Surface Smoothing of Rough Amorphous Films by Irradiation-Induced Viscous Flow

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Surface roughening and smoothing reactions on vapor codeposited glassy $Zr_{65}Al_{7.5}Cu_{27.5}$ films by 1.8 MeV Kr^+ ion beam irradiation is investigated. Irradiation causes significant smoothing of initially rough surfaces, and nearly atomically smooth films can be achieved. Smooth surfaces roughen at high doses and long wavelengths. By a Fourier analysis, radiation-induced viscous flow is identified as the dominant surface relaxation mechanism. Two noise terms are identified, which operate on different length scales: One is due to sputtering and the other to thermal spikes. The irradiation-induced viscosity is compared with radiation-enhanced diffusion.

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Kinetic roughening of surfaces in open dissipative systems has become of broad scientific interest owing to its significance for such diverse processing methods as vapor deposition, oxidation, and ion beam irradiation [1]. For ion irradiations the surfaces of solids generally undergo roughening and smoothing reactions acting in competition, and for many crystalline and amorphous materials, this competition leads to roughening instabilities and even patterning [2]. Most studies undertaken on kinetic roughening have utilized low-energy ion bombardments for which the external forcing could reasonably be associated with atomic level sputtering reactions. It is now recognized, however, that bombardment with higher energy ions has a dramatic effect on the surface morphologies owing to collective, thermal spike effects. Simulations have shown, for example, that local melting in the surface region can cause flow of molten material onto the surface, crater formation, and dislocation loop punching [3,4]. Scanning tunneling microscopy [5] and transmission electron microscopy [6] measurements have corroborated this type of behavior. The perturbations to the surface of this type are characterized by a far coarser length scale than that typical of sputtering, exceeding several nanometers in many cases [7]. The present work considers the effect of this mesoscopic noise source, on the surface roughening behavior, acting in parallel with atomic level noise from sputtering.

We chose for this investigation near-normal, 1.8 MeV bombardment of the metallic glass, $Zr_{65}Al_{7.5}Cu_{27.5}$. These conditions eliminate the complications introduced by step edge anisotropies in crystalline materials and minimize ripple formation due to preferential sputtering. The choice of an amorphous metallic target was further motivated by the conclusion drawn in earlier works that smoothing of amorphous materials derives from a viscous flow mechanism [8,9]. While irradiation-induced viscous flow has been explained by a thermal spike mechanism for high-energy bombardments, where electronic stopping powers can exceed 1 keV/Å, the mechanisms when nuclear stopping is dominant [10] are less clear. This is particularly true for low-energy light-ion irradiation of targets like Si and SiO_2.

$Zr_{65}Al_{7.5}Cu_{27.5}$ [11] was selected for the current experiments since the thermodynamical and mechanical properties of this alloy are understood in detail [12]. The crystallization temperature of $Zr_{65}Al_{7.5}Cu_{27.5}$ is over 80 K above the glass temperature. This makes it possible to anneal initially rough thin film specimens above the glass temperature and obtain atomically smooth samples so that both smoothing and roughening could be studied on the same alloy. In addition, ion beam mixing has been measured on similar alloys. These data provide the possibility to compare the irradiation-induced diffusion coefficient directly with irradiation-induced viscous flow through the Stokes-Einstein relationship.

The alloys were evaporated under UHV conditions (base pressure $\leq 3 \times 10^{-10}$ Torr) onto thermally oxidized Si(100) wafers at room temperature. The irradiations with 1.8 MeV Kr^+ ions were also performed at room temperature under high vacuum conditions (pressure 3×10^{-8} Torr). The applied doses were measured to an accuracy of 10%, although the relative doses are known to a few percent. Beam heating of the samples, which were attached to a water-cooled Cu block, was negligible for the applied currents below 300 nA/cm^2 employed here. The surface topographs $h(\vec{x})$ [considered on a two dimensional coordinate system parallel to the substrate with $\langle h(\vec{x})\rangle_{\vec{x}} = 0$; $\vec{x} = (x, y)$] for different irradiation doses were measured using a commercial atomic force microscope (AFM) applying primarily contact mode, and scanning tunneling microscopy in constant current mode. The surface structures were characterized quantitatively by the root mean square (rms) roughness

$$\sigma = \sqrt{\langle (h(\vec{x}))^2 \rangle_{\vec{x}}} \qquad (1)$$

and the lateral correlation length R_C. The latter is defined as the abscissa of the first maximum of the height-height correlation function (e.g., [13])

$$C(r) = \langle h(\vec{x}) h(\vec{x} + \vec{R}) \rangle_{\vec{x}, |\vec{R}| = r} . \qquad (2)$$

The roughnesses of selected samples were checked using x-ray reflectivity measurements, as described elsewhere [14]. Amorphicity before and after irradiation is verified using x-ray diffraction (Cu K_α).

The smoothing action of ion irradiation is illustrated in Fig. 1 where surface topographs of 480 nm thick amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ films show the closure of the gaps (Fig. 1b) of the initially cusplike surface (Fig. 1a), followed by a strong decrease of the corrugations (Fig. 1c) with almost unchanged lateral structure size ($R_C \approx$ 21 nm). The rms roughness during this irradiation sequence is plotted in Fig. 2 as a function of dose. Following a rapid initial decrease with dose, the roughness reaches a minimum at 2×10^{16} ions/cm^2. Additional irradiation results in added roughness and mesoscopic fluctuations on the surface, as shown in Fig. 1d. The process of surface smoothing, notably, is accompanied by nearly complete relaxation of the tensile mechanical intrinsic film stresses generated during evaporation [15], a finding in agreement with earlier stress relaxation measurements reported on amorphous Si [16]. Identification of the smoothing processes is possible using stochastic rate equations for the evolution of the surface $h(\vec{x}, t)$ in Fourier space (e.g., [17])

$$\frac{\partial h(\vec{q}, t)}{\partial t} = -h(\vec{q}, t) \sum_{i=1}^{4} a_i q^i + \eta(\vec{q}, t) , \qquad (3)$$

where $a_i \geq 0$ denotes constants and η temporally and spatially uncorrelated Gaussian noise with

$$\langle \eta(\vec{q}, t) \eta(\vec{q}\,', t') \rangle = 2D(q) \delta(\vec{q} + \vec{q}\,') \delta(t - t') . \qquad (4)$$

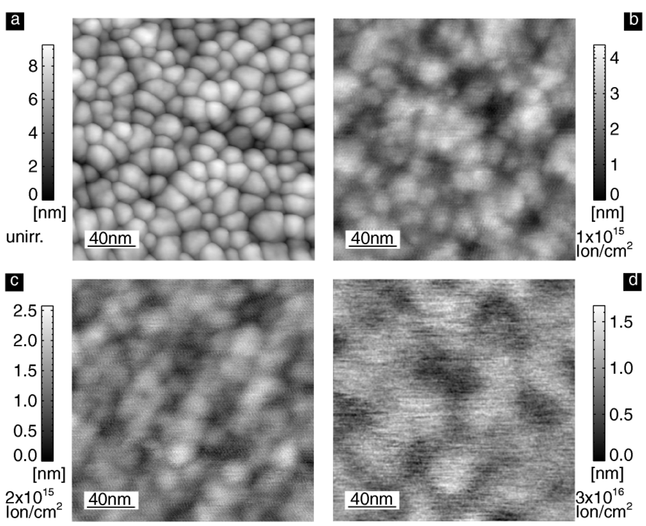

FIG. 1. Surface topographs, as measured by AFM, for a 480 nm amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ film, irradiated with different doses of 1.8 MeV Kr^+.

Each term in the sum in Eq. (3) can be identified with a specific surface relaxation process, as pointed out by Herring [18]. Starting from a surface of arbitrary structure, it can be shown (similar to derivations in [19]) that the radially averaged spectral power density

$$\hat{C}(q, t) = \langle |h(\vec{q}, t)|^2 \rangle_{|\vec{q}| = q} \qquad (5)$$

[normalized to $C(q, t)$] behaves like

$$C(q, t) = C_0(q) e^{-2t \sum_{i=1}^{4} a_i q^i} + D(q) \frac{1 - e^{-2t \sum_{i=1}^{4} a_i q^i}}{\sum_{i=1}^{4} a_i q^i} \qquad (6)$$

for which the steady state solution at long times $t \to \infty$ is $C(q, t) = C(q) = D(q) / \sum_{i=1}^{4} a_i q^i$.

The dominant surface relaxation mechanism can then be obtained from a log-log plot of $C(q)$. Figure 3 shows $C(q)$ before and after irradiation to two doses. While unirradiated samples reveal a q^{-4} behavior characteristic of surface diffusion [12] in the high frequency regime (B), irradiated samples show a q^{-1} dependence, which is characteristic of viscous flow. The region showing q^{-1} extends to smaller q with irradiation dose. The growth of this region is expected since the relaxation time τ, for smoothing by viscous flow depends on q as

$$\mu / \tau = \gamma q , \qquad (7)$$

where μ is the viscosity of the sample during irradiation and γ is the surface energy [20]. An important feature in Fig. 3 is that at the largest values of q, the film undergoes roughening, illustrating that the surface has reached a steady state in this regime between roughening and smoothing reactions. We examined the roughening and steady state behavior at all length scales by irradiating specimens that were initially smoothed by thermal annealing. These data are shown in Fig. 4. The main observation here is that at both doses a q^{-1} dependence is obtained at high and at low q, but with a transition in the level of

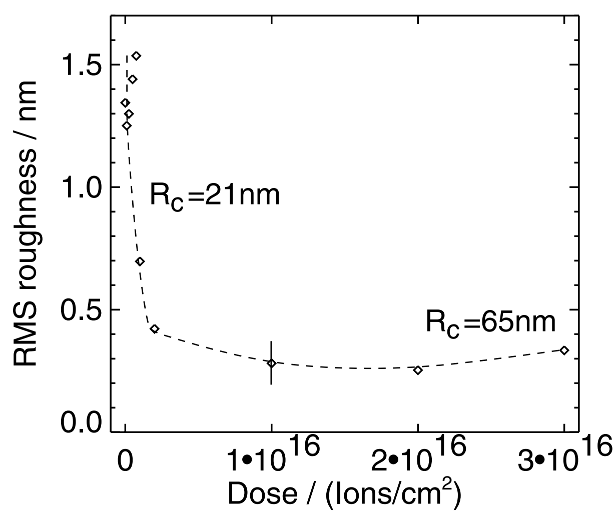

FIG. 2. Evolution of surface roughness and lateral structure size R_C in dependence of the radiation dose.

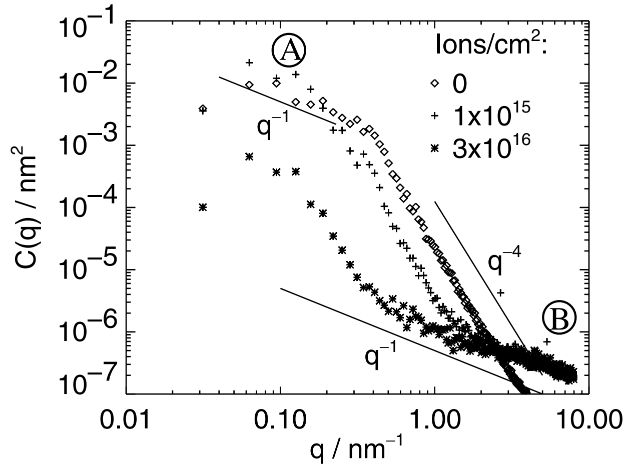

FIG. 3. Radially averaged spectral power densities for unirradiated and irradiated amorphous $Zr_{65}Al_{7.5}Cu_{27.5}$ films.

$C(q)$ in the region $q = 0.3$ nm^{-1}. While both the small q (region A in Fig. 4) and large q (region B) vary as q^{-1}, only region B reaches a steady state.

We explain the present data by considering the surface roughening mechanism introduced by the thermal spike effects mentioned above, within a linear theory. For simplicity we treat these roughening mechanisms as an additional noise term that operates over a larger length scale than the atomic level noise arising from sputtering. The total noise η is thus composed of two contributions, considered to be statistically independent:

$$\eta(\vec{x}, t) = \zeta(\vec{x}, t) + \xi(\vec{x}, t). \tag{8}$$

Following a suggestion of Edwards and Wilkinson [21], the contribution of noise due to bump formation to the total noise is estimated assuming a simple uniform Gaussian shape located at $\vec{x}_0$ with the lateral width a, and total volume ϵ

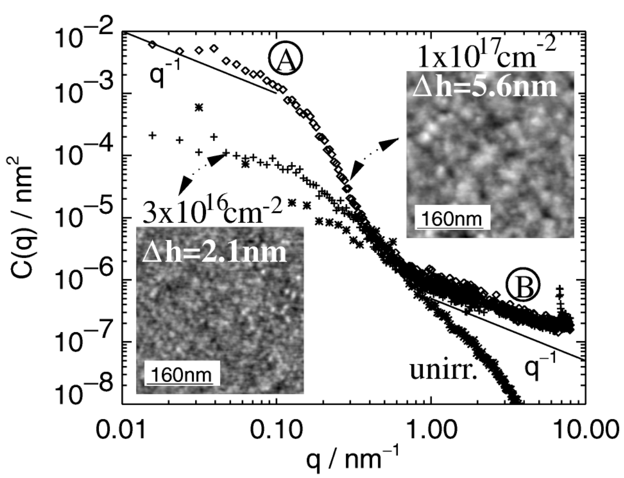

FIG. 4. AFM images and radially averaged spectral power densities for an initially smooth film irradiated with high doses of 1.8 MeV Kr^+.

$$f(\vec{x} - \vec{x}_0) = \frac{\epsilon}{2\pi a^2} \exp\left(-\frac{(\vec{x} - \vec{x}_0)^2}{2a^2}\right). \tag{9}$$

The noise thus generated by each such individual thermal spike i can be written as

$$\xi_i(\vec{x}, t) = \delta(t - t_i) f(\vec{x} - \vec{x}_i), \tag{10}$$

leading for N independent events to the total noise $\xi(\vec{x}, t) = \sum_{i=1}^{N} \xi_i(\vec{x}, t)$ where the times and positions are randomly distributed in a sufficiently long interval of time $t_i \epsilon [0, T]$ and space $\vec{x}_i \epsilon [-L/2, L/2]^2$. With the Fourier transformation of the bump shape function $f(\vec{q}) = FT[f(\vec{x})]$, the noise in Fourier space is

$$\xi(\vec{q}, t) = f(\vec{q}) \sum_{i=1}^{N} \delta(t - t_i) \exp(-i\vec{q}\vec{x}_i). \tag{11}$$

Averaging over all x_i and t_i, the expectation values can be calculated, with the average ion flux $I = N/(L^2 T)$:

$$\langle \xi(\vec{q}, t) \xi(\vec{q}', t') \rangle = I \epsilon^2 \delta(\vec{q} + \vec{q}') \delta(t - t') \exp(-a^2 q^2). \tag{12}$$

Thus, the noise on an atomic level $\zeta(\vec{q}, t)$ can be mainly attributed to sputtering effects with an average sputtering yield ν per incident ion on the surface. Having a vanishing lateral extent in the continuum limit, an expression can be easily gained simply as a limit $a \rightarrow 0$ and by replacing $I \rightarrow \nu \cdot I$ and $\epsilon \rightarrow \Omega$ in Eq. (12), where Ω denotes the atomic volume. The total noise intensity in Eq. (4) can be written as

$$2D(q) = I[\nu \Omega^2 + \epsilon^2 \exp(-a^2 q^2)], \tag{13}$$

which shows (for $\epsilon \gg \Omega$) a transition from $2D = I\epsilon^2$ for very low q to an atomic noise dominated regime $2D = \nu I \Omega^2$ for very high q, with a transition region for frequencies corresponding to the lateral extent of the bumps $a = 1/q_T$. Taking the lowest q_T, observable from the experimentally determined spectral power densities $C(q)$ (Figs. 3 and 4), a maximum lateral extent of the bumps $a \leq 7.5$ nm can be estimated, which is in good agreement with the typical lateral dimensions expected for viscous flow due to thermal spikes for the present irradiation conditions [7]. Finally, we return to the question of whether viscous flow can indeed account for the observed smoothing by comparing the irradiation-induced viscosity with the measured irradiation-induced diffusion coefficient. The relaxation time, τ, for smoothing of a surface feature by viscous flow, is given by Eq. (7). In Figs. 2 and 3 we see that at an irradiation dose of 10^{15}/cm^2 the initial roughness is reduced by a factor of e^{-1} at $q \approx 0.3$ nm^{-1}, and with $\gamma \approx 1.4$ J/m^2 we obtain $\frac{\mu}{\tau} \approx 4 \times 10^8$ N/m^2. In the diffusivity measurements (we use data for the amorphous alloy $Zr_{50}Ni_{50}$, which should be very similar to $Zr_{65}Al_{7.5}Cu_{27.5}$ [22]) the normalized diffusion constant is given by $\hat{D} = D\tau/(\Phi F_D) \approx 25$ Å^5/eV, where Φ is the ion fluence and F_D is the damage energy deposition per unit length normal to the specimen surface. With Stokes-Einstein and the atomic radius r this leads to

$$\frac{\mu}{\tau} = \frac{kT}{6\pi r\hat{D}\Phi F_D} \approx 1.4 \times 10^6 \ \frac{\mathrm{N}}{\mathrm{m}^2} \tag{14}$$

using $T \approx 1500$ K, $r \approx 0.2$ nm, $F_D \approx 160$ eV/Å [23], and $\Phi = 10^{15}$ cm^{-2}. The diffusion data illustrate that the irradiation-induced viscosity is indeed sufficiently small to explain the observed smoothing; in fact, it suggests that the smoothing should occur 2 magnitudes faster. Part of the discrepancy surely arises from the approximate nature of the analysis; for example, ballistic mixing during irradiation contributes to diffusion but not viscous flow. A more significant error presumably arises from neglecting the fact that viscous flow is restricted to the local region of the thermal spike; that is, only a local region becomes hot during each impact. This has little effect on diffusion, since each atom diffuses only one or two atomic jumps during a spike, but it can restrict the flow of matter. In this regard, it raises the question whether viscous flow can be operative for low-energy light ion bombardments of surfaces.

In conclusion, we have illustrated that high-energy irradiation can lead to surface roughening mechanisms that operate on a larger length scale than sputtering, and this dramatically affects the surface morphology. This finding presents the possibility that the morphologies of surfaces are tunable by appropriate selection of ion beam mass and energy. We have also demonstrated that smoothing of rough amorphous alloys can occur by viscous flow for irradiations where nuclear rather than electronic stopping is predominant, and we have provided a semiquantitative account for the rate of smoothing by comparison with irradiation-induced diffusion experiments.

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