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Activation energy spectra for annealing of ion irradiation induced defects in silica glasses

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Abstract

In situ stress measurements were performed on alkali-borosilicate glass samples during and after 2 MeV Xe ion irradiation at several temperatures between 95 and 580 K. After switching off the ion beam, stress changes are observed that are related to the annealing of ion beam generated defects. The activation energy spectra for defect annealing are obtained from the data at each irradiation temperature. Defects are observed in the energy range from 0.26 to 1.85 eV. At each temperature the spectrum increases monotonously with activation energy. At each energy the defect density per unit energy is smaller at higher temperatures. This behavior can be explained using a binary collision model. The data are contrasted against the results obtained for 4 MeV Xe ion irradiation of thermally grown SiO_2 films, which can be explained using a thermal spike model. Measurements of the radiation induced viscosity support these ideas.

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1. Introduction

The effect of ion irradiation on the structure of silica glasses has been studied for many years, and many of the radiation-induced phenomena that can occur are now well established. For example, ion irradiation can cause structural transformations in which rearrangements in the glass network topology take place [1]. When the irradiated region is constricted by a substrate, such changes may lead to the build-up of mechanical stress in the material. This stress can be relaxed by radiation-induced viscous flow [2,3]. In addition, irradiation at high (MeV) energies may cause anisotropic deformation, leading to stress in the plane perpendicular to the direction of the ion beam [2,4–6].

Ion irradiation also leads to the generation of point defects or larger defect agglomerates. Spectroscopic techniques have been used to try to identify the charge state and bonding nature of these defects [1,7]. Little is known, however, about the typical annihilation activation energies of these defects and their steady state concentration as a function of activation energy. One way to study this is by measuring the mechanical stress in an irradiated region that has built up due to the excess

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volume generated by such defects [2]. In this paper, we present stress measurements during and after 2 MeV Xe ion irradiation of alkali-borosilicate glass. Measurements are performed at different irradiation temperatures in the range from 95 to 580 K. The results are compared with similar measurements that were recently performed on 4 MeV Xe irradiated SiO_2 films, thermally grown on Si [3,8]. Some striking differences between the defect spectra are found, and are related to a fundamental difference in the nature of the defect generation process.

2. Experimental

Measurements were performed on 150 μm thick rectangular bulk alkali-borosilicate glass samples (6×23 mm^2, Menzel cover glasses). Rutherford backscattering spectrometry and elastic recoil detection show that this glass contains (besides Si and O) approximately 4.7 at.% Na, 3.7 at.% B and also small concentrations of K, Ca, Ti and Zn. One end of the samples was clamped to a temperature-controlled copper block, leaving the other end free to bend. The bare glass-side of the samples was homogeneously irradiated with a 2 MeV Xe ion beam that was electrostatically scanned over the sample with an ion flux of $4–9\times10^{10}$ ions/cm^{2}s. The maximum ion range was about 1.0 μm [2]. During irradiation the radius of curvature of the sample was measured using a sensitive scanning laser technique, from which the average in-plane stress σ in the irradiated region was derived [9]. In order to obtain a good reflection from the sample a 50 nm thick Cr film was evaporated on the backside of the sample. The measurements were performed at fixed temperatures between 95 and 580 K.

3. Results and analysis

Fig. 1(a) shows a typical stress measurement as a function of time during and after ion irradiation at a temperature of 580 K. The ion beam is switched on at $t = 54$ s and switched off at $t = 893$ s. In this paper, compressive stress is defined to be positive. After switching on the ion beam there is small initial increase in the stress. The stress then becomes tensile and reaches a maximum tensile stress at $t = 130$ s, corresponding to a Xe fluence of 7.3×10^{12} cm^{-2}. The stress then turns towards compressive values and saturates at a value of –3 MPa after ~500 s, corresponding to a fluence of about 4×10^{13} Xe cm^{-2}.

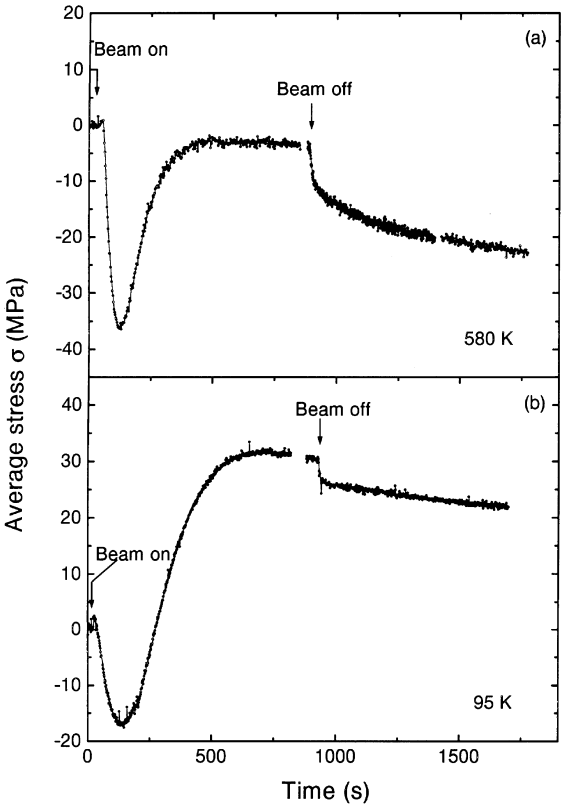

Fig. 1. In situ measurements of the average in-plane stress σ of alkali-borosilicate glass before, during and after 2 MeV Xe irradiation as a function of time. Results are shown for a sample temperature of 580 K (a), and 95 K (b). The ion beam was switched off after a total irradiation fluence of 8×10^{13} Xe/cm^2 (a), 4.3×10^{13} Xe/cm^2 (b).

As shown previously, the stress changes during ion irradiation are caused by different processes that occur simultaneously [3,8]. The small initial peak is caused by stress induced by the creation of volume occupying defects in the glass as the ion beam is switched on. The subsequent change towards tensile stress is attributed to a structural

change of the glass [8]. At the same time, radiation-induced viscous flow occurs, a continuous stress-driven process that eventually relaxes the stress to zero. Fig. 1(b) shows a stress measurement at a temperature of 95 K. It shows the same features as the data in Fig. 1(a), except that the stress saturates at a positive value. As described earlier, this is due to an anisotropic stress generation phenomenon in the silica glass, that occurs at low temperature [2,4–6].

After switching off the ion beam the stress changes towards tensile values as can be seen in Fig. 1 both at 95 and 580 K. The same effect was also observed in measurements performed at intermediate temperatures [10]. This stress change is attributed to the annealing of volume occupying defects (generated by the ion beam) that have a spectrum of annealing times. The densification is given by [8,11,12]

$$\Delta\rho = \Delta\rho_\infty - \int_0^\infty D(Q)\, \mathrm{e}^{-t'/\tau(Q)}\, \mathrm{d}Q, \tag{1}$$

where $D(Q)$ is the density change per unit energy, t' is time after switching off the beam and $\tau(Q)$, given by

$$\tau(Q) = \frac{h}{kT}\, \mathrm{e}^{Q/kT}, \tag{2}$$

is the characteristic annealing time of defects with an activation energy Q. In Eq. (2) k and h are Boltzmann's and Planck's constants, respectively, and T is temperature.

From Eq. (2) it follows that at a time t' after switching off the ion beam defects with activation energies in a small band of order kT around:

$$Q_{t'} = kT\ \ln(t'kT/h), \tag{3}$$

are annealing out, resulting in a certain stress change. The spectrum $D(Q)$ can be calculated from the measured stress change by [8]

$$D(Q) = \frac{-3\rho}{kTY_\mathrm{b}}\, \frac{\mathrm{d}(\Delta\sigma)}{\mathrm{d}(\ln[t'kT/h])}, \tag{4}$$

where $\Delta\sigma$ is the stress change after switching off the ion beam with respect to the saturation stress, ρ is the density of the silica glass (6.9×10^{22} atoms/cm^3) and Y_b the biaxial modulus of the modified region of the glass (90 GPa) [2].

Fig. 2 shows the transient stress change from Fig. 1 after switching off the ion beam on a logarithmic time scale. According to Eq. (4) the spectra $D(Q)$ can now be calculated by taking the derivative of $\Delta\sigma$ with respect to $\ln(t'kT/h)$. This is done by fitting a third order polynomial to the data and then taking the derivative of these curves versus $\ln(t')$. The result is shown in Fig. 3(a), where $D(Q)$ is plotted versus Q for the temperatures between 95 and 580 K. To avoid possible contributions from beam heating on the stress measurement only data for $t' > 30$ s are used. This explains why the spectra $D(Q)$ do not begin at $Q = 0$ eV.

4. Discussion

As can be seen in Fig. 3(a), at each temperature the spectrum for $D(Q)$ increases with increasing Q over the whole range. It can be seen that at a fixed activation energy the defect density per unit energy decreases with increasing sample temperature.

We will compare these spectra of alkali-borosilicate glass with activation energy spectra derived from stress measurements performed on 2.4 μm thick, thermally grown SiO_2 films on Si [8], that

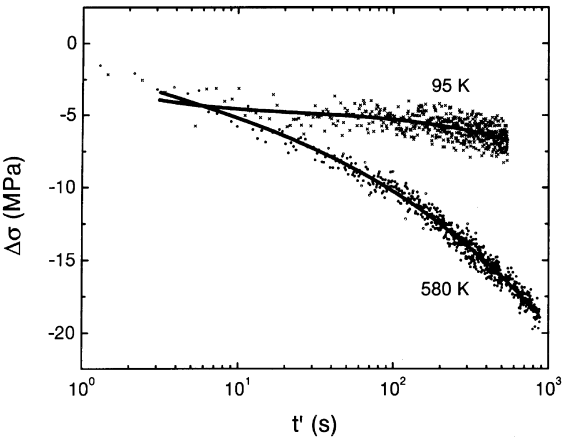

Fig. 2. The stress change $\Delta\sigma$ from Fig. 1 (relative to saturation stress) after switching off the ion beam, plotted as a function of the time after switching off the ion beam (t'). Results are shown for the alkali-borosilicate glass at sample temperatures of 580 and 95 K (from Fig. 1). At both temperatures the samples were first irradiated to reach a saturation stress value. The drawn lines are polynomial fits through the data.

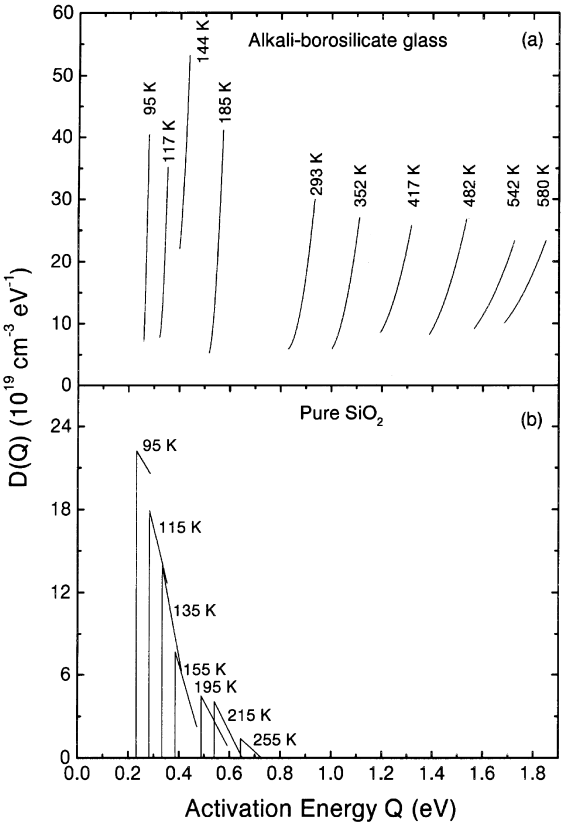

Fig. 3. (a) Defect annihilation activation energy spectra for alkali-borosilicate glass derived from the data in Fig. 2 and from additional data taken at other temperatures (all after irradiation with 2 MeV Xe at a flux of $4–9\times10^{10}$ ions/cm^{2}s). (b) The same for thermally grown SiO_2 films on Si (after irradiation with 4 MeV Xe at a flux of 5×10^{12} ions/cm^{2}s).

are shown in Fig. 3(b). These measurements were done with a 4 MeV Xe^{4+} beam at an ion flux of 5×10^{12} Xe/cm^{2}s.

In contrast to the case of alkali-borosilicate glass, for SiO_2 no stress change due to defect annealing was observed for temperatures higher than 255 K. Therefore the annihilation activation energy spectrum calculated from the data shows no contributions for $Q>0.75$ eV as can be seen in Fig. 3(b). Furthermore, all spectra decrease gradually as a function of the activation energy Q. By comparing all spectra for pure silica measured at different temperatures they seem to fit one 'universal' continuous spectrum.

Comparing the spectra of the two glass types it can first be concluded that defects are more stable in alkali-borosilicate glass, because the spectrum for alkali-borosilicate glass has non-zero values up to at least 1.85 eV whereas for the thermal oxide the spectrum vanishes above 0.75 eV.

The universal behavior of the spectra for thermal SiO_2 can be explained using a thermal spike model [8]. The defect generation is independent of sample temperature, as the temperature in the thermal spike [3,8,13] is much higher than the sample temperature. The defect population that is probed by the stress measurement is generated during the thermal spike that causes local melting of the SiO_2 film, and quenched in during rapid cooling.

The fact that this 'universal' behavior is not found for alkali-borosilicate glass implies that in this glass the steady state concentration of defects depends on sample temperature. This can be explained by a binary collision model for which in contrast to a thermal spike, an ion impact does not cause local melting but produces isolated defects as a result of binary collisions. In this case, a steady state defect population builds up due to a temperature independent defect generation and a temperature dependent defect annihilation. Therefore the steady state defect population then depends on the activation energy Q, the sample temperature and the maximum concentration of defects that can be generated for each Q. Because the annihilation rate (Eq. (2)) is larger for higher temperatures, the steady state defect population for a fixed activation energy is smaller for higher temperatures, which is in agreement with the data in Fig. 3.

The different nature of the defect generation in the two cases can also be seen by comparing the temperature dependencies of the radiation-induced viscosity η_{rad} [2,3,6,8] for both glass types. These data are derived from stress relaxation measurements during ion irradiation. We estimated η_{rad} by fitting an exponential function to the part of the curve between $\sim$300 and 700 s (fluence $\gtrsim 1.5\times10^{13}$ Xe/cm^2), the same method as used in [3]. The results are shown in Fig. 4. As can be seen, the viscosity for alkali-borosilicate glass (triangles) slowly increases with increasing temperature from $(0.75\pm0.10)\times10^{23}$ Pa ion/cm^2 at 95 K to

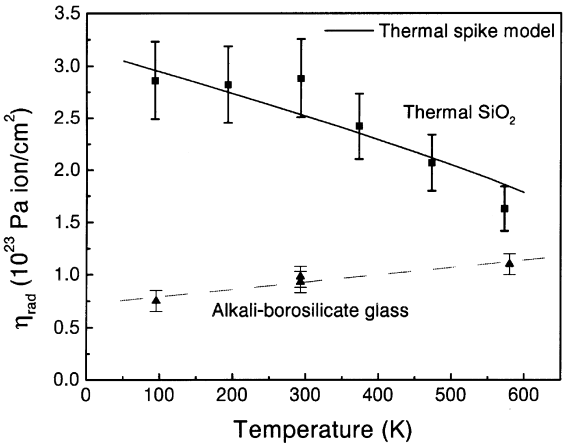

Fig. 4. The radiation-induced viscosity η_{rad}, derived from stress relaxation data during ion irradiation, plotted as a function of temperature for both alkali-borosilicate glass (triangles) and thermally grown SiO_2 films (squares). The solid line is a calculation of η_{rad} according to a thermal spike model [3]. The dashed line is a guide to the eye for the alkali-borosilicate glass.

$(1.1 \pm 0.10) \times 10^{23}$ Pa ion/cm^2 at 580 K. For comparison, the data for pure SiO_2 (squares) are included, which shows an opposite behavior of η_{rad} in agreement with calculations using a thermal spike model (the drawn line in Fig. 4) [3]. This provides independent evidence that the defect generation in alkali-borosilicate glass is not governed by a thermal spike process.

The different behavior observed above for pure silica and alkali-borosilicate glass may be due to the difference in the beam flux that was used (5×10^{12} Xe/cm^{2}s for pure SiO_2 versus $4–9 \times 10^{10}$ Xe/cm^{2}s for alkali-borosilicate glass), or the difference in the composition of the glass. Indeed it has been shown that the presence of boron affects the stability and the density of ion irradiation induced defects in silica glass [7,14].

5. Conclusions

In conclusion, we determined the defect activation energy spectra and the temperature dependence of the radiation-induced viscosity for alkali-borosilicate glass under ion irradiation with 2 MeV Xe at a flux of $4–9 \times 10^{10}$ Xe/cm^{2}s. We compared these results with data for thermally grown SiO_2 films irradiated with 4 MeV Xe at a flux of 5×10^{12} Xe/cm^{2}s.

We find that defects in alkali-borosilicate glass are more stable than in pure silica. A binary collision model explains the shape of the obtained defect activation energy spectra. This contrasts with data for pure silica that were explained using a thermal spike model. In addition, the temperature dependence of the radiation-induced viscous flow in alkali-borosilicate glass deviates from a thermal spike behavior.

Note added in proof

In the meantime, additional measurements have been performed on the structural relaxation behaviour after 2 Mev Xe irradiation of pure SiO_2 at a flux of 1.5×10^{11} Xe/cm^{2}s. It was found that the activation energy spectra are very similar to what was found for 4 MeV Xe irradiation at a flux of 5×10^{12} Xe/cm^{2}s in this paper. This indicates that the different behaviour for pure silica and alkali-borosilicate glass is not due to the difference in flux or energy, but must be due to the difference in glass composition.

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