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# Photoluminescence of Se-related oxygen deficient center in ion-implanted silica films

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## ABSTRACT

The results of low-temperature time-resolved photoluminescence (PL) investigation of thin SiO<sub>2</sub> films implanted with Se<sup>+</sup> ions are presented. The films demonstrate an intensive PL band in the violet spectral region, which is attributed to the triplet luminescence of a new variant of selenium-related oxygen deficient center (ODC). The main peculiarity of the defect energy structure is the inefficient direct optical excitation. Comparison with spectral characteristics of isoelectronic Si-, Ge- and SnODCs show that the difference in electronic properties of the new center is related to ion size factor. It was established that the dominating triplet PL excitation under VUV light irradiation is related to the energy transfer from SiO<sub>2</sub> excitons. A possible model of Se-related ODC is considered.

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## 1. Introduction

Amorphous silicon dioxide (SiO<sub>2</sub>) and its low-dimensional modifications are of technological importance in the growing fields of optoelectronics and photonics [1]. Complex silica-based functional materials, including structures containing semiconductor quantum dots, are often created by means of ion implantation. Required compatibility with the current technology in the semiconductor industry induces an extensive research on Si-based emitting materials in which photoluminescence (PL) properties of Si-, Ge-, and Sn-implanted SiO<sub>2</sub> layers were studied [2–4]. Such ion-beam synthesis is inevitably accompanied by generation of point defects which affect the optical properties of the host matrix. However detailed information concerning the point defects nature and energy parameters is required in order to understand the regularities and mechanisms of optical properties formation for SiO<sub>2</sub>-based structures [5].

The majority of group IV elements: silicon (Si), germanium (Ge) and tin (Sn) are known to form ODC-type defects in SiO<sub>2</sub> matrix. Among the optically active defects the most studied are silicon and germanium oxygen deficient centers (SiODC and GeODC) [5]. The models of neutral oxygen vacancy ≡Si–Si≡ (≡Ge–Ge≡) and twofold-coordinated silicon =Si: (germanium =Ge:) had been proposed for them. Though the former model has not been totally disproven, the latter is now chosen by the most of authors [6]. The principal optical bands related to these defects refer to the so-called B-type

activity, consisting of an optical absorption (OA) band, centered at 5 eV, and of two photoluminescence (PL) emissions centered at 4.2–4.4 and 2.7–3.1 eV [6]. A similar optical activity is also present in Sn-doped silica and has been attributed to SnODC centers [2,3,8–10]. Some authors have shown that the UV optical absorption (OA) of Sn-doped silica is dominated by a band peaked at 4.9 eV, which excites two photoluminescence (PL) emissions at 4.1 eV, decaying in few nanoseconds, and at 3.2 eV, decaying in few microseconds [8–10]. The overall B-type activity has been associated with a single structural model: the twofold coordinated atom also indicated as =Sn: [6].

Thus the oxygen deficient centers of the isoelectronic series (Si, Ge and Sn) demonstrate similar spectroscopic and structural features. But is this list exhaustive? Though this group of elements contains also the carbon (C) and lead (Pb), they are not presently known to form ODC-type defect. The Pb atom seems too large and heavy (207 amu) to substitute silicon in the silica lattice, while carbon may react with silicon and oxygen to form stable compounds and therefore it is unlikely to create substitution defects. Nevertheless one might imagine the existence of ODC-defects modified by atoms having electronic configuration different from that of IV group elements. The aim of the present work is detection and investigation of the ODC-type defects formed during selenium ion implantation in thin SiO<sub>2</sub> film.

## 2. Materials and methods

Time-resolved PL spectra in the region of 1.5–6.0 eV, time-resolved PL excitation spectra (3.7–18.0 eV) and the PL decay

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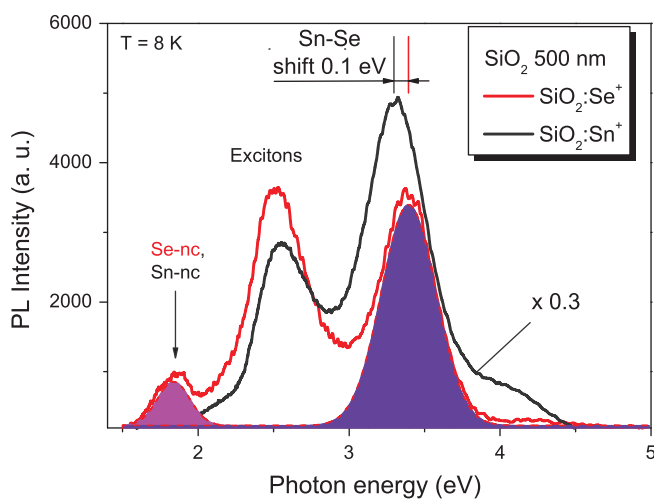
E-mail addresses: [a.f.zatsepin@ustu.ru](mailto:a.f.zatsepin@ustu.ru), [zats@2-u.ru](mailto:zats@2-u.ru) (A.F. Zatsepin)

kinetics were measured at room and low temperatures using synchrotron radiation (SR) on a SUPERLUMI station (Beam-line I, HASYLAB, DESY). Samples were mounted in a sample holder attached to a He-flow cryostat with vacuum not less than  $7 \times 10^{-10}$  Torr. At the storage ring DORIS the full width at half maximum (FWHM) of SR pulses was 130 ps with the repetition period of 192 ns. The 2 m vacuum monochromator (Al-grating, spectral resolution 3.2 Å) was used to excite of the PL in 3.7–18 eV range. The 0.3 m ARC Spectra Pro-300i monochromator equipped with either R6358P (Hamamatsu) photomultiplier was used as a registration system. Time-resolved PLE spectra were measured in two independent time spans  $\Delta t_1 = 21$  ns (the fast component) and  $\Delta t_2 = 72$  ns (the slow component), which were delayed relative to the beginning of the SR-excitation pulse for  $dt_1 = 3.7$  ns and  $dt_2 = 101$  ns respectively. Time-integrated (TI) spectra were recorded within the full time range available between two sequential excitation pulses (192 ns). The excitation spectra were normalized to the same number of SR-exciting photons using sodium salicylate. The PL emission spectra were not corrected to the spectral sensitivity of the recording system.

As samples we have used amorphous, thermally grown  $\text{SiO}_2$  layers, 500 nm thick, wet oxidized at 1100 °C on a crystalline Si substrate. The ion implantations of  $\text{Se}^+$  were performed with energy of 330 keV, with a uniform dose of  $5 \times 10^{16}$  ions/cm<sup>2</sup>. This implantation energy and dose led to an atomic dopant fraction of about 4 at% at nearly the half depth of the oxide layers. The  $\text{Sn}^+$ -implanted samples with similar characteristics (400 keV,  $5 \times 10^{16}$  ions/cm<sup>2</sup>) were used as a reference. A post-implantation thermal annealing for both types of samples was performed at temperature  $T_a = 900$  °C for 1 h in dry nitrogen. An additional 1 h air annealing at 500 °C was applied to selenium-implanted films in order to investigate the oxidation processes.

### 3. Results

The ion-implanted and once annealed  $\text{SiO}_2:\text{Se}^+$  and  $\text{SiO}_2:\text{Sn}^+$  samples show similar sets of PL bands at the 1.5–3.8 eV region (Fig. 1). The most pronounced maxima for selenium-implanted samples are 2.5 eV (green band) and 3.4 eV (violet band) ones. The violet band demonstrates a weakly pronounced fine structure containing equally spaced oscillations, intensity of which in the time-integrated spectrum, however, is higher than the noise level.



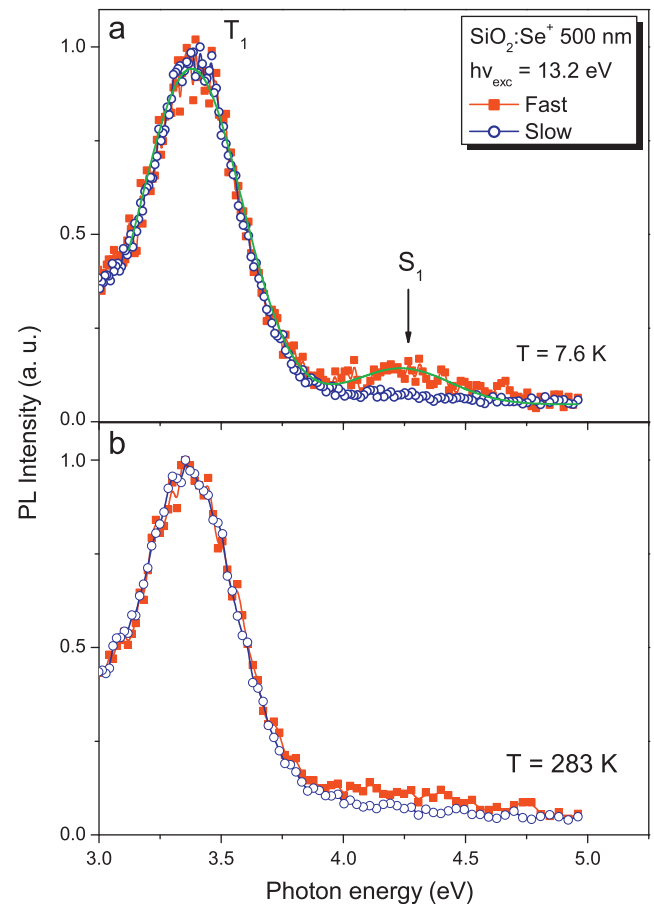
**Fig. 1.** Time-integrated PL spectra of  $\text{SiO}_2:\text{Se}^+$  films annealed at  $T=900$  °C in  $\text{N}_2$  atmosphere registered under 13 eV excitation. Deconvoluted Gaussian components are denoted by dashed lines. A reference spectrum of  $\text{SiO}_2:\text{Sn}^+$  film (annealed at  $T=900$  °C in  $\text{N}_2$ ) is shown by black line. (For interpretation of the references to color in this figure, the reader is referred to the web version of this article.)

These oscillations may correspond to the vibronic states of the luminescent defect.

Besides, there are some weak peaks in the 1.7–2.0 spectral range that may be related to the selenium and tin nanoclusters [2]. In principle, there might be another interpretation of the long wavelength bands appeared due to the possible interactions of synchrotron radiation with the  $\text{SiO}_2$  matrix. For example, the band around 1.9 eV is often observed in silica and related to nonbridging oxygen hole centers (NBOHC). Messina et al. [7] have demonstrated that NBOHC may be induced by vacuum UV synchrotron radiation. Determination of their nature requires a detailed research and goes beyond the scope of the present study.

Gaussian deconvolution of the green band reveals two components (2.5 eV and 2.6 eV bands having different halfwidths) responsible for its nonelementary shape. The components may be ascribed to the photoluminescence of self-trapping excitons [11–13], silica point defects or impurity-related centers [8,14]. Contrary, the violet band has truly Gaussian profile. The latter band is implanted ion-specific: as compared to tin-containing films one can observe a 0.1 eV spectral shift of the violet band from 3.3 eV to 3.4 eV in selenium-implanted ones.

The fragment of time-resolved spectra in the 3–5 eV region is shown in Fig. 2. The fast component of spectrum dominates over the slow one in the 4–4.75 eV range, indicating the existence of a weak 4.26 eV band with nanosecond-order kinetics. This maximum loses its intensity with growing temperature (see Fig. 2a, b). At low temperatures the PL lifetime of the 3.4 eV band is more than 200 ns. The room temperature measurements reveal a complex PL decay law for the violet band under high energy excitation



**Fig. 2.** Time-resolved PL spectra of the  $\text{SiO}_2:\text{Se}^+$  films at helium (a) and room (b) temperatures recorded under 13.2 eV excitation. The fast and slow components of PL spectra have been normalized to compare their shape.

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