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Structure and Morphology of the $Zn_x Mg_{1-x}O$ Nanowires Studied Using Shape Memory Composite Nano-tweezers

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***Abstract*— Nanowires (NWs), nano rods, nano whiskers are an important class of materials with the great potential for applied and fundamental basic research. The cross section of NWs is typically cylindrical, hexagonal, square, or triangular and is uniform with a high aspect ratio. Recently the new technology of 3D-nanomanipulation is proposed based on composite bimetallic structures with shape memory effect (SME). The present paper reports application of the new nano-tweezers system for experimental investigation of the individual nanowires of $Zn_xMg_{1-x}O$, which is the example of submicron-sized objects whose individual properties are difficult to study by standard methods. We describe the technology of preparation of $Zn_xMg_{1-x}O$ NWs, the process of the selection of individual NWs by composite nano-tweezers with SME in vacuum chamber of FIB device and experimental study of their structure and morphology by TEM.**

Keywords—nanowires; 3D nanomanipulation; nanotweezers; composites with shape memory effect; ZnO; Ti_2NiCu

I. INTRODUCTION

In the past 20 years, one-dimensional (1D) carbon nanotubes and semiconducting inorganic nanowires (NWs) have been extensively studied as potential building blocks for nanoscale electronics, photonic devices, optoelectronics, sensors, and energy producing devices due to their unique physical and functional properties [1-6]. Among nanostructures, nanowires (NWs) [7-9] are an important class of material that exhibit one-dimensional (1D) electrical properties and attractive optical properties with great potential for applied and fundamental basic research. NWs are usually single-crystalline, highly anisotropic with different functional properties, particularly promising in electronics, sensorics, photonics and solar energy.

As it was manifested in [10], NWs with flat end facets can be exploited as optical resonance cavities to generate coherent light on the nanoscale. Room temperature UV lasing has been demonstrated for the ZnO and GaN nanowire systems with epitaxial arrays [11], combs [12], and single nanowires [13, 14]. ZnO is wide bandgap semiconductors (3.37, 3.42 eV) suitable for UV-blue optoelectronic applications. The large binding energy for excitons in ZnO (~60 meV) permits lasing via exciton-exciton recombination at low excitation conditions. Well-faceted nanowires with diameters from 100 to 500 nm support predominantly axial Fabry-Perot waveguide modes (separated by $\lambda = \lambda 2/[2Ln(\lambda)]$, where L is the cavity length and $n(\lambda)$ is the group index of refraction owing to the large diffraction losses suffered by transverse trajectories [10].

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In the present work, we study the doping of ZnO with magnesium, which allows controlled increasing of the width of the forbidden zone from 3.37 eV (for ZnO) to 7.8 eV (for MgO) by increasing the concentration of Mg. The purpose of the present study is to demonstrate a simple method of producing arrays ("forest") of nanowires $Zn_xMg_{1-x}O$ with a high concentration of Mg by annealing ZnO vapor Mg. Another purpose of our work is to improve the technology of 3D manipulation of submicron objects based on composite shape memory nano-tweezers controlled by external heating in vacuum chamber of FIB device and to perform selection of NWs from the forest, harvesting, transportation into TEM vacuum chamber and detailed study of their morphology, crystallographic structure and composition.

2. $ZN_xMG_{1-x}O$ NANOWIRES FABRICATION

In the present study, we suggest a simple method of producing of arrays of nanowires $Zn_xMg_{1-x}O$ with a high concentration of Mg by annealing ZnO in the vapor of Mg. (See Fig. 1). Among the various wideband semiconductors, zinc oxide is one of the most promising for creating optoelectronic devices such as UV lasers. The main characteristic features of this materials are wide band gap (Eg ~ 3.37 eV at 300 K) and high exciton binding energy (60 meV at 300 K).

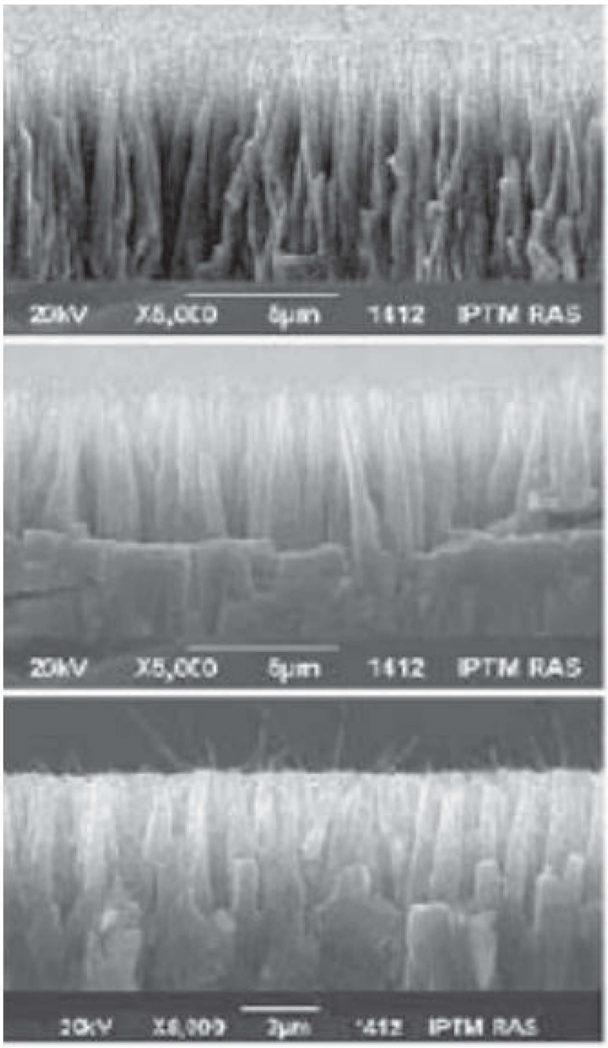

Fig. 1. SEM image of the forest of ZnxMg1-xO nanowires at different magnifications.

The doping ZnO with magnesium allows controlled to increase of the width of the forbidden zone with 3.37 eV (for ZnO) to 7.8 eV (for MgO) by increasing the concentration of Mg. The ionic radii of Mg^{2+} (0.57 Å) and Zn^{2+} (0.6Å) allows one to embed Mg in the crystal lattice without changing the crystalline structure in the nodes of the crystal lattice, replacing zinc.

As it can be seen on the Fig. 2, where SEM images at different magnifications are shown of the $Zn_xMg_{1-x}O$ NWs forest grown on the sustrate and processed by annealing in vapor of Mg, the dementions, morphology, end facet flatness are dispersed. The representatives of the NWs forest for further treatment and UV lasing application tests should be selected carefully. For the sake of a carefull selection of individual $Zn_xMg_{1-x}O$ NWs, the 3D nanomanipulation system based on comopsites nanotweezers with shape memory effect was applied [15-22].

II. 3D MANIPULATION SYSTEM BASED ON COMPOSITE NANOTWEEZERS WITH SHAPE MEMORY EFFECT

We report the experiments on utilization of a new 3D nano-manipulation method using bimetallic composite nano-tweezers based on a Ti_2NiCu alloy with shape memory effects to select and to manipulate individual $Zn_xMg_{1-x}O$ NWs.

Standard FIB processing was applied for the preparation of the nano-tweezers using thinned and strained Ti_2NiCu melt spun ribbon with shape memory effect as described elsewhere [15-22]. The FIB device used was a FEI Strata 201 equipped with an OmniProbe® or Kliendiek ® nano-manipulator. The nano-tweezers system on the tip of the OmniProbe® nanominipulator tungsten micro wire was controlled using distant heating control by laser radiation in vacuum chamber of FIB system or by resistive microheater placed on the tip of microwire of nanopositioning system. The temperature of the actuation is determined by Ti_2NiCu alloy martensitic transition and is close to 50-60 °C.

The process of the NW manipulation includes the following steps:

(1) The selection of the individual NW from the forest as shown on the Fig. 2. The controlled gap of the nano-tweezers is about 0.8 μm. The gap width and relative orientation of the nano-tweezers and the selected NW limit the choice of the NWs to be selected.

(2) The harvesting of the selected object (one or several NWs) and its separation from the environment. It often demands cutting of the part of the $Zn_xMg_{1-x}O$ NW by ion beam as shown on Fig. 3.

(3) The transportation of the selected individual object to the copper grid of TEM and attaching it by the Pt layer chemical vapor deposition (CVD) as shown Fig. 4.

(4) Study of the properties of the selected NWs by TEM JEOL JEM-2100, including composition, morphology, perfection of the end facets and crystallographic structure.

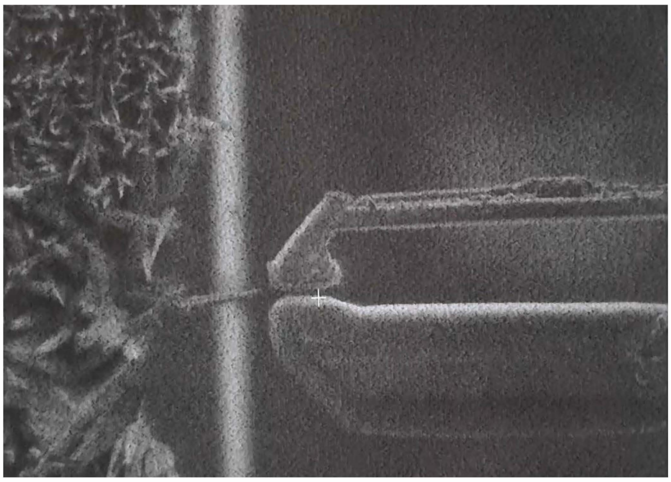

Fig. 2. The selection of the individual NW from the forest. The controlled gap of the nanotweezers is about 0.8 μm.

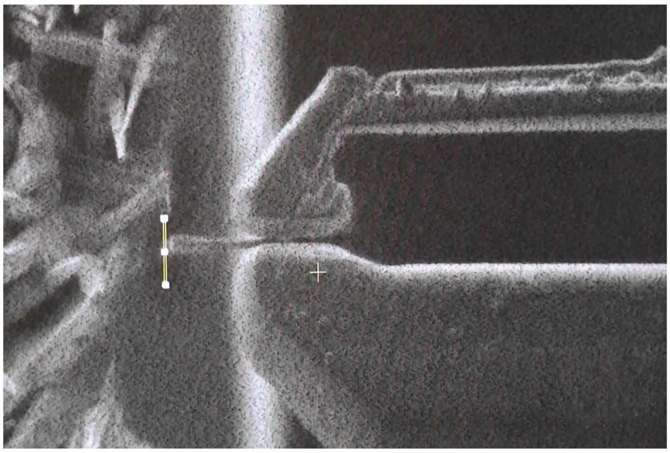

Fig. 3. The harwesting of the slected individual object and its separation from the invironment by cutting of the part of the NW by ion beam.

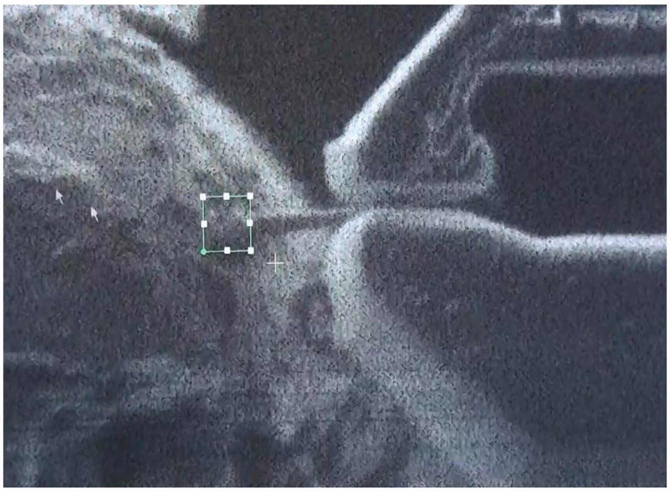

Fig. 4. The operation of ZnxMg1-xO NW attaching by Pt layer using FIB CVD to copper grid for further TEM study.

III. STRUSTURE AND MORPHOLOGY OF $\mathrm{ZN_XMG_{1\text{-}X}O}$ NANOWIRES

Figures 5 and 6 illustrate the results of the study of the ZnxMg1-xO NWs by HR TEM. The most of the samples of NWs that were selected by 3D manipulation from the forest have demonstrated the single crystalline structure with some quantity of defects and twins. The dimensions of the NWs are in the range: length 5-50 μm, diameter 100 – 1000 nm. The common morphology of the $Zn_xMg_{1\text{-}x}O$ NWs is cylindrical, conical and comparatively rarely dendrite.

The electron diffraction studies of the samples of $Zn_xMg_{1\text{-}x}O$ NWs in TEM usually demonstrate the single crystalline structure (Fig. 6). Structural twins sometimes disturb the pure crystallographic structure and defect arrays, which can probably affect optical properties in UV rang of 100 – 500 nm to be generated by $Zn_xMg_{1\text{-}x}O$ NW based laser.

TEM observation of the end facet of NWs often shows the non-regularities of its surface (Fig. 5). Composition measurements give information about common contaminations. Among them the thin Pt layers are the most pronounced, as it can be seen on the NW's surface on Fig. 5. This contamination is due to FIB assisted process of CVD deposition of the Pt layer for NW's attaching to the surface of the copper grid. This circumstance stresses the demand for further improvement of the system of 3D manipulation of NWs. In order to accomplish not only fundamental studies of the NWs, but also to go over to hybrid assembly of the NW based devices to IC and photonic structures, the clean, fast, automated and precise including also low price of the tools for 3D manipulation technology should be developed. One of the possible technological bases for such technology could be composite shape memory materials.

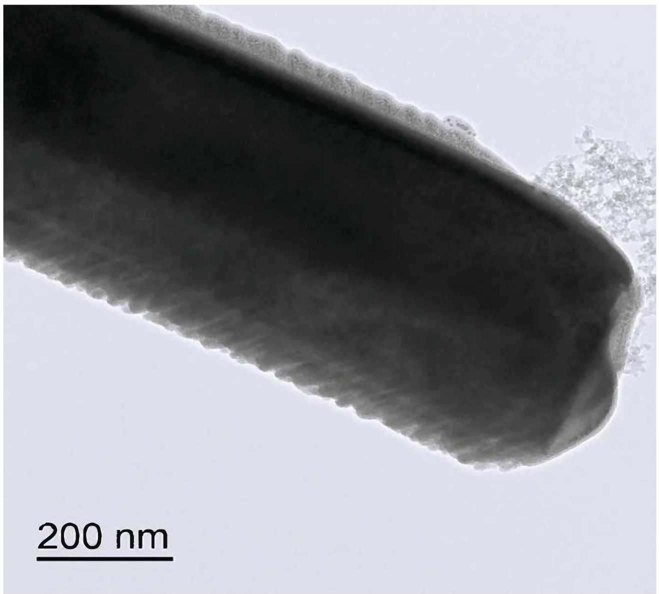

Fig. 5. The end facet of the $Zn_xMg_{1\text{-}x}O$ NW stuied by TEM. The thickness of the NW near end facet is about 400 nm.

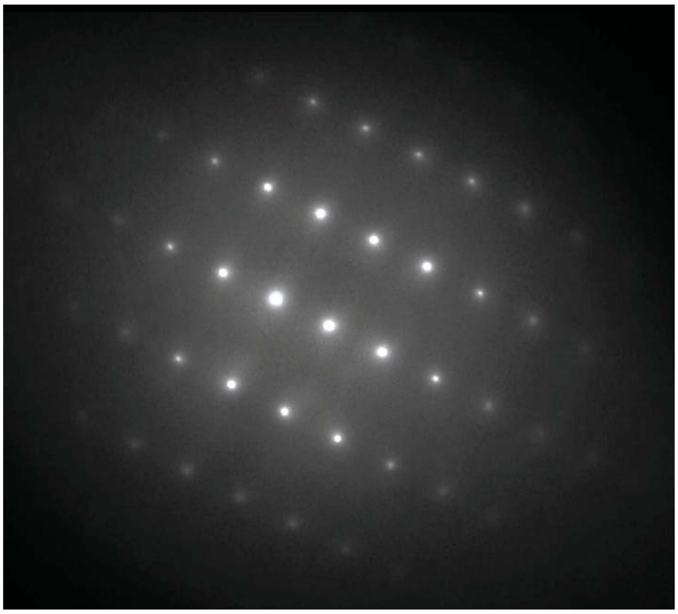

Fig. 6. The single crystalline structure of the $Zn_xMg_{1-x}O$ NW revilled by electron diffraction in TEM.

IV. CONCLUSION

We can conclude that in the present work we have performed the experimental study of the doping of ZnO with magnesium which allows controlled increasing of the width of the forbidden zone from 3.37 eV (for ZnO) to 7.8 eV (for MgO) by increasing the concentration of Mg. It was demonstrated that producing of the arrays of ZnxMg1-xO MWs with a high concentration of Mg by annealing ZnO vapor Mg allows growing forest of regular NWs with relatively perfect structure and shape.

Using the improved technology of 3D manipulation of submicron objects based on composite shape memory nano-tweezers controlled by external heating in vacuum chamber of FIB device there were perform selection NWs from the forest, harvesting, transportation to TEM vacuum chamber and detailed study of their morphology, crystallographic structure and composition. The most of the samples studied demonstrated single crystalline structure sometimes accompanied by the regular defect arrays and twins.

3D manipulation system based on shape memory composite nano-tweezers in vacuum chamber of FIB device have proved its flexibility and reliability. The selection of individual NWs, transportation and attaching to copper grid of TEM is accomplished routinely.

The continuation of the applied study of the possibilities of creating of UV nano lasers in wide range of wavelengths using $Zn_xMg_{1-x}O$ NWs is on the way. Further improvement of the 3D manipulation system can lead to the creation of production technology of UV nano lasers on the principle of top-bottom for the next generation optoelectronic and photonic devices.

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