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Conf-9311153--1

**DENSITY REDUCTION:
A MECHANISM FOR AMORPHIZATION AT HIGH ION DOSES**

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ABSTRACT

At cryogenic temperatures, the accumulation of vacancy-interstitial pairs in Al_2O_3 from atomic displacements associated with ion implantation produces amorphization. At room temperature, these pairs recombine, and amorphization occurs only at high doses. X-ray reflectivity measurements show that amorphization of the surface of Al_2O_3 implanted at room temperature with 160 keV Cr^+ ions is preceded by a progressive reduction in near-surface density. Monte Carlo simulations show that this density reduction can be accounted for by high-energy-transfer collisions which knock atoms deep into the target, leaving widely separated vacancies and interstitials, which do not recombine. Electron microscopy shows that at least some of these vacancies condense into voids. We propose that this reduction in near-surface density can lead to amorphization at high doses. We present simple approximations for the density reduction expected for different ions and targets.

INTRODUCTION

The mechanisms by which ion implantation causes amorphization can be broadly categorized as structural and chemical. Chemical effects occur in the end-of-range (eor), where implanted ions come to rest, changing the chemical composition of the target. Structural effects are dominant in the midrange: as the ions pass through they displace target atoms from lattice sites. At relatively low temperatures, midrange amorphization typically requires a dose producing on the order of one displacement per target atom (dpa), while at higher temperatures structural damage is annealed out, and amorphization does not occur.¹⁻⁴

Room temperature amorphization occurs at much higher ion doses for Al_2O_3 , ZrO_2 , MgO , and WC . While a dose ~ 1 dpa produces amorphization at cryogenic temperatures, ~ 100 dpa is required at room temperature.^{1,5-8} The mechanism for this high-dose amorphization has been unclear. We address the origin of this anomalously high-dose amorphization by examining the density and microstructure of Al_2O_3 films implanted with ion fluences below the amorphization threshold. Implantation with Cr^+ was chosen to minimize chemical effects: it has been shown⁹ that elements such as Cr which occupy substitutional sites induce amorphization at a higher dose. Room temperature amorphization of Al_2O_3 occurs at a dose between 1×10^{21} and 6×10^{21} Cr^+/m^2 [Ref. 6]; we examine samples implanted with 4×10^{20} and 1×10^{21} Cr^+/cm^2 .

We summarize x-ray reflectivity, electron microscopy, and Monte Carlo simulation results¹⁰ which show that amorphization is preceded by a progressive reduction in near-

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surface density. We derive approximate formulae for the expected density change as a function of the choice of target and incident ion.

X-RAY REFLECTIVITY

X rays with wavelength λ are totally reflected by a material with density ρ , average atomic number Z , and average atomic weight M below a critical incident angle $\theta_c = (A\rho Z\lambda^2/M)^{1/2}$, where $A = 2.70 \times 10^{10} \text{ m}$.¹¹ Because x rays penetrate only $\sim 5 \text{ nm}$ under conditions of total reflection, the critical angle for total external reflection provides a sensitive measure of near-surface density. As shown in Fig. 1, implantation increases this critical angle. The calculated reflectivity profiles (Fig. 1, lines) are derived from simple models¹⁰ including surface roughness, the thickness of the implanted layer, and the degree to which the midrange density is decreased and the eor density is increased. Here we defer discussion of complete models of the density profile and emphasize the simple, model-independent correspondence between the decrease in reflectivity at the critical angle (triangles, Fig. 1) and the near-surface density. The critical angles observed in Fig. 1 are used to compute the near-surface densities in Fig. 2.

Note that the density decrease is *not* caused by a lattice expansion, in contrast to observations at low temperature.¹² It has been shown using glancing-incidence x-ray diffraction¹³ that lattice expansion accounts for just 0.3% of the 12% reduction in density produced by $10^{21} \text{ Cr}^+/\text{cm}^2$. At low temperature, vacancy-interstitial pairs produced by implantation lead to a large lattice expansion, while at room temperature these pairs recombine. Rather, the density reduction results from the accumulation of excess vacancies in the midrange.

Fig. 1 X-ray reflectivity from Al_2O_3 . (•) unimplanted, (○) implanted with $10^{21} \text{ Cr}^+/\text{m}^2$, (▲, △) critical angles, lines are models from Ref. [10].

Fig. 2 Near-surface density as measured by x-ray reflectivity and computed by Monte Carlo simulations. Dashed line is a guide to the eye.

MONTE CARLO SIMULATIONS

Monte Carlo simulations of atomic displacements provide a quantitative model for the density reduction observed with x-ray reflectivity. We have applied the TRIM89 code^{10,14} to calculate the effects of implantation. Because each ion is assumed to pass through structureless Al_2O_3 , unaffected by implantation, the results are linear in incident ion fluence. The effects of substrate crystal structure are neglected, but because the density reduction is predominantly caused by high-energy-transfer collisions which do not depend on crystal structure, we expect the results to be accurate. More seriously, the calculation does not include recovery mechanisms. The simulated density profile is shown in Fig. 3, and the near-surface density is plotted in Fig. 2. The fluctuations in the Monte Carlo result in Fig. 3 is statistical, because we simulated only 30,000 ions.

ELECTRON MICROSCOPY

Monte Carlo simulations demonstrate that an excess of vacancies over interstitials is produced as atoms are pushed deeper into the target. Transmission electron micrographs (TEM) of cross-sections of implanted samples are used to determine how these excess vacancies are accommodated. Figure 4 shows a TEM of Al_2O_3 implanted with $4 \times 10^{20} \text{ Cr}^+/\text{m}^2$. While a dense array of dislocations is apparent in the eor (60 - 230 nm), the midrange (0 - 60 nm) is free of visible dislocations and contains a high density ($\sim 5 \times 10^{23}/\text{m}^3$) of small ($\sim 2 \text{ nm}$) features which exhibit contrast consistent with that of voids. Electron microdiffraction demonstrated that the midrange remains crystalline for both doses.

Fig. 3 Density profiles calculated based on Monte Carlo simulations, x-ray reflectivity data, and approximate Eqs. (4) and (7).

Fig. 4 Cross-section TEM showing the microstructure observed in Al_2O_3 following implantation with $4 \times 10^{20} \text{ Cr}^+/\text{m}^2$.

ANALYTIC APPROXIMATION

While density changes can be calculated most accurately using Monte Carlo simulations, a simple order-of-magnitude approximation may prove useful. We consider a model where ions of mass M_1 , atomic number Z_1 , fluence f/a_B^2 , and energy $E_0 E_R$ impinge on an elemental target with atomic mass M_2 , atomic number Z_2 , and number density n/a_B^3 . Factors of the Rydberg energy $E_R = 13.6$ eV and the Bohr radius $a_B = 5.3 \times 10^{-11}$ m are included to make parameters dimensionless. We neglect straggling and use the approximate ranges given by Sigmund.¹⁵ For the incident ions the range is

$$R_i(E_0)/a_B \approx 0.12 E_0 \bar{Z}^{1/3} (1 + M_2/M_1) / (n Z_1 Z_2) , \quad (1)$$

where $\bar{Z} = (Z_1^{2/3} + Z_2^{2/3})^{3/2}$. When an incident ion transfers energy TE_R to a target atom, the atom penetrates to depth

$$R_s(E_0, T)/a_B \approx 0.34 T^{3/2} / (n E_0^{1/2} Z_2^{5/3} \mu^{1/2}) , \quad (2)$$

which includes a factor of $2\sqrt{T/T_m}$ to approximately account for the effect of scattering angle on penetration depth; $\mu = M_1 M_2 / (M_1 + M_2)^2$, and $T_m = 4\mu E_0$ is the maximum energy transfer to target atoms. Because we will consider high-energy-transfer collisions, we use the unscreened Rutherford cross-section,

$$d\sigma/d\tau \approx 4\pi Z_1^2 Z_2^2 a_B^2 \mu / (E_0 T^2) . \quad (3)$$

These approximations are valid for $0.001 < E_0 \bar{Z}^{1/3} / Z_1 Z_2 < 10$.

Two effects contribute to a midrange density reduction. The first depends on the proximity of the target surface:

$$\frac{\Delta n_1(x)}{n} \approx \int_0^{T(E_0, x)} \frac{d\sigma}{dT} dT - \int_0^{T_*(E_0)} \frac{d\sigma}{dT} dT \approx \frac{-6.2 f n^{1/3} Z_1^2 Z_2^{8/9} \mu^{2/3}}{E_0^{4/3} (x/a_B)^{2/3}} , \quad (4)$$

where $T(E_0, x)$ is the energy required for a scattered ion to penetrate to depth x . The first integral is the density gain to shallower target atoms being scattered to depth x ; the second integral is the density loss due to target atoms being scattered from depth x deeper into the target. Due to the surface, no high-energy atoms are scattered to shallow depths, and density is reduced. Near the surface, Δn_1 becomes large in magnitude; its average over the ion penetration depth is

$$\langle \Delta n_1 \rangle / n \approx -75.3 f M_1^{1/3} \mu Z_1^{8/3} Z_2^{14/9} / (E_0^2 M_2^{1/3} \bar{Z}^{2/9}) .$$

A further reduction in midrange density arises because the scattering cross-section increases with decreasing ion energy. Because the incident ion energy is reduced as the ion penetrates the target, again more atoms are scattered *from* any depth, deeper into the target, than are scattered from shallower depths *to* that depth. At depth x , target atoms are scattered deeper by an average distance

$$M(x) \approx f \int_0^{T_+(E(x))} R_s(E, T) \frac{d\sigma}{dT} dT \quad (6)$$

where $E(x)$ is the incident ion energy at depth x , and density will be reduced by

$$\Delta n_2/n \approx (dE/dx)(dM/dE) \approx -142 f Z_1^3 Z_2^{4/3} M_1^{1/2} / (E_0^2 \bar{Z}^{1/3} M_2^{1/2} \mu^{3/2}) . \quad (7)$$

Noting that $M \sim 2Z$, we see that the surface effect Δn_1 dominates for $Z_1 < Z_2$ and $Z_1 > Z_2$, and is of similar magnitude to the energy-loss effect Δn_2 for $Z_1 \approx Z_2$.

In Fig. 3, we compare measured density changes with the more accurate Monte Carlo result with the approximations of Eqs. (4) and (7). While the Monte Carlo approximation overestimates the density reduction due to neglect of recovery processes, the analytic approximation used here underestimates the density reduction due to the neglect of multiple scattering processes.

DISCUSSION

The pairs of vacancies and interstitials created when ion bombardment displaces target atoms may be accommodated in three ways. Firstly, pairs may simply recombine. While thermal diffusion in Al_2O_3 is negligible at room temperature,^{16,17} and the low amorphization threshold of Al_2O_3 at cryogenic temperature demonstrates that ion bombardment alone does not bring about vacancy-interstitial recombination, the resistance of Al_2O_3 to amorphization at room temperature shows that thermal effects and ion bombardment synergistically cause recombination.

Secondly, vacancies or interstitials may precipitate into dislocation loops. Electron microscopy (Fig. 4) shows that dislocations form in the eor but not in the midrange. Because implantation leads to an excess of vacancies in the midrange and of interstitials in the eor, this is consistent with observations that dislocation loops in Al_2O_3 are formed from interstitials but not from vacancies.^{18,19}

Finally, isolated vacancies or interstitials may condense into other defects such as microvoids, vacancy clusters, or regions of amorphous Al_2O_3 . While recombination or dislocation loop formation will restore the density to its unimplanted value, formation of these other defects will preserve the reduced midrange density. Because Monte Carlo simulations predict twice the observed density reduction, we conclude that half the excess midrange vacancies recombine, either with interstitials deeper in the target or at the surface, while half are stabilized as low-density point defects. Since observable voids account for only ~0.2% density reduction, whatever defect accounts for most of the density reduction is

not apparent in TEM. For targets which are resistant to low-dose amorphization, such as Al_2O_3 at room temperature, the accumulation of these low-density defects may eventually destabilize the lattice and amorphize the target.

Self-implantation (e.g. stoichiometric implantation of Al_2O_3 with Al and O) minimizes chemical effects; this might provide clearer evidence that high-dose amorphization is due to displacement effects. Self-implantation, however, requires higher doses to produce large density changes than does implantation with heavier ions. Effective sample cooling would be required to achieve such high doses in a reasonable time, to avoid beam heating associated with high-flux irradiation..

ACKNOWLEDGEMENTS

This work was sponsored by the Division of Materials Sciences and by the Office of Fusion Energy, U.S. Department of Energy, under contract DE-AC05-84OR21400 with Martin Marietta Energy Systems, Inc.

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