Interface-Limited Grain-Boundary Motion during Ion Bombardment

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Ion bombardment of polycrystalline Ge, Si, and Au films results in grain-boundary migration rates which are weakly temperature dependent, and which greatly exceed thermal migration rates. The enhanced migration rate is proportional to the rate of nuclear collisions at or very near the grain boundary. We present a transition-state model which accounts for the observed kinetics of grain-boundary migration during bombardment. The ratio of atomic jumps at grain boundaries to the local collision-induced Frenkel-defect generation rate is characteristic of each material.

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The enhancement of atomic and interfacial rearrangement during ion bombardment has been the subject of several recent experimental studies.[1-7] Although models have been developed for thermally induced interface motion,[8-10] little progress has been made to date in describing interface motion during ion bombardment. Central to the discussion of bombardment-enhanced kinetic processes in solids is the determination of whether the kinetic enhancement is limited by migration of beam-generated Frenkel defects to the region where the process occurs, or by a direct elastic or inelastic collisional process at the interface. Investigations of bombardment-enhanced epitaxial crystallization of Si have yielded models for motion of the amorphous-crystalline interface based on both mobile Frenkel defects[1] and also direct interfacial interactions.[2] Recently, studies of bombardment-enhanced grain growth in Ge[3,4] and Ni[5-7] have shown that grain-boundary motion is proportional to the energy deposited in elastic collisions in the solid. Here we propose that grain-boundary motion is limited by a direct interfacial interaction and develop a transition-state model for that interaction. Comparison is made with experimental results for grain-boundary motion in thin polycrystalline films of Ge, Si, and Au.

A simple analysis of the time dependence of grain-boundary motion favors a kinetic process based on a direct interfacial interaction. To show this, we compare the kinetics predicted from this proposition with that based on defect migration. The average rate of boundary motion can be taken to be

$$dr/dt = \lambda \Delta k, \tag{1}$$

where λ is the jump distance and Δk is the jump rate in the direction of boundary motion. Turnbull has shown that this can also be written as[8]

$$dr/dt = -M\Delta\mu, \tag{2}$$

where M is the atomic mobility per atom during ion bombardment. The change in the chemical potential per unit volume $\Delta\mu$ accompanying normal grain growth is due to the elimination of grain-boundary area, and is proportional to the average radius of curvature of the grain boundaries. When the radii of curvature are assumed equal to the average grain radius, r, then $\Delta\mu = 2\gamma_{gb}/r$, where γ_{gb} is the grain-boundary energy per atom.

If the grain-boundary mobility enhancement during bombardment is due to elastic collisions at grain boundaries, and if a spatially uniform ion flux is assumed, the mobility is independent of grain size. In this case, the predicted time dependence for grain growth is $r \propto t^{0.5}$. The same conclusion is reached from a more complex analysis of thermally induced grain growth.[11]

If we assume that defects generated throughout a grain volume contribute to boundary motion, the atomic mobility, M, is not independent of r. The volume defect generation rate is estimated by $N_v = \Delta k_{Gd} \frac{4}{3}\pi r^3$, where Δk_{Gd} is the defect generation rate per atom. The grain-boundary area is approximately $4\pi r^2$, and so that atomic mobility, which is proportional to the rate of defect arrival at the boundary per unit area, is proportional to r. This leads to a time dependence of grain growth of $r \propto t$.

The rate of grain growth has been studied for Ge, Si, and Au during bombardment with a constant ion flux. The experimental methods and results are described elsewhere.[4,12] For 50-nm-thick Ge films bombarded with 50-keV Ge^+ at 600 °C and at a constant ion flux, the grain size, r, varied with time as $r \propto t^{0.28-0.35}$. Si films 100 nm thick bombarded with 70-keV Si^+, 100-keV $Ge,^+$ and 150-keV Xe^+ exhibited a variation in grain size of $r \propto t^{0.47-51}$. In 50-nm Au films bombarded with 80-keV Kr^+ and 200-keV Xe^+ at 23 °C, $r \propto t^{0.33}$. Clearly, the experimental data are in better agreement with the first assumption that M is not a function of r.

Measurements of the temperature dependence of bombardment-enhanced grain growth have been carried out for Ge and Si. For 50-nm-thick Ge films bombarded with 50-keV Ge^+ 450 °C and 700 °C at a constant ion flux, the activation energy for grain-boundary motion is 0.15 eV.[4] This is lower than measured or calculated values for vacancy migration in Ge. This suggests that the thermal migration of defects generated away from

the boundary is not limiting the grain-growth rate. Similar results have been obtained for 100-nm-thick Si films bombarded with 150-keV Xe^+ ions between 750 °C and 850 °C. The apparent activation energy for grain-boundary motion in Si films under bombardment was found to be ≤ 0.1 eV,[12] which is lower than the energy for vacancy migration in bulk Si of 0.33 eV.[13] There is some evidence which suggests that self-interstitials migrate essentially athermally during irradiation of bulk Si.[14] The small but nonzero measured activation energies, together with the time dependence, suggest that neither bulk interstitial migration nor bulk vacancy migration are limiting grain-boundary motion. Hence we propose that elastic collisions at or very near grain boundaries limit enhanced grain growth.

We now develop a simple model for normal grain-growth kinetics during ion bombardment. Grain-boundary motion is assumed to be due to some combination of independent bimolecular processes. Each process consists of (a) vacant-site formation at the grain boundary and (b) atomic migration across the boundary into the vacant site, as shown in Fig. 1. In principle, each of these steps can be due either to a thermal or to a collision-induced event. The net rate of forward jumps at the boundary for the jth process, Δk_j, is the product of the probability of forming a vacant site on the low-energy side of the boundary and the net jump rate Δk_{jump_j} into the vacant site

$$\Delta k_j = [\mathcal{P}_j\{\text{vacancy}\}][\Delta k_{\text{jump}_j}]. \tag{3}$$

We propose that in an expression such as Eq. (1), the jump rate during ion bombardment has terms corresponding to each of n possible processes;

$$\frac{dr}{dt} = \lambda \sum_{j=1}^{n} \Delta k_j. \tag{4}$$

Since the thermodynamic driving force was assumed to be equal for all processes, these terms simply correspond to different kinetic paths for grain-boundary motion during ion bombardment, or different terms in the expression for the atomic mobility.

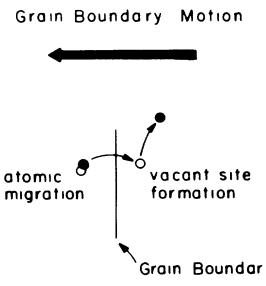

FIG. 1. Bimolecular model for grain-boundary motion during ion bombardment, consisting of vacant-site formation and atomic migration. Either event can be induced by thermal processes or by irradiation.

One possible bimolecular process for grain-boundary motion, which we will call process 1, consists of thermal formation of a vacancy at the grain boundary and migration of the vacancy across the boundary. Vacancy migration across the boundary is equivalent to an atomic jump across the boundary in the opposite direction. In a second process, process 2, a vacant site is created at the boundary by ion bombardment, and migration of the vacancy occurs as a result of a thermal process. In process 3, a thermally induced vacancy is formed at the boundary and a collision-induced interstitial migrates to the vacant site. In process 4, a collision-induced interstitial migrates to a collision-induced vacant site at the boundary.

For process 1, the apparent activation energy for thermal boundary migration is expected to be equal to the sum of the energies of formation of a vacancy at a grain-boundary site and migration of the vacancy across the boundary. The net rate of forward jumps in process 1, Δk_1, is given by

$$\Delta k_1 = [e^{-Q_{\text{vf}}/kT}][k_0 e^{-Q_{\text{vm}}/kT}(1 - e^{-\Delta\mu/kt})], \tag{5}$$

where k_0 is an attempt frequency, Q_{vm} is the energy of vacancy migration across the boundary, Q_{vf} is the energy of vacancy formation, and $\Delta\mu$ is the change in the chemical potential. Process 1 is assumed to be the process characteristic of thermally induced boundary migration, which experiments have shown to be of negligible importance in the low-temperature regime where bombardment-enhanced boundary motion is evident.

For process 2, the net rate of forward jumps across the boundary is

$$\Delta k_2 = [\Delta k_{Gd}\tau][k_0 e^{-Q_{\text{vm}}/kT}(1 - e^{-\Delta\mu/kT})], \tag{6}$$

where Δk_{Gd} is the generation rate of collision-induced

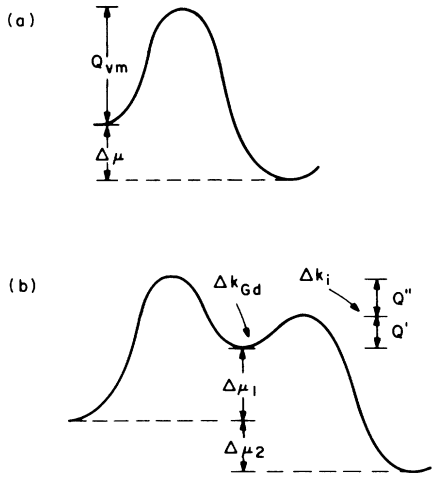

FIG. 2. (a) Transition-state diagram for vacancy migration in processes 1 and 2. (b) Transition-state diagram for intermediate state in processes 3 and 4.

defects at the boundary and τ is the lifetime of such a defect. The generation rate, in defects per atom, is

$$\Delta k_{Gd} = J\bar{R}/qN_l h, \tag{7}$$

where J is the ion-beam current density, q is the electronic charge, N_l is the lattice atomic density, h is the film thickness, and $\bar{R}$ is the yield of Frenkel defects generated in the solid per incident ion.

Figure 2(a) depicts the thermally induced vacancy migration event for processes 1 and 2. If process 2 characterizes boundary motion during ion bombardment, the apparent activation energy would be only the energy of vacancy migration across the boundary.

In processes 3 and 4, we assume that bombardment populates an intermediate interstitial state at the boundary with rate Δk_{Gd}, as illustrated in Fig. 2(b). In principle, the interstitial could be generated either at the boundary or in the bulk. The net rate of forward jumps out of the intermediate state is Δk_i, and the activation energy for forward jumps is Q'. Structural models of high-angle grain boundaries in the diamond lattice suggest possible locations for this intermediate state.[15,16] For example, for a [110] tilt boundary, it is possible to generate a structure with boundary interstitial sites which have greater volume than the bulk interstitial site, for many orientations. The net jump rate for process 3 is

$$\Delta k_3 = [e^{-Q_m/kT}]\left[\frac{\Delta k_{Gd}\Delta k_i}{\Delta k_{Gd}+\Delta k_i}\right], \tag{8}$$

where Δk_i is the net jump rate in the forward direction from the intermediate state, and is given by

$$\Delta k_i = k_0 e^{-Q'/kT}[(1-e^{-(\Delta\mu_1+\Delta\mu_2)/kT}) - e^{-Q''/kT}(1-e^{-\Delta\mu_1/kT})]. \tag{9}$$

If Q'' is sufficiently large, the activation energy is approximately equal to Q', the energy for a thermal jump out of the intermediate state.

We believe that process 3 is unlikely to describe boundary motion during bombardment, since the activation energy for process 3 is at least equal to the energy of thermal vacancy formation at the boundary. The activation energy for vacancy formation at the boundary is probably similar to the energy for bulk vacancy formation, and the thermally induced vacancy population is smaller than the collision-induced defect population in the regime of our experiments.

Process 4 involves collision-induced formation of both defects. The net rate of forward jumps is

$$\Delta k_4 = [\Delta k_{Gd}\tau]\left[\frac{\Delta k_{Gd}\Delta k_i}{\Delta k_{Gd}+\Delta k_i}\right]. \tag{10}$$

There are two limiting cases for boundary motion in process 4. The first case, when $\Delta k_i \ll \Delta k_{Gd}$, has an activation energy equal to the energy of migration out of the intermediate state, Q', and $\Delta k_4 \propto \Delta k_{Gd}$. In the second case, when $\Delta k_i \gg \Delta k_{Gd}$, the activation energy is zero, and $\Delta k_4 \propto \Delta k_{Gd}^2$. This latter case implies that boundary motion is expected to exhibit a *second-order dependence on the rate of collision-induced defect formation,* and hence also the ion-beam current density. Based on our measurements of the dependence of grain growth on the concentration of collision-induced defects, which were not extensive, bombardment-enhanced grain growth appears to exhibit a first-order dependence on the rate of collision-induced defect formation, arguing against the latter limiting case for process 4.

Both process 2 and the former limiting case for process 4 are consistent with a first-order dependence on Δk_{Gd}, and also a weak (but nonzero) temperature dependence. Our experimental results do not allow us to distinguish between these processes. Therefore, we believe that either the dominant process in bombardment-enhanced grain growth is process 2, or it is process 4 in the limit where the jump out of an intermediate boundary site is rate limiting.

If we assume that the net rate of forward jumps at the boundary has a first-order dependence on the number of defects generated at the boundary, that is,

$$\Delta k = \mathcal{C}\Delta k_{Gd} = \mathcal{C}J\bar{R}/qN_l h, \tag{11}$$

then the proportionality constant $\mathcal{C}$ is the number of atomic jumps at the boundary per defect generated at the boundary,

$$\mathcal{C} = \Delta r N_l h/\lambda Q_d \bar{R}, \tag{12}$$

where the ion dose $Q_d = J\Delta t/q$ and Δr is the distance over which the boundary moves. The variation of Δr

TABLE I. Values for number of jumps at a grain boundary per defect generated for various polycrystalline films. Films are unsupported unless denoted as supported on SiO_2.

Projectile ion	Target	Temp. (°C)	$\bar{R}$	$\mathcal{C}$
50-keV Ge	500-Å Ge	500	1131	2.7
50-keV Ge	500-Å Ge	600	1131	2.5
50-keV Ge	500-Å Ge/SiO_2	600	1131	1.1
50-keV Ge	500-Å Ge/SiO_2	500	1131	1.3
50-keV Ar	500-Å Ge/SiO_2	600	762	1.7
50-keV Kr	500-Å Ge/SiO_2	600	983	1.7
100-keV Xe	500-Å Ge/SiO_2	600	2104	1.6
40-keV Kr	250-Å Au	23	608	4.1
60-keV Kr	250-Å Au	23	890	4.0
80-keV Kr	250-Å Au	23	1175	5.9
100-keV Kr	250-Å Au	23	1421	7.4
60-keV Ar	250-Å Au	23	703	7.3
200-keV Xe	250-Å Au	600	2681	5.2
70-keV Si	1000-Å Si/SiO_2	1050	450	1.5
100-keV Ge	1000-Å Si/SiO_2	800	1141	1.4
150-keV Xe	1000-Å Si/SiO_2	850	1810	1.3

with Q_d has been measured and values for $\bar{R}$ have been calculated with TRIM, a Monte Carlo code for simulation of ion transport in solids.[17] The values for $\mathcal{C}$ have been computed for studies of 50-nm Ge, 100-nm Si, and 50-nm Au films, and are shown in Table I.

It is noteworthy that the number of jumps per defect, $\mathcal{C}$, is approximately constant for a given material, even though $\bar{R}$ varied widely. The value of $\mathcal{C}$ is higher for Au, which may be an indication that the grain-boundary vacancy migration energy is different for Au than for the covalently bonded Si and Ge. However, it should be noted that the calculation of $\bar{R}$ is quite sensitive to the assumed displacement energy, E_d, in the solid. For Si and Ge, $E_d = 15$ eV was assumed, and for Au $E_d = 25$ eV.

In conclusion, we have shown that bombardment-enhanced grain-boundary motion is limited by interfacial rearrangements which occur at the boundary. In the bombardment-enhanced regime, the boundary migration rate is weakly temperature dependent, and proportional to the energy deposited in nuclear collisions at or very near the boundary. A transition-state model has been developed for grain-boundary motion during bombardment which accounts for these observations. The model may be more generally applied to bombardment-enhanced motion of other interfaces; e.g., the amorphous-crystalline interface.

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