Temperature dependence of MeV heavy ion irradiation-induced viscous flow in SiO_2

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In-situ wafer curvature measurements were performed to determine the mechanical stress in thermally grown SiO_2 films on Si during 4 MeV Xe ion irradiation at various temperatures in the range from 90 to 575 K. Radiation induced viscous flow is observed and the radiation induced viscosity is determined at various temperatures. It ranges from 2.9×10^{23} at Pa ion/cm^2 90–300 K to 1.6×10^{23} Pa ion/cm^2 at 500 K. Both its magnitude and temperature dependence can be explained in terms of a phenomenological model in which stress relaxation takes place in locally heated, mesoscopic regions of low viscosity, centered around individual ion tracks. According to this model, stress relaxation occurs in ~10 ps and within ~3 nm of the ion track. © *1997 American Institute of Physics.* [S0003-6951(97)02138-4]

When a keV or MeV ion penetrates a thin surface layer of a material, it loses energy by ionization events and atomic collisions. If the irradiated film is constrained by a substrate, the ion beam induced excitations can lead to the generation or relaxation of mechanical stress in the film.[1–5] One of the most striking ion irradiation-induced effects that has been observed is radiation-induced plastic flow, in which the ion beam causes macroscopic stress relaxation in the film. In this letter, we present temperature dependent measurements of the radiation induced viscosity for heavy ion irradiation in the MeV energy range, with typical energy loss in the keV/nm range. We compare the data with numerical simulations based on a model in which the macroscopic stress relaxation is calculated from the stress relaxation in hot regions of mesoscopic dimensions centered around the individual ion tracks.[6]

Experiments were performed on 2.4 μm thick SiO_2 films grown by wet thermal oxidation (1100 °C) on 95 μm thick (100) Si substrates. Rectangular samples (5×25 mm^2) were clamped to a copper block at one end, leaving the other end free to bend. The sample temperature was kept constant in the range from 80 to 575 K by cooling with liquid N_2 or resistively heating the copper block. Subsequently, the SiO_2 films were homogeneously irradiated by electrostatically scanning a 4.0 MeV Xe^{4+} beam over the sample at an ion flux of around 10^{11} ions/cm^2 s. The mean projected range of the Xe ions was well within the oxide film thickness. A scanning laser technique was used to *in-situ* measure the radius of curvature from the back of the sample while it was irradiated from the front. Details of this technique are described elsewhere.[4] From the radius of curvature, the average in-plane stress in the SiO_2 film, σ, can be derived, using the biaxial elastic modulus, $Y_{Si}=181$ GPa[7] of (100) Si. Local variations in film and wafer thickness limit the absolute determination of the stress to ±6 MPa.

Figure 1 shows two measurements of σ in the SiO_2 film as a function of Xe fluence taken at 90 and 575 K. At both temperatures, ion irradiation causes the initially compressive stress to turn tensile, reach a maximum tensile stress at a fluence of $\sim10^{13}$ Xe/cm^2, increase, and finally saturate. Although the two curves show essentially the same qualitative behavior, quantitative differences are evident and will be discussed below.

The initial compressive stress is attributed to the strain caused by the difference in the thermal contraction of the SiO_2 film and the Si substrate upon cooling the wafer from the oxidation temperature to the measurement temperature. The stress decrease at low fluences is mainly the result of changes in the SiO_2 network structure, such as a decrease in the mean Si–O–Si bridging bond angle.[8] As we have shown previously,[1–3] the relaxation for fluences above 10^{13} Xe/cm^2 is due to radiation induced viscous flow. This flow is Newtonian, i.e., the strain rate is proportional to the stress.[1] Furthermore, it has been shown that the stress behavior as a function of fluence is independent of the ion flux so that a flux-independent viscosity can be defined as $\eta_{rad}=\eta d\phi/dt$, where $d\phi/dt$ is the ion flux. The nonzero saturation stress value in Fig. 1 is ascribed to an anisotropic stress generating effect discussed in detail in Refs. 2, 3, 9, and 10. The magnitude of η_{rad} can be determined from the high fluence part of the data ($\phi>2\times10^{13}$ cm^{-2}). Here, the stress dependence on fluence is determined by the combined effect of Newtonian flow and anisotropic stress generation:

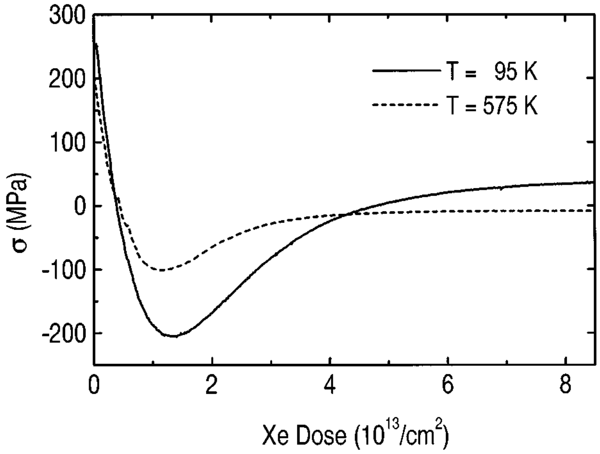

FIG. 1. *In-situ* measurements of the in-plane stress in a 2.4 μm thick SiO_2 film on a 95 μm thick Si (100) substrate as a function of the 4 MeV Xe fluence. Results are shown for substrate temperatures of 90 and 575 K. Each drawn line represents a set of ~200 data points.

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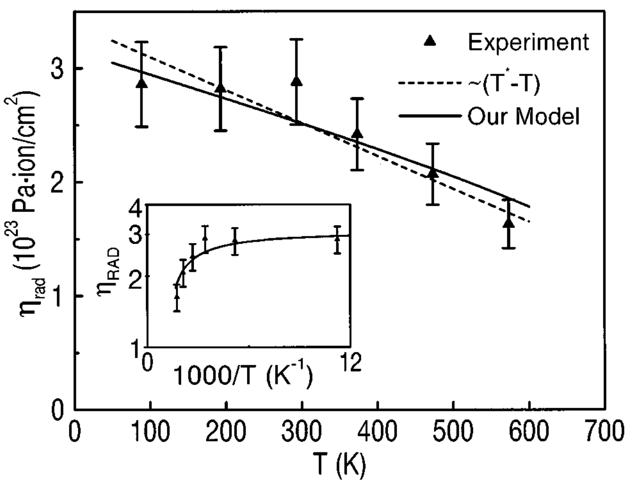

FIG. 2. Radiation induced viscosity, η_{rad}, as obtained from stress measurements at temperatures in the range from 90 to 575 K. An Arrhenius plot of the same data is shown as an inset. The solid curve is a calculation of η_{rad} based on our thermal spike model as described in the text. The dashed line shows a prediction by Trinkaus, with T^* the so-called flow temperature (Ref. 6).

$$\frac{d\sigma}{d\phi}=Y_{\text{OX}}\left(A-\frac{\sigma}{6\,\eta_{\text{rad}}}\right), \tag{1}$$

with $Y_{\text{OX}}=1\times10^{11}$ Pa the biaxial modulus of the oxide film and A the in-plane strain generated per ion.[2,3] From this equation, it follows that σ will exponentially decrease to the saturation value $\sigma_{\text{SAT}}=6A\,\eta_{\text{rad}}$. Fitting Eq. (1) to the fluence region $\phi>2\times10^{13}$ cm^{-2} of the 90 K curve in Fig. 1 results in $\eta_{\text{rad}}=(2.9\pm0.2)\times10^{23}$ Pa ion/cm^2 and $A=(2.5\pm0.3)\times10^{-17}$ cm^2/ion. Dividing η_{rad} by the ion flux yields $\eta=2.9\times10^{12}$ Pa s, roughly equal to the thermal viscosity of SiO$_2$ at 1500 K.[11] This shows that the ion beam causes an effective macroscopic softening of the SiO$_2$ film similar to that caused by thermal flow at 1500 K. The value of η_{rad} derived from the data taken at 575 K is even lower than that at 90 K: $\eta_{\text{rad}}=(1.6\pm0.2)\times10^{23}$ Pa ion/cm^2.

More measurements of η_{rad} have been performed at several other temperatures in the range from 90 to 575 K and are shown in Fig. 2. The inset shows the same data in an Arrhenius plot. Below 300 K, the radiation-induced viscosity does not show a significant temperature dependence. This is similar to that found by Zhu and Jung for light ion irradiation.[5] Above 300 K, a decrease of η_{rad} is observed characterized by an apparent activation energy of 0.2 eV. This is a low value for viscous flow, a process that involves the breaking and rearrangement of covalent bonds, and suggests that the apparent activation energy is not the true activation energy for flow. Thermal spike models have been successfully applied to describe radiation induced ion beam mixing and diffusion for which the temperature dependence is also characterized by a temperature independent regime and a thermally activated regime with a low activation energy.[12] The following outlines how a thermal spike model can be applied to describe both the absolute value and the temperature dependence of the radiation induced viscosity.

The basic idea of a thermal spike model describing the relaxation of an applied stress has been formulated by Trinkaus.[6] When an ion enters a solid, it deposits energy in nuclear collisions and electronic excitations, which results in a sharp rise of the local temperature and a concomitant drop of the viscosity. As a result, the shear stress can relax in the locally heated region, and upon cooling down the associated strain change freezes in. Using this model, and not taking into account the time and temperature dependence of the thermal viscosity, a linear dependence of the radiation reduced viscosity on temperature is predicted.[6] A linear dependence of η_{rad} on T is shown by the dashed line in Fig. 2 and provides a good fit to the data.

In this letter, we perform a numerical calculation of the radiation-induced viscosity using a spatial and temporal integration of the (temperature dependent) relaxation rate. The temperature evolution in the spike can be calculated by assuming that the initial temperature distribution has the form of a δ function along a linear ion track.[13] The temperature distribution then evolves according to the laws of classical heat conduction. In cylindrical coordinates, the temperature, $T(r,t)$, at distance r from the ion track and time t is given by

$$T(r,t)=\frac{F_d}{4\pi\kappa t}\exp(-\rho C r^2/4\kappa t)+T_s, \tag{2}$$

with T_S the substrate temperature, ρ the density of the film (2.23 g/cm^3), and F_d the energy deposited into the track per unit length, which is composed of energy lost in nuclear collisions and electronic excitations (3.1 keV/nm total). Since most of the flow will take place at high temperatures, it is justified to approximate the thermal conductivity by $\kappa=2.4$ W/m×K, and the heat capacity by $C=75$ J/mol K.[11] For many amorphous materials, the thermal viscosity can be approximated by $\eta=\eta_0\exp(E/kT)$ where η_0 is a material dependent prefactor, E is the activation energy for flow, and k is Boltzmann's constant. While the values of η_0 and E are not exactly known for the wet thermal oxide used in these experiments (e.g., they are strongly dependent on OH concentration),[11,14] we have used first order estimates of $\eta_0=10^{-3}$ Pa s and $E=1.0$ eV. This relatively low activation energy is chosen in analogy with ion beam mixing experiments that show a low activation energy for diffusion under ion irradiation.[12]

Using the temperature profile from Eq. (2), the local viscosity in the spike can now be calculated for all r and t. Figure 3(a) shows a calculation of η as a function of r at a fixed time t of 1 ps and a substrate temperature of 100 K. It is clear that a region of low viscosity ($<10^{-2}$ Pa s), characteristic of a liquid, forms in a several nm wide region around the ion track. From the calculated viscosity, the shear stress relaxation rate $R=\mu/\eta$ can be determined, with μ the shear modulus (for SiO$_2$: $\mu=3.55\times10^{10}$ Pa).[11] For example, the relaxation rate in the center of the spike at $t=1$ ps is 2×10^{13} s^{-1}, corresponding to a relaxation time of 50 fs. This implies that in the center of the spike the viscosity is low enough to lead to full stress relaxation on the ps time scale of the thermal spike. The total amount of stress relaxation up to a time τ after ion impact can be calculated at every distance r by integrating R over time

$$\Omega(r,\tau,T_s)=1-\exp\left[\int_0^{\tau}-R(r,t,T_s)\,dt\right], \tag{3}$$

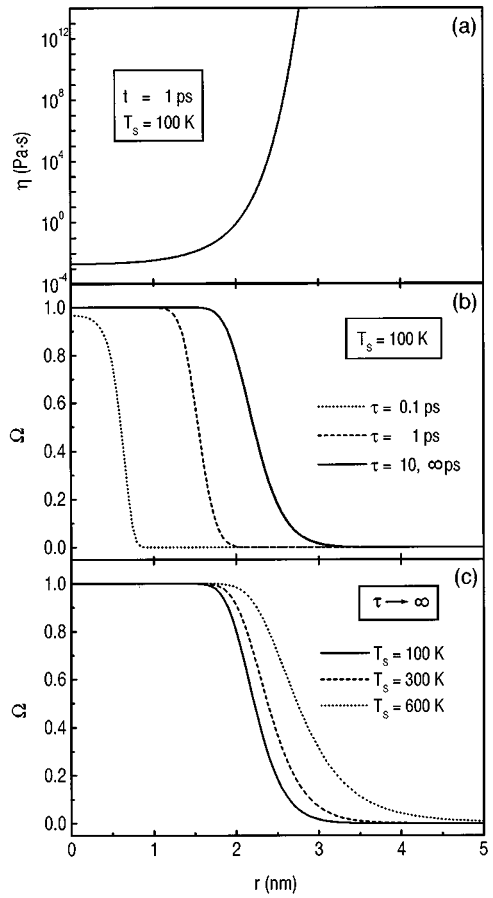

FIG. 3. (a) Calculation of the local thermal viscosity, η, as a function of the distance from the ion track. Data are shown for the case of a 4 MeV Xe ion, 1 ps after it entered the SiO_2 film ($T_s = 100$ K). (b) Calculations of the total amount of stress relaxation at $T_s = 100$ K up to a time $\tau, \Omega(r,\tau,100\text{ K})$, for four different values of τ: 0.1 ps, 1 ps, 10 ps, and $\tau \rightarrow \infty$. (c) The total amount of stress relaxation, $\Omega(r,\infty,T_s)$, as a function of distance from the ion track. Calculations are shown for substrate temperatures of 100, 300, and 600 K. $\Omega(r,\tau,T_s) = 1$ corresponds to full relaxation.

in which $\Omega(r,\tau,T_s) = 1$ corresponds to full relaxation. Figure 3(b) shows calculations of $\Omega(r,\tau,T_s)$ at $T_s = 100$ K for four different values of τ: 0.1 ps, 1 ps, 10 ps, and $\tau \rightarrow \infty$. As can be seen, at a time $t = 0.1$ ps, the stress has almost fully relaxed in a cylinder with a radius of about 0.4 nm. The region in which substantial stress relaxation has taken place grows for larger values of τ up to roughly 10 ps. At 10 ps, full stress relaxation has occurred in a region with a radius of about 2 nm. The amount of relaxation then sharply drops for increasing r, and virtually no relaxation is found for distances >3 nm from the ion track. The final profile $\Omega(r,\tau,T_s)$ for $\tau \rightarrow \infty$ is virtually identical to that for $\tau = 10$ ps, indicating that all stress relaxation takes place within 10 ps. It can be argued that starting the integration over time at $t = 0$ has no physical meaning since on time scales shorter than an atomic vibration time the velocity of the moving atoms has not yet assumed a Boltzmann distribution and, as a consequence, a temperature can not be defined. However, it can be shown that the final profile $\Omega(r,\infty,100\text{ K})$ is insensitive to the initial time integration value as long as it is less then roughly 0.5 ps. Figure 3(c) shows calculations of $\Omega(r,\infty,T_s)$ for three different substrate temperatures, 100, 300, and 600 K. Comparing these curves, it can be seen that the higher the substrate temperature the larger the region in which the relaxation is complete.

The macroscopic stress relaxation in the SiO_2 film can be described by Trinkaus' model in which it is assumed that each ion causes full stress relaxation in a cylinder with cross-section $\theta_{\text{eff}}(T_s)$. The value of $\theta_{\text{eff}}(T_s)$ can be determined by integrating $\Omega(r,\infty,T_s)$ over the area of the film. The macroscopic stress relaxation as a function of ion dose is then described by

$$\frac{d\sigma}{d\phi} = Y_{\text{OX}}\left[A - \frac{\sigma B \theta_{\text{eff}}}{2\mu}\right], \tag{4}$$

with B a geometric factor that depends on Poisson's ratio, ν ($B = 6[1-\nu]/[5-4\nu] = 1.15$, and $\nu = 0.17$).[11,6] Comparing Eqs. (1) and (4), it follows that η_{rad} is given by $\eta_{\text{rad}} = \mu/[3B\theta_{\text{eff}}(T_s)]$. Using a thermal spike calculation of θ_{eff} at 95 K, we find that $\eta_{\text{rad}} = 0.6 \times 10^{23}$ Pa ion/cm^2. Considering that no fitting parameters are used, this is close to the experimentally determined value from Fig. 1 (2.9×10^{23} Pa ion/cm^2). To obtain quantitative agreement between the model and the measured data, the η_{rad} values obtained from Eq. (4) were multiplied by a factor of 4.7. The result is shown by the drawn line in Fig. 2. From this figure, it can be seen that the calculations also successfully predict the observed temperature dependence. The fact that the calculated radiation induced viscosity is lower than the measured value may indicate that not all energy loss contributes to flow. The discrepancy may also be caused by uncertainties in the geometric factor B and the values taken for η_0 and E.

In conclusion, we have performed measurements of the radiation-induced viscosity during 4 MeV Xe irradiation of SiO_2. The viscosity ranges from 2.9×10^{23} Pa ion/cm^2 at 90–300 K to 1.6×10^{23} Pa ion/cm^2 at 500 K. The data can be fully explained by a thermal spike model, in which macroscopic stress relaxation is caused by viscous flow in hot regions of mesoscopic dimensions that result from the energy deposition of individual Xe ions.

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[1] C. A. Volkert and A. Polman, Mater. Res. Soc. Symp. Proc. **235**, 3 (1992).
[2] E. Snoeks, A. Polman, and C. A. Volkert, Appl. Phys. Lett. **65**, 2487 (1994).
[3] E. Snoeks, T. Weber, A. Cacciato, and A. Polman, J. Appl. Phys. **78**, 4723 (1995).
[4] C. A. Volkert, J. Appl. Phys. **70**, 3521 (1991).
[5] Z. Zhu and P. Jung, Nucl. Instrum. Methods Phys. Res. B **91**, 269 (1994).
[6] H. Trinkaus, J. Nucl. Mater. **223**, 196 (1995).
[7] W. A. Brantley, J. Appl. Phys. **44**, 534 (1973).
[8] R. A. B. Devine, Nucl. Instrum. Methods Phys. Res. B **91**, 378 (1994).
[9] H. Trinkaus and A. I. Ryazanov, Phys. Rev. Lett. **74**, 5072 (1995).
[10] S. Klaumünzer, Li Changlin, S. Löffler, M. Rammensee, G. Schumacher, and H. C. Neitzert, Radiat. Eff. Defects Solids **108**, 131 (1989).
[11] H. Scholtze, *Glass* (Springer, New York, 1991).
[12] M. Nastasi and J. W. Mayer, Mater. Sci. Eng. R. Rep. **12**, 1 (1994).
[13] G. H. Vineyard, Radiat. Eff. **29**, 245 (1976).
[14] G. Hetherington, K. H. Jack, and J. C. Kennedy, Phys. Chem. Glasses **5**, 130 (1964).