Densification, anisotropic deformation, and plastic flow of SiO_2 during MeV heavy ion irradiation

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The response of SiO_2 thin films and implantation masks to 4.0 MeV Xe irradiation is studied. Trenches in silica deform dramatically after irradiation with 3×10^{15} ions/cm^2. *In situ* wafer curvature measurements show that thin planar silica films first densify by 3.6% during irradiation. The resulting stress then relaxes viscously by radiation-enhanced Newtonian flow. At a flux of 3×10^{10} Xe ions/cm^{2}s the measured shear viscosity was 6×10^{13}Pa s. We find evidence that an irradiation induced anisotropic deformation mechanism is present in the silica films. In equilibrium, this deformation leads to an average compressive saturation stress as large as 4.5×10^7 Pa. © *1994 American Institute of Physics.*

General studies of radiation damage in silica have been performed for many years,[1] because of the potential use of silica in nuclear reactors and waste containers, and its current use in optical fibers. Some of the studies showed that ion irradiation causes densification of the amorphous SiO_2, due to both ionization events and atomic collisions.[1,2] The densification eventually saturates with fluence. When a thin film of SiO_2, constrained by a substrate, is irradiated, densification results in a tensile stress in the irradiated region. Stress can be relieved by radiation enhanced plastic flow, as shown for irradiation with Si and Au at energies below 800 keV.[3] Presently, ion implantation is being used to dope materials with heavy ions at MeV energies,[4] for instance to modify optical properties. It is therefore important to determine the response of silica to irradiation with heavy ions at MeV energies.

In this letter we present a study of deformation in amorphous SiO_2 films during 4.0 MeV Xe irradiation at room temperature. Scanning electron microscopy (SEM) shows a dramatic macroscopic deformation of trenches in SiO_2, after irradiation to a fluence above 10^{15} ions/cm^2. This observation is correlated to *in situ* wafer curvature measurements of stress in planar SiO_2 films on Si during irradiation. Densification, plastic flow, and a nonsaturating anisotropic deformation phenomenon, not present at lower irradiation energy, are observed.

Experiments were performed on 1.85-μm-thick SiO_2 films, obtained by wet thermal oxidation at (1100 °C) of one side of double-side polished, undoped, (100) Si wafers. Trenches, 1.0 μm deep and 5.0 μm wide, were etched in such a SiO_2 film on a thick substrate (325 μm) using reactive ion etching. The trenches were separated from each other by 15 μm. The trenches were studied in cross section by SEM with 12 keV electrons before and after Xe irradiation of the SiO_2 film at 4.0 MeV.

A thin Si substrate (100 μm), also covered with 1.85 μm SiO_2, was used for *in situ* stress measurements during ion irradiation. Rectangular pieces (5×25 mm^2) were cleaved and clamped at one end to a copper block, leaving the other end free to bend. By scanning a He-Ne laser beam up and down on the back of the sample, the sample curvature was measured *in situ* while the sample was implanted at the front. Details of this technique are described in Ref. 5. The integrated in-plane stress (in N/m) was derived from the measured radius of curvature,[6] using the biaxial elastic modulus of (100) Si: 181 GPa.[7] The average local stress in the film (σ, in pascal) can be obtained by dividing the integrated stress by the film thickness. Local variations in wafer and oxide thickness limited the absolute determination of the intergrated stress to ±15 N/m. The 4.0 MeV Xe^{4+} beam was electrostatically scanned through an aperture, at ion fluxes in the range $(0.8-15)\times10^{10}$ ions/cm^{2}s. All irradiations were performed at room temperature. The oxide thickness and ion range and concentration were determined by Rutherford backscattering spectrometry (RBS), using 4.0 MeV $^4He^+$.

Figures 1(a)–1(d) show cross-section SEM images of a 5.0-μm-wide trench etched in SiO_2 before and after Xe irradiation

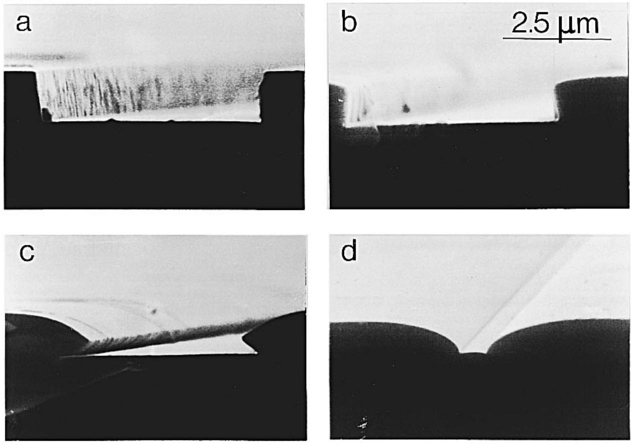

FIG. 1. Cross-section SEM images of a 5.0-μm-wide trench in a thermally grown SiO_2 film (a) before irradiation, and after 4.0 MeV Xe irradiation by (b) 1.0×10^{15}, (c) 3.0×10^{15}, and (d) 1.0×10^{16}/cm^2. All images were taken with the same magnification. The ion beam is directed perpendicular to the surface.

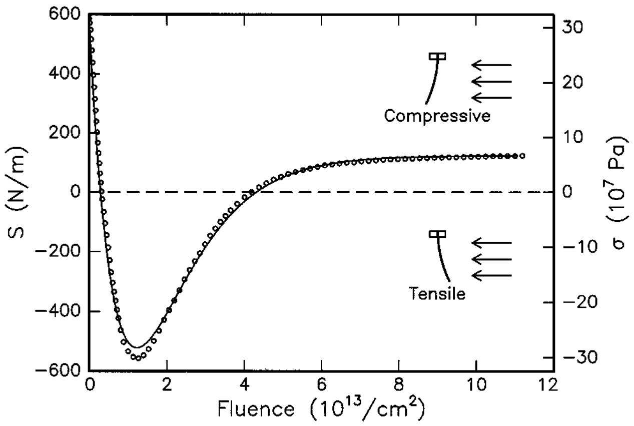

FIG. 2. The integrated in-plane stress of an SiO_2 film on a Si substrate during irradiation with 4.0 MeV Xe. The right-hand axis shows the average local stress. The solid line is a fit according to Eq. (1).

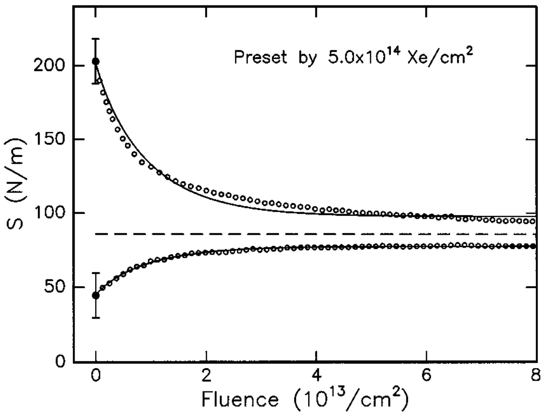

FIG. 3. The integrated in-plane stress during 4.0 MeV Xe irradiation, of samples which were first set in two different stress states. The "set" stress is indicated by the closed circles. The solid lines are fits using Eq. (2). The dashed horizontal line denotes the equilibrium stress value.

diation to fluences ranging from 1.0×10^{15} to 1.0×10^{16} Xe/cm^2. The silica shows a dramatic macroscopic deformation: the material expands in the plane perpendicular to the ion beam and contracts in the direction along the ion beam. A small effect is first seen in the near-surface region after $1.0\times10^{15}/cm^2$. After $3.0\times10^{15}/cm^2$ the sides of the trench have almost collapsed, and after $1.0\times10^{16}/cm^2$ the surface has deformed so much that the trench is nearly filled.

Figure 2 shows the measured integrated in-plane stress of planar film, without trenches, during Xe irradiation at the same energy, but a much lower fluence. The right axis shows the corresponding average local stress. The initial integrated compressive stress ($S_0=580\pm15$N/m) is caused by the elastic strain due to the difference in thermal contraction of SiO_2 and the Si substrate upon cooling the wafer after oxidation. As the sample is irradiated, the stress first decreases, and becomes tensile. At the fluence of $1.3\times10^{13}/cm^2$ the integrated stress reaches a minimum of -550 N/m. For higher fluences the stress increases and finally saturates at a compressive value of $S_{sat}=120$ N/m, corresponding to $\sigma=6.5\times10^7$ Pa. The maximum implanted Xe concentration is 20 ppm, so that volume changes due to the implanted Xe can be excluded. The stress behavior was independent of ion flux, in the range of $0.8-3.1\times10^{10}$ ions/cm²s.

Previous wafer-bending studies of SiO_2 during ion irradiation[1,2] have attributed the initial stress decrease to densification of the silica network. Densification is a result of both electronic and nuclear stopping processes, and has been shown to saturate when $\sim10^{20}$ keV/cm³ is deposited into atomic collisions. Indeed, a Monte Carlo calculation of the implantation damage (TRIM '89)[8] at the observed minimum at 1.3×10^{13} Xe/cm^2 shows that 1×10^{20} keV/cm³ is deposited in atomic collisions in the silica.

More recent measurements[3] have demonstrated that stress in SiO_2 can relax without a density change by radiation-enhanced Newtonian plastic shear flow, in which the strain rate is proportional to the stress. From these experiments it is inferred that ion irradiation can strongly reduce the effective shear viscosity compared to the thermal value. A similar relaxation is indeed observed in Fig. 2 for fluences $>1.3\times10^{13}/cm^2$, but in this case the stress becomes compressive again. By viscous flow, stress can only relax to zero; therefore, in addition to densification and viscous flow, a third process must participate in the behavior. This is attributed to the higher beam energy with respect to that used in Ref. 3.

For very high energy ion irradiation (up to 360 MeV), anisotropic deformation was reported in a variety of amorphous materials,[9,10] in which the materials contract along the direction of the beam and expand in the perpendicular plane. The deformation was found to be nonsaturating, and the rate of deformation was linearly dependent on the (electronic) energy loss, with a threshold of ~2 keV/nm. The electronic energy loss for 4.0 MeV Xe ions in SiO_2 is ~2.3 keV/nm, in addition to a nuclear energy loss of ~0.8 keV/nm (i.e., 26%).[8] Therefore we suggest that the same anisotropic deformation found for bulk samples[9,10] plays a role in our thin films. The nonzero saturation in Fig. 2 can be ascribed to a dynamic equilibrium determined by the rate of anisotropic deformation (expansion perpendicular to the beam) which increases the in-plane stress, and radiation enhanced flow which serves to relax the stress. Note that in the 360 MeV, experiments on bulk samples the ion range was much larger than the sample thickness, so that the deformation was uniform through the sample. In this case no stress builds up.

To demonstrate the idea of equilibrium, samples with nonequilibrium stress states were prepared by clamping samples in cylindrical armatures[5] with fixed radii of curvature (10.00 cm convex and 7.50 cm concave) and irradiating them with 5×10^{14} Xe/cm^2 at 4.0 MeV. In this way, any changes in density saturate, and plastic flow should occur, driven by the stress imposed by the armatures. When the samples were removed from the armatures, they had acquired different stress states (see the closed circles in Fig. 3), indicating that plasticity indeed had occurred. No curvature was induced in samples clamped in the armatures for a similar length of time without being implanted, indicating that the flow was radiation induced rather than thermally activated.

Figure 3 shows the stress of the two "set" samples during subsequent irradiation with 4.0 MeV Xe (open circles). The integrated stress of the sample with an initial value of 45 N/m increases to a steady state value of 80 ±15 N/m during irradiation. The stress of the other sample, set at a value of 200 N/m, decreases during irradiation and saturates at 93 ±15N/m, within the error the same saturation value.

RBS shows that the Xe projected range in the 1.85-μm-thick SiO_2 films, is 1.70 μm. A fraction of the Xe ions have entered the Si substrate, damaging an 0.18-μm-thick Si layer. This gives a small contribution to the measured integrated stress,[5] which was found to be less than $+30$ N/m in S_{sat} by measuring the substrate curvature after etching the SiO_2 layer from the substrate after irradiation.

Under the assumption that the local stress is uniform through the oxide layer, the integrated in-plane stress in the SiO_2 film as a function of fluence ϕ can be described by a rate equation in which the three radiation induced processes (densification, anisotropic deformation, and radiation induced plastic flow) are included

$$\frac{dS}{d\phi}=Y_{ox}t_{ox}\left(\frac{d\epsilon_\rho}{d\phi}+A\right)-\frac{Y_{ox}}{6\eta_{rad}}S. \tag{1}$$

Here, t_{ox} is the oxide layer thickness, $Y_{ox}=1\times10^{11}$ Pa the biaxial elastic modulus, ϵ_ρ the strain due to densification, A the strain per ion due to nonsaturating anisotropic deformation, and η_{rad} the radiation induced viscosity as defined in Ref. 3. Viscous flow is negatively proportional to the stress. When density changes have saturated, $d\epsilon_\rho/d\phi=0$, the solution to Eq. (1) is

$$S(\phi)=S_{sat}+(S_0-S_{sat})\exp\left[-\frac{Y_{ox}}{6\eta_{rad}}\phi\right], \tag{2}$$

where $S_{sat}=6A\eta_{rad}t_{ox}$ is the saturation stress. Fits, according to Eq. (2), are given in Fig. 3 by solid lines, and indeed describe the data reasonably well. The fits yield $\eta_{rad}=(1.67\pm0.17)\times10^{23}$ Pa ions/cm^2 (or a shear viscosity of 6×10^{12} Pa s at 3.1×10^{10} ions/cm^{2}s). This is at least seven decades lower than the pure thermal viscosity at room temperature. The low viscosity presumably results from broken bonds either directly created by the incoming Xe ions, or indirectly by a local heating effect in the vicinity of the ion track. Indeed, such fluid behavior is found in a recent molecular dynamics simulation of low energy irradiation of Au.[11] The general behavior of these simulations may apply to silica as well. Using S_{sat} and η_{rad} from Fig. 3, the anisotropic deformation constant $A=(5.0\pm1.5)\times10^{-17}$cm^2 is derived.

Finally, Eq. (1) can be applied to model the behavior in Fig. 2. It is assumed that the densification is described by a damage overlap model, in which the densification rate exponentially decreases to zero, $d\epsilon_\rho/d\phi\propto\exp[-\phi/\phi_\rho]$, and that η_{rad} is constant. The solid line in Fig. 2. was fitted yielding a saturation density change of (3.6±0.6)%, with $\phi_\rho=1.0\times10^{13}$/cm^2, $\eta_{rad}=(1.67\pm0.17)\times10^{23}$ Pa ions/cm^2 and $A=(5.7\pm1.5)\times10^{-17}$cm^2. As can be seen, the calculation resembles the measured data quite well. Small deviations for low Xe fluences may be explained by some variation of η_{rad} during densification.[3] The observed density increase agrees with previously established values.[1] The deformation constant and the radiation induced viscosity agree with values found in Fig. 3. The latter is in the same range as the values found in Ref. 3 for irradiations with Si and Au below 800 keV.

An independent measure of A can be obtained from the SEM pictures in Fig. 1. From the relative length change of the 15 μm SiO_2 regions between adjacent trenches in Fig. 1, a lower limit for the in-plane expansion coefficient of $A=(2.9\pm0.5)\times10^{-17}$cm^2 can be extracted, which is consistent with the values obtained from Figs. 2 and 3. This leads to the conclusion that both the nonsaturating anisotropic expansion seen in Fig. 1 and the final compressive stress observed in Figs. 2 and 3 are caused by the same mechanism. An extrapolation of A values obtained from very high energy experiments on bulk samples at 115 K,[10] using the electronic stopping as a scaling parameter, yields $A\sim3\times10^{-17}$cm^2.

The deformation in Fig. 1 seems to be most pronounced in the very surface, where the electronic stopping power is high. Electronic stopping causes a local heating of a cylindrical ion track, with a strong temperature gradient perpendicular to the cylinder, which may result in an elastic expansion of the silica. Apparently, the beam-directional cylindrical symmetry, which occurs only at high beam energy, can give rise to anisotropy as observed. Note that a significant fraction of the ion energy is deposited in atomic collisions, which also contributes to the heating effect.

In conclusion, densification, anisotropic deformation, and radiation enhanced plastic flow have been observed in thin SiO_2 films at room temperature during 0.4 MeV Xe irradiation. These processes were flux independent in the range $(0.8–3.1)\times10^{10}$ ions/cm^{2}s. Nonsaturating anisotropic deformation is possibly caused by local heating and thermal expansion around the ion tracks. This causes a dramatic deformation of SiO_2 implantation masks, and may be observed for other materials, as well.

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