Monday Morning, December 12, 2016

Biomaterial Surfaces & Interfaces
Room Milo - Session BI-MoM

Buddy Ratner's 70th Birthday Session

Moderator: Lara Gamble, University of Washington, USA

8:20am **BI-MoM2 Genetic Level Programming of Molecular Assembly of Intrinsically Disordered Proteins***, **Gabriel López**,* University of New Mexico, NSF Research Triangle Materials Research Science and Engineering Center, Duke University, USA **INVITED**

A number of dynamic, protein-rich intracellular structures containing phase separated, unstructured proteins comprising low-complexity amino acid sequences have recently been shown to serve a variety of important cellular functions, including signaling, compartmentalization and stabilization. The understanding of these structures, and the ability to synthesize models of them, has been limited. This talk will present simple methods for programming diverse assemblies comprised of a series of elastin-like polypeptides, model intrinsically disordered proteins possessing sequences of low-complexity. By encoding the stimulus-induced aqueous phase behavior of proteins at the amino acid sequence level, we demonstrate the reversible formation of a variety of protein-rich structures, ranging from uniform nano-, meso-, and micro-scale puncta (small, distinct particulates) to multilayered, orthogonally-phase-separated, multicomponent microgranules. We further show how such nanoscale assemblies (i) can be stabilized by controlled biomineralization, (ii) can be used for simple bioassays for diagnostic or drug discovery applications, or (iii) can be used as building blocks for the hierarchical formation of micellar hydrogels with surprising mechanical properties and potential use in controlled delivery of nanoparticles for drug delivery applications. The talk is dedicated to Prof. Buddy Ratner, a mentor and friend of mine and of my collaborator, Prof Ashutosh Chilkoti, on the occasion of Buddy's birthday this year.

9:00am **BI-MoM4 Surface Activation of the VWF A1 Domain: The Relationship between Platelet Activity and Absorbed A1 Structure***, H. Tronic, E. Thomas, **David Castner**,* University of Washington, USA

When a material is placed in a biological environment, the surface of the material acts as the interface between that material and the biological environment. Upon contacting blood, plasma proteins attach to these surfaces and mediate platelet adhesion and activation and thrombosis. A key protein in this process is the clotting protein von Willebrand Factor (VWF) which binds to platelet receptor glycoprotein 1bα (GPIbα) when VWF is activated by chemicals, high shear stress, or immobilization onto surfaces. Activation of VWF by surface immobilization is an important problem in the failure of cardiovascular implants, but is poorly understood. Here we investigate whether some or all surfaces can activate VWF at least in part by affecting the orientation or conformation of the immobilized GPIbα-binding A1 domain of VWF. Platelets translocate rapidly on A1 adsorbed onto PS surfaces, and demonstrate shear-enhanced adhesion in that they detach at low rather than high shear stress. In contrast, platelets translocate more slowly on A1 adsorbed onto TCPS surfaces and are nearly stationary on A1 adsorbed onto glass surfaces, and demonstrate shear-inhibited adhesion in that they detach at high but not low shear stress. Both X-ray photoelectron spectroscopy and conformation independent antibodies reported comparable A1 amounts on all surfaces. Time-of-flight secondary ion mass spectrometry (ToF-SIMS) suggested differences in orientation on the three surfaces, but none that could explain the biological data. Instead, ToF-SIMS determined Cys exposure and conformation-sensitive antibody binding suggest that A1 retains its native conformation when adsorbed onto PS surfaces, while TCPS surfaces and especially glass surfaces stabilized an alternative activated conformation of A1 that likely resembles the activated form of A1 that is also stabilized by disease-causing mutations. Regardless of the specific structure of the activated forms of A1, these studies demonstrate that it is not enough to determine the amount of various proteins that bind to different biomaterials placed in contact with the blood; instead, it is necessary to understand how different surfaces control the conformation of the many blood proteins that are capable of undergoing activating conformational changes. In particular, these studies demonstrate that the A1 domain of VWF has fundamentally different biological activity when adsorbed onto different surfaces. This is important when interpreting or designing *in vitro* experiments with surface-adsorbed A1 domain, and is also of likely relevance for blood-contacting biomaterials.

9:20am **BI-MoM5 Nanotechnology and Ultrasound for Targeted Delivery of Drugs and Nucleoti***, **Joseph Kost**,* Ben-Gurion University, Israel

The basic approach that drug concentration-effect relationships are significantly invariant as a function of time in man has led to the development of constant rate drug delivery systems. Nevertheless, there are a number of clinical situations where such an approach may not be sufficient. Thus, in recent years several research groups have been developing targeted and stimuli responsive systems that could more closely resemble the normal physiological process. Advances in protein engineering and materials science have contributed to novel nanoscale targeting approaches that may bring new hope to patients. Several nanocarriers have been approved for clinical use. However, to date, there are only a few clinically approved nanocarriers with drugs to selectively bind and target cancer cells. Nanoparticles used as drug delivery carriers consist of different biodegradable materials such as natural or synthetic polymers, lipids, or metals. Nanoparticles are taken up by cells more efficiently than larger micromolecules and therefore, could be used as effective delivery systems. For therapeutic applications, drugs can either be integrated in the matrix of the particle or attached to the particle surface. A drug targeting system should be able to control the fate of a drug entering the biological environment. An effective approach for achieving efficient drug delivery would be to develop nanosystems based on the understanding of their interactions with the biological environment, cellular and intracellular barriers, target cell population and cell-surface receptors, mechanism and site of drug action, drug retention, molecular mechanisms, and pathobiology of the disease under consideration. Reduced efficacy could be due to instability of therapeutic agent, cellular and intracellular transport barriers, toxicity of the carrier, changes in signaling pathways with the progression of disease, or drug degradation. Better understanding of the mechanism of uptake, intracellular trafficking, retention, and protection from degradation inside a cell are required for enhancing the efficacy of the therapeutic agent. Physical approaches to increase efficacy and targeting to specific tissues have been also studies. In the presentation the drug delivery aspects of nanomedicine, the molecular mechanisms underlying the interactions of nanoparticles with cell-surface receptors, biological responses and ultrasound as a triggering and targeting tool and its effect on cellular transport would be discussed.

9:40am **BI-MoM6 SIMS Surface Science from SAMs to 6S Scaffolds***, **Daniel Graham**, L.J. Gamble,* University of Washington, USA

Time-of-flight secondary ion mass spectrometry (ToF-SIMS) generates chemically rich, complex data that can encode information about surface composition, molecular conformation, orientation and more. However, due to the complexity and magnitude of the data, it is imperative that research projects be carefully planned out before the researchers attempt to extract this information using ToF-SIMS. Professor Ratner understood this challenge and recognized that, after utilizing a well planned research strategy, applying multivariate analysis methods (MVA) could aid to better understand ToF-SIMS data and use it more efficiently. This idea, generated more than 20 years ago, led me on a journey exploring the complexities of ToF-SIMS through the use of self-assembled monolayers (SAMs) that has continued into exploring complex organic systems such as cells, tissues and tissue engineered scaffolds. In this presentation I will highlight the work pioneered by the ideas of Buddy Ratner that helped start the MVA revolution in SIMS analysis and has led to the development of methods that help to more efficiently process and better understand secondary ion mass spectrometry data. Examples will be shown from controlled experiments with SAMs, cells, tissues and tissue engineering scaffolds. Work with SAMs helped demonstrate that combining MVA with SIMS and well controlled substrates could help us better understand the SIMS fragmentation process and discover new information encoded in the relative intensities of the peaks. This set the foundation for processing more complex systems and using MVA and SIMS to characterize the chemical differences in more complex systems. This has led to one of our current projects involving characterizing tissue engineering scaffolds with cells in 2D and 3D.

10:20am **BI-MoM8 Plasmas, Proteins and Other Things Buddy has Inspired me to Play with in Vacuum Chambers***, **Sally L. McArthur**,* Swinburne University, Australia **INVITED**

Control and the ability to elicit specific responses from a biological system lies at the heart of most bioengineering. We want to immobilize proteins on biosensors but ask them to behave as they would in the body, stimulate cells to assemble into tissues, reconstructing our bodily functions. We want methods that prevent bacteria forming biofilms and better still we would like them to stop bacteria attaching to surfaces full stop. But biology is soft and normally has lots of water associated with it, so how and why would you want to use vacuum based techniques to create coatings or characterise these systems? This talk will explore how in my group and our collaborators, have tackled the challenges associated with interfacing vacuum deposited plasma polymers with water, proteins, lipids and cells to create a wide number of model systems and devices. At the same time, we have developed methods for chemically characterising these systems in vacuum, integrating XPS and ToF-SIMS with a range of other surface analytical and biological tools to gain insight into the materials we create and their interactions with biological systems.

Energy Harvesting & Storage
Room Lehua - Session EH-MoM

Surfaces & Interfaces for Environmental Processes

Moderator: Jun Yoshinobu, University of Tokyo

8:40am **EH-MoM3 Nuclear-spin State Filtering and Conversion of H_2 with Solid Surfaces for Efficient Hydrogen Liquefaction***, G. Nakamura, K. Takeyasu, S. Ohno, D. Ivanov, S. Ogura,* ***Katsuyuki Fukutani,*** University of Tokyo, Japan

Hydrogen is a clean energy source, and storing hydrogen in a liquid form is a high-density storage method. Molecular hydrogen exists in nuclear-spin isomers of ortho and para species according to the total nuclear spin [1]. Since these species are correlated to the rotational states with even and odd rotational quantum numbers (*J*) because of the symmetry of the total wavefunction with respect to the permutation of the two nuclei, the stable state at the liquid hydrogen temperature is the para state. Although the ortho-para conversion in an isolated state is strictly forbidden, the conversion is promoted at solid surfaces [1], which has been used for efficient hydrogen liquefaction. Due to the symmetry of the H_2 molecule, on the other hand, the molecule-surface interaction is anisotropic depending on the molecular orientation, which can be analyzed with the *J*-state selective temperature-programmed desorption (TPD) [2]. In the present work, we have investigated the potential anisotropy of H_2 on a Pd(210) surface with resonance-enhanced multiphoton ionization (REMPI). With the anisotropic potential, furthermore, we propose that the ortho and para species can be separated by surface scattering, which is potentially used for efficient hydrogen liquefaction. We demonstrate such nuclear-spin state filtering on a TiO_2(110) surface.

When the Pd(210) surface is exposed to H_2 at ~30 K, H_2 is molecularly chemisorbed on a H-covered surface, which is revealed by a TPD peak at ~70 K [3]. When this desorption is *J*-state selectively detected, the *J*=0 para H_2 is desorbed at 74 K, while the *J*=1 ortho H_2 is desorbed at a higher temperature of 78 K. This indicates that the adsorption energy of the ortho species is larger than that of the para species. This is due to the lifting of the degeneracy of the ortho state induced by the potential anisotropy. From the population ratio of the ortho and para states, the ortho-para conversion time in this adsorption state is found to be shorter than ~10 s, which is much faster than Ag surfaces [1]. By applying a pulsed supersonic H_2 beam, the angular distribution of H_2 scattered from TiO_2(110) is state-selectively measured. Whereas the *J*=1 ortho H_2 reveals a broad distribution in the near-specular direction, the *J*=0 para H_2 shows a slightly shifted distribution. We discuss the scattering of H_2 via an anisotropic potential and resultant nuclear spin-state filtering.

References

[1] K. Fukutani, T. Sugimoto, Prog. Surf. Sci. 88, 279 (2013).

[2] T. Sugimoto, K. Fukutani, Phys. Rev. Lett. 112, 146101 (2014).

[3] P. K. Schmidt et al., Phys. Rev. Lett. 24 87, 096103 (2001).

9:00am **EH-MoM4 Closing Open Questions on Gold(111)-thiol Interfaces***, E. Pensa, E. Cortés,* Imperial College London, UK*; R. Salvarezza,* Institute of Theoretical and Applied Physicochemical Research, Argentina*; P. Carro,* University of La Laguna, Spain*; C. Hernández, C. Ocal, E. Barrena,* ***Xavier Torrelles,*** Institute of Materials Science of Barcelona, Spain

The gold-sulphur interfaces of alkanethiols and dialkenethiols have been extensively studied with the main objective to understand how thiols bind to gold surfaces to form self-assembled monolayers. Nowadays, the preparation and characterization of these systems are still experiencing a tremendous progress as consequence of their applicability in emergent areas of nanotechnology as protective gold clusters. In contrast to the models developed for self-assembling the gold-thiolate interface of thiolate-protected gold clusters reveal the presence of gold adatoms flanked by two sulphur atoms. This new situation together with the observation of gold vacancy islands on Au(111) single crystals is causing a review of the different proposed models obtained from the experiment and theory that still leave unresolved issues.

The work performed using X-ray diffraction at the ID03 beamline of the ESRF permitted to acquire a data set of enough quality to unravel the basic structural blocks linked to the interface structure between molecule and gold substrate, i.e. adatoms, vacancies, molecular orientation, gold layer relaxation and more. The experiment was designed to accomplish or give basic answers to fundamental questions concerning alkanethiol adsorption on Au(111) surface as: Is the gold reconstructed upon thiol adsorption?, Which is the origin of the adatoms during self-assembly? Are there vacancies/adatoms on the ordered/disordered thiol areas? Answers to these questions are the basis to understand new type of experiments that are already being done at nano level.

9:20am **EH-MoM5 Chemical Gradients Formation on Polymer Surfaces for Directed Molecular Transport***,* ***Hyung-Jun Koo,*** Seoul National Univeristy of Science and Technology, Republic of Korea*; P.V. Braun,* University of Illinois at Urbana-Champaign, USA*; K.V. Waynant,* University of idaho, USA*; C. Zhang,* University of Illinois at Urbana-Champaign, USA

Surfaces containing defined microscale chemical gradients are important for various applications including a sample library with an extremely dense variable set and a smart platform to direct 2D-molecular transport. In this regard, reliable methods to form mili- to micron-scale chemical gradients are required. We present two facile microfluidic methods to form narrow surface chemical gradients in a tertiary amine functionalized polymer brush via a selective quaternization. Two methods are on the basis of different physical mechanisms: permeation into porous media vs. diffusion at liquid/liquid laminar interface. Concentration and separation as well as directional transport driven by surface-gradient on highly hydrated polymer films will be also demonstrated. Such a new concept to control 2D transport of molecules could generally be applied for signal enhancement in chemical sensors to detect tiny amount of harmful molecules, e.g., pollutants, toxins, etc..

References:

1. **H.-J. Koo**, K. V. Waynant, C. Zhang, R. T. Haasch, P. V. Braun, “General Method for Forming Micrometer-Scale Lateral Chemical Gradients in Polymer Brushes”, ***Chemistry of Materials,*** 26, 2678 (2014).

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3. C. Zhang, A. Sitt, **H.-J. Koo**, K. V. Waynant, H. Hess, B. D. Pate and P. V. Braun, “Autonomic molecular transport using hydrogel films containing programmed chemical potential gradients”, ***Journal of the American Chemical Society***, 137, 5066 (2015)

9:40am **EH-MoM6 Selectivity Control in the Electroreduction of CO_2 over Nanostructured Catalysts***,* ***Beatriz Roldan Cuenya,*** Ruhr University Bochum, Germany

The electrocatalytic reduction of CO_2 to industrial chemicals and fuels is a promising pathway to sustainable electrical energy storage and to an artificial carbon cycle, but is currently hindered by the low energy efficiency and low activity displayed by traditional electrode materials.

Using colloidal synthesis, nanoparticles (NPs) with well-defined size and interparticle distance were prepared and tested as catalysts for CO_2 electroreduction. Cu NP catalysts displayed a drastic increase in activity and selectivity for H_2 and CO with decreasing NP size below 5 nm. Hydrocarbon (methane and ethylene) selectivity was increasingly suppressed with decreasing NP size. For Au NPs, a drastic increase in current density was observed with decreasing NP size, along with a decrease in faradaic selectivity towards CO. The H_2/CO product ratio could be specifically tailored for different industrial processes by tuning the size of the Au NPs. In addition, we demonstrated that interparticle distance (IP) is also a critical parameter for controlling reactivity. For largely spaced NPs, selectivity to CO is enhanced, since this reaction intermediate is less likely to readsorb on neighboring NPs after formation. On the contrary, for closely spaced NPs we find that hydrocarbon selectivity is enhanced, since the re-adsorption of reaction intermediates on neighboring NPs can facilitate the multi-step pathway required for hydrocarbon production. This study addresses previously unexplored aspects of how product selectivity can be controlled using mesoscale transport processes during CO_2 electroreduction.

Another critical parameter for selectivity control in nanostructured electrocatalysts is the chemical state. We will discuss new oxide-derived metal catalysts that can reduce CO_2 with lowered overpotential and improved ethylene selectivity. We will also present critical insights into the catalyst reaction mechanism which were unraveled using structural and chemical information on the sample obtained under *operando* conditions via X-ray absorption fine-structure spectroscopy. Finally, the role of the NP shape, in particular, the presence of (100) facets in Cu nanocubes and the evolution of the NP structure and dispersion under reaction conditions will be discussed based on *operando* electrochemical AFM data.

10:20am **EH-MoM8 Activation of CO_2 using Heterogeneous Catalysts***, **Junji Nakamura**,* Tsukuba University, Japan **INVITED**

Methanol synthesis by hydrogenation of CO_2 using Cu catalysts is one of the promising reactions to convert CO_2 into useful chemicals. Formate species is the pivotal intermediates formed as the initial step of CO_2 hydrogenation ($CO_2 + H_a \rightarrow HCOO_a$). The reaction rate of formate synthesis is very low and the reaction probabilities are about 10^{-12} at 340K. The formate synthesis must be accelerated in order to convert CO_2 to methanol efficiently. Our previous kinetic measurements have suggested that formate is synthesized via Eley-Rideal typed mechanism, in which CO_2 molecules directly attack adsorbed hydrogen atoms on Cu surfaces. The structure insensitivity observed for formate synthesis experiments on Cu(111), Cu(100), and Cu(110) were well explained by the Eley -Rideal mechanism based on DFT calculations. In addition, sharp angular desorptions of CO_2 have been observed for formate decomposition as the reverse reaction of formate synthesis, indicating thermal non- equilibrium reaction. We thus performed molecular beam experiments to prove the Eley-Rideal typed mechanism, in which CO_2 molecules with controlling vibrational and translational energies were reacted with adsorbed hydrogen on cold Cu(111) and Cu(110) surfaces (TS =150-215 K). The formation of formate was found by infrared spectroscopy and temperature programmed desorption measurements of CO_2 and H_2 from decomposition of formate. We confirmed the formation of formate species on Cu(111) and Cu(110) with reaction probabilities of 10^{-5} by heating nozzle above 1000 K, while no formate is formed at nozzle temperatures below 1000 K. The results indicate the Eley-Rideal typed mechanism with thermal non-equilibrium character. DFT calculations also reproduce the Eley-Rideal typed mechanism, in which translational and vibrational excitations of CO_2 are required to overcome the barrier of formate synthesis, 0.6-0.7 eV. The understanding on dynamics of CO_2 activation is expected to apply for the state-to state chemistry of methanol synthesis. That is, selective energy supply for an energy-efficient methanol synthesis process.

Nanomaterials
Room Hau - Session NM-MoM
Nanofabrication and Nanodevices

Moderator: Kaifu Huo, Huazhong University of Science and Technology

8:20am **NM-MoM2 Fabrication of Nanoplasmonic Pore on the Pyramid for Single Molecule Analysis***, **SeongSoo Choi**, M.J. Park, C.H. Han, S.J. Oh, T. Yamaguchi,* Research Center for Nanobio Science, SunMoon University, Republic of Korea*; Y.S. Kim,* Sungkyunkwan University, Korea, Republic of Korea*; N.K. Park,* School of Electrical Engineering, Seoul National University, Republic of Korea

There have been tremendous interests about the portable single molecule sensor device by using nanopore detection techniques. Recently the portable genome sequencing device based on the electrical detection technique was fabricated, however, the very high error rate during detection process was reported. In this report, we will report the nanoplasmonic Au nanopore fabrication by using diffusion of atoms, or drilling a freestanding thin film under high electron beam irradiation. For diffusion techniques, the Au apertures with ~ 100 nm diameter were fabricated by using focused ion beam technique followed by electron beam irradiations. The Au nanoclusters were formed on the diffused membrane several months later under the room environment after electron beam irradiations. In addition, drilling a freestanding 40 nm thick Au membrane was successfully carried out. Due to unstable electron beam irradiation on the nanoscale spot, we observed a crescent shape aperture with 0.75 nm width on the freestanding Au film. The fabricated nanopore surrounded with periodically patterned grooves can enhance the optical transmission and enhance the optical intensity due to plasmonic hot spot at the pore area. The controlled nanopore can be utilized as single molecule translocation and analysis by using optical detection and optically driven technique.

8:40am **NM-MoM3 Reversible Diels-Alder attachment of Organic Molecules to Single Atoms on Hydrogenated Semiconductors***, **Szymon Godlewski**, M. Kolmer,* Jagiellonian University, Poland*; M. Engelund,* Donostia International Physics Center, Spain*; H. Kawai,* Institute of Materials Research and Engineering*; R. Zuzak,* Jagiellonian University, Poland*; A. Garcia-Lekue,* Donostia International Physics Center, Spain*; A.M. Echavaren,* Institute of Chemical Research of Catalonia*; D. Pena, D. Perez, E. Guitian,* Universidad de Santiago de Compostela*; C. Joachim,* CEMES-CNRS, France*; D. Sanchez-Portal,* Donostia International Physics Center, Spain*; M. Saeys,* Ghent University, Belgium*; M. Szymonski,* Jagiellonian University, Poland

In recent years the on-surface, local chemistry attracts growing attention, inspired by the interest in fundamental processes occurring on surfaces, as well as by potential technological applications. In particular, the controlled and reversible bonding between single molecules and atoms could be advantageous in construction of prototypical molecular switches, rotors and electronic circuits. To control the electronic properties of organic species the isolation from the underlying substrate is required. This could be achieved by application of passivated surfaces that enable retention of originally designed properties [1-3]. Hydrogen passivated silicon and germanium surfaces are of particular interest enabling creation of atomic scale defects – hydrogen vacancies that could interact with organic molecules and form artificial wiring [4-5].

In the presentation we will demonstrate reversible Diels-Alder attachment of prototypical three-branch conjugated molecules to paired surface dangling bonds. We will show that molecules initially undergo the [4+2] cycloaddition forming chemical bonds with the unsaturated surface dangling bonds [6]. Further, it will be discussed that the bonds could be broken and restored using the low temperature scanning tunnelling microscope. We will demonstrate that at low temperature the molecules located on surface dangling bonds could be switched between the chemisorbed configuration and the physisorbed one held by van der Waals interactions only. Interestingly, the molecules adsorbed in the latter configuration could be controllably switched rotationally with the STM tip, which constitutes the first molecular switch on a passivated surface. Further it will be shown that by tuning the structure of the molecules the attachment geometry could be controlled with high selectivity. Finally we will introduce prospects for utilization of the control over connecting individual molecules with surface single atoms.

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[3] Szymon Godlewski et al. Phys. Chem. Chem. Phys. 18 (2016) 3854

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9:00am **NM-MoM4 Full Color Light Emitting Diodes using Perovskite Quantum Dots as Emissive Materials***, Y.-H. Suh,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; J.-W. Chio,* Gwangju Institute of Science and Technology (GIST), Republic of Korea*; T. Kim,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; S.-H. Han,* Mokpo National Maritime University, Republic of Korea*; J. Park,* Ulsan National Institute of Science and Technology (UNIST), Republic of Korea*; **Chang-Lyoul Lee**,* Gwangju Institute of Science and Technology (GIST), Republic of Korea

The cesium lead halide ($CsPbX_3$, X = Cl, Br, and I) based perovskite quantum dots (QDs) were synthesized using precipitation and hot-injection methods. And also, the device performance of QD-LEDs using inorganic perovskite ($CsPbX_3$) as emissive layer was characterized. The $CsPbX_3$ showed excellent properties, such as high quantum yield (>~80%), easily tunable band gap, and high color purity as well as high stability. The PL spectra of $CsPbX_3$ were varied by changing the composition of halides. The inverted structure QD-LEDs consisted of ITO/ZnO/poly-electrolyte/PeQDs/MoO_3/Ag showed the high color purity EL (Blue : ~480 nm, Green: ~510 nm, Red : ~680 nm) and high brightness (Blue : ~200cd/m^2, Green: ~1,200cd/m^2, Red : ~300cd/m^2).

9:20am **NM-MoM5 Nanoarchitecture Design for Independent Control of Carrier and Phonon Transports*, Yoshiaki Nakamura,*** Osaka University, Japan **INVITED**

Thermoelectric (TE) conversion has been expected to be one of the ideal energy sources, where waste heat is converted to be usable electrical energy. Therefore, TE performance enhancement had drawn much attention. TE performance is related to dimensionless figure of merit, $ZT=S^2\sigma T/\kappa$, where S is Seebeck coefficient, σ is electrical conductivity, κ is thermal conductivity, and T is absolute temperature. This means that the materials with high S, σ, and low κ are required. However, high σ and low κ are difficult to achieve simultaneously because they are correlated. Therefore, the identical control of σ and κ has been a vital goal in thermoelectric study for long.

We proposed the nanoarchitecture where phonon was scattered effectively at the nanostructure interfaces, but carriers could go through them using ultrasmall epitaxial nanodots (ND) with well-controlled interfaces. Herein, carriers feel that nanomaterials are single crystal because crystals of NDs are oriented. On the other hand, the interfaces of ultrasmall NDs scatter phonon. In this study, we use our original technique for forming epitaxial ND structures. We achieve the identical control of phonon and carrier transports using the above nanoarchitecture design.

Clean Si surfaces were oxidized at 500°C at the O_2 pressure of 2×10^{-4} Pa to form ultrathin (~0.3 nm) SiO_2 films. Si or Ge was then deposited to form epitaxial Si or Ge NDs grown on Si substrates with ultrahigh density of $\sim10^{12}$ cm^{-2} as the following. At first stage of Si of Ge deposition, nanowindows were created in the ultrathin SiO_2 films through the reaction of $Si+SiO_2 \rightarrow 2SiO\uparrow$, or $Ge+SiO_2 \rightarrow GeO\uparrow+SiO\uparrow$. By subsequent deposition, Si or Ge NDs formed on the ultrahigh density nanowindows. In the case of Ge NDs, Si layers were formed on Ge NDs at 400°C. The above formation of Si NDs or Si layer/Ge NDs and the oxidization process were repeated to fabricate the ND stacked structures.

The formation of the epitaxial nanoarchitectures including NDs was succeeded. The κ values were measured by 2ω method. The smallest κ value of stacked Si NDs with 3 nm diameter was close to the amorphous value. In the case of Ge NDs, the κ values were also drastically reduced compared with bulk Si. The σ of Ge ND structures was enhanced to be a similar value to the bulk Si cases by the interface designing, indicating the independent control of κ and σ. This demonstrates the possibility of our nanostructure as a Si-based thermoelectric material with high ZT.

This work was partially supported by JSPS KAKENHI Grant Number 16H02078 for Scientific Research (A) and 15K13276 for Challenging Exploratory Research. In part, this work was supported by CREST-JST program.

10:20am **NM-MoM8 DNA self-assembled Nanostructures using a Scaffold with a Minimum Size*, Enrique Samano,*** Universidad Nacional Autónoma de México, México*; T.H. LaBean,* North Carolina Central University, USA

Artificial DNA nanostructures such as DNA origami have garnered significant interest as templates for sub-20 nm assembly of materials because their design allows for the incorporation of binding sites to assemble nanocomponents with 6nm resolution. The DNA origami strategy for assembling designed supramolecular complexes requires ssDNA as a scaffold strand. A system is described that was designed using approximately one third of the M13 bacteriophage genome as a scaffold. Folding of the short 2404-base ssDNA scaffold into a variety of two-dimensional origami shapes (rectangle, triangle, and circle) with high assembly yields is demonstrated. DNA origami templates, modified to have DNA binding sites with a uniquely coded sequence, can be used to produce complex metallic nanostructures of programmable design. Gold nanoparticles functionalized with a complementary DNA sequence were attached to specific binding sites on the scaffold in a highly controllable manner to form a predesigned metallic array on two nanostructures.

10:40am **NM-MoM9 Feedback-Controlled Electromigration (FCE) Method with Automatically Optimized Parameters*, Noriaki Numakura,*** *Y. Iwata, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

Feedback-controlled electromigration (FCE) has been used as a useful technique for fabricating quantum point contacts (QPCs) and nanogaps [1]. The conventional FCE method is performed on a general-purpose operating system (GPOS). In contrast, real-time operating system (RTOS) is specifically designed to run applications with precise timing and reliability. Hence, we have previously reported the FCE method using RTOS, in order to run FCE algorithms time-deterministically and to control quantized conductance of Au nanowires, at room temperature in ambient air [2]. In this report, we propose a new FCE system with automatically optimized parameters for the improvement of control performance of FCE using RTOS.

In this system, we designed the FCE algorithms with randomly varying parameters. First, FCE experiments for the Au nanowires were repeatedly performed to obtain various FCE experimental data. Then, the FCE parameters were evaluated using cost functions, and stored in a database. Finally, we performed the FCE experiments with a suitable set of evaluated FCE parameters, which was generated using the stored data. As a result, the conductance of Au nanowire was successfully quantized and decreased without catastrophic break. Therefore, it is considered that the FCE system based on automatically optimized parameters can show the conductance quantization of Au nanowires even at room temperature in ambient air.

References

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[2] S. Sato, Y. Kanamaru, Y. Katogi and J. Shirakashi, 43rd International Conference on the Physics and Chemistry of Surfaces and Interfaces (PCSI-43), Mo0950, January 17-21, 2016, Palm Springs, CA, USA.

Thin Films
Room Mauka - Session TF-MoM
Advances/Innovation in Synthesis & Characterization

Moderator: Franz Himpsel, University of Wisconsin Madison, USA

8:00am **TF-MoM1 ToF-SIMS Depth Profiling of Full Organic/inorganic Hybrid Devices with Low-Energy Cesium Ions*, Céline Noël,*** University of Namur, Belgium*; L. El Fissi, L.A. Francis,* Université Catholique de Louvain*; L. Houssiau,* University of Namur, Belgium

In the last few years, growing attention has been brought to devices based on hybrid (organic/inorganic) multilayered materials as they allow for highly versatile properties, such as tunable optical and electronic features, malleability, transparency and cost-efficiency that could find applications in a large variety of devices such as OPVs, OLEDs, sensors, microfluidics, fuel cells, etc. . Forthcoming technological advances will require detailed knowledge of layers and interfaces composition and morphology in order to optimize device efficiency, stability, processing conditions.

ToF-SIMS is a well-suited technique to obtain key information such as the in-depth molecular composition of each layer and diffusion at the interfaces. However, for hybrid materials, depth profiling remains challenging as ion sources which are efficient on organic materials are generally not efficient on inorganic ones. Numerous dynamic-SIMS studies of interfacial migration between organic/inorganic layers have been reported, but no molecular signal could be monitored. Recently, low-energy (500 eV) Cs^+ ions were shown to possibly offer a reliable solution for depth-profiling hybrid systems [1]. Using this novel approach, the present work presents molecular depth-profiling on complex OLEDs interfaced materials showing that each layer, until the substrate, could be successfully identified by its specific molecular signal within a reasonable sputtering time.

In parallel, oxide/polymer hybrid materials were investigated with future applications in microfluidics, BioMEMS and lab-on-chip devices. Samples consisted of TiO_2 or Al_2O_3 coating on three different polymers, namely cyclic olefin copolymer (COC), polyimide (PI) and SU-8 (a negative photoresist). Again, all samples were easily depth profiled by low-energy Cs+, with characteristic molecular fragments monitored on each polymer even after the oxide layer is sputtered. This again proves that low-energy Cs^+ is an efficient solution to depth profile hybrid materials. We also compared metal diffusion in different oxides coating and polymers. Issues like homogeneity, contamination or non-stochiometry near the interface could be addressed by ToF-SIMS analyses; matrix effects and ion beam induced modifications were discussed based on complementary XPS measurements.

With the development of new technologies, an increasing number of applications are expected to require in-depth molecular information of organic/inorganic materials. The present work shows how ToF-SIMS can answer this demand, opening the way for the characterization of such novel applied materials.

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8:20am **TF-MoM2 Amplitude Contrast High Resolution Electron Microscopy of A-site Associated Oxygen Octahedral Rotations in Artificial Perovskite Superlattices***, **Dean Miller**, J.G. Wen,* Argonne National Laboratory, USA*; X. Wu,* Temple University, USA

Artificially structured perovskite superlattices offer rich opportunities for novel ferroelectricity. We have developed a new high-resolution TEM imaging technique that allows the direct observation of A-site associated oxygen octahedral rotations in perovskite oxide superlattices that reveals the underlying mechanisms of enhance ferroelectricity in complex heterostructures. By combining the amplitude-contrast high-resolution electron microscopy and DFT calculations, we show that a highly polar $CaTiO_3$ phase with a $BiFeO_3$-like structure can be stabilized in $(CaTiO_3)_n/(BaTiO_3)_n$ superlatice. Amplitude contrast imaging (ACI) relies on both spherical and chromatic aberration correction for TEM imaging. Under ACI conditions, atomic resolution channeling contrast can be realized, allowing one to obtain directly interpretable high-resolution electron microscopic images with discrimination between light and heavy atomic columns. Using this imaging approach, we were able to image the atomic structure in a $BaTiO_3/CaTiO_3$ superlattice with high spatial accuracy and discrimination between Ba and Ca columns, providing direct visualization of the Ca and Ba associated oxygen octahedral rotations. Combined with the first-principles calculations, we found that a highly polar metastable “interface phase” of CaTiO3 with a structure of BiFeO3 is stabilized by the mechanical and electrical boundary conditions of the BaTiO3/CaTiO3 superlattice. Under this new mechanism, a large number of perovskites with the CaTiO3 type structure will become good candidates for novel highly-polar multiferroic materials.

8:40am **TF-MoM3 Controlled Growth of Transition-Metal Nitride Alloy Films via Hybrid HIPIMS/Magnetron Co-Sputtering using Synchronized Metal-Ion Irradiation***, **Grzegorz Greczynski**, J. Lu, O. Tengstrand,* Linköping University, Sweden*; I. Petrov, J.E. Greene,* Linköping University, Sweden, University of Illinois at Urbana-Champaign*; W. Kölker, S. Bolz, C. Schiffers, O. Lemmer,* CemeCon AG, Germany*; L. Hultman,* Linköping University, Sweden **INVITED**

Growth of thin films by physical vapor deposition (PVD) typically requires elevated substrate temperatures and/or ion irradiation to ensure high adatom mobilities necessary for film densification. However, obtaining densification via high incident gas-ion energies extracts a steep price in the form of residual ion-induced compressive stress resulting from both recoil implantation of surface atoms and trapping of rare-gas ions in the lattice. Our solution for these issues employs high-power pulsed magnetron sputtering (HIPIMS) owing to the high ionization degree of sputter-ejected metal atoms, and the time separation of metal- and gas-ion fluxes incident at the substrate. The former implies that ion fluxes originating from elemental targets operated in HIPIMS are distinctly different from those obtained during dc magnetron sputtering (DCMS). The latter feature allows us to suppress the role of gas-ion irradiation, by synchronizing the pulsed substrate bias with the metal-rich-plasma portion of the HIPIMS pulse.[1]

We carry out experiments in a hybrid configuration with one target powered by HIPIMS and the other operated in DCMS mode (HIPIMS/DCMS).[2,3] This allows us to probe the roles of intense metal-ion fluxes from HIPIMS-powered targets on film growth kinetics, microstructure, and physical properties over a wide range of transition metal nitride M_1M_2N alloy compositions. Model materials systems include TiAlN, TiSiN, TiTaN, and TiAlTaN. In a series of extensive experiments, we established that the essential factors determining film growth pathways include (i) the average metal-ion momentum transfer per deposited atom , (ii) metal-ion charge state, and (iii) mass of metal ion assisting the growth.[4]

Based on the above results, a new PVD approach is proposed which relies on the hybrid concept to grow dense, hard, and stress-free thin films with no external heating.[5] TiTaN and TiAlTaN film densification is achieved by pulsed synchronized bombardment with Ta^+/Ta^{2+} metal ions which are film constituents; this, in turn, minimizes film stress. The preliminary results are very promising. For example, with as little as 8 mol% of TaN, fully-dense TiTaN alloys with high hardness and low residual stress can be obtained at temperatures T_s < 150 °C (due to plasma heating). This novel approach expands the PVD process envelope to allow the use of temperature-sensitive substrates, including plastics.

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[2] G. Greczynski, J. Lu, M. Johansson, J. Jensen, I. Petrov, J.E. Greene, and L. Hultman, *Surf. Coat. Technol.* 206 (2012) 4202.

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[5] G. Greczynski, J. Lu, I. Petrov, J.E. Greene, S. Bolz, W. Kölker, Ch. Schiffers, O. Lemmer and L. Hultman, *JVSTA* 32 (2014) 041515

9:20am **TF-MoM5 Evaluation of Perturbation Induced by Ionic Clusters Bombardmen: XPS and Electrochemical Coupled Approach***, **Arnaud Etcheberry**,* Paris Saclay University, France

Evaluation of perturbation induced by ionic clusters bombardmen: XPS and Electrochemical coupled approach.

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The XPS profiling is a key technique to provide quantitative compositional profiles of ultra thin and thin films. XPS profiling needs ion guns etching which can induce perturbations of the XPS probed films. It is particularly true when fragile films are submitted to the etching procedure as for example organic films, oxide etc. Rational evaluation of the exact nature of the perturbation is an very important question which needs accurate approach to compare different etching procedure and to propose calibrated etching strategy. In this paper we treat the evaluation of perturbation induced by ionic argon cluster gun which is a very interesting method to provide very different conditions to perform XPS profiling as soon as possible close to the actual compositional profile. To perform that we use as supporting material InP a well known semiconductor for which problem of preferential etching is well documented. We chose to combine on same samples (n,p & undoped) XPS, UPS and electrochemical characterizations to evaluate the impact of a ionic or ionic cluster bombardment on the responses of the surface. We show that modifying the size of the cluster, the energy, the angle we induced very important modulation of the perturbations. The interesting feature of our proposal is that XPS modification: position of Peak Energy, valence band, fwhm, atomic ratio are related to the electric ones: capacitive response, I-V toward electrochemical processes, anodic dissolution. This coupling approach gives rise to a set of experimental data which are used as calibration information to provide adapted perturbation by an ion cluster bombardment. Moreover electrochemical diode has the advantage to be easily broken so it is compatible with XPS, Electrochemistry sequences which allows very fast experimental cycles. For example perturbation induced by ionic bombardment can be eliminated by dissolution of the semiconductor induced by chemical etching or by anodic oxidation. Both provide quantitative evaluation of the depth of the perturbed zone before a complete recovering of the initial XPS or electrochemical responses. We propose in this paper to detail several facets of this interfacial chemistry study

9:40am **TF-MoM6 TOF-SIMS Parallel Imaging MS/MS - Making Data Interpretation Easier***, **John Newman**, S.R. Bryan, G.L. Fisher, P.E. Larson, J.S. Hammond,* Physical Electronics, USA*; R.M.A. Heeren,* Maastricht University*; S. Iida, H. Chang, T. Miyayama,* Ulvac-PHI

Over the last quarter century Time-of-Flight Secondary Ion Mass Spectrometry (TOF-SIMS) has been successfully used to characterize the molecular composition of the outermost layers of solid surfaces. However, even with mass resolutions greater than 15,000 *m/Δm* and mass accuracies better than 10 ppm, making definitive chemical assignments of higher mass peaks above ~200 *m/z* has continued to be a challenge. This problem has become even more pronounced with the advent of cluster beams (e.g. Au_3, Bi_3, C_{60} and Ar gas cluster) which provide substantially improved yields for higher mass fragment ions. To overcome this shortcoming, Physical Electronics has developed a revolutionary TOF-SIMS tandem mass spec method specifically designed to unambiguously identify the composition of higher mass secondary ions [1]. The method allows for MS/MS spectra (MS^2) of select secondary ions of interest (precursor ions) to be acquired in parallel with conventional TOF-SIMS spectra (MS^1); both being simultaneously generated from the same analytical volume. The precursor ion, defined by a 1 Da selection window, is deflected from the MS^1 secondary ion stream into an argon filled high energy (1.5 keV) collision-induced-dissociation (CID) cell. In the CID cell, the precursor ions collide with argon atoms which results in partial fragmentation of the precursor ions. The precursor and its fragment ions are then accelerated into a linear TOF analyzer and recorded by a pulse-counting detector. In both the MS^1

and MS^2 data, a full mass spectrum is collected for each image pixel, with spatial resolutions in the tenths of a micrometer. As the MS^2 spectra are predominantly generated from single molecular ions, they are much cleaner and simpler than conventional MS^1 spectra which usually contain secondary ions from multiple chemical species. The MS/MS fragmentation spectrum (MS^2) is used to identify the composition of the precursor ion by either identification of the fragmented ions and/or comparison to spectra contained in on-line databases. Applications of this new method will be shown for a variety of materials including polymers, pharmaceuticals, tissue cross sections, and other organics.

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10:20am **TF-MoM8 Atomic Layer Deposition of Thin VO$_2$ Films to Enable Smart, Functional Coatings***, **Virginia Wheeler**, B. Downey, M. Currie, M. Tadjer, A. Kozen,* US Naval Research Laboratory, USA*; R. Bell, M. Thompson,* Cornell University, USA*; D. Meyer, F. Kub, C. Eddy Jr.,* US Naval Research Laboratory, USA

VO$_2$ is a phase change material that exhibits significant changes in thermal emittance, optical transmittance and reflectance, and intrinsic electrical properties due to a metal-insulator phase transition (MIT) at a critical temperature (T$_c$). Electrical and optical properties across the MIT are strongly reliant on microstructural characteristics which are dependent on deposition technique. While several different methods have been explored to deposit VO$_2$ films, atomic layer deposition (ALD) provides a way to obtain large area film uniformity, abrupt interfaces and angstrom-scale control of thickness conformally across planar and high surface area nanostructures. Thus, this method could be used to integrate VO$_2$ films into complex electronic and optical devices for additional functionality. Moreover, as-deposited films are amorphous which can be subsequently annealed to tailor the crystallinity and thus the MIT properties. Here, we will show the properties of amorphous and crystalline ALD VO$_2$ films and discuss their integration with other materials to achieve functional optical and electrical coatings.

Amorphous ALD VO$_2$ films were deposited at 150°C using TEMAV and ozone precursors. XPS revealed that beneath ~1nm of atmospheric contamination, there was no residual carbon impurities and only a single VO$_2$ peak was evident. Electrical measurements showed an exponential change in resistance of ten orders of magnitude from 77-500K, though no characteristic sharp transition was detected. This resulted in an average activation energy of -0.20eV and temperature coefficient of resistance of 2.39% at 310K.

To realize sharp MIT transitions, ALD VO$_2$ films were crystallized with an optimized ex-situ anneal at 650°C in 1.5x10^{-5} Torr of oxygen for 1-4hrs depending on film thickness. Electrical measurements showed that the R$_{off}$/R$_{on}$ ratio increased from 3.4 to 7083 as VO$_2$ thickness increased from 12 to 92nm. The T$_c$ also increased with increasing thickness, while all films exhibited relatively low hysteresis (<8°C). Temperature dependent near-IR measurements also show an increase in the change in reflectivity (up to 80%) and decrease in transmission (up to 60%) with film thickness.

ALD is a preferred method to deposit on soft materials due to its low deposition temperature. However, for VO$_2$ films, this benefit is negated by the higher anneal temperatures required for crystallization. To overcome this problem, laser annealing was investigated as an alternative crystallization approach. Initial results show that by varying the laser power one can tailor the local temperature within the VO$_2$ film to attain the required crystallinity without affecting the underlying substrate.

10:40am **TF-MoM9 Nitridation of High-k Dielectric Nanofilms through Remote Plasma***, J.A. Torres-Ochoa, **Alberto Herrera Gomez**,* CINVESTAV-Unidad Queretaro, México

The diffusion of indium and gallium through alumina,[1] hafnia[2] and zirconia[3] nanofilms has been well documented. Nitridation of the dielectric could represent a solution to this diffusion problem.[4] We found that nitridation of silica can be carried out at relatively low temperatures and in a substitutional fashion if remote-plasma is employed.[5] It saturates at a ratio of one nitrogen atom for three oxygen atoms.[5] We also found that the binding energy of N 1*s* for substitutional nitrogen in hafnia is ~ 398 eV. [6] We are carrying out a series of studies comparing the nitridation mechanism (i.e., substitutional vs interstitial) in high-k dielectric nanofilms under remote plasma. We compared the nitridation degree of 2 nm films of silica and hafnia under a certain conditions (power: 2,500 W, pressure: 4×10^{-2} Torr, temperature: 400 °C, time: 5 min). While the nitridation of silica reaches saturation (SiO$_{1.67}$N$_{0.46}$), the composition of hafnia changes from HfO$_2$ to HfO$_{1.8}$N$_{0.15}$. This suggest that nitrogen is incorporated in a substitutional manner. The binding energy of N 1*s* (399 eV) is about 1 eV higher that the value previously found;6 however, the O 1s peak is also shifted by the same amount, confirming the substitutional nature of the incorporation of nitrogen in hafnia.

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Biomaterial Surfaces & Interfaces
Room Milo - Session BI-MoE

Soft Surface & Biofunctional Coatings

Moderator: Duncan McGillivray, University of Auckland

5:40pm **BI-MoE1 Functionalisation of Polymeric Biomaterials by Graft Copolymerisation***, **Lisbeth Grondahl**,* The University of Queensland, Australia **INVITED**

The surface of a material is the first contact with the cellular environment upon inoculation (in vitro) or implantation (in vivo) and as such these surfaces must, at minimum, possess properties amenable to cell adhesion. However, many polymers used as biomaterials lack functional moieties and the overall hydrophobic nature of the polymers encourage non-specific protein adsorption and make them less than ideal for controlled protein attachment and hence directed cell attachment and expansion.

One method of changing the surface properties of polymeric biomaterials is graft copolymerisation of functional polymers thereby providing functional groups and/or reduced hydrophobicity to the material. Work will be presented on graft copolymerisation of both the biodegradable polymer polycaprolactone (PCL), an FDA approved aliphatic semicrystalline polyester studied extensively for tissue engineering, and the biostable polymer expanded polytetrafluoroethylene (ePTFE), used for example in facial reconstruction. The ability to modify the interior of scaffolds and membranes as well as introducing various functional groups (eg. phosphate, carboxylate and amine) will be illustrated. Recent studies on creation of dual functional materials will show how the approach taken (one-pot or consecutive grafting) affects the material properties.

Protein adsorption studies using albumin, lactoferrin and lysozyme illustrate that the surface density of carboxylate groups does not correlate to the amount of adsorbed protein rather a correlation to the degree of grafting was observed indicating penetration of the proteins into the grafted layers. Furthermore, the topology of the graft copolymer is shown to be more important than the functional group in regards to the outcome of in vitro mineralisation when comparing a series of phosphate and carboxylate functionalised surfaces.

6:20pm **BI-MoE3 Blood Compatibility Evaluation of Fluorinated Bioresorbable Polylactic Acid For Coronary Artery Stents***, **Razieh Khalifehzadeh**, B.D. Ratner,* University of Washington, USA

Bioresorbable stents are an emerging, novel treatment for improving long-term stent outcomes. Rigid metallic stents are associated with failure over time partly due to their permanent presence in vessel walls inhibiting physiologic vasomotion and stimulating neointimal hyperplasia. Among various polymers, poly(lactic acid) (PLA) has been extensively used for making bioresorbable stents. PLA undergoes degradation through hydrolysis of ester bonds. The degradation products are lactic acid and oligomers that later metabolize into CO_2 and water.

Despite the various long-term advantages of bioresorbable stents, their reported thrombosis is higher than metallic stents. In an attempt to improve blood compatibility of PLA, we used radio frequency glow discharge (RFGD) to modify the surface of this polymer with perfluoro compound. Fluoropolymers have been shown to lower thrombogenicity and platelet reactivity, and are extensively used in blood contacting materials.

Here, we have developed a process to coat the surface of PLA with perfluoro compound. Electron spectroscopy for chemical analysis (ESCA) was used to analyze the surface composition of these polymers. In addition, contact angle measurements, cell cytotoxicity, and degradation profile were evaluated.

Finally, we will assess the blood compatibility of these modified surfaces by using radiolabeled blood plasma proteins (albumin and fibrinogen) adsorbed onto their surface. The adsorption of plasma proteins is the central event in the biofouling of blood-contacting surfaces, which occurs immediately upon exposure of blood to biomaterial. We hypothesiz that tight binding of adsorbed albumin on fluoropolymers accounts for its success in blood-contacting applications.

6:40pm **BI-MoE4 Multifunctional Bionanotubular Implant Surfaces***, **Tolou Shokuhfar**,* University of Illinois at Chicago, USA

Bionanotubular surfaces offer exciting progress toward the design of multifunctional medical implants. To bring this to reality, we have synthesized and optimized the mechanical, physical, biocompatibility, and interfacial properties of titania nanotube surfaces using in-situ TEM, SEM, FIB, FTIR, and WCA measurements. We have observed that the fabrication of bionanotubular titania surfaces with elastic modulus close to actual bone promotes osteoblast growth and prevents stress shielding. In addition, bionanotubular titania surfaces could be considered a suitable alternative route for the development of drug-eluting and antimicrobial implants due to the fact that these nanostructures are not an added coating but rather are rooted in the implants and will not delaminate from the surface. Such drug-eluting implants can prevent unnecessary side effects caused by oral administration of drugs, increase drug efficiency, and prevent infection related implant complications and failures.

7:00pm **BI-MoE5 NAP-XPS and EnviroESCA – Surface Analysis Entering New Fields of Applications: XPS from Liquids and Solid-Liquid Interfaces***, **Thomas Schulmeyer**,* SPECS Surface Nano Analysis, Inc.

For decades XPS has been the well-accepted standard method for non-destructive chemical analysis of solid surfaces. To fulfill this task, existing XPS tools combine reliable quantitative chemical analysis with comfortable sample handling concepts integrated into fully automated compact designs.

Recently however, it has been possible to develop XPS systems that can work far beyond the standard of high or ultrahigh vacuum conditions. Near Ambient Pressure (NAP) XPS has become a rapidly growing field in research, inspiring many scientist to transfer the method to completely new fields of application. By crossing the pressure gap, new insights in complicated materials systems have become possible using either synchrotron radiation or laboratory X-ray monochromators as excitation sources under NAP conditions.

Based on this experience, SPECS Surface Nano Analysis GmbH has developed two lines of products: a portfolio of research instruments with various setups optimized for different applications of NAP-XPS, and EnviroESCA. Both of these revolutionary tools realize the long existing dream in many analytical laboratories: reproducible chemical surface analysis under any environmental condition. EnviroESCA^{TM} allows for different applications, such as extremely fast solid surface analysis of degassing (but also non-degassing) samples, XPS analysis of liquids or liquid-solid interfaces, chemical analysis of biological samples, materials and device analysis under working conditions (in situ/in operando studies of catalysts, electrochemical devices etc.).

In this presentation, the various basic designs showcasing their different applications are introduced. The results primarily show how measurements can be taken from liquids or solid/liquid interfaces, and the essential bits of information that can be derived from these measurements. The applications range from measurements on static and dynamic liquids, biological samples and fuel cells to in-operando measurements on electrodes under potential in static and dynamic electrochemical cells. For the first time, systematic XPS analysis from liquids is possible and evidenced. Thus, realistic opportunities as well as experimental challenges in liquid-XPS analysis will be discussed and summarized.

Nanomaterials
Room Hau - Session NM-MoE

Nanocatalysis

Moderator: Svitlana Pylypenko, Colorado School of Mines, USA

5:40pm **NM-MoE1 Electrocatalysis - Ensemble versus Single Nanoparticle Investigations***, **Kristina Tschulik**,* Ruhr-Univ. Bochum, Germany **INVITED**

Nanomaterials play a crucial role in catalysis thanks to their large surface-to-volume ratio and the possibility to adjust their electronic structure, i.e. reactivity. As it provides several promising routes to sustainable energy, electrocatalysis is a strongly expanding research topic to date. It provides a route to both, the production of sustainable fuels by water electrolysis or CO_2 reduction, and to their environmentally friendly utilization in hydrogen or alcohol fuel cells. The fact that these reactions occur at the solid liquid interface and that electronic and ionic charge carriers are involved, make the characterization of nano-electrocatalysts a challenging task. The overlapping effects of altered mass transport at nanoparticle modified surfaces and of changed electronic connection add to the changes in reaction kinetics. Hence, it is difficult to directly extract kinetic information from experimental data.

To overcome the obstacles of poor electronic conductivity and slow diffusional mass transport, nanomaterials are typically mixed with a conductive binder and thick films of this mixture are immobilized on rotating disc electrodes for electrocatalysis studies. However, this conventional procedure fails if porous films result or the influence of the binder material is not known. Thus, new methods for binder-free electrocatalyst characterization are being developed to enable fast and reliable electrochemical characterization of new catalyst materials. Two new approaches are presented that facility binder-free testing of electrocatalysts either using (sub-)monolayer films of nanomaterials [1] or single nanoparticle impact studies. In the first case, ensembles of nanoparticles on an electrode are produced [1], while the latter approach utilizes the Brownian motion based impacts of nanoparticles at an electrode to study their [2] electrocatalytic performance [2]. Both methodologies avoid thick films and convection. Hence, conductivity effects are minimized, while changes in the mass transport of reactants can be quantified using numerical simulations of the diffusional processes at nanoparticle modified electrodes. Accounting for these overlapping effects, the experimental electrochemical response during electrochemical reduction of CO_2, O_2 or H^+, can be deconvoluted to reveal the true kinetic performance of novel catalysts. These methods may thus enable a more rational design and testing of new catalyst materials in the future.

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6:20pm **NM-MoE3 Formation and Migration of a Au-CO Complex in Gold-assisted Catalysis***, **Monica McEntee**,* University of Virginia, USA*; J. Wang,* Oak Ridge National Laboratory, USA*; W. Tang, M. Neurock,* University of Virginia, USA*; A.P. Baddorf, P. Maksymovych,* Oak Ridge National Laboratory, USA*; J.T. Yates, Jr.,* University of Virginia, USA

Fabrication of highly active, stable and selective nanocatalysts requires an understanding of the mechanisms that control charge transfer and the activation of adsorbate interactions at specific surface sites. Here I report on the nature of low coordinated Au sites (likely to be on Au nanoparticles) by creating nano-pits on a Au (111) single crystal surface using scanning tunneling microscopy (STM). At room temperature, CO molecules adsorb on Au atoms and form Au-CO complexes, which allow for Au atom extraction from dislocation sites of the herringbone reconstruction. These complexes migrate and form Au clusters on elbows and edges of the Au surface. In conjunction with STM, transmission infrared (IR) spectroscopy and density functional theory (DFT) calculations were used to understand this new mechanistic motif. The mechanism for the Au atom extraction involves electron transfer from CO to Au forming positive charge on CO that creates stronger bonding with Au atoms of lower coordination number. Nanocatalysts involving Au nanoparticles with an abundance of low coordinated Au sites likely exhibit similar properties and these studies could foster future enhanced catalysts.

6:40pm **NM-MoE4 Advanced Nanostructures as Electrocatalysts for Energy Applications***, **Vojislav Stamenkovic**,* Argonne National Laboratory, USA

Electrocatalysis is a subclass of heterogeneous catalysis that is aimed towards increase of the electrochemical reaction rates that are taking place at the surfaces. Real-world electrocatalysts are usually based on precious metals in the form of nanoparticles due to their high surface-to-volume ratio, which enables better utilization of employed materials. Ability to tailor nanostructure of an electrocatalyst is critical in order to tune their electrocatalytic properties. Over the last decade, that has mainly been achieved through implementation of fundamental studies performed on well-defined extended surfaces with distinct single crystalline and polycrystalline structures. Based on these studies, it has been demonstrated that performance of an electrocatalyst could be significantly changed through the control of size, composition, morphology and architecture of employed nanomaterials. This presentation will outline the most important in development of an efficient electrocatalyst: 1) electrochemical properties of well-defined surfaces, 2) synthesis and characterization of different electrocatalysts, and 3) correlation between physical properties (size, shape, composition and morphology) and electrochemical behavior (activity and durability). In addition, a novel research platform in the development of functional nanomaterials for energy conversion and storage applications such as fuel cells electrolyzers and batteries will also be presented.

Besides activity, our results have demonstrated that durability of an electrocatalyst can also be tailored by manipulating the catalyst structure. For instance, in order to address this issue a core-shell electrocatalyst where an Au core was coated by a multilayered MPt_3 shell was developed. Such core-shell Au/MPt_3 electrocatalysts showed negligible activity loss after 60,000 cycles between 0.6 – 1.1 V (vs. RHE). In the most recent example, an entire gold core was replaced by Ni core which was coated by gold and then encapsulated by Pt-bimetallic shell, creating a core-interlayer-shell structure with unique electrochemical properties. In addition, a highly functional hollow type multimetallic structures will be discussed as efficient electrocatalysts for oxygen reduction, hydrogen oxidation and evolution reactions.

Common ground for all systems relies on distinguished approach that includes collection of fundamental knowledge from well-defined highly crystalline systems and connects them to the real world nanomaterials.

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7:00pm **NM-MoE5 Metal Nanoparticles Intercalated in Mesoporous Silica as Robust Catalyst Platforms***, **Ryan Richards**, S. Gage, Y. Ji, M. Menart, M. Davidson, S. Pylypenko, B. Trewyn,* Colorado School of Mines, USA

Metal nanoparticles have been in the research spotlight for decades for their activity as efficient and highly selective heterogeneous catalysts. Similar to many nanoscale metal particles, the catalytic activity of for example Pd and Au NPs also depends on particle size. At high temperatures however the particles often undergo aggregation and sintering resulting in an increase in particle size and a corresponding loss in activity. In order impart robustness to Pd and Au NPs catalysts, supporting NPs on another material is a common approach. Amongst support materials, silica is attractive for its relative chemical inertness and thermal stability. Here, we present a sol-gel process by which we intercalated Pd and Au into the wall framework of mesoporous silica yielding a catalytic material termed PdMS or GMS here (Pd or Au in the walls of mesoporous silica). The PdMS material has been shown to be stable (maintaining both porous silica framework and Pd nanoparticle size) at temperatures as high as 650 °C making them attractive for high temperature processes.

7:40pm **NM-MoE7 Development of Noble-metal Free and Durable Nanoporous Catalysts for Exhaust-Gas Conversion***, **Takeshi Fujita**,* Tohoku University, Japan

Precious metals (Pt and Pd) are typical materials for heterogeneous exhaust-gas catalysts in automotive systems. During a catalytic reaction in conventional nanoparticulate systems, such as Pt, active nanoparticles (typically less than 5 nm) aggregate, resulting in a significant reduction of performance. In addition, their limited resources and high market-driven prices are principal issues in realizing the path toward a more sustainable society.

Herein, we developed an earth-abundant nanoporous NiCuMnO catalyst by leaching Mn from a CuNiMn precursor. The developed catalyst was catalytically active and durable for NO reduction and CO oxidation. During catalytic reactions, the nanostructure self-transformed into a more active nanostructure; in particular, the Cu/CuO regions derived from the nanostructure were very active, and further significant coarsening was not observed without the loss of activity, as these regions were tangled with a stable nanoporous NiMnO network. The self-transformed nanostructure successfully completed a long-term durability test for NO reduction at 400 °C for 10 days. The *in situ* TEM under NO reduction clearly provided evidence for the instant reaction-induced self-transformation of the nanostructure. This result demonstrates an important implication of this work: even when nanoporous alloys are coarsened to significantly greater than 100 nm, as long as the metal phase is entangled and sustained within a stable nanoporous network of oxides, geometrically necessary surface defects can be retained as catalytically active sites and further enhanced catalytic performance exhibited because of the metal-oxide interfaces (i.e. perimeter); thus, catalytic activity can be retained with durability.

Although the nanoporous NiCuMnO catalyst requires more improvement at low temperatures, the temperature of the catalyst bed in an automobile system is typically higher than 400 °C, where nanoparticles become significantly unstable. Production of the nanoporous catalysts can be easily scaled up, and they may be a rational alternative to traditional precious-metal catalysts for automotive systems in the near future [1].

References

[1] T. Fujita *et al.*, Adv. Func. Mater. **26** (2016) 1609-1616.

8:00pm **NM-MoE8 Atomic Layer Deposition of MoS_2 Catalyst for Electrochemical Hydrogen Evolution Reaction***, Z. Jin, S. Shin,* ***Yo-Sep Min,*** Konkuk University, Republic of Korea

Atomic layer deposition (ALD) has emerged as a useful tool for design and synthesis of catalysts with atomic scale precision owing to its self-limiting growth mechanism. Here, we report ALD of MoS_2 which has attracted great attention as an electrocatalyst for hydrogen evolution reaction (HER). MoS_2 catalysts are grown at 100 ^oC using molybdenum hexacarbonyl and dimethyldisulfide as precursors of Mo and S, respectively. The crystallographic phases of the catalysts grown at 100 ^oC by ALD depend on the selection of a supporting substrate. The ALD-MoS_2 is amorphous on Au but a mixture of amorphous and nano-crystalline phases on carbon fiber paper (CFP). The most important advantage of the ALD-MoS_2 is its high turnover frequency for the HER, and the electrocatalytic performance of the ALD-MoS_2 can be improved by choosing a porous supporting substrate of CFP with a large specific surface area. To unveil the inherent activity of the ALD-MoS_2, we discuss the effects of chemical states and crystallographic phases of MoS_2 on the electrocatalytic activity.

Thin Films
Room Mauka - Session TF-MoE

Nanostructured Surfaces & Thin Films I

Moderator: Alberto Herrera Gomez, CINVESTAV-Unidad Queretaro, Mexico

5:40pm **TF-MoE1 Reducing Losses In Magnetic Thin Films by Surface Patterning***,* ***Goran Rasic****, BV. Vlahovic,* North Carolina Central University, USA*; J. Schwartz,* North Carolina State University, USA

As technology advances the demand for smaller and faster devices with reduced power losses becomes increasingly important. For high-frequency devices, such as antenna and sensors, two loss mechanisms are relevant, electrical and magnetic. Electrical losses are reduced by forming laminate structures and/or choosing materials with high electrical resistivity. Magnetic losses, however, arise from the magnetic hysteresis of the material, and thus are intrinsic. At frequencies above 1 GHz, these losses become immense. To reduce magnetic losses, the hysteresis losses must be reduced without losing desirable magnetic properties; reduced coercivity is needed, while retaining high saturation magnetization.

Textured nickel ferrite ($NiFe_2O_4$) thin films were deposited onto a c-plane sapphire substrate using chemical solution deposition. Surface of the films was patterned with a polydimethylsiloxane (PDMS) stamp using a modified nanoimprint lithography technique. A series of pattern masters with periods ranging from 500 nm to 1500 nm was used for patterning. In addition, samples with different thicknesses were prepared. Atomic force microscopy showed that the pattern was faithfully copied from the pattern masters to the thin films. X-Ray diffraction revealed all samples to be textured single phase inverse spinel nickel ferrite with preferential orientation along the <111> easy axis direction. Magnetic measurements showed the magnetic field response in the patterned samples to be unchanged as compared to plain samples, indicating there was no loss in magnetic properties. Similarly, the patterned samples showed appreciable and consistent saturation magnetization values. The coercivity of all samples showed significant reduction as compared to the plain samples. In addition, two distinct regimes were identified. For the out-of-plane measurements, the coercivity reduction increases with increasing feature size, whereas for the in-plane measurements the opposite is observed. These polar trends for the in-plane and out-of-plane measurements allow us to further fine tune the material for specific applications by not only controlling the feature size but also the orientation of the film with respect to the field. Finally, the origin of the coercivity reduction was shown to be the surface morphology anisotropy by MFM measurements. Magnetic domains were shown to be strongly affected by the surface features and oppositely oriented, reducing magnetostatic energy and leading to coercivity reduction. These results, in combination with the theoretical investigation, confirmed the origin of the coercivity reduction to be a direct consequence of altered surface topography.

6:00pm **TF-MoE2 Orientational Control of Polar Molecules in Macroporous Systems and their Dielectric Properties***,* ***Ryosuke Yamamoto****, N. Kimizuka,* Kyushu University, Japan

Organic ferroelectric materials have been attracting much interest as a new family of memory materials that operate under lower electric field. However to date, most of the reported organic ferroelectric materials are solid and they show dielectric hysteresis only in the presence of high electric field. Accordingly, there is a compelling need for new dielectric materials working at a lower electric field and ambient temperature. In this light, we have focused on supramolecular gels as organic soft dielectric materials. Gelator molecules were dissolved in solvents with large dipole moment such as nitrobenzene by heating and succeeding cooling of the mixture afforded organogels. In the electron microscopes (SEM, TEM) observations, extended nanofibrous aggregates were abundantly observed for the dried gel. In this gel, polar solvent molecules are confined and their molecular motion are expected to be limited since they interact with fibrous gel networks which contain extended hydrogen bonding networks. Thus, the dielectric properties of these supramolecular gels were investigated systematically. The gels showed increase in the magnitude of polarization with distinctive polarization-electric field hysteresis loop, though such hysteresis was not observed for the polar solvents without gelators. In addition, in contrast to the gels formed with polar solvents, gels formed with non-polar solvents didn’t show the hysteresis loop. From these findings, confinement of polar solvent molecules in the suramolecular gel fiber networks play an important role to control mobility of solvent molecules, thus leading to orientational polarization.

To better understand this confinement effect and to generalize the approach, we employed porous polymer films with controlled pore-size as matrixes. Dielectric properties of polar molecules introduced into these porous polymer systems were investigated, which show similar hysteresis. We also found that polar molecules trapped in the different pore-sized polymer films showed distinct phase transition and dielectric behaviors. From these observations, it is suggested that polar molecules in the pores exert interactions with the pore surfaces and accordingly, their orientation is maintained even after cutting off the electric field. Furthermore, this system works at low electric fields. We believe that our approach would provide a new concept to design soft ferroelectrics.

6:20pm **TF-MoE3 Control and Understand the Impacts of Nano and Microstructures on Perovskite Solar Cell Performance***,* ***Guozhong Cao,*** University of Washington, USA **INVITED**

Organometallic halide perovskite materials have a variety of remarkable optoelectronic properties, such as suitable band gap (1.5eV), high absorption coefficient, long carrier diffusion lengths and lifetimes. All these unique characters pave the way for perovskite-based devices, especially the photovoltaic cells. Its conversion efficiency have surged to 20.1% in several years and perovskite solar cells have been viewed as the new generation high efficiency thin-film cells at low cost. This presentation will include (1) study of charge transfer and surface potential as a function of surface morphology of TiO_2 compact layer, (2) control the morphology of TiO_2 compact layer, and (3) control of the perovskite film morphology with the specifics detailed below.

The variation of the surface potential, photo-generated voltage, and photocurrent networks of the perovskite solar cells (PSCs) with different film topography has been studied by coupling scanning Kelvin probe force microscopy (SKPM) and photoconductive atomic force microscopy (pcAFM). These results suggest that the performance of PSCs can be improved through better control of morphology.

A series of TiO_2 compact films was prepared by sol-gel method with different sol aging time resulting in change of, thickness, surface roughness and compactness. High roughness of the films benefits the light absorption of perovskite layer and the injection efficiency at interface. The films with better compactness perform better hole blocking effect. The Ag@TiO_2 nanoparticles made by polyol solution method are embedded in perovskite films, resulting in an enhanced short-circuit current density due better light absorption and reduced charge recombination.

CH_3NH_3Cl was introduced into the pristine $CH_3NH_3PbI_3$ precursor for antisolvent precipitation at low temperature and fabricated high quality perovskite films with desired morphology, crystallinity and optical properties. CH_3NH_3Cl exerted significant impacts on the perovskite crystallization process by controlling the delivery speed of PbI_2 from the intermediate phase $CH_3NH_3I_2Cl$. The resultant solar cells demonstrated an average power conversion efficiency around 16.63% and a best efficiency at 17.22% under the standard light illumination condition.

7:00pm **TF-MoE5 Atomic Layer Deposition of Al_2O_3 films on Various Two-Dimensional Materials***, **Taejin Park**,* Samsung Electronics, Republic of Korea*; H.J. Kim, M. Lim, W.S. Ahn, S.H. Choi,* Sungkyunkwan University, Korea, Republic of Korea*; J.B. Kim, J. Uh, B.S. Kim, Y.S. Hwang, H.S. Hong,* Samsung Electronics, Republic of Korea*; S.J. Jeong, S.J. Park,* Samsung Advanced Institute of Technology, Republic of Korea*; Y.S. Kim, H.S. Kim,* Sungkyunkwan University, Korea, Republic of Korea

The atomic layer deposition (ALD) of high-*k* films usually fails on two dimensional (2D) materials due to the absence of dangling bonds on their surface, which only allows physisorption of a precursor that can be easily detached *via* thermal desorption [1].

In this presentation, the surface coverage of the ALD-Al_2O_3 films on various 2D flakes (MoS_2, WS_2, WSe_2, and *h*-BN) was examined as a function of the substrate temperature to extract the adsorption energy (E_{ads}) of a trimethyl-aluminum (TMA) precursor . The film coverage exhibited a strong dependence on the ALD temperature and the 2D substrate. The E_{ads} values of TMA on various 2D material surfaces were experimentally determined using the measured film coverage after 10-cycled ALD at different temperatures. The E_{ads} values were in the range of 0.05-0.26 eV, which corresponded to the values for van der Waals physisorption and could be well explained by different induced dipole polarizability of 2D materials.

[1] H. Liu *et al*., Appl. Phys. Lett. **100**, 152115 (2012).

7:40pm **TF-MoE7 Self-Assembled Monolayers of Alkynes on Au (111) – Structure and Stability***, T. Żaba,* Jagiellonian UnUniversity, Poland*; A. Noworolska, J. Ossowski,* Jagiellonian University, Poland*; C.M. Bowers,* Harvard University, USA*; A. Krzykawska,* Jagiellonian University, Poland*; G.M. Whitesides,* Harvard University, USA*; **Piotr Cyganik**,* Jagiellonian University, Poland

Self-assembled monolayers (SAMs) of *n*-alkynes ($HC{\equiv}C(CH_2)_nCH_3$, n = 5, 7, 9, and 11) on Au(111) were prepared at elevated temperatures (60^oC), and characterized with scanning tunneling microscopy (STM), infra-red reflection absorption spectroscopy (IRRAS), X-ray photoelectron spectroscopy (XPS), secondary ion mass spectrometry (SIMS), and contact angles of water. In contrast to previous spectroscopic studies, our microscopic and spectroscopic experiments confirm the formation of highly-ordered SAMs having structure, packing density, and molecular chain orientation that is similar to those of alkanethiols on Au(111). The preparation of high-quality SAMs from alkynes requires careful preparation and manipulation of the reactants in a rigorously oxygen-free environment: trace quantities of oxygen lead to oxidized contaminants and disordered surface films. Once formed, the high-quality SAMs of alkynes are resistant to further oxidation in ambient conditions. We demonstrated that SAMs of alkynes are more stable than analogous alkanethiols by performing exchange experiments and monitoring the effects of thermal desorption. Following our recent methodology based on SIMS, the relative stability of chemical bonds at the molecule-substrate interface of alkynes and thiols was also analyzed. Our study indicates that the stability of alkynes on Au(111), together with their high structural order, provides the basis for potential applications of this new type of SAM.

8:00pm **TF-MoE8 Crystal Growth Simulation of ZnO Thin Film on α-Al_2O_3 Substrate by Molecular Dynamics Simulation***, **Shunsuke Kawagishi**, J. Xu, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, M. Kubo,* Tohoku University, Japan

A ZnO thin-film semiconductor is used as light emitting devices and quantum hall effect devices because of its broad wide band gap of 3.2 eV and large exciton binding energy of 60 meV. In the previous research, optical properties of the ZnO thin film depend on the crystal orientation and quality [1]. Therefore, in order to obtain the high-quality thin film, it is necessary to understand crystal growth process such as physical vapor deposition. However, it is difficult to observe the crystal growth process at atomic scale by experiments. In this study, to elucidate the crystal growth process of ZnO, we performed crystal growth simulation of a ZnO thin film on an α-Al_2O_3 substrate by our molecular dynamics simulator and analyzed crystal quality of the formed ZnO thin film.

At first, to investigate crystal growth process of the ZnO thin film, we irradiated ZnO molecules on an α-Al_2O_3(0001)substrate at a velocity of 900 m/s at 700, 900, and 1200 K. The ZnO thin films are formed on the substrate at 700, 900, and 1200 K. Next, to evaluate crystal quality of the formed ZnO thin films, we analyzed radial distribution function of the formed thin films. The first and second peaks of the radial distribution function at 1200 K are sharper than those at 700 and 900 K. This indicates that crystallinity of the formed thin film at 1200K is higher than that at 700 and 900 K. Our simulation result is in good agreement with the experimental result in which crystal quality is improved by increasing the substrate temperature [2]. Next, we investigated the atomic behavior in the growth process. At only 1200 K, some of the irradiated ZnO molecules dissociate on the thin film. Then, the Zn and O atoms diffuse into the formed thin film. Finally, 6-membered rings are formed by diffusion of the Zn and O atoms in the formed thin film. This indicates that atomic mobility of the Zn and O atoms on the substrate is promoted due to raising substrate temperature and this high mobility of the Zn and O atoms contributes to the quality of the formed thin film. Thus, we succeeded in crystal growth simulation of a ZnO thin film on an α-Al_2O_3 substrate and found difference in the growth process of the thin film at 700, 900, and 1200 K.

[1] S. Dutta et al., Progress in Materials Science, 54, 89-136 (2009).

[2] A. El-shaer et al., Superlattices and Microstructures, 38, 265-271 (2005).

8:20pm **TF-MoE9 Nucleation and Aggregation of Nanoparticles during Atomic Layer Deposition on High-Surface-Area Substrates***, **Fabio Grillo**, H. Van Bui,* Delft University of Technology,The Netherlands*; J.R. van Ommen,* Delft University of Technology, The Netherlands

Atomic layer deposition (ALD) is proving to be an attractive technique for depositing nanoparticles (NPs) in a controlled fashion. By relying on self-limiting surface reactions, ALD lends itself to the decoration of high-surface-area substrates with NPs for various applications such as enhanced catalysts and batteries. However, the mechanisms underlying the nucleation and growth of NPs during ALD are still poorly understood. Understanding the evolution of the particle size distribution of NPs during ALD is essential for fabricating supported NPs with predictable morphology and functionality. ALD growth is generally explained in terms of self-limited layer-by-layer growth, and although such picture applies to the deposition of a variety of metal oxides, especially at low temperature, it does not apply to the nucleation and growth of metal NPs. In fact, the evolution of the particle size distribution (PSD) of NPs is governed by kinetic processes such as surface diffusion, aggregation and coalescence. Here, we study the evolution of the PSD of Pt and Pd NPs deposited in time scales relevant to thermal ALD based on oxidative chemistries on high-surface-area substrates. To unravel the relevant processes underlying the evolution of the shape of the PSD, we devise a kinetic model based on the Smoluchowski equation that incorporates the generation of adatoms on both the substrate and the pre-existing NPs due to surface reactions, surface diffusion, adatom capture and NP aggregation. In doing so, we show that, during the first cycles, NP growth proceeds mostly due to NP diffusion and coalescence. The evolution of the PSD during dedicated sintering experiments of the ALD-grown NPs suggests that NPs aggregation takes place mostly during the oxygen exposure. In fact, the oxygen exposure not only regenerates the active surface for the subsequent precursor exposure but also mediates the metal-support interaction. Finally, we show that by varying the deposition temperature, while adjusting the exposure times to retain saturation conditions, the determining mechanism for NPs growth shifts from accretion due single-atom capture, at low temperatures (T<100 °C), to NPs diffusion and coalescence at high temperatures (T>150 °C). The insights obtained in this study open up new avenues to the rational design of novel composite materials based on supported metals NPs.

8:40pm **TF-MoE10 Tight-Binding Quantum Chemical Molecular Dynamics Simulation on Water Lubrication Mechanism of Silicon Nitride***, **Jun Chida**, N. Takahashi, Y. Wang, Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, K. Adachi, M. Kubo,* Tohoku University, Japan

Silicon nitride (Si_3N_4) is used as a low friction material under water lubrication. It is suggested that the low friction is caused by the $SiO_2\cdot n(H_2O)$ (silica gel) layer generated by chemical reactions between the Si_3N_4 and the water at a friction interface [1]. Thus, the understanding of formation mechanisms of the silica gel is required to improve the friction properties. However, it is difficult to directly observe the chemical reaction dynamics at atomic scale by experiments. In this work, we investigated the formation mechanism of the silica gel by our tight-binding quantum chemical molecule dynamics simulator [2].

We performed the sliding simulation of Si_3N_4 under water lubrication. The simulation model consists of two amorphous Si_3N_4 substrates and H_2O molecules. The top of the upper substrate was slid by 100 m/s with a load of 3 GPa. The Si atoms and the N atoms on the surfaces were terminated by OH groups and H atoms, respectively.

First, we employed the flat substrate model. During the friction simulation, an H atom of a Si-OH bond on the Si_3N_4 surface transferred to a nearby N atom. Then, the O atom of the Si-O bond approached another Si atom in the surface, and a Si-O-Si bond was generated. The Si-OH groups changed to the Si-O-Si groups at the friction interface. This process leads to the formation of Si-O-Si bond network which is the main component of the silica gel.

Next, in order to reveal the influence of surface roughness on the formation mechanism of the silica gel, we employed the Si_3N_4 substrates with a rough surface. During the friction simulation, the Si-O-Si bonds were generated on the surface of the convex parts, as observed in the simulation with the flat substrates. When the two convex parts collided, the chemical bonds were generated between the two substrates. Then, the convex part of the lower substrate combined with the upper substrate was scraped off. H_2O molecules dissociated and adsorbed on a newly generated surface to saturate the dangling bonds. Finally, the flat Si-O-Si chain was formed on the surface. This result indicates that the collision of the convex parts leads to the formation of the flat Si-O-Si bond network.

In this work, we found that the Si-O-Si network, which is the main component of silica gel, is generated at the friction interface of Si_3N_4 by the chemical reaction of the Si-OH groups and the collision of the convex parts. Remarkably, the flat Si-O-Si network was formed after the scraping the convex parts.

[1] M. Chen et al., Tribol. Lett. 11 (2001) 23.

[2] K. Hayashi, M. Kubo et al., *J. Phys. Chem. C*, 115, 22981-22986 (2011).

Biomaterial Surfaces & Interfaces
Room Milo - Session BI-TuM

Bioimaging & Bionanotechnology

Moderator: Sally L. McArthur, Swinburne University, Australia

8:20am **BI-TuM2 ToF-SIMS Imaging for Nano-Bio Applications*, Tae G. Lee,*** Korea Research Instutue of Standards and Science (KRISS), Republic of Korea **INVITED**

Although the collisional cascade process in ToF-SIMS is unable to produce secondary ions with a molecular weight of over m/z 2,000 without the use of noble metals or special matrixes, time-of-flight secondary ion mass spectrometry (TOF-SIMS) imaging is a powerful technique for producing chemical images of small biomolecules (ex. metabolites, lipids, peptides) “as received” because of its high molecular specificity, high surface sensitivity, and submicron spatial resolution. For large biomolecules, matrix-assisted laser desorption/ionization mass spectrometry (MALDI-MS) has been used for molecular identification of proteins in the discovery of disease-related biomarkers as a key platform technique in proteomics.

For this talk, I will show that the label-free ToF-SIMS imaging technique can be a platform technology for characterization of organic-conjugated nanoparticles, disease diagnosis and drug screening. In addition, I will discuss the potential capability of Ar-cluster SIMS to study omics, particularly proteomics and lipidomics for brain studies.

9:00am **BI-TuM4 Label-Free Imaging of Biological Tissue with Micron Spatial and 240k Mass Resolution using a New Sims Hybrid Mass Analyzer*, Nathan Havercroft,*** ION-TOF USA, Inc.*; A. Pirkl, R. Moellers, H. Arlinghaus, F. Kollmer, E. Niehuis,* ION-TOF GmbH, Germany*; A. Makarov, S. Horning,* Thermo Fisher Scientific, Germany*; M.K. Passarelli, R. Havelund, P. Rakowska, A. Race, A.G. Shard,* National Physical Laboratory, UK*; A. West, P.S. Marshall, C.F. Newman,* GlaxoSmithKline, UK*; M.R. Alexander,* University of Nottingham, UK*; C.T. Dollery,* GlaxoSmithKline, UK*; I.S. Gilmore,* National Physical Laboratory, UK

Time-of-flight secondary ion mass spectrometry (TOF-SIMS) is an established, highly sensitive analytical technique for mass spectrometry (MS) imaging applications with a lateral resolution below 100 nm. Application of this technique for the localization of drugs and their metabolites in drug-doped cells could be used to find regions in which a pharmaceutical compound accumulates. This information would be extremely helpful for selection of possible drug candidates in pre-clinical studies, thereby reducing the development costs for new pharmaceutical products. Furthermore, surveying biologically relevant molecules, such as lipids, in tissue can give valuable information on the molecular fundamentals of diseases and the effects of treatments.

However, in complex biological samples identification of unknown compounds can be hampered by mass interferences and a high number of possible assignments for a single mass peak. In order to overcome these limitations, the 3D nanoSIMS project [1] is developing a revolutionary new SIMS instrument that combines the high lateral resolution and speed associated with TOF-SIMS (TOF.SIMS 5, ION-TOF GmbH, Muenster, Germany) with the high mass resolution and high mass accuracy of an orbital trapping mass analyzer (QExactive^{TM} HF [2], Thermo Fisher Scientific^{TM}, Bremen, Germany). The instrument is equipped with a newly developed gas cluster ion beam column which provides the capability to image with a lateral resolution down to the micron level with minimum sub-surface damage. In this contribution we will report about results obtained from different biological application areas such as tissue imaging, lipidomics, and single cell analysis. From coronal mouse brain tissue slices, we fully separate the (3'-sulfo)Gal-Cer(d18:1/24:1(2-OH)) and (3'-sulfo)Gal-Cer(d18:1/25:0) sulfatides, which reveals a difference in spatial distribution. In the low mass region, mass resolving powers of >400,000 are achieved allowing clear separation of the low abundance metabolite dopamine from other peaks, which has not been possible before.

Analyzing NR8383 cells, we show the ability to image the drug amiodarone with sub-cellular resolution and show that the mass spectra are not affected by sample topography.

Furthermore the MS/MS capability of the QExactive Instrument is used to confirm proposed assignments on tissue and from single cells.

[1] The 3D nanoSIMS project, http://www.npl.co.uk/news/3d-nanosims-label-free-molecular-imaging

[2] Scheltema, et al. Mol Cell Proteomics (2014).

9:20am **BI-TuM5 Advancing our Understanding of Tumor Biology with Imaging Time-Of-Flight Secondary Ion Mass Spectrometry (ToF-SIMS)*, Lara Gamble*,** *D.J. Graham, B. Bluestein,* University of Washington, USA

Imaging time-of-flight secondary ion mass spectrometry (ToF-SIMS) can provide images of tissues with chemical and molecular specificity. These chemically specific images can improve our understanding of biological processes. Our current research has utilized this technique to map the chemical changes in the composition and distribution of metabolic related molecules within a tumor and the tumor microenvironment in order to study tumor development and progression in inducible and regressible mouse pancreatic β-cell neoplasia. Using ToF-SIMS, the chemistry of tumor microenvironments and lipid metabolomics relationship to cancer and tissue can be visualized on a cellular and sub-cellular level. Samples mounted on ITO substrates can be analyzed with ToF-SIMS and directly correlated with immunohistochemical and/or H&E images taken on the same sample. Imaging principal component analysis (PCA) is used to identify chemical regions that correlate with the tumor and the surrounding tumor environment. Preliminary results using PCA analysis of ToF-SIMS image data easily separate the tumor chemistry from the surrounding tissue within the first principal component. Differences in chemistry between the tumor and surrounding tissue suggest a preferential uptake of fatty acids 18:3, 18:2 within the tumor. The data shows an absence of Mg^+ within the islet tumor and small, higher signal regions on the periphery of the tumor that correlate with increased CN^-, CNO^-, $C_7H_{10}O^+$, and Fe^+ ToF-SIMS peaks. This work demonstrates the high resolution capability of ToF-SIMS as the data clearly reveals intratumor chemical heterogeneity as localized high intensity regions for specific chemical signatures. It also highlights the utility of acquiring ToF-SIMS images and traditional H&E images on the same sample.

9:40am **BI-TuM6 Multi-stain Live Confocal Microscopy of *Balanus Amphitrite* Provides New Insight on Interfacial Processes*, Kenan Fears*,** *C. So,* US Naval Research Laboratory, USA*; B. Orihuela, D. Rittschof,* Duke University, USA*; K. Wahl,* US Naval Research Laboratory, USA

The adhesion of hard foulers (e.g., barnacles and tubeworms) has plagued the maritime community for as long as mankind has been setting sail. Since the biological processes responsible for adhesion occur at buried interfaces, elucidating the mechanisms by which foulers adhere is challenging. Through the use of multiple fluorescent probes, peptides, and antibodies, we have been able to discern an unprecedented level of detail about biological processes that occur at the interface between acorn barnacles (Balanus Amphitrite) and the underlying substratum during the barnacle growth cycle. Barnacles secrete a lipidaceous substance around the outside of their shell, prior to expansion that dislodges microorganisms and biofilms to present a cleaned surface. During molting, epithelia cells build a new interfacial cuticular layer, which becomes autofluorescent as it is sclerotized, above the existing cuticle whose degradation coincides with the exuviation of the main body's cuticle. Rather than being directly secreted onto the substrate, nanostructured barnacle cement accumulates in the space in between the new and old cuticle. As the barnacle expands, the cuticular layers are stretched and pulled around the outside of the side plate. The strain causes the old cuticle to randomly tear, allowing the new cuticle to deposit cement into the interface as it is dragged across the substrate. Furthermore, antibody staining allowed us to spatially and temporally identify where different cement proteins are presenet. These results illustrate that the methodologies we have developed to break down and analyze barnacle cement collection are yielding a more accurate representation of the proteins at the buried interface, and providing insight on their roles which will lead to improved strategies to both combat and mimic barnacle adhesives.

10:20am **BI-TuM8 Nanodiamonds for Targeted Biolabeling*, Olga Shimoni,*** *K. Bray, L. Cheung, I. Aharonovich,* University of Technology Sydney, Australia

In the last decade, nanodiamonds (NDs) have attracted much interest from the biological community as the ultimate agent for biomedical applications, such as biomarkers, drug and gene delivery and biocatalysts, owing to their chemical inertness, biocompatibility, prolonged photostability and negligible toxicity. Their fluorescence emanates from point defects (centres) that possess an unprecedented photostability and exhibit visible emission at room temperature. One of the most well-known centres is nitrogen-vacancy (NV) defects, mostly because of its potential use in quantum computer and nanomagnetometry applications. Here, we will demonstrate the utilisation of commercially available NDs with NV centres and in-house fabricated NDs with silicon-vacancy (SiV) defects for application in bio-imaging. We will discuss their optical properties, luminescence differences and opportunities for fluorescence enhancement. An additional advantage of using NDs in bio-imaging is that they are purely made of carbon, and carbon can be readily modified with functional groups to attach biomolecules using standard organic chemistry procedures. Therefore, we demonstrate surface functionalisation of NDs to achieve selective intracellular targeting. In summary, our results bring new advancement in fabrication and utilisation of NDs as targeted biomarkers.

10:40am **BI-TuM9 Encapsulation of Selected Natural Novel Nutraceutical Biomolecules**, ***Selim Kermasha,*** McGill University, Canada*; S. Karboune,* McGill Universit, Canada

Although there is an increasing interest in the development of novel natural nutraceuticals, it is important to ensure their preservation and delivery by their encapsulation, a technology that is gaining popularity in the food industry. The encapsulation of selected nutraceuticals, including enzymatically-synthesized phenolic lipids and self-assembly polymers of proteins and polysaccharides, was carried out. Our research group succeeded in the production of novel biomolecules of high nutritional value and antioxidant capacity, phenolic lipids (PLs), by a biotechnological process involving the esterification of selected phenolic acid models and endogenous edible oils. The encapsulation of PLs was carried out by the development of a process to yield gelatin-gum Arabic multinuclear microcapsules, via complex coacervation. The overall experimental findings indicated that the microencapsulation of PLs was effective for preventing their oxidation and hence by maintaining their antioxidant potential. On the other hand, the self-assembly of selected proteins (patatin and lysozyme)/polysaccharides (galactan, gum Arabic and xanthan gum)-based nanoparticles was investigated. The results indicated that the nanoparticles have spherical shape and their sizes were dependant on the pH and the molar ratio of protein to polysaccharide. Through the zeta (ζ) potential measurements, the formation mechanism of amphoteric patatin/xanthan gum and lysozyme/galactan nanoparticles was illustrated.

11:00am **BI-TuM10 Sequential Drug Release by pH/redox Dual Responsive Non-covalent Polymer Gatekeepers in Hollow Mesoporous Silica Nanoparticle**, ***Ja-Hyoung Ryu,*** Ulsan National Institute of Science and Technology, Republic of Korea

Nanoscopic delivery vehicles capable of encapsulating drug molecules and releasing them in response to

external stimuli are of great interest due to implications in therapeutic applications. Sequential drug delivery with dual

stimulus responsive nanotherapeutics is highly desirable for disease specific treatment in cancer therapy with

minimized adverse effects. In addition to this, on-demand therapy received considerable attention among the

treatment techniques. Herein, we present the design of robust, new and simple pH dependent charge conversional

non-covalent polymer gatekeepers technique by preparing the hydrophilic and hydrophobic drug loading at high

capacity and improved encapsulation stability in hollow mesoporous container for target specific cellular uptake for

cancer treatment. The di-isopropyl methacrylate functionalized monomer facilitates the fast cellular uptake at acidic

environment of cancer cells and allows the on-demand release of hydrophillic drug at acidic pH of endosomes upon

protonation. Pyridine disulfide facilitates the strong encapsulation of loaded cargo upon crosslinking by thiol-disulfide

exchange and releases the cargo upon exposure with increased intracellular glutathione concentration. The codelivery

of the multi-drugs in single carrier enables a synergistic chemotherapeutic effect. Based on this new design, a

wide range of sequential and synergistic therapy can be achieved to satisfy varied clinical requirements.

11:20am **BI-TuM11 Development Of Biometric Identification Technique Of High Reliability Based On Atomic Force Microscopy**, ***Vlad Ageev,*** Biomaging and Bionanaotechology, Russia

In this paper a method of biometric identification with high reliability based on measuring the elastic properties of the skin of a human finger while scanning his finger prints is presented. This method is shown to allow with a high degree of veracity to distinguish the skin from the inorganic materials used to create the fingerprint. It is found that the elasticity of the skin varies at 15% with increasing interval between the cut and measurement of the skin from 5 to 30 minutes. The elasticity of the skin also depends on the age of the person and is 60,2 ± 4,2 and 42,4 ± 2,6 kPa to 20 and 40 years, respectively. These dependencies can be used for creating additional levels of protection of biometric identification method and preventing such methods of its comprometation as the use of moulds and pre-made cuts of skin. The results can be used in the development of biometric identification systems with a high level of protection that verifies either the fingerprint pattern of skin of human finger or its elasticity.

Nanotechnology; biometrics; biometric identification; skin; elasticity; atomic force microscopy

Energy Harvesting & Storage
Room Lehua - Session EH-TuM

Surfaces & Interfaces for Solar Cells and Solar Fuels

Moderator: Charles Eddy Jr., US Naval Research Laboratory, USA

8:00am **EH-TuM1 Electrospun Photoelectrodes for Dye-Sensitised Solar Cells**, *J. Macdonald,* University College London, UK*; D. Tune,* KIT, Germany*; R. Dewi,* Zeiss, Australia*; T. Gibson, G. Shapter,* Flinders University, Australia*;* ***Thomas Nann,*** Victoria University of Wellington, New Zealand

The performance of dye-sensitised solar cells (DSSCs) depends to a large degree on the material and surface structure of the photoelectrodes (most commonly only the anode is a photoelectrode). Electrospun photoelectrodes offer a very high surface area and inter-connectivity, which should be ideal for this particular application. We will present a study on electrospun titania and nickel oxide photoelectrodes and their application in DSSCs.

Titania (TiO_2) photoanodes are by far the most studied system for DSSCs. We have shown that the performace of electrospun titania (anatase) fibre-photoelectrodes can be significantly increased by forming a single walled carbon nanotube (SWCNT) composite material [1]. Figure 1 shows scanning electron micrographs (SEMs) of a typical photoanode of this type.

Photocathodes are much less efficient compared with anodes and are replaced by platinum group metal catalysts frequently. We have studied photocathodes that are based on nickel oxide (NiO). The base semiconductors have been 'sensitised' with quantum dots and organic fluorophores. The morphology and nanostructure of the materials have been varied and finally, electrocatalysts have been added. It was found that sensitising can improve the performance of some *p-type* photocathodes significantly, but even the best performing photocathodes did not compare with equivalent TiO_2 photoanodes.

References

[1] T. J. Macdonald, D. D. Tune, M. R. Dewi, C. T. Gibson, J. G. Shapter, T. Nann, *ChemSusChem***2015**, *8*, 3396–3400.

8:20am **EH-TuM2 Combinatorial in-situ Photoelectron Spectroscopy Investigation of Sb_2Se_3/ZnS Heterointerfaces**, ***Sebastian Siol,*** *P. Schulz, M. Young, K. Borup, G. Teeter, A. Zakutayev,* NREL, USA

Energy band alignments at heterointerfaces play a crucial role in defining the functionality of semiconductor devices. The search for material systems with suitable electronic band alignments is one of the key challenges in developing novel photovoltaic technologies. Particularly the tuning of band offsets has enabled significant advances in efficiency for several state of the art thin film solar cell technologies. While the theoretical prediction of band alignments at semiconductor heterointerfaces is often very limited, interface experiments utilizing X-ray photoelectron spectroscopy (XPS) measurements can be employed to track the evolution of the electronic structure at the interface. In particular the V-IV binary chalcogenide Sb_2Se_3 has been identified as a prospective absorber material for the next generation of thin film solar cells [1], yet the understanding of interfacing this compound semiconductor to commonly employed buffer layers such as ZnS is still in its very infancy.

In recent years high throughput, combinatorial materials science methodology has gained tremendous interest [2]. In this work we demonstrate how combinatorial techniques can be utilized to increase the throughput of *in-situ* experiments to investigate the interface formation for respective semiconductor heterojunctions. Thin films are grown with intentional thickness gradients on the substrate, to minimize the required number of depositions and transfers. In addition, other deposition parameters such as the deposition temperature or composition can be systematically co-varied with thickness to cover several individual interface experiments on one substrate.

Using orthogonal thickness and temperature gradients a combinatorial *in-situ* interface experiment was set up, that provided a comprehensive dataset for the extensive investigation of the band alignment at the prototypical Sb_2Se_3/ZnS heterojunction. Our findings point to a large conduction band offset of ΔE_{CB}= 1.75 ±0.05 eV along with a potentially detrimental interfacial reaction at the junction. With this result, the study reveals why the choice of a ZnS buffer layer would limit device parameters and gives initial guidelines for alternative buffer layer materials with smaller electron affinities.

The method presented in this contribution can easily be applied for other material systems and will enable other researchers to quickly acquire comprehensive data for a more accurate picture of electronic processes across potential device interfaces.

[1] Y. Zhou et al. *Nat. Photonics* **2015**, *9*, 409.

[2] M. L. Green et al. *J. Appl. Phys.* **2013**, *113*, 231101.

8:40am **EH-TuM3 High Performance Transparent Electrode Based on Silver Nanowires with Plasma Treatment for Flexible Solar Cell Applications**

Sunghoon Jung, *W. Ahn, D,G. Kim,* Korea Institute of Materials Science, Republic of Korea

The random networks of silver nanowires (AgNWs) have been noticed as next generation transparent electrode which satisfies the high conductivity, transmittance and flexibility at the same time. Thus, AgNWs have a great potential for replacement of indium-tin-oxide (ITO) transparent electrode which have been used most widely. Although the nature of the superb self-electrical, optical and mechanical properties, some disadvantages of the transparent electrode such as chemical, environmental stability and contact resistance are bottle-necks for practical applications.

A simple approach to improve the stability of AgNW electrode is to form low-reactive materials such as graphene, graphene oxide and alumina on the top of AgNWs as passivation layers. Chemical and environmental stability is increased and electrical resistance is decreased. However, there are some negative aspects which are losses of transmittance, increasing vertical electrical resistance and upper layer and unisotropic chemical etching.

In this study, plasma techniques are applied to augment the electrical and environmental properties of AgNWs transparent electrode. The electrical resistance is decreased and environmental stability is improved. Moreover, AgNWs with plasma treatment showed much improved thermal stability compared to untreated AgNWs. We applied the plasma treated AgNWs to flexible organic photovoltaic devices as transparent electrode, and its power conversion efficiency is similar to organic photovoltaics based on ITO/Glass.

9:00am **EH-TuM4 Visible Light Responsive Photocatalysts toward Solar Hydrogen Production**

Ryu Abe, Kyoto University, Japan **INVITED**

Water splitting into H_2 and O_2 using semiconductor photocatalysts has received much attention recently due to the potential for the clean production of H2 from water utilizing solar energy [1]. Because almost half of all incident solar energy at the Earth's surface falls in the visible region, the efficient utilization of visible light remains indispensable for realizing practical H2 production. We have developed a new type of photocatalytic water splitting system, mimicking the mechanism of photosynthesis in green plants [2-6]. In this system, the water splitting reaction is broken up into two stages: one for H_2 evolution and the other for O2 evolution; these are combined by using a shuttle redox couple (Red/Ox) in the solution. Over a H_2 evolution photocatalyst, the photoexcited electrons reduce water to H_2 and holes oxidize a reductant (Red) to an oxidant (Ox). The Ox is reduced back to the Red by photoexcited electrons generated over an O_2 evolution photocatalyst, where the holes oxidize water to O_2. This system reduces the energy required to drive each photocatalysis process, allowing visible light to be utilized more efficiently than in conventional system. We have achieved water splitting using various visible light responsive photocatalysts, such as SrTiO3 doped with Cr [3], tantalum oxynitrides (TaON or $BaTaO_2N$) [4], and organic dyes [5], which work as a H_2 evolution photocatalyst, combined with tungsten oxide (WO_3) for O_2 evolution in the presence of a shuttle redox mediator such as iodate/iodide. Some oxyhalides such as Bi4NbO8Cl have also been proven as stable and efficient O2-evolving photocatalysts under visible light, enabling a Z-scheme overall water splitting with iron redox [6]. We have also demonstrated that the porous photoanodes of tantalum oxynitrides can stably oxidize water with significantly high quantum efficiency, after loading of IrO_2 or CoO_x nanoparticles as a cocatalyst; enabling water splitting under visible light with a relatively small applied bias [7].

References

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[5] J. Am. Chem. Soc. 135 (2013) 16872.

[6] J. Am. Chem. Soc. 38 (2016) 2082.

[7] a) J. Am. Chem. Soc., 132 (2010) 11828; b) Energy Environ. Sci. 4 (2011) 4138; c) J. Am. Chem. Soc. 134 (2012) 6968; d) J. Am. Chem. Soc. 135 (2013) 10238.

9:40am **EH-TuM6 *In Situ* Growth and Degradation Mechanisms in Methylammonium Lead Halide Perovskites for Graphene-Based Solar Cells**

Muge Acik, *S.B. Darling,* Argonne National Laboratory, USA

High power conversion efficiency of perovskite-based solar cells offers promise for low-cost and scalable production of renewable energy. The need to harness solar energy has recently motivated the search to alternate ETL/HTL hybrid materials, specifically graphene/perovskite films. Hybrid organic-inorganic methylammonium lead halides, $MAPbX_3$ (X=I, Br, Cl)/mixed-halides ($I_{3-x}Cl_x$, $I_{3-x}Br_x$) have been reported as light harvesting layers with their superior optoelectronic properties: tunable bandgap, long electron-hole diffusion lengths and high electron/hole mobility. Nevertheless, halide-based perovskites require *in situ* investigation for film growth, degradation and perovskite formation mechanisms to overcome detrimental effects of incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination. Graphene-derived hybrids have recently emerged as an ETL/HTL replacement in these devices, however understanding the origin of interfacial chemical reactions between deposited perovskite films over graphene-derived materials is still lacking, especially at the ETL/perovskite/HTL interfaces. Moreover, effect of film thickness, stoichiometry control, overlayer/ underlayer morphology/composition, stability issues and cation-anion electrostatic interactions ought to be examined for better charge transport. To address scalability and stability issues, we examined degradation, nucleation and growth mechanisms in reduced graphene/graphite oxide (RGO) upon halide-based (I, Cl, Br) perovskite deposition. Chemical interactions were interpreted at perovskite/RGO interfaces for the grain size, orientation, boundaries, and surface/bulk effects using variable-temperature (≤600°C, Ar(g)) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, luminescence) and SEM, XRD, XPS, TEM, and AFM for morphology characterization. Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting in improved chemical stability with heat (vs. iodide derivative). Overall, perovskite decomposition and oxygen-induced chemical reactions occurred at ≤150°C, eliminated hydroxyls/carboxyls in RGO, and maintained ethers/epoxides upon perovskite decomposition. Poor perovskite formation was observed on RGO due to varying electron affinity and reactivity of precursor halides, resulting in film degradation in air (O_2, H_2O). References: (1) M Acik, SB Darling. J. Mater. Chem. A (2016) 4, 6185-6235. (2) J Gong, SB Darling, F You, Energy Environ. Sci. (2015) 8, 1953-1968 (3) M Acik, G Lee, C Mattevi, M Chhowalla, K Cho, YJ Chabal. Nature Materials (2010) 9 (10), 840-845.

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Science User Facility under Contract No. DE-AC02-06CH11357. M.A. also acknowledges support from the Joseph Katz Named Fellowship at Argonne National Laboratory.

10:20am **EH-TuM8 Back Contact Passivation via Atomic Layer Deposition for Increased Device Performance of Earth-Abundant $Cu_2ZnSn(S,Se)_4$ Solar Cells**, ***Priscilla Antunez***, *D.B. Farmer, D.M. Bishop, R.A. Haight,* IBM T.J. Watson Research Center, USA

Thin film solar cell absorbers composed of earth-abundant elements such as $Cu_2ZnSn(S,Se)_4$ (CZTSSe) are particularly attractive due to their relative low toxicity and their record maximum power conversion efficiency of 12.6% using an antireflective coating. Despite rapid progress, further improvements in efficiency are needed to enable the commercial-scale implementation of CZTSSe as a solar cell absorber. Our recent efforts have identified the deleterious impact of recombination at the interface between the CZTSSe absorber and the molybdenum back contact, which results in decreased lifetime, compared to the bulk, and a reduced open circuit voltage (V_{oc}), compared to theoretical expectations. To address this limitation, we have employed two approaches designed to increase device performance. The first approach involves the deposition of Al_2O_3, via ALD, onto the Mo/glass substrate prior to the CZTSSe growth. In the second approach, the CZTSSe device is exfoliated to expose the back surface of the absorber, and a thin Al_2O_3 layer is then deposited to passivate the back of the solar cell. The passivating ALD step is then followed by the deposition of a high work function back contact. The high work function material further reduces recombination by imposing an electrostatic field, which drives the separation of electrons and holes to increase device performance. These effects are supported by device simulations and confirmed with experimental results that show an increase in several performance parameters, like V_{oc} and J_{sc}, when high work function back contacts are employed in conjunction with careful control of absorber thickness. With this approach, along with the inclusion of the Al_2O_3 passivating layer designed to inhibit recombination, efficiencies as high as 11.6% have been achieved without the use of an antireflective coating.

10:40am **EH-TuM9 Nanoscale Imaging of Charge Carrier Transport in Monoclinic Bismuth Vanadate Photoanodes Via Atomic Force Microscopy**, ***Johanna Eichhorn***, *J.K. Cooper, L.H. Hess,* Lawrence Berkeley Lab, USA; *D. Ziegler,* Scuba Probe Technologies LLC, USA; *D.M. Larson, M.K. Gilles, I.D. Sharp, F.M. Toma,* Lawrence Berkeley Lab, USA

Photoelectrochemical water splitting is a promising route for efficient conversion of solar energy to chemical fuel. Among different photoelectrode materials, bismuth vanadate ($BiVO_4$) is one of the most actively investigated oxide semiconductors due to its moderate bandgap, favorable conduction band position, and relatively long photocarrier lifetimes.[1] However, under relevant operating conditions, pristine $BiVO_4$ thin films are subjected to degradation at the exposed surface facets. The degradation process in solution is accelerated by photoexcitation, which causes trapping of photogenerated holes at localized surface sites.[2] Therefore, developing approaches to stabilize these efficient semiconductor nanostructures requires a detailed understanding and control of charge separation, transport, and recombination mechanisms at their relevant length scales.

Here, we use photoconductive atomic force microscopy in combination with Kelvin probe force microscopy to correlate local surface morphology with generated photocurrent and contact potential difference maps at individual grain facets in polycrystalline $BiVO_4$ films. Furthermore, we employ scanning transmission X-ray microscopy to trace the changes in local chemical structure and composition in pristine and photodegraded $BiVO_4$.

The photocurrent and contact potential difference maps reveal the impact of different working conditions, such as bias voltage, excitation energy or excitation power, on the local charge carrier dynamics. Both for excitation above the bandgap (405 nm) and sub-bandgap illumination (532 nm), the photocurrent maps resolve the contributions from individual grains with nanometer spatial resolution. The photoelectrochemical performance of $BiVO_4$ can be significantly enhanced by varying the oxygen vacancy defects and hydrogen impurities, through hydrogen annealing. Therefore, we compare the photocurrent generation of pristine and hydrogen annealed $BiVO_4$. This careful analysis allows us to identify locally the charge transfer and loss mechanisms in these materials which ultimately contribute to desired photocurrent generation or undesired photocorrosion.[3]

[1] J. K. Cooper et al., The role of hydrogen in defining the n-type character of $BiVO_4$ photoanodes, *Chem. Mater.* **2016**.

[2] F. M. Toma et al., Mechanistic insights into chemical and photochemical transformations of bismuth vanadate photoanodes, *Nat. Commun.* **2016**.

[3] J. Eichhorn et al., Nanoscale photocurrent imaging of monoclinic $BiVO_4$ films via atomic force microscopy, **2016** (in preparation).

11:00am **EH-TuM10 Energy Level Alignment at Interfaces in Hybrid Lead Halide Perovskite Photovoltaics**, ***Philip Schulz***, *A.A. Dameron, P.F. Ndione, M. Yang, K. Zhu, J.J. Berry,* NREL, USA

Hybrid organic/inorganic perovskites define an emerging class of solar cell absorber materials which advances to the lead in maximum power conversion efficiencies in the area of thin-film solar cells.[1] In the photovoltaic device the electronic interaction between the perovskite absorber and adjacent charge extraction and transport layers is key to maximize cell functionality. We identified that device characteristics such as the open circuit voltage can be affected by the alignment of the electronic energy levels of an organic charge extraction layer with the electronic transport levels in the perovskite film.[2] Furthermore, we found that the doping characteristic of the underlying oxide substrate can be used to rigidly tailor the Fermi level position in a subsequently deposited perovskite film. For future applications such as the integration of a perovskite subcell into a tandem device, precise control over the electronic alignment processes is required.[3]

Here we present our recent findings in which we examine a selection of incrementally deposited oxide charge carrier transport layers on top of methylammonium and formamidinium lead iodide perovskite films. Functional *n*-type (e.g. TiO_2, MoO_x), *p*-type (e.g. NiO) and intrinsic oxides (e.g. Al_2O_3) are grown by pulsed laser and atomic layer deposition techniques on top of the perovskite absorber layer. We then use ultraviolet and X-ray photoemission spectroscopy (UPS/XPS) to determine the electronic energy level alignment at the oxide/perovskite interface while at the same time tracking changes in the interface chemistry. Using this approach we are able to explain band offset changes induced in the perovskite layer by chemical interactions with the oxide on top, changes in the electrostatic potential and the formation of defective surface layers. The results are not only used to give guidelines about how to embed oxide layers into perovskite photovoltaic devices but also inform to what extent the electronic structure of the perovskite is subject to extrinsic perturbations on a more universal scale.

[1] K. Emery, Best research-cell efficiencies. http://www.nrel.gov/ncpv/images/efficiency_chart.jpg, Ed. NREL: 2016

[2] P. Schulz, E. Edri, S. Kirmayer, G. Hodes, D. Cahen, A. Kahn, *Energy Environ. Sci.***2014**, *7*, 1377

[3] P. Schulz. L. L. Whittaker-Brooks, B. A. MacLeod, D. C. Olson, Y.-L. Loo, A. Kahn, *Adv. Mater. Interfaces* **2015**, *2*, 1400532

Nanomaterials
Room Hau - Session NM-TuM

Nanocharacterization

Moderator: Kristina Tschulik, Ruhr-Univ. Bochum, Germany

8:20am **NM-TuM2 Solution Phase Synthesis, Electron Microscopy Characterization and Catalytic and Medical Applications of Nanoparticles**, ***Richard Tilley***, University of New South Wales, Australia **INVITED**

Liquid phase synthesis is a powerful method for the formation of uniform sized nanoparticles and nanoparticles with a faceted morphology. General strategies for the formation of nanoparticles and through chemical synthesis will be outlined. The results presented will include the formation of catalytic metals such as gold core palladium shell nanoparticles, below and branched nanostructures of gold, palladium and ruthenium. The growth mechanism of how the particles form will also be presented along with HRTEM observations. Biomedical and catalytic applications will be discussed.

9:00am **NM-TuM4 Atomic Species Identification at the (101) Anatase Surface by Simultaneous Scanning Tunnelling and Atomic Force Microscopy**, *O. Stetsovych,* NIMS, Japan; *M. Todorović,* Universidad Autonoma de Madrid, Spain; *T.K. Shimuzu,* NIMS, Japan; *R. Perez,* Universidad Autonoma de Madrid, Spain; ***Oscar Custance***, NIMS, Japan

Titanium dioxide (TiO_2) is an important material in a number of energy-related applications such as photocatalytic water splitting, and the conversion of solar energy to electricity. Most of these applications rely on nano-crystalline TiO_2 samples that consist principally of two polymorphs: anatase and rutile. In some commercial TiO_2 samples, anatase nanocrystals account for up to 75% of the product, and anatase is generally regarded as having a higher surface reactivity than rutile.

Despite the pivotal role of anatase as reactive component in TiO_2 samples used as the active phase in commercial catalysts, there is still a relatively scarce amount of experimental studies on anatase surfaces in comparison with rutile. More research is required to better understand the surface properties that define anatase as such a good photocatalyst. In particular, the real space characterization of anatase substrates at the atomic scale is essential to elucidate the basic principles that govern the photocatalytic and photovoltaic applications of this TiO_2 polymorph.

In this contribution, we combine atomic force microscopy (AFM) and scanning tunneling microscopy (STM), supported by first-principles calculations, for the simultaneous imaging and unambiguous identification of atomic species at the (101) anatase surface [1]. By using single water molecules as atomic markers, we demonstrate that AFM images the topmost oxygen atoms of the surface, while the main contribution to the STM signal comes from the titanium atoms at the third atomic layer. We show that the STM signal is sensitive to sub-surface defects, and that simultaneous AFM-STM allows the acquisition of STM images with atomic resolution within the surface band gap, where standard STM imaging is challenging.

Based on key distinguishing features extracted from experiments and first principles calculations, we identify candidates for the most common surface defects of the (101) anatase surface and characterize the surface local chemical reactivity with the AFM probe at atomic scale.

The findings reported here provide the foundation for future work on anatase, and pave the way for the study of more complex anatase systems related to water splitting and organic photovoltaics, including the adsorption geometries and binding sites of photoactive molecules as well as metal dopants to enhance hydrogen production.

[1] O. Stetsovych et al. Nature Communications 6, 7265 (2015)

9:20am **NM-TuM5 Electrochemically-generated Nanomaterials Studied by In situ Flow Spectro-electrochemical Scanning Transmission X-Ray Microscopy**, ***Adam Hitchcock,*** *V. Prabu,* McMaster University, Canada*; S.M. Rosendahl,* Canadian Light Source, Canada*; M. Reynolds, H. Hosseinkhannazer,* Norcada Inc, Canada

We are using soft X-ray scanning transmission X-ray microscopy (STXM) [1] to investigate Cu thin film and dendritic electrochemical growth on a Au surface under variable pH conditions. Electrochemical reduction of Cu(II) under acid conditions is commonly used to deposit copper for integrated circuit interconnects, and in many other technologically important applications of thin films and nanoscale Cu metal. Improved understanding of the fundamental steps of the reaction and how to control undesirable phenomena such as dendritic growth is needed to further optimize this process. The reduction of Cu(II) to Cu(0) proceeds via a Cu(I) intermediate, which can be detected under weakly acidic to neutral conditions. We have developed a novel device for *in situ* STXM studies of electrochemical reactions which can operate under flow or static conditions [2]. The ability to change electrolyte during an experiment is being used to better understand the role of Cu(I) species in the deposition process. Spectromicroscopy at the Cu 2p and O 1s edges is used to analyze initial and final states, follow the process *in situ*, and search for intermediate species. The apparatus and techniques for spectro-electrochemical-microscopy will be described and results will be presented from deposition & stripping of copper from $CuCl_2$(aq) and $CuSO_4$(aq) electrolytic solutions as a function of pH.

STXM performed using BL10ID1 at CLS and BL 5.3.2.2 at ALS . Research supported by NSERC and the Catalyst Research for Polymer Electrolyte Fuel Cells (CaRPE-FC) network.

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G. Van Tendeloo, D. Van Dyck and S. J. Pennycook 2012. (Wiley)

[2] A.P. Hitchcock, Z. Qin, S.M. Rosendahl, V. Lee , M. Reynolds and H. Hosseinkhannazer, *Electro-deposition of Cu studied with in situ electrochemical scanning transmission x-ray microscopy* Am. Inst. Phys. Conf Series 1696 (2016) 02003 (1-5)

9:40am **NM-TuM6 Structural and Chemical Study of the Stability of Pt-based Fuel Cell Electrocatalysts via 3D Electron Tomography***, **Karren More**, D.A. Cullen, B.T. Sneed,* Oak Ridge National Laboratory, USA

Polymer electrolyte membrane (PEM) fuel cell performance and materials degradation, particularly associated with the cathode catalyst layer (CCL), can be directly attributed to the structure and chemistry of individual material components, as well as their uniformity/homogeneity within a CCL. The individual material constituents used to form the CCL within the membrane electrode assemblies (MEAs), e.g., the electrocatalyst (Pt or Pt-alloys), catalyst support (C-based), and ionomer films (proton conductor), and especially the critical interfaces that are formed between these various constituents, are critically importance in controlling fuel cell performance. Understanding the specific microstructural characteristics of the individual materials within the CCL, and how the materials interact during fuel cell operation/aging, is important for identifying materials optimization parameters that can significantly enhance performance and durability.

Research efforts at Oak Ridge National Laboratory are focused on the high-resolution microstructural and microchemical characterization of MEAs fabricated using different Pt-based electocatalysts and catalyst loadings, carbon-based support materials, and ionomer solutions, as well as the same MEAs subjected to accelerated stress tests (ASTs) designed to degrade specific MEA components and assess durability. High-resolution analytical microscopy methods are used to study the distribution and chemistry of materials and interfaces within CCLs, which are combined with high-resolution imaging and 3D electron tomography techniques to provide unprecedented insight into the structure and interfaces (ionomer/support, ionomer/catalyst, catalyst/support, ionomer/pore) in "real" MEAs before and after aging. This presentation will focus on understanding materials distributions within the CCL as a function of processing variables, e.g., initial ionomer and/or ink chemistry, electrocatalyst (type, loading, and dispersion), and the type of carbon support used. The stability of the ionomer films, electrocatalyst, and support structures in CCLs after ASTs will be evaluated.

Research sponsored by (1) the Fuel Cell Technologies Office, Office of Energy Efficiency and Renewable Energy, U.S. Department of Energy and (2) Oak Ridge National Laboratory's Center for Nanophase Materials Sciences (CNMS), which is a U.S. Department of Energy, Office of Science User Facility.

10:20am **NM-TuM8 Challenges in Synthesis and Characterization of Non-precious Transition Metal Carbide/Nitride Catalysts***, S. Gage, M. Davidson, C. Ngo, C.A. Cadigan,* Colorado School of Mines, USA*; D. Esposito,* Max-Planck Institute for Colloids and Interfaces*; B. Trewyn, R. Richards, **Svitlana Pylypenko**,* Colorado School of Mines, USA

Metal carbides/nitrides have demonstrated unique properties for various catalytic reactions and are attractive as earth-abundant alternatives to precious group metals (PGM). However, synthesis of nanoscale transition metal carbides and nitrides has proven difficult, and obtaining structures with high surface areas and controlled morphologies have been elusive. Additional challenges arise from the complex nature of these nanomaterials and there is limited characterization available in the literature. Through unique synthetic approaches, we have created a wide array of unsupported and supported nickel-based nanomaterials, and utilized bulk and surface characterization techniques to identify synthesis-composition-property relationships.

10:40am **NM-TuM9 Stacking of AlOOH Nano-Rods and Plates: The Effect of Surface Termination Chemistry on the Preferential Interacting Crystal Zones in Solution***, **Michele Conroy**, J. Soltis, S. Chatterjee, E. Buck,* Pacific Northwest National Laboratory, USA

Aluminum oxyhydroxide (boehmite) nanoparticles are used for a wide variety of applications including catalysis and adsorption. It has been shown that boehmite nanoparticles with 010 plane as the largest exposed surface area have increased catalysis and adsorption rate, due to the relatively high OH density of this plane. Additionally synthesizing these nanoparticles in a hierarchical structures instead as mono-dispersed, has been reported to increase the reactivity even further. In this study we utilize cryo-transmission electron microscopy (TEM) and in-situ liquid TEM to achieve fundamental insights into the mechanisms of nanoparticle aggregation and reactivity. Although there is a lot of theoretical debate around the preferential interacting zones of AlOOH crystalline nanoparticles in solution, there has been no experimental confirmation to date. Our initial results show that the particles aggregate along a preferred crystal orientation (the main flat (010)), irrespective of pH and solution content, forming large stacked agglomerates and decreasing the exposed surface area.

Aluminum oxide nanoparticles formed by the dehydration of boehmite are also widely used in industrial catalysis including petrochemical, chemical, and automotive due to their stability at high temperatures. Although the shape of the nanoparticle during the thermal treatment of boehmite remains the same the terminating planes of course change with the removal of water. This enabled us to study any change in the aggregation due to the terminating chemistry without the shape of the nanoparticle itself being a possible variable.

11:00am **NM-TuM10 Nanoscale Chemical Imaging with Photo-induced Force Microscopy**, ***Sung Park***, Molecular Vista, USA

Infrared Photo-induced Force Microscopy (IR PiFM) is based on an atomic force microscopy (AFM) platform that is coupled to a widely tunable mid-IR laser. PiFM measures the dipole induced at or near the surface of a sample by an excitation light source by detecting the dipole-dipole force that exists between the induced dipole in the sample and the mirror image dipole in the metallic AFM tip. This interaction is strongly affected by the optical absorption spectrum of the sample, thereby providing a significant spectral contrast mechanism which can be used to differentiate between chemical species. Due to its AFM heritage, PiFM acquires both the topography and spectral images concurrently and naturally provides information on the relationship between local chemistry and topology with sub 10 nm spatial resolution on a variety of samples. PiFM spectral images surpass spectral images that are generated via other techniques such as scanning transmission X-ray microscopy (based on synchrotron source), micro confocal Raman microscopy, and electron microscopes, both in spatial resolution and chemical specificity. The breadth of the capabilities of PiFM will be highlighted by presenting data on various polymer systems. By enabling imaging at the nm-scale with chemical specificity, PiFM provides a powerful new analytical method for deepening our understanding of nanomaterials and facilitating technological applications of such materials.

11:20am **NM-TuM11 CNC Modification for the Development of Active Food Packaging**, ***Monique Lacroix***, INRS-Institut Armand-Frappier, Canada

Irradiation treatment of CNC was performed at doses of 5-20 kGy followed by reaction with a redox group of ascorbic acid (AA) and hydrogen peroxide in order to promote the formation of radicals on the macromolecule to enhanced the interaction of CNC with gallic acid. Our results have demonstrated that both of these pre-treatments induce the formation of carboxylic acid groups on CNC surface by conductometric titration. Derivates of carboxylic acid are known as food stabilizers and preservers due to their antiradical and antimicrobial effects. Since gallic acid has carboxilic acid groups, it was found that its interaction with pre-teated CNC with gamma-irradiation in the presence of redox group (CNC-g-GA) can impart to native CNC antiradical properties. A solution of 20% of CNC-g-GA was then added to a 1% (w/w) gellan in order to produced antiradical gellan-based film packaging. A significant improvement of the tensile strength (TS), the tensile modulus (TM) and the elongation at break (EB) and the water resistance was observed when CNC-g-GA was added to the film packaging formulation ($p \leq 0.05$). These results bring to a new application of antiradical film packaging or coatings which could be applied for food industry to preserve fruit and vegetables during storage.

Thin Films
Room Mauka - Session TF-TuM

Nanostructured Surfaces & Thin Films II

Moderator: Guozhong Cao, University of Washington, USA

8:00am **TF-TuM1 Ways to Increase the Strength of Langmuir Monolayers of Particles at Air/aqueous Interfaces**, ***Cathy McNamee***, Shinshu University, Japan; *S. Fujii*, Osaka Institute of Technology, Japan; *S. Yusa*, University of Hyogo, Japan; *M. Kappl*, MPIP, Germany

The use of Langmuir monolayers of polymer particles stabilized at air/liquid surfaces in medical and industrial applications are affected by their physical properties, e.g., stiffness (deformability), their resistance against breakage upon impact of other materials, and their adhesion to other surfaces. We previously studied the physical properties of a Langmuir monolayer of polystyrene particles loaded with poly(*N,N*-dimethylaminoethyl methacrylate) (particle abbreviation: "PDMA_PS") at air/aqueous interfaces by using the Monolayer Particle Interaction Apparatus [1]. A particle was attached to an Atomic Force Microscope cantilever (probe), which acted as the colliding material. The probe was brought from the bulk water to the monolayer of PDMA_PS particles at the air/water interface and then returned back into the bulk water, during which time the forces between the probe and the monolayer were measured. A monolayer of PDMA_PS particles at the air/water interface was seen from the force-distance curves to give a low stiffness, a result explained by the induced movement of the particles in the monolayer at the air/water interface by the probe, when the probe was brought into contact with the monolayer from the bulk water.

In this study, we aimed to create a Langmuir monolayer of polymer particles at an air/water interface that showed a high stiffness, even after the collision of a probe or another material. This was achieved by adding a poly(2-hydroxyethyl methacrylate) ("PHEMA") polymer to a Langmuir monolayer of PDMA_PS particles at an air/water interface. The mixed PHEMA- PDMA_PS monolayer gave a polymer-like monolayer at low surface pressures and a particle-like monolayer at high surface pressures. The PDMA_PS particles formed small aggregates that were dispersed throughout the PHEMA monolayer at low surface pressures, a result suggesting that the particles were trapped in the PHEMA network. The stiffness of the mixed monolayer was independent of the surface pressure, but increased as the ratio of PHEMA in the mixed monolayer increased. The stiffness increase was explained by the PDMA_PS particles being embedded in the PHEMA polymer network, which inhibited the movement of the PDMA_PS particles by the probe. A PHEMA polymer monolayer containing a small amount of PDMA_PS particles gave a stiffer film than a pure PHEMA polymer monolayer. It was therefore concluded that the stiffness of a particle monolayer could be changed by adding a polymer to a Langmuir monolayer of particles.

[1] McNamee, C.E.; Fujii, S.; Yusa, S.; Azakami, Y.; Butt, H.-J.; Kappl, M. Colloid Surf. B-Biointerfaces, **2015**, *470*, 322-332.

8:20am **TF-TuM2 Carbon Incorporation into the Si(111)-7x7 Surface**, *E. Seo, D. Eom*, Korea Research Institute of Standards and Science (KRISS), Republic of Korea; *J.-M. Hyun, H. Kim*, Sookmyung Women's University, Republic of Korea; ***Ja-Yong Koo***, Korea Research Institute of Standards and Science (KRISS), Republic of Korea

Carbon incorporation into Si wafer has attracted much attention due to the important role of carbon in developing high-performance, Si-based devices. The isovalent C atoms may induce systematic surface strains for building nanostructures on Si wafer without the doping effects. However, the extremely low solubility of C atoms in bulk Si (below 0.001%) has been considered as an obstacle to C incorporation into Si surface.

C atoms can be incorporated into the 4th delta-layer (0.4 nm deep) under the Si(001) surface upto the density of 0.125 monolayer with the c(4x4) surface reconstruction.

We investigated the incorporation of C atoms into Si(111)-7x7 surface by using scanning tunneling microscopy. The C atoms are extracted by thermal dissociation of CO molecules adsorbed on the Si(111)-7x7 surface. Previous studies negate adsorption of CO molecules on this surface even at low temperatures near 10 K. However, we find that every surface dangling bond on the Si(111)-7x7 surface can bind strongly with the C atom of a CO molecule even at temperatures higher than room temperature. Especially CO molecules bind with Si adatoms in three configurations; one <on-top> and two <back-bond inserted> structures.

By thermal annealing, C atoms are incorporated under the Si adatoms of Si(111)-7x7 surface. The maximum density of incorporated C atoms on Si(111)-7x7 is low compared with that on Si(001)-2x1. At high density, C atoms are swept away from the 7x7 reconstructed surface due to the excessive surface stress, forming irregular SiC phases along the step edge.

Regular and uniform C-incorporated Si(111)-√3x√3 reconstruction is not formed on this Si wafer surface.

8:40am **TF-TuM3 Optical, Electronic and Structural Properties of Eu and Gd bis-phthalocyanines Thin Films for Optoelectronics**, *E. Maresova, **Michal Novotny**,* Institute of Physics of the Czech Academy of Sciences, Czech Republic*; P. Fitl, J. Vlcek,* University of Chemistry and Technology Prague, Czech Republic*; M. Vondracek, P. Hubik, L. Fekete,* Institute of Physics of the Czech Academy of Sciences, Czech Republic*; M. Vrnata,* University of Chemistry and Technology Prague, Czech Republic*; J. Bulir,* Institute of Physics of the Czech Academy of Sciences, Czech Republic*; B. Paruzel, J. Pfleger,* Institute of Macromolecular Chemistry of the Czech Academy of Sciences, Czech Republic*; R. Slota,* Faculty of Chemistry, Opole University, Poland*; J. Sebera,* Institute of Physics of the Czech Academy of Sciences, Czech Republic*; I. Pis,* Elettra - Sincrotrone Trieste S.C.p.A., Italy*; I. Kratochvilova, J. Lancok,* Institute of Physics of the Czech Academy of Sciences, Czech Republic

Phthalocyanines (Pcs) exhibit unique properties, i.e. semiconductivity, photoconductivity, chemical stability and optical absorption in the UV-VIS-NIR region. These properties make the Pcs suitable candidates for optoelectronic devices, small molecular organic solar cells, laser printers or chemiresistive gas sensors. Pcs belong in the most efficient class of organic semiconductors for solid state photovoltaic conversion. Metal 'mono'-Pc compounds, i.e. ZnPcs, CuPcs, are most commonly utilized. Lanthanide bis-phthalocyanines ($LnPc_2$) based on two macrocycles coordinated by the rare earth metal offer additional possibilities since their arrangement allows changing the distribution of electronic density within the cores of the particular phthalocyanine moieties whereas the molecular structure of the sandwich complex remains intact.

Bis-phthalocyanine thin films of $GdPc_2$ and $EuPc_2$ were grown by vacuum evaporation from effusion cell. The optical properties were characterized by spectrophotometry and spectral ellipsometry. The spectra exhibited well pronounced Q, B, N and C bands and a band around 460 nm that could be attributed to radical band (X band) – transition $[2e_g(\pi)\text{-}2a_{1u}(\pi)]$ suggesting $Ln^{3+}Pc_2$. Relatively high values of conductivity ($1.3\cdot10^{-5}$ $S.cm^{-1}$ for $EuPc_2$ and $6.1\cdot10^{-5}$ $S.cm^{-1}$ for $GdPc_2$) were obtained in open air at room temperature with interdigital surface Au electrodes arrangement. The conductivity was found to be sensitive to the thermal annealing and ambient conditions. Electronic structure was analyzed by XPS, resonant PES and NEXAFS. Well pronounced individual components of core level spectra of C 1s, N 1s, Eu 4d and Gd 4d and resonating lanthanide 4f levels in valence band were obtained and analyzed. The analyses confirmed Ln^{3+} ionic state. NEXAFS measurement supported by density functional theory calculations revealed rather inclined orientation of $LnPc_2$ molecules on the substrate. The molecular orientation could be manipulated by deposition pressure and depends on the film thickness. Morphology was studied by SEM and AFM. The surface roughness was found to be lower than 1 nm. FTIR characterization suggested low deterioration of $LnPc_2$ in the films.

The obtained results suggest both $GdPc_2$ and $EuPc_2$ as promising candidates for application in photovoltaics.

9:00am **TF-TuM4 Defect-induced lOcalized States on Nitride-Based HEMT and Their Influence on the Radiative Recombination Processes**, ***Manolo Ramírez López**,* Instituto Politécnico Nacional, Mexico*; L. Janicki, R. Kudrawiec, M. Baranowski, J. Misiewicz,* Institute of Physics, Wroclaw University of Technology, Poland*; M. Zhao, K. Kai Cheng,* IMEC, Belgium

Intensive efforts have been made to improve electrical performance of GaN-based HEMT transistors but it has not been identified factors that limit the breakdown voltage, electrical mobility and lead to the early device failure[1]. Incorporation of impurities, point defects, dislocations and grain boundaries formed at semiconductor layers of the device are good candidates to explain their electrical limitations. This work was focused to study the effect of non-intentional carbon concentration on optical recombination processes in AlGaN buffer layer and GaN channel of HEMT transistors grown by MOCVD technique. Samples were grown by changing growth temperature from 950 to 1040 ^{o}C, which reduced carbon concentration from $8x10^{19}$ to $5x10^{17}$ $atoms/cm^3$ (measured by SIMS). Low temperature photoluminescence (PL) spectra of AlGaN buffer layers where show yellow band(YL), blue band(BL) and near band emissions (NBE), whose relative intensities are well related with dislocation density and carbon incorporation. Optical quenching phenomena on YL, BL and NBE was observed as temperature increases and NBE peak position suffers a redshift as carbon concentration decreases [2]. In samples with high carbon concentration ($8x10^{19}$ and $2x10^{19}$ $atoms/cm^3$) only carrier redistribution within localized state was observed, while for samples with lowest carbon concentration ($5x10^{17}$ to $3x10^{18}$ $atoms/cm^3$) two optical quenching process were identified (carrier redistribution and delocalization). Carrier delocalization was confirmed by yellow-band intensity increase when this process was thermally activated at 150 K. Results are explained in terms of carbon-generated localized states with different depth and aluminum fluctuations within AlGaN buffer layers. High-resolution PL spectra of C-doped layers show free A exciton and acceptor bound-exciton whose intensities are correlated with crystal quality and carbon concentration. Complementary analysis will be presented for GaN channel of HEMT transistors.

[1] E. Zanoni, M. Meghini, A. Chini, D. Marcon and G. Meneghesso, IEEE Transactions On Electron Devices, **60**, 10 (2013).

[2] M. A. Reshchikov, D. O. Demchenko, A. Usikov, H. Helava, and Yu. Makarov, Phys. Rev. B **90**, 235203 (2014).

This work was performed within the grant of the National Science Center (NCS) (OPUS 5 No. 2013/09/B/st7/02395), and supported by SIP-IPN project No. 20160610. The authors acknowledge to CONACYT for financial support though postdoctoral scholarship No. 265970.

9:20am **TF-TuM5 Comparative Study of the Ni-Silicide Films formed on Si and Strained Si:P**, ***Seongheum Choi**, J. Kim, J. Choi, S. Cho,* Sungkyunkwan University, Korea, Republic of Korea*; M. Lee, E. Ko,* Yonsei University, Korea*; I. Rho, C.H. Kim,* SK Hynix Inc.*; D.-H. Ko,* Yonsei University, Korea*; H.S. Kim,* Sungkyunkwan University, Korea, Republic of Korea

The epitaxially-grown strained Si:P film can be used as an uni-axial stressor and/or a low resistance contact material in the n-channel metal-oxide-semiconductor field-effect transistors (NMOSFETs) [1]. Because an additional silicidation process is expected on top of the strained Si:P layer, there have been a few attempts to synthesize metal-silicide films, such as Ti- and Ni-silicides [2, 3].

In this presentation, we will compare the microstructural properties of the NiSi films formed on a Si substrate and a strained Si:P film. The strained Si:P film (P concentration of ~1.9%) was epitaxially grown on Si using a low-pressure chemical vapor deposition system. After HF cleaning and Ni deposition, silicidation was performed by rapid thermal annealing at 400~800 °C for 1 min in N_2 ambient. According to microstructural and electrical comparison with the NiSi film formed on Si, a number of large-sized grains with a flat interface existed and a delay of thermal agglomeration was observed in the NiSi film on Si:P. The possible difference in the grain-growth mechanism of the NiSi films on Si and Si:P will be discussed.

9:40am **TF-TuM6 Low Temperature Chemical Vapor Deposition of Manganese and Iron Nitride from Bis(2,2,6,6 Tetramethylpiperidido)metal (ii) and Ammonia**, ***Elham Mohimi**, B.B. Trinh, S. Babar, G.S. Girolami, J.R. Abelson,* University of Illinois at Urbana-Champaign, USA

Manganese and iron nitride phases are an interesting class of materials for applications such as optoelectronics, microelectronics, magnetic recording, and spintronics. Since chemical vapor deposition (CVD) can conformally coat high aspect ratio (deep) features used in design of nanoscale devices, it is highly desirable to develop CVD routes for manganese and iron nitride films. However, the lack of suitable precursors has hindered this development.

Here, we report CVD growth of manganese and iron nitride films from a novel and practical precursor, bis(2,2,6,6 tetramethylpiperidido)metal (II), $M\ (tmp)_2$, with ammonia as co-reactant. The manganese and iron tmp complexes can be synthesized in high yield and are thermally stabile at room temperature. Growths are done in a cold wall, high vacuum chamber at substrate temperature of 50-350 °C. Precursors are heated to 60-75°C and delivered to the chamber using Ar carrier gas at flow rates of 5-40 sccm. Anhydrous ammonia is delivered through a separate line to afford a partial pressure of 0-13 mTorr.

XPS reveals a compositional ratio of Mn:N = 2.6:1 to 2.8:1 for manganese nitride (Mn_xN_y) and Fe:N = 4.1:1 for iron nitride (Fe_xN) films grown in the temperature range examined, with no carbon contamination within the detection limits of instrument. All films show a slightly columnar microstructure in cross-section SEM. While there was a few min of nucleation delay for Mn_xN_y growth at 150 °C, no nucleation delay was observed for Fe_xN under the same growth conditions. There is no film growth at all in the absence of ammonia; this indicates that transamination is required to create $Mn\text{-}NH_2$ groups that react on the substrate surface to form the nitride film, as seen for film growth from other metal amido precursors in the presence of ammonia. Films are conformal in micro-trenches of aspect ratio 3; the thickness profiles are, however, characteristic of film growth from two reactive species, one with high and one with low sticking coefficient at the film surface. Copper diffusion barrier properties of a 12 nm manganese nitride film are investigated by annealing a test structure of 200 nm Cu / 12 nm Mn_xN_y / 300 nm SiO_2 / Si at 500 °C under Ar for 1 hour. Auger electron spectroscopy depth profiles show that manganese nitride performs well as copper diffusion barrier for microelectronic applications.

10:20am **TF-TuM8 Multi-functional Thin Film Coatings formed via Nanoscale Grinding***, R. Sapkota,* ***Chris Papadopoulos,*** University of Victoria, Canada

Nanostructured surfaces and thin films composed of nanoscale particles can be created using a variety of nanofabrication methods for applications in electronics, photonics, energy, biotechnology, etc. Generally, such nanostructures can take many forms depending on the various top-down to bottom-up fabrication methodologies [1]. *Nanoscale grinding*, or colloidal grinding, is a unique approach to nanoparticle thin film synthesis that can directly produce large amounts of nanoscale particles in an appropriate solvent without the use of complex chemical or physical processing. Planetary ball milling is typically used to grind a starting bulk powder into a nanoscale colloidal suspension suitable for thin film coating of various functional materials from solution. Efficient energy transfer during planetary ball motion leads to a fast and inexpensive process for the creation of nanostructured films. By adjusting the grinding parameters, the size and dispersion of the particles can be controlled and optimized for applications.

Here we describe results using the nanoscale grinding approach to fabricate multi-functional nanostructured thin film coatings. Nanogrinding allows tunability of film properties that can lead to novel functions depending on the particular combination of material, solvent and nanoparticle geometries/dimensions used. These unique abilities produce a general solution-based processing approach for thin film surface coatings and devices (including non-planar geometries).

Nanostructured thin films based on grinding high-purity powders (Si and TiSi) and characterization via electron microscopy, scanning probe, electronic transport and contact angle measurements are presented. Zirconia beads in a planetary ball mill with readily available powders initially consisting of ~10-50 micron particles in solvent were used. Grinding speeds and times varied between approx. 300-1000 rpm and 10-250 minutes, respectively. The resulting colloidal dispersions are deposited on a substrate for analysis. As grinding time is increased, the particles and films display good uniformity with sizes reaching below 100 nm. Both electrical conductance and contact angle could be tuned over a wide range depending on grinding conditions thereby creating unique multi-functional nanostructured materials and films. We also discuss preliminary results on optical and photocatalytic properties of the nanostructured surfaces. Thin films created via nanogrinding possess unique and varied electrical, optical and mechanical properties, which can be used to create advanced materials and devices.

[1] C. Papadopoulos, "Nanofabrication: Principles and Applications", Springer, 2016.

10:40am **TF-TuM9 Optimization of the ZnO Passivation Process on p-type $In_{0.53}Ga_{0.47}As$ Using Atomic Layer Deposition***,* ***Changmin Lee,*** *Y. An, S. Choi, J. Song,* Sungkyunkwan University, Republic of Korea*; Y.-C. Byun, J. Kim,* University of Texas at Dallas, USA*; H.S. Kim,* Sungkyunkwan University, Republic of Korea

For the performance enhancement of the inversion-type III-V metal-oxide-semiconductor field-effect transistors (MOSFETS), it is essential to improve the interface quality between the high-*k* gate dielectric and the p-type III-V substrate. Recently, ZnO passivation using an atomic layer deposition (ALD) process was reported to be effective in removing the interface oxides and improving the electrical properties on both p-type GaAs [1] and p-type $In_{0.53}Ga_{0.47}As$ [2].

In this study, the ALD-ZnO treatment was performed on the sulfur-passivated p-type $In_{0.53}Ga_{0.47}As$ substrates with different numbers of cycles at 150 °C. According to the electrical measurement of the MOS capacitors with HfO_2 gate dielectrics (ALD at 200 °C), a minimum capacitance increased with a flat band voltage shift when the number of treatment cycles was increased after an optimal condition. The possible origin for the observed changes in the electrical properties will be discussed based on various characterization results, such as the low temperature C-V measurement and chemical analysis using X-ray photoelectron spectroscopy.

[1] Y.-C. Byun et al., ACS Appl. Mater. Interfaces, 6, 10482 (2014).

[2] A. T. Lucero et al., Electron. Mater. Lett., 11, 769 (2015).

11:00am **TF-TuM10 Electrical Properties of the Atomic-Layer-Deposited Al_2O_3 on GaSb pretreated with TMA and TDMAT***,* ***Youngseo An,*** *C. Lee, S. Choi, J. Song,* Sungkyunkwan University, Republic of Korea*; Y.-C. Byun, J. Kim,* University of Texas at Dallas, USA*; H.S. Kim,* Sungkyunkwan University, Republic of Korea

GaSb is one of the possible candidates for a p-channel layer in the high-speed metal-oxide-semiconductor field-effect transistors (MOSFETs). However, its poor thermal stability and high reactivity with ambient air produce a poor interface with the high-*k* gate dielectrics, and there have been several attempts to resolve these problems [1-3].

In this presentation, the sample loading temperature was varied to find an optimal atomic layer deposition (ALD) condition of an Al_2O_{-3} film on p-type GaSb substrates. Then, we compared *in situ* substrate treatments of two metal precursors, trimethylaluminum (TMA) and tetrakis(dimethylamino)titanium (TDMAT), at the same loading temperature prior to the ALD-$Al\text{-}_2O\text{-}_3$ process. According to various electrical characterizations of the capacitors, lowering the loading temperature was beneficial in reducing the Fermi level pinning effect, and further suppression could be achieved by the subsequent TMA/TDMAT pretreatments. Although the TDMAT treatment showed more efficient relief of Fermi level pinning than the TMA treatment, it undermined the frequency dispersion characteristics in an accumulation region, as an adverse effect. The interface characterization results using X-ray photoelectron spectroscopy will also be discussed to understand the observed electrical properties.

[1] A. Nainani et al., J. Appl. Phys., 109, 114908 (2011).

[2] M. Yokoyama et al., Appl. Phys. Lett., 106, 122902 (2015).

[3] L. B. Ruppalt et al., Appl. Phys. Lett., 101, 231601 (2012)

11:20am **TF-TuM11 Using Surface Chemistry for Morphological Control of Metal Oxides and Chalcogenides on Organic Surfaces***, J.K. Hedlund, Z. Shi,* ***Amy Walker,*** University of Texas at Dallas

We describe recent progress in our laboratories to build robust complex two- and three-dimensional composite metal oxide and chalcogenide - molecular constructs. This work has important applications in photovoltaics, molecular and organic electronics, sensing, photonics and other technologies. Several recent developments will be discussed including the chemical bath deposition of ZnO transition metal dichalogenides, the atomic layer deposition of ZnO and ZnS and the formation of semiconducting nanowires and other nanostructures on micron-scale patterned surfaces. Optimization and further development of these techniques requires a detailed understanding of the reaction pathways involved in the interaction of organic thin films with organometallic compounds, ions, and other compounds in both solution and gas phases.

11:40am **TF-TuM12 Ultra-High-Density Arrays of Defect-Free AlN and GaN Nanorods: A "Space-Filling" Approach for Heteroepitaxial Thin Film Growth***, M. Conroy,* Pacific Northwest National Laboratory*;* ***Haoning Li,*** *V. Zubialevich, J. Holmes, P. Parbrook,* Tyndall National Institute

Nanostructured semiconductors have a clear potential for improved optoelectronic devices, such as high-efficiency light-emitting diodes (LEDs). However, most arrays of semiconductor nanorods suffer from having relatively low densities (or "fill factors") and a high degree of nonuniformity, especially when produced by self-organized growth. Ideally an array of nanorods for an optoelectronic emitter should have a fill factor close to 100%, with uniform rod diameter and height. In this paper we present a "space-filling" approach for forming defect-free arrays of AlN nanorods, whereby the separation between each rod can be controlled to 5 nm due to a self-limiting process. These arrays of pyramidal-topped AlN nanorods formed over wafer-scale areas by metal organic chemical vapor deposition provide a defect-free semi-polar top surface, for potential optoelectronic device applications with the highest reported fill factor at 98%. We then applied this method to GaN, in particular investigating the desorption factor that was not an issue for the AlN growth. Here we show that the etched nanorods change morphology during the annealing step even before additional GaN is deposited, forming 6 non-polar side walls.

Biomaterial Surfaces & Interfaces
Room Makai - Session BI-TuP

Biomaterial Surfaces & Interfaces Poster Session

BI-TuP1 A Real Time Observation of Nano/Bio Interface of Protein Nanoparticles Using Graphene Liquid Cell ELectron Microscopy*, Tolou Shokuhfar,* University of Illinois at Chicago, USA

Investigation of crystalline structure and chemistry of biomaterials including biopolymers, bacteria cultures and proteins has always been a great interest for both materials and biomedical communities. The difficulties associated with the imaging of biological structures can be listed as follows: 1) If the imaging is conventional in Scanning / Transmission Electron Microscope (S/TEM), all liquid phase will be evaporated in the vacuum environment when inserted into the microscope, otherwise room temperature fixation, dehydration, infiltration, fixation, embedding and staining should be applied, but in this case, the sample will go through several chemical and thermal processes which involves loss of liquid phase and artificial contrast improvement through preferential staining so that the sample will not be in its native state. 2) If cryogenic imaging is utilized, the sample will be frozen, so all these steps mentioned in 1 will be eliminated. By lowering diffusion rates at liquid nitrogen temperatures, the electron beam induced sample damage will be less, which is good for imaging, but the other energy activated processes, which again depend on the electron beam-sample interaction, are not possible for these frozen samples to occur. 3) In order to see the dynamic processes, *in situ* fluid cell holders can be used. Even though electron beam related dynamic processes can be visualized with these holders, the sample thickness will be too much including the two silicon nitride windows and the liquid sandwiched in between the windows. 4) To characterize the chemistry and crystal structure knowledge at the native state with the highest resolution, the material needs to be thin and should be sealed/sandwiched in between two single layers of graphene sheets forming graphene liquid cell (GLC), so that the Selected Area Electron Diffraction (SAED) and Electron Energy Loss Spectroscopy (EELS) studies can be carried out in the Cs corrected S/TEMs with the highest resolution available in terms of the crystal structure and chemistry, respectively. We have shown even individual iron ions can be detected in the liquid state when released from the ferritin structures encapsulated in GLC and which proves the necessity of using GLC for the achievement of this sort of resolution [1-2].

[1] T Shokuhfar *et al.*: High resolution electron microscopy and spectroscopy of ferritin in biocompatible liquid cells and graphene sandwiches, Advanced Materials, 26, 3410, pp. 3410-3414.

[2] The authors acknowledge funding from the National Science Foundation- CAREER award- Grant No- DMR- 1350734.

BI-TuP2 Combined Effect of Antimicrobial Coatings, Gamma Radiation and Negative Air Ionization with Ozone on *Listeria Innocua*, *Escherichia coli* and mesophilic bacteria on ready-to-eat cauliflower florets*, Monique Lacroix,* INRS-Institut Armand-Frappier, Canada

The objective of this study was to evaluate the effect of an antimicrobial bioactive edible coating on the microbiological quality of ready-to-eat cauliflowers. Combined treatments using antimicrobial coating in combination with a low γ-radiation dose or negative air ionization (NAI) with ozone on the microbiological quality of ready-to-eat cauliflowers was also evaluated. The antimicrobial coating was based on a microemulsion of citrus and lemongrass extract in mixture. The microemulsion was also mixed with a polymeric formulation based on maltodextrin and methylcellulose.

Results showed that each treatment alone was effective on *Listeria innocua*, *Escherichia coli* and mesophilic bacteria.

The antimicrobial coating was able to reduce by 2 Log CFU/gr, the level of *E. coli* and *L. innocua* and by 1.5 log CFU/gr, the level of total mesophilic bacteria. The bioactive coating acts also in synergy with γ-radiation, inducing no bacterial growth of *L. innocua* and *E. coli*, as well as a control of the growth of mesophilic bacteria during 7 days of storage. However, the use of NAI + ozone did not act in synergy with the antimicrobial coating to reduce the level of the pathogens under study. However, storage of coated vegetables under NAI + ozone atmosphere would be a good technique to reduce and control bacterial growth during storage to prevent cross-contamination.

BI-TuP3 Antibacterial Nano-film Fabrication for Ophthalmic Application*, Minwook Chang,* Dongguk university, Republic of Korea*; J. Hong,* Chungang university, Republic of Korea

Super-hydrophilic coatings have been extensively studied because of their diverse applications, especially for anti-bacteria films. Anti-bacterial coatings in biomedical devices need to be durable and bio-compatible, but super-hydrophilic films are commonly very fragile due to a porous structure, which is essential for super-hydrophilic functionality, chemical contamination, and thermal stability. To overcome these drawbacks of antibacterial coatings, we introduced polymeric silsesquioxane into the nano-coating, resulting in superior thermal stability and matrix structure based on siloxane groups. Layer-by-layer assembly was used as a multilayer fabrication method to exquisitely control morphology, thickness, and functionality of the nano-coating, and fabricate suitable structures for super-hydrophilic films through simple dipping and washing steps. Antimicrobial and nanoindentation tests were carried out to demonstrate the successful enhancement in the antibacterial and mechanical properties of the nano-coatings.

BI-TuP4 Micro/Nano-Bioactive Structure of Titanium Implant Surface*, Zhoucheng Wang,* Xiamen University, China

Multi-level micro/nano-structure on titanium surface was constructed by Al_2O_3 sandblasting, acid etching in H_2SO_4 and HCl solution, and then anodizing in HF solution at a constant potential. The biological activities of different treated titanium samples were observed in vitro experiment . Scanning electron microscopy (SEM), [app:ds:Energy] [app:ds:Disperse] [app:ds:Spectroscopy] ([app:ds:EDS]) and X-ray diffraction (XRD) were employed to characterize the morphology, composition and crystalline phase of the different treated titanium samples. The results showed the multi-level micro/nano-composite structure in which approximately consisting of 10~20 μm diameter hollow by sandblast, 5~8 μm diameter pit by acid etching and 10 nm diameter nanotexture by anodizing. The results of vitro experiments showed that the multi-level micro/nano-composite structure had better biological activity than the control group. After modification and heating treatment of the surface, the multi-level micro/nano-composite structure sample showed [app:ds:excellent] hydrophilic property and biological activity.

BI-TuP5 Single-vesicle Fusion Assay Provides Insight into ER Fusion Mediated by the Dynamin-like GTPase Sey1p*, Sanghwa Lee,* Gwangju Institute of Science and Technology (GIST), Republic of Korea

It is known that dynamin-like GTPase Sey1p protein maintain the structure of endoplasmic reticulum(ER) that constantly forms interconnected network in the cell. There is not yet consensus on how Sey1p mediate homotypic ER fusion in detail, however. Through the conventional ensemble measurements, where the individual interaction of vesicles cannot be distinguished, they have limitations for reveal how Sey1p works. To elucidating the detailed mechanism of Sey1p, we performed FRET-based single-vesicle lipid-mixing assay. It turns out that Sey1p can easily mediate tethering while it can hardly stimulate vesicle fusion by itself. On the other hand, the time it takes to switch from "tethering" to "fusion" is not affected by the GTP & Mg^{2+} concentration and protein density on vesicle. These results suggest that Sey1p requires additional factors to support ER fusion in vivo.

BI-TuP6 Assembly of Proteins and Oriented Purple Membrane on Functionalized Carbon Nanomembranes*, Natalie Frese,* Bielefeld University, Germany*; D. Rhinow,* Max Planck Institute of Biophysics, Germany*; A. Turchanin,* Friedrich Schiller University, Germany*; N. Hampp,* Philipps University, Germany*; A. Gölzhäuser,* Bielefeld University, Germany

This presentation is about hybrid structures comprising carbon nanomembrane (CNM) as a functional substrate and oriented assembled purple membranes (PMs). CNMs are monomolecular cross-linked layers of aromatic amphiphilic molecules with lateral dimensions of several square centimeters and a thickness of about 1 nm. PM from Halobacterium salinarum is a membrane consisting of bacteriorhodopsin (BR), which is a light-driven proton pump, and lipids.

CNM has already been successfully tested as a substrate for electron cryo-microscopy of PM. To realize the oriented assembly of PM patches on CNM, we used a PM mutant, which has histidine (HIS) tags selectively on one side of the membrane and a nitroliotriacetic acid (NTA) terminated NBPT-CNM. The functionalized CNM has also been tested with different HIS-tagged proteins.

BI-TuP7 Detection Fecal Occult Blood for Early Colorectal Cancer by TOF-SIMS*, C.C. Yu,* Vanung University, Taiwan, Republic of China*; W.J. Lin, S.M. Wang,* Central Police University, Taiwan, Republic of China*; **Fu-Der Mai**,* Taipei Medical University, Taiwan, Republic of China

Due to a dramatic change in both the lifestyle and eating habits, a steady increase in risk of gastrointestinal diseases every year. Early detections and treatments can reduce the mortality caused by gastrointestinal diseases. Fecal occult blood (FOB) is a small amount of blood in the stool which is invisible to human eye. If blood is detected in FOB, the cause may be gastrointestinal disorders, such as colorectal polyps, colorectal cancer and, etc. Fecal occult blood test (FOBT) is a rapid and non-invasiveness method for early diagnostics about gastrointestinal diseases. In this study, we present an alternative method for FOBT other than the traditional methods by using the time-of-flight secondary ion mass spectrometry (TOF-SIMS). TOF-SIMS can analyzes the molecular composition of the sample surface with a simple pre-treatment or even without any pre-treatment. Furthermore this method can avoid the potential pitfalls found in the traditional FOBT, such as the false positive results due to the interfere of food and drugs in the chemical method and the false negative responses due to the hemoglobin degradation during the storage in the immunization method. Preliminary results shown that there are significant differences at m / z = 86 and m / z = 184 for the stool samples with FOB. Currently we test different pre-treatments to achieve consistency and accuracy of the experimental results.

BI-TuP8 Preparation of Water-Based Cationic Polyurethane Dispersion for Antibacterial Applications*, G.H. Wu, **Cheng-Tien Hsieh**,* National Taiwan University, Taiwan, Republic of China*; S. Hsu,* National Taiwan University,Taiwan, Republic of China

Waterborne biodegradable cationic polyurethane (WCPU) nanoparticle dispersion was synthesized by reaction of polycaprolactone, isophorone diisocyanate, and N-methyldiethanolamine under 75 °C and vigorous stirring under acidic condition. The nanoparticles dispersed in the aqueous medium were uniform with an average size of ~80 nm and a zeta potential of ~60 mV. The WCPU nanoparticle dispersion may be cast into films. The contact angle of the films was ~67°and the zeta potential was ~16 mV. The WCPU nanoparticles demonstrated excellent antibacterial activity against Escherichia coli (E. coli) and Staphylococcus aureus (S. aureus) (100% inhibition with a contact time of 3 h). Meanwhile, the antibacterial ratio of WCPU films to E. coli and S. aureus reached 100% after 24 h of contact. Moreover, The WCPU nanoparticles could be used as a transfection reagent without significant toxicity for concentrations less than 1000 mg/mL and showed the ability to condensate plasmid DNA. The transfection efficiency for HEK293T cells was ~60% after 48 h of transfection. Moreover, the WCPU dispersion can be made into microspheres conveniently. The WCPU dispersion prepared in the study has potential antibacterial and biomedical applications.

BI-TuP9 Hydrophilic Itaconic Acid Based Material Coating on Silicone Implants Surface for Inhibition of Capsular Contracture*, M. Birajdar,* Chung Ang University*; YB. Choy,* Seoul National University, Korea*; S. Lee,* CHA*; **Hansoo Park**,* Chung Ang University

The capsular contracture has been a serious problem for silicone implants, leading to surgical removal or surgical replacement. Recently, the silicone implants were modified with textured surface and coated with biomimetic materials to overcome this complication. In this work, we modified the surface of silicone implants with highly hydrophilic itaconic acid (IA) based materials having antibacterial properties and investigated their effect on inhibition of capsular contracture. Various formulation including IA alone, Oligo IA, IA-gelatin polymers, gelatin particles containing IA were tested. The results confirmed the coating of silicone surface with thin layers of IA based materials with concentration dependent manner. It was also found that the contact angle was decreased in all groups, confirming the increase in hydrophilicity. In vitro cell adhesion and protein adsorption were also tested on the modified silicone and compared to the unmodified silicone. These surface modification of IA based materials could be used as a potential alternative to inhibit the formation of capsular contracture.

BI-TuP10 Photoacoustic Microscopic Imaging with Bone Targeted Near Infrared Fluorophore*, **TaeJoong Eom**, H.D. Lee,* Gwangju Institute of Science and Technology (GIST), Republic of Korea

In order to obtain 3D bone structure images, we should regard x-ray dose for CT imaging or ultrasound image confusing from other organs. By using a bone-specific near infrared (NIR) fluorophore functionalized by phosphonate groups, we demonstrate photoacoustic microscopy (PAM) system for in-vivo bone imaging with out regarding x-ray dose. The NIR light has certain key advantages for biomedical imaging, including relatively ultra low tissue absorption with red blood cell, reduced scatter, and minimal autofluorescence. Especially, the phosphonated NIR fluorophore targets bone tissue with high specificity and this property is inherent to the chemical structure of the fluorophore. Since the heptamethine indocyanine structure has absorption/emission spectrum at ~780/ ~800 nm and the quantum yield of fluorophore is around 10-20 %, the NIR fluorophore can be applied for PA imaging system. The most of surplus optical energy is transferred to the thermal energy which can generate acoustic signal. For the NIR pulse excitation, we applied a high power pulsed laser, which has output power of 600 mW, pulse duration of 1 ns, and repetition rate of 10 kHz at the center wavelength of 780 nm. The NIR fluorophores were administered intravenously into nude mouse to obtain in-vivo PA bone imaging. The foot and tail bone structures of mouse image were successfully obtained by scanning a PAM system with a single ultrasound transducer.

BI-TuP11 Histological Analysis of Bone Regeneration with Hydroxyapatite Isolated from Two Natural Sources (Gallus Domesticus and Sciaenops Ocellatus) in Bone Defects induced in Tibiae of Rabbits*, D.I. Balleza-Ovalle,* Universidad Autónoma de Tamaulipas, México*; H. Hernández-Cocoletzi,* Benemérita Universidad Autónoma de Puebla, México*; **J.H. Luna-Domínguez**, C.A. Luna-Lara, H. Tellez-Jimenez,* Universidad Autónoma de Tamaulipas, México*; E. Águila-Almanza,* Benemérita Universidad Autónoma de Puebla, México

In the field of dentistry, biomaterials that meet the requirements for optimal bone tissue formation have play a vital role for the treatment of bone reabsortion caused by periodontal disease, dental extractions or periapical lesions. Hydroxyapatite (HA) is a biocompatible nonabsorbable material chemically similar to the mineral component of bones and hard tissues, therefore, it can be used as a scaffold. HA can be isolated from natural sources by the thermal calcination method. The aim of this study is to assess the osteoconductive effect of hydroxyapatite isolated from two natural sources (Gallus domesticus and Sciaenops ocellatus) by histological analysis applied in bone defects induced in tibiae of rabbits over a period of four weeks. In this experimental study, five healthy adult male rabbits of New Zealand strain, weighing approximately 3.5 kilograms, which were kept in cages according to the Mexican Official Standard NOM 062 Z00-1999 for the use of laboratory animals were used. Four defects with a size of 4 mm in diameter and 6 mm of deepness were made in the proximal metaphyseal planodiáfiso of both tibias and HA was applied to the defect according to the grouping. After four weeks of the surgery, both tibias were recovered in blocks containing all the graft area for histological analysis. Results: In the hydroxyapatite groups the new bone growth involved an area of 78.53% (Sciaenops ocellatus) and 72.23% (Gallus domesticus). The control group involved 15.97%. Conclusion: After four weeks, HA groups shown to be osteoinductive agents and they allowed the growth of bone tissue to a higher growth rate and bone of higher quality than in the control group.

Nanomaterials

Room Makai - Session NM-TuP

Nanomaterials Poster Session

NM-TuP1 On the Possibility of the Development of Vicinal Superlattices in Quantum Wires on Semiconductor Low - Index Surfaces*, **Victor Petrov**,* Institute of Radio Engineering & Electronics, Russian Academy of Science,Moscow,125009,Russia, Russian Federation

As is well known, vicinal superlattices (VSLs) are realized in 2D electron systems on semiconductor high-index Miller surfaces. The possibility of existence of such VSLs was predicted theoretically (V.A.Petrov, 1977) [1,2]; simultaneously and independently they were realized (T.Cole et al.1977) [3]. At the present time, all these VSLs are developed only in 2D systems.

In this work we suggest a new method of development of the VSL in the quantum wires (QWR).where superlattice effects should be maximal. The special feature of this method is the combination of the main properties of the VSL - the separation in the system by some way of the long translation period A - with the possibility of developing this situation in the QWR on semiconductor low - index surfaces. It is easy to see that this situation is possible when the axis of the QWR which lies on the low - index surface will be oriented at the necessary angles to the basic translation vectors along the surface. In this case the translation symmetry of the QWR will be determined by its orientation on the crystal surface since the possibility of a free motion only along the axis of the wire selects in the initial two -

dimensional translation group along the surface a one - dimensional translation subgroup along the wire with the basic period A. Thus, in the one-dimensional VSL the period A is selected by the orientation of the wire on the surface. For example, if the QWR is realized in the MOS system with the use of a narrow gate (V.A.Petrov 1978)[4] then the orientation of the wire will be determined simply by the appropriate orientation of the gate.

The analytic expressions of the new periods A were obtained as a function of the angles which determine orientation of the QWR for the different low-index surfaces GaAs and Si. The positions of minigaps in the one-dimensional k-space were determined. It is should be noted that in the region of the particle wave function localization in the QWR there are many crystallographic planes which form a superlattice energetic spectrum of the particle. Illustrative estimates of the magnitude of the minigaps for the QWR of the rectangular cross-section made in the weak coupling approximation demonstrate their dependence on the geometric parameters of the cross-section, on the period A as well as on the crystal potential.

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NM-TuP2 Influence of Electron Interference Effects on Reflection of Electron Waves From Potential Barrier in 2D Semiconductor Nanostructures, ***Andrey Nikitin****, V.A. Petrov,* Institute of Radio Engineering & Electronics, Russian Academy of Science,Moscow,125009,Russia, Russian Federation

The influence of the interference of electron waves in the case of their reflection from potential barrier on the spatial distribution of the density of quantum-mechanical current $ej_x(x,z)$ (e – electron charge) in 2D semiconductor nanostructure which is represented by rectangular narrow ($x < 0, QW_1$) and wide ($x > 0$, QW_2) quantum wells (QWs) sequentially oriented along the direction of the propagation of electron wave has been studied theoretically. It is supposed that the wave falls from the narrow QW_1 on the semi-infinite potential barrier V_0 in height in the wide QW_2, the energy of the falling wave being less than V_0. Differing widths of QW_1 and QW_2 provide the non-orthogonality of wave functions of particles in these regions and the corresponding existence of electron interferential effects in this kind of nanostructure. In particular cases these effects lead to the appearance of spatially inhomogeneous distributions $ej_x^{(1)}(x,z)$ in QW_1 and $ej_x^{(2)}(x,z)$ in QW_2. It has been analytically demonstrated that in case of an electron wave falling along the first (lower) quantum-dimensional subband in QW_1 and its kinetic energy E_x being less than the energy positions of all the other subbands in QW_1 (*i.e.*, the undamped propagation of the wave reflected from the barrier with real quasi-momentum is possible only along this lower subband) $ej_x^{(1)}(x,z)$ and $ej_x^{(2)}(x,z)$ are equal to zero. However, if a particle has such an energy that the refection of the wave with real quasi-momenta is possible along more than one (lower) subband, then the situation completely changes due to the interference of the reflected waves. In this case the interference leads to an existence of a complicatedly oscillating spatially inhomogeneous distribution $ej_x^{(1)}(x,z)$, and under the barrier in QW_2 it provides the appearance of exponentially damped at $x \to \infty$ and possessing a coordinate dependence of leakage $ej_x^{(2)}(x,z)$ under the barrier. Besides, three regions of the symmetric along z axis propagation $ej_x^{(2)}(x,z)$ are formed under the barrier. They are the central one, in which the current is directed in axis x positive direction, and two side regions in which the current is directed in negative direction. The presence of the regions of that kind provides the charge flow from under the barrier. The numerical calculations of $ej_x^{(1)}(x,z)$ and $ej_x^{(2)}(x,z)$ have also been made taking into account 31 subbands. It should be noted that these kinds of effects have a general nature and exist in 1D and 2D nanostructures with arbitrary profiles of QWs and barriers.

NM-TuP3 Understanding Ligand-Surface Passivation of Cation-Rich Colloidal Quantum Dots: First-Principles Study, *J.-H. Ko, D. Yoo,* ***Yong-Hyun Kim,*** Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

Colloidal quantum dots (CQDs) are attractive nanomaterials for optoelectronic and photovoltaic applications because they are useful for mass production and easy to tune optical and electronic properties by controlling the size of CQDs. Generally, stable CQDs with good ligand-surface passivation are essential for such CQD applications. Yet, microscopic understanding how CQD surfaces are stabilized with passivating ligands is not clear in the colloidal environment. In this study, we performed first-principles density-functional theory (DFT) calculations for understanding ligand-surface passivation of cation-rich surfaces of IV-VI, II-VI, and III-V CQDs. Calculation results indicate that while non-polar surfaces of CQDs are self-passivated, polar surfaces of cation-rich CQDs, i.e., (100) and (111) for zinc blende semiconductors, have reactive surface dangling electrons that should be properly coordinated with passivating anionic ligands. We will discuss how such polar surfaces of CQDs could be stabilized by organic and inorganic ligands based on electron counting rule and coordination chemistry.

NM-TuP4 Ar Plasma Treated Transparent Silver Nanowire Electrodes for Flexible Quantum Dot Light-Emitting Diodes, *J-W. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea; ***Jiwan Kim,*** Kyonggi University, Republic of Korea

A smooth, ultra-flexible, and transparent electrode was developed from Ag nanowires (AgNWs) embedded in a colorless polyimide (cPI) by utilizing an inverted film-processing method. The resulting AgNW-cPI composite electrode is highly transparent and has an ultra-smooth surface with a low sheet resistance. The thickness of this conductive composite film was reduced to less than 100um with extreme flexibility. This film exhibited mechanical durability up to a bending radius of 5 mm. Green quantum dots light-emitting diodes (QLEDs) were fabricated using these composites as bottom electrodes (anodes). Hole-injection in QLEDs was poor, because AgNWs were largely buried beneath the composite's surface. Thus, we used a simple plasma treatment to remove the thin cPI layer overlaying the nanowires without introducing other conductive materials. As a result, we were able to finely control the flexible QLEDs electrical/optical properties using the enlarged conductive pathways. The fabricated flexible devices showed only slight performance degradation after a repeated bending test.

NM-TuP5 High-throughput Synthesis of Emissive Glass Microcomponents via Contact Flow Lithography, ***Jiseok Lee,*** Ulsan National Institute of Science and Technology, Republic of Korea

We report a high-throughput synthesis of emissive microcomponents with rare-earth-doped upconverting nanocrystals (UCNs) using a contact flow lithography. Upconverting nanocrystals were synthesized using hydrothermal reaction and used as anti-Stokes emitters that absorb near-infrared (NIR) light and emit in visible spectrum. We utilized contact flow lithography for massive production of nonspherical composite microcomponents. Emissive composite microcomponents with a variety of shapes was synthesized and corresponding glass microcomponents were obtained through polymer burn-off. The synthesized particles with UCNs are stable at high temperature and have great potential to use as anti-counterfeiting platform.

NM-TuP6 Effect of Redox-Induced Conformational Changes in Charge Transport Characteristics of a Ferrocene-Alkanethiolate Molecular Device: Temperature-Dependent Transition Voltage Spectroscopy Analysis, ***Hyunhak Jeong****, Y. Jang, D. Kim, W.-T. Hwang, J.-W. Kim, T. Lee,* Seoul National University, Republic of Korea

The ultimate aim of molecular electronics is to overcome the limit of the conventional silicon based solid-state electronics by utilizing either single molecules or a bundle of molecules as an active electronic device component. For example, Nijhuis et al. recently reported a robust molecular diode using ferrocene-alkanethiolate self-assembled monolayers (SAMs) and eutectic Ga and In (EGaIn) electrodes.[1] They demonstrated a large rectification ratio of up to ~1000 and reported that the strong asymmetric electrical characteristics could be interpreted by hopping assisted tunneling transport arising from the ferrocene-alkanethiolates and the electrodes.

Similar to these studies, we have also examined the possibility of the electronic device application by fabricating a large number of molecular devices based on ferrocene-alkanethiolate (denoted as FcC) SAMs using a conventional solid-state device fabrication technique both on rigid and flexible substrates.[2] Specifically, we observed a distinctive temperature dependence on the electrical characteristics; that is, the current density decreased as the temperature increased in a certain temperature range when a sufficient voltage was applied with a certain voltage polarity. This behavior was in contrast to the usually expected thermally activated charge transport in the molecular device junction or other device junctions in which, most times, the current density increases as the temperature increases. In that study,[2] we suggested the unusual thermal characteristics are probably due to the redox-induced conformational changes of the FcC in the molecular junctions. While the analysis was quite reasonable and consistent with the experimental results, further evidence was needed to support our suggested explanation. We also performed temperature-dependent transition voltage spectroscopy (TVS) analysis based on a multibarrier tunneling model, which supports the occurrence of the proposed redox-induced conformational changes in the FcC molecular junctions.[3]

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NM-TuP7 High Elastic Modulus, High Extensibility Nanorods Constructed of pH-Responsive Cyclic Peptide Polymer*, **Kenan Fears**, M. Kolel-Veetil, D. Barlow, N. Bernstein, C. So, K. Wahl,* US Naval Research Laboratory, USA

Due to their ability to self-assemble into supramolecular nanorods in solution, cyclic β -tripeptides (CBTPs) have been used as molecular scaffolds that predictably display functional groups along the axis of the assembly. To enhance the mechanical strength and processability of such nanostructures, we synthesized a linear polymer of amide-bonded CBTP subunits using previous computational analysis on the conformational stability and tunability as guidance. Two amino acids in each subunit (β -HLys or β -HGlu) form "hinges" with neighboring subunits, and electrostatic repulsions between the third, β -HOrn, forced the polymer to adopt a disordered conformation when protonated. When deprotonated, atomic force microscopy revealed rigid nanorods exhibiting an elastic moduli (51.3 GPa) stiffer than any report peptide-based material. The hinges also allow the nanorods to elongate under tension which should impart the polymer with high extensibility and resilience. Nanorods were decorated with Au nanoparticles to demonstrate the ease in functionalizing the polymer, greatly expanding its potential applications beyond a structural material. The solubility and structural control achieved by combining covalent bonds, non-covalent bonds, and electrostatic interactions suggest the polymer may not only exhibit excellent processability but also mimic toughness and elasticity found in nature.

NM-TuP8 Growth and Optical Properties of Catalyst-free Ga(In)N Nanorods with Different Top Shapes*, **Moon-Deock Kim**, B.-G. Park, J.-W. Hwang,* Chungnam National University, Republic of Korea*; W.-C. Yang, D.-Y. Kim, K.-B. Chung,* Dongguk university, Republic of Korea

In this work, we have investigated the kinetic process and adatoms mechanism of four different top shapes of catalyst-free Ga(In)N nanorods (NRs) namely flat, taper, hammer, and mushroom structures were grown in holes of a patterned Si (111) substrate by plasma-assisted molecular beam epitaxy. Arrays of nano-holes with diameter of 80 nm on the Si substrate were obtained by using of self-assembled silica nanospheres as a nano-hole mask. The silica nanospheres coated on the Si substrate and then spread using a spin-coating method. A 10 nm-Ti deposited after dry etching to sizes control and then removed silica nanospheres by chemical etching. Different top shapes of Ga(In)N were obtained by varying the growth conditions namely growth temperature and N2 plasma power, and the morphology evolution was explained based on the interrelation between sidewall diffusion and direct impingement during the NRs growth. GaN NRs grown at the growth temperature (T_g) and *Ga* flux of 650 °C and $5x10^{-7}$ Torr, respectively, were used as the buffer for the subsequent growth of GaN NRs with different top shapes. GaN NRs with flat top (Fig. 1(a)) was obtained without altering the growth conditions that was used for the buffer growth. When the T_g was increased gradually from 590 °C to 650 °C under *Ga* flux of $1x10^{-7}$ Torr, we obtained GaN NRs with top tapered shape (Fig. 1(b)). On the other hand, hammer shaped GaN NRs (Fig. 1(c)) were obtained when the T_g was reduced gradually to 570 °C, while keeping the Ga flux $1x10^{-7}$ Torr during the growth of GaN NRs. Furthermore, mushroom shaped Ga(In)N nanostructure (Fig. 1(d)) on top of GaN NRs were obtained when introducing *In* flux of $1x10^{-7}$ Torr at T_g ~ 350 °C under the same Ga flux. The variations in the shape of GaN NRs are explained by the interrelation of sidewall diffusion and the supersaturation of adatoms at the top surface [1, 2]. Photoluminescence measurements revealed higher light emission for tapered GaN when compared to non-tapered structure. APSYS simulations were further conducted to theoretically confirm the observed experimental results. We believe that our results can provide crucial information for the shape controlled growth of GaN NRs with diverse nanostructures and promising approach for the realization of high brightness LEDs.

Fig. 1 SEM images of GaN NRs with different top shape (a) flat, (b) tapered, (c) hammer and of GaInN with (d) mushroom

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NM-TuP9 Semi-green Synthesis and Characterization of Superparamagnetic Fe_3O_4-MNPs with Aqueous Extracts from C. Verum and Natural Extract from V. Planifolia*, A.L. Ramírez-Núñez,* Doctoral Program in Nanosciences and Nanotechnology CINVESTAV-IPN, Mexico*; **Jaime Santoyo-Salazar,*** Nanosciences and nanotechnology, CINVESTAV-IPN, México*; L.F. Jiménez-García,* Faculty of Sciences, UNAM, México*; G. Goya Rossetti,* Instituto de Nanociencia de Aragón, Spain

Recently biosynthetic methods employing either biological entities or plant extracts have emerged as an easy, fast and economical alternative to chemical and physical síntesis procedures for the production of safer nanomaterials for human use. An eco-friendly semi-green method was used in order to obtain magnetite magnetic nanoparticles (Fe_3O_4-MNPs). Besides the know effect of polyphenols as therapeutical agents in cancer diseases, biomolecules from aqueous extracts can act as capping and reducing agents wich effectively replace toxic chemical reductans. Plant extracts with a rich mixture of active biological phytochemicals (i.e. polyphenol compounds, tannins, saponnins, flavonoids) control and shape the growing nanoparticles. Superparamagnetic properties have been studied extensively due to their potential use in hyperthermia in cancer treatment. The green synthesis of Fe_3O_4-MNPs with aqueous extracts represent a major advantage in the synthesis of superparamagnetic materials for biomedical usage, due to their diminished toxicity to biological organisms and more efficient drug delivery carriers for specific cancer diseases. In order to explore the diversity of biomolecules in the obtention of Fe_3O_4-MNPs, in this work an aqueous extract from *Cinnamomun verum* and *Vanilla planifolia* (natural pods and synthetic extract) were used during the synthesis of magnetite.

The Fe_3O_4 MNPs obtained were identified by XRD (PDF-19-0629) corresponding to an inverse spatial group *Fd3m* (227) inverse spinel FCC structure, *a*= 8.355 Å in synthetic vanilla and a=8.362 Å in vanilla pods extract (*V. planifolia),* and *a*=8.366 Å in *C. verum*. IR peaks at 576 cm^{-1} correspond to Fe-O bonding formation; vibrational peaks at 576-1641 and 3415 cm^{-1} suggest phenol molecules involved in bio-reduction process. XRD and HRTEM diffraction patterns overlap with the corresponding Fe_3O_4 peaks (220),(311),(400),(511),(440). The *d* spacing 2.4 Å in *V. planifolia* and 2.7 Å in *C. verum* match the main diffraction plane 35° (311). The particle size calculated by Scherrer´s equation by Scherrer´s equation *(t=Kl/b cos Θ)* in *V. planifolia* was 12 nm and 14 nm in *C. verum*. AFM-MFM data show a monodomain arrangement of 2-3 nm in *V. planifolia* and 5-6 nm in *C. verum.* VSM data indicate that magnetization increases rather using *C. verum* extract (64.89 emu/g) than *V. planifolia* (46.6 emu/g). The SPA values suggest that vanilla pods extract has an advantageous performance during Fe_3O4-MNPs synthesis due to their increased heating capability (64.51 W/g). The bio-synthesis of Fe_3O_4 MNPs obtained by aqueous plant extracts are commensurable to those obtained by a chemical method with a better performance than synthetic extract.

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NM-TuP10 Nanostructure Surface Design for Increased Photovoltaic Responses in Ethanol Photochemical Fuel Cells*, K. Hirakawa, D. Rodriguez, K. Anderson, **Yong Gan**,* California State Polytechic University Pomona, USA

Electro-spun Titanium nanofibers can be applied to the surface of photoanode to create a multi-catalyst anode. The electrospinning process is considered in this study and found that it is as one of the simplest ways to create nanofibers with varying diameters ranging from 50 to 500 nm. When combined with a polyvinylpyrrolidone (PVP) composite, titanium oxide creates a nanofiber with high surface area while containing the intrinsic semiconductor properties of . The effects of using silicon nanowires (SiNW) on the surface of doped silicon as a substrate was also studied in this work. SiNWs create a porous surface feature due to the electrodeposited silver on silicon. Silver has a plasmonic effect which allows free electrons to oscillate on the surface of the metal when exposed to light. This plasmonic effect allows Silver to be used as a photocatalyst. Silicon can also be easily etched which creates another photocatalyst . The porous SiNWs enhances the phonon scattering about the interfaces of the nanowires due to its high anti reflectivity causing higher absorption. The functionality of a PEC cell is driven by many factors. nanotubes are the primary interest in this research. The purpose of this work is to determine the effects of type of the surface modified nanostructured photocatalyst anode, the ethanol concentration levels, on the response time of the photoelectrochemical (PEC) reaction when exposed to UV light source. Over a short period of UV irradiation exposure, the response time influences how much the potential difference changes between the anode and cathode. Creating multi-catalyst anodes using doping techniques, electrospinning applications, and electrodeposition methods change the photocatalytic properties. Varying the concentration of the fuel by lowering the energy density present in the electrolyte also effects the response time of the photoanode. By inspecting the various response times, the efficient photoanode in this study is identified.

NM-TuP11 Microfluidic Capacitive Sensors Using Ionic Liquid Electrodes and CNT/PDMS Composites for Multimodal Sensing Applications*, **SunGeun Yoon**, S.M. Lee,* Chung Ang University, Republic of Korea

There are many studies of demonstrating capactive sensors for various purposes such as detecting pressure, body motions, and temperature variation. However, its perfoming principle is mainly dependent on physical and geometrical changes of dielectric layers. In this study, we developed a new class of microfluidic capacitive sensors with utilizing ionic liquid serving as electrodes and CNT/PDMS composites (CPCs) as a dielectric layer. The working principle of our microfluidic sensors was investigated with geometrical changes of microfluidic channel and variations of electric double layer (EDL) capacitance. Our microfluidic capacitive sensors showed detection of localized pressure, lateral pressure movement, and even temperature variations with high sensitivity. By using multimodal capability, the microfluidic capacitive sensor was successfully performed as a keypad and applied to a bottle and human skin. This microfluidic capacitive sensors could offer great opportunity of development for future stretchable and flexible electronic devices such as wearable electronics, soft robotics, electronic skin, and human healthcare systems.

Thin Films
Room Makai - Session TF-TuP
Thin Films Poster Session

TF-TuP1 P-Type Nitrogen Doped Zinc Oxide Films Prepared By Magnetron Sputtering*, J.Y. Chen,* Ming Chi University of Technology, Taiwan*; H.T. Zhang, G. Zhao, Q. Chen,* Beijing Institute of Graphic Communication, China*; **Jyh-Shiarn Cherng**,* Ming Chi University of Technology, Taiwan, Republic of China

P-type nitrogen doped zinc oxide (NZO) was prepared on a glass substrate by RF magnetron sputtering using N_2 as the nitrogen source. The structural, electrical and optical properties of the NZO films were investigated by X-ray diffractometry, X-ray photoelectron spectroscopy, Raman spectroscopy, Hall effect and Seebeck effect measurements, and UV-Vis spectroscopy. The electrical properties of the p-type NZO showed a conductivityof 7.6×10^{-2} $(\Omega\text{-cm})^{-1}$ and remained stable for over 259 days at the optimized process conditions. With the increase of N_2 flow rate during sputtering, the conductivity of the NZO films exhibited an n-p-n transition. The corresponding mechanism of this transition and the origin of the p-type conductivity were discussed accordingly.

TF-TuP2 Low Temperature Deposition of nc-Silicon Thin Films using SiH_4/H_2 Mixture*, **Moniruzzaman Syed**,* Lemoyne Owen College, USA*; B. Goh, N. Nazarudin,* University of Malaya, Malaysia*; J. Alam,* University of Memphis*; Y. Hamada,* Lemoyne Owen College, USA*; A. Ali,* King Khalid University, Saudi Arabia

Nanocrystalline-silicon (nc-Si) films were simultaneously deposited on glass and single-crystal Si substrates that were exposed to H_2 plasma excited using RF $_{power}$ = 80 W prior to the film deposition, under 250°C by plasma enhanced chemical vapor deposition using a SiH_4/H_2 mixture. Structural changes of the nc-Si films were investigated by X-ray diffraction, Raman spectroscopy, infrared absorption, UV-VIS and AFM measurements. All nc-Si films were deposited as a function of RF power conditions. <110> preferentially oriented nc-Si films were observed to grow suddenly with RF power of 80 W resulted in improved crystalline qualities. These results were examined on the basis of the effect of various mechanisms on the crystalline properties, although these mechanisms may jointly determine the properties.

TF-TuP3 Effect of Laser Assisted Local Heating on Mechanical Properties during Indirect Hot Stamping of Tubes*, M.N. Chowdhury, T.T. Nguyen, **GiDong Park**, T.K.A. Dinh, S.-T. Hong,* University of Ulsan, Republic of Korea*; J.W. Jung, H.N. Han,* Seoul National Univeristy, Republic of Korea

Mechanical behaviors of a hot stamping steel tube are experimentally investigated using laser assisted local heating. A partial surface with spiral shape along the length of tube is heated to austenitic temperature by combining the linear movement of the laser and the rotation of the tube. The result of axial crush tests suggests that the laser assisted local heating is capable to enhance mechanical strength and hardness of the tube. A microstructural analysis shows that the laser locally induces a martensitic phase transformation in the heated region along the length of the tube.

TF-TuP4 High Quality ALD of Silicon Nitride Films Via Microwave Plasma*, **Kihyun Kim**,* Samsung Electronics, Republic of Korea*; J. Provine, P. Schindler, Stephen. Walch, Y. Kim, HyoJin. Kim, F.B. Prinz,* Stanford University, USA

Modern integrated circuit processing for DRAM, flash, and logic devices require silicon nitride (SiN) spacer layers with exacting requirements for chemical, physical, and electrical performance. High quality SiN thin films can be achieved by low pressure chemical vapor deposition (LPCVD) at elevated deposition temperatures (>800°C). However, modern device design rules require low thermal budget (<400°C) for these and other applications.

In this abstract, we demonstrate with a custom built PEALD system utilizing a high power (~1kW) microwave plasma source. Utilizing this system, we can achieve composition with low oxygen, carbon, and hydrogen content similar to what is achieved in higher temperature LPCVD reactions.

The dependence of the SiN film properties on processes parameters including plasma power and plasma treatment cycle, are investigated. Specifically, the wet etch rates in dilute hydrofluoric acid (H_2O:HF 200:1) with respect to plasma power and treatment cycle times can be varied because of the effects of radicals and ions generated by the plasma source during deposition. Wet etch rates comparable to LPCVD SiN films can be demonstrated at significantly reduced temperature by PEALD. X-ray reflectometry (XRR) and X-ray photoemission spectroscopy (XPS) studies show the higher plasma power and extended plasma treatment cycles can vary the density and the composition of SiN films.

TF-TuP5 Homeotropic Liquid Crystal Alignment on Aluminum Oxide Films and its Application for Liquid Crystal Display*, **Hong-Gyu Park**,* Changwon National University, Republic of Korea*; H.Y. Mun, H.-C. Jeong, J.H. Lee,* Yonsei University, Korea, Republic of Korea*; B.-Y. Oh,* ZeSHTech Co. Ltd., Republic of Korea*; D.-S. Seo,* Yonsei University, Korea, Republic of Korea

Liquid crystal display (LCD) technology is still occupying a strong position in the display industry. The orientational control of liquid crystal (LC) molecules is essential for high-quality LCDs and interactions between LC molecules and solid-substrate surfaces are still significant in both fundamental research and industrial applications Achieving sophisticated control and uniform alignment of LCs with a regular pretilt angle on the alignment layer is an important step in the manufacture of LC displays (LCDs). Intensive research on the use of organic or inorganic films as LC alignment layers has been conducted to obtain uniform LC alignment using various alignment techniques such as rubbing, ultraviolet (UV) photoalignment technique, nanoimprint lithography, oblique deposition, and ion-beam (IB) irradiation. Among these, the rubbing process has still attracted much attention in terms of simplicity, high cost-effectivity, and reliability. Recently, transparent inorganic materials have been investigated by many research groups as alignment layers, because of their low power consumption achieved via the reduction of LC threshold voltage. In addition, oxide-based inorganic materials are more durable than organic materials and are insensitive to oxygen and water, which slows the degradation of the device performance compared to organic materials.

We previously reported on LC alignments on aluminum oxide (Al_2O_3) films deposited using various techniques including atomic layer deposition (ALD), RF magnetron sputter, and e-beam evaporation via IB irradiation. In this paper, we demonstrate the effects of LC alignment on Al_2O_3 films using a rubbing process. Through a simple technique, uniform and vertical LC alignment was achieved on the Al_2O_3 films. Optical retardations and contact angles were observed on the Al_2O_3 films to measure the effect of the rubbing treatment on Al_2O_3 films. Finally, the electro-optical (EO) characteristics of vertically aligned (VA) cells on Al_2O_3 films were measured.

TF-TuP6 A Pulsed Supersonic Valve System for Researches on Collision-Induced Reactive Thin Film Etching Phenomena*, **Masahito Tagawa**, K. Yokota, T. Yasukochi,* Kobe University, Japan*; S.K. Chee,* Mechano Transformer Corporation, Japan

A pulsed supersonic valve (PSV) with fast operation capability is essential for many molecular/atomic beam experiments. A reliable PSV is a key device for not only scientific molecular beam experiments, but also engineering applications such as future digital molecular beam epitaxy (MBE) and molecular beam-induced etching. Among these applications, laser-detonation hyperthermal beam source, which has been applied for space environmental effect studies on thin film erosion, requires highly reliable and fast response PSV system. We have developed a fast and reliable piezoelectric-driven PSV system. It consists of conventional low-voltage piezoelectric actuator (max 150V) with a displacement enlargement mechanism (displacement is greater than 0.1mm) . These mechanisms are covered by a stainless steel body. Size of PSV is approximately 15 x 10 x 4 cm. Gas is ejected by a 1 mm hole. The poppet clearance is adjustable by the micrometer. The poppet system with a Viton O-ring and Au reflector was specially designed for laser-detonation applications, which requires the focusing 7 J laser pulse near the O-ring. A pressure profile of ejected gas from the nozzle was measured. It is clearly indicated that the PSV is able to operate less than 100 microseconds. It should be mentioned that even faster operation is possible with a high-current PSV driver. It was also confirmed the specification below;

Max. Pressure of supply gas: > 0.8 MPa, Max. Repetition rate: > 50 Hz, Poppet life: > 0.6 million shot (with CO_2 laser irradiation)

One of the unique features of this system is that two PSVs independently eject gas pulses into one hole, such that time-variation of the composition of a gas pulse could be controlled. This capability provides controllability of the dissociation of molecules in a pulsed laser plasma.

Time-of-flight spectra of "thermal" molecular beam generated with this PSV system were measured. It was obvious that the velocity distribution was consistent with the Maxwell-Boltzmann distribution. Also the capability of forming "hyperthermal" atomic beam with laser-detonation for space environmental simulation of thin film erosion problems as well as a wide variety of applications on applied surface sciences of this fast and reliable PSV system will also be discussed.

A part of this research was supported by the Grant-in-Aids for Scientific Research from JSPS under contract Nr. 25289307, 26289322, 15K14252 and 15K14253. Financial support through the Coordination Funds for Promoting Aerospace Utilization from the MEXT was also appreciated.

TF-TuP7 Synthesis of High-quality MoS_2 Atomic Layers with Inorganic Seeding Promoters by Chemical Vapor Deposition*, **Woochul Yang**, S.H. Choi, Y.J. Kim,* Dongguk university, Republic of Korea*; K.K. Kim,* Dongguk University, Republic of Korea

Molybdenum disulfide (MoS_2) is highlighted due to their unique physical and electrical properties such as ultrathin layered structure, high on/off ratio, and high mobility. The Band gap of layered-semiconductor MoS_2 is changed from 1.2 eV to 1. 9 eV depending on the layered thickness. Monolayer MoS_2 with direct band gap is an optimal material to develop novel optoelectronic devices. There are many method to prepare monolayer MoS_2 such as mechanically, chemically exfoliation, and chemical vapor deposition (CVD) method. Among them, the CVD method is inexpensive and easy to synthesize MoS_2 films with large scale and uniform thickness. In the CVD process, the absorption of vapor phase molybdenum and sulfur on the substrate is a problem for laterally layered growth of MoS_2. Recently, organic aromatic molecules helps the nucleation of MoS_2 in the CVD process. However, the organic materials are easily decomposed due to their thermal instability at the growth temperature. Herein, we first report the inorganic seeding promoter including alkali metal ions to grow high quality MoS_2 flakes. The size of the grown flakes was up to 200 um. The crystalline quality and the thickness of the MoS_2 were confirmed by AFM, Raman, and PL. The difference of typical Raman peaks of E_{2g} and A_{1g} is lower than ~19 cm^{-1} with full width half maximum values of 3.8 cm^{-1} and 4.5 cm^{-1}, respectively. This high quality is similar with mechanically exfoliated MoS_2. In addition, the size of the grown MoS_2 flakes can be tuned by concentration of the seeding promoters. The growth process with seeding promoters will be suggested in terms of surface reaction and nucleation of participating atoms and promoters on the surface. Our suggested inorganic seeding promoter will open the way to grow high quality monolayer MoS_2 flakes with scalable size.

TF-TuP8 Effect of Al_2O_3 Passivation Layer on the Stability of Al-IZO Thin-film Transistors*, **Ji-in Park**, Y.S. Lim, M.H. Jang, S.I. Choi, N.G. Hwang, M.S. Yi,* Pusan National University, Republic of Korea

We investigated the effect of aluminum oxide (Al_2O_3) passivation layer on the stability of aluminum-indium-zinc oxide (Al-IZO) thin-film transistors (TFTs) under positive bias stress (PBS) and negative bias illumination stress (NBIS). 20-nm thick Al-IZO channel layers were deposited by radio-frequency (RF) magnetron co-sputtering, and then annealed in air for 1h at 250℃Processing parameters such as the IZO, Al_2O_3 target power (50, 10W) and oxygen partial pressure (13%) were fixed. After depositing the channel layers, 20-nm thick Al_2O_3 passivation layers were deposited by RF magnetron sputtering at room temperature, and annealed again at 250℃

The TFTs without any passivation were taken as reference devices for comparison (device A). Fig. 1 shows the cross-sectional schematic diagram of Al_2O_3 passivated Al-IZO TFTs (device B). The measured electrical parameters of each device were summarized in Table 1, and it indicates that Al-IZO channel layer is not degraded during the passivation layer deposition by sputtering.

Fig. 2 (a) and (b) show the transfer characteristic curves the device A and B depending on the stress durations (7200 s) under the positive bias stress (V_{GS}= +20V, V_{DS}= 0V, PBS) in dark, respectively. It can be easily seen that threshold voltage shift (ΔV_{th}) of the device B is much smaller than that of the device A, and indicates that more charge trapping sites ($O_2+e^- \rightarrow O_2^-$) is created in device A during PBS condition. In other words, Al_2O_3 passivation layer could effectively prevent the oxygen absorption on surface of the Al-IZO film under the influence of gate voltage stress.

To investigate the stability of the TFTs under bias illumination stress, a negative bias stress (V_{GS}= -20V, V_{DS}= 0V, NBS) were repeatedly applied to the device A and B under green light illumination in air for 7200s. The brightness of the green light source was 2047cd/m^2. Fig. 3 (a) and (b) show the evolution of the transfer characteristic curves of each device for various stress durations under NBIS condition, and it can be concluded that the stability of device B is better than that of device A under NBIS condition. In general, the degradation mechanism of the NBS under illumination of Al-IZO TFTs is dominated by the photo-generated hole trapping states ($V_o \rightarrow V_o^{2+}+2e^-$) at gate insulator and/or interface between insulator and channel. In this result, the Al_2O_3 passivation layer could effectively passivate the defect in the Al-IZO films. We demonstrated that the Al_2O_3 could be an effective passivation layer to suppress O_2 absorption on Al-IZO back channel and decrease photo-excitation on Al-IZO films.

TF-TuP9 Extreme Ultraviolet Emission from Laser-induced O_2+Ar Plasmas Relevance to Ground-based Simulation of Thin Film Etching Reactions in Low Earth Orbit*, **Kumiko Yokota**, T. Ohyabu, J. Ohira, K. Morimoto, M. Tagawa,* Kobe University, Japan

The environmental factors in space, for example, ultraviolet (including EUV and VUV wavelength), x-rays, ion and electron radiations, thermal cycling, and neutral species such as atomic oxygen (AO), give serious effects on many thin film materials used in space systems. The incompleteness of the ground-based simulation technology arises problems on the accuracy of assessment of the material survivability in real space environment. It has been reported that FEP Teflon eroded much faster in ground-based facilities than in space. This discrepancy is believed due to the ultraviolet which is a byproduct from the oxygen plasma. A laser detonation AO source, which has widely been used as a ground-based AO environmental simulator, uses high-power CO_2 laser to create laser-induced oxygen plasma. The basic configuration of laser detonation AO beam source is similar to that of EUV light source using xenon gas. However, EUV from laser-detonation AO beam source has not been evaluated.

In this presentation, EUV spectra from laser-induced oxygen (and mixed gas) plasmas were reported. The flat-field EUV spectrometer especially designed for this purpose was equipped to laser-detonation AO beam source, and confirmed the capability to measure EUV spectra from oxygen plasma. Also, the cross relationship between EUV spectra, time-of-Flight (TOF) spectra of AO beam and effect of addition of Ar were investigated related to the low altitude orbital applications.

It was clearly observed that EUV emission intensity from 100%Ar plasma was greater than that from 100%O_2 plasma. However, Ar emission was not observed from the laser-sustained plasma consisting of 50%Ar+50%O_2 gas mixture, i.e., EUV lines only originated from oxygen were observed. Emission intensities originated from O increased with Ar content and disappeared in the pure Ar plasma. The EUV emission property was considered to be related to the collisional processes in the mixed plasma. This hypothesis was proved by the TOF spectra, i.e., dissociation reaction of O_2 into AO was promoted by adding Ar in the gas. It was also observed that the EUV emission intensity decreased with increasing the supply gas pressure of the PSV. This could be a practical way to reduce the side effect of EUV on the ground-based AO simulations.

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TF-TuP10 Structural and NO Adsorption Properties of One Layer Thick Fe Oxides on Ag(100) and Ag(111)*, **Mikhail Shipilin**, E. Lundgren, J. Gustafson, C. Zhang,* Lund University, Sweden*; F. Bertram,* DESY Photon Science, Germany*; C. Nicklin,* Diamond Light Source, UK*; C. Heard, H. Grönbeck,* Chalmers University of Technology, Sweden*; F. Zhang, J. Choi, V. Mehar, JF. Weaver,* University of Florida, USA*; LR. Merte,* Lund University, Sweden

The interplay of structural and chemical properties of ultra-thin films grown on various substrates has an immense importance from both fundamental research and technological application points of view. The possibility to tune the functionality of these materials by changing the substrate and/or growth conditions has attracted an increased attention [1-5]. Iron oxides, in particular, were shown to be catalytically active in e.g. reactions of selective oxidation and dehydrogenation [6].

In this contribution, we report results of Scanning Tunneling Microscopy (STM), Low Energy Electron Diffraction (LEED) and Surface X-ray Diffraction (SXRD) structural studies of FeO(111) monolayers grown on a Ag(100) and a Ag(111) single crystal surfaces. Additionally, we report our findings regarding surface adsorption sites probed by Temperature Programmed Desorption (TPD) and Reflection Absorption Infra-Red Spectroscopy (RAIRS) of NO molecules. We show that the NO adsorption properties on FeO(111)/Ag(100) and FeO(111)/Ag(111) are similar despite the difference in the coincidence periodicity due to the underlying substrate. The fact that NO does not adsorb on FeO(111)/Pt(111) [7] despite the theoretically found similarity in electronic properties of the films on both Pt and Ag surfaces [8] allowed us to assign the difference in adsorption properties of the films on these substrates to steric effects. Namely, the film on Pt has a smaller unit cell size resulting in a higher degree of the internal rumpling of the O and the Fe atoms in the FeO(111) layer in comparison with the films on both Ag substrates. The oxygen atoms protruding upwards therefore sterically hinder the NO adsorption on FeO(111)/Pt(111) while the flat film on Ag(100) and Ag(111) leave the Fe ions accessible to adsorption.

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TF-TuP11 Device Performance of Tungsten doped InZnO Thin Film Transistor depending on Active Layer Thickness*, **Hyun-Woo Park**, D.-Y. Kim,* Dongguk university, Republic of Korea*; W.-C. Yang,* Dongguk University, Republic of Korea*; M.-D. Kim,* Chungnam National University, Republic of Korea*; K.-B. Chung,* Dongguk university, Republic of Korea

Tungsten doped InZnO thin film transistors (WIZO-TFTs) were fabricated using by radio frequency (RF) sputtering system as a function of active layer thickness. In order to explain the degradation of the device performance depending on the active layer thickness, we investigated the correlations between the device performance and physical properties including the film density, surface/interface roughness, band edge state below the conduction band, refractive index and composition along the depth direction. The 10 nm-thick WIZO film is showed the highest film density and the flat interface roughness. In addition, increase of the band edge state and thickness of interface layers could be related to the device performance, which resulted in changes of interfacial trap density.

TF-TuP12 Influence of Macro-Confinement on the Thermochromic Transition Temperature of VO_2 Thin Films*, **Adetayo Adedeji**, T. Patel, A.D. Agyapong,* Elizabeth City State University, USA

Vanadium dioxide (VO_2) in bulk and thin film forms are well known thermochromic materials. VO_2 switches optically from IR transparent to IR reflecting at a transition temperature of about 68ºC (about 150ºF). Because of the easily accessible transition temperature, researchers are interested in driving the transition temperature to lower or higher values depending on the intended application. The goal of this research is to investigate the effect of thin film macro-size confinement on the transition temperature of VO_2. To achieve this goal, pure vanadium metal was deposited on clean quartz substrate using magnetron sputtering system. Different sizes of copper mesh were used as template for the depositions. The samples were oxidized in 800 mtorr N_2/O_2 gas mixture at 500°C for 4 hours. Surface morphology of the sample and chemical composition were obtained using SEM with EDS. Various grain sizes and orientations were observed at different depth from the quartz-VO_2 interface with aberration corrected Scanning Tunneling Electron Microscope (STEM). Optical transmittance in air ambient was measured as the samples were taken through thermal cycle. It was observed that the transition temperatures of samples deposited through Cu meshes are different from those obtained from plain 2D VO_2 films and films shielded with transparent Ta-Si-N barrier layer.

TF-TuP13 Nitrogen Plasma Treatment of Polytetrafluoroethylene*, P. Garcia, C. Rangel, **Steven Durrant**,* UNESP - Sorocaba, Brazil

Cold plasma treatment is well established for the modification of metal, glass and polymers. Treatments of polymers in plasmas of inert gases can alter the degree of cross-linking, release hydrogen, and produce dangling bonds, thus affecting the surface morphology and reactivity. In addition to such effects, treatments in plasmas of gases such as oxygen, carbon tetrafluoride or nitrogen, can cause etching and introduce new elements, such as O, F or N, to the polymer surface. It is known that cold nitrogen plasma treatment of polytetrafluoroethylene (PTFE) can strongly modify its properties; for example, reducing its surface contact angle to zero. There is still much to be learnt, however, about the effect of the system parameters on the modifications produced. In this study, PTFE is treated in cold nitrogen plasmas as a function of the gas pressure, P, RF plasma power, W, and exposure time, t. The variables P, W and t range from zero to 100 mTorr, 200 W, and 30 min. respectively. The induced chemical structural and compositional changes are examined using Infrared spectroscopy with attenuated total reflection (ATR) and Energy dispersive X-ray spectroscopy (EDS). Surface roughness and morphology are examined using Scanning electron microscopy (SEM). Surface contact angles are measured using goniometry.

TF-TuP14 Effects of Photogenerated Carrier Scattering on the Decay Process of Coherent Longitudinal Optical Phonons in an *i*-GaAs/*n*-GaAs Epitaxial Structure Investigated by Terahertz Time-domain Spectroscopy*, **Hideo Takeuchi**, T. Sumioka, M. Nakayama,* Osaka City University, Japan

Terahertz (THz) electromagnetic waves are generated by illumination of femtosecond (fs) laser pulses on semiconductor surfaces. The THz wave, therefore, supplies time-domain information on the dynamical phenomena around the surface. In the THz-wave emission from the coherent longitudinal optical (LO) phonons, initial polarization, which corresponds to the LO-phonon amplitude, is launched by a surge current of carriers generated by laser-pulse illumination. Subsequently, the coherent LO phonon, the dynamical polarization, starts oscillating and the THz wave is emitted. Here, we point out the possibility that the surge current scatters the coherent LO phonon in the launch stage. For clarifying the above possibility, we investigated the coherent LO phonon in an *i*-GaAs/*n*-GaAs epitaxial structure, focusing our attention on the decay time.

The sample used was grown by MOVPE. The *i*-GaAs (*n*-GaAs) layer thickness was 100 nm (300 µm). The doping density of the *n*-GaAs layer was $3x10^{18}$ cm^{-3}. In the *i*-GaAs/*n*-GaAs structure, a uniform built-in electric field is produced in the *i*-GaAs layer, which induces the initial polarization. The THz wave was measured at room temperature and at the humidity below 10%. We used an optical gating method. The fs laser pulse had a photon energy of 1.55 eV and a pulse duration of 60 fs. The laser beam had a Gaussian shape. The pump powers were varied from 30 to 110 mW.

The THz waveforms show a monocycle signal from the surge current, which is followed by long-lived oscillations due to the coherent LO phonon. The

Fourier power spectra of the waveforms show the surge current and coherent LO phonon bands. In addition, two bands, the frequencies of which depend on the pump power corresponding to the photogenerated carrier density, were observed. The frequencies of the latter two bands were evaluated using the Gaussian decomposition, and compared with the dispersion curve of the LO-phonon-plasmon coupled (LOPC) mode. We consider that the THz wave from the coherent LOPC mode is emitted from almost the center position of the Gaussian beam spot on the sample surface because of the presence of sufficient photogenerated carriers forming the plasmon. In contrast, the coherent LO phonon is generated around the beam-spot tail. The waveform shows only the coherent LO phonons in the time-delay range larger than 1.0 ps. The decay time of the coherent LO phonon, which is 3.0 ps at the pump power of 30 mW, is monotonically decreased with increasing the pump power: The decay time is 1.3 ps at 110 mW. Since the increase in the pump power enhances the surge current, we conclude that the surge current disturbs the coherent LO phonon through the scattering.

TF-TuP15 Effect of Anodization Voltage on Formation of $BaTiO_3$– Al_2O_3 Composite Oxide Films*, **Lian Xiang**, S.S. Park,* Kyungpook National University, Korea, Republic of Korea

$BaTiO_3$–Al_2O_3 (BT–Al) composite oxide films were fabricated on high-voltage etched aluminum foils by vacuum infiltration using sol and anodization. The specimens coated with the $BaTiO_3$ films were annealed under 550 °C for 30 min and then anodized at 100–700 V. The specimens were analyzed using field emission scanning electron microscopy and field emission transmission electron microscopy. The withstanding voltage and specific capacitance value of the specimens were also measured. The results show that the tunnels of the BT-coated specimens after anodization had a multi-layer structure, which consisted of an Al_2O_3 outer layer, a BT–Al composite oxide middle layer, and an aluminum hydrate inner layer. The specimens could withstand the corresponding operating voltage and the specific capacitances of the BT-coated specimens were all higher compared with the specimens without the BT film coating. The dominant contribution of specific capacitance changed from BT–Al composite oxide films to Al_2O_3 films for the anodization voltage increasing form 100 to 700 V. These results also suggest the successful fabrication of BT–Al composite oxide films on high-voltage etched Al foils by vacuum infiltration using sol and anodization. Composite oxide films with high dielectric constants could be used for enhancing the specific capacitance of high-voltage electrolytic capacitors.

TF-TuP16 Effects of Borate Polyester Electrolyte on the Anodizing Behaviors and Electrical Properties of ZrO_2-Coated Al Foil*, **Kaiqiang Zhang**, S.S. Park,* Kyungpook National University, Korea, Republic of Korea

ZrO_2-Al_2O_3 composite oxide films are promising dielectric material for future use in aluminum electrolytic capacitors. The films were prepared on etched Al foils by ZrO_2 coating and anodizing. The anodizing of Al foils has been carried out generally in aqueous boric acid solution. But when Al foils are anodized above about 700V, boric acid solution is not suitable as electrolyte due to severe O_2 evolution. In this study, we used borate polyester solution as electrolyte to inhibit the O_2 evolution, and discussed the effects of the borate polyester concentration on anodizing behaviors and electrical properties of the ZrO_2 coated Al foils. The results show that borate polyester electrolyte can effectively inhibit the O_2 evolution during anodizing, and increase the withstanding voltage of the samples. The specific capacitance of the samples decreases with the increasing of borate polyester concentration. Compared to anodization in boric acid electrolyte, the use of borate polyester electrolyte led to increases in the specific capacitance of 25.9 % for 700 V, 15.6 % for 800 V and 8.9 % for 900 V.

TF-TuP17 Selectivity of Plasma Treatment Effects on Wettability Modulation between Silicon, Glass, Polyimide and PMMA, Using Several O_2, CF_4 and CHF_3 Gas Ratios*, **Shogo Uehara**, P. Wood,* SAMCO Inc., USA

Surface wettability of materials is influenced by surface energy as well as surface roughness, and the surface energy can be modulated by changing surface chemistries. Plasma treatment is one of the techniques to control the surface chemistries, and is used for the surface wettability modulation of materials in device fabrication. However, few papers have investigated the selectivity of plasma treatment effects on the wettability modulation between two or more materials in a batch process [1], [2]. In this research, the roles of reactive species of oxygen- and fluorine-based plasma chemistries were investigated for selective surface wettability modulation of materials. Using a reactive ion etching system (RIE-10NR, SAMCO Inc.), various plasma chemistries with several gas flow ratios of O_2, CF_4 and CHF_3 were formed over inorganic (silicon and glass) and organic (polyimide and PMMA) materials. Static contact angle and XPS were utilized to study the surface wettability and surface chemical bonding structure before and after plasma treatment. The contact angle was also investigated over the course of 20+ days storage in a N_2-purged desiccator in order to examine the stability of the wettability modulation effects.

With a gas flow ratio adjustment, a large contact angle contrast was observed between the materials. In pure CF_4 plasma treatment, the inorganic materials showed contact angle reduction after the plasma treatment, while the organic materials showed significant contact angle increase. XPS analysis revealed that the silicon surface retained 9.5 at.% fluorine, while 35.4 at.% fluorine was observed on PMMA surface after the pure CF_4 plasma treatment. This indicates that the PMMA wettability modulation was caused by the fluorine-containing chemical functional groups at the outermost surface layers.

After ageing the samples in storage, the contact angle contrast was gradually decreased due to a contact angle increase of the inorganic materials after pure O_2 or CF_4 plasma treatment. On the other hand, samples processed in a plasma using a gas mixture of CF_4 and CHF_3 showed stable contact angles. This difference is attributed to the existence of a thin fluorocarbon layer deposited during the CHF_3 based plasma treatment.

These results indicate that the reaction of oxygen and fluorine-containing active species on substrate surfaces influences wettability modulation effects of materials and also the stability of these effects.

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TF-TuP18 Annealing Behaviors for High-k ZrO_2 Grown on Ge*, **Deuk-Young Kim**, W.-C. Yang, K.-B. Chung, S. Lee,* Dongguk University, Republic of Korea*; M.-D. Kim,* Chungnam National University, Republic of Korea*; H. Lee, N. An, Y. Lee,* Dongguk University, Republic of Korea

The thermal annealing behaviors of electrostatic properties for high-k ZrO_2 layers were investigated. ZrO_2 layers were grown on p-type Ge substrates at 500°C by RF magnetron sputtering. To reduce the native defect density in ZrO_2, we adopted the higher oxygen-partial pressure (*i.e.*, O_2/Ar > 1). The RF power was 150 W, and the growth time was 20 min. After the growth of ZrO_2, the samples were annealed at 600-700°C in Ar ambient by using a rapid thermal annealing method. For the capacitance-voltage characteristics, the as-grown sample exhibited its maximum electrostatic capacitance (*i.e.*, C_{max} at the accumulation mode) to drastically decrease with increasing the frequency of ac signals. However, the dielectric characteristics of ZrO_2 were much improved after thermal annealing at temperatures above 600°C. Particularly, the magnitude of C_{max} was increased by more than 3-times after annealing at 600°C. In addition, C_{max} was much stabilized at wide frequency ranges. For higher annealing temperatures, the above feature became more significant. This indicates that the defects in ZrO_2 could be effectively eliminated by thermal annealing; particularly, at temperatures above 600°C. Through x-ray photoelectron spectroscopy measurements, we confirmed the above thermal-annealing behaviors to arise from the stabilization of Zr-O bonds due to the interdiffusion of Ge at the interface between ZrO_2 and Ge. The best electrostatic permittivity was more than 20, and the equivalent-oxide-thickness was less than 4 nm. Owing to the improvement of interface bonding structures at ZrO_2/Ge, the dielectric breakdown field was increased up to ~1 MV/cm. The results suggest that sputter-grown high-k dielectric ZrO_2 can be utilized for Ge-based MOS devices, and that thermal annealing is effective to improve the dielectric characteristics of ZrO_2.

TF-TuP19 Surface Energy Controlled Patterning of Carbon Nanomaterials for Electronic Devices*, **SungMin Lee**, S.G. Yoon,* Chung Ang university, Republic of Korea

Comparing with traditional coating technique, solution-based patterning method has its strength in process cost as it can be proceeded in room temperature and pressure condition. Because of its merits, solution-based patterning method has been actively exploited in various application such as field effect transistor, flexible transparent electrode, solar cell. However there are some drawbacks in these techniques: controllability of pattern thickness, high material consumption, extended process time. In our study, we design high speed, low cost, thickness controllable, solution-based patterning technique by controlling surface energy of substrate and demonstrate its application to electronic device. Furthermore we also study application for deposition of nano particles. Solution based metal deposition process is very competitive to currently used method vacuum based deposition in point of cost and processing time.

TF-TuP20 Physicochemistry of Chemical Bath Deposited ZnS Films at Near Ambient Temperatures*, **Irving Gonzalez**, I. Oliva Arias,* Centro de Investigación y de Estudios Avanzados del Instituto Politécnico Nacional, Unidad Mérida, Mexico

Zinc sulfide (ZnS) is a semiconductor material that has increased its importance in recent years due to its wide range of applications. For solar applications, ZnS has shown great potential as optical window for developing high efficiency CIGS solar cells. Chemical bath deposition (CBD) technique has been used for several years to obtain ZnS thin films. Deposition time, bath temperature and chemical reagents concentration are some parameters that have been investigated through time. However, there are scarce reports conducted to understand the physicochemistry of the CBD technique. In recent years, the development of physicochemical tools such as the species distribution diagrams (SDDs) and the solubility curves (SCs) gives light to understand the growth mechanisms to obtain the growth parameters for depositing high quality ZnS films. Nevertheless, most of these contributions have been carried out at temperatures between 60 and 90 °C leaving aside near ambient temperatures. Research on these conditions could bring benefits for industrial applications. This work aims to provide the physicochemical conditions in which high quality ZnS films at near ambient temperature can be obtained. A chemical bath containing $ZnCl_2$, KOH, NH_4NO_3, and $SC(NH_2)_2$ as chemical reagents was used for depositing the ZnS films. Temperatures of 25, 40, and 55 °C were selected for films deposition. The SDDs and SCs were obtained for each temperature at three conditions (by varying $[SC(NH_2)_2]$) in order to study the influence of the chemical species onto the ZnS formation. The $R=[HS^- /]/[Zn(OH)_2^{2-}]$ ratio as a main parameter for CDB-ZnS films deposition was investigated. The SCs show that higher values of R assure enough amount of HS^- ions and better conditions for depositing ZnS, avoiding the formation of $Zn(OH)_2$. The SDDs show that at near ambient temperatures the ZnS formation is attributed to the $Zn(OH)_3^-$ and $Zn(OH)_4^{2-}$ complexes and the HS^- ions.

ZnS films deposited onto glass substrates were characterized by x-ray photoelectron spectroscopy, atomic force microscopy, x-ray diffraction, and spectrophotometry techniques. Results indicate that when the R ratio and temperature are increased, better stoichiometry is obtained. The Zn is bonded mainly to hydroxide ions for lower R ratios, but when R increases bonding changes to S ions. The band gap energy of films was measured between 3.4 and 3.7 eV. The lower values are due to that samples contained ZnS and $Zn(OH)_2$ because of the low value of R. ZnS films deposited at 55 °C presents a (111) cubic orientation (sphalerita); meanwhile, films deposited at 25 °C present an orthorhombic orientation due to the $Zn(OH)_2$ formation.

TF-TuP21 Imaging of Deformation of a Polypropylene Separator Due to Immersion in Electrolyte in a Li-ion Battery*, **Keiji Takata**, Y. Matsushita, T. kitaura, R. Osaka, K. Butsugan,* Kansai University, Japan

A separator play an important role in a Li-ion battery. The separator must electrically isolate the anode and the cathode of the battery. On the other hand, the separator should allow Li ions to pass through smoothly, and so the separator is porous. Large pores degrade the ability of electric isolation but enhance the permeability; thus, we must determine the best pore size for optimal performance. The pore size of the separator can be observed precisely before its incorporation into the battery, but the size may not be maintained in the electrolyte.

Here, we present the differences in the separator structures before and after immersion in the electrolyte.

Atomic force microscopy images of a 25-mm-thick single-layer polypropylene separator before and after immersion in the electrolyte clearly showed the lamellar alignment and the the fibrillae between the lamellae. The electrolyte is ethylene carbonate with $LiPF_6$. The spacing between the lamellar layers was around 0.8 mm before immersion, but expanded to 1.4 mm after immersion. The pores expanded like sponge when they immersed in the liquid electrolyte. Expansion of the separator occurs when it is bound tightly inside the battery. Thus, expansion of the pores of the separator must be considered to achieve good performance.

Biomaterial Surfaces & Interfaces
Room Milo - Session BI-TuE

Medicinal Applications

Moderator: Michael Grunze, KIT

5:40pm **BI-TuE1 Challenges in Translating Surface Designs to Clinical Medical Device Applications***, David Grainger,* University of Utah, USA **INVITED**

Surface strategies for translational clinical performance for 1) medical devices with antimicrobial properties, and 2) nanomaterials in imaging and drug delivery are discussed.

1. Antimicrobial medical devices.[1-5] Increasing medical devices are used in clinical implants: in aging populations, diverse patient genetic profiles, ethnicity and health status, and increasing developing countries. Notably, infection related to implanted devices is a primary concern both for patient risk and healthcare cost reasons. Medical device surfaces and interfaces have long been a focus to produce diverse antimicrobial strategies, yet few translate to clinical use. A classic problem is lack of in vitro-in vivo correlation, validation or efficacy for surface methods and antimicrobial approach in vivo. A second issue is lack of commercial enthusiasm to take approaches forward thru regulatory pathways to clinical use. Improved methods are required to assess and validate new antimicrobial technologies that reduce implant-associated infections and risks in translation.

2. Nanomaterials exposure to the human physiome.[6-10] Human exposure to engineered nanotechnology is an increasing concern. Importantly, medical grade standards of purity and contamination validation and analysis are difficult for nanomaterials and not commonly followed in most in vivo studies. Since surface area is critical nanomaterials property, surface analysis is critical but rarely performed.[6] Much published data demonstrate that particles placed in blood circulation are rapidly filtered by the reticuloendothelial system (RES) comprising liver, spleen, lung, kidney, and marrow, performing blood scavenging. Particle removal is mostly independent of size or chemistry, and refractory to targeting strategies by coatings. Wide variations in circulating nanomaterials properties produce quite similar results in mammalian biodistributions and RES clearance (>90% RES filtration). Issues with connecting nanomaterials surface properties to complex biological interactions will be discussed.

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6:20pm **BI-TuE3 Metal Oxides, Hydroxyapatite and Bone Healing***, Håkan Nygren,* University of Gothenburg, Göteborg, Sweden*; P. Malmberg, L. Ilver,* Chalmers University of Technology, Sweden

Magnesium alloy, Zinc and Manganese have been explored extensively for application as degradable metal implants, but there is still a lack of understanding of the biological response to the corrosion products and their influence on the local tissue repair process at the implantation site. The approach, in this study is to correlate the effect of corrosion products on human embryonic stem cells *in vitro* and on bone healing with and without stainless steel implants *in vivo* in rat tibia by preparing a paste of MgO or $MgCO_3$, ZnO and MnO. The metals and the formation of mineral were analysed by ToF-SIMS, EDX and XPS. Metal oxides, incubated in tissue culture medium (DMEM), induced the formation of hydroxyapatite (HA), covering the oxide grains. The apatite was low crystalline and carbonated. We found that when cultured human embryonic stem cells were presented with the HA-coated corrosion products they were able to maintain viability and proliferate over time. The presence of HA-coated metal corrosion products resulted in the up-regulation of hydroxyapatite formation by the stem cells *in vitro* and enhanced bone formation *in vivo*, preceded by the formation of hydroxyapatite in the tissue. The results of the present study suggest that metal corrosion products catalyse the formation of hydroxyapatite in the tissue, that the formation of apatitite is amplified by stem cells and that the hydroxyapatite is an active species in promoting osteogenesis.

6:40pm **BI-TuE4 Microstructure Evaluation of Chill Cast Co-Cr Alloys for Biomedical Applications***, Julio Juarez-Islas, A.L. Ramirez-Ledesma,* Universidad Nacional Autonoma de Mexico, Instituto de Investigaciones en Materiales, México

Binary Co-Cr alloys containing various Cr contents were vacuum induction melted and cast into wedge shaped copper molds with the aim of produce a microstructure free from interdendritic segregation and porosity with minimal intermetallic precipitates and suitable for biomedical applications. The resultant microstructures were evaluated from sections obtained longitudinally and centrally in the plane normal to the diverging wedge faces. All ingots showed a dendrite microstructure with some characteristics, for instance, in Co-20 to 30 wt. % Cr alloys, chill cast microstructures consisted of columnar dendrites without interdendrite segregation, a minimum of precipitates and observed for the first time, the presence of a predominant athermal HCP e-martensite (>80 wt .%) and the metastable FCC γ-Co phase which were identified by x-ray diffraction means and scanning electron microscopy. In the case of 35 to 44 wt. % Cr cobalt alloys a eutectic constituent including the s-phase were found to develop in the interdendritic regions. In particular, a Co-20 wt. % Cr alloy was chosen for further investigation after heat treating below the γ/e transition temperature. The resultant tensile strength and ductility of the heat-treated alloy were then determined including its corrosion resistance in artificial saliva.

7:00pm **BI-TuE5 Modulation of Macrophage Polarization Using Surface Immobilized Bioactive Molecules***, Alex Chen, B.D. Ratner,* University of Washington, USA

Introduction: The polarization of macrophages is highly influential in modulating the foreign body response. Macrophages characterized by the M2 (anti-inflammatory) phenotype are believed to reduce the formation of the foreign body capsule. It is hypothesized that surface immobilizing M2 promoting bioactive molecules will reduce the formation of the foreign body capsule by increasing M2 polarization as well as decreasing M1(inflammatory) polarization of macrophages. Collagen VI (col6) and α-1 acid glycoprotein (AGP) have been shown to induce M2 polarization of macrophages when introduced in solution. This work demonstrates the feasibility of modulating macrophage polarization via immobilization of col6 and AGP onto hydrogel coated surfaces.

Methods: 2-hydroxyethyl methacrylate (HEMA) was plasma deposited onto 10mm circular glass slides. HEMA coated glass slides were washed three times in p-dioxane and then surface activated by incubation with 100mM carbonyl diimidazole (CDI) in dioxane for 2.5 hours at 40°C. CDI activated glass slides were then incubated in either 440µg/mL AGP only or 250µg/mL AGP plus 62.5 µg/mL col6 solutions in pH 10.2 sodium carbonate/bicarbonate buffer for 24 hours at 40°C. Bone marrow derived macrophages (BMDMs) were cultured by harvesting marrow from the femurs of sacrificed mice, which was then dispersed and cultured in RPMI with macrophage colony stimulating factor for 7 days. BMDMs were then transferred to glass slides coated with immobilized bioactive molecules and cultured for 48 hours. CDI activated HEMA coated glass slides without immobilized bioactive molecules was used as a control. Macrophage polarization was assessed via ELISA measurements of tumor necrosis factor-α (TNF-α), a cytokine released by M1 macrophages, as well as RT-qPCR of arginase 1 (Arg1), an enzyme highly expressed by M2 macrophages. ELISA experiments involved the addition of 10uM lipopolysaccharide(LPS) to culture media in order to induce an M1 polarization of macrophages. RT-qPCR experiments did not involve the use of LPS and solely focused on the expression of Arg1.

Results and Conclusions: ELISA experiments showed a decrease of TNF-α expression in macrophages cultured on surfaces with immobilized AGP (~30%). RT-qPCR experiments showed an increase in Arg1 expression of macrophages cultured on surfaces with immobilized AGP (2.6x) or immobilized AGP + col6 (5.85x).

These experiments show the potential of using immobilized bioactive molecules to modulate the polarization of macrophages, which can potentially be used to reduce the foreign body response and foreign body capsule formation.

Energy Harvesting & Storage
Room Lehua - Session EH-TuE

Battery/Supercapacitor Coatings, egs., Li* Batteries & Thermo-/Piezo-electrics

Moderator: Takuya Masuda, NIMS (National Institute for Materials Science), Japan

5:40pm **EH-TuE1 Electrochemistry at Well-defined Interfaces in Organic Environments*, Nenad Markovic,*** Argonne National Laboratory, USA

In recent years, improvements in the fundamental understanding of electrochemical interfaces and their role in electrocatalytic processes have started to revolutionize the development of alternative energy systems for clean energy production, storage and conversion. In many respects the subject of surface electrochemistry in aqueous environments is more advanced than the corresponding understanding of interfaces in organic solvents. This is due to a long-standing difficulty associated with developing in-situ methods that are capable of characterizing interfaces at atomic-/molecular levels in organic solvents. This intrinsic disparity in understanding, however, has a tendency to mask the inherently close ties that exist between interfacial phenomena in aqueous and organic environments [1]. In this presentation, by building a bridge between these two artificially differentiated types of interfaces will allow for us to define the landscape of parameters that control the coupled roles of surface structure, chemical identity, electrostatic field, solvation and other related factors that determine the functional links between activity, selectivity and stability of any electrochemical interface. Selected example will be discussed, ranging from oxygen electrochemistry to metal deposition of Mg all the way down to intercalation processes on well-defined single crystal oxide materials. We identify the profound impact of trace levels of H_2O (<3ppm) on the kinetics of Mg deposition as well Mg intercalation in a layered V_2O_5 compound. Two types of water has been found; a “bad water”, that via the formation of MgO and $Mg(OH)_2$ passive films inhibits Mg deposition as well as a “good water” that helps intercalation of Mg^{2+} into V_2O_5 structures [2]. We conclude that understanding the complexity of electrochemical interfaces would open new avenues for design and deployment of alternative storage systems.

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6:00pm **EH-TuE2 Coupling in-situ TEM and Ex-Situ Analysis to Understand Heterogeneous Sodiation of Antimony*, David Mitlin,*** Clarkson University, USA

We employed an in-situ electrochemical cell in the transmission electron microscope (TEM) together with ex-situ time-of-flight, secondary-ion mass spectrometry (TOF-SIMS) depth profiling, and FIB - helium ion scanning microscope (HIM) imaging to detail the structural and compositional changes associated with Na/Na^+ charging/discharging of 50 and 100 nm thin films of Sb. TOF-SIMS on a partially sodiated 100 nm Sb film gives a Na signal that progressively decreases towards the current collector, indicating that sodiation does not proceed uniformly. This heterogeneity will lead to local volumetric expansion gradients that would in turn serve as a major source of intrinsic stress in the microstructure. In-situ TEM shows time-dependent buckling and localized separation of the sodiated films from their TiN-Ge nanowire support, which is a mechanism of stress-relaxation. Localized horizontal fracture does not occur directly at the interface, but rather at a short distance away within the bulk of the Sb. HIM images of FIB cross-sections taken from sodiated half-cells, electrically disconnected and aged at room temperature, demonstrate non-uniform film swelling and the onset of analogous through-bulk separation. TOF-SIMS highlights time-dependent segregation of Na within the structure, both to the film-current collector interface and to the film surface where a solid electrolyte interphase (SEI) exists, agreeing with the electrochemical impedance results that show time-dependent increase of the films’ charge transfer resistance. We propose that Na segregation serves as a secondary source of stress relief, which occurs over somewhat longer time scales.

6:20pm **EH-TuE3 Polymer-based Piezoelectric Nanogenerators for Energy Harvesting Applications*, Sohini Kar-Narayan,*** University of Cambridge, UK **INVITED**

Harvesting energy from ambient sources in our environment has generated tremendous interest as it offers a fundamental energy solution for ‘small power’ applications, including, but not limited to, ubiquitous wireless sensor nodes; portable, flexible and wearable electronics; biomedical implants and structural/environmental monitoring devices. Energy harvesting from ambient vibrations is particularly attractive as these are ever present and easily accessible, originating from sources such as moving parts of machines, fluid flow and even body movements. In this context, piezoelectric materials offer the simplest means of directly converting mechanical vibrations into electrical power and are well suited for microscale device applications, thus offering a means of superseding traditional power sources such as batteries that require constant replacing/recharging and that do not scale easily with size. In particular, nanoscale piezoelectric energy harvesters, or *nanogenerators*, are capable of converting small ambient vibrations into electrical energy, thus paving the way for the realisation of the next generation of self-powered devices. A recent review article from our group [1] highlighted the fact that nanogenerator research to date has mainly focused on traditional piezoelectric materials in the form of ceramics, but these are stiff and prone to mechanical failure. On the other hand, piezoelectric polymers [1-3], although less well studied, have several advantages over ceramics such as being flexible, robust, lightweight, easy and cheap to fabricate, lead free and bio compatible. However, they do suffer from inferior piezoelectric properties in comparison to ceramics. The field thus faces orthogonal difficulties associated with these two classes of materials. In this talk, I will discuss work from our group aimed at developing novel hybrid polymer-ceramic nanocomposites [2,4,5] combining the best of both materials, while developing scalable nanofabrication techniques for flexible, low-cost and highly efficient polymer-based nanogenerators and sensors.

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7:00pm **EH-TuE5 High-Resolution Observation of Electronic Properties of a Cathode Material in a Li-ion Battery*, Ryuma Osaka,*** Kansai University, Japan

Li-ion batteries are widely used in many portable electronic devices and are recognized to be energy storage devices for mass-produced electric vehicles. However, to improve of power density, durability and safety, it is crucial to optimize the structure of the electrode as well as exploring new materials because the kinetics of the electrode reaction depends on the structure of the composite electrode.

The main elements are positive electrodes, negative electrodes, separators, and electrolytes. The electrolyte is typically a nonaqueous mixture of organic carbonates containing complexes of Li ions, which are noncoordinating anion salts such as Li hexafluorophos phate ($LiPF_6$). The separator is, for example, monolayer polypropylene. The electrode materials hold the key to determine the performance of the batteries. They are generally intercalated lithium compounds. Depending on the materials, the voltages, capacities, and lifetimes of the batteries greatly change. Therefore, they have been actively investigated.

The cathode material is also an oxide such as lithium cobalt oxide ($LiCoO_2$). Concerning the cathode materials, some materials, Li_2MnO_3, $Li_{1.2}Mn_{0.4}Fe_{0.4}O_2$, $LiNi_{0.3}Mn_{0.3}$-$Co_{0.3}O_2$, etc., have been proposed, developed, and investigated. Redox of the transition metal oxides or valence fluctuation of transition metals play important roles of charge neutral. Therefore, not only ionic conductivity but also electronic conductivity is important for battery operation. However, electric conductivity varies with valence fluctuation of the transition metals due to extraction or insertion of Li ions. We present results on a change in band structure of $LiCoO_2$ corresponding to the Li-ion concentrations, which were obtained via a scanning probe microscope.

Nanomaterials
Room Hau - Session NM-TuE
Nanofabrication and Nanodevices

Moderator: Adam Hitchcock, McMaster University, Canada

5:40pm **NM-TuE1 Surface and Screening Effects on Optical Properties of Carbon Nanotubes**, ***Yuichiro Kato,*** RIKEN, Japan **INVITED**

Screening is limited in single-walled carbon nanotubes because of their one-dimensional nature, and the strong Coulomb interactions result in optical spectra dominated by excitons with binding energies lager than half an eV. Also because of the limited screening, a charged carrier can be bound to an exciton to form a trion that is stable at room temperature. Adsorption and desorption of molecules on the surface of nanotubes can readily modulate such interactions.

Here we discuss experiments aimed at highlighting the behaviors of excitons and trions in individual suspended carbon nanotubes. Simultaneous photoluminescence and photoconductivity spectroscopy show evidences for spontaneous dissociation of excitons [1], despite the expectation that free carrier generation from such a tightly-bound state would be difficult. As the field is increased, we observe an emergence of new absorption peaks in the excitation spectra, which can be explained by electrical activation of dark excited states [2]. Although trion formation has been thought to be difficult in suspended nanotubes due to low exciton-carrier scattering rates, we have succeeded in identifying trion emission under an application of gate voltages [3]. More recently, we have observed optical bistability of exciton emission, which is attributed to resonance shifts caused by molecular adsorption and desorption.

Work supported by KAKENHI, The Canon Foundation, The Asahi Glass Foundation, and the Photon Frontier Network Program of MEXT, Japan.

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6:20pm **NM-TuE3 Low-temperature Localized Growth of High Aspect-Ratio Multi-Wall Titanium Dioxide Nanotubes for Orthogonal Frequency Coded SAW Gas Sensors**, ***William Clavijo,*** *C. Castano,* Virginia Commonwealth University, USA; *W. Wilson,* NASA Langley Research Center, USA; *G. Atkinson,* Virginia Commonwealth University, USA

We expand the potential application and sensitivity of solid acoustic wave (SAW) gas sensors by incorporating ultra-high surface area, multi-wall TiO_2 nanotubes into orthogonal frequency coded (OFC) SAW gas sensors. This process relies on synthetization of multi-wall tube-in-tube polycrystalline TiO_2 nanotubes utilizing nanoporous anodic aluminum oxide (AAO) templates in a thin (2.5µm) aluminum film deposited on a lithium niobate substrate. We have demonstrated this method by integrating multi-wall nanotubes onto the delay line of an OFC SAW device to form an integrated sensor structure. The multi-wall TiO_2 nanotube growth uses a combination of multi-stage aluminum anodization, alumina barrier layer removal, TiO_2 and Al_2O_3 atomic layer deposition (ALD), and wet release etching. This growth process selectively forms TiO_2 nanotubes on the delay line while the aluminum film remains intact for interdigital transducers (IDT) and reflector banks. The self-assembled high density AAO template was selectively formed in an ultra-smooth (R_a=1.5nm) 2.5 µm thick aluminum layer deposited through e-beam evaporation. The resulting AAO template consists of nanopores of 100 nm in diameter and 1.5 µm in height with an aerial density of 1.3×10^{10} nanopores/cm^2. This AAO template was then filled with successive ALD nanotubes by alternating Al_2O_3 sacrificial spacers and TiO_2 at 200 ˚C. The alumina template and Al_2O_3 sacrificial spacers were then removed, leaving free standing multi-wall coaxial TiO_2 nanotubes of 1.5 µm in height and 100 nm in diameter, offering an increase in 112X the surface area over a standard flat TiO_2 film for sensing applications. The TiO_2 nanostructures were characterized by SEM, and TEM to examine internal structure, composition, and verify crystal structure. In addition, the OFC SAW gas sensor with a center frequency of 229 MHz and 3 reflectors on each side of the IDT was tested using 200 ppm NH_3 to demonstrate functionality and measure sensitivity. Mass loading induced by the NH_3 gas absorbed onto the multi-wall TiO_2 nanotube resulted in amplitude shift of 0.027 dB upon exposure to 200 ppm NH_3 at room temperature during interrogation of the 3rd reflector in sensitive channel. The sensor shows a promising room temperature operation with reproducible performance. Furthermore, OFC SAW gas sensors may be coded and implemented both passively and wirelessly in addition of taking advantages of the benefits of SAW technology.

6:40pm **NM-TuE4 Epitaxial Graphene Based Sensors for Gigahertz Detection**, ***Anthony Boyd,*** US Naval Research Laboratory, USA; *A. El Fatimy, P. Barbara,* Georgetown University, USA; *A. Nath, PM. Campbell, M. Currie, RL. Myers-Ward, KM. Daniels, DK. Gaskill,* US Naval Research Laboratory, USA

There is a clear need for fast, high efficiency, and broadband sensitive detectors. Graphene demonstrates great promise to fill this void, possessing high room temperature carrier mobility, up to 60000 $cm^2V^{-1}s^{-1}$, and absorption of incoming radiation, ~2.3%. This absorption is impressive considering graphene is a single atomic layer thick. In the gigahertz (GHz) frequency range, the absorption is enhanced due to the Drude contribution of the free carriers. Synthesizing epitaxial graphene (EG) on SiC has the advantages of wafer scale size, low defect density, and being single crystal.[1] Growing high quality, conformal dielectric films with Atomic Layer Deposition (ALD) on EG is challenging due to the lack of dangling bonds which serve as nucleation sights for film growth. Researchers at this laboratory have developed a fluorine functionalization approach to overcome the challenge without negatively impacting graphene's morphology and electronic properties to enable ALD of high-κ dielectrics onto EG for gated devices.[2]

We investigate two types of GHz detectors fabricated on EG. The first is an antenna coupled device. It utilizes two dissimilar contact metals, one for the source and the other for the drain, and the metal work function difference translates into asymmetric Seebeck voltages at each contact. We fabricated these devices with two types of EG: 1) a quasi-free standing bilayer graphene (QBLEG) and 2) a standard one monolayer EG (1ML). The second device is a field effect transistor constructed using 1ML EG with an asymmetric top gate that creates a PN junction and facilitates tuning the photovoltaic response . Both device types were fabricated using a lift off resist-based clean lithography process, have low contact resistance [3] and use metal work function asymmetry for detection, consistent with recent studies of the photothermoelectric effect mechanism.[4]

The devices were electrically characterized and then irradiated with a Backwards Wave Oscillator from 100 to 177GHz. The antenna coupled devices response varies with frequency, incident power, and demonstrates a distinct antenna coupling. The QBLEG shows a 3 to 4X increase in response over the standard 1ML. The response of the PN junctions depends on the radiation frequency and the gate voltage. At a fixed frequency, the device response can be doubled by tuning the gate voltage, consistent with the known dependence of the Seebeck coefficient with charge concentration.

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7:00pm **NM-TuE5 Structural and Electrical Properties of Electromigrated Au Nanogaps**, ***Tomoyuki Ito,*** *K. Inoue, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

Au nanogaps have been attractive for the fabrication of single-molecule devices. For this reason, many different approaches of Au nanogaps have been reported, including electromigration [1], break junction [2] and electroplating [3]. We have already reported on fabricating narrower Ni nanogaps by controlling tunnel resistance of the nanogaps using field-emission-induced electromigration. We call this method "activation" [4, 5]. In this report, the application of activation to Au nanogaps is investigated in comparison with that of Ni nanogaps.

Under room temperature and vacuum condition, the activation was applied to initial Au nanogaps with a separation of around 50 nm. The initial Au nanogaps showed high tunnel resistance of more than 500 TΩ. After performing the activation with the preset current I_s of above 300 nA, the tunnel resistance of Au nanogaps gradually decreased to less than 10 MΩ. Activation properties of Au nanogaps are quite similar to those of Ni nanogaps ever reported [4, 5]. Thus, the results imply that the tunnel resistance of Au nanogaps can be controlled in the same way as that of Ni nanogaps using activation.

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7:40pm **NM-TuE7 Micronization of Carotenoids using Solution-Enhanced Dispersion by Supercritical Fluid**, ***Motonobu Goto**, C. Uemori, H. Nerome, W. Diono, H. Kanda,* Nagoya University, Japan

The absorption of compounds such as carotenoids in the human body is promoted by micronization. There are many micronization techniques with the use of supercritical fluids. In this work, one of the supercritical antisolvent process called solution-enhanced dispersion by supercritical fluids (SEDS) is applied. In this process, the solution and the antisolvent fluid are injected into the precipitation vessel continuously, and particles are formed when supersaturation of the mixture is achieved.

We used lycopene and beta-carotene as carotenoid. The type of precipitation section was investigated, where vessel type and tube type was compared. Mixing part of solvent containing carotenoids and supercritical carbon dioxide as antisolvent is also important.

By using the SEDS process, carotenoids were successfully micronized to nano to micro particles. Composite particle consisting of carotenoids and cyclodextrin was also prepared. The effects of operation parameters such as temperature, pressure, and flow rates are investigated.

8:00pm **NM-TuE8 Investigation of Electromigration Induced by Field Emission Current Flowing through Au Nanogaps in Ambient Air**, ***Kazuki Inoue**, T. Ito, J. Shirakashi,* Tokyo University of Agriculture & Technology, Japan

We have proposed a simple method for the fabrication and control of nanogaps, called "activation" [1]. In the activation scheme, electromigration (EM) is induced by field emission current passing through the nanogaps. Hence, the control of tunnel resistance of Ni nanogaps was achieved using the activation method [1, 2]. As expected, the activation method has been applied to Ni nanogaps in vacuum conditions. On the other hand, controlled EM technique is generally applicable to Au nanowires in ambient air conditions [3]. Here, we investigate activation properties for Au nanogaps in ambient air conditions, from the point of view of practical use of activation method. First, initial nanogaps of Au, separated by several tens of nanometers, were fabricated on SiO_2/Si substrate by electron-beam lithography and lift-off process. Then, the activation method was performed in ambient air at room temperature. The tunnel resistance of the Au nanogaps after performing the activation became smaller than that of before performing the activation, resulting in a decrease in the separation of the Au nanogaps. Thus, these results suggest that the activation method can be applied to Au nanogaps even in ambient air conditions.

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8:20pm **NM-TuE9 Nanoparticles and Nanostructures Synthesis by High-Power Pulsed Hollow Cathode Sputtering**, ***Ulf Helmersson**, S. Askari, N. Brenning, S. Ekeroth, R. Gunnarsson,* Linköping University, Sweden

The use of high-power pulses for synthesis of nanoparticles in the gas phase is of interest because of the effective ionization of the supplied gases and the sputtered source material. The advantage of ionizing the source material is the effective trapping of positive ions onto the negatively charged nanoparticles in the plasma resulting in a significant increase in growth rate and utilization of material. A cylindrical metal hollow cathode was used where sputtering occurs on the internal surface of the cylinder. Apart from that a cathode configuration with a linear slit was employed suitable for roll-to-roll deposition. The sputtered material of ions and neutrals is ejected from the cathode due to the the pressure buildup by the high voltage pulse, due to the outward directed ambipolar electric field structure at the hollow cathode opening and due to the flow of the gas through the cathode. This results in rapid expansion of the sputtered material and it leads to nucleation and growth of nanoparticles. A range of materials has been synthesized by this technique including Fe, Cu, Ti, Ag, Mo, In and Zn. By adding a reactive gas to the process nanoparticles containing Ti-O, Ti-N Zn-O and In-N has been synthesized. Several process parameters were identified to affect the size, size distribution, shape and structure of the nanoparticles. These parameters include pulse power, pulse frequency, sputtering gas composition, gas pressure and geometry of the setup. By tuning these parameters, the nanoparticle size can range from a few nm to more than 250 nm in diameter. Depending on the employed process parameters, the crystal structure of nanoparticles varies from a single crystal with well-defined crystallographic faces to polycrystalline and amorphous cauliflower structures consisting of randomly oriented agglomerates of nano-crystals. In the presentation it will also be shown that the nanoparticles can be used for assembling of different nanostructures.

Thin Films
Room Mauka - Session TF-TuE

Growth & Characterization of 2D Materials

Moderator: Gregory Abadias, Institut Pprime, CNRS-Université de Poitiers

5:40pm **TF-TuE1 Characterizing 2D-materials and Hetero-structure of MoS_2 and WSe_2 by Spectroscopic Imaging Ellipsometry**, ***Sebastian Funke**,* Accurion GmbH, Germany; *U. Wurstbauer, E. Parzinger, B. Miller,* Walter Schottky Institute and Physics Department, TU München; *P. Thiesen,* Accurion GmbH, Germany

Characterizing 2D-materials and Hetero-structure of MoS_2 and WSe_2 by Spectroscopic Imaging Ellipsometry

Sebastian Funke[1], Ursula Wurstbauer[2,3], Eric Parzinger [2,3], Bastian Miller[2,3] , Peter H. Thiesen[1]

1. Accurion GmbH, Stresemanstraße 30, 37079 Göttingen, Germany

2. Walter Schottky Institute and Physics-Department, TU München, Garching 85748, Germany

3. Nanosystems Initiative Munic 80799, Germany

By stacking different 2D-materials into hetero-structures new optoelectronic devices are formed[1,2]. The advantage of these new hetero-structures compared to conventional devices may be superior material properties and its significant lower height. For the design of efficient hetero-structures the knowledge of the materials properties is essential. We show that spectroscopic imaging ellipsometry (SIE) is capable of measuring the optical properties of different types of 2D-materials. With the lateral resolution down to 1 µm SIE is able to localize and characterize small flakes of e.g. 2D-materials. It also enables the characterization of stacked materials.

In the talk we present spectral investigations on Molybdenum-disulphide from the UV- to NIR. To describe the dispersion for MoS_2 an anisotropic approach is shown[3]. It reveals an anisotropic behaviour in the out-of-plane direction. Further, investigations on a hetero-structure of MoS_2 and WSe_2 are done as seen in Figure 1. All regions can be measured simultaneously, so a comparison of the spectral response of the single 2D-materials can be compared to the stacked response. Spectral investigations around the bandgap of MoS_2 at around 650 nm will be shown and discussed for the overlapping and non-overlapping regions.

Figure 1: Heterostructure of MoS_2 and WSe_2. Green area denotes the overlapping hetero-structure.

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6:00pm **TF-TuE2 Synthesis & Characterization of Atomic and Electronic Properties of Graphene-based Heterostructure***, Q. Wu, **YoungJae Song**,* Sungkyunkwan University, Korea, Republic of Korea

Electronic structure of graphene is affected by number of graphene layers and stacking order. Control of layer number as well as scalability has been the main issues for device applications based on graphene. A new and unique CVD method is proposed to synthesize epitaxial multilayer graphene on copper by an iterative process of graphene growth and h-BN etching in chemical vapor deposition (CVD). A h-BN thin film is utilized to provide a gap of well-defined thickness for introducing the precursors and to play the role of the epitaxial growth of multilayer graphene. A thin h-BN film, initially-CVD grown on copper, is locally etched out by hydrogen atoms decomposed from CH4 during the sequential graphene growth, which generates additional growth channels of graphene adlayers again under the first graphene layer. The crystallinity with AB stacking was confirmed by Raman analysis and selected-area electron diffraction measurements as well as statistical studies of optical microscope images. Graphene growth with a h-BN template suggests a potential way for controlling the specific layer number of large-area graphene in CVD for the device applications of graphene.

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6:20pm **TF-TuE3 2D vs. 1D Structures at Stepped Si Surfaces and in Organic Molecules***, **Franz Himpsel**,* University of Wisconsin Madison, USA*; J.M. García Lastra,* Technical University of Denmark, Denmark*; A. Rubio,* Universidad del Pais Vasco*; I. Boukahil,* University of Wisconsin Madison, USA*; R. Qiao,* Advanced Light Source, LBNL, USA*; S.C. Erwin,* Naval Research Laboratory, USA*; I. Barke,* University of Rostock, Germany **INVITED**

The dimensionality of a structure plays an important role in its electronic properties, as demonstrated recently by a variety of layered compounds who behave very differently as single layer. This raises the question what happens when reducing the dimensionality further to one-dimensional atomic chains - the finest conceivable nanowires. Theory predicts exotic behavior, such as the elusive Luttinger liquid. Strong correlations are established between electrons propagating along an atomic chain, since they are not able to avoid each other. One might also expect reduced dielectric screening and higher chemical activity in 1D structures due to the reduced number of neighbors.

This talk focuses on two types of atomically-precise structures that bridge the gap between 2D and 1D. Both their preparation and their electronic structure are considered. Stepped surfaces can be prepared on vicinal Si with great precision (less than one kink in 10^4 edge atoms), since the high energy cost of a broken Si-Si bond leads to stable surface reconstructions. These can be decorated with a wide variety of metal atoms, frequently leading to metallic wires on a semiconducting substrate. The transition from 2D to 1D is explored by varying the step spacing. A variety of interesting phases have been found in these wires, such as charge density waves [1], spin-polarized energy bands, and an ordered array of spin-polarized Si edge atoms [2].

The other approach uses organic molecules to compare π-bonded carbon sheets and chains [3]. First-principles calculations show that 1D wires exhibit very simple molecular orbitals which mimic the overtones of a vibrating string, while 2D structures form more complex orbital patterns related to the modes of a drum. The dielectric screening is found to scale with the number of atoms in a molecule rather than the number of neighbor atoms, suggesting delocalized screening.

Looking into the future, we discuss molecular complexes combining 2D and 1D structures with atomic precision, such as the donor-π-acceptor complexes used in dye-sensitized solar cells [4]. Computational screening of the energy levels for thousands of dye molecules provides the blueprint for tandem solar cells where two π-absorbers are connected by molecular wires [5].

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7:00pm **TF-TuE5 Probing Atomic Structure of 2D TMDs by High Resolution STEM***, **Moon Kim**, Q. Wang, J. Wang,* The University of Texas at Dallas, USA

As the scaling of various functional devices continues, the future of these devices will rely on new class of materials. Research in graphene and the methodology of preparing ultrathin layers has led to the exploration of other 2D materials. In particular, single layers of transition metal dichalcogenides (TMDs) with lamellar structures similar to those of graphite have drawn significant attention because of their tunable bandgaps. TMDs exhibit diverse properties that depend on their composition: semiconductors, semimetals, metals, or superconductors. TMD properties also strongly depend on the crystalline structure, including the number and stacking sequence of layers. In exploring and developing these emerging materials, nanoscale characterization becomes ever more important. In particular, high resolution electron microscopy-based techniques now are capable of analyzing these 2D nano-materials and devices with better than 0.1 nm resolution. Here, we present our recent studies on the characterization of 2D layered materials by means of Scanning Transmission Electron Microscopy (STEM), specifically High Angle Annular Dark Field (HAADF) imaging and *in-situ* Transmission Electron Microscopy (TEM). We have identified the atomic arrangements and defects in single layer MoS_2, 2H stacked TMDs, 1T stacked TMDs, and distorted 1T stacked TMDs by HAADF STEM imaging . The location and nature of individual atoms, defects, phase transformation, and layer by layer shearing of 2D crystals will be presented and discussed in detail.

7:40pm **TF-TuE7 Synthesis of Transitional Dichalcogenide Films by Chemical Transformations of Thin Films***, **Shaul Aloni**,* Lawrence Berkeley National Laboratory, , USA*; C.T. Chen, T.R. Kuykendall,* Lawrence Berkeley National Laboratory, USA*; C. Kastl,* Lawrence Berkeley National Laboratory, USA*; T.P. Darlington, P.J. Schuck, N.J. Borys,* Lawrence Berkeley National Laboratory, USA*; A.M. Schwartzberg,* Lawrence Berkeley Lab, USA

The promising properties of transition metal chalcogenides (TMD's) continue to inspire great deal of research on optical and electronic devices. However, the progress in this field is limited by challenges in materials synthesis and device fabrication. In this work we present a new approach for the synthesis of TMD's with digital control of layer thickness. This method utilises chemical transformation of solid thin films of oxides deposited with submonolayer precision by ALD. Following their deposition the films are exposed to a chalcogen containing gas resulting in smooth and continuous TMD films whose thickness is defined by the thickness of the ALD deposited oxide film.

Typical experiments involve deposition of metal oxide, WO3 or MoO3, followed by a short conversion procedure involving annealing of the oxide film in presence of a chalcogenation agent, *e.g.* hydrogen disulfide gas or organochalcogen vapor. Typical composition of the gas phase is equivalent to 1% of H2S in argon. However, precise control of water content in the gas phase composition provides means for controlling the reaction mechanism. At low water vapor content (2-10 ppm) metal oxide films are chalcogenized in place with the thickness of the continuous TMD film defined by the thickness of the oxide layer. The resulting WS2 thin films are nanocrystalline, and moderately luminescent . At higher water concentrations (> 200 ppm) the process is dominated by vapor transport. Under these conditions, the volatility of the oxide species is significantly enhanced, resulting in minimal residual metal disulfide after growth. Under optimized conditions, highly luminescent, triangular monolayer WS2 and MoS2 islands with good island-to-island uniformity can be grown directly on the previously metal-oxide-coated substrate or onto a bare substrate placed downstream of a source. Carefully controlled humidity (~ 100 ppm) consistently produces high quality highly luminescent triangular WS2 and MoS2 islands.

The chemical transformation of solid films by a gas phase precursors offers additional benefits. In addition to precise control of thickness and compatibility with many transition metals, it is also compatible with any substrate that is not adversely affected by the chalcogenation agent. We present deposition of WS2 on variety of substrates including amorphous SiO2 and Si3N4 as well as SiC, TiO2 and GaN. Moreover, we suggest that the use of controlled amounts of water vapor is a new knob by which to tune growth of these materials, and these results demonstrate a route to improved material quality and unprecedented reproducibility of chemical vapor transport of many transition metal dichalcogenides.

8:00pm **TF-TuE8 Growth and Characterization of hBN/Graphene Heterostructures on Metal Substrates***, **Boris Feigelson,*** U.S. Naval Research Laboratory, USA*; K. Sridhara,* Texas A & M, USA*; J.K. Hite,* U.S. Naval Research Laboratory, USA*; A. Nath,* George Mason University*; J.A. Wollmershauser,* U.S. Naval Research Laboratory, USA

The development of 2D hBN/graphene heterostructures is still in the early stages and largely depends on possibility to grow these heterostructures as well as on rapid and accurate characterization of the grown hBN/graphene layers. Along with graphene, atomically thin two dimensional hexagonal boron nitride (2D hBN) is one of the key materials in the development of new van der Waals heterostructures due to its outstanding properties including an atomically smooth surface, high thermal conductivity, high mechanical strength, chemical inertness and high electrical resistance.

In this work, hBN/graphene films were grown by atmospheric-pressure CVD on metal substrates (mainly Cu, but also Cu-Ni alloys). A vertical custom-made CVD reactor was used to grow 2D hBN/graphene films. The design of the vertical reactor allows the simultaneous growth of a few samples of hBN/graphene layers on different substrates in the same run.

As it was shown in our previous work [1], Fourier transform grazing-incidence infrared reflection absorption spectroscopy (FT-IRRAS) can be used to characterize monolayer and few-layer h-BN films directly on metal substrates. Two sub-bands of the A_{2u}(LO) vibrational mode were found for thin 2D h-BN films in contact with Cu and Ni. The lower-energy A_{2u}(LO)1 sub-band around 819 cm^{-1} is related to 2D h-BN coupled with Cu substrate, while the higher energy A_{2u}(LO)2 sub-band around 824 cm^{-1} is related to decoupled (essentially free standing) 2D h-BN.

The IR-active out-of-plane vibrational mode was exploited to identify and characterize 2D hBN in grown heterostructures directly on metal substrates, while graphene was characterized by micro Raman spectroscopy. Combining FTIR and Raman spectroscopy allows express and in-depth characterization of hBN/graphene heterostructures directly on metal substrates used for growth.

The approach also provides an opportunity to determine which growth conditions lead to the absorption of foreign species on the substrate prior to the heterostructure deposition. Such interfacial layers were shown to result in easily-recognizable shifts in the A_{2u}(LO) peak. The degree to which the interaction of the hBN layer with the substrate is uniform and homogenous can also be assessed easily by examining the width and fine structure of the A_{2u}(LO) band.

B. N. Feigelson, V. M. Bermudez, J. K. Hite, Z. R. Robinson, V. D. Wheeler, K. Sridhara, and S. C. Hernandez, Nanoscale **7,** 3694 (2015)

Biomaterial Surfaces & Interfaces
Room Milo - Session BI-WeM

Biomolecule/Material Interactions

Moderator: Duncan McGillivray, University of Auckland

9:00am **BI-WeM4 Reconstruction Process and Orientation of Membrane Proteins in Artificial Cell Membrane Systems***, **Ryugo Tero,*** Toyohashi University of Technology, Japan **INVITED**

The lipid bilayer is the fundamental structure of cell membranes, at which the transportation of materials and signals in and out of cell membranes take place. Ion channels are one of representative membrane proteins promoting these reactions. They retain their proper structures and function only when they are incorporated in lipid bilayer membranes. It is necessary to reconstruct the membrane proteins into artificial lipid membranes to investigate the structure and function of membrane proteins out of cells. n this study we reconstructed the ion channels into solid-supported lipid bilayers (SLBs), which is an artificial lipid bilayer at solid-liquid interfaces, using proteoliposomes. We investigated the distribution and orientation of ion channels in the SLBs using fluorescence microscopy and atomic force microscopy (AFM).

9:40am **BI-WeM6 Surface Adsorbed Antibody Characterization using ToF-SIMS with Principal Component Analysis and Artificial Neural Networks***, N.G. Welch, R.M.T. Madiona, T.B. Payten, R.T. Jones, N. Brack,* La Trobe University, Australia*; B.W. Muir,* CSIRO, Australia*; **Paul Pigram,*** La Trobe University, Australia

Artificial neural networks (ANNs) form a class of powerful multivariate analysis techniques, yet their routine use in the surface analysis community is limited. Principal component analysis (PCA) is more commonly employed to reduce the dimensionality of large time-of-flight secondary ion mass spectrometry (ToF-SIMS) data sets and highlight key characteristics. The strengths and weaknesses of PCA and ANNs as methods for investigation and interpretation of a complex multivariate sample set will be considered. Using ToF-SIMS, spectra were acquired from an antibody and its proteolysis fragments with three primary-ion sources to obtain a panel of 72 spectra and a characteristic peak list of 775 fragment ions. The use of ANNs as a means to interpret the ToF-SIMS spectral data is explored, highlighting the optimal neural network design and computational parameters, and considering the technique limitations. Employing Bi_3^+ as the primary-ion source, ANNs can accurately classify antibody fragments from the parent antibody based on ToF-SIMS spectra.

10:20am **BI-WeM8 Controlled Peptide Surfaces of Various Ratios that Guide Neural Stem Cell Differentiation.***, **HalaShakib Dhowre,** C. Towlson, HS. Sahaf, N.A. Russell,* University of Nottingham, UK

Cell instructive biointerfaces represent an essential aspect for the advancement of regenerative medicine. Currently, a major issue in biointerface design is the limited ability to mimic the complex interactions of the natural processes in the extracellular matrix (ECM) with artificially designed surfaces and interfaces [1]. While biomaterial surfaces have been shown to be able to elicit specific cell responses (e.g. adhesion, proliferation, differentiation), precise control akin to that of natural cellular environments is still lacking[2].

AIM:

The present work aims to address this challenge by designing new synthetic peptide surfaces with well controlled composition and functionality able to impact control over the differentiation of neuronal stem cells with the ultimate goal to understand and control how neuronal networks function.

METHODS:

Compositionally well defined surface concentrations of two short laminin peptide sequences, Arg-Gly-Asp (RGD) and Ile-Lys-Val-Ala-Val (IKVAV) were prepared of various ratios via the “grafting from” stepwise approach and the surface modification was confirmed with surface analysis techniques to indicate successful peptide functionalisation. The neural stem and progenitor cells (NSPC) were set up from embryonic rat hippocampi (E18). Immunocytochemistry (ICC) observed cell viability and differentiation to specific NSPC lineages for Nestin, βIII-Tubulin and GFAP.

RESULTS:

Surface characterising techniques (WCA, AFM and ToF-SIMS) verified the successful amino acid build-up to peptides on the surfaces, allowing modification of the surfaces with RGD and IKVAV. Enhanced NSPC adhesion, proliferation and differentiation were observed on the peptide surfaces. ICC demonstrated Nestin expression decrease after the removal of the growth factors (EGF and FGF) and an increase in the expression of βIII-Tubulin and GFAP; thus illustrating cells differentiating from stem cells to neurons or astrocytes due to peptide surface influence.

CONCLUSION:

Well defined peptide surfaces were designed successfully, the various ratios of RGD and IKVAV surfaces demonstrated cell adhesion, proliferation and influences desirable effects in controlling different populations of stem cell fate. These surfaces may advance new insight in understanding how surface properties affect the regulation of physiological relevance in directing neural cell differentiation, which will be essential to understand how neural networks function.

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10:40am **BI-WeM9 Inelastic Neutron Spectroscopy Studies of Biosurfaces: the Chemistry of Hydrogen Surface Interaction***, **Anton Stampfl,*** Australian Nuclear Science and Technology Organisation, Australia

Adsorption, surface complexation and reactivity of biological molecules on inorganic surfaces and interfaces is pervasive throughout an enormous range of fields such as chemistry (geochemistry, biochemistry), biotechnology (medical implants, biosensors, tissue engineering, bioelectronics, biomimetics and artificial photosynthesis), radiation technology (radiation damage and detection), colloid chemistry, surface chemistry and physics. Hydrogen and its interaction at surfaces clearly plays a pivotal role in the ultimate functionality of many biologically-based surfaces. Through the hydrogen’s subtle interaction with the tethering surface, or interface, and the surrounding wet environment can and does lead to a multifaceted response to changes in temperature, pH, radiation etc.

Inelastic neutron spectroscopy is the domain of vibrational spectroscopic studies on bulk materials. At first sight, surface studies using such a method, with relatively low neutron flux rates and largish sample size, seems a totally hopeless task. There are, however, exceptions to this rather bullish view, where the surface dominates the scattered signal due to huge surface to volume ratios and large scattering cross-sections from adsorbate molecules, that incorporate for example, hydrogen, which neutrons are supremely sensitive to.

The deposition of amino acids and carbonyl-sulphide onto oxide surfaces is a fruitful area of discovery in the field of prebiotic formation of peptides and an example of how neutron spectroscopy makes significant contributions to the understanding of the subtle chemistry between adsorbate, substrate and surrounding environment. In this series of studies the deposition of amino-acids onto alumina from solution and in the presence of OCS is investigated by both inelastic neutron spectroscopy and high resolution photoemission which allows both the vibrational and electronic structure to be determined for these incredibly interesting systems. Studies focused on the extent of adsorption at various pH's, the character of each adsorbate (zwitterionic, basic, acidic), and the number of discrete surface sites of adsorption. Results show strong chemisorption of amino acids through an ester type bond with the alumina surface across a range of pH. Direct sorption of the amine group with alumina is observed only at pH 9. Formation of multilayers and/or peptides can also occur in conjunction with OCS absorption.

11:00am **BI-WeM10 Exploring Protein and Mesoporous Silica Nanoparticle Interactions***, **Brian Trewyn,** M. Moyer,* Colorado School of Mines, USA

Tandem and cascade reactions have the potential to save time and resources, advantages not frequently observed in individual, stepwise reactions. The versatile, ordered pore structure of mesoporous silica nanoparticle (MSN) materials is an ideal support for multiple, active catalysts that potentially have orthogonal optimal conditions. Herein, we will demonstrate that enzymes covalently tethered to MSN can be paired to inorganic species to catalyze multistep reactions. Additionally, MSN can be used to entrap large, multisubunit proteins as individual subunit monomers. Upon release, we will demonstrate that the subunits reassociate to form biochemically active proteins.

Nanomaterials
Room Hau - Session NM-WeM
Electronic & Magnetic Properties

Moderator: Yoshiaki Nakamura, Osaka University, Japan

8:20am **NM-WeM2 Effect of Segregation of sp-Impurities on Surface and Grain Boundary Magnetism in Nanocrystalline Nickel and Cobalt***, **Mojmir Sob**, M. Vsianska, H. Vemolova,* Masaryk University, Czech Republic

We present a systematic ab initio study of segregation of 12 non-magnetic sp-impurities (Al, Si, P, S, Ga, Ge, As, Se, In, Sn, Sb and Te) at Σ5(210) grain boundary (GB) and (210) free surface (FS) in fcc nanocrystalline ferromagnetic cobalt and nickel and analyze their effect on structure, magnetic and mechanical properties. In nanocrystalline nickel, most of the above impurities nearly kill or substantially reduce the magnetic moments at the FS and, when segregating interstitially (i.e. Si, P, S, Ge, As, Se), also at the GB so that they provide atomically thin magnetically dead layers which may be very desirable in spintronics. We demonstrate that the existence of magnetically dead layers is a common phenomenon at the sp-impurity-decorated GB and FS in nickel. It is caused by a strong hybridization of sp states of the impurities with the d states of nickel and a redistribution of electron states in both majority and minority bands. Reduction of magnetic moments at the Σ5(210) GB in fcc nanocrystalline cobalt is, in absolute values, very similar to that in nickel. However, as the magnetic moment in bulk cobalt is higher, we do not observe magnetically dead layers here. It turns out that by focused impurity segregation we can generate atomically thin magnetic layers with tailored magnetization, which can contribute to a new development of technologically important materials.

8:40am **NM-WeM3 Reversible Single-Molecular Manipulations of Spin Trans-Effect in Co-porphryin/Au(111) with Conserved Spin Moment***, M.H. Chang,* Korea University, Republic of Korea*; Y.H. Chang,* orea Advanced Institute of Science and Technology (KAIST), Korea*; H. Kim,* Korea University, Republic of Korea*; S.-H. Lee,* Korea University*; Y.-H. Kim,* Korea Advanced Institute of Science and Technology (KAIST), Korea*; **Se-Jong Kahng**,* Korea University, Korea

Controlling spin interactions in magnetic-molecules/metal is essential for spintronic molecular device applications. It has been considered that small molecule coordination to magnetic-molecules/metal can be used to reset molecular spins from 1/2 to zero and from zero to 1/2. However, the study on the control of spin interactions without changing spin moment of magnetic-molecules has been rare. Here, we demonstrate that spin interactions in Co-porphyrin/Au(111) can be controlled while spins being conserved, by coordination and de-coordination of small gaseous molecules, using scanning tunneling microscopy and spectroscopy (STM and STS). With small moleculecoordination, we observed that a zero-bias peak at Co-porphryin, a signature of Kondo effect in STS, remained but was clearly showed reduced width i.e. Kondo temperature, and that it could be reversibly retrieved by single molecular STM manipulations. Based on our density functional theory calculation results, the reduced Kondo temperature is explained with the relocation of unpaired spins in d_z2 orbitals of Co-porphyrin by vertical coordination of small molecules. Our study shows that with conserved spin moment in magnetic-molecules/metal, spin version of trans-effect can be directly probed through Kondo effect with STS.

9:00am **NM-WeM4 Two-dimensional Manganese Gallium NitrideSurface Structure Showing Ferromagnetism at RoomTemperature***, **Yingqiao Ma**, A. Smith,* Ohio University, USA

Ferromagnetic semiconductors are very promising materials for the spintronic applications, as they are good spin-polarized carrier sources and easy to be integrated into semiconductor devices. The search for ferromagnetic semiconductors with Curie temperature above the room-temperature has been a long-standing goal, since the Curie temperature Tc of most ferromagnetic semiconductors are at the cryogenic level with little possibility of improvement, which hinders their future practical spintronic applications.

Here, we observed the ferromagnetic domain structure at room-temperature on a GaN-based two-dimensional MnGaN semiconducting surface alloy, using spin-polarized scanning tunneling microscopy/spectroscopy which is sensitive to the surface magnetic nanostructures and can completely rule out the extrinsic origin of the ferromagnetism such as magnetic elements segregation by its ultimate spatial resolution. In contrast to the randomly doped dilute magnetic semiconductors, the two-dimensional surface structure has a unique and well-ordered hexagonal-like Mn √3 x √3 - R30° symmetry. The total density of states of the Mn √3 x √3 - R30° structure calculated by the density functional theory agree well with our normalized differential tunneling dI/dV spectroscopy, which clearly reveal the spin-polarized and spin-split Mn surface density of states peaks and prove the semiconducting nature of the surface as the normalized dI/dV goes to zero at the Fermi level. By applying a small magnetic field to the sample, the magnetic hysteresis is mapped out, which further proves its ferromagnetic nature. In conclusion, we demonstrated the room-temperature ferromagnetic nature of the two-dimensional Mn √3 x √3 - R30° structure, which makes it a promising material for future realistic magnetic storage, field-controlled, and quantum computing nano spintronic devices.

9:20am **NM-WeM5 Current-induced Magnetic Domain Wall Motion and its Application***, **Teruo Ono**,* Kyoto University, Japan **INVITED**

Current-induced magentic domain wall motion has been attracted much attention both from scientific and technological points of view [1]. When a magnetic DW is driven by electric current via adiabatic spin torque, the theory predicts a finite threshold current even for a perfect wire without any extrinsic pinning [2]. We have shown that this intrinsic pinning determines the threshold current, and thus that the adiabatic spin torque dominates the DW motion resulting in DW motion along electron flow direction, in a perpendicularly magnetized Co/Ni system sandwiched by a symmetric capping and seed layers [3-9]. On the other hand, current-induced DW motion against electron flow direction has been observed in ultrathin magnetic films in which the structural inversion symmetry (SIA) was broken [10, 11]. Recently, this DW motion against electron flow direction has been explained by the combination of a chiral DW and spin Hall torque [12, 13].In this presentation, I will show the systematic investigation by changing thickness of Co/Ni layer and discuss the contribution of adiabatic spin transfer torque, and spin Hall torque in the current-induced DW motion. I will also discuss possible applications using the current-induced DW motion.

This work was partly supported by a Grant-in-Aid for Scientific Research on Innovative Areas, Grant-in-Aid for Specially Promoted Research, and R & D Project for ICT Key Technology of MEXT.

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10:20am **NM-WeM8 Reconfigurable Nano-Structured Magnetic Metamaterials for Magnonic Logic***, **Andrei Slavin**, I.V. Lisenkov, V.S. Tyberkevych,* Oakland University, USA

Artificial magnetic metamaterials formed by arrays of dipolarly coupled magnetic nanodots are promising candidates for applications in microwave signal processing. It has been shown recently, that an array of magnetic dots can be used as a reconfigurable magnonic metamaterial (RMM), since its metastable static state (and the corresponding microwave characteristics) can be switched by application of a pulse of a bias magnetic field [1-3].

In this work we present a theory of switching of a metastable static state in a magnetic metamaterial formed by an array of identical dipolarly coupled nanodots under the action of a short (duration of the order of 10-100 ns) magnetic field pulse. It is shown that a large array of magnetic dots cannot be switched into a perfect periodic antiferromagnetic state (AFM). Instead, the final state of an array after the end of the switching pulse comprises a set of clusters with the local AFM periodicity. The properties of the array's final state strongly depend on the duration of the trailing front τ_f of the switching field pulse. In particular, the average size of the AFM clusters in the final state increases as $A \sim \tau_f^{2/3}$. This increase in the regularity of a final state is limited by the thermally activated dot magnetization reversals that become possible if the switching field decreases too slowly. In particular, our results show that the distance of the signal propagation in a chain of magnetic dots may be increased by application of a clock pulse having a long trailing front. It is also demonstrated that using magnetic metamaterials it is possible to design of a magnonic phase shifter operating without an external bias magnetic field. The phase shifter uses a localized collective spin wave mode propagating along a domain wall "waveguide" in a dipolarly-coupled magnetic dot array with a chessboard antiferromagnetic (CAFM) ground state. It is also demonstrated numerically that the remagnetization of a single magnetic dot adjacent to the domain wall waveguide introduces a controllable phase shift in the propagating spin wave mode without significant change to the mode amplitude. Thus, it is possible to realize a logic XOR gate in the same system.

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10:40am **NM-WeM9 Controlled Switching and Charge State Alteration of Surface Dangling Bond Nanostructures, Realization of a Quantum Hamiltonian Boolean Logic Gate***, S. Godlewski,* ***Rafal Zuzak,*** Jagiellonian University, Poland*; M. Kolmer,* Jagiellonian University, Poland*; M. Engelund,* Donostia International Physics Center, Spain*; H. Kawai,* Institute of Materials Research and Engineering, Singapore*; G. Dridi,* CEMES-CNRS, France*; A. Garcia-Lekue,* Donostia International Physics Center, Spain*; C. Joachim,* CEMES-CNRS, France*; D. Sanchez-Portal,* Donostia International Physics Center, Spain*; M. Szymonski,* Jagiellonian University, Poland

In recent years we observe an increasing interest in the precise atomic-scale fabrication of surface nanostructures. This is because the miniaturization of various electronic devices has pushed many fundamental research efforts toward creating atomic-scale circuits [1]. Among different substrates, the hydrogen passivated silicon and germanium surfaces are regarded as the promising ones due to the fact that they allow precise fabrication of complex dangling bond (DB) nanostructures, which introduce new electronic states within the intrinsic band gap of the substrate [2]. These structures could be further utilized in fabrication of atomic scale devices [3] or may be directly applied in quantum circuitry.

In the presentation we will describe fabrication of various surface DB nanostructures. Their geometrical and electronic properties will be analysed on the basis of scanning tunnelling microscopy/spectroscopy (STM/STS) measurements corroborated by density functional theory (DFT) calculations. We will show that upon electron/hole injection dangling bonds exhibit dynamical behaviour, which due to the high frequency of oscillations leads to smooth STM appearance. A new imaging model, based on a dynamical two-state rate equation, which allows detailed reproduction of observed STM pattern will be introduced [4]. Moreover, the influence of single dangling bond charging on the STS spectra will be analysed [5]. We will further envision that our new model might be applied to simulate other bi-stable systems where fluctuations arise from transiently charged electronic states. Finally, we will present successful design and construction of the first prototypical QHC (Quantum Hamiltonian Computing) atomic scale Boolean logic gate operated by the STM tip [6].

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This research was supported by the National Science Centre, Poland (contract no. UMO-2014/15/D/ST3/02975) and the 7th Framework Programme of the European Union Collaborative Project PAMS (contract no.610446).

11:00am **NM-WeM10 Synthesis of Transition Metal Dichalcogenide Heterostructures and Nanodevices by Atomic Layer Deposition***,* ***Christoph Kastl,*** *C.T. Chen,* Lawrence Berkeley National Laboratory, USA*; B. Shevitski,* University of California, Berkeley, USA*; T.R. Kuykendall, S. Aloni, A.M. Schwartzberg,* Lawrence Berkeley National Laboratory, USA

Interest in layered transition metal dichalcogenides (TMDs) has been renewed since the discovery of emergent properties when reduced to single two-dimensional layers. The current state-of-the-art fabrication of heterostructures involves exfoliation from bulk crystals and subsequent manual stacking of the atomic layers. The lack of reproducible and large scale synthetic methods for high quality, consistent TMD samples has become a major bottleneck to research on and application of these materials.

The following two-step process involving atomic layer deposition (ALD) and chalcogenization can be used as a scalable and highly versatile method for TMD synthesis. First, high quality transition metal oxide films are deposited by ALD. Second, the transition metal oxide films are converted into layered TMDs by chemical chalcogenization, i.e. annealing under H2S atmosphere in a high temperature furnace. [1] We leverage the particular advantages of ALD to further develop this approach into a fabrication process for encased nanodevices and heterostructures. Planar films of MoO3 and/or WO3 are deposited on the growth substrate, and SiO2 is used as an inert capping layer. Then, device structures are defined by photolithography and reactive ion etching. In the subsequent conversion step, the nucleation starts at the exposed cross sections of the heterostructure, and the TMD growth proceeds laterally from the nucleation site. Cross-sectional TEM reveals that this lateral growth mode forms highly crystalline MoS2 (WS2) layers which are aligned parallel to the substrate. We characterize the optical and electronic properties of the encased heterostructures by photoluminescence spectroscopy, ultrafast transient absorption spectroscopy, and field effect measurements. Furthermore, controlling the extent of the lateral growth via annealing time and temperature, we show that encased TMD nanoribbons can be fabricated with lateral dimension down to ~10 nm.

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11:20am **NM-WeM11 Growth and In situ Electronic Transport and Scanning Probe Studies of Topological Materials Bi_2Se_3 and Na_3Bi***,* ***Michael Fuhrer,*** Monash University, Australia **INVITED**

Topological materials are fascinating novel electronic phases with important device implications. Topological insulators are insulating in their interiors but conduct on their boundaries; two-dimensional topological insulators can realize dissipationless conduction along their one-dimensional edges. Topological Dirac semimetals lie at the boundary between conventional and topological insulators, and can be pushed toward one or the other by electric or magnetic fields, realizing new types of switches.

I will discuss the development of a novel experimental capability combining the growth of topological materials by molecular beam epitaxy (MBE) with *in situ* magnetotransport and low-temperature scanning tunneling microscopy at 5 K. This capability has been used to study the transport properties of topological insulator Bi_2Se_3 *in situ* during MBE growth, monitoring the carrier concentration and mobility as a function of film thickness[1]. More recently, topological Dirac semimetal Na_3Bi thin films have been prepared on α-Al_2O_3(0001) substrates with low temperature charge carrier mobilities exceeding 6000 $cm^2V^{-1}s^{-1}$ with n-type carrier densities below 1×10^{18} cm^{-3}, comparable to the best single crystal values[2]. Perpendicular magnetoresistance at low field shows the perfect weak-antilocalization behaviour expected for Dirac fermions in the absence of intervalley scattering. Our ongoing efforts to tune the carrier density using physical and chemical schemes to realize topological devices will also be discussed [3].

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Thin Films
Room Mauka - Session TF-WeM
Plasma-based Film Growth, Etching, & Processing

Moderator: Davide Sangiovanni, Linköping University, Sweden

8:00am **TF-WeM1 Flexible Electrochromic Electrodes on the Substrate of Crystalline Indium Tin Oxide with Graphene***, **Yekyung Kim**, SJ. Lee, JW. Seo, S.H. Han, H. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

Electrochromic technology is recently getting attention due to the requirement of the energy saving technology and the advancement of paired technology which shows synergistic effect together, such as light-responding mirrors, smart window, light shutter, etc. Nickel oxide are the most well-known anodic coloration material which is generally used as a counter electrode with enhancing coloration efficiency together with tungsten oxide, the main determinant of the coloration efficiency of whole device. The enhancement of electrochromic and cyclic stability of the electrochromic device is performed, in this study, by conditioning of nickel oxide with various methods of tungsten alloying, optimization of sputtering condition, lithiation, and so on. Also, to concrete a flexible electrochromic device, transparent conducting oxide should be deposited on a plastic substrate under the electrochromic layer. In this study, nickel and tungsten oxide were deposited on the crystalline indium tin oxide (*c*-ITO)/graphene/polyethylene terephthalate (PET) film. The thermally and mechanically stable graphene helps to prepare *c*-ITO on PET film which is hardly fabricated due to the high temperature requirement for ITO crystallization. The prepared flexible electrochromic electrodes on *c*-ITO)/graphene/PET showed reasonable coloration performance. Also, the electrochemical and cyclic properties of electrochromic full-cell were determined.

Acknowledgement

This work was supported by the Energy Efficiency & Resources of the Korea Institute of Energy Technology Evaluation and Planning (KETEP) grant funded by the Korea government Ministry of Knowledge Economy (No. 20142010102980). This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT & Future Planning (NRF-2015M3A7B4050452)

8:20am **TF-WeM2 Maximizing Retention of Complex Chemical Functionality in Plasma Polymers Via the Alpha-Gamma Transition***, **Andrew Michelmore**, S. Saboohi, B.R. Coad,* University of South Australia, Australia*; R.D. Short,* University of Lancaster, UK*; H.J. Griesser,* University of South Australia, Australia

There is increasing need for fabrication of thin polymeric films with complex chemical functionality for a variety of applications including cell therapies, biosensing, microelectronics and as platforms for surface initiated atom-transfer radical polymerization (ATRP). Conventional polymerisation techniques are not suitable in many instances as control of film thickness and topography is difficult. Plasma polymerisation is a technique which can overcome these issues, but has typically suffered from difficulty in retaining chemical structure due to fragmentation in the plasma phase and/or ion bombardment on the surface.

We have shown that pressure plays a critical role in plasma processes. By tuning the plasma from collisionless to collisional sheaths (the alpha to gamma transition) the chemistry of the plasma and the plasma polymer are drastically changed [1]; in gamma mode, the plasma chemistry is biased towards protonated precursor ions and the contribution of ions to the deposit increases. For example, we have studied deposition of ethyl a-bromoisobutyrate (EBIB) for fabricating surfaces for initiating ATRP [2]. This requires that the intact a-bromoisobutyryl structure be retained on the surface of the plasma polymer. Using plasma phase mass spectrometry we show that at the transition from alpha to gamma mode protonated EBIB are formed which arrive at the surface intact and dominate the deposition process. This results in high retention of groups capable of initiating ATRP. High pressure also limits the ion energy, such that ions can be 'soft landed' and do not scramble chemical structures on the surface by ion bombardment.

More recent results on a family of ester compounds will be presented which highlight the critical roles of pressure, power and ion energy. Methods for predicting optimum conditions will also be discussed. These results open possibilities to fabricate functionalized surfaces with higher retention of chemical structure than has been possible previously.

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8:40am **TF-WeM3 Layer-by-layer Etching of LaAlSiOx***, **Mitsuhiro Omura**, K. Furumoto, K. Matsuda, T. Sasaki, I. Sakai, H. Hayashi,* Toshiba Corporation, Japan **INVITED**

With downscaling of metal-oxide-semiconductor (MOS) devices, high dielectric constant (high-k) oxide materials have been proposed as gate oxide, to reduce the gate leakage current. LaAlSiOx is one of the attractive candidates. In gate transistor fabrication, removal of high-k oxide films after gate electrode etching is a critical step for the formation of ohmic contacts on source and drain regions. Dry etching is a potential process to minimize the recess of the Si substrate which leads to the degradation of device performances. The conventional approach is to use an etching process with high selectivity to the Si substrate. Sasaki et al. have achieved a high LaAlSiO$_x$-to-Si selectivity of 6.7 using C_4F_8/Ar/H_2 plasma [1]. Another approach to reduce the Si substrate recess is precise control of etching depth using atomic layer etching (ALE) or layer by layer etching. ALE is defined to be an etching technique that uses sequential self-limiting reactions consisting of two steps, surface modification to form a reactive layer, followed by a removal step which takes off only this modified layer keeping the underlying film intact [2]. It is reported that by ALE using an energetic Ar beam and BCl3 gas in HfO2 etching, drain current and leakage current characteristics of MOSFET device improved, compared with conventional reactive ion etching (RIE) [3]. To control the etching depth of LaAlSiOx, layer by layer etching using a sequential process has been studied, focusing on the selective removal of surface modification layer and repeatability of the sequential process.

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9:20am **TF-WeM5 Effect of Ar$^+$ Ion Assist on the Properties of a-C:H Films Deposited on a Trench***, **Yuki Hirata**,* Tokyo University of Science, The University of Tokyo, Japan*; K. Onishi,* The University of of Tokyo, Japan*; S. Sasaki,* Tokyo University of Science, Japan

Hydrogenated amorphous carbon (a-C:H) film have attracted considerable interest because of their high hardness, extremely low friction, high wear resistance, chemical inertness, and excellent gas barrier properties. These aforementioned characteristics make a-C:H films suitable for use in a wide range of applications such as tribological, anti-corrosional and gas barrier applications.

In our previous study, a-C:H film was prepared using the bipolar PBII&D technique on a trench-shaped target (20 mm pitch and 10 mm depth), and the coating uniformity was evaluated. In the bipolar PBII&D process, glow discharge plasma is generated by a positive pulse voltage applied to the target, and subsequently, a high-voltage negative pulse is applied for omnidirectional ion implantation and/or deposition to the target. However, this study revealed that the mechanical or structural properties of the a-C:H film differed greatly depending on whether the coating area was the top, sidewall, or bottom surface of the trench-shaped target. To reveal them, behavior of the ions or radicals around the trench-shaped target was analyzed through plasma simulation. Then it became apparent that these results were attribute to the nonuniformities of the incident flux or energy of the ions. Thus, in this study, non-reactive Ar gas was added to a toluene gas for deposition of a-C:H films to enhance the incident energy of the ions, and such ion-assisted effect was investigated simultaneously. The mechanical properties of the a-C:H film, including the internal stress in the thickness direction, were measured using a surface profilometer, the hardness and adhesiveness were measured using a nanoindentation hardness test and micro-scratch test, respectively. Furthermore, to evaluate the a-C:H film structure, Raman spectroscopy and Fourier transform infrared spectroscopy (FTIR) were also conducted.

As a results, the uniformity of the film thickness was improved as the amount of introduced argon gas increased. Moreover, the hardness, internal stress, and adhesiveness were also improved in the case of an a-C:H film coated on a Si plate or at the top or bottom surface of a trench-shaped target. Such superior tendencies were considered to be caused by ion-assisted effects. On the other hand, in the case of the a-C:H film coated on the side wall, no improvement in film properties was seen. According to the Raman spectroscopy and FTIR, structure of a-C:H films were destroyed by Ar^+ ion sputtering. That's why, it could be considered that Ar gas addition did not lead to the improvements for its properties but lead to the destruction of its structure.

9:40am **TF-WeM6 Characterization of PECVD a-C:H:Si:O:Cl Films***, D. Rossi,* UNESP - Sorocaba, Brazil*; R. Landers,* Ifgw - Unicamp, Brazil*; J.R. Bortoleto,* ***Steven Durrant,*** UNESP - Sorocaba, Brazil

Thin films were produced by plasma enhanced chemical vapor deposition (PECVD) of tetramethylsilane, chloroform, argon mixtures. The partial pressure of chloroform in the chamber feed, C_{Cl}. was varied from 0 to 40%. Amorphous hydrogenated carbon films also containing silicon, oxygen and small amounts of chlorine, a-C:H:Si:O:Cl, were produced at deposition rates of up to about 220 nm min^{-1} (for a C_{Cl} of 40%). Transmission infrared-analyses revealed the presence of OH groups in the chlorinated films, along with, amongst others, CH, C=C, Si-CH, Si-CH_2 and Si-O-Si groups. As revealed by X-ray photoelectron analysis, the films could be doped with chlorine to a maximum of about 2 at%. Surface morphology and roughness were examined using Scanning electron microscopy (SEM) and Atomic force microscopy (AFM). Tauc band gaps, calculated from transmission ultraviolet-visible near infrared spectra, tend to decrease from ~3.4 eV for the unchlorinated film to around 2.5 eV for those doped with chlorine.

10:20am **TF-WeM8 Plasma-assisted Atomic Layer Deposition of SiN_x Films***, R.A. Ovanesyan, N. Leick, R.J. Gasvoda, J.M. Klein,* Colorado School of Mines, USA*; D.M. Hausmann,* Lam Research Corporation, USA*;* ***Sumit Agarwal,*** Colorado School of Mines, USA **INVITED**

The introduction of 3-D device architectures in integrated circuits has created a need for atomic layer deposition (ALD) of highly conformal ultra-thin films. In particular, ALD of low-dielectric-constant, carbon-containing silicon nitride (SiC_xN_y) films at temperatures ≤400 °C is required. However, controlled incorporation of C atoms into SiN_x during ALD remains challenging. In this work, we report the C incorporation mechanism during two plasma-enhanced SiC_xN_yALD processes. The first ALD process consisted of three steps, Si_2Cl_6/thermal CH_3NH_2/N_2 plasma, while the second process consists of two steps, Si_2Cl_6/CH_3NH_2 plasma. In both ALD processes, we have determined the film composition, reactive sites, and adsorbed surface species using *in situ* attenuated total reflection Fourier transform infrared (ATR-FTIR) spectroscopy. In addition, the growth per cycle (GPC) and refractive index were determined using in situ four-wavelength ellipsometry.

Our IR spectra show that in the first ALD process, the CH_3NH_2 thermally reacts with –$SiCl_x$surface species created after the Si_2Cl_6 half-cycle to form -CH_xterminated surface amides. During the subsequent N_2 plasma half-cycle, in addition to nitridation of Si, a fraction of the surface CH_xgroups were incorporated into the SiC_xN_yfilm as -N=C=N- species, which appear as a strong vibrational mode at ~2170 cm^{-1}. The composition of the SiN_xfilms in the two-step ALD process was very similar, with C incorporated primarily as -N=C=N- groups created during the CH_3NH_2 plasma half-cycle. We find that during the exposure of the film to Si_2Cl_6 following an CH_3NH_2 plasma half-cycle, surface carbodiimides (-N=C=NH) react to nitriles (-NH-C≡N), while most of the surface is terminated with -$SiCl_x$species. The subsequent CH_3NH_2 plasma half-cycle, shows that the -NH-C≡N species formed during the Si_2Cl_6 half-cycle are removed, and the N=C=NH surface species are restored along with –NH_xgroups. For the Si_2Cl_6/CH_3NH_2 plasma ALD process, SiN_xfilms grown at 400 °C show a carbon content of ~4 at.% as measured through Rutherford backscattering spectroscopy combined with hydrogen forward scattering. Transmission electron microscopy shows a conformality of >95% for the SiC_xN_yfilms. The GPC for both processes was ~0.9 Å, with a refractive index of 1.95 and 1.86 for the N_2 plasma and CH_3NH_2 plasma ALD processes, respectively.

11:00am **TF-WeM10 Atomic Scale Analyses of Plasma Surface Reactions using Molecular Dynamics Simulations and Ion/radical Beam Experiments***,* ***Satoshi Hamaguchi,*** *H. Li, T. Ito, M. Isobe, K. Karahashi,* Osaka University, Japan

As the sizes of semiconductor devices continue to diminish and are now approaching atomic scales, the downsizing of transistors following Moore's law is bound to end in the near future. However, the continuing market demand for higher performance and lower energy consumption of large-scale integrated (LSI) circuits has driven a series of innovations in device technologies, such as three-dimensional (3D) device structures and devices based on non-silicon materials. Manufacturing of these non-conventional devices also poses new challenges for processing technologies. For example, magnetic materials used in magnetoresistive random-access memories (MRAMs) cannot be etched efficiently by the existing reactive ion etching (RIE) technologies, which has so far limited the level of integration of MRAM devices. The modern near-atomic-scale devices also require atomic level precision in their manufacturing processes, which has also driven new technologies such as atomic layer deposition (ALD) and atomic layer etching (ALE). In this work, we have developed analytical techniques to examine plasma-surface interactions at the atomic scale using molecular dynamics (MD) simulation and multi-beam (i.e., ion and radical beam) injection experiments [1], in order to understand atomic layer reaction mechanisms that largely determine efficiencies of such atomic-level processing technologies. Some of our recent analyses include surface chemical reactions for magnetic materials [2,3] metal oxides[4], Si-based materials [5] as well as damage formation mechanisms [6,7] due to ion bombardment during RIE processes.

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11:20am **TF-WeM11 Low-temperature Fabrication of Amorphous Zinc Tin Oxide Thin Film Transistors without Annealing Process***,* ***Sungmin Kim,*** *J.M. Kim, H.J. Kim,* Seoul National University, Korea, Republic of Korea

Amorphous oxide semiconductor (AOS) such as $InGaZnO_x$ (IGZO) and $ZnSnO_x$ (ZTO) attracts an attention as a new channel material for thin film transistors (TFT). It has outstanding properties such as high field effect mobility (>10cm^2/V-s) as well as transparency and uniformity. Therefore, display industry has named it as a prime candidate of channel material for large-sized and flexible display devices. However, considering that substrates in use for flexible display devices are polymer materials like PEN or PI, AOS has a critical drawback that it requires annealing process over 350°C This is a quite low temperature compared to conventional silicon-based process(over 800°C), but the process temperature must be under 200°Cto prevent deformation of polymer substrates.

In this study, the fabricated ZTO TFTs have a ZTO bottom gate and ITO top contacts, and all of them were made by RF magnetron sputtering system. And we replaced post annealing step with heating up the sputter stage up to 200°Cduring sputtering and forming 10% oxygen atmosphere. Electrical properties such as threshold voltage (V_{th}), mobility and subthreshold swing (SS) of ZTO TFTs were compared to convince that our new process could replace post annealing over 350°C. Analyses for morphology and chemical compositions are also conducted.

Saturation mobility of ZTO TFTs with 350°Cannealing process and with our novel process were measured to be 17.4 and 11.7cm^^{2}/V-s, respectively. Post annealing at 200°Ccannot activate ZTO TFTs at all, but by heating up the sputter stage, heating of 200°Cwas sufficient to activate TFTs. There was a little reduction of mobility, but 11.7cm^^{2}/V-s is still good enough giving that mobility of 10cm^^{2}/V-s is enough for large sized display (>70 inches). And SS values of 350°Cannealed sample and one sputtered at 200°C was 0.31V/decade and 0.50 V/decade, respectively. Also, chemical composition and surface roughness was analyzed by XPS and AFM. These results also show that our new low temperature process is suitable for manufacturing AOS TFTs.

The main reason of this phenomenon can be served by combination of plasma and thermal energy in sputter chamber. Generally, it is obvious that as-deposited AOS channel needs oxygen curing to connect broken bonds between metal and oxygen atoms. While Ar/O_2 plasma in sputter chamber redeem relatively low thermal energy(200°C), curing reaction immediately occurs on as-deposited ZTO. Consequently, we made ZTO TFTs below 200°C process, rather than post annealing over 350°C. Performances of them were still applicable for next generation display. But it shows a little bit poor performance, so there must be further study to advance properties

Energy Harvesting & Storage
Room Makai - Session EH-WeP

Energy Harvesting & Storage Poster Session

EH-WeP1 Multifunctional Polymeric Binder for Silicon Anode in Li-ion Battery*, Ja-Hyoung Ryu,* Ulsan National Institute of Science and Technology, Republic of Korea

Silicon as an anode material in lithium-ion batteries has great potentials due to its high charge capacity. However, the practical application of Si is quite challenging because severe volume change during charging/discharging process results in breaking anode film and fading the reversible charge capacity. Therefore, the efficient polymeric binder to stably accommodate active materials in the anode is highly demanded. We demonstrated the systematic molecular design and synthetic approaches of novel binder is one of the solution which is capable of preserving electrode integrity and maintaining electrical contact during expansion/contraction of silicon anode. We have introduced multifunctional group-containing poly(acrylic acid-*co*-vinyl alcohol) copolymer binders. Polymeric binders with three different functional groups, namely, carboxylic acid (COOH), carboxylate (COO–), and hydroxyl (OH), in a single polymer backbone have been synthesized and characterized via 1H NMR and FTIR spectroscopies. A systematic study that involved varying the ratio of the functional groups indicated that a material with an acid-to-alcohol molar ratio of 60:40 showed promise as an efficient binder with an initial columbic efficiency of 89%. The strong interaction of the polymer binder with Si nanoparticle from PAA, and high viscosity form PVA could give a synergetic effect on making uniform anode film. Further more, three dimensionally interconnected networks provide sufficient mechanical properties to prevent the destruction of the electrode during numerous cycling.

EH-WeP3 Strain imaging of a LiCoO2 Cathode in a Li-ion Battery*, Keisuke Nakayama,* Kansai University, Japan

In recent years, world's energy consumption has been steadily increasing, and prompt efforts are needed to decrease CO_2 and other greenhouse gas emissions. Li-ion batteries are becoming increasingly important in the world market of energy storage and conversion devices. Compared with other commonly used batteries, Li-ion batteries have advantages including high energy density, high output voltage, and the absence of the memory effect, and so are recognized as promising candidates for energy storage. Li-ion batteries are applied to mobile electronic devices and these are an essential part of the full hybrid electric vehicles (HEVs) and/or plug-in electric vehicles (PHEVs) owing to their high energy densities and low weight-to-volume ratios.

Li-ion batteries are operated by the Li ions migration. Therefore, it is important to observe the migration of lithium-ions with a high spatial resolution and non-destruction.

The active materials in the electrodes of the lithium-ion batteries have been generally used $LiCoO_2$ cathode and graphite carbon anode that were layered materials. Graphitic materials, which are representative of carbon materials have been used the most for anode materials because of their low working potential, which is close to the metallic lithium anode. During charging and discharging, Li-ions migrate between $LiCoO_2$ and graphite, and intercalation/deintercalation are induced. Intercalation/deintercalation induce changes in volume. Scanning probe microscopy (SPM) can allow high resolution imaging of these volume changes, which enables us to investigate Li-ion migration without destruction.

Our samples to observe were as follows. $LiCoO_2$ particles around 10 µm in diameter were coated with the Al current collector. The thickness of the coated layer was around 30 µm. A 20-µm-thick polypropylene separator with the electrolyte was sandwiched between the $LiCoO_2$ cathode and the graphite anode.

We observed volume changes in the $LiCoO_2$ cathode using SPM, and successfully imaged the distribution of the volume changes corresponding to the $LiCoO_2$ particles. Volume changes in the interspace were significantly larger than those in the particles. Therefore, the large volume changes are caused by electrolyte flux induced by changes in concentration of Li ions.

EH-WeP4 Imaging of dry-out in a $LiCoO_2$ Cathode in a Li-ion Battery*, Yukiho Okuno,* Kansai Univerisity, Japan

Lithium ion batteries have attracted an attention in the field of portable electronic devices and electric vehicles due to high energy density, high output voltages, and no memory effect. Therefore, Li-ion batteries are recognized as promising candidates for energy storage. The main elements of Li-ion batteries are positive electrodes, negative electrodes, separators, and electrolytes. $LiCoO_2$ and graphite that are layered materials are commonly used as electrode materials for Li-ion batteries.

Lithium ion batteries operate through migration of Li-ions between the electrodes. During charging and discharging, Li-ions migrate between $LiCoO_2$ and graphite, and Li-ions are inserted into or extracted from particles of electrode materials. Insertion/extraction of Li-ions induce changes in volume. The volume change causes dry-out of electrolyte.

Dry-out of electrolyte is one of the most important issues in Li-ion batteries. The volume changes of the electrode materials induce dry-out of electrolyte, which greatly degrades the batteries. Our samples to investigate dry-out were as follows. $LiCoO_2$ particles around 10 µm in diameter were coated with the Al current collector. The thickness of the coated layer was around 30 µm. A 20-µm-thick polypropylene separator with the electrolyte was sandwiched between the $LiCoO_2$ cathode and the graphite anode.

We observed volume changes in the $LiCoO_2$ cathode using SPM. The observed volume changes are caused by electrolyte flux induced by changes in concentration of Li-ions. However, the volume changes were greatly reduced when the electrolyte dried out. The dry-out and infiltration of electrolyte between the $LiCoO_2$ particles and the current collector spread out with the procedure of degradation of the batteries. The boundaries between the dry-out and infiltration regions acted as barriers of electrolyte flux.

EH-WeP5 Application of XPS and UPS to the Characterization of LixPOyNz Surfaces*, David Surman,* Kratos Analytical Inc.*; J. Counsell, S.J. Coultas,* Kratos Analytical Ltd., UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield,* Kratos Analytical Ltd., UK

Lithium ion batteries are commonly found in home electronic equipment. In recent times there have been significant efforts to improve the durability, cycle time and lifetime decay of the batteries and in particular the electrode/electrolyte material. Novel materials have been developed that also increase the energy storage density. Lithium phosphorus oxynitride (LiPON) has become one of the most commonly used solid electrolyte thin-films in energy storage devices. Obviously, due to the widespread use of this material, there is significant interest in understanding the characteristics and properties with a view towards optimization.

We have applied both XPS and UPS to explore the surface and bulk properties of several $Li_xPO_yN_z$ surfaces prepared via atomic layer deposition ALD [1]. The distribution of elements below the surface is explored using ion and angular-resolved depth profiling methods. This technique has been used extensively across a broad range of applications however the damage caused by impinging ions on the structure of the analyzed material has always been a concern for the analyst. Recently Argon gas cluster ion sources have been employed to reduce the chemical damage of organic materials and broaden the range of materials amenable to this type of analysis. Here we extend the application of cluster ions beyond organics to inorganic oxides. We will present how, with the use of Ar250-3000+ ions, where the energy per atom can be 2.5-40 eV, it is possible to obtain more accurate information regarding the true nature of the LiPON thin-film. A comparison is made with conventional monatomic depth profiles and in particular the differences in stoichiometry that is obtained with the two different ion sources. Ion implantation is also discussed as are the unfortunate chemical effects of carbon deposition from organic cluster ions. We will demonstrate how the analyst can now confidently depth profile through inorganic metal oxide thin-films without the worry of reduction or preferential sputtering.

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EH-WeP6 Study on Double Perovskite as a Solid Oxide Regenerative Fuel Cell Cathode Material*, Youngjin Kwon,* *J.M. Bae,* Korea Advanced Institute of Science and Technology (KAIST), Republic of Korea

It has been increasing interest in hydrogen(H_2) as an alternative energy carrier. Because the H_2 has high energy density, pure emission and it is easy to be transported by using a pipeline. But H_2 doesn't exist on the earth as a fuel. For this reason, it must be generated. There are several ways of producing H_2 such as by photocatalytic water splitting, gasification of biomass, solar thermochemical water splitting and water electrolysis driven by solar cell or wind turbine. Among these technologies, Solid oxide regenerative fuel cell(SORFC) is a practical and efficient method for the industrial field. High operating temperature improves the electrode kinetics and reduce the SORFC electrolyte resistance, leading to lower losses in cell performance.

Due to similarity to Solid oxide fuel cell(SOFC), advances have been made in the development of SORFC based on cell assemblies with structure nickel-yttria stabilized zirconia(Ni-YSZ) fuel electrode / YSZ electrolyte / lanthanum strontium manganite-YSZ(LSM-YSZ) air electrode. The previous study show that the performance discrepancies of the cell in operation between the electrolytic and galvanic modes could be varied, depending on the electrode materials. Moreover, the Ni-YSZ most widely used fuel electrode has several problems even though its great catalytic performance. One of them is degradation of the fuel electrode because of Ni particle's redox reaction and agglomeration. Therefore it is necessary to develop an alternative fuel electrode material.

Double perovskite electrode material is one of the promising candidate for the fuel electrode of the SORFC because of its high catalytic performance and stability at SOFC mode. In this study, We studied on the Double perovskite $Pr_{0.5}Br_{0.5}MnO_{3-\delta}$(PBMO) as a fuel electrode material of SORFC. PBMO was infiltrated into the scaffold structure of the electrolyte, $La_{0.8}Sr_{0.2}Ga_{0.85}$ $Mg_{0.15}O_{3-\delta}$ (LSGM) and synthesized at the low temperature because second phase generated when it annealed at high temperature. The Half cell test was conducted to investigate the electrochemical performance of the electrode material at the steam rich atmosphere.

EH-WeP7 PtNi Extended Surface Catalysts for Oxygen Reduction in PEMFC*, S. Shulda, C. Ngo,* Colorado School of Mines, USA*; J. Nelson Weker,* SLAC National Accelerator Laboratory, USA*; S. Mauger, KC. Neyerlin, S. Alia, B. Pivovar,* National Renewable Energy Laboratory, USA*;* ***Svitlana Pylypenko,*** Colorado School of Mines, USA

Extended surface platinum nickel (PtNi) nanowires are a promising alternative to the current state-of-the-art catalysts in polymer electrolyte membrane fuel cells (PEMFCs). In this work, PtNi nanowires were synthesized via galvanic displacement and showed high specific activity for the oxygen reduction reaction. Post-synthesis treatments were explored to tune activity and durability of the PtNi nanowires, and various ink formulations were investigated to improve membrane electrode assembly (MEA) performance. Scanning transmission electron microscopy (STEM), x-ray photoelectron spectroscopy (XPS), extended x-ray absorption fine structure (EXAFS), x-ray absorption near edge structure (XANES), and transmission x-ray microscopy (TXM) were carried out to understand, on a fundamental level, how the post-synthesis treatments affected composition, structure, and morphology of the nanowires and electrodes. The results guide future work on scalable synthesis of these materials and optimization of their performance in MEA.

EH-WeP8 Unoccupied Surface State Induced by Ozone and Ammonia on H-Terminated Diamond Electrodes for Photo-Catalytic Ammonia Synthesis*, I. Boukahil, P.S. Johnson,* University of Wisconsin Madison, USA*; R. Qiao,* Advanced Light Source, LBNL, USA*; J. Bandy, R.J. Hamers,* ***Franz Himpsel,*** University of Wisconsin Madison, USA

Recently, the use of H-terminated diamond electrodes for photo-catalytic conversion of N_2 to NH_3 in aqueous solution was demonstrated [1]. This concept uses energetic electrons, created in diamond by UV-light and injected into the solution. The negative electron affinity of H-terminated diamond surfaces makes them efficient electron emitters [2], and their chemical inertness enables applications as electrodes in reactive environments [1]. A limiting factor was the build-up of O at the interface during the photo-catalytic reaction.

We investigated the surface electronic structure of H-terminated, polycrystalline diamond films prepared the same way as those used for ammonia synthesis in [1], before and after treatment with ozone or ammonia. X-ray absorption spectroscopy (XAS) served as atom- and bond-specific probe (compare [3] for the methodology). For ozone treatment, a sharp C1*s* transition to an unoccupied surface state is found at -2.5 eV below the onset of the bulk conduction band transitions (289.2 eV). A similar transition is found at -2.6 eV after ammonia treatment.

It is surprising to obtain such a well-defined surface state at complex, real-life electrode materials. That suggests a characteristic local bonding configuration. An extensive comparison with spectra from reference molecules reveals two compatible configurations for the ozone-treated surface, a keto group (>C=O) and a hydroxyl group attached to π-bonded carbon (=C-OH). Both lead to low-lying π^* transitions similar to those observed at the C1*s* and O1*s* edges.

Possible roles of the surface state in the photo-injection of electrons from diamond into electrolytes are discussed. Thereby the electron-hole interaction [4] is taken into account which affects both the position of the surface state in the core level spectra and the barrier for electron injection.

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EH-WeP9 Improved Thermo-stability of $(NH_4)_2SiF_6$ Fluorescent Microparticles with the Phosphoric Acids*,* ***Aoi Tokiwa,*** Tokyo Denki University, Japan

Ammonium hexafluorosilicate ($(NH_4)_2SiF_6$) microparticles, are one of novel phosphor, possess excellent features such as a high-efficient fluorescence and robust photo-stability, compared to other silicon (Si)-based ones. Because of these advantages, they are a promising candidate for the applications to light emitting diodes (LEDs), opto-electronic integrated circuits (OEICs) and solar cells. However, the microparticles may be restricted the adaptable environment so as to cause the rapid degradation of fluorescence intensity under temperature above 200℃ Therefore, the improvement of heatproof temperature is of crucial importance. As a one of the heat-resistance materials, the phosphoric acids are known to have effective features for the products such as flame-retardant plastics and rubber. In this presentation, we will discuss the thermo-stable effect of the $(NH_4)_2SiF_6$ fluorescent microparticles with the phosphoric acids. The fluorescent microparticles were synthesized by the chemical reaction of vaporized hydrofluoric nitric acid with Si powders and P powders in closed container. The obtained microparticles had a mean diameter of approximately 10 - 30 µm, and were composed of $(NH_4)_2SiF_6$/phosphorus oxide composites as major ingredients. To investigate the thermo-stability of the fluorescent microparticles, they were annealed from room temperature to 300 °C for 30 min in the atmosphere. The microparticles could be dramatically enhanced the heatproof temperature by adding the phosphoric acids, showing the stable fluorescence even after 300 °C annealing. It is clarified from Fourier transforms infrared (FT-IR) analysis that the improved thermos-stability is mainly due to the formation of Si-O bond with the stronger binding energy at the interface region between the $(NH_4)_2SiF_6$ and the phosphorus oxide. It should be noted that the annealed microparticles at 300 °C could be visible to the naked eye. Therefore, the introduction of the phosphoric acids into the $(NH_4)_2SiF_6$ fluorescent microparticles would become a dominant tool for the development of the thermally stable phosphor.

EH-WeP10 Optimization of Si Quantum Dot Arrays in Inorganic-organic Solar Cells*,* ***Yuuki Sugano,*** Tokyo Denki University, Japan

Currently, silicon (Si)-based solar cells have been used extensively because of the possession of greater advantages such as high performance and high reliability. To expand the versatility and to reduce the production cost of the solar cells, inorganic-organic solar cells that combine Si quantum dots (SiQDs) with conducting organic polymers have been developed over the past several years. In the design of the highly efficient solar cells, the usage of strong wavelength range, i.e., 450-520 nm of sunlight is of crucial importance. The SiQDs can be freely controlled the bandgap width by the variation of size, enabling the selective absorption of sunlight. Therefore, it is necessary to uniform form the SiQDs on the substrate so as to maximize the potential abilities of the SiQDs. In this presentation, we will discuss the correlation between the morphology of the substrate surface and the configuration state of the SiQDs. The uniform arrangement of the SiQDs could be achieved by the formation of the micro-textured structures onto the substrate surface. Additionally, to investigate the absorbance characteristics of the substrates with SiQD arrays, we conducted the UV-vis analysis. As a result, the substrates with the SiQD arrays led to the higher absorbance compared to substrates without the SiQD arrays. Therefore, the optimizing the arrangement of the SiQDs becomes the most important factor in the performance improvement of SiQDs based on the inorganic-organic solar cells.

EH-WeP11 Upgradation in Photoelectrochemical Performances and Stability of CdS cased ZnIn$_2$S$_4$/TiO$_2$ Heterojunction *via* Improved TiO$_2$/FTO Interface and Ni(OH)$_2$ Cocatalyst*, **_Mahadeo Mahadik_**, *P. Shinde,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Republic of Korea*; D. Selvaraj,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Korea*; H.H. Lee,* Pohang Accelerator Laboratory (PAL), Pohang University of Science and Technology (POSTECH), Republic of Korea*; M. Cho, J.S. Jang,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Republic of Korea

A simple and effective strategy was used to fundamentally improve the performance of a Ni(OH)$_2$ loaded CdS cased ZnIn$_2$S$_4$/TiO$_2$ heterostructured photoanode. TiO$_2$ nanorods grown hydrothermally on fluorine-doped tin oxide (FTO) and annealed at 500°C yielded an optimal photocurrent density of ~ 988 µA cm^{-2} at 0.1 V vs. Ag/AgCl under simulated one sun illumination. The annealing effect minimized the defects in TiO$_2$ and assisted the formation of compact contacts between the FTO and TiO$_2$ nanorods for efficient electron transport. The stepwise introduction of ZnIn$_2$S$_4$ and CdS on annealed TiO$_2$ enhanced the absorption in the visible spectrum range and electron/hole separation in CdS cased ZnIn$_2$S$_4$/TiO$_2$. Additionally, the Ni(OH)$_2$ cocatalyst functioned in hole trapping and improved the stability of the photoelectrode through timely consumption of the photogenerated charges, particularly the holes. The photoelectrical performances studied under AM1.5G illumination shows the 3D heterostructure generate a photocurrent of approximately 1.9 mA cm^{-2}, and is stable up to 60 min.

EH-WeP12 Surfaces And Interfaces Of Methylammonium Lead Halide Perovskite/ Graphene Oxide Films Studied By Spectroscopy, **_Muge Acik_**, *S.B. Darling,* Argonne National Laboratory, USA

Power conversion efficiency in perovskite-based solar cells has recently improved to ≥20%, however, there is insufficient understanding of the underlying optoelectronic device function. Among all perovskite materials as candidates for the light harvesters in such solar devices, organolead halide perovskites, MAPbX$_3$ (X=I, Br, Cl), have stood out with their outstanding optoelectronic properties such as tunable bandgaps, long electron-hole diffusion length and high electron/hole mobility. Indeed, replacement of ETL/HTL with graphene-derived materials (graphene oxide, reduced graphene oxide, n/p-doped graphene, etc.) has emerged as a pathway to improve device performance. Nevertheless, unclear film growth, nucleation and degradation mechanisms at the graphene/perovskite hybrid interfaces require understanding of interfacial mechanisms during perovskite growth. Moreover, graphene/perovskite structure-property relationships are not well understood due to unclear chemistry/poor characterization at the interfaces of ETL/perovskite/HTL hybrids. To explore interfacial working mechanisms and perovskite film formation in graphene-derived perovskite solar cells, we performed variable temperature (≤600°C) *in situ* spectroscopy (infrared absorption, micro-Raman, UV-vis-NIR, x-ray photoelectron and luminescence), and *ex situ* XRD, SEM, TEM, and AFM for film morphology studies. Our studies targeted perovskite/graphene interfaces and perovskite growth mechanisms to overcome detrimental effects of stability factors such as incomplete lead precursor conversion, inconsistent crystallite formation/film uniformity, and weak cation-anion-solvent coordination. Effect of film thickness, stoichiometry control, underlayer/overlayer composition, and perovskite growth temperature were optimized. To address film scalability and stability, we studied opto-thermal changes in reduced graphene/graphite oxide (RGO) upon halide-based (CH$_3$NH$_3$PbI$_3$, CH$_3$NH$_3$PbBr$_3$, CH$_3$NH$_3$PbCl$_3$) perovskite deposition, and performed spectroscopic analysis derived from the intensity and peak areas of perovskite vibrational modes of C-H (~2800-3200 cm^{-1}) and N-H (~2000-2800 cm^{-1}). Controlled perovskite formation was achieved at room temperature for bromide/chloride-based perovskites resulting improved chemical stability with heat (*vs.* iodide derivative). Poor perovskite formation was monitored on RGO resulting in film degradation in air (O$_2$, H$_2$O) by *in situ* characterization. (1) M Acik, SB Darling. J. Mater. Chem. A (2016) 4, 6185-6235. (2) J Gong, SB Darling, F You, Energy Environ. Sci. (2015) 8, 1953-1968. (3) M Acik, G Lee, C Mattevi, M Chhowalla, K Cho, YJ Chabal. Nature Mater. (2010) 9 (10), 840-845.

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EH-WeP13 Kesterite Cu$_2$ZnSnS$_4$ (CZTS) Thin Films Using Sn/Cu/ZnS Stack Layers and H$_2$S Sulfurization, *M.S. Choi, D.H. Lim, Y.J. Kim, H.H. Han, S.K. Son, J.H. Lee,* Hanyang University, Seoul, Korea, Republic of Korea*; R.C. Choi,* Inha University, Incheon, Korea, Republic of Korea*;* **_Changhwan Choi,_** Hanyang University, Seoul, Korea, Republic of Korea

We synthesized and characterized Cu$_2$ZnSnS$_4$ (CZTS) thin film as an absorber layer using hybrid physical vapor deposition methods with a Sn/Cu/ZnS stack order on the Mo coated SLG (Soda lime glass) or SLG substrates. Considering melting temperature of each element, the first Sn layer was thermal-evaporated, followed by deposition of Cu and ZnS layers using Radio-Frequency (RF) magnetron sputtering. For the complete precursor, the final sulfurization process was carried out at 550 ^{o}C for 1 hour under the mixture gases of N$_2$ + H$_2$S (5%). ZnS was intentionally adopted to provide more sulfure into the film instead of using single Zn because some sulfur is lost during thermal processing. In order to investigate the effects of the elemental composition ratio within CZTS thin film on the structural, electrical and optical properties, the ratio of Sn: Cu: ZnS was modulated by adjusting the thickness of each element layers as following: (1) Sn (110 nm)/Cu (97 nm)/ZnS (243 nm), (2) Sn (132 nm)/Cu (109 nm)/ZnS (209 nm), (3) Sn (135 nm)/Cu (117 nm)/ZnS (198 nm), (4) Sn (134 nm)/Cu (138 nm)/ZnS (178 nm), and (5) Sn (134 nm)/Cu (158 nm)/ZnS (158 nm).

The CZTS thin film was turned out to be kesterite structure and the strongest preferred (112) orientation peak was detected to Cu/(Zn+Sn) ratio with 1.04. The Cu/(Zn+Sn) ratio substantially affects the peak intensity as well as growth and creation of secondary phases in the kesterite-structured CZTS films. In addition, the optical energy band gap (E_g) is significantly influenced by the composition ratio. Generally, increasing Cu/(Zn+Sn) ratio induced the growth of CZTS particle size leading to surface morphology improvement while the E_g was reduced. The moderate Cu/(Zn+Sn) ratio in the range between 0.53 and 1.04 led to enhance the kesterite structure of CZTS single crystal phase and reinforce growth direction of (112) preferred orientation. However, the Cu-rich films having Cu/(Zn+Sn) ratio greater than 1.0 showed much larger grain size due to agglomeration with adjacent grains. The Cu-rich CZTS thin film exhibited high carrier concentration (1.60×10^{20} cm^{-3}) and hall mobility (9.8 cm^2/V·sec), but lower (1.18 eV) was attained. Instead, the E_g of Cu-poor CZTS thin film was 1.53 eV, favorable to the optimal CZTS absorber layer. Our results indicate that the optical energy band gap, an indicator to determining the optical properties of the CZTS thin film, is very sensitive to the composition ratio of constituent elements and PVD-based CZTS thin film should be carefully processed to get the optimum optical properties.

EH-WeP14 Charge Transfer Dynamics between Carbon Nanotubes and Hybrid Organic Metal Halide Perovskite Films, **_Philip Schulz_**, *M. Yang, R. Ihly, K. Zhu, J.L. Blackburn, J.J. Berry,* NREL, USA

The ongoing development of hybrid organic inorganic perovskite photovoltaics has revealed that the numerous interfaces in perovskite solar cells (PSC) play crucial roles for device efficiency and stability. Importantly, many critical interfacial properties are still poorly understood, a deficiency that often limits efforts to improve device performance. Carbon nanotubes have been identified as viable transport layer components in high efficient PSC with enhanced cell characteristics. In this talk I will present our most recent results exploring the mechanisms by which carbon nanotubes enable advantageous charge carrier extraction from the absorber layer and how carbon nanotube interlayers can ideally be embedded in the device geometry.

First, we demonstrated in a detailed photoemission spectroscopy study of semiconducting single-walled carbon nanotubes (s-SWCNT) on top of methlyammonium lead iodide (MAPbI$_3$) absorber films that the formation of an interfacial dipole leads to beneficial band bending in the s-SWCNT film. This observed alignment allows for rapid hole extraction at this interface from the absorber onto the s-SWCNT transport layer as seen from the clear spectroscopic signatures of both phases (MAPbI$_3$ and s-SWCNT) in transient absorption spectroscopy.[1] Subsequently, we were able to show that this enhanced hole extraction process impacts the kinetics of charge transfer at multiple interfaces within the device stack by unambiguously tracking charge carrier dynamics with a combination of time resolved photoluminescence, transient absorbance and time resolve microwave conductivity measurements.[2] Eventually, we showed that integrating a thin s-SWCNT interlayer between the $MAPbI_3$ absorber and a conventional organic hole transport layer leads to a significant improvement of device characteristics and cell performance. In my outlook I will sketch how the ensemble of these studies opens up an avenue to tailor-made charge carrier extraction interlayers for the next generation of transport layers in PSC.

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EH-WeP15 Combinatorial Reactive Sputtering of In_2S_3 as an Alternative Contact Layer for Thin Film Solar Cells*, Sebastian Siol,* NREL, USA*; T. Dhakal,* Binghamton University, USA*; G. Gudavalli, P. Rajbhandari,* Binghamton University, USA*; C. DeHart, L. Baranowski, A. Zakutayev,* NREL, USA

High-throughput computational and experimental techniques have been used in the past to accelerate the discovery of new promising solar cell materials. An important part of the development of novel thin film solar cell technologies, that is still considered a bottleneck for both theory and experiment, is the search for alternative interfacial contact (buffer) layers. The research and development of contact materials is difficult due to the inherent complexity that arises from its interactions at the interface with the absorber. A promising alternative to the commonly used CdS buffer layer in thin film solar cells that contain absorbers with lower electron affinity can be found in β-In_2S_3. However, the synthesis conditions for the sputter deposition of this material are not well established.

Here, In_2S_3 is investigated as a solar cell contact material utilizing a high throughput combinatorial screening of the temperature-flux parameter space, followed by a number of spatially-resolved characterization techniques. It is demonstrated that by tuning the sulfur partial pressure, phase pure β-In_2S_3 could be deposited using a broad range of substrate temperatures between 500°C and ambient temperature [1]. Combinatorial photovoltaic device libraries with $Al/ZnO/In_2S_3/Cu_2ZnSnS_4/Mo/SiO_2$ structure were built at optimal processing conditions to investigate the feasibility of the sputtered In_2S_3 buffer layers and for an accelerated optimization of the device structure. The performance of the resulting In_2S_3/Cu_2ZnSnS_4 photovoltaic devices is on par with CdS/Cu_2ZnSnS_4 reference solar cells with similar values for short circuit currents and open circuit voltages.

Overall, these results demonstrate how a high-throughput experimental approach can be used to accelerate the development of contact materials and facilitate the optimization of thin film solar cell devices.

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EH-WeP16 Higher Voltage Li-rich Cathode Materials for Lithium-ion Battery Applications*, Chandrasekar M Subramaniyam,* *H.K. Liu, S.X. Dou,* Institute for Semiconducting and Electronic Materials AIIM facility, Innovation Campus, University of Wollongong, Australia

- Li-rich layered cathode material exhibited excellent specific capacity (250 mAh/g) over 100 cycles exhibiting 95-99% coulombic efficiency.
- Therefore, these materials in combination with appropriate electrolytes are expected to perform at high voltage (up to 5 V) which in turn could foresee the requirement for plug-in/ hybrid electric vehicles

A quest to replace fossil fuels so as to ignite the automotive and electronic devices with high-performing, economical and safe power storage simulates R&D in the field of chemical power sources. The past two decades research on lithium-ion batteries (LIBs) proven it to be robust technology in electrify electronic devices and in developing plug-in and hybrid electric vehicles as they delivers high energy and power capabilities. However, the present R&D aimed at beefing up it's the current state-of-art technology to develop "5 V" cell without sacrificing high specific charge capacity, excellent cyclability and safety[1-4]. Therefore, the current focus is on the development of cathode materials as the anode materials possess working voltage approximately close to Li metal.

In order to foresee these objectives, herein, we have attempted to synthesis spinel-layered[4-7] Li-rich Li-Mn-M-O based composites as cathode material for lithium-ion batteries applications via simple, low temperature - solvothermal method. Both as-obtained and annealed samples were characterized for their phase, morphology using x-ray diffraction (XRD) and field emission scanning electron microscopy (FESEM), respectively. When electrochemically tested against Li^+/Li^0 between 2.0 – 4.8 V, the annealed Li-rich spinel-layered exhibited excellent specific capacity and rate capability even at high current density, making it as a probable next generation cathode material for LIBs.

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EH-WeP17 High-Resolution Observation of Electronic Properties of an Anode Material in a Lithium-Ion Battery*, Yuki Matsushita,* Kansai University, Japan

The electrochemical energy storage devices have attracted an attention in the field of mobile electric devices and electric vehicles. Lithium-ion batteries are one of the most significant devices because of high energy density, high output voltage, and no memory effect.

The primary components of a lithium-ion battery are negative-electrode material, positive-electrode material, separator, and electrolytes along with current collectors. Lithium-ion batteries operate through the migration of lithium- ions between the electrodes. During charging and discharging, electrode reactions occur in the active materials corresponding to lithium-ion migrations.

The active materials in the electrodes of the lithium-ion batteries have been commonly used $LiCoO_2$ and graphite that were layered materials. Also, the electrolyte is a lithium salt in an organic solvent. The lithium-ion batteries based on graphite are approaching the theoretical limit for capacity. Therefore, Si particles have attracted an attention. Si has a high theoretical specific energy density for anode materials in lithium-ion batteries. However, the cycle life of batteries with Si anode is poor as large volume changes are associated with the lithiation and delithiation cycle according to electrode reactions, resulting in the pulverization of the electrode. In addition, lithium-ion batteries have a risk of ignition because of using flammable organic liquid electrolyte. All-solid-state lithium-ion batteries using the non-flammable inorganic solid electrolyte instead of flammable organic liquid electrolyte have been attracted an attention to improve safety. Lithium-ion batteries have been widely studied for additional improvement of performance and safety.

When Si or Li_2TiO_3 particles lithiated or delithiated with lithium ions in a battery, the electrons also are transferred to maintain charge neutral. Therefore, the anode materials in the electrodes of the lithium-ion batteries are required to both electronic conductivity and ionic conductivity. We focused on change in electronic properties of the anode materials especially Si due to the chemical reactions with lithium ions. We present results in observation of changes in electric properties of Si particles in the anode corresponding to the lithium-ion concentrations, which were obtained via a scanning probe microscope.

EH-WeP18 Activated Carbon-like Graphene Assembly for Supercapacitor Applications*, Kwang Bum Kim*, Yonsei University, Korea, Republic of Korea

Graphene has been extensively stuided as an electrode material for supercapacitors due to its large specific surface area, high electrical conductivity and excellent chemical/mechanical stabiity. Due to the 2D nature, however, graphene tends to easily restack to form layered microstructures on a current collector during electrode fabrication. Restacking of the graphene sheets in an electrode greatly reduces the effective surface area of graphene and limits ion transport within a graphene electrode, which in turn leads to a decrease in the specific capacitance.

Here, we developled new approaches to improve capacitive properties of graphene: nanomesh graphene and activated graphene microsphere. The activated graphene microsphere is like an activated carbon-like graphene assembly which is prepared through graphene assembly into microspheres followed by an activation treatments.

In this study,we report on the activated carbon-like graphene assembly as high specific capacitance electrode materials for supercapacitor applications. Detailed synthetic procedure and electrochemical properties of the activated graphene microsphere assembly will be discussed in the meeting.

Nanomaterials
Room Makai - Session NM-WeP
Nanomaterials Poster Session

NM-WeP1 Quantum Confinement Effect and Photocatalytic Properties of Cu$_4$SnS$_4$ and Cu$_4$SnS$_4$-Au Quantum Dots*, Wenchao Liu,* Nanjing Tech University, China

We developed an improved hydrothermal method with water-oil two-phase reaction system to synthesize size-controllable and oil-soluble Cu$_4$SnS$_4$ (CTS) quantum dots (QDs). The formation and growth mechanism of CTS QDs was proved to proceed via three steps: nucleation of C$_{31}$S$_{16}$ nanoparticles, diffusion of Sn^{4+} into Cu$_{31}$S$_{16}$ nanoparticles and formation of regular hexagonal nanoprisms via Ostwald ripening. The water-oil interface plays an important role in controlling nuclei process and growth speed of CTS QDs. The average size and size distribution of CTS QDs can be controlled efficiently through adjusting the solvent ratio of toluene/water. Nearly monodisperse CTS QDs can be synthesized when the toluene volume is larger than 30 mL. More importantly, this improved hydrothermal method is a general and low cost method to synthesize not only chalcogenide based QDs but also other complex compound QDs. The blue-shift of absorption edge and broadening of Raman bands were observed due to the quantum confinement effect. The exciton Bohr radius of CTS QDs was calculated to be 3.3-5.8 nm by using the first principle calculation. We further use the CTS quantum dots as seeds to produce CTS-Au heterostructured nanoparticles. Such heterostructured nanoparticles are shown to have excellent photocatalytic properties.

NM-WeP2 Magnetic Strain Imaging of a Main Pole Tip and an Upper Shield in a Hard Disk Drive*, Kenta Butsugan,* Kansai University, Japan

Hard disk drives (HDDs) play an important role as large-scale information storages. Currently, in perpendicular recording, the main pole is keenly confined to apply magnetic fields to a finite portion. Therefore, remanent magnetization tends to appear at the pole tip. The magnetic fields produced by the remanent magnetization erase data recorded on magnetic media. The head-induced data erasure, especially erase-after-write, is a serious problem for the single-pole writer. We observed a head to reveal the erase-after-write phenomenon using magnetic strain imaging.

Scanning probe microscopes (SPMs) can sensitively detect changes in the gap between the tip and sample, with high in-plane resolutions. Strain imaging, based upon the excellent capabilities of SPMs, detects changes in the gap induced by the modulation of a physical property to be imaged, and images the modulated property of the sample together with its topography. Strain imaging was applied to observe the piezoelectric/ferroelectric properties of samples, and then magnetic observation was presented.

When a magnetic sample is subjected to a magnetic field, strains are generated in the sample. Because the strains involve factors that depend on the magnetization of each domain, we can observe the magnetic domain structures by imaging the strains via an SPM. We pointed out magnetostriction, magnetic forces, and electromagnetic interaction between the magnetization and eddy currents as the causes of the strains. Any magnetic probe is not required with this method, because domain structures are imaged by the detection of surface displacements. The applied magnetic fields are well-estimated and precisely controllable, while the stray fields from the magnetic probes used in magnetic force microscopy are not controllable and not easy to estimate.

Our observed samples were heads having the main pole tips of 60-nm and 30-nm width. One of them was multilayer pole tip. We observed magnetic imaging of the tips with respect to the write coil currents. We present these results.

NM-WeP3 Electrical and Optical Properties of Barium Titanate Nanoparticles Contained in Mesoporous Silicate Thin Film*, Atsushi Kohno,* *T. Tajiri,* Fukuoka University, Japan

Integration of size-controlled nanoparticles into thin films is attractive for applications to functional materials and devices owing to their unique properties related to the reduced size. We have synthesized the nanoparticles of dielectric materials in the one-dimensional pores of mesoporous silicate SBA-15 thin films formed on silicon and quartz substrates and have investigated the characteristics of nanoparticles. Ferroelectric nanoparticles are attractive for memory application especially as ultra-small scale devices, and the ferroelectricity of nanoparticle is interesting from the viewpoint of materials sciences. In this research we focus on the nanoparticles of perovskite-type ferroelectric materials. The synthesis of barium titanate (BaTiO$_3$) nanoparticles in the pores of SBA-15 thin film were developed, and the electrical and optical properties of the nanoparticles have been investigated.

Mesoporous silicate SBA-15 has been synthesized using Ethylene oxide/propylene oxide/ethylene oxide triblock copolymer and tetraethylorthosilicate. The mixture solution was coated on p-Si(100) and quartz substrates by spin-coating, and then the coated samples were dried and sintered. The SBA-15 thin film samples were dipped in BaTiO$_3$ precursor solution. The SBA-15 films which contained BaTiO$_3$ precursor solution in the pores were sintered in a furnace at 700 °C for crystallization. In the case of electrical measurement Au electrodes were made on the films.

X-ray diffraction showed that the one-dimensional pores in SBA-15 thin film were aligned parallel to the surface and stacked keeping well-ordered hexagonal symmetry. The pore diameter was estimated to be about 5 nm from the analyses of X-ray diffraction and reflectivity, as detail of the evaluation method was reported elsewhere. It was confirmed that the stacked pore structure was never affected by the synthesis of BaTiO$_3$ nanoparticles. The elemental composition and chemical states of BaTiO$_3$ nanoparticles in the thin films were checked by XPS measurement as compared with the bulk material. The optical absorption of BaTiO$_3$ nanoparticles was clearly observed and the absorption edge is estimated to be about 3.7 eV which is much larger than the bandgap of the bulk material.

The clockwise hysteresis was clearly observed in the capacitance-voltage characteristics of Au/BaTiO$_3$-containing SBA-15/p-Si capacitor and the hysteresis voltage width was increased and saturated as increased the applied voltage. These results suggest that the hysteresis was caused by ferroelectricity of BaTiO$_3$ nanoparticles. The properties of the BaTiO$_3$ nanoparticles will be discussed in the conference.

NM-WeP4 Structural Analysis of Hydroxyapatite Nanoparticles by Rietveld Refinement and Electron Diffraction*, Magdalena Méndez-González,* ESFM-National Polytechnic Institute of México*; G.M. González,* UPIBI-National Polytechnic Institute of México*; M.M. Méndez,* ESFM-National Polytechnic Institute of México

It was studied by Rietveld refinement and electron diffraction structural behavior of hydroxyapatite nano-particles, synthesized by chemical precipitation under normal temperature and pressure. Rietveld refinement using the data applied to XRD structural parameters of the nano-particles, its crystal size and the crystalline phases were obtained. Electron diffraction semi spherical and slightly elongated morphology, defined in relation to time and aging temperature used in the synthesis, distinguishing normal hexagonal prism morphology observed in natural hydroxyapatite crystals micrometer size was observed.

NM-WeP5 Fe$_3$O$_4$@Zn$_3$K$_2$[Fe(CN)$_6$]$_2$ for Cesium Removal from Radioactive. Aqueous Waste Solutions: A Mössbauer and XPS Study*, Arely Cano,* CICATA Legaria, National Polytechnic Institute, México*; A.A. Lemus-Santana,* CICATA Legaria, National Polytechnic Institute, Mexico*; J. Tóth, L. Kövér,* Institute for Nuclear Research (ATOMKI), Hungarian Academy of Sciences, Hungary*; E. Reguera,* CICATA Legaria, National Polytechnic Institute, México

Zn$_3$A$_2$[Fe(CN)$_6$]·xH$_2$O with A= Na$^+$, K$^+$, Rb$^+$ shows a high ability for Cs$^+$ removal from aqueous solutions by ionic exchange.These solids have a porous framework formed by six large ellipsoidal cavities per hexagonal unit cell with dimensions close to 15.5x11.1x7.9 Å. The neighboring cavities remain connected by elliptical windows of about 6.8x8Å. Within a given cavity two charge balance cations A$^+$are found. These cations are located close to N corners of the ZnN$_4$ tetrahedron [1]. For Cs$^+$ the ionic exchange is highly favorable due of its large volume [2], the Cs$^+$ ion is found interacting with two N neighboring atoms. This explains that when Zn$_3$A$_2$[Fe(CN)$_6$]$_2$·xH$_2$O is immersed in an aqueous solution containing Cs$^+$, the ionic exchange is quantitative. On the other hand, the iron oxides nanoparticles have attracted attention as simple, efficient and economical materials for pollutant removal, including heavy metals. Their physicochemical properties as large surface areas, surface reactivity and strong adsorption capability can be modified and enhanced to obtain effective adsorbents materials. In addition, the iron oxide behaves as ferrimagnetic or ferromagnetic material; such property can be used to allow the separation process using an applied magnetic field. This is the case of the system under study in this contribution. In this study, paramagnetic magnetite nanoparticles were synthesized and covered with a thin shell of $Zn_3A_2[Fe(CN)_6]_2$, then the shell was progressively growing at the surface. The nanocomposi tes obtained were evaluated for Cs^+ removal from aqueous solutions. For evaluation, the nanocomposites were prepared with different iron oxide particles sizes and $Zn_3A_2[Fe(CN)_6]$ thin shell . The structural study was carried out from XRD powder patterns and Electron Microscopy data.

The interactions at the interface between the core of magnetite nanoparticles and the zinc hexacyanoferrate shell were studied by X-ray Photoelectron Spectroscopy (XPS) and Mössbauer spectroscopy. The nanocomposites studied were prepared by two different successive adsorption cycles of shell growth, $Fe_3O_4@[Fe(CN)_6]^{4-}$ and Zn^{2+}. The quantitative analysis by XPS allows determine the shell thickness using an appropriate model and supported with Mössbauer data which allows the identification of species formed and their interactions at the interface.

NM-WeP6 Subwavelength Color Printing with Wide Viewing Angle*, HuiJoon Park,* Ajou University, Republic of Korea

Color filter has been considered as an essential component of various display technologies such as LCDs and OLEDs, because the quality of image and resolution of those displays are significantly affected by the performance of color filters. Existing color filter systems, however, utilize colorant pigments or dyes, whose properties are easily affected by numerous factors including constant UV illumination, longstanding heat exposure and moisture, thus causing the performance degradation of display devices in a relatively short period of time. Furthermore, their low stability with respect to diverse processing chemicals and complicated patterning processes for creating individual pixels are also the biggest concern of the traditional color filter systems.

As an alternative to the present color-generating systems, a structural color filter scheme, which exploits a physical interaction of light with nano- and micro-structures (*e.g.* photonic and plasmonic resonances), has been widely investigated due to their potential advantages such as ultra-compactness, long-standing stability and simple manufacturability as compared to the conventional color filters.

Particularly, with the growing popularity of high-definition devices, the ability of attaining high spatial resolution by tightly localizing the light energy into neighboring gaps at the deep subwavelength scale, thus being able to create color pixels beyond the diffraction limit, has been another key feature of the structural color filter system. Therefore, in recent years, with the rapid developments of large-scale nanofabrication techniques such as nanoimprint lithography, colloidal self-assembly and laser interference lithography, substantial amount of attention has been given to the various nanostructure-based color filtering systems, which could provide unique and distinct possibilities for enabling a color printing with sub-diffraction resolution. However, there have been great difficulties in retaining optical resonances at the same wavelength over a wide angular range and simultaneously creating vivid full colors in a pixel unit through a one-step process.

Here, an angle-insensitive structural color filtering scheme based on strong interference effects in ultrathin subwavelength semiconductor gratings on metallic substrates is introduced. The proposed color filter devices, which are fabricated over a large area using nanoimprint lithography, produce distinctive colors that are easily tuned by altering a width of the nanostructured gratings even with the fixed thickness of the structure, thus allowing all the individual color pixels to be patterned via one-step fabrication.

NM-WeP7 Ultrasonic Assisted Preparation of Liposomes using Supercritical Carbon Dioxide*, Chiho Uemori,* Nagoya University, Japan*; W. Diono,* Nagoya University*; T. Kon,* Shalom Co.*; H. Kanda,* Nagoya University*; M. Goto,* Nagoya University, Japan

A liposome is a spherical vesicle having single or multiple lipid bilayers. Liposomes are generally composed of phospholipids. Lipophilic or hydrophilic compounds can be encapsulated in liposomes either in the phospholipid bilayer or in the inner aqueous phase. Liposomes are prepared conventionally by the Bangham method, the detergent depletion method, the reverse phase evaporation method, and emulsion method. Recently, supercritical carbon dioxide has been applied to produce liposome instead of organic solvent.

In this work, liposomes were produced utilizing supercritical fluid technology with ultrasonic mixing. Since no organic solvent was used in this process, solvent-free liposomes were prepared. As a lipid, we used sphingomyelin or phosphatidylcholine. Phospholipids and water were charged in high pressure vessel. Then, pressurized carbon dioxide was pumped into the vessel. The vessel was placed in thermostatted water bath and applied ultrasonic power to mix phospholipids, water, and carbon dioxide phase in order to produce liposome structure. The obtained liposomes were identified as multi-lamella form by TEM analysis. The effects of operation parameters such as ultrasonic frequency, pressure, and temperature, particle size of liposomes were studied.

NM-WeP8 Method development and Determination of Trace Metal Impurities in Silicon Based Nanopowder in Solvent Mixture by Inductively Coupled Plasma Mass Spectrometry*, Mohsina Islam,* *S. Liu,* Chemtrace Analytical Testing and Solutions

In Semiconductor industry, the silicon based nanoparticles showed great promises in various applications like thin- film transistors for liquid crystal displays (LCD TFTS), solar cells and printed semiconductor materials because of its superior properties such as feasibility of surface functionalization, size dependent multicolor light emission and stability against photobleaching.

In this work a novel analytical method was developed for the determination of trace metal impurities in silicon based nanoparticles dispersed in solvent mixture using Inductively Coupled Plasma Mass Spectrometry (ICP-MS). For this purpose silicon nanoparticles with metal dopants, e.g, phosphorous and boron dopant nanoparticles dispersed in various solvents like Isopropyl alcohol, PGMEA and Terpineol were studied. The sample was prepared by evaporation to solvent boiling point followed by Silicon dissolved and digestion with mixed acid solution. The trace metal (TM) residue was dissolved and reconstituted in dilute acid solution which is analysed through ICP-MS. Following the same method, a spiked sample was prepared with known TM level in the range of 3.0 to 6.0 ppb. The spike recoveries with this method is in the range of 75 to 125% for all elements. The dopant levels were measured as 0.05-0.3 wt.% for B and P following the dissolution and dilution of sample in mixed acid solution. The method detection limit as low as 0.1 to 10 ppb were achieved for different TM contaminants.

NM-WeP9 Optical and Morphological Characterization of ZnSe Nanoparticles Processed by Laser Ablation in Liquid*, Patricia Maldonado-Altamirano,* *R.Y. Ponce-Cano, L.A. Martinez-Ara,* ESFM-IPN, México*; M.A. Hernandez-Perez,* ESIQIE-IPN, México*; J.R. Aguilar-Hernandez,* ESFM-IPN, México

In this work we present results and analysis concerning the processing of semiconducting ZnSe nanoparticles obtained by laser ablation of diluted ZnSe powder in acetone. A Nd-YAG pulsed laser was used for ablation, tuned at the first harmonic, 1064 nm, 50 Hz frequency repetition during 60 minutes. The experiment was performed as a function of the laser power intensity. UV-Vis and Raman spectroscopies were used to characterize the ZnSe particles, whereas scanning electron microscopy, transmission electron microscopy and X ray diffraction were used to determine the morphology and size of the particles. According to the UV-Vis results it was confirmed a shift of the band gap towards high energy (blue shift) from 2.7 to 3.3 eV. Raman spectroscopy show the LO phonon at 250 cm^{-1} and also the so called surface mode at 230 cm^{-1}, for the case of the smaller particles, approximately 10 nm, which was estimated through SEM and TEM images. The cristalline planes were also observed in the TEM images. X-Ray diffractograms confirmed that the particles show the wurtzite structure. A deep analysis of the results is presented and discussed.

NM-WeP10 New Method Of Synthesis Of Graphene From Cvd In Steady State*, Alejandra Moreno-Barcenas,* Centro de Investigacion y de Estudios Avanzados Del Intituto Politecnico Nacional, Mexico*; J.F. Perez-Robles, A. Garcia-Garcia,* Centro de Investigacion y De Estudios Avanzados Del Intituto Politecnico Nacional, Mexico*; L.M. Avilez-Arellano,* CINVESTAV Querétaro México, Mexico*; Y.V. Vorobiev,* CINVESTAV-Unidad Queretaro, Mexico

The Graphene is a material used in a wide range of applications due to its unique structure and excellent electronic, optical, mechanical and thermal properties. Currently, several techniques are being developed to obtain graphene, one of this techniques that has highlighted which chemical vapor deposition (CVD) technique is the most reported. The fastest progress in graphene methodology in recent years have been obtained by this way. In this sense, the aim of the investigation in graphene is to increase the graphene production by CVD with high quality and at low cost. However, usually to produce graphene, it is necessary to use high vacuum equipment and temperatures about 1800 °C, which represents a very high cost. In this paper a new method is proposed to obtaining monolayer graphene with good quality and low cost operation. Using acetylene and nitrogen as precursors by CVD is possible to obtained monolayer graphene by CVD, instead of methane and argon. Also a mix of nitrogen:hydrogen (90:10, respectively) was used instead pure hydrogen. All the components are subjected to temperatures about 1000 °C and atmospheric pressure, on polycrystalline copper foil. The synthesis of the graphene is carried out in steady state, reducing the synthesis time around a minute. The amount of gas flow is determined taking into account the reactor volume per unit mass. The presence of graphene is shown by transmission electronic microscopy and Raman spectroscopy confirmed the monolayer of graphene.

NM-WeP11 Synergistic Effect of Orange (II) Dye Degradation by Surface Treated and Metal Loaded Rutile TiO_2 NRs Photocatalyst*, **Love Kumar (L.K.) Dhandole**, M.A. Mahadik, S. Kim, M.H. Cho,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Republic of Korea*; J.H. Ryu,* Korea Institute of Geoscience and Mineral Resources, Korea*; J.S. Jang,* Division of Biotechnology, Brain Korea 21 Plus Program, Advanced Institute of Environment and Bioscience, College of Environmental and Bioresource Sciences, Chonbuk National University, Republic of Korea

Transition metal oxides (MnO, NiO, Co_2O_3 and CuO) 1 w % loaded on acid treated TiO_2 nanorods were successfully prepared by chemical treatment and wet impregnation method. The catalyst were characterized by X-ray diffraction (XRD), field emission scanning electron microscopy (FESEM), transmission electron microscopy (TEM), X-ray photoelectron spectra (XPS), Fourier transform infrared spectroscopy (FT-IR) and UV-visible diffuse reflectance spectroscopy (UV-DRS). FT-IR results confirmed the presence of H_2O and OH groups on the surface of acid treated photocatalyst and TEM and XPS results confirmed the fine dispersion of metal and their oxide on TiO_2 nanorods. The photocatalytic activity of as-prepared, acid treated, metal oxide loaded and metal oxide loaded on acid treated nanorods were compared and rate constant values were determined from kinetics of the degradation of Orange (II) dye. Cobalt oxide 1w% loaded on 1.0 M acid treated TiO_2 nanorods exhibited the higher photocatalytic Orange (II) degradation efficiency 98.57% (within 120 min) than as-prepared and metal loaded acid treated samples under the solar irradiation. The synergistic effect of cobalt oxide 1w% loaded on 1.0 M acid treated TiO_2 nanorods over Orange (II) degradation is considered due to fine dispersion of metal oxides on the OH rich surface of acid treated TiO_2 nanorods. The mechanism of enhanced photocatalytic activity and photoelectrochemical analysis of photocatalyst also studied

NM-WeP12 Composition-tuned Porous Pd-Ag Dendrites for the Enhancement of the Ethanol Oxidation Reaction*, S.Y. Lee, Y.G. Jo, **SungMin Kim,*** Korea Aerospace University, Korea*; J.-W. Kim,* InCheon University, Korea

Porous Pd-Ag bimetallic dendrites of various compositions were prepared using a galvanic replacement reaction between Ag dendrites and $Pd(NO_3)_2$, in which the compositional variation could be effectively controlled by adjusting the concentration of $Pd(NO_3)_2$. The structural and morphological results revealed that the Ag-rich bimetallic dendrites had hollow structure with porous surface layers, whereas the Pd-rich bimetallic dendrite structures collapsed into large aggregates composed of Pd fragments. The electrochemical measurements for the ethanol oxidation revealed that in terms of electrocatalytic activity, the $Pd_{40}Ag_{60}$ bimetallic dendrites were superior to the other Pd-Ag catalysts. This could be attributed to the geometric and electronic effects of the porous Pd-Ag bimetal dendritic structure.

Thin Films
Room Makai - Session TF-WeP
Thin Films Posters Session II

TF-WeP1 High Hardness and Oxidation Resistance of Ti– Al –Si– N Nanocomposite Coatings for Machining of Aircraft Mechanical Parts*, **Wang-Ryeol Kim,*** Korea Institute of Industrial Technology, Korea*; T.H. Nam,* University of Ulsan, Republic of Korea*; I.-O. Baek, E.Y. Choi, J.B. Jeon,* Korea Institute of Industrial Technology, Korea

Superhardness Ti –Al –Si –N nanocomposite coatings were deposited on SKD 61 and inconel substrates by hybrid coating system (AIP+Sputtering) in various Si target powers for maching of aircraft mechanical parts. The relationship among microstructures, mechanical properties, and tribologiacal properties was investigated. The synthesized Ti –Al –Si –N coatings were characterized using x –ray diffraction (XRD) and x –ray photoelectron spectroscopy (XPS). These analyses revealed that the Ti –B –N –Si coatings are nanocomposites consisting of solid-solution (Ti,Al)N crystallites distributed in an amorphous SiNx matrix. The addition of Si into the Ti –Al –N coating led to percolation of amorphous SiNx and BN phases. The Ti –Al –Si –N coatings exhibited high hardness and H/E values, indicating high fracture toughness, of approximately 42 GPa and 0.097, respectively. Furthermore, the minimum friction coefficient of the Ti –Al –Si –N coatings was approximately 0.25 at low Si target powers. A systematic investigation on the microstructures, mechanical properties, and tribological properties of Ti –Al –Si –N coatings prepared from three Ti-Al composite targets and pure Si target is reported in this study.

TF-WeP2 Microstructure, Mechanical Properties and Tribological Properties of ZrN Based Nanocomposite Hard Coatings Deposited by a Hybrid Coating System*, **Yeongha Song,*** Korea Institute of Industrial Technology (KITECH), Pusan National University, Republic of Korea*; H.D. Kim,* University of Ulsan, South Korea*; K.-S. Kim, S.M. Shin,* Korea Institute of Industrial Technology (KITECH)*; J.-H. Kim,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

Zr–Si–N coatings with various Si contents were synthesized by a hybrid coating system combining arc ion plating and d.c. magnetron sputtering techniques. The influence of the Si content on the microstructure, mechanical properties and tribological properties of the Zr–Si–N coatings were investigated. The results showed that as the Si content increased from 0 to 5.8 at.%, the coatings transformed from a columnar ZrN to nanocomposite structure with a nano-sized ZrN crystallites embedded in amorphous Si3N4 matrix and further increases of Si content lead to amorphous-like coatings. The maximum hardness (H) of 33 GPa, Young's modulus (E) of 265 GPa, and H/E* value of 0.12 were obtained at Si content of 5.8 at.% in the Zr–Si–N coatings, respectively. The coating with the lowest friction coefficient and the best wear resistance was also obtained at Si content of 5.8 at.%, which was mainly contributed to high value of H/E* and formation of SiO2 or Si(OH)4 self-lubricating layer due to the interface tribo-chemical reaction.

TF-WeP3 Advanced High Toughness Hard Coatings for Tribological Applications*, **Sung-bo Heo**, U.C. Jung,* Korea Institute of Industrial Technology (KITECH), Republic of Korea*; H.J. Son,* University of Ulsan, Republic of Korea*; I.W. Park,* Korea Institute of Industrial Technology (KITECH), Republic of Korea

A number of multi-component, nanostructured coatings have been produced for a range of tribological applications. The paper will discuss four such nanocomposite coating systems: (i) Ti-B-C-N; (ii) Ti-Al-Si-N; (iii) Cr-Al-Si-N; and (iv) Zr-Al-Si-N produced by hybrid coating deposition system in which the deposition parameters have been varied to control the structure and properties of the films. In each case, the coating system needs to exhibit a range of tribological properties to meet the required application, such as high wear resistance, low coefficient of friction, self-lubrication, high oxidation and/or corrosion resistance. In particular, the effect of the film chemistry, pulsing the magnetron and utilizing a closed field configuration will be discussed as suitable control parameters in tailoring the structure and properties of the coatings to meet specific tribological applications.

TF-WeP4 Effects of Various Interlayers on the Adhesion and Tribological Properties of the CrZrSiN Coatings on Tungsten Carbide Substrate*, S.Y. Lee, **HoeKun Kim**, J.H. La,* Korea Aerospace University, Republic of Korea

CrZrSiN coatings have been paid much attention to the cutting tool's coating applications due to many advantages, such as high hardness, very low surface roughness, and high oxidation resistance. It was reported that the interlayer with the median hardness to elastic modulus ratio (H/E ratio) between the value of the coating and the substrate improved the wear resistance of the coating. In this work, influence of the H/E ratios of the various interlayers on wear and adhesion properties was investigated. The CrZrSiN coatings with the Cr, CrN, CrN/CrZrN interlayers were synthesized by an unbalanced magnetron sputtering system on the WC-6 wt.% Co substrate. A field emission scanning electron microscopy and energy dispersive spectroscopy were used to investigate microstructure and chemical composition of the coatings and interlayers. Mechanical properties of the coatings were evaluated by a nano-indentation, ball-on-disc wear tester, and scratch tester.

The hardness and elastic modulus of all the CrZrSiN coatings with various interlayers were measured to be in the ranges of 31.2 to 32.5 GPa and 213.2 to 219.4 GPa, and they were not significantly affected by the type of the interlayer. Wear and scratch test showed that the CrZrSiN coating with CrN/CrZrN interlayer exhibited the lowest friction coefficient of 0.31 and the highest adhesion strength of 68 N. These improved wear and adhesion properties could be attributed to the H/E ratio of the interlayer between the CrZrSiN coating and WC substrate. In view of the coating structure, there exists a gradual decrease in the H/E ratio from the CrZrSiN coating (H/E, 0.148), to the CrZrN interlayer (H/E, 0.131) and CrN interlayer (H/E, 0.076), and the WC substrate (H/E, 0.040). The CrZrN and CrN interlayers induced a smooth transition of the stress effectively under loading conditions during the wear and scratch test. Therefore, wear and adhesion properties could be improved significantly by structuring the coating with an optimal gradient of the H/E ratio of the coating/interlayer/substrate.

TF-WeP5 Migration-enhanced Epitaxy using Ga Droplets of GaAsNSe Thin Films on Si(110) Substrates*, Katsuhiro Uesugi*, *T. Ozawa, Y. Igarashi, Y. Shimomura, S. Kimura, K. Obara,* Muroran Institute of Technology, Japan

The development of strain relaxation buffer layers between GaAs and Si(110) that controlled large lattice mismatch and surface orientation influences are expected to integrate GaAs-based optical-fiber communication devices to Si(110) wafers. The growth of Ge and GeSi layers is mainly studied on Si(001) substrates, but absorb light signal of 1.55 µm wavelength due to the narrow bandgap energy of ~0.67 eV. A two-dimensional growth technique of GaAs(110) films on Si(110) surfaces is also necessary. In this paper, we report the migration-enhanced epitaxy of n-type GaAsNSe thin films with Ga droplets prepared on Si substrate surfaces, as the strain relaxation layers between GaAs and Si(110).

GaAsNSe films were grown by using metal-organic molecular beam epitaxy (MOMBE) equipped with the nitrogen radio-frequency discharge plasma system. MO precursors used were triethylgallium, trisdimethylaminoarsenic (TDMAAs), trisdimethylaminoantimony (TDMASb), and ditertiarybutylselenide. The Si(110) substrate surfaces were thermally cleaned at 550 °C with the simultaneous supply of TDMAAs. Ga droplets were formed on Sb-terminated Si surfaces which prepared by the supply of TDMASb at the substrate temperature of 470 °C. Then GaAsNSe films were grown at the temperature of 370-510 °C. The growth process of the films was characterized by using RHEED, AFM, and x-ray diffraction methods.

The Si- and As-terminated Si(110) surfaces were not covered with Ga layers, and Ga droplets of 40-75 nm height were formed at a density of 1×10^{8} cm^{-2}. On the other hand, small Ga droplets of 2 nm height were formed on the Sb-terminated Si surfaces at a high density of 2×10^{10} cm^{-2}, which suggest the anti-surfactant effect of Sb surface atom. The growth of a GaAsNSe ring structure occurred by the isotropic Ga diffusion from the droplet at low temperature. The step-flow growth mode of GaAsNSe was promoted as the increase of growth temperature. The activation energy of the Ga diffusion from the droplet during the growth was estimated to be 0.46 eV. At a high growth temperature of 510 °C, the two-dimensional growth of GaAsSe(110) with a large lattice mismatch of 3.5% was promoted considerably by using the effect of the surface Ga diffusion from the droplets. The formation of the pits and three-dimensional islands was suppressed in comparison with the films prepared by normal MOMBE growth. The migration enhanced MOMBE using surface Ga nano-droplets is a very useful technique for the fabrication of the flat GaAsNSe lattice relaxation layers on Si(110) substrates.

TF-WeP6 Formation of Low Friction Interface Utilizing Diamond-like Carbon Coating Containing Molybdenum Disulfide in Vacuum, Oxygen and Nitrogen*, Junko Masuda*, *K. Adachi, T. Takeno,* Tohoku University, Japan

Molybdenum disulfide (MoS_2) is widely used as a solid lubricant in vacuum. It produces very low friction due to its lamellar structure. However, one of the drawback of MoS_2 is weak for oxidation. Recently, the coating that MoS_2 nanoparticles are dispersed into diamond-like carbon (DLC) host matrix is proposed to overcome this problem utilizing gas barrier effect of DLC in addition, its hardness increases . Such coating is called MoS_2-containing DLC (MD). The coating shows lower friction, m ~ 0.01, than MoS_2 in vacuum when the coating is prepared under specific condition. When it shows low friction, unique transfer layer onto counter surface is formed. The structure of the transfer layer is consisted of 5 nm carbon layer on counter surface and mixed layer composed of MoS_2 and C on it. These facts clearly indicate that such specific structure is organized thanks to the coating. We have also demonstrated that low friction can be achieved depending not only on MoS_2 concentration but also bias voltage during deposition. Carbon matrix is important for achieving low friction. It is indicated that in order to form unique transfer layer, carbon has something potential to support MoS_2 to arrange lamellar structure. The purpose of this study is to clarify mechanisms of low friction.

Friction tests were conducted with ball-on-disk type apparatus in well-controlled environmental conditions. Dry nitrogen, dry oxygen and humid nitrogen gases are used to change atmospheric condition during friction tests. Various observation techniques including scanning electron microscope (SEM) and transmission electron microscope (TEM) equipped with energy dispersive X-ray spectrometer (EDS) are employed in this study.

Under nitrogen gases, both MoS_2 and MD coatings show low friction with vacuum. Actually, it is natural that MD coating shows low friction in nitrogen because MoS_2 and DLC give low friction in this condition. In case of oxygen condition, MoS_2 shows higher friction coefficient, ~ 0.2, in oxygen condition than in vacuum. On the other hand, friction coefficient of 0.02 is achieved utilizing MD coating, and very thin transfer layer was formed on the counter surface, which clearly shows the potential for low friction utilizing MD coating. A cross-sectional TEM image of the layer shows that structure of the transfer is also same as the one obtained in vacuum. In addition, EDS mapping on the TEM image revealed that oxygen from atmosphere is included in the whole transfer. It suggests that composite structure of MD coating can contribute the formation of a thin transfer layer.

TF-WeP7 Stability on O_2 Plasma Treatment of DLC Coating as Biocompatibility*, Kyoichi Terai,* Tokyo Denki University, Japan

Diamond-like carbon (DLC) films have been investigated in domestic fields because of their many attractive properties. In especially, mechanical high hardness, low wear resistance and gas barrier property of DLC films can be mentioned as the dominant advantages. DLC coating has already applied to surface finishing technology of metallic molds, cutting tools and polyethylene terephthalate (PET) bottles. In recent, many researchers have reported the characteristics of chemical stabilities, blood compatibilities and cell affinities on the DLC films. Modification of the surface condition of DLC films has been rapidly expected to demand of the advanced medical care.

In order to improve the biocompatibility of DLC films, plasma treatment of oxygen (O_2) and nitrogen (N_2) gases are proposed on the DLC surfaces1). Surface conditions of the DLC films are delicate because bonds between carbon and oxygen are not so strong. The stability of effect of plasma treatment for DLC films has to investigate by systematic approach. In this study, we investigate that stability of the surface characteristics for time of O_2 plasma treatment. DLC films were prepared on Si substrate by using r. f. plasma chemical vapor deposition (r. f. plasma CVD) in methane (CH_4) gas. After DLC films deposition, surface modification was carried out by O_2 plasma. To evaluate stabilities of the plasma treatment on surface characteristics, surface conditions were analyzed by contact angle measurement and X-ray photoelectron spectroscopy (XPS). The cell affinity is estimated by *in-vitro* examination with a cell proliferation test using mouse-derived fibroblasts.

In case of contact angle measurement, DLC films without plasma treatments have water repellency and are almost constant. Hydrophilicity of surfaces immediately O_2 plasma treatments is stables for several days, after that their change to the saturation value.

From the result of XPS, intensity ratio of oxygen and carbon peak on the surfaces of the DLC films without plasma treatment is increased as function of time. In contrast, the intensity ratio between oxygen and carbon is decreased with time in case of sample with O_2 plasma treatments. The results revealed that adsorption and desorption of oxygen play important role to shift of the wettability in the plasma treatment on DLC films.

Reference

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TF-WeP8 Characterization of Compound Thin Films of CeO_2 and SiO_2 deposited by MOCVD*, Tomonari Furuya,* Hosei University, Japan*; T. Matsumura,* TOSHIBA Corporation, Japan*; K. Kikuchi,* Hosei University, Japan*; K. Ishibashi, S. Suzuki,* COMET Inc., Japan*; Y. Yamamoto,* Hosei University, Japan

Chemical states and electrical properties of the CeO_2 based compound oxide doped with SiO_2 as the promising gate stuck material for MOS devices were investigated, based on the consideration that the crystallization could be suppressed by mixing materials having different crystalline structures. The X-ray photoelectron spectroscopy (XPS) analysis revealed that the compound oxide was successfully prepared on p-type Si (100) substrates by pyrolytic MOCVD using $Ce(OCEt_2Me)_4$ at the substrate temperature of 350 °C for 30 min with the intermittent introduction of TEOS (TetraEthoxyOrthoSilicate) for 10 sec every 3, 5, or 10 min. The decomposition temperature of TEOS was lowered by the hydrolysis utilizing H_2O generated from Ce source decomposition. In the X-ray diffraction (XRD) patterns, the pure CeO_2 films represented the distinct cubic CeO_2 peaks, while CeO_2 peaks decreased to the trace level for the samples with TEOS introduction; the CeO_2 films with TEOS introduction were essentially amorphous.

From the X-ray photoelectron spectroscopy (XPS) spectra of Ce3d, Si2s and O1s, the average molar concentrations of SiO_2 in the films with the introduction of TEOS for 10 sec every 3, 5, or 10 min were determined to be 15%, 6% and 6%, respectively. Although TEOS was intermittently introduced during CeO_2 deposition, the distribution of Si in CeO_2 films was uniform and the amount of incorporated Si was not directly related to the TEOS supply rate. Cerium silicate formation in the film prepared with TEOS introduction was confirmed from Si2s peaks at 153.5 eV and O1s spectra appearing with the shoulder at the higher binding energy.

The electrical properties after annealing at 500°C for 30 min in the ambient of O_2 were analyzed by I-V and C-V measurements using the Pt dot electrodes. The sample with TEOS introduction for 10 sec every 3 min represented the lowest leakage current around 1.0×10^{-5} A/cm^2 at 1.5 MV/cm, which was one order of magnitude lower than that of the pure CeO_2 films. The relative dielectric constant ranged between 16.6 and 21.6 depending on the TEOS introduction interval. These values were rather higher than that of pure CeO_2 films without Si doping which was usually lower than that of bulk relative dielectric constant of 26. These results suggest that Si doping brought about the change in the interface structure between Si substrates and deposited films such as the disappearance of the interfacial layer with lower dielectric constant. The flat band voltage shifted toward lower gate voltages for the samples prepared with TEOS introduction probably due to the introduction of fixed positive charge by silicate formation.

TF-WeP9 Development of Visualization System of Permeated Hydrogen Map on Stainless Steel Membrane

Naoya Miyauchi, Toho University, Japan*; Y. Murase,* National Institute for Materials Science, Japan*; H.A. Sakaue,* National institute for fusion Science, Japan*; A.N. Itakura,* National Institute for Materials Science, Japan*; S. Takagi,* Toho University, Japan

Hydrogen outgassing from an inside wall is the most important issue for vacuum chambers in ultrahigh vacuum (UHV) and extremely high vacuum (XHV). In addition, the behavior of hydrogen in metals should be made clear to understand the mechanisms of hydrogen embrittlement and storage. We have observed the behavior of hydrogen in metals by visualizing sequentially spatial distributions of permeated hydrogen on the surface of stainless steel membrane. The distributions of surface hydrogen were obtained using ions emitted by the method of desorption induced by electronic transition (DIET) process with the scanning electron microscope (SEM).The diffusion pass of hydrogen can be revealed from comparison of hydrogen maps obtained by this technique with the surface grain structure. In addition, physical information on permeation, which contains the processes of solution, diffusion, adsorption, is obtained by conjunction with a measurement on time dependence of permeated hydrogen pressure in the vacuum.The experimental setup is shown in Figure 1. We equipped the SEM (JEOL JAMP10) to the sample holder with hydrogen supply system and collecting electrode of DIET ions, the detection system of DIET ions and the quadrupole mass analyzer (Pfeiffer Vacuum QMG220). The collecting electrode is attached due to focusing DIET ions on the detector system. The DIET signals are measured in two-dimensional pulse counting system constructed by LabVIEW. This two-dimensional pulse counting system is synchronized with the scanning electron beam. The sample is SUS304 stainless steel, which has austenite structure with martensite dislocations caused by cold working of 20 %. The sizes of austenite grains are about 100 µm. The thickness of membrane is 200 µm. After outgassing of hydrogen in the sample (573K: 48 hours) the following experiments were performed under the outgassing temperature. The back side of SUS membrane was exposed to hydrogen (2.7×10^5 Pa) and the permeated hydrogen on the opposite observation side was observed by DIET method. The vacuum chamber was evacuated by the sputter ion pump (100 l/s) under the experiments. The pressure was 1×10^{-7} Pa under the experiment. Both H_2 and D_2 gases were used to investigate an isotope effect for permeation.

Figures 2 and 3 are the secondary electron image and the permeated hydrogen map, which is obtained by accumulating DIET ions for 50 hours at 473 K, respectively. A comparison of two kinds of image suggested that the hydrogen permeation from the inside of grain and more permeation in austenite grains than martensite grains.

TF-WeP10 Hydrogen Diffusion in Stainless Steel and the Surface Stress Due to the Hydrogen

Akiko N. Itakura, *Y. Murase, T. Yakabe, M. Tosa,* National Institute for Materials Science, Japan*; N. Miyauchi, S. Takagi,* Toho University, Japan

Hydrogen in metals causes hydrogen embrittlement, which is the process of various metals to become brittle and fracture. Surface stress measurement is an effective technique for gas detection. In this study we focused on the stress of hydrogen contained in metals. We have detected a surface stress of stainless steel coated micro-cantilever under hydrogen irradiation. Meanwhile, it is not known the existing position of hydrogen in an alloy attributed to the complex structure of the alloy.

Metal thin films with the thickness of 20-50nm were deposited by RF magnetron sputtering on silicon micro cantilever (MCS: thickness of 1 micron and length of 500 micron). We found both of austenite and martensite structure in the film. The stress under hydrogen plasma irradiation was measured in-situ using a bending of cantilever beam [1]. MCS bended toward compressive surface stress and saturated under the irradiation. Probably it was a stress change due to hydrogen absorption although the bending might include temperature effect. After the irradiation stop, the bending curve decreased gradually. In 2nd experiment running, the saturated value of the bending was smaller than the 1st. After 10 times of the irradiation experiments (10 h irradiation) the bending did not decrease more.

In this study we tried to investigate hydrogen behavior in metal alloys from observation of two-dimensional hydrogen distribution on metal surface using a method of DIET (Desorption Induced by Electronic Transition). For the experiment we divided a vacuum container into two rooms. A part of a vacuum wall, between the two rooms, was a sample. Surface of the sample membrane thickness of 200 mm, had ring shape lines of 40micron pitch. The lines, which is a trace of the blade, were formed when the surface was flattened by a lathe. Cutting blade made un-uniformity of dislocations, too. H_2 gas was supplied from the backside room, H atom (ion) permeated through a sample and was desorbed into the vacuum room by electron irradiation. DIET mapping shows the hydrogen concentration reflects a density of dislocations, which has 40micron pitch [2]. It should be considered more by the comparing of DIET experiments with the structure measurement, grains, grain boundaries and dislocations [3]. Schematic diagram of the new experiment is shown in fig1. In the presentation we will show higher resolution images of DIET mapping, which can be compared with grains in SEM picture.

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TF-WeP11 Tight-Binding Quantum Chemical Molecular Dynamics Simulations on Tribochemical Reaction Dynamics of Carbon Nitride Thin Films

Miho Nakamura, Tohoku University, Japan*; S. Sato,* Tohoku University*; Y. Ootani, Y. Higuchi, N. Ozawa, K. Adachi, M. Kubo,* Tohoku University, Japan

Recently, carbon nitride (CNx) has gained much attention as solid lubricant in automotive engines, aerospace instruments, etc. Experimentally, one of the authors, Adachi, discovered that CNx gives super-low friction coefficient. However, the super-low friction mechanism of CNx has not been clarified experimentally. It is experimentally pointed out that CNx shows lower friction coefficient than diamond-like carbon under specific condition. It means that the role of nitrogen in CNx is very important. However, the function of nitrogen in CNx has not been elucidated. Therefore, the theoretical approach is desired to reveal the role of nitrogen in CNx. In the present study, we employed our original tribochemical reaction simulator based on the tight-binding quantum chemical molecular dynamics method [1-3]. The friction dynamics of H-terminated CNx is simulated under 1 GPa pressure. The simulation result shows low friction coefficient of 0.05. We found that hydrogen-hydrogen repulsion is source of the super-low friction. However, this reason is same with that of H-terminated diamond like carbon films. It means that the role of nitrogen has not been clarified. Then, we investigate the effect of water molecules on the friction dynamic of H-terminated CNx. It is very interesting to see the generation and evaporation of NH3 molecules by the tribochemical reaction of CNx and water. The generation and evaporation of NH3 molecules give low density diamond-like carbon thin films. Therefore, we propose that low density diamond-like carbon generated by the tribochemical reactions of CNx and water gives super-low friction coefficient.

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TF-WeP12 Detection of 2-nitrotoluene – Comparison of Thin Film Sensors and Ion Mobility Spectrometry*, **Premysl Fitl**, D. Tomecek, M. Pajkova, J. Vlcek, L. Fiser, E. Maresova, S. Havlova, P. Hozak, M. Vrnata,* University of Chemistry and Technology Prague, Czech Republic

Our work deals with comparison of detection abilities of thin film chemiresistors based on silver phthalocyanine with metallic nanoparticles and ion mobility spectrometry. In our study we focus to the detection of widely used taggant in explosives - 2-nitrotoluene.

The sensing layers of chemiresistors were deposited by vacuum evaporation (AgPc) and DC magnetron sputtering (metallic nanoparticles) on ceramic substrates with platinum interdigital electrodes. We varied type of metallic nanoparticles (Au, Pd and Ag), their amount (equivalent thickness in the range of 1 to 50 nm) and also the deposition sequence of used techniques (bottom AgPc + top nanoparticles vs top AgPc layer - bottom nanoparticles). For underlying metal nanoparticles the substrates were heated during deposition (temperature range of 20 - 600 °C) to investigate and tailor nanoparticle shape and conductivity properties.

Growth of metallic nanoparticles was continuously monitored by in-situ resistance measurements during sputtering and annealing operations. These measurements enable also detection of percolation threshold. The morphology of prepared layers was investigated by electron microscopy.

For as-deposited layers of metal on AgPc it was found that when the amount of metal is relatively low (i.e. less than layer with equivalent thickness of 4 nm for Pd, 5 nm for Au and 8 nm for Ag) metal clusters on organic surface are created. Continuous but incompact layers are formed for slightly greater amounts of sputtered metals. Finally, continuous and compact layers were observed when equivalent thicknesses achieved ≈ 15 nm. When the layers are annealed the percolation threshold is in general shifted to greater amounts of sputtered metal.

Optimized sub-threshold layers containing metallic cluster arrays on chemiresistor substrates were used for detection of 2-nitrotoluene. The taggant vapors were detected in two modes: without or with photoactivation ($\lambda = 266$ nm). While the dc-response of AgPc/Au(10 nm) sensor to 189 ppm of non-activated 2-nitrotoluene vapors was negligible, after photoactivation the dc-response rose to 373.

The sensing properties of thin films were compared with sensitivity of commercially available GC-IMS system. The detection limit of our thin film sensors is in range of hundreds of ppb. The ion mobility spectrometer is cable to reach lower detection limits (ppt). Although the ion mobility spectrometry shown the higher sensitivity, the possibility of overexposure and contamination of sampling valve and drift tube may cause fatal ion mobility spectrometer failure. Our phthalocyanine thin film sensors can be used as low cost alternative for detection of 2-nitrotoluene.

TF-WeP13 Development of SiC-DLC cOatings for Super Low Friction Mechanical Systems in Water*, **Takanori Takeno**, T. Hayase, K. Adachi,* Tohoku University, Japan

Water is environmentally friendly liquid. When we used it as a lubricant, it gives very low friction. Silicon carbide and silicon nitride can produce very low friction, < 0.01, under water lubricating condition. However, one of the drawback is low load carrying capacity due to low viscosity of water. With increase of load, direct contact between the materials occurs, which leads to seizure. Some researchers have shown increase of load-carrying capacity thanks to DLC that can reduce friction under direct contact condition. Although it works as protective coating to avoid seizure, friction under such severe condition is still high, ~0.1-0.2. So, the target of this study is to produce the coating to show low friction and high load carrying capacity under water lubricating condition. To achieve the goal, we are developing SiC-containing DLC coatings.

Investigated coatings are prepared by RF generated methane plasma and DC magnetron co-sputtering of silicon carbide target (Purity: 99.99%). Silicon carbide disk is used as a substrate material. Various coatings are deposited by changing methane and argon flow rate (CH4/Ar). Composition, structural analyses and hardness are measured by Rutherford backscattering spectroscopy (RBS), X-ray photoelectron spectroscopy (XPS) and nanoindentation technique. Friction tests are performed using ball-on-disk tribometer. Silicon carbide ball is used as a counter material. Ball and disk are immersed in water and friction tests are carried out.

By changing flow rate of methane and argon, various coatings with different composition are achieved. Hardness of the coatings decreases with increase flow rate. Friction properties also vary with composition of the coatings. With CH4/Ar = 0.1, coating is removed at very beginning of the friction test. When the coating is deposited with CH4/Ar = 0.2, very low friction of 0.05 can be achieved. Almost similar friction curve is obtained with further increase of the ratio but fluctuation of the friction coefficient is also observed with CH4/Ar = 0.3. It suggests that these is optimum structure or composition of the coating. We also changed speed and load for friction tests. Surprisingly, friction coefficient of the coating with CH4/Ar = 0.2 decreases with increase of load and decrease of speed condition, meaning lower friction is obtained with more severe contact condition. According to the literature, lowering friction coefficient is due to the termination of OH bonds by reacting SiC surface with water. Thanks to the hydrogen bonding between O from OH and H from H_2O, water is captured on the frictional surface and friction force can be derived from shearing the low viscos water.

TF-WeP14 Atomic Layer Deposition of 2D MoS_2 on Si/SiO_2 and Quartz Substrates*, A. Valdivia, **John Conley, Jr.**,* Oregon State University, USA

The synthesis of high quality single layer 2D MoS_2 on large area substrates remains challenging. Mechanical exfoliation is capable of producing high quality material, but it is limited to small areas, requires transfer to the device substrate, is not scalable, and is impractical for manufacturing. Chemical vapor deposition (CVD) has been shown to yield MoS_2 on a variety of substrates, but is limited by non-uniform electrical properties, poor process stability, and high deposition temperature (>600°C). A natural method for the synthesis of 2D materials is atomic layer deposition (ALD) in which alternating, purge separated, self-limiting surface reactions allow for precise thickness control, high conformality, and scalability to large surface areas. Although reports of ALD MoS_2 are beginning to emerge, ALD of *single layer* MoS_2 has typically required specialty sapphire substrates and high temperature (800°C) post deposition anneals and/or has been limited to small diameter wafers.

In this work, we demonstrate low temperature ALD of single to few monolayer MoS_2 uniformly across 150 mm diameter patterned SiO_2/Si and quartz substrates.[1] Purge separated cycles of $MoCl_5$ and H_2S precursors were used at ALD reactor temperatures ranging from 375°C to 475°C. Raman scattering measurements show clearly the in-plane (E^1_{2g}) and out-of-plane (A_{1g}) modes for ALD films deposited at 375°C or 475°C, indicating the presence of mono- to few layer MoS_2. The separation of the E^1_{2g} and A_{1g} peaks is a function of the number of ALD cycles, shifting closer together with fewer layers. Films deposited at 475°C are of much higher quality than films deposited at 375°C. While the E^1_{2g}-A_{1g} peak separation of the 375 °C film corresponds to bulk-like MoS_2, the smaller peak separation of the 475°C film suggests a thickness of approximately two monolayers. Raman polarization tests confirm the MoS_2 crystals have the desired orientation parallel to the surface. High temperature H_2S and sulfur annealed films produce a sharpening of the E^1_{2g} and A_{1g} peaks as well as the appearance of the band edge PL and spin orbit splitting peaks, a further indication of the presence of monolayer MoS_2. High resolution transmission electron microscopy images confirms the presence of monolayer to bilayer MoS_2 films. X-ray photoelectron spectroscopy indicates that a sub-stoichiometric sulfur ratio in the as-deposited films is increased to the stoichiometric S/Mo ratio after annealing in H_2S at 600°C and above. Results suggest that ALD may be a promising method for production of 2D MoS_2.

Support provided by Sharp Labs of America.

7. A. Valdivia, D.J. Tweet, and J.F. Conley, Jr., J. Vac. Sci Tech A **34**, 021515 (2016).

TF-WeP15 Corrosion Protection of Silver-Based Telescope Mirrors using Hybrid Barrier Layers Fabricated by PVD and ALD*, **David Fryauf**, A. Phillips, N. Kobayashi,* University of California Santa Cruz

An urgent demand remains in astronomy for high-reflectivity silver mirrors that can withstand years of exposure in observatory environments. The University of California Observatories Astronomical Coatings Lab has undertaken development of protected silver coatings suitable for telescope mirrors that maintain high reflectivity at wavelengths from 340 nm through the mid-infrared spectrum. We present results on superior protective layers of transparent dielectrics produced by evaporation and atomic layer deposition.

Several novel coating recipes have been developed with ion-assisted electron beam deposition (IAEBD) of various fluorides, oxides, and nitrides in combination with conformal layers of aluminum oxide (AlOx) deposited by atomic layer deposition (ALD) using trimethylaluminum as a metal precursor and water vapor as an oxidizer. Extending on our previous results demonstrating the superior durability of ALD-based AlOx top barrier layers over IAEBD AlOx, this work investigates the effects on mirror barrier durability comparing different IAEBD anti-oxidation layers on Ag with an identical AlOx top barrier layer deposited by ALD. Samples of coating recipes with different anti-oxidation layers undergo aggressive environmental testing, including high temperature/high humidity (HTHH), in which samples were exposed to an environment of 80% humidity at 80°C for ten days in a simple test set-up. While most samples show fairly successful endurance after HTHH testing, visible results suggest that AlOx and aluminum nitride anti-oxidation layers offer enhanced robust protection against chemical corrosion and moisture in an accelerated aging environment, which is attributed to superior adhesion and intermolecular bonding between the Al-based anti-oxidation layers and the AlOx top barrier layer. Mirror samples are further characterized by reflectivity/absorption before and after deposition of oxide coatings, and the roles of stress and adhesion characterization of the films are discussed.

TF-WeP16 Optical and Structural Study of GaN Films Grown by Pulsed Laser Deposition in Nitrogen Atmosphere*, **LuisArturo Martinez-Ara**, P. Maldonado-Altamirano, R.Y. Ponce-Cano, J.R. Aguilar-Hernandez,* ESFM-IPN, Mexico*; M.A. Hernandez-Perez,* ESIQIE-IPN, Mexico*; G.S. Contreras-Puente,* ESFM-IPN, Mexico

Results about processing and characterization of gallium nitride (GaN) films grown by pulsed laser deposition technique are presented. The films were grown on sapphire (0001) and silicon (111) substrates, under the following conditions: substrate temperature of 850 °C, time deposition of 60 minutes and pressure of $4.2x10^{-6}$ torr. A Nd: YAG laser was used with wavelength of 1064 nm, repetition frequency of 50 Hz and power of 2.8 W. To study the GaN films structural properties, X-ray diffraction was used obtaining peaks around 34.5° corresponding to GaN. To study the optical properties, UV-Vis absorption spectroscopy, photoluminescence (PL) and Raman spectroscopy were used. From the UV-Vis spectroscopy a band-gap value of 3.2 eV was obtained. Photoluminescence at room temperature was observed, the PL spectra shows two bands, one of these associated to yellow band of GaN at 2.2 eV, and the other one around 3.0 eV associated with recombination centers, such as interstitials Gallium or Nitrogen atoms. Raman shift in 722 cm^{-1} was obtained corresponding to GaN in its wurtzite structure.

TF-WeP17 Electrical and Chemical Properties of HfO_2/Al_2O_3 on $In_{0.53}Ga_{0.47}As$ Annealed at Different H_2 Pressures*, **Sungho Choi**, Y. An, C. Lee, J. Song,* Sungkyunkwan University, Republic of Korea*; M.-C. Nguyen,* Inha University, Repubilc of Korea*; Y.-C. Byun, J. Kim,* University of Texas at Dallas, USA*; R.C. Choi,* Inha University, Republic of Korea*; H.S. Kim,* Sungkyunkwan University, Republic of Korea

Passivation of a high-*k*/III-V interface is the most important process to be developed for future III-V-based transistors. Recently, there have been several attempts to passivate the interface defects by performing H_2 annealing after the high-*k* deposition on $In_{0.53}Ga_{0.47}As$: forming gas annealing [1] or H_2 high pressure annealing [2].

In this study, we deposited a HfO_2/Al_2O_3 gate stack using atomic layer deposition on the $In_{0.53}Ga_{0.47}As$ substrates with different doping types and carried out H_2 high pressure annealing (400 °C) at different pressures (10 bar and 30 bar). According to the time-of-flight secondary ion mass spectrometry and X-ray photoelectron spectroscopy measurements, out-diffusion of In and Ga atoms toward the high-*k* film was escalated as the H_2 pressure increased. The relationship between the observed H_2-induced out-diffusion and the resulting electrical properties will be discussed.

[1] K. Tang, R. Droopad, and P. C. McIntyre, ECS Transactions, **69**, 53 (2015).

[2] T.-W. Kim, H.-M. Kwon, S. H. Shin, C.-S. Shin, W.-K. Park, E. Chiu, M. Rivera, J. I. Lew, D. Veksler, T. Orzali, and D.-H. Kim, IEEE Elec. Dev. Lett. **36**, 672 (2015).

TF-WeP18 *In-situ* Visualization of Graphene Grain Boundary by Optical Microscopy*, K.-P. Hong, S.-H. Park, D.-J. Oh, **Yekyung Kim**,* Korea Electronics Technology Institute (KETI), Republic of Korea*; K.-S. Kim,* Sejong University, Republic of Korea*; K.-H. Kim, J.-B. Choi,* Sungkyunkwan University, Republic of Korea*; H. Kim,* Korea Electronics Technology Institute (KETI), Republic of Korea

The graphene consisting with carbon atoms to honeycomb structure has the excellent properties about mechanical, chemical and thermal and it has been research in a variety of fields. In order to commercialize graphene with these outstanding properties, as well as a large area, mass production is essential for precise and fast measurement. In this study, for measuring the shape and size of the oxidation graphene fast and precisely, we configured the measuring system with an optical microscope, a heating stage and 3 W level laser. Through the configured system we can keep the graphene in a vacuum and wet condition to 200 ℃and measure the grain boundary of the oxidation graphene by irradiating the laser to locally. Later by proceeding the additional experiment and analyzing the correlation between the degree of graphene oxide and the laser irradiation time, through this process we develop the optimized visualization method of the graphene defects.

Acknowledgement

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TF-WeP19 Suppression of the Co Spin-state and Metal-insulator Transitions in Epitaxial Thin Films of $Pr_{0.50}Ca_{0.50}CoO_3$ on $LaAlO_3$*, **Xavier Torrelles**, J. Padilla-Pantoja,* Institute of Materials Science of Barcelona, Spain*; J. Herrero-Martin,* ALBA synchrotron, Spain*; B. Bozzo,* Institute of Materials Science of Barcelona, Spain*; J. Rubio-Zuazo,* ESRF Synchrotron Facility, France*; J. Blasco,* ICMA-CSIC, Spain*; J.L.. Garcia-Munoz,* Institute of Materials Science of Barcelona, Spain

$Pr_{0.50}Ca_{0.50}CoO_3$ has received considerable attention in bulk form due to the charge transfer from Pr to Co ions at the metal-insulator transition as well as being the first strongly correlated oxide able to offer large an ultrafast photoresponse in the insulating phase. Thin films of PrCaCoO3 (PCCO) were deposited on (100) $LaAlO_3$ (LAO) substrates by pulsed laser deposition technique. The film grows epitaxially on the surface with two times the substrate periodicity and with the long *b*-axis of the *Pnma* cell of the bulk PCCO perpendicular to it. Compared to the latter, the film structure is noticeably relaxed, as denoted by a reduction of the space group symmetry from P*nma* (bulk) to $P2_12_12_1$ (film). Other remarkable differences were found in comparison to the bulk material. The film is ferromagnetic below 170 K and exhibits metallic conductivity in the whole temperature range, in contrast to the non-magnetic insulating behaviour of the bulk system at low temperature. We have found that the $P2_12_12_1$ structure of the film persists down to low temperatures, confirming the suppression of the Co spin-state and metal-insulator transitions recently described in PCCO ceramic samples.

TF-WeP20 Combining XPS and UPS Measurements in Thin Film Depth Profiles*, A. Bushell, J. Treacy, C. Deeks, P. Mack, T. Nunney, **Joseph Robinson**,* Thermo Scientific, USA

X-ray Photoelectron Spectroscopy (XPS) depth profiling has been widely utilized to provide detailed elemental and chemical state information of thin films, such as those used in microelectronic devices and protective coatings. These measurements have often been combined with valence electronic information obtained using the related technique of Ultraviolet Photoelectron Spectroscopy (UPS). Such detailed and complementary information is essential when attempting to fine-tune specific thin film parameters for best device or coating performance. While useful information is acquired from XPS and UPS in isolation, a more powerful insight into the structure of a material comes from using these two techniques in conjunction, allowing a more complete material characterisation to be performed. Previously, switching between techniques throughout the course of an experiment has been an involved and often laborious process, discouraging more widespread use. Recently the automation of UPS has allowed acquisition of XPS and UPS data at each level of a depth profile, providing a much sought after insight into the correlation between chemical and electronic structure at within a substrate at various depths. Of particular interest is the ability to access the valence electronic structure at mixed oxide interfaces using small argon ion gas clusters, which was not previously possible due to the loss of electronic structure in semiconductors or organic materials on exposure to monatomic argon ion beams. This presentation demonstrates the wealth of information that can be acquired by performing combined XPS-UPS depth profiles and the ease with which this information can be acquired and processed, due to recent instrumentation and software developments.

TF-WeP21 Thin Films of Sustainable Materials by UV Photo-transformation

***Lopamudra Das**, M.J. Kelley,* College of William & Mary, USA

The expanding availability of narrow-wavelength deep UV lamps and powerful tools for numerical modelling afford growing opportunity to create precisely tailored organic thin films by transformation of an original substrate. Having begun with synthetic polymers (polyesters), application to natural materials (cellulose) is now proving successful, as revealed by surface spectroscopies (XPS and ToF-SIMS), AFM and wetting.

TF-WeP22 Nanostructured Oxide Thin Films as an Active Layers of Chemiresistive Sensors for Detection of Chemical Warfare Agents and Their Simulants

***Jan Vlcek**, P. Hozak, D. Tomecek, E. Maresova, P. Fitl, L. Fiser,* University of Chemistry and Technology Prague, Czech Republic*; T. Rozsypal, M. Hoskovcova, Z. Kobliha, Z. Skalican,* University of Defense, Czech Republic*; J. Lancok, L. Fekete,* Institute of Physics, Academy of Science of the Czech Republic*; M. Vrnata,* University of Chemistry and Technology Prague, Czech Republic

The aim of this work is to investigate the response of nanostructured chemiresistive gas sensors with an active layers based on nanostructured metal oxides (nanoporous structures) to a significant group of chemical warfare agents (CWAs) - (G-series: sarin, cyclosarin, soman, choking agent: diphosgene) and their simulants - (diethyl-malonate, ethyl-chloroacetate and difenyl-phosphochloridate). The active layers of sensors (based on SnO_2 , ZnO, PdO) with thicknesses of 100 - 400 nm were prepared on sensor substrates by *(i)* sputtering of source metal and subsequent anodic oxidation, *(ii)* sputtering of source metal and subsequent thermal oxidation in oxygen atmosphere, *(iii)* thermal evaporation of source material metal and subsequent oxidation in oxygen atmosphere. Sensor platform consists of a planar sensor aluminium oxide substrate with interdigital platinum electrodes.

We present results of morphology investigation of nanostructured oxide films by AFM and SEM microscopy and structural analysis by XRD. Conventional dc-sensitivity of sensors S_{dc} was evaluated as a ratio of their resistance in air containing given concentration of analyte and that in "pure" air respectively. Detection was tested for concentrations of CWAs up to 50 ppm in air. SnO_2-based sensors feature a high sensitivity towards CWAs, where S_{dc} reaches a values of 3 - 10. On the other hand ZnO-based sensors exhibit significant selectivity to CWAs, whereas the responses to a common interferents are negligible. We show the connection between material morphology properties (porosity, crystalline size) and detection ability of CWAs.

Energy Harvesting & Storage
Room Lehua - Session EH-WeE

Surfaces & Interfaces for Efficient Power Conversion

Moderator: Junji Nakamura, Tsukuba University, Japan

5:40pm **EH-WeE1 Influence of Annealing Treatment on Optical, Electric and Thermoelectric Properties of MBE Grown ZnO*, Khalid Mahmood,*** Government College University Faisalabad, Pakistan

In this paper, we have reported the influence of annealing temperature and annealing environment on optical, electrical and thermoelectric properties of MBE grown ZnO thin films on Si substrate. A set of grown ZnO thin films was annealed in oxygen environment at 500^oC – 800^oC with a step of 100^0C and another set was annealed in different environments (vacuum, oxygen, zinc and successively annealed vacuum and zinc) for one hour in a programmable furnace. Room temperature Seekbeck measurements showed that Seebeck coefficient and power factor increased from 222 to 510 µV/K and 8.8×10^{-6} to 2.6×10^{-4} $Wm^{-1}K^{-2}$ as annealing temperature increased from 500 to 800 ^0C respectively. This observation was related with the improvement of crystal structure of grown films with annealing temperature. X-ray diffraction (XRD) results demonstrated that full width half maximum (FWHM) of ZnO (002) plane decreased and crystalline size increased as the annealing temperature increased. Photoluminescence study revealed that the intensity of band edge emission increased and defect emission decreased as annealing temperature increased because the density of oxygen vacancy related donor defects decreased with annealing temperature. This argument was further justified by the Hall measurements which showed a decreasing trend of carrier concentration with annealing temperature

6:00pm **EH-WeE2 Hard X-ray Photoelectron Spectroscopy: Applications To Energy Materials*, Jeff Terry,*** Illinois Institute of Technology

We have recently commissioned a new Hard X-ray Photoelectron Spectroscopy (HAXPES) system on the undulator beamline at the Materials Research Collaborative Access Team (MRCAT). This system was built to study materials of interest in energy storage and generation. There are a number of problems where knowledge of the electronic structure of materials is of great interest. Specifical, how is the electronic structure modified due to chemistry, irradiation, structural change, disorder, etc. The MRCAT HAXPES system is designed to operate with photon energies between 6 keV and 12 keV. This will allow us to study the electronic structure of these materials as a function of depth. Our initial measurements have been on thin films utilized in lithium ion batteries and in claddings used in nuclear reactor fuels. We will discuss these results and describe other experiments that can be conducted at the new HAXPES facility.

6:20pm **EH-WeE3 Bridging the Gap between Model Catalyst Systems and Industrial Type Fuel Cell Catalysts*, Matthias Arenz,*** University of Bern, Switzerland **INVITED**

An overview of our work is given which aims at characterizing and developing catalysts for proton exchange membrane fuel cells (PEMFCs). We investigate both model systems as well as applied catalysts, i.e. high surface area catalysts that can be used in industry or industrial samples. In our work, we focus on determining their activity for key electrochemical reactions as well as their electrochemical stability. The measurements are performed in electrochemical half-cells, which allows us to focus on a single electrode under relatively defined conditions as compared to measurements of membrane electrode assemblies (MEAs). Thereby we try to establish general trends and to reveal mechanistic information.

We argue that in many investigations there is still a large gap between the insight gained on model systems and its utilization in applied catalysts. To meet this goal, we strive to improve experimental methods and procedures for characterizing catalyst performance. We introduced for example the method IL-TEM to follow catalyst corrosion in more detail. More recently we started to develop a synthesis platform that allows systematic investigations of industrial type catalysts. We coined this a colloidal tool-box approach. In this presentation we discuss the benefits and limits of our approach to combine basic and applied research.

7:00pm **EH-WeE5 First-Principles Study on Influence of Metal Oxide on Poisoning Tolerance of Pt Nano-Particle Catalyst in Polymer Electrolyte Fuel Cell*, Tsuyoshi Kaji,*** *Y. Ootani, T. Nishimatsu, Y. Higuchi, N. Ozawa, M. Kubo,* Tohoku University, Japan

Platinum (Pt) catalyst is used in an anode of polymer electrolyte fuel cell. It is reported that carbon monoxide (CO) in the fuel adsorbs on an active site of Pt catalyst and degrades the catalytic activity. Thus, a development of a CO tolerant catalyst is required. Some experiments show that an addition of metal oxide nano-particles improves the CO tolerance of the Pt-based catalyst[1]. This result may be due to a decrease in an adsorption energy of CO on the Pt-based catalyst, but the detail mechanism is under consideration. In order to develop a higher CO tolerant catalyst, it is necessary to reveal an effect of the metal oxide nano-particle on the CO tolerance. In this work, we calculated an adsorption energy of a CO molecule on a Pt_4 cluster on an anatase $TiO_2(101)$ surface with first-principles calculation to investigate the effect of the metal oxide on the CO tolerance of the Pt catalyst.

First, we placed the Pt_4 cluster on the anatase $TiO_2(101)$ surface with several configuration, and decided the stable configuration. The Pt_4 cluster had a tetragonal structure. Three Pt atoms adsorbed on two-coodinated O atoms on the $TiO_2(101)$ surface. Then, we calculated the adsorption energy of the CO molecule on each adsorption sites of the Pt_4 cluster. The adsorption energies are defined by the difference of a total energy between the adsorption structure and dissociation structure. The largest adsorption energy of –49.31 kcal/mol was obtained for the on-top site on the Pt atom which is located on the undermost layer of the Pt_4 cluster. Whereas, the adsorption energy of the CO molecule on the on-top site of the isolated Pt_4 cluster is –68.66 kcal/mol. These results indicate that the adding of TiO_2 improves the CO tolerance of the Pt catalyst.

Next, we examined the effects of the doping elements on TiO_2. Since the doping modifies electronic structure of TiO_2, improvement of the CO tolerance of the Pt catalyst is expected. Thus, we substituted a F atom for the O atom or a Nb atom for the Ti atom of the $TiO_2(101)$ surface. When we substituted the F atom and the Nb atom, the adsorption energies of the CO molecule on the Pt_4 cluster are –41.75 and –40.61 kcal/mol, respectively. These adsorption energies are lower than the adsorption energy on Pt_4 cluster on the undoped $TiO_2(101)$ surface. Thus, we suggest that the substitution of F and Nb atoms improves the CO tolerance of the Pt cluster on the TiO_2 surface. At the conference, we discuss the reason why the doping of F and Nb atoms decrease the adsorption energy of a CO molecule on the Pt_4 cluster on the $TiO_2(101)$ surface based on the density of states.

[1] T. Takeguchi et al., *Catal. Sci. Technol.*, **6,** 3214 (2016).

7:40pm **EH-WeE7 In Situ Observation of Electrochemical Processes at Solid/Liquid Interfaces*, Takuya Masuda,*** NIMS (National Institute for Materials Science), Japan **INVITED**

In order to design highly efficient and durable materials for energy conversion devices such as fuel cells and batteries, it is important to understand the key electrochemical processes occurring at solid/liquid interfaces. We have utilized various x-ray techniques to investigate those interfacial processes under electrochemical potential control. In this talk, in situ XAFS studies on electron transfer reactions on electrocatalysts and development of an in situ electrochemical XPS apparatus for the solid/liquid interfaces will be presented.

The rate of oxygen reduction reaction (ORR) was significantly enhanced when cerium oxide (CeO_x) was utilized as a co-catalyst together with Pt catalyst. The promotion effect of CeO_x for ORR at Pt was investigated by in situ XAFS measurements of the Pt-CeO_x/C and a conventional Pt/C catalyst. Upon the incorporation of CeO_x into Pt, not only Ce^{4+} species corresponding to CeO_2 but also Ce^{3+} species were observed due to the formation of the Pt/CeO_x interface. After cleaning the Pt surface by oxidation/reduction cycles in an aqueous solution, Ce^{4+} species is preferentially eluted in the solution, so that 3−5 nm Pt nanoparticles coated with a few CeO_x layers were formed. At the Pt L_3 edge of the Pt/C, the white line intensity increased as the potential was made more positive than 1.0 V (vs. Ag/AgCl), showing the formation of Pt oxide because the white line intensity reflects the *d*-band vacancies. In contrast, for the Pt-CeO_x/C, the formation of Pt oxide was significantly suppressed by the CeO_x layer. This suggests that the intrinsic ORR activity of bare Pt was maintained at the Pt-CeO_x/C while the Pt surface is partly covered by insulating Pt oxide at the pure Pt/C. At the Ce L_3 edge of the Pt-CeO_x/C, a singlet peak due to the Ce^{3+} species formed at the Pt surface turned into a doublet peak characteristic to the CeO_2, suggesting that Ce^{3+} species was oxidized to Ce^{4+} species to inhibit the formation of Pt oxide.

XPS is a powerful technique to analyze the surface compositions and oxidation states. However, it is difficult to carry out *in situ* XPS analysis of electrode surfaces in contact with electrolyte solutions under electrochemical potential control because of requirement of vacuum. Recently, we constructed an *in situ* XPS apparatus, which is applicable to electrochemical processes at solid/liquid interfaces, using a micro-volume cell equipped with an ultrathin photoelectron window. Electrochemical growth of Si oxide in contact with water was observed as a first demonstration of the capability of this system and effect of potential and time on the thickness of Si and Si oxide layers was quantitatively determined.

Nanomaterials
Room Hau - Session NM-WeE
Nanocomposites

Moderator: Richard Tilley, University of New South Wales, Australia

5:40pm **NM-WeE1 Engineering Nanomaterials for Electrochemical Energy Storage and Biosensing*, Kaifu Huo,*** Huazhong University of Science and Technology, China **INVITED**

With depleting fossil fuels and growing concern on environmental protection, urgent research efforts are needed to find alternative energy resources and efficient and economical energy storage devices. Li-ion batteries (LIBs) and supercapacitors (SCs) constitute the two main types of electrochemical energy storage devices for powering portable electronics, electric vehicles (EVs), and hybrid electric vehicles (HEVs). Electrode materials are the key components of SCs and LIBs as well as electrochemical biosensors, largely determining the device performance. The development of nanomaterials and nanotechnology has enabled exciting opportunities to design materials with desirable electronic, ionic, and electrochemical properties, which has also contributed to the advance in electrode materials and led to high-performance electrochemical energy storage devices and biosensors. Herein, we will introduce our recent work by rational designing nanostructured materials for high-performance LIBs, SCs as well as electrochemical biosensors. Four specific material systems will be discussed: i) biomass-derived alloy anodes for LIBs, ii) nanostructured sulfur, selenium cathodes for Li-batteries, iii) nanostructured metal nitride electrodes for electrochemical capacitors, and iv) core-shell carbon nanofiber arrays for high-performance electrochemical biosensors and supercapacitors.

6:20pm **NM-WeE3 Functionally Graded Nanocarbon-reinforced Metal Matrix Composite Materials*, Hansang Kwon,*** *G.J. Park,* Pukyong National University, Republic of Korea*; S. Lim, J.H. Park,* Next Generation Materials Co., Ltd, Republic of Korea

Functionally graded nanocarbon particles reinforced aluminium (Al) matrix composites have been successfully fabricated by solid-state spark plasma sintering process [1]. The multiwalled-carbon-nanotubes (MWCNT) were used as a main reinforcement and the MWCNT were well dispersed in the Al particles using high energy ball milling process. Several different types of MWCNT were used in the same volume. The ball milled Al-MWCNT powder mixtures were fully densified and demonstrated good adhesion with no serious micro-cracks and pores within a multilayer composite. Each multilayer contained different amounts of the MWCNT, showed different microstructures and mechanical properties. It is possible to control the mechanical, thermal and electrical properties of the functionally graded multilayer composite through the efficient design of an MWCNT reinforced gradient layer.

[Reference]

[1] KWON, H., LEPAROUX, M. & KAWASAKI, A. 2014. Functionally Graded Dual-nanoparticulate-Reinforced Aluminum Matrix Bulk Materials Fabricated by Spark Plasma

6:40pm **NM-WeE4 Boron Nitride Nanotube-Titanium Alloy Nanocomposites*, John-Andrew Hocker,*** NASA Langley Research Center, USA*; S-H. Chu, V. Yamakov,* National Institute of Aerospace, USA*; J. Newman, S. Messina, E. Judd,* NASA Langley Research Center, USA*; C. Rohmann, D. Bernhardt,* The University of Queensland, Australia*; C. Park, C. Fay,* NASA Langley Research Center, USA

Titanium alloys, such as Ti-6Al-4V, are used in aerospace applications that require light weight, high strength and corrosion resistance. Boron nitride nanotubes (BNNT) are a unique high strength, high aspect ratio, neutron absorbing nanomaterial with good thermal and chemical stability. Adding low density BNNT enables structural mass savings and may impart multifunctional capabilities such as the piezoelectric effect, and increased thermal conductivity. Recent theoretical studies indicate that BNNTs should exhibit a stronger interfacial binding with titanium than they do with aluminum or copper. Guided by those results, a series of nanocomposites was fabricated to experimentally investigate the reinforcing effect of BNNTs on the Ti-6Al-4V alloy. BNNT-Ti-6Al-4V nanocomposites were prepared by first consolidating the powder/BNNT blends at several loadings, 0.01 to 10 weight percent BNNT, in a circular die at elevated temperature and pressure. These consolidated specimens were then placed in a furnace and sintered under vacuum at ~1300°C. The resulting physical and mechanical properties of the metal matrix nanocomposites will be discussed, and compared with morphological results from X-ray diffraction, and optical, scanning electron, and scanning probe microscopies.

7:00pm **NM-WeE5 Fabrication and Applications of Nanocomposites Based on Anodic Aluminium Oxide*, Jinghua Fang,*** University of Technology Sydney, Australia

Engineering a new class of nanocomposite-metamaterials can achieve ultra-sensitive sensors for bio-imaging, gas detection, air and food contamination control. This is critical to meet the global challenges of environmental conservation and efficient use of energy and mineral resources, especially for point-of-use applications. Using anodic aluminium oxide (AAO), here we report the fabrication of metamaterials with different metal nanostructures, we also investigate the applications of these fabricated metamaterials based on AAO templates.

7:40pm **NM-WeE7 Graphene-based Nanocomposite Hydrogels for Contaminant Removal*, Nathalie Tufenkji,*** *N. Yousefi, K. Wong, A. Angulo,* McGill University, Canada

Due to its exceptionally high specific surface area and abundance of surface functional groups, graphene oxide (GO) is of great interest as a high performance sorbent for dyes, heavy metal ions, oils, toxins and organic solvents from contaminated waters. However, recovery of GO after the water treatment process is difficult due to its high stability in water. Thus, self-assembly of GO sheets into porous 3D macrostructures such as hydrogels has been explored as a technique to exploit their high surface area while facilitating easy recovery from treated water. Nonetheless, creating mechanically robust hydrogels with acceptable adsorption capacities is not straightforward. We report a simple method for preparation of ultra-strong nanocomposite GO hydrogels at low pressure using vitamin C as a natural cross-linker. The structure and chemical compositions of the hydrogels are examined using microscopy and spectroscopy techniques. We demonstrate that hydrogels with high storage moduli can be used to effectively remove model dyes such as methylene blue, heavy metal ions and emerging contaminants such as the pharmaceutical products diclofenac and sulfamethoxazole from aqueous solutions. We will describe the novel aspects of the hydrogel synthesis that give rise to its exceptional mechanical strength and adsorption capacity.

8:00pm **NM-WeE8 Nanocrystal-in-Glass Composite Thin Films for Electrochromic Smart Windows*, Delia Milliron,*** University of Texas at Austin, USA

Degenerately doped metal oxide semiconductors, like ITO, exhibit plasmonic resonance at near and mid-infrared wavelengths tunable by varying their composition. Nanocrystals of many such materials have now been synthesized and applications are emerging that leverage the responsiveness of their localized surface plasmon resonance (LSPR) to electronic charging and discharging. In this talk, I'll focus on how we are applying this concept to develop electrochromic glass that can dynamically control heat loads and daylighting in buildings. We demonstrated that dual-band electrochromism (voltage control over near infrared and visible light transmittance independently) is achievable by embedding plasmonic ITO nanocrystals in a redox-active niobium oxide glass matrix. To develop a practical technology on the basis of this concept, the component materials and their mesoscale architecture can both be optimized so that we now can modulate a large fraction of incident solar radiation on demand. To enable low-cost manufacturing, we have recently developed low-temperature processing strategies and have now fabricated complete dynamic glass prototypes. The materials innovations needed to enable this progress will be emphasized.

8:20pm **NM-WeE9 Towards Producing Bulk Monolithic Core/Shell Nanocomposites***, B.N. Feigelson,* ***James Wollmershauser,*** *K. Manandhar,* U.S. Naval Research Laboratory, USA

With designed bulk nanostructured solids, one could potentially combine properties that are mutually exclusive in a single bulk material, and, as a result, dramatically improve the desired performance. However, a major research challenge and roadblock is how to produce 3D nanostructured materials consistently with the required phases arranged in designated spatial order that are at the same time fully dense without porosity and detrimental phases. Known state-of-the-art techniques for producing bulk nanostructures cannot simultaneously meet all these requirements. As a

result, the inherent properties of such bulk monolithic nanostructured materials are greatly unknown and unexplored.

We developed an Enhanced High Pressure Sintering (EHPS) process to consolidate oxide, metal, and semiconductor nanoparticles into 3-dimensional monolithic nanostructured materials. EHPS incorporates stringent environmental control and utilizes high pressures to break agglomerates while simultaneously exploiting the increased pristine surface potential of nanoparticles for surface-energy-driven densification without microstructural changes. Using this approach, monolithic nanocrystalline transparent ceramics with grain size bellow 30 nm are demonstrated. Such ceramics exhibit a 30% increase in hardness over a corresponding order of magnitude reduction in grain size and suggest that Hall-Petch type (strengthening via grain size reduction) relations exist in ceramics at least down to 30nm [1].

Core/shell nanoparticles offer fundamentally new means for nanostructured solids design and tailoring basic properties of these artificial materials. To provide flexibility in core/shell nanoparticles design, a particle atomic layer deposition (pALD) reactor was incorporated in the EHPS facility. The new setup allows to controlling environment during all stages of the nanoparticles processing, atomic layer deposition and sintering. Spinel/alumina core/shell nanoparticles were the first material system tested for producing the first core/shell ceramic nanocomposite. Alumina shell was grown on spinel nanoparticles, and then core/shell nanoparticles sintered under pressure without exposing to atmospheric air. The developed nanocomposite ceramics demonstrated better hardness and fracture toughness than pure nanocrystalline spinel.

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8:40pm **NM-WeE10 Nanoscale Bioinspired Interfaces in Carbon Fibre Reinforced Polymer Composites***, **Bronwyn Fox**,* Swinburne University, Australia

Carbon fibre composites, where bundles of carbon fibres are embedded in a polymer matrix, offer enormous design flexibility due to the ability to tailor properties such as strength and modulus. They are used to lightweight aerospace and automotive structures and are seeing an exponential increase in demand with the global market predicted to grow to $36 billion by the year 2020. The Achilles heel of these materials lies in their ability to withstand damage from impact loads. Once damaged, the ultimate strength of the material is reduced via the formation of microcracks that lead to delamination failure. The microcracks are often found to originate at the interface between the fibre and the matrix, yet interfacial adhesion in composite materials is poorly understood and still hotly debated in the literature. The relative influence of fibre grade (standard, intermediate or high modulus), fibre surface roughness and chemistry in interfacial adhesion and therefore microcracking is required. This new knowledge will lead to the development of engineered interfaces in composites for improved performance. There are many examples of tailored interfaces in nature from which we can draw inspiration. Nacre (mother of pearl) is a natural high-performance composite comprising nanocrystals of CaCO3, aragonite, embedded in a multi-layered, multi-component soft organic matrix. The CaCO3 crystals do not bind directly to the organic chitin layer, but are separated by an intermediate protein layer. This intermediate phase creates a soft/soft/hard interface that can be likened to an engineered interphase in carbon fibre composites. Commercial carbon fibres are usually electrolytically oxidised and then coated with either an epoxy or a polyurethane sizing to protect the fibre during processing and to facilitate handling. The nature and presence of this sizing may influence the chemistry of the surrounding polymer matrix to create an interphase region. We have explored a range of strategies to tailor the fibre surface roughness and chemistry to ensure compatibility with the polymer matrix. The electrolytic treatment was systematically varied to ensure that the fibre surface was free of amorphous carbon debris, a range of chemical treatments were used including the attachment of small molecules to the fibre surfaces. Novel sizing systems and plasma polymer coatings have also been applied to the fibres. This paper will describe our recent results on the effect of a range of fibre treatments to improve interfacial performance in carbon fibre composites.

Thin Films
Room Mauka - Session TF-WeE
Microstructure & Surface Morphological Evolution in Organic & Inorganic Films

Moderator: Satoshi Hamaguchi, Osaka University, Japan

5:40pm **TF-WeE1 Characterizing the Packing Density of Amorphous Sputtered SiO2 Thin Films with Positrons***, **Eric Charrault**,* University of South Australia, Australia*; J. Sullivan,* The Australian National University, Australia*; C. Hall, D. Evans, P. Murphy,* University of South Australia, Australia

Sputter deposited thin films are widely used as a way to modify a substrate and change its properties (electrical, mechanical, optical etc…). The resulting structure of the film (at the micro-and nanoscale) depends on a whole range of deposition parameters and is typically assessed by the residual stress of the film, which is widely used to evaluate the performance and quality of the film. Depending on the targeted applications and film properties, variable levels of stress are desirable. Much recent studies demonstrated direct correlation between the residual stress in multilayers thin films and their performances under certain conditions. For instance, by tuning the stress in an amorphous SiO_2 layer, which was part of a multilayer thin film, corrosion resistance could be improved. Over the past decades, extensive studies have been carried out to give more insights about the structure/stress relationship. However, a morphous dielectric films present some challenges regarding their characterization: for example, classical diffraction techniques reporting crystallinity are of little interest as the films herein do not present short or long range order, typical electron microscopy is also challenging because of charge accumulation effect. One particularly important parameter in designing thin films by sputter deposition is the substrate. Crystallinity, temperature, DC bias are as many properties of the substrate that can be changed in order to modify the residual stress of the deposited film. However, very little attention has been focused on the effect of the mechanical properties of the substrate. Recently, it has been shown using atomic force microscopy that the size of the grains of sputtered films depend on the hardness of the substrate. The need to better characterize dielectric thin films could shed some light on their critical impact in new products development. By using positron annihilation lifetime spectroscopy (PALS) to investigate the physical structure of SiO2 films we aim at correlating the size of pores to their seeding and growth processes and to their residual stress.

6:00pm **TF-WeE2 Growth and Characterization of Epitaxial Cu2O,CuO Thin Films & Cu2O/MgO Superlattices***, **Paritosh Wadekar**, Y. Chen, W.C. Hsieh,* National Sun Yat Sen University, Taiwan, Republic of China*; C. Wei,* National Sun Yat Sen University,Taiwan, Republic of China*; H.C. Huang, LWT. Tu, C.W. Lin, M.J. Yang, J.W. Chou,* National Sun Yat Sen University, Taiwan, Republic of China*; C.H. Liao,* Military Academy, Taiwan, Republic of China*; C.F. Chang, S.T. You, I.K. Lo, N.J. Ho,* National Sun Yat Sen University, Taiwan, Republic of China*; H.W. Seo,* Jeju National University, Korea*; S.W. Yeh,* National Kaohsiung University of Applied Science and Technology, Taiwan, Republic of China*; H.H. Liao,* Enli Technology, Taiwan, Republic of China*; W.K. Chu,* University of Houston, USA

Oxides of copper such as cuprite(Cu2O) and tenorite (CuO) have potential application for harvesting solar energy. By combing these with a wide band gap oxide such as MgO, one could design artificial quantum structures such as Cu2O/MgO or Cuo/MgO. However, the narrow growth regime and strict oxygen pressure requirements can cause oxidation or reduction resulting in local mixed phases in epitaxial thin films. In this report, we aim to study the grown mechanism of Cu2O as well as CuO on various substrates such as Al2O3(0001), Al2O3(11-20), Al2O3(10-10), MgO(100), MgO(110). The samples were grown using DC magnetron sputtering on the above mentioned substrates. They were further characterized for epitaxy using XRD, TEM measurements. Temperature dependent optical properties were studied using cathodoluminescence measurements. We also tried to grow superlattices of Cu2O/MgO on Al2O3 substrates. We also investigated the effect of buffer layers on the physical properties of these superlattices. Samples were characterized using XRD, TEM, SEM measurements. Our results indicated that while single phase epitaxy of Cu2O on above mentioned substrates can be achieved, growth of superlattices is difficult owing to formation of rough surfaces at the interfaces.

6:20pm **TF-WeE3 Understanding Organic-Organic Quasiepitaxy***, **Richard Lunt**,* Michigan State University, USA **INVITED**

The presence of excitons in organic materials offer new opportunities for low-cost photovoltaics and electronic systems and provide prospects for unique energy science and applications. In this talk I will review our understanding of organic quasepitaxy. I will then discuss our demonstration of the growth of ordered organic-organic hetero-quasieptiaxial supperlattices, composed of incommensurate organic semiconductors with sustained registry grown from the bottom up via a new step-edge nucleation driven growth mechanism. By probing a range of molecular pairings with in-situ and real-time diffraction, we further uncover driving forces that can broadly enable this type of growth, which are completely distinct from the requirements of inorganic epitaxy. It is well known that crystalline order, orientation, and quantum confinement of highly anisotropic organic semiconductors can significantly alter the properties and performance of organic electronics. Thus, these demonstrations can enable entirely new photophysical phenomena and provide opportunities for manipulating energy in a variety of excitonic structures.

7:00pm **TF-WeE5 Characterization of Aluminum Nitride Grown by Atomic Layer Epitaxy with real time Grazing Incidence Small Angle X-ray Scattering***, **Virginia Anderson**, N. Nepal, S.D. Johnson,* US Naval Research Laboratory, USA*; Z. Robinson,* The College at Brockport SUNY, USA*; A. Nath, A. Kozen,* US Naval Research Laboratory, USA*; A. DeMasi,* Boston University, USA*; J.K. Hite,* US Naval Research Laboratory, USA*; K.F. Ludwig,* Boston University, USA*; C.R. Eddy, Jr.,* US Naval Research Laboratory, USA

A focus area of research on III-nitrides attempts to lower the growth temperature of films, because molecular beam epitaxy and metalorganic chemical vapor deposition (MOCVD) must be done at relatively high temperatures to produce a high quality material. As an example, aluminum nitride MOCVD takes place at over 1000°C. Tunable band gaps, high breakdown voltages, and piezoelectric properties are attractive qualities of aluminum nitride films, and thus motivate the search for alternate fabrication methods. Atomic layer epitaxy (ALE) of GaN, AlN, and InN films have been shown at temperatures far below that required for MOCVD. [1] Further exploration of the growth parameters of these films is underway. Research during the actual growth process allows much more information on early stages of film deposition, and eliminates many of the *ex-situ* issues with surface oxidation upon sample removal from the reactor. The X-ray photons available at some synchrotrons allow insight into the growth process from grazing incidence small angle X-ray scattering (GISAXS), a technique that can be carried out at ALE pressures and is extremely sensitive to surface morphological evolution.

The work presented will describe film growth of aluminum nitride using trimethylaluminum and a nitrogen/argon or hydrogen/nitrogen/argon plasma. Based on *ex-situ* examinations, aluminum nitride ALE on MOCVD GaN at 500°C was previously seen to exhibit single crystal character, with a full-width at half maximum of 670 arc-seconds. [2] Work presented here describes results on changing the temperature and the plasma conditions for ALE AlN. The substrates were sapphire and the growth took place at Brookhaven National Laboratory and at the Cornell High Energy Synchrotron Source in a custom reactor designed to facilitate GISAXS monitoring during growth.

These results suggest that surface feature distances are related to the final quality of the aluminum nitride films. Samples grown at 350-400°C have higher impurities than samples grown at 450-500°C, and GISAXS shows closer features at the lower temperatures. In addition, holding the flow constant and changing the nitrogen to argon ratio resulted in changes in the atomic species present in the plasma source, and changes in nucleation and growth behavior.

References:

1 N. Nepal et al., *Thin Solid Films* **589** 47 (2015)

2 N. Nepal et al., *Appl. Phys. Lett.* **103** 0 82110 (2013)

7:40pm **TF-WeE7 Study of Structural Phase Transitions during Growth of Tetracene and Pentacene Films on H/Si(001) via NEXAFS and AFM***, **Xiaorong Qin**, J. Shi,* University of Guelph, Canada*; T. Regier,* Canadian Light Source, Canada*; D.T. Jiang,* University of Guelph, Canada

To understand the formation of organic thin films and substrate influences to the molecular structures, we investigated the orientation of polyacene molecules (i.e., tetracene, pentacene) on hydrogen-passivated Si(001) as a function of coverage, using polarization-dependent C1s near-edge x-ray absorption fine structure spectroscopy (NEXAFS). Molecular films were prepared via vacuum molecular beam deposition, and in situ NEXAFS measurements were performed on the films of different coverage (from 0.2 ML to 12 ML). We report that under the film growth condition, at the early stages of the film growth the average orientation of the molecules is largely disordered. Clear upwards tilting of the molecules start when coverage exceeds a significant portion of a monolayer. With further increasing the film coverage to around 3-4 ML, a structural phase transition occurs, leading to the average molecule tilting angle around the bulk value. We conclude that, in both tetracene and pentacene growth, after the coverage of 3-4 ML, the molecules adopt the organization similar to that in the bulk-phase structure due to strong the self-assembly effect and less influence from the molecule-substrate interface. Atomic force microscopy (AFM) imaging of the films was carried out ex situ to show the morphology of the surfaces at different coverage. The film formation mechanisms and their impact to the charge transport properties of the film will be discussed.

8:00pm **TF-WeE8 Copper Native Oxidation at Room Temperature Studied by Reflectometry-Ellipsometry***, **David Fryauf**, J. Diaz Leon, N. Kobayashi,* University of California Santa Cruz, USA

Native oxidation of copper has been a nuisance in electrical devices due to the added electrical resistance to copper electrodes. However, copper oxide, known to have two primary stable phases, cuprous oxide (Cu2O) and cupric oxide (CuO), is an interesting materials system for the prospective application of resistive switching in memory devices. Cu2O and CuO often form concurrently within the native oxide. Because of their similar refractive index and extinction coefficient, optically differentiating these two phases is a challenge, yet it is critical for designing devices. In this study, thin copper films were deposited using electron-beam evaporation at different deposition rates, and copper film crystalline structure and surface morphology were modified by annealing and argon ion bombarding. A native oxide was grown on the prepared copper films over 5 months in air and periodically evaluated with reflectometry-ellipsometry. Similar samples were also subjected to accelerated oxidation in atmospheric conditions and periodically measured. XRD, XRR, and AFM measurements were also performed on the samples aged for 5 months to supplement and confirm the confirm the characteristics of oxide growth. A comprehensive analysis on the progressive formation of native oxide on copper is discussed.

8:20pm **TF-WeE9 Spatio-Time-Resolved Cathodoluminescence Study of Thick III-polar and N-polar InGaN***, **Zakaria Al Balushi**, J. Redwing,* The Pennsylvania State University, USA

InGaN quantum wells (QWs) have been well established as active layers in LEDs and laser diodes. Recently, there has been interest in the growth of thick InGaN to serve as strain-reducing layers for deep-green and red emitters. The growth of thick layers is, however, challenging. The miscibility gap between InN and GaN leads to InGaN phase separation and indium clustering. In addition to low indium incorporation at high growth temperatures, a high density of V-pits are observed in InGaN films grown in the III-polar direction. Alternatively, the growth of films in the N-polar direction offers advantages that are attractive for the growth of thick InGaN. N-polar growth enables higher indium incorporation and V-pits are less favorable to form. Despite these advantages, limited studies on thick N-polar InGaN films have been reported. This is because N-polar InGaN grown by MOCVD typically suffer from high densities of hexagonal hillocks that originate from low quality N-polar GaN templates. Therefore, in order to assess the quality of thick N-polar InGaN films, it is necessary to probe the local structure and optical properties of high quality grown films.

In this study, we compare the structural and optical properties of thick III-polar and N-polar InGaN. Both III-polar and N-polar InGaN growth was carried out by MOCVD under identical conditions (130 nm, 780°C, 300 Torr, V/III=2450) on high quality GaN base layers. The N-polar InGaN films were free of hexagonal hillocks and exhibited a reduced RMS roughness of 0.66 nm in comparison to the RMS roughness of 2.30 nm for III-polar InGaN. High resolution XRD, SIMS and EDX measurements revealed higher indium incorporation in the N-polar films (13%) when compared to III-polar InGaN (7.5%). From PL measurements, two distinct peak emissions located at different depths of the film were observed for both film polarities, one peak originating from a pseudomorphically strained region and the other from a partially relaxed region. To further investigate the optical properties of InGaN films, we performed both steady state and time-resolved cathodoluminescence mapping of the III-polar and N-polar films at room and liquid helium temperatures. From CL measurements, distinct emission from indium clusters and threading dislocation around V-pits were observed in III-polar InGaN films. In the case of N-polar InGaN, CL emission was homogenous across the film surface. With the combination of spectroscopic techniques, this study elucidates the differences in the luminescence in thick InGaN as a function of film polarity and gives new insights into possible mechanisms of luminescence quenching commonly observed N-polar InGaN.

8:40pm **TF-WeE10 3D Image of Coating and Diffusion Species*, Lei Zhang,*** Shenyang National Laboratory for Materials Science, Institute of Metal Research, Chinese Academy of Science, China

Morphology, composition and crystallography are three common objects for microanalysis in material science. The developments of 3D techniques in material microanalysis facilitate researchers to explore in 3D space. 3D chemical analysis is of important in 3D microanalysis family but need to be improved and promoted. Combining 2D imaging in lateral with sputtering in depth, layered SIMS imaging can be reconstructed in 3D. Detailed 3D-SIMS analysis of interfaces between phases, such as concentration change and inhomogeneity of diffused species near interface, provide diffusion information between coating and substrate with new view. Such 3D-SIMS technique become a useful and popular tool to generate full-view images in 3D space for various specimens with layered or complex structure from inorganic, organic and biological research. It provides a wealth of composition information and gives deep insights that cannot easily be attained in other interfacial analysis.

Normal approach in 3D-SIMS can display the species in layered or complex structure. However, detailed analysis of interfaces between phases, such as concentration change and inhomogeneity of diffused species near interface, attract more attention that need to be explored. For example, diffused interface is expected to be a sign of solid bonding for the safety of coating service life. New 3D imaging approach is developed to separate the diffused species through the interface. In terms of the ion imaging of CsAl+ in diffusion region, diffused Al at the interface between the ceramic coating and Zircaloy substrate were investigated in both as-deposited and annealed states.

The new analytics toolkit to resolve diffused species is a key evaluation to develop coating layer on alloys. The new method based on 3D-SIMS analytics is expected to provide diffusion information between coating and substrate with new view. It will continue to advance and gives more information about the formation of diffusion interface which facilitate the interface analysis from variety of research interest.

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Biomaterial Surfaces & Interfaces
Room Milo - Session BI-ThM

Plasma for Biomedical Applications

Moderator: David Castner, University of Washington, USA

9:00am **BI-ThM4 Fundamentals of Plasma Interactions with Biological Systems***, **Endre Szili**, R.D. Short,* University of South Australia, Australia **INVITED**

There is significant optimism that cold atmospheric plasma could play a role in the treatment of diseases and infection, particularly those that are refractory and potentially life-threatening such as non-healing chronic wounds and cancers. The medical benefits from plasma are assigned to reactive oxygen and nitrogen species (RONS) that are generated by plasma upon interaction with air and liquids. However, we still do not have a sufficient understanding of (1) what RONS are delivered by plasma, (2) the rate RONS are delivered, (3) how the RONS are perturbed by tissue and (4) how RONS interact with cellular membranes. This knowledge is essential in order to obtain a quantitative mechanistic understanding of plasma in biology and medicine. In this talk, I will discuss simple biological mimics of 3D tissue or cells membranes, which are utilized to gain new insight into the plasma generation and transport of RONS and molecular oxygen into tissue fluid, tissue and cells. Surprisingly, we discovered that plasma can directly transport RONS and molecular oxygen deep within tissue to millimeter depths and across cellular membranes without physically damaging the tissue or cell membrane. In addition, I will discuss how the combined dynamic changes in the concentrations of RONS and molecular oxygen in the biological fluid can significantly impact cell viability during and after the plasma treatment. Finally, I will discuss how the above assays can support the future development of plasma sources to deliver metered doses of RONS and molecular oxygen within tissue for treatment of diseases such as chronic wounds and cancers.

9:40am **BI-ThM6 Plasma Engineered Surface for Managing Growth Factor Release in Stem Cell Culture***, **Jason Whittle**,* University of South Australia, Australia

The surface modification of materials used in biomedical applications is one of the earliest successful applications of gas plasma treatment. Such "Tissue Culture Plastics" are the mainstay of cell culture facilities to this day.

More recently, the ability to use plasma polymerisation to engineer novel surfaces has opened up the possibility of more advanced surfaces for cell culture. Products based around this technology are now also widely available.

In our laboratory we have developed plasma deposited surfaces that bind glycosaminoglycans from solution, and which are subsequently able to bind and release growth factors and other signalling molecules into solution. The presence of these growth factors enables the culture of primary- and stem cells without the need to add these growth factors to the media formulation. The development and application of this surface in the culture of human cells will be described, in addition to some of the challenges associated with commercialisation of plasma deposited films, where better knowledge of the physics and chemistry of depositing plasmas is needed.

10:20am **BI-ThM8 Principles for Retention of Fragile Chemical Functionality Structures in Plasma Polymer Thin Films***, **Solmaz Saboohi**, B.R. Coad, A. Michelmore,* University of South Australia, Australia*; R.D. Short,* University of Lancaster, UK*; H.J. Griesser,* University of South Australia, Australia

There is a growing need for thin films which are functionalized with specific surface chemical motifs that impart new physical, chemical or biological properties. The design and fabrication of thin films with specific surface groups has the potential to provide further insights into bio-interfacial interactions as well as to yield novel coatings for products such as cell culture ware. Plasma polymerization (PP) provides a one-step, solvent-free process, irrespective of material type and format, and supports several large-scale industrial applications on the basis of advantages such as excellent uniformity and adhesion of coatings and their reproducibility. We have studied how volatile ester compounds can be plasma polymerized with retention of a high density of intact structural elements. However, in PP there usually occurs extensive fragmentation of the volatile precursor molecule ("monomer") and re-assembly of the various fragments from the plasma gas phase into a solid polymeric coating. Considerable scrambling of molecular structural elements is evident even where functional group retention has been the objective. High energy electron impact events in the plasma results in loss of specific functional groups in the plasma phase. In addition, a strong negative electric field, which develops in the vicinity of the surface, may cause positive ions to arrive at the surface with significant energy. Sputtering / reorganization at the surface due to ion impingement also results in loss of specific functional groups. Retention of chemical functional groups can be optimized by considering the pressure where the plasma transitions from the alpha to the gamma regime.[1] Operating the plasma in the collisional regime biases the deposition towards increased contributions by ions rather than neutral/radical grafting.[2] This study demonstrates that relatively complex structural motifs in precursor molecules can be retained in plasma polymerization if the chemical and physical processes occurring in the plasma phase are controlled by tuning the plasma to deliver a high flux of polyatomic ions and suitable energy of the ions to deposit films.

References

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10:40am **BI-ThM9 Cell-Surface Modification for Biomaterial Applications using Furfuryl Methacrylate Plasma Polymer***, **Hanieh Safizadeh**, A. Michelmore, J.D. Whittle,* University of South Australia, Australia

Cell-surfaces interaction plays a significant role in biomedical applications and cell therapies. In many cases, materials which are convenient for manufacturing biomedical devices and culture ware exhibit poor cell adhesion. Therefore, it is important to modify cell-surface interactions using surface engineering. Poly(furfuryl methacrylate) (p(FMA)) is a promising polymer surface that recently has been recognized for stem cell adhesion and proliferation due to the furan ring in its structure. However controlling the thickness and topography of surface coatings of p (FMA) is difficult, which inhibits scale-up. Plasma polymerization offers a simple, solvent-free method for coating surfaces with FMA which is substrate independent, with fine control of film thickness and topography.

Herein, FMA plasma polymer coatings were prepared with different powers, deposition times and flowrates. Furan ring retention on these surfaces has been determined using chemical analysis such as XPS and ToF-SIMS. SEM demonstrated the existence of particle aggregates under certain plasma conditions. Through judicious choice of plasma polymerization parameters the formation and quantity of the particle aggregates was reduced and the fabricated plasma polymer coatings became chemically uniform and smooth and the furan ring retention was maximized. These optimised surfaces support cell proliferation, comparable to results with tissue culture plastic, while maintaining cell fate. These findings show not only the chemistry of surfaces is important but also that surface morphology plays an important role in cell adhesion and proliferation.

11:00am **BI-ThM10 Quasi-zwitterionic Glow-Discharge Radio Frequency Plasma Coatings Reduce IgG Protein Adsorption***, **Marvin Mecwan**, B.D. Ratner,* University of Washington, USA

Introduction: Glow discharge plasma-treated surfaces have been used to create non-fouling surfaces, and can be readily applied to implants. For successful plasma polymerization it is important that the monomer of interest be easily volatilized. Zwitterionic polymer hydrogels in mice have shown to resist foreign-body reaction. However, zwitterionic polymer precursors, such as carboxybetaine methacrylate (CBMA) and sulfobetaine methacrylate (SBMA) are solids with high boiling points which would not make them ideal candidates for glow-discharge plasma treatment to coat surfaces. This study investigates the preparation of quasi-zwitterionic surfaces via glow-discharge plasma treatment prepared by the simultaneous deposition of a positively charged (allylamine or AAm), and negatively charged (acrylic acid or AAc) monomer, and its ability to act as a non-fouling surface.

Methods: Glass substrates were cleaned with MeOH in a sonication bath for 10 mins x 2. Substrates were loaded into the reactor, Ar etched (40W for 10 min), followed by a CH_4 layer (80W for 5 min). The monomer of choice—AAc and AAm—was introduced into the chamber either by itself or simultaneously and plasma deposition was carried out at 150mT pressure; 80W for 1 min (adhesion) followed by 10W for 10 mins (deposition). Samples were quenched for 5 mins before venting the chamber and retrieving coated samples resulting in 3 treatment groups: AAc, AAm and AAc-AAm. Plasma-treated samples were washed using DI water x 3 and ESCA was used to assess coating composition before and after washing.

ESCA analyses were done using an S-Probe ESCA (with monochromatic Al K-alpha X-rays focused to 800μm spot size) using survey and detailed C1s scans. Protein adsorption studies were performed using bovine IgG, and the amount of IgG adsorbed was determined by substrate based ELISA. Cytotoxicity studies were performed using NIH3T3 mouse fibroblast cells.

Results: ESCA scans of plasma-treated substrates showed absence of substrate associated peaks implying that plasma coatings on substrates are at least 10 nm thick (coating thickness will be measured using AFM). Furthermore, experimental and theoretical elemental compositions of the surfaces align well. Moreover, AAc-AAm coatings were able to reduce protein adsorption by 50% compared to untreated controls, and were non-cytotoxic.

Conclusions: The preliminary data demonstrates that quasi-zwitterionic surfaces can be successfully created, reduce IgG protein adsorption and are non-cytotoxic. Further optimization is required to reduce protein adsorption further in order to create a new generation of materials that perform efficaciously as non-fouling surfaces.

11:20am **BI-ThM11 Titanium Films Deposited by HiPIMS for Medical Applications***, K. Thorwarth,* Empa, Switzerland*; S. Jin,* Sungkyunkwan University, Korea, Republic of Korea*; S. Gauter,* Christian-Albrechts-University Kiel, Germany*; **Joerg Patscheider,*** Empa, Switzerland

The metallization of polymer substrates by metallic titanium films provides many attractive applications, e.g. in biomedical applications. In contrast to conventional techniques in orthopaedic implants such as plasma spraying, which lead to a high thermal load of the substrates' surface and thereby to the undesired loss of surface structural feature, magnetron sputter deposited films maintain the surface topography of PEEK substrates

In this work Ti coatings were deposited on PEEK (polyether ether ketone) by chopped HiPIMS, a technique where HiPIMS pulses are decomposed into a sequence of short micropulses. The combination of these pulse trains distinctly influence the properties of titanium coatings prepared by this technique. The plasma was characterized using voltage/current measurements, optical emission spectroscopy and Langmuir probing, along with caloric measurements during deposition. The prepared coatings were examined using X-ray diffraction, scanning electron microscopy and X-ray photoelectron spectroscopy. It is shown that the pulse sequence is decisive for the applicability of Ti coatings on polymeric substrates, as it strongly influences properties such as process stability, deposition rate, morphology and thermal load during deposition, which can be improved with respect to standard HiPIMS and DC sputter deposition. The coatings' microstructure shows increased smoothening of the coating surface and shallower surface oxidation for samples deposited using chopped HiPIMS

Thin Films
Room Mauka - Session TF-ThM

Advanced Protective Coatings including Hard Coatings Exhibiting Toughness

Moderator: Grzegorz Greczynski, Linköping University, Sweden

8:00am **TF-ThM1 XPS Analysis of a Super-hard Material – Application of Ar Cluster Ions to Probe New Depths in Surface Analysis***, **David Surman,*** Kratos Analytical Inc.*; J. Counsell, S.J. Coultas,* Kratos Analytical Ltd., UK*; C. Moffitt,* Kratos Analytical Inc.*; C.J. Blomfield, A.J. Roberts,* Kratos Analytical Ltd., UK

Super-hard inorganic multilayers have emerged in recent times as a distinct class of material, currently used in coatings of cutting tools for machining and in the aerospace industry. There has been significant effort to develop new coatings due to increased need for wear protection and friction reduction.

One such material we will discuss in this work is a TiN/CrN superlattice consisting of alternating TiN and CrN layers of nanometer-scale, deposited by the means of the reactive magnetron sputtering technique. This superlattice has been studied previously, examining performance properties under stress and temperature and the mechanisms of wear [1,2]. This material has been shown to have high oxidation resistance as well as superior mechanical properties. The hardness, high wear resistance and inertness of transition metal nitrides has been attributed to the unique bond structure. Typically 12-52 layers are deposited in a lattice with the extent of alloying, contamination, and roughening all critical to the performance of the lattice. Also, as the layers thin there are distinct changes in crystallinity and alloying affecting the tribological properties. As expected, deposition is difficult due to differences in the heat of formation of CrN and TiN – they each require different partial pressures of N_2 to form stoichiometric coatings.

To explore the stoichiometry and the extent of alloying in a TiN/CrN superlattice, we have employed the traditional surface analysis techniques of ion etch depth profiling with XPS. It has been historically accepted that monatomic Argon will typically suffice for this process however in this presentation a comparison will be made between conventional monatomic Ar^+ ions and the more recent cluster Ar_n^+ ions. The choice of impinging ion will be discussed with respect to stoichiometry and blending as will the practicalities of the depth profiling experiment and analysis. A novel method is proposed for the analysis of these materials, free of erroneous results.

S. Gallegos-Cantú *et al.,Wear*, **330–331**, 2015, pp 439–447.

H. C. Barshilia et al., *J. Mater. Research*, **19**, 2004, pp 3196–3205

8:20am **TF-ThM2 Hydrogen Permeability of Hydrogenated Amorphous Carbons***, **Motonori Tamura,*** The University of Electro-Communications (UEC-Tokyo), Tokyo, Japan

Diamond-like carbon **(**DLC**)** is an amorphous carbon with a significant fraction of CC *sp^3* bonds. Tetrahedral amorphous carbon **(**ta-C**)** is the DLC with the maximum *sp^3* content. These hydrogenated amorphous carbons have been classified into several types, such as a-C:H and ta-C:H.

Films of a-C:H with the highest H content (40–60 at. %**)** can have up to 70% *sp^3*. However, most of the *sp^3* bonds are hydrogen terminated and this material is soft and has low density. Films of a-C:H with intermediate H content (20–40 at. %**)** have better mechanical properties. Even if these films have lower overall *sp^3* content, they have more C-C *sp^3* bonds. These films have the advantage of possessing high hardness levels –in the range of conventional tribological PVD coatings (1500 – 3200 HV), coupled with a coefficient of friction that is less than half of the conventional coatings.

In this study, hydrogen permeability of a-C:H films with intermediate H content was measured. Films were deposited by PVD + plasma-assisted CVD (PACVD) on stainless-steel substrates Type 316L. Hydrogen-permeation tests were performed on the coated stainless steel samples. These tests were based on the differential-pressure methods described in ISO15105-1:2007, the international standard for determination of gas-transmission rates.

The permeation of hydrogen through solid materials involves a series of steps including adsorption, dissociation, diffusion, and recombination coupled with desorption. In our experimental conditions, it was indicated from the relation between the permeation flux and driving pressure of hydrogen (100～800 kPa) that hydrogen passed through the samples in the diffusion-limited permeation mode.

Hydrogenated amorphous carbon films (2.0-mm-thick) were effective to reduce the rate of hydrogen permeation through stainless steel (0.1-mm-thick) less than 1/100 at 573-773 K. Effect of hydrogen content in films to hydrogen permeation behavior was studied.

8:40am **TF-ThM3 Mass Transport and Plastic Deformation in Refractory Nitrides via Density Functional Theory and Ab Initio Molecular Dynamics***, **Davide Sangiovanni,*** Linköping University, Sweden **INVITED**

Surface dynamics during film growth and mobility of defects such as vacancies, dislocations, and grain boundaries in bulk determine the properties and performances of refractory nitride thin films. *Ab initio* calculations, carried out at 0 K, provide useful information regarding adatom and admolecule migration on surfaces as well as defect formation and mobility in bulk. However, phase stability and mass transport are also strongly affected by lattice vibrations at finite temperatures. This results in molecular dynamics (MD) becoming the primary computational tool for evaluating the rate of thermally activated processes and revealing the occurrence of non-intuitive reactions. Estimating the rate of rare events via accurate, but computationally expensive, ab initio MD is a challenging task, thus requiring the use of acceleration techniques.

I present the results for mass transport and plastic deformation in transition metal nitride compounds and alloys determined via density-functional theory and ab initio MD. I show that lattice vibrations significantly affect adatom, admolecule, point-defect, and dislocation mobilities, with dramatic effects on surface reaction rates and bulk properties.

9:20am **TF-ThM5 Anticorrosion yet Conductive Hf Coatings on AZ91D Magnesium Alloy by Magnetron Sputtering***, **Zhoucheng Wang**, D.F. Zhang,* Xiamen University, China

Magnesium and its alloy are prone to corrosion due to the high electrochemical activity, although they are promising materials in electronics and aerospace industries . Surface coating technique has become an effective method to enhance the corrosion resistance of the Mg alloys. In addition to offering high corrosion resistance, the protective coatings should be conductive to avoid static buildup and maintain other advantageous properties when Mg alloy been used in the electronics and aerospace applications. In this study, anticorrosion yet conductive Hf coatings were fabricated on the AZ91D Mg alloys by magnetron sputtering with different bias voltages. The microstructure and corrosion behavior were investigated as a function of bias voltage range from 0 to -125 V. Both potentiodynamic polarization and neutral salt spray tests reveal that the Hf coating deposited at -100 V exhibits the best protective performance. It possesses the lowest corrosion current density of 1.032 mAc/m^2 and the highest protection rate of 6, respectively. This perfect anticorrosion property is due to the dense structure and low porosity induced by applying the appropriate bias voltage. The chemical inert Hf oxide formed on the coating's surface also contributes to improve the corrosion resistance. Various types of corrosion sites after corrosion tests are examined by scanning electron microscope (SEM) and energy-dispersive X-ray spectroscopy (EDS). The results indicate that the coating failure is determined by the synergy between the defects in coating and the random phase distribution in substrate.

9:40am **TF-ThM6 Effect of Oxygen on the Self-formation of Carbonaceous Tribo-layer with Carbon Nitride Coatings under a Nitrogen Atmosphere***, **Naohiro Yamada**, T. Takeno, K. Adachi,* Tohoku University, Japan

Carbon nitride (CN$_X$) is an expected coating material which shows high hardness and relatively low friction under a nitrogen atmosphere. These properties make it a good candidate for small precision machines in order to reduce energy consumption and material losses. We have already reported that a carbonaceous tribo-layer, whose structure is altered from that of the deposited coating, has been found on the worn surface of counterpart. Thus, a structural change of carbon is necessary condition for super-low friction. However, the outstanding properties cannot be achieved in the presence of oxygen or humidity, which has meant these coatings has not been used in practical applications under ambient air. In contrast, CN$_X$ coatings can give super-low friction under ambient air when they are heated to 100 ˚C. Besides, we have reported that hydrogen atoms derived from water molecules in a nitrogen atmosphere chemisorb the worn surfaces, which provides super-low friction. These results indicate that CN$_X$ coating has possibility to reduce friction and wear regardless of whether the nitrogen gas is mixed with oxygen and humidity. In this study, the effect of oxygen and humidity on friction and wear of CN$_X$ coatings are clarified in detail. The possibility of super-low friction under an oxygen-contained humid nitrogen atmosphere is discussed from the viewpoint of formatting carbonaceous tribo-layer.

The CN$_X$ coating is produced on the surfaces of SiC ball and disk using an ion beam assisted deposition system. We conduct a ball-on-disk friction and wear test in a glove box, which allows for control of the relative humidity (RH) and oxygen concentration within the range of 0.01-40 %RH and 0.01-25 vol.%, respectively.

When friction and wear tests of CN$_X$ coatings are conducted, friction coefficients and wear volumes increase with increasing RH (3-40 %RH) and oxygen concentration (0.01-25 vol.%). However, friction coefficients and wear volumes remain low values regardless of RH and oxygen concentration when CN$_X$ slides against hydrogenated-CN$_X$ (CN$_X$:H) coating. Besides, we found that CN$_X$ coatings gave specific wear rate below $3*10^{-8}$ mm^3/Nm when they achieved low friction coefficients below 0.05. These results indicate that there is a critical value of specific wear rate for formatting carbonaceous tribo-layer on the worn surfaces. TOF-SIMS depth analysis provides evidences that carbon derived from CN$_X$:H transfer to the surface of CN$_X$. This means that the carbonaceous tribo-layer is self-formed during friction. CN$_X$ slid against CN$_X$:H achieved low friction coefficient below 0.05 regardless of RH and oxygen on the condition that the carbonaceous tribo-layer is self-formed.

10:20am **TF-ThM8 Complex Stress Evolutions during Sputter-deposition of Metal Films: Interface Reactivity, Alloying and Phase Transformation***, **Gregory Abadias**, J. Colin, C. Furgeaud, A. Michel,* Institut Pprime, CNRS-Université de Poitiers, France **INVITED**

The understanding of morphological and microstructural development during thin film growth is of particular relevance to control islands shape, nucleation and growth of nanoparticles, phase transformation, texture or surface roughness. Due to oversaturated vapour fluxes employed in physical vapor deposition (PVD) techniques, dynamics usually prevails over thermodynamics in dictating growth and microstructural evolution in PVD films. Depending on the material type and process conditions, the film can develop different stress levels, evolving usually with film thickness. Recently, real-time wafer curvature measurements have contributed to increase our knowledge on the underlying mechanisms of stress development during growth, and to propose comprehensive physical models [1].

In this presentation, we will provide some examples of *in situ* and real-time diagnostics based on optical techniques (wafer curvature, surface differential reflectance spectroscopy) and electrical resistance measurements to probe with high sensitivity the early growth stages of a variety of metal films on Si during sputter-deposition. We will first review some typical compressive-tensile-compressive stress evolutions observed for high-mobility metals (e.g. Ag, Cu, Au) [2]. The influence of interface reactivity (using different buffer layers- SiO$_x$, *a*-Si or *a*-Ge) will be highlighted, and for the specific case of Cu, alloying with Ge (using co-sputtering) will be addressed.

In the second part of the talk, special focus will be placed on low-mobility metal systems (e.g., Mo, Ta, W) deposited on amorphous Silicon (a-Si), which exhibit a complex stress development with film thickness. In the case of Mo and Fe films, our *in situ* measurements reveal a structural transition at a film thickness of ~ 2-3 nm manifested by a concomitant tensile stress variation [3] and decrease in electrical resistance. Insights on the kinetics of the amorphous-to-crystalline phase transformation were gained from *in situ* synchrotron studies, coupling simultaneously X-ray diffraction, X-ray reflectivity and wafer curvature during sputter-deposition of a series of $Mo_{1-x}Si_x$ alloys.

[1] E. Chason, P.R. Guduru, J. Appl. Phys. 119 (2016) 191101.

[2] G. Abadias, L. Simonot, J.J. Colin, A. Michel, S. Camelio, D. Babonneau, Appl. Phys. Lett. 107 (2015).

[3] A. Fillon, G. Abadias, A. Michel, C. Jaouen, P. Villechaise, Phys. Rev. Lett. 104 (2010) 096101.

11:00am **TF-ThM10 First Steps Towards Accessing Aluminum's Far UV Reflectance for Space-based Telescopes***, **David Allred**, R.S. Turley, S.B. Perry, S.M. Thomas, S.G. Willett,* Brigham Young University, USA

We report on our progress on vacuum removal of protective layers on aluminum mirror surfaces using hydrogen plasmas and/or heating. One of NASA's flagship astrophysical missions of the 2020's or 30's will likely be a LUVOIR (large, UV-optical-IR) telescope. This space-based observatory will employ the largest mirrors ever flown. The reflective coating will almost certainly be aluminum since such telescopes would profit from truly broad-band mirrors. The top surface of such aluminum mirrors, however, need to be bare without the oxide layers that naturally form in air. (The local space environment for the observatory should be sufficiently oxygen-free that a pristine surface should remain bare for decades.) We will discuss our research into protecting as-deposited aluminum mirrors before atmosphere exposure with a robust, protective layer, or layers, that could be deposited to coat the aluminum immediately after its deposition, before it comes in contact with air, and cleanly and relatively easily removed once the mirror is in space. This removal must be gentle enough to not roughen the mirror surface nor redepositing material removed from the protec-tive layer on the mirror or other spacecraft components. Thus our choice of hydrogen plasmas. We will specifically discuss the deposition and removal of organic and inorganic (Cd-containing and Zn) films that were evaporated onto the aluminum immediately after its deposition. This could open up the 11-15eV band for space-based astrophys-ics without sacrificing IR, visible and UV reflectance.

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