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E-beam induced damage in SiO_2–Ge crystalline α-quartz, comparison with silica glass

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Abstract

Electron beam induced transformation in crystalline α-quartz doped with germanium was studied by mean of cathodoluminescence and of phase shift interferometric microscope. E-beams with low current (below 50 nA), defocused (diameter of spot about 40 μm) and with acceleration energy of 15 kV produce swelling of the irradiated volume about 100 nm above the non-irradiated surface. The luminescence of the self-trapped near germanium exciton (GeSTE) is observed mainly. No luminescence of the germanium related oxygen deficient center with bands at 290 and at 395 nm, usual for Ge-doped silica glass (GeODC), was observed. Defocused e-beam with higher current (about 200 nA), the same energy and similar dose, produces depression about 100 nm deep. In this case, we observed the band at 280 nm typical for SiODC in pure silica glass in the same time than the GeSTE already appearing for low current. However, we could not detect the band at 460 nm also typical for SiODC. It was, probably, obscured by the intensive band of GeSTE. We deduced that high density e-beam produces glass-like phase in the irradiated volume of α-quartz exhibiting the luminescence characteristic of pure silica glass. We explain, the absence of both bands related to GeODC in glass-like phase by a disappearance of germanium from this phase under irradiation.

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1. Introduction

The use of germano-silica core in telecommunication optical fibers stimulated the need of complete fundamental understanding of all the properties of complex system such as germano-silicate glasses. Clear picture of the germanium behavior is not yet achieved. It should include knowledge about geometric and energetic structure, photostimulated transformation, etc.

Germanium impurity in crystalline and glassy SiO_2 creates luminescence centers and it is thus fruitful to compare the luminescence properties of these materials to better understand the nature of these centers.

The luminescence properties of germanium centers in silica and germano-silicate glasses never resemble the one in SiO_2 or GeO_2 crystals with α-quartz structure [1]. The Ge related center luminescence in glasses is mainly connected to oxygen deficiency. The luminescence excitation spectrum of germanium related oxygen deficient center named GeODC began at 3.6 eV (triplet–singlet transitions) with a strong band at 5 eV (singlet–singlet transition) [2]. The luminescence spectrum contains two bands: a blue one with maximum at about 3.15 eV and an ultraviolet (UV) band at 4.3 eV. Both bands are polarized when the excitation is done with polarized light. The blue band polarization changes sign with change of excitation energy. The structure of the center is a twofold coordinated germanium [2].

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The α-quartz doped with Ge possesses optical absorption threshold at 7.5 eV and the luminescence excitation bands are started there as well. There is only one luminescence, it exhibits large band with strong Stoke's shift and is located at 2.3 eV. Its properties are very similar to those of self-trapped exciton (STE) in pure silicon dioxide or germanium dioxide crystals with the structure of α-quartz [3]. We deal thus in any case with STE in tetrahedral lattice. The structure of the STE could be imagined as Si(Ge)–O bond rupture with following relaxation of non-bridging oxygen toward a bridging oxygen situated on opposite site of *c*-channel or *x*, *y*-channel. So, in spite of possible existence of oxygen deficiency in crystal, we never observed glass-like luminescence centers in crystalline quartz either pure or germanium doped. That is true even for the case of irradiation of crystal with 'soft' ionising radiation such as X-rays.

We put thus here a question: is it possible by destructive irradiation to produce glass-like center in crystalline quartz? For answering, we have to check if germanium related center in crystalline quartz could be transformed by electron beam irradiation to germanium oxygen deficient center of silica glass.

We reported above the luminescence properties deduced from UV light excitation i.e. photoluminescence. Previous experiments using e-beam irradiation i.e. cathodoluminescence (CL) shows some time the existence of SiODC(II) luminescence in CL of α-quartz [4], some time does not detect any [5] and the causes of that are not yet understood. On the contrary, the surface related red luminescence of non-bridging oxygen was detected every time. The cathodoluminescence of silica glass and thin film of silicon dioxide were studied in details (see for example [4–7]). It was shown that cathodoluminescence of the sample with oxygen deficiency possesses strong blue band and smaller UV band from SiODC(II). The luminescence intensity drops down with the irradiation dose. Cathodoluminescence from silica glass samples elaborated in 'normal' melt conditions i.e. without oxygen deficiency, contains the same luminescence bands but with relatively small intensity at the beginning of the irradiation. It is, here, growing with dose. The luminescence of thin film of silicon dioxide, elaborated by silicon oxidation, grows with e-beam dose excitation from a negligible level. The main spectral content is the same as the one of bulk silica samples: the two luminescence bands from SiODC and the red luminescence from non-bridging oxygen luminescence center.

The germanium containing silica glass and thin films of silicon dioxide on silicon, where germanium was implanted, contains GeODC luminescence as prevailing luminescence. The change on dose is depending on sample treatment [8].

In this work, we find that neither X-ray nor e-beam irradiation produce GeODC(II) in Ge doped α-quartz crystal. However, e-beam irradiation under high current (200 nA in a spot with diameter of about 40 μm during 5 min) produces glass-like UV luminescence of SiODC, but low current irradiation (below 50 nA) does not produce glass-like luminescence at all.

Comparing the e-beam induced volume changes in crystal and glass. It was obtained two cases were also distinguished: for low current, we got volume expansion, usual for crystals and for high current, we got depression of the irradiated surface, like it was previously observed for Ge doped silica glass [9].

2. Experimental

The samples for the investigations were synthetic crystalline quartz, pure and activated with germanium 0.1 wt%, grown by hydrothermal method in the Institute of Mineral synthesis (Alexandrov, Russia) and pure silica glass. The samples were polished plates of $10 \times 10 \times 1\ mm^3$. Experiments were performed on scanning electron microscope LEO 260 with used electron energy 15 kV and current up to 200 nA. Defocused electron beam with spot diameter about 30 μm was used. Carbon layer covered the surface of the samples in order to screen the implanted charge. Cathodoluminescence spectra were detected during irradiation with Jobin Yvon polychromator with CCD camera, all monitored with Spectramax 32 program. Volume changes were measured with a PC monitored phase shift interferometric microscope, which allow visualizing the surface of the sample with horizontal sensitivity of about 1 μm and vertical precision about less than nm. Experiments were performed at room temperature. A X-ray tube with W anticathode (15 mA, 40 kV) was used to study luminescence under X-ray radiation through beryllium window.

3. Results

First of all, we investigated X-ray irradiation of crystalline quartz doped with germanium. Here, we did not detect the luminescence of GeODC(II) even after X-ray irradiation during many hours neither at 290 K, nor at 77 K. Only luminescence of self-trapped exciton was observed. No other trace of luminescence has been detected. We can thus deduce that X-ray irradiation in α-quartz does not induce transformation of germanium to oxygen-deficient center in spite of the high Ge concentration (up to 1 wt%).

Similar situation was observed for low dense e-beam irradiation (e-beam current about 50 nA). The material damage is observed by the topographer as well as by luminescence. Luminescence intensity decreases with dose, showing on radiation-induced damage of