

(In preparation for submission to *Physical Review Letters*)

Spontaneous nanoscale corrugation of ion-eroded SiO₂: the role of ion irradiation-enhanced viscous flow

Christopher C. Umbach,¹ Randall L. Headrick,²

Kee-Chul Chang,³ and Jack M. Blakely⁴

^{1,3,4} *Dept. of Materials Science and Engineering,* ²*Cornell High Energy Synchrotron Source,*
Cornell University, Ithaca, NY 14853

Grazing incidence x-ray scattering was used to determine the temperature and ion-energy dependence of nanoscale corrugations that form on an amorphous SiO₂ surface eroded by Ar⁺ ions. The corrugation wavelength λ shows a nearly linear dependence on ion energy. Between room temperature and ~300° C, λ depends weakly on temperature and above ~300° it shows an Arrhenius-like increase. Ion-assisted viscous relaxation in a thin surface layer is shown to be the dominant smoothing process during erosion; the rate of viscous smoothing scales with λ as $(\lambda)^{-4}$.

PACS numbers: 68.35.Bs, 61.10.Kw, 81.16.Rf, 81.65.Cf

The spontaneous formation of patterns on surfaces during deposition, annealing, or ion bombardment is of interest for producing useful nanoscale textured materials. Ion-induced surface corrugations are a notable type of such self-organization. First observed on silicate glasses [1], corrugations also form on crystals (Si [2], Ge [3], GaAs [4], Ag [5]) under experimental conditions similar to those for glasses but with longer corrugation wavelengths. Corrugation formation depends on a balance between microscopic processes that smooth the surface, and hence eliminate curvature gradients, and processes that increase curvature, such as atom removal by ion bombardment. Surface diffusion is the dominant smoothing process on some crystals such as Si for both thermally activated diffusion [6] and diffusion enhanced by ion-bombardment [2]. Thermally activated viscous flow dominates smoothing at micron length scales on silicate glasses [7], but its influence relative to that of surface diffusion at submicron dimensions and under conditions of ion-bombardment is unknown.

In this Letter we report using real-time x-ray scattering to monitor the formation of nanoscale corrugations on SiO₂ produced by bombardment with Ar⁺ ions, demonstrating that x-rays can determine the wavelength of corrugations at length

scales (from 20 to 200 nm) where near-visible light scattering methods [8] cannot be applied. We find the primary smoothing mechanism to be ion-enhanced viscous flow confined to a near-surface region (model SV, for ‘surface viscosity’). The depth of this region is on the order of the ion range, which is much smaller than the corrugation wavelength λ and on the same order as the corrugation amplitude (Fig. 1 inset). Without ion bombardment, the corrugations do not smooth at temperatures of 800° C and lower, where the viscosity of SiO₂ is quite high. SV provides better quantitative agreement with the data and is more consistent with previous measurements of ion-induced relaxation in SiO₂ than the other possible models: (i) ion-enhanced diffusive transport at the surface (SD, for ‘surface diffusion’) and (ii) ‘diffusionless smoothing’ in which erosion processes mimic surface diffusion [9] (SE, for ‘surface erosion’). The chief features of SV can be summarized as follows. *Temperature dependence:* We attribute the observed temperature dependence of λ to changes in ion-induced viscosity with temperature. From a weak temperature dependence of λ below 300° C, we deduce that at low temperatures the viscosity is temperature-independent, implying that the rate of network rearrangement associated with viscous relaxation is dominated by collision processes. At higher temperatures λ shows an Arrhenius-like increase with temperature; thermally induced rearrangements of the network become significant enough to aid the rearrangements initiated by atomic collisions. Such a temperature independent viscosity at low temperatures and an activated viscosity at elevated temperatures has also been deduced from the rate at which stress in SiO₂ is relaxed by ions with MeV energies [10]. *Energy dependence:* In SV the effect of thermal excitations on the network rearrangement is assumed to be independent of the effect of the ion-induced collision cascade. Hence the dependence of λ on temperature is separable

from its ion energy dependence, which is predicted to be a power law varying with ion energy as λ^* as 0.77 , quite close to the observed dependence of 0.85 . In SD, physically plausible models predict a weaker dependence of λ^* on ion energy, as does SE.

*Magnitude of λ^** : Like SV, SE predicts a temperature-independent wavelength at low temperatures. However SE predicts a much smaller λ^* than is observed.

The corrugated surfaces were produced in an ultra-high vacuum chamber (base pressure of 5×10^{-10} torr) mounted on an x-ray beamline at the Cornell High Energy Synchrotron Source (CHESS)[11]. The SiO_2 films were 500 nm thick and formed by conventional wet oxidation of a Si(001) wafer. The bombarding Ar^+ ions were incident at an angle of 45° from normal at fluxes of several μ / cm^2 with a background Ar pressure of 1×10^{-4} torr. The ion beam was rastered over the sample surface to insure uniform erosion of the surface in the area illuminated by the incident x-rays. The amount of erosion was determined ex-situ by methods standard for characterizing oxides on Si wafers; erosion rates ranged from $2 \text{ \AA} / \text{min}$ to $20 \text{ \AA} / \text{min}$, depending on ion energy and flux. Typical x-ray fluxes at a beam energy of 10 keV were 10^{12} photons/sec in a beam 0.5 mm high by 2.0 mm wide. The scattered intensity was probed in a glancing incidence geometry near where the diffuse scattering is peaked (the so-called "Yoneda wing" [12]).

Figure 1 illustrates the real-time development of corrugations during erosion by 1.0 keV ions. The diffuse intensity at different intervals is plotted as a function of scattering vector. The detector was scanned along the corrugation wavevector (which is in the plane of ion incidence). The single peak at time $t=0$ is the Yoneda wing whose height is related to the initial roughness of the sample. As the surface erodes, two peaks on either side of the central peak develop due to the corrugation periodicity. The heights

of the peaks increase after the periodicity is well-developed, indicating growth of the corrugation amplitude, although the periodicity remains relatively constant. The angular separation of these peaks can be related to the corrugation wavelength λ by assuming a simple asymmetric sawtooth shape for the surface for which the Fourier transform has been determined analytically [13]. Figure 2 shows a fit using this model. Both the 2nd order peaks associated with increasing spatial coherence of the corrugations and the asymmetric lineshape are well reproduced by the model. The asymmetric lineshape, which is fit by a difference in sidewall slope of $\sim 1^\circ$, likely arises from the off-normal ion bombardment geometry. The corrugation amplitudes and wavelengths from the fit are consistent with atomic force microscope (AFM) images of the surface; the inset of Fig. 2 is an ex-situ AFM image of the sample acquired after the x-ray measurements. The amplitudes of the corrugations are typically 10 to 20 Å. The rate of amplitude increase does vary with flux, but the value of λ is insensitive to flux for the ion energies studied (0.5 to 2 keV) within the factor of three range in flux accessible in the experiments.

During corrugation formation curvature gradients increase because of a morphological instability by which regions of negative surface curvature (pits) erode faster than regions of positive curvature (bumps) [14]. Other curvature-gradient increasing processes may occur on crystalline surfaces. The increases in curvature gradients are opposed by curvature-dependent smoothing processes in which there is net transport of material from regions of high curvature to regions of low curvature. Bradley and Harper (BH) showed that for the case of smoothing by surface diffusion, a stable sinusoidal surface morphology of constant wavelength develops during off-normal sputtering, although the amplitude of the sinusoid increases exponentially in

time [15]. Hence the surface amplitude $h(x, t)$ as a function of spatial coordinate x and time t can be written as $h(x, t) = h_0 \cos(qx) e^{rt}$, where h_0 is the initial amplitude, q is given by $2\pi/\lambda$, (λ is the corrugation wavelength) and r is the exponential growth rate. Mayer, Chason and Howard (MCH) developed a version of the BH model to determine an ion-induced surface diffusivity consistent with their observation of 300 Å wavelength corrugations formed by sputtering SiO₂ with 1 keV Ar⁺ ions [16]. MCH included in the growth rate for a sinusoid those terms due to smoothing by viscous flow as well as by surface diffusion. The viscous smoothing can be found from solutions to the two-dimensional Navier-Stokes equations with appropriate boundary conditions for a sinusoid (attempting to describe viscous smoothing using local spatial derivatives [17] overlooks the non-local character of viscous flow). Two geometric limits are relevant. In the first limit (that used by MCH), fluxes extend into the bulk a distance on the order of the wavelength of the sinusoid. In the second limit (that proposed by the present authors), viscous flow occurs only in a surface layer of thickness d where d/λ is small. Smoothing by bulk viscous flow [18], contributes a negative term $-F_b q$ to the rate of growth; smoothing by surface-confined viscous flow [19] contributes a term $-F_s d^3 q^4$. Here F_b (F_s) is proportional to $\eta_b / \eta_s (\eta_b / \eta_s)$, where η_b and η_s are the bulk and surface viscosities, respectively, and γ is the surface tension, assumed to be constant and isotropic.

The growth rate r of a sinusoid for bulk viscous relaxation [16] will be $r_b = Sq^2 - F_b q - Bq^4$, where S is a roughening prefactor related to the curvature-dependent erosion rate and B is a prefactor proportional to the surface diffusivity. For the limit of surface viscous relaxation, the growth rate r becomes $r_s = Sq^2 - F_s d^3 q^4 - Bq^4$. Differentiating r_b or r_s with respect to q will determine whether there is a dominant corrugation wavevector q^* for

which r is positive and maximum; the corrugation with wavevector q^* will grow faster than all others. For bulk viscous relaxation with $B=0$, it is found that there will be no such wavelength selection. When either surface diffusion or surface viscous relaxation dominates, then there will always be some q^* for which r is maximized.

Because ion-induced viscous flow occurs in a thin surface layer with a depth on the order of the ion range (50 Å and less for the energies used in the experiments described here), the limit of surface confined viscous flow can be used to determine q^* for the case when surface diffusion is negligible: solving for the wavelength with the largest rate r gives $q_{sv}^* = 2 \sqrt{(2F_s d^3 / S)}$. For ions incident with angle θ measured from the normal, $S = (fa/n)Y(\theta) \cos(\theta)$, where f is the ion flux, a is the average depth of energy deposition by the ions, n is the atomic density, $Y(\theta)$ is the sputter rate per ion, and $\cos(\theta)$ is a parameter related to the curvature dependence of the erosion rate. Experiments on viscous relaxation in SiO₂ indicate that $1/r$ and can be expressed as $1/r = \tau_r/f$, where $1/\tau_r$ is a flux-independent measure of the viscous *relaxation* per ion which varies with ion energy as $1/\tau_r \propto E^{-1/2}$. From measurements of ion-induced viscosities in bulk SiO₂ a value of 0.5 was deduced [20] whereas from measurements of the rate of smoothing of surface roughness due to light-ion bombardment of SiO₂, it can be concluded that $1/\tau_r = 1$ [16]. Equating the depth of energy deposition a and the depth of the reduced viscosity layer d gives

$$q_{sv}^* = 2 \sqrt{d^3 / [(f \cos(\theta) Y(\theta) \tau_r)]^{1/2}}. \quad (1)$$

Here q_{sv}^* is independent of flux, which is consistent with our observations. Simulations of sputter yield using the ion-collision simulator TRIM indicate that both d and

λ vary as $\lambda^{-0.55}$, where λ depends very weakly on energy. Hence

$$\lambda_{sv}^* = e^{(E/k_B T)^{0.27}}. \text{ For surface viscous relaxation } \lambda_{sv}^* = 1 \text{ and } \lambda_{sv}^* = 0.77.$$

Figure 3 shows the dependence of corrugation wavelength on inverse temperature for three different ion energies. Samples were pre-annealed to 800°C and then sputtered at temperature until a well-defined λ_{sv}^* developed. We separate the energy dependence from the temperature dependence in Eqn. 1 as $\lambda_{sv}^* = E(\lambda)W(T)$, where $E(\lambda) = c \lambda^p$ and $W(T) = [e^{-E/k_B T} + 1]^{-1/2}$. Here c is a proportionality constant, p represents the dependence on energy of $d(\lambda)/d\lambda$, E is a barrier for the thermally activated rearrangement of the network, and λ is a parameter introduced to account for the temperature independent ion-induced viscosity at low temperatures. A value of $p=0.85$ is found in a non-linear least squares fit to the data (the solid line in Fig. 3), which is quite close to the predicted value of 0.77. The inset in Fig. 3 shows each λ_{sv}^* divided by the term $W(T)$; the power law dependency derived from the fit is also plotted. A power law dependence of $\lambda_{sv}^* \propto \lambda^{-0.8}$ has been observed for corrugations formed by sputtering Si with O_2^+ ions[21], suggesting that our model may also describe corrugations formed when sputtering disorders a crystalline surface. A value of $E = 0.4$ eV is found in the fit, which is quite small compared to the bond energies in SiO_2 . However activation energies with approximately the same value have been observed in other measurements of ion-assisted viscous flow [10]. It is likely that 0.4 eV represents the average energy associated with a collective motion of defect structures within the network.

Models based on surface diffusion (SD) in some cases predict a flux-independent λ_{sv}^* but not the strong energy dependence observed here. In SD transport occurs by the motion of individual atoms or molecules, either through a thin layer or constrained to the surface. Vajo *et al.* used a simple ion-induced mixing model in which the diffusivity

in the thin layer is enhanced by the excess defects created by the ion collisions. In this model $\dot{\rho}_{SD}^*$ is flux-independent and given by $\dot{\rho}_{SD}^* \propto Y^{0.5}$ for a sputter yield dependency of $Y(\epsilon) \propto \epsilon^{0.85}$ [21]. For the value of $\alpha = 0.55$ appropriate for our experiments, $\dot{\rho}_{SD}^*$ becomes nearly independent of ion energy. For the case of surface diffusion at the surface, Erlebacher *et al.* proposed that a flux-independent $\dot{\rho}_{SD}^*$ arises when surface traps dominate the recombination of defects created on the surface [2]. In this model $\dot{\rho}_{SD}^* = [Z/d \cdot Y(\epsilon)]^{1/2}$, where Z is the number of diffusing molecules per incident ion and d is the areal density of surface traps. Assuming that the density of traps and the density of diffusing molecules each increases with energy at the same rate, then the energy dependence becomes $\dot{\rho}_{SD}^* \propto \epsilon^{-1/2}$. The detailed surface diffusion processes on SiO₂ would have to be radically different from those proposed in these models to reproduce the observed $\epsilon^{0.85}$ dependence. In real physical systems where surface diffusion is thought to dominate smoothing, such as Ge and Si, $\dot{\rho}_{SD}^*$ has not been found to be flux independent. In the case of Ge, $\dot{\rho}_{SD}^*$ actually decreases with increasing ion energy [22].

In model SE erosion processes appear to smooth the surface. Expanding the rate of height change $dh(x, t)/dt$ as a function of surface spatial derivatives produces a term in $dh(x, t)/dt$ that mimics surface diffusion in its curvature dependence [9]. A dominant wavelength λ_{SE}^* that is independent of temperature and flux results, giving SE certain of the important observed attributes. However it is straightforward to show that the values of λ_{SE}^* must be on the order of the width of the spatial distribution of energy deposited by an ion. This width varies as $\epsilon^{0.5}$ at the experimental energies and is

approximately 10 times smaller than the observed values of τ^* , suggesting that SE alone cannot account for the observed low-temperature behavior.

In summary, a model of corrugation formation based on surface viscous relaxation better explains the data presented here than current literature models based on surface diffusion or surface erosion. Consistent with other experiments on ion-induced surface smoothing, our model indicates a strong dependence of the ion-induced viscosity on ion energy. The microscopic processes responsible for this dependency can likely be elucidated by molecular dynamics simulations; such simulations have previously proved effective for describing changes in glass structure due to radioactivity-induced atomic collisions [23].

We acknowledge helpful discussions with E. Chason, D. Cahill, L. Barabasi, M. Rauscher, and J. Sethna. This work was supported by the National Science Foundation through grants DMR-96-32275 to the Cornell Center for Materials Research and grant DMR-97-13424 to CHESS. [24-28]

FIG.1 : Diffuse intensity from SiO₂ sputtered by 1 keV Ar + versus time and x-ray scattering vector k . The arrows show different orders of the corrugation periodicity as determined by the fit to the final lineshape (see Fig. 2). Inset: Geometry of incident ions, scattering vector k , and corrugation wavelength λ . The viscosity near the surface is reduced in a region of thickness d , comparable to the ion range.

FIG. 2: Diffuse scattering from sample of Fig.1 after 185 minutes of sputtering. The data is fit for an asymmetric sawtooth surface with a wavelength of 270 Å and sidewall slopes of 6° and 7°; arrows indicate the different orders of the corrugation wavevector

determined by the fit. Upper Inset: AFM image taken ex-situ after the x-ray measurements showing the projected ion beam direction. Lower inset: Model geometry.

FIG. 3. Corrugation wavelength λ^* as a function of inverse temperature for different ion energies. The solid line is a fit for surface viscosity. Inset: λ^* scaled for temperature dependence versus ion energy E . The measurement error is comparable to the height of the symbol. The power law dependence of $\lambda_{\text{corr}}^{0.85}$ is plotted.

- [1] M. Navez, C. Sella, and D. Chaperot, *Comptes Rendus J. de Phys.* **254**, 240 (1962).
- [2] J. Erlebacher *et al.*, *Phys. Rev. Lett.* **82**, 2330 (1999).
- [3] E. Chason *et al.*, *Phys. Rev. Lett.* **72**, 3040 (1994).
- [4] S. W. MacLaren *et al.*, *J. Vac. Sci. Technol. A* **10**, 468 (1992).
- [5] S. Rusponi, C. Boragno, and U. Valbusa, *Phys. Rev. Lett.* **78**, 2795 (1997).
- [6] M. E. Keeffe, C. C. Umbach, and J. M. Blakely, *J. Phys. Chem.* **55**, 965 (1994).
- [7] D. C. Cassidy and N. A. Gjostein, *J. Amer. Cer. Soc.* **53**, 161 (1970); G. De With and A. J. Corbijn, *J. Mat. Sci.* **30**, 3155 (1995); K. Hirao and M. Tomozawa, *J. Amer. Cer. Soc.* **70**, 43 (1987); A. Kishi, K. Fueki, and K. Kitazawa, *J. Non-Cryst. Sol.* **33**, 95 (1979); J. M. Blakely, C. C. Umbach, and S. Tanaka, in *Dynamics of Crystal Surfaces and Interfaces*, edited by P. M. Duxbury and T. J. Pence (Plenum, New York, 1997), p. 23.
- [8] E. Chason *et al.*, *Appl. Phys. Lett.* **72**, 3276 (1998).
- [9] M. A. Makeev and A. L. Barabasi, *Appl. Phys. Lett.* **71**, 2800 (1997).
- [10] M. L. Brongersma, E. Snoeks, and A. Polman, *Appl. Phys. Lett.* **71**, 1628 (1997).
- [11] R. L. Headrick *et al.*, *Phys. Rev. B* **54**, 14686 (1996).
- [12] S. K. Sinha, E. B. Sirota, and S. Garoff, *Phys. Rev. B* **38**, 2297 (1988).

- [13] M. Yoon *et al.*, Surf. Sci. **411**, 70 (1998).
- [14] P. Sigmund, J. Mat. Sci. **8**, 1545 (1973).
- [15] R. M. Bradley and J. M. E. Harper, J. Vac. Sci. Technol. A **6**, 2390 (1987).
- [16] T. M. Mayer, E. Chason, and A. J. Howard, J. Appl. Phys **76**, 1633 (1994).
- [17] G. Carter, Phys. Rev. B **59**, 1669 (1999).
- [18] S. Pai, *Viscous Flow Theory, Vol .1* (Van Nostrand, 1956); W. W. Mullins, J. Appl. Phys. **30**, 77 (1959)
- [19] S. E. Orchard, Appl. Sci. Res. **11A**, 451 (1962).
- [20] E. Snoeks *et al.*, J. Appl. Phys. **78**, 4723 (1995).
- [21] J. J. Vajo, R. E. Doty, and E.-H. Cirlin, J. Vac. Sci. Technol. A **14**, 2709 (1996).
- [22] E. Chason, T. M. Mayer, and B. K. Kellerman, Mat. Res. Soc. Sympo. Proc. **396**, 143 (1996).
- [23] J. M. Delaye and D. Ghaleb, J. Nucl. Mater. **244**, 22 (1997)..