Low Temperature Photoluminescence of SiO₂ Films Implantated With Sulfur Ions

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Ion implantation in general leads to structure modification and therefore to the occurrence of new luminescent and non-luminescent defect centers in the host matrix. It can be used as a tool for the tuning of functional characteristics of SiO₂-based materials for optoelectronic and photonic devices. The role of intrinsic (Si, O) ions implantation on thin film silica luminescence properties have been extensively studied (see, for example [1, 2]). Implantation of extrinsic elements with similar electronic structure could shed the light on emission centers formation mechanisms. The present work is devoted to investigation of S⁺-implanted SiO₂ films luminescence, determination of luminescence centers formation regularities as well as their influence on energy structure of the material.

The objects of study were thin “wet” SiO₂ films synthesized by silicon thermal oxidation (500 nm). All measurements were carried out at T = 9 K. The steady-state (Stat) and time-resolved photo luminescence (PL) spectra, the PL decay kinetics were measured under selective VUV-excitation at SUPERLUMI station (beam-line I). The primary monochromator with Al-grating had a typical spectral resolution of 3.2 Å. The PL spectra was measured using a 0.3-m monochromator model ARC Spectra Pro-308i and an R6358P photomultiplier (Hamamatsu) in two time spans Δt₁ = 16 ns (the fast component) and Δt₂ = 69 ns (the slow component), which were delayed relative to the beginning of the SR-excitation pulse for δt₁ = 3.3 ns and δt₂ = 16 ns respectively. Excitation spectra were normalized to the same number of SR-exciting photons using sodium salicylate.

The PL spectra of the unirradiated films include several ODC bands at 2.5-3.5 and 4.3-4.5 eV, usually observed for SiO₂ glass and films [3]. After implantation of S⁺ ions (the fluence of 5·10¹⁶ cm⁻² and the energy of 150 keV) and subsequent annealing (900°C, 1 hour), the luminescence properties of the samples under study change considerably. The most intensive band appears at 2.8 eV (Figure 1). Its excitation spectra (Figure 2) have a complex shape but mostly rises starting from 9 eV. Low-intensity maxima within the SiO₂ optical transparency gap correspond to matrix point defects. Peaks at 10 and 11 eV are in the excitons part of the spectrum. It should be noted that after a year of storage in air ambience the implanted samples show excitation spectrum degradation. Such behavior is probably due to gradual oxidation and passivation processes. PL decay kinetics measured for 2.8 eV peak show microsecond kinetics in the entire excitation range except the 4.3 eV band demonstrating single monoexponential component with τ = 18.5 ns. This band also exhibits equidistant oscillations with the step ΔE = 0.05 eV (see inset graph on Figure 2).

![Figure 1](image1.png)  
**Figure 1:** PL spectra for implanted SiO₂:S⁺ films recorded under different excitation energies hvexc.

![Figure 2](image2.png)  
**Figure 2:** PL excitation spectra of 2.84 eV band for measured two times after a year-long delay.
Along with the PL band described, the 1.75-1.9 eV maximum appears under 9.9 eV excitation which match known wavelengths for surface and bulk non-bridging oxygen hole centers (NBOHCs) [4]. Contrary to O+ ions that are native for oxide matrix, sulfur ones create more complex excitation pattern. The explanation would be as follows: during the annealing extrinsic S+ ions form sulfur nanoinclusions which introduce additional point defects at the nanocluster-silica interface. These defect states are capable of low-intensity excitation maxima creation within the SiO2 band gap. As it was shown in the work [5], the absorption band with a maximum at 4.4 eV has a resolved vibrational structure and is assigned to the S2 molecules weakly bound to the SiO2 network. Later in [6] the same luminescence was attributed to S2+ ion because the locations of the vibrational lines and their mean vibrational frequency for this ion are in better agreement with experimental ones. Exact coincidence of our oscillations period ΔE with the value obtained in [5, 6] further proves sulfur nature of luminescent center observed. The fast kinetics of this peak also suggests direct intracenter excitation character, while at higher energies the indirect excitation takes place.

The most interesting effect of the ion implantation is appearance of high-energy excitation bands. Similar peaks were observed for oxygen-implanted silica film [2]. Thus the luminescence in 2.4 – 3.2 eV region together with 9 – 10 eV excitation seems to be present regardless of the implanted ion type, at least for VI group elements. VUV excitation is capable of free excitons creation followed by either self-trapping or nonradiative relaxation. According to [4], such synchrotron radiation leads to O-H bond breaking and excited NBOHC formation. Such assumption agrees well with 1.9 eV band appearance under hνexc > 9 eV. Indeed, wet silica itself can have considerable hydrogen concentration, and subsequent ion implantation should further supply some amount of OH groups. Remaining portion of self-trapped excitons transfer their energy to S-related centers and emits light with 2.5-3.2 eV spectrum. The superposition of relaxation processes described results in nonelementary shape of 10 eV excitation maximum (Figure 2).

Thus sulfur-implanted samples in their comparison with oxygen ones allowed clear discrimination of implant-dependent, defect- and exciton-related emission. However the set of low-energy excitation within the silica band gap remains a subject for future investigations.

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References