



Luminescence of unfused 95%SiO₂–5%GeO₂ amorphous films with fluorine additive: No evidence for presence of GeODC(I) defects found

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ABSTRACT

Photoluminescence (PL) of unfused amorphous germanosilicate films with fluorine additive is studied in 2–8.5 eV spectral range. Experiments are based on films deposited on silica substrates by means of the surface-plasma chemical vapor deposition (SPCVD). Films of about 100 μm in thickness with “high F” (~4.2 wt.%) and “low F” (~0.5 wt.%) fluorine content have been fabricated for the experiments. KrF (248 nm), ArF (193 nm) and F₂ (157 nm) excimer lasers are used to pump PL. It is found that absorption and luminescence associated with germanium oxygen deficient centers (GeODCs) in “high F” and “low F” films differ. In the “high F” unfused film absorption coefficient of the band at 5 eV as well as intensity of the blue PL band at 3.1 eV are significantly greater. This film proves features of the so called GeODCs(II), which symbolize twofold coordinated germanium defects in silica network. In the “low F” unfused film absorption band at 5 eV is feebly marked. Poorly resolved PL intrinsic to GeODCs(II) can be detected in this film under the KrF laser pump. The most significant PL features are revealed under deeper UV pump by ArF and F₂ lasers. Spectral positions of PL bands excited by these lasers correspond to GeODCs(II). However PL decay kinetics dramatically differs from that one intrinsic to GeODCs(II). Noticeable growth of PL intensity caused by permanent (half an hour and more) exposure to ArF and/or F₂ lasers takes place, indicating GeODC(II) formation. It is found that considerable body of fluorine additive has the same effect as profusion for “low F” and/or fluorine free germanosilicate amorphous material synthesized by SPCVD. In the “high F” film yield of GeODC(II) PL pumped by the F₂ laser remains high. This speaks for the suppression of the competitive 7.6 eV absorption band associated with SiODCs(I) by fluorine additive indicating a decrease in the content of this type of defects in the material. High yield of GeODC(II) luminescence pumped by deep UV photons as well as hypothetical similarity of SiODC(I) and GeODC(I) permit one to conclude that GeODCs(II) are the only defects dominating in the materials under study.

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1. Introduction

Current investigation is aimed at search of experimental evidence of presence of germanium oxygen deficient centers in the form of GeODCs(I) in Ge-doped amorphous silica with fluorine additive. Under defect marked GeODCs(I), we shall imply all types of oxygen deficient imperfections associated with germanium in the glass network except twofold coordinated germanium, which unique name is GeODC(II).

Presence of the two types of oxygen deficient centers in pure silica denoted as SiODC(I) and SiODC(II) is testified by numerous experimental and theoretical studies. SiODC(I) defects are characterized by the absorption band at 7.6 eV and frequently appear as a result of sample preparation in oxygen deficient conditions [1]. Defects named as SiODC(II) are present in oxygen deficient pure silica in the form of twofold coordinated silicon [2].

Difference between SiODC(I) and SiODC(II) is based on diversity in spectral and kinetics parameters of photoluminescence (PL) bands associated with them. In particular, decay of the UV PL band associated with SiODC(I) is faster (see e.g. [1] and references therein). Other distinctive feature of SiODC(I) is the suppression of the 7.6 eV absorption band intensity by fluorine admixture to glass network [3–5].

Analogously to SiODC(II) a model for twofold coordinated germanium or GeODC(II) is developed for oxygen deficient centers in germanosilicate glass. The model is based on similarity of PL spectral, kinetics, and polarization characteristics of these defects to SiODCs(II). GeODCs(II) possess a blue band at 3.1 eV with the exponential decay time constant of about 110 μs [6] and a UV band at 4.3 eV with the decay time constant equaling 6–9 ns [7,8]. Polarization properties of SiODC(II) and GeODCs(II) PL bands are similar [2,6]. Both centers can be excited mainly via intra center processes, because of a low probability of inter center energy transport [9,10].

If we assume availability of hypothetical GeODCs(I) as an equivalent to SiODC(I), there should be corresponding manifestations of these defects observed. It could be an absorption band somewhere at 7.6 eV, which would be uncorrelated with the absorption band

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centered at 5 eV. Other manifestation would be the difference in decay kinetics of PL excited by 5 eV and by higher energy photons. We would expect to find out influence of fluorine admixture on absorption and luminescence in germanosilicate glass.

Our searching of the GeODCs(I) defects is based on absorption and luminescence measurements proceeded with unfused germanosilicate films containing fluorine additive. Amorphous materials under study are fabricated by means of the surface-plasma chemical vapor deposition (SPCVD) [11]. Specific feature of unfused germanosilicate films fabricated by this technology is the absence of manifestation of GeODCs(II) until profusion of deposited material [12]. Caused by profusion activation of GeODCs(II) is associated with the escape of chlorine contamination from the melt.

There are two significant features, brought by the addition of fluorine to SPCVD chemistry. Firstly, fluorine effectively replaces chlorine, which is an inevitable contamination for silica, if SiCl_4 is used as a raw material for deposition. Secondly, addition of fluorine to silica significantly reduces its softening temperature. For this reason heavily F-doped silica layer could be considered as fused material in conditions of deposition at substrate temperature of about 1100 °C [13].

2. Experimental

Samples composed as $\text{Si}_{0.95}\text{Ge}_{0.5}\text{O}_2$ in the form of 100 μm thick films are synthesized on high purity silica substrates. To produce fluorine doped material, high purity CF_4 is added to the gas mixture. Fluorine content in the glass is controlled by setting a ratio of SiCl_4 and CF_4 flows. Substrate temperature during the deposition is maintained at a level of 1100 °C.

Two kinds of samples are synthesized for the experiments. The “high F” with relatively high fluorine content amounting to 4.2 wt.% and the “low F” with smaller (0.5 wt.%) fluorine concentration. No post deposition annealing is applied to the samples.

ArF (193 nm wavelength), KrF (248 nm wavelength) and F_2 (157 nm wavelength) excimer lasers, model PSX-100 of Neweks (Estonia) are used to excite PL. For ArF and KrF lasers, pulse energy amounts to 5 mJ, whereas for the F_2 laser it is by an order of magnitude smaller. Pulse duration is 5 ns for all lasers. Samples are illuminated by unfocused beams ensuring predominance of one photon excitation. Luminescence emission is collected in a direction perpendicular to the exciting laser beam. Samples are carefully cleaned and mounted on a holder, no glue is used. Measurements are performed at 60–350 K sample temperatures. The lower temperature limit corresponds to the temperature of liquid nitrogen under pump. Luminescence and absorption measurement techniques are detailed in [12]. The errors of measurements estimated from a scatter of several registration runs typically do not exceed 5–10%. For the cases of small signals, the influence of PM noise and stray currents of excitation sources is marginally larger, which is reflected via corresponding error bars in the figures. In some figures the noise of the presented curves shows precision of measurements.

3. Results

Fig. 1 illustrates absorption spectra of the samples under study as well as intensity and decay time constant (τ) spectra of PL pumped by the KrF laser. Significant difference in the absorption spectra of “high F” and “low F” films in the vicinity of photon energy of about 5 eV is clearly seen. Absorption intensity there is low in “low F”. Measured optical density of the “high F” film in this spectral band is as high as 2, which is close to the detection limit of our spectrometer due to insufficient power of the light source used. The similar absorption band in the “low F” film is shifted to higher energy. Shapes of PL spectra of both samples are similar for the case of KrF laser, but PL intensity of “low F” sample is much smaller.

PL excited in the “low F” film by the ArF laser is quite a different story. PL intensity is very weak, although a growth of the blue PL

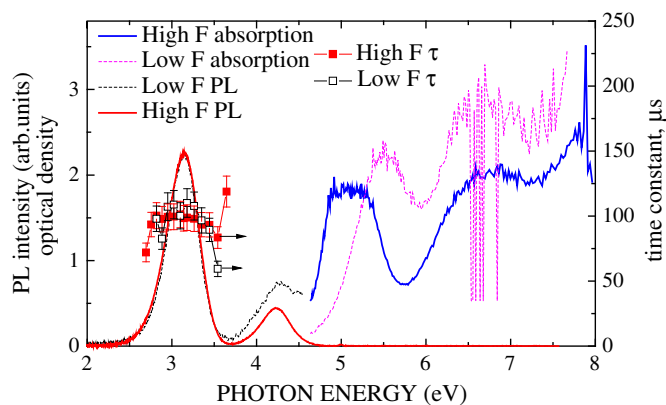


Fig. 1. Absorption, time average luminescence intensity and decay time constant (τ) spectra in germanosilicate films with different volumes of fluorine additive. PL is pumped by the KrF laser. The noise of the curves shows precision of the measurements. The lines between points are drawn as guides to the eyes.

band intensity under permanent laser exposure is clearly seen (see inset in Fig. 2). Decay kinetics is strongly non-exponential and happens faster than in the case of KrF laser excitation, Fig. 2.

The “high F” film spectra and decay kinetics of PL excited by ArF and KrF lasers are similar. Greater PL intensity for the “high F” film makes it possible to measure photoluminescence excitation (PLE) spectra for both bands of UV at 4.3 eV and blue at 3 eV, which are plotted in Fig. 3 together with PL and absorption ones for 293 K and 80 K. The effect of temperature is usual for germanium doped silica [6]. Temperature 293 K is better for the observation of the blue band and 80 K is better for the observation of the UV band. The spectra are very similar to already known (see e.g. [9]). Ratio of PLE and absorption spectra provides the spectrum of a relative quantum yield, which for the blue PL band is also depicted in Fig. 3. It is seen, that the peak of quantum yield spectrum in the vicinity of 5 eV is shifted to higher energies. That could be related to depopulation of the singlet excited state of the GeODC(II) over UV photon emission. Due to this process, the UV PL band pumped by the KrF laser decays faster (6 ns at 80 K) than that one pumped by the ArF and/or F_2 lasers (10–25 ns). Some increase of quantum yield at a bit higher photon energies in the vicinity of 5.5 eV is due to a greater transition probability to triplet state from higher vibration levels of the singlet state. At photon energies corresponding to the direct excitation of the triplet state (T_2) quantum yield is high, whereas efficiency of the UV PL band excitation is low. The highest efficiency of PL excitation in the vicinity of 7.6 eV testifies to the absence of non-radiation channels

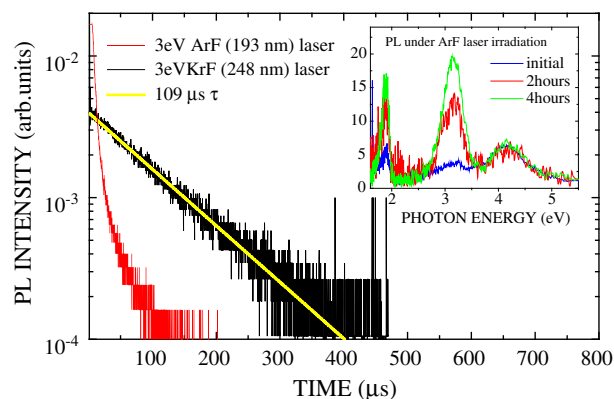


Fig. 2. Decay kinetics of the blue and PL bands excited by ArF and KrF excimer lasers in the “low F” germanosilicate film. Insertion illustrates growth of time average PL intensity resulted from permanent exposure to the ArF excimer laser. The noise of the curves shows precision of the measurements.

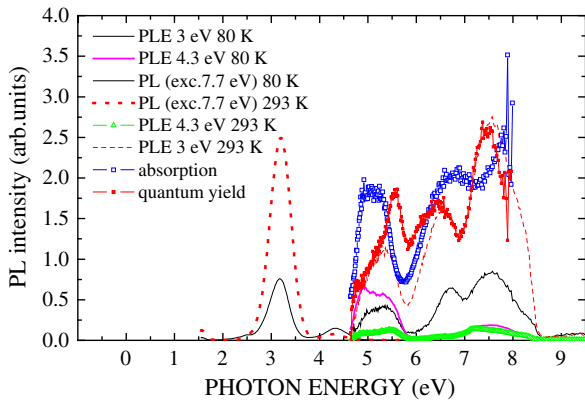


Fig. 3. Absorption, PL and PL excitation (PLE) spectra of the “high F” germanosilicate film. The noise of the curves shows precision of the measurements.

for excitation deactivation or to the presence of competitive pathway for exciting photon absorption.

Fig. 4 illustrates the decay time constants for UV and blue PL bands together with corresponding PL spectra excited by the ArF and KrF lasers in “low F” sample. If within the spectrum bandwidth of the blue PL band decay time constants are concentrated in a range in the vicinity of $105 \pm 10 \mu\text{s}$, the ones for the UV PL band are about 6 ns for KrF laser pump. The PL of “low F” sample under ArF laser is very weak and blue band is very fast (see below Fig. 6a). For the case of “high F” film excitation with ArF laser provides UV band with time constant about 25 ns and for the blue band the same $105 \pm 10 \mu\text{s}$ as in the case of KrF laser for both types of samples.

Time resolved PL spectra and corresponding decay time constants for PL bands pumped by the F₂ laser (157 nm) are presented in Fig. 5. The “high F” film emits blue PL with decay time constant of $110 \pm 10 \mu\text{s}$ for 293 K and 80 K temperatures. Decay time constant measured at the peak of the UV PL band amounts to $9 \pm 3 \text{ ns}$ and decreases when shifting to the higher energy side of the PL band. Spectral positions and decay time constants of the bands are typical for the GeODCs(II). Blue luminescence of the “low F” film is very fast, decay time constant being of $5 \pm 3 \text{ ns}$. Its position in the time resolved spectrum coincides with that one for the “high F” sample. The UV PL band in “low F” film is practically undetectable by the PMT operating in current regime. In time average spectrum recorded by CCD Hamamatsu mini-spectrometer only a trace of the UV PL band could be distinguished (not shown in Fig. 5).

Decay kinetics curves of the UV PL band in the samples under study are presented in Fig. 6a, b. Decay time constants are determined by convolution of a probe decay exponent with recorded pattern curve of the laser pulse. Measured curves are strongly influenced by

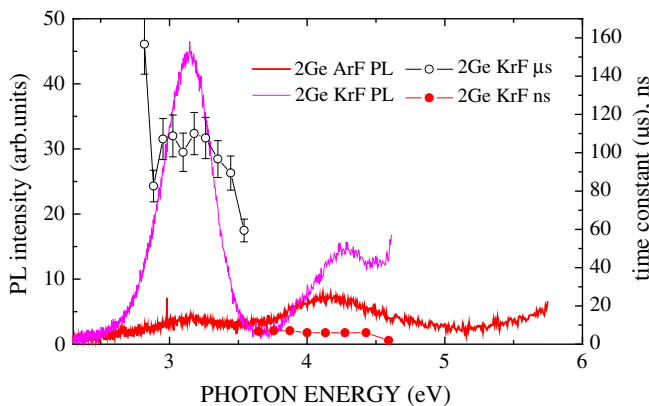


Fig. 4. Time average intensity and decay time constant (τ) spectra of PL excited by ArF and KrF excimer lasers in “low F” germanosilicate film (this sample labeled 2Ge). The lines between points are drawn as guides to the eyes.

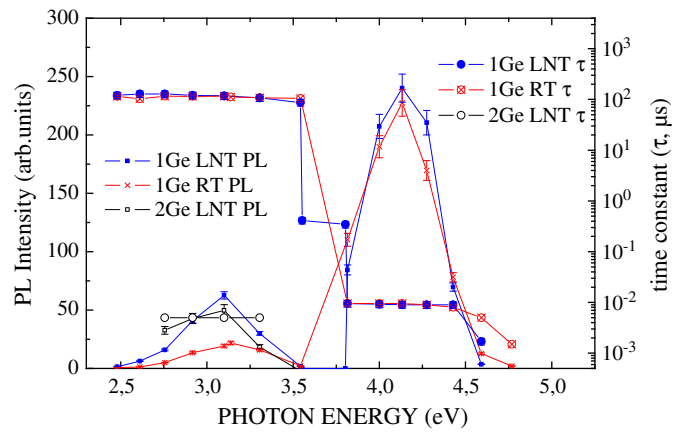


Fig. 5. Time average PL intensity and decay time constant (τ) spectra in “high F” (1) and “low F” (2) germanosilicate films pumped by the F₂ laser pulses. The lines between points are drawn as guides to the eyes.

noise pick up caused by electric discharge in a laser cavity. Magnitude of time constant is estimated by the probe exponent, which provides best match to the recorded decay curve when convoluted with the pattern curve. The decay in the case of ArF laser excitation in the “low F” sample is very fast and is below limit of determination of decay time constant that is below 0.5 ns and that takes place within whole luminescence of the “low F” sample including blue range, Fig. 6a. In Fig. 6b the kinetics curves are shown for that case of KrF laser excitation. In this case the time constants of the “low F” and the “high F” are on the same level – 6 ns at 80 K and about 2 ns at 293 K.

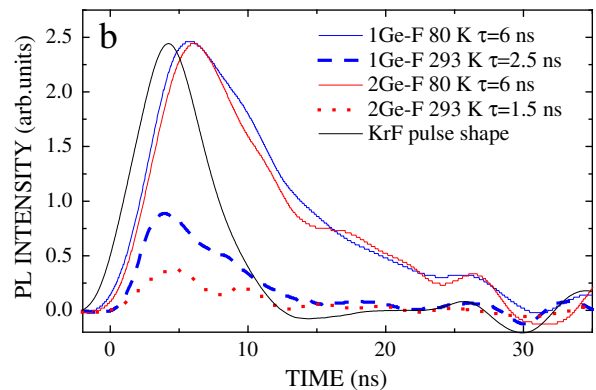
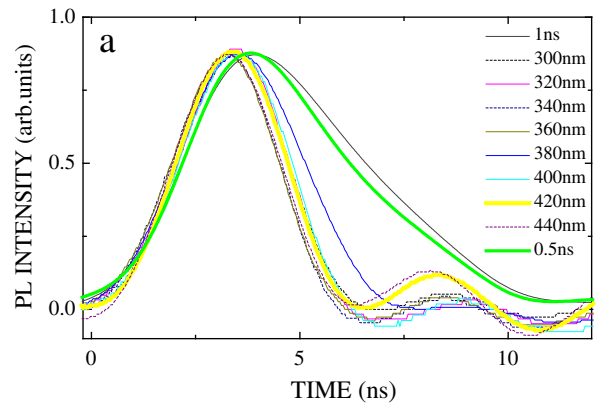


Fig. 6. The bending decay curves are due to the stray current induced by laser discharge and that determines precision of the measurements. a). UV band PL decay curves at different wavelengths. Excitation with ArF laser (193 nm) of the “low F” germanosilicate film. b). Excitation with KrF laser (248 nm) of the “low F”(2) and “high F” (1) germanosilicate films at different temperatures. UV band PL decay curves.

Fig. 7 shows temperature dependence of PL intensity excited in the “low F” sample by passed through a vacuum monochromator 7.7 eV photons of a hydrogen discharge light source. Measurements are performed with the help of the PMT in a photon counting mode. This dependence looks similarly to the process of self-trapped hole thermal release [14] that permits one to suppose that the origin of this dependence is associated with a recombination process. It should be noted that for the “high F” sample this dependence is much weaker.

4. Discussion

Specific feature of unfused germanosilicate films formed by oxidation of silicon and germanium tetrachloride vapors in dry SPCVD process consists in the absence of any spectroscopic manifestation of GeODCs [12]. Effect mentioned above is associated with the termination of the GeODCs by chlorine atoms inevitably contaminating amorphous silicon and germanium oxides synthesized by SPCVD. As a result absorption and luminescence activities are terminated by chlorine. GeODCs stay in a latent state, in which they can provide only short living luminescence after permanent irradiation by the ArF laser. Profusion of the material is accompanied by chlorine outcome and leads to uprising of absorption and bright luminescence band characteristic for the GeODCs.

To a great extent the similar behavior is observed for the “low F” sample. The GeODC PL bands arise only as a result of permanent irradiation by the ArF and/or F₂ lasers. The only difference is that GeODC PL in the “low F” sample can be excited by the KrF laser with decay time constant of about 100 μs for the blue PL band and a few ns for the UV one. This PL intensity remains unchanged after permanent exposure to the KrF laser. Contrarily, the ArF laser excites the blue PL band, which decays faster via a drastic non-exponential manner. The F₂ laser excites only very fast blue PL band in the “low F” film and a weak UV band undetectable against noise pickup caused by an electric discharge in a laser cavity. However, time average PL of both blue and UV bands is observed with the help of the Hamamatsu mini-spectrometer.

In the “low F” unfused film substitution of chlorine by fluorine acts similarly upon PL properties of the GeODCs. Faster decay of PL excited by the KrF as compared to ArF and F₂ lasers is explained by the presence of fluorine in the vicinity of GeODCs. Photon energy of the KrF laser appears to be insufficient for detachment of fluorine atoms. On the contrary photons of the ArF and F₂ lasers are able to do that thus preventing the effect of fluorine proximity on the singlet–singlet transition probability.

In the case of the “high F” sample typical for GeODC(II) blue band with time constant of $110 \pm 10 \mu\text{s}$ is observed under the excitation by all three excimer lasers. This means that triplet–singlet transition probability appears to be weakly affected by neighboring fluorine. Decay time constants measured for the UV band amount to $6 \pm 1 \text{ ns}$ for KrF,

10–25 ns for ArF and 9 ns for F₂ lasers. This permits one to conclude that the main impact of a high content fluorine admixture consists in a decrease of softening temperature so that fabricated by SPCVD material can be considered as fused. Excitation of GeODC(II) PL by the F₂ laser as well as by high energy photons of the deuterium discharge light source takes place with the same quantum yield as it does by 5 eV and 6.5 eV photons. No shortening of PL decay process when switching excitation from KrF to F₂ lasers is observed, which could be presumed if hypothetical GeODC(I) exists. Contrarily, even shorter decay of the UV PL band excited by the KrF laser is observed (Figs. 4 and 6b). Possible origin of this effect is related to fluorine interaction with GeODCs(II). Features of PL mentioned above testify to the absence of SiODCs(I) in fluorine containing samples as well as hypothetical GeODCs(I), which could influence PL characteristics in the spectral band in the vicinity of 7.6 eV. Fluorine is known to suppress SiODCs(I), our observation speaks to the absence of the GeODCs(I) either (see Fig. 8). Indeed, in fluorine free sample the PLE band in the range of 7.6 eV (position of the SiODCs(I)) is smaller than that in the fluorine containing sample. Fluorine leads, because of passivation of the SiODCs(I), to increase germanium related luminescence, which after decay kinetics is the luminescence of GeODCs(II), as mentioned above. The GeODC(I) is absent in fluorine-free SPCVD fused germano-silicate sample. That we can prove by comparison of the decay kinetics of UV band in fluorine-free fused sample [12] and fluorine containing unfused sample, object of this article, Fig. 9. The decay in those samples are similar within noise, therefore hypothetical shortening of that decay presumed for GeODC(I) in fluorine-free sample, when excited at 7.6 eV, was not observed. So, we conclude that GeODC(I) does not exist at all.

5. Conclusion

Based on the results of experiments we can conclude that addition of 4.2 wt.% of fluorine to germanosilicate films fabricated by SPCVD technology leads to the formation of GeODCs(II) without subsequent profusion of the deposited material. We attribute this effect to viscosity decrease of germanosilicate glass caused by addition of considerable body of fluorine, which makes it already melted at typical for the SPCVD substrate temperatures. Smaller concentration of fluorine additive is not sufficient for the development of the typical GeODC(II) PL bands.

Similar to pure silica fluorine admixture is found to decrease intensity of the absorption band attributed to SiODCs(I). We did not find any evidence for the presence of hypothetical GeODCs(I) in samples with fluorine. This allows us to conclude that the absorption

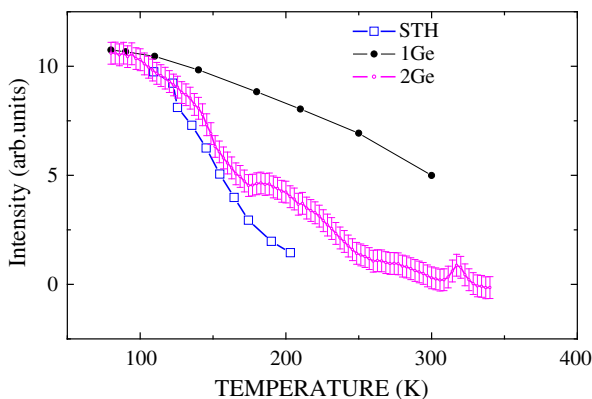


Fig. 7. Temperature dependences of PL intensities excited by 7.7 eV photons in “high F” (1Ge) and “low F” (2Ge) samples as well as self-trapped holes ESR signal taken from [14]. The lines between points are drawn as guides to the eyes.

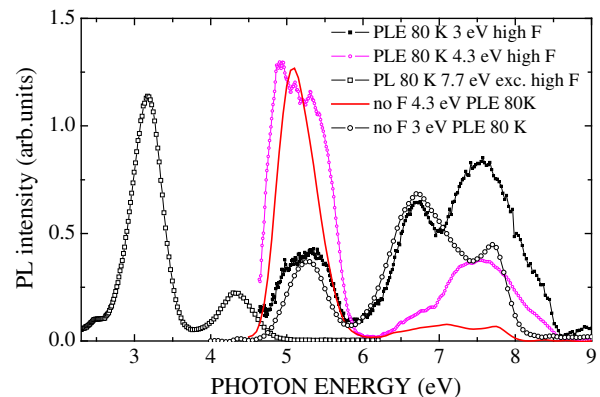


Fig. 8. PL excited at 7.7 eV and PLE spectra for 3 eV and 4.3 eV PL bands of SPCVD germanosilicate films with (unfused, high F) and without fluorine (fused, no F) additive. The noise of the curves shows precision of the measurements. Presence of fluorine removes absorption band of SiODCs(I) at 7.6 eV and enhances PL excitation efficiency of GeODCs(II).

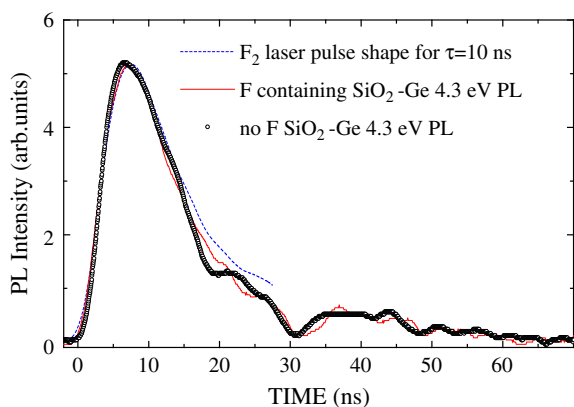


Fig. 9. PL at 4.3 eV decay kinetics of SPCVD germanosilicate films with (unfused) and without fluorine (fused) additive at 80 K under F_2 laser (157 nm) excitation. The shape of laser pulse convoluted with exponent with time constant 10 ns is presented for comparison. The bending decay curves are due to stray current induced by laser discharge and that determines precision of the measurements.

band centered at 7.6 eV in germanosilicate glasses is totally associated with SiODCs(I).

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