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Irradiation induced densification and its correlation with three-membered rings in vitreous silica

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ABSTRACT

Suprasil silica glass was irradiated by 50 keV electron beam with doses within the range of 3.1–191.1 kC/m^2. Volume changes induced by electron irradiation were monitored by means of Atomic Force Microscopy (AFM). Raman spectra were taken from irradiated spots to observe structural changes. Irradiated glasses were annealed at temperatures 500–1000 °C. After annealing irradiated spots were again examined by AFM and Raman spectroscopy in order to observe volume and structural relaxation of radiation-induced changes. Electron beam caused volume compaction that was correlated with D2 peak area for lower doses. D2 peak evolution under irradiation and subsequent annealing showed that topological changes in glass structure are possible deeply below the glass transition temperature.

1. Introduction

Silica glass is important technological material, which is used in a wide variety of applications spanning from construction industry to special purposes in detectors, cosmic research, and nuclear waste deposition or as an insulation material in nuclear power plants. Moreover, silica glass can be considered as the model system for silicate glasses, because network formed by silica interconnections creates a natural backbone of all silicate glasses and therefore radiation effects in silica glass can provide better understanding of radiation processes in more complex systems. Electron irradiation causes many changes in the structure of the glasses, because of the ionization and ballistic interactions of electrons with solid constituents. Because incoming electrons have a low mass, they are not able to induce many displacement events (Frenkel pairs), but most of the deposited energy is dissipated by ionization processes, through Coulombic interactions, which represent a major source of damage [1,2]. Depending on the dose and the energy of the electrons introduced effects may vary from creation of point defects up to the phase transitions [3]. The other possible changes are amorphization, changes of volume and refractory index, and/or formation and growth of oxygen-filled gas bubbles [4–7]. Some authors also observed changes of mechanical properties of electron-irradiated glasses [8,9]. Electron irradiation is accompanied by the decay of alkali X-ray intensities in alkali-silicate glasses [10]. Macroscopic migration of alkali ions may be conveniently observed by EPMA (Electron Probe Microanalysis) by recording the decay curve (X-ray intensity versus time) [11].

Some previous papers documented the volume changes in various types of glasses caused by electron irradiation of various doses [3,12–14]. The glass is very sensitive to the irradiation, partially because the glass state is not in the thermodynamic ground state. Incoming electrons inject the energy and the charge into glass structure, leading to many changes (e.g. shifts of the equilibrium positions of atoms) [3]. Previous experiments [14–16] showed the response of the vitreous silica to the electron irradiation leads either to densification or to volume expansion, depending on the OH content. The volume compaction was explained as follows: incoming electrons deliver the energy to the glass structure via elastic scattering between electrons and atoms. This causes a local increase of the energy and momentum and enables relaxation of Si–O–Si bonds and optimization of their angles [13]. Similar effect was observed at borosilicate glasses, which revealed only volume compaction, because of apparent prevailing role of the silicate phase [12,13]. Volume compaction was observed also for alkali-silicate glasses, but

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only for lower doses [3,12]. The densification of the glass can be also reached also by means of laser [17].

The important effect of electron irradiation on silicate structure is also the creation of the stable point defects and the changes of the valence states of the lattice atoms, because point defects can alternate the physical properties of the glass and limit its technological applications [18]. Formation of the point defects under electron irradiation has been studied in many papers [19–22] and it was also assumed that these defects are mainly responsible for the abovementioned volume compaction (densification). But recent estimates [20] suggested that this defect creation may cause 0.1% volume change at most. On the contrary, according to calculations, energy dissipated in the nuclear displacements, at which macroscopic variations seem to saturate, is about 3.4 eV per one Si–O bond [20]. This energy is approximately equal to the bond energy, which suggests reorganization and rebonding of the network.

Besides point defects, irradiation is expected to cause other structural changes in the glassy matrix. Devine [20] suggested that radiation-induced densification is correlated with a size decrease of rings. A few methods are able to observe structural changes on the microscale, e.g. EELS (Electron Energy Loss Spectroscopy), EXAFS (Extended X-ray Absorption Fine Structure), and mainly Raman spectroscopy. A number of Raman spectroscopic studies concerning the glass structure were carried out on oxide glasses [23,24]. The evolution of Raman spectra of silica glass under β-irradiation was observed by Boizot [23]. He observed evolution of the sharp peak at 602 cm^{-1}, denoted as D2 defect peak in the spectrum of irradiated silica glass. That peak corresponds to the symmetric oxygen breathing vibrations of the three-membered rings consisted of $(SiO_4)^{4-}$ tetrahedra [23,25] and it was found to increase as a function of a dose. Another structural process induced by β-irradiation is formation of molecular oxygen, which was determined from the Raman spectra of irradiated glasses as the sharp peak at 1550 cm^{-1} [26].

Despite of number of papers dealing with radiation effects in glasses, the microscopic structure-related processes leading to the macroscopic changes of density are not elucidated. The presented paper attempts to correlate the volume changes estimated by AFM with structure variance observed on Raman spectra. Silica glass, as a representative of silicate glasses, is chosen for this study to avoid possible influence of other species in glass. In addition, thermal relaxation of the induced defects is very seldom. Here, subsequential annealing at temperatures below the glass transition should help to differentiate thermally removable changes from those, if there are any, requiring larger intervention.

2. Experimental

Annealed silica glass samples Suprasil 1, supplied by Heraeus, were used in our experiments. The OH content is 400–1200 ppm according to the producer. All samples were rectangle-shaped to a size of 5×3 mm^2. Thickness of the glass was 0.5 mm. First, the surfaces of the samples were cleaned up by acetone to avoid possible surface contamination. Then, samples were coated by 10 nm layer of Au/Pd alloy by means of vacuum sputtering to ensure surface conductivity and to avoid charging of samples during electron irradiation. Glasses were then subsequently irradiated by the series of electron doses from 3.1 kC/m^2 to 191.1 kC/m^2; each dose was continual and independent (irradiated places were well separated on the surface not to influence each other). Glass surface was also investigated by an optical microscope before electron irradiation to avoid locations with evidently worse quality of their surface. Accelerating voltage was set to 50 keV (penetrating range of electrons is about 20 μm), the probe current was 50 nA. The diameter of the beam was set by the optical microscope to 60 μm, so that a widening of the defocused beam caused by electron scattering may be neglected in comparison to the adjusted beam diameter. The increase of temperature under electron irradiation was evaluated [10,27] and also experimentally verified [28]. Based on results of these papers the temperature increase during irradiation can be neglected under irradiating conditions used here. Subsequently, the morphology of the irradiated spots was examined by Atomic Force Microscopy, AFM, (Topometrix TMX 2000). All electron doses caused depressions on the silica surfaces. Hence, the volume change of the irradiated place can be related to a difference between the point in the centre of the irradiated area and the line of the unirradiated glass surface. AFM pictures of 100×100 μm^2 were used to describe morphology of each pit; each picture was accompanied with a corresponding Z-profile through the centre of the pit (see Fig. 1).

For the correct evaluation of the depth of the pit it is necessary to take into account that a contamination layer is continuously growing with the irradiation time/dose. The rate of the contamination thickness was determined during the long-term expositions using SEM [14] and was set to 0.02 nm/s. Although AFM has an excellent vertical resolution, the precise determination of the depth of the pit depends strongly on the smoothness of the scanned profile as well as glass surface. On the other hand the precise calculation of the electron dose is affected by the beam fluctuation and the coefficient of backscattered electrons that depends on both composition and morphology of glass surface. The total error of measuring of the dose is estimated up to 5%, for low doses is about 1%. The reproducibility of the volume evaluation is within 10%, mostly influenced by the surface non-uniformity and smoothness of the pit profile.

The next step was to measure the Raman spectra from both clean pristine surface and the centres of the irradiated spots. Collections of Raman spectra were confined to linear regime of volume compaction, i.e. up to 15.92 kC/m^2. Raman spectra were collected using Renishaw InVia Raman Spectrometer equipped with 1800 lines/mm grating with a Leica DM2500 microscope. The 514 nm Ar^+ laser with output of 500 mW (about 150 mW on the sample) was used to excite the Raman scattering. The resolution/intensity variations of the Raman measurements can be estimated up to 2 cm^{-1}/2%, respectively.

To study relaxation after electron irradiation glass samples were irradiated by 31.8 kC/m^2 dose (the dose slightly beyond linear regime of the glass densification) and subsequently were heated to the temperatures 500 °C, 600 °C, 700 °C, 800 °C, 900 °C, and 1000 °C, one glass sample was used for one particular temperature only. Samples were heated by using Linkam High Temperature Stage TMS 1500. After 60 min of annealing Raman spectra were recorded from the irradiated and annealed spots again in order to evaluate the relaxation of the radiation-induced changes. In order to minimize accidental errors multiple spectra were taken from each irradiated spot. In addition, AFM profiles of the annealed spots were measured in order to evaluate volume changes.

3. Results

Fig. 2 presents two typical images of the irradiated spots recorded by AFM. Each image is accompanied with a corresponding Z-profile. Image on the left (*a*) represents a depression caused by a low electron dose (5 min or 5.3 kC/m^2) and image on the right (*b*) represents a depression caused by a large electron dose (180 min or 191.1 kC/m^2) for comparison. These two pictures document the typical evolution of morphology with an increasing dose. Starting the irradiation (lower dose), local glass structure is being shrunk and the rate of compaction is very high. Larger doses seemed to cause some expansion (as for alkali-silicate glass), but this effect can be fully attributed to the increase of the contamination layer, which is significant for the long exposure times [14]. Actually, after the subtraction of the thickness of the contamination layer it is obvious that the volume expansion is but apparent and only compaction occurs, see Fig. 3, which presents the dependence of the volume compaction on the electron dose. The linear fit through the first four doses (plus an unirradiated spot) proves the linear dependence of densification on dose for low doses (correlation coefficient is 0.995).

The Raman spectra of the pristine and silica glasses irradiated by doses up to 15.92 kC/m^2 (from the linear part of densification, see