Amorphization Processes in Electron- and/or Ion-Irradiated Silicon

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Amorphization has been studied in electron- (e^-) and ion-irradiated Si. Si irradiated at < 10 K with 1.0- or 1.5-MeV Kr^+ became amorphous at <0.4 displacement per atom (dpa), whereas Si irradiated at 10 K to a fluence of ≈ 14 dpa of 1-MeV e^-, in an electron microscope, failed to amorphize. However, Si subjected to a simultaneous e^- and Kr^+ *in situ* irradiation at < 10 K to a Kr^+ fluence of 1.5 dpa retained crystallinity. The critical ratio, at < 10 K, of the e^- to Kr^+ ion displacement rates to maintain a degree of crystallinity is ≈ 0.5. Atomistic models for these phenomena are presented.

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The crystalline (c)-to-amorphous (a) phase transition for silicon in a particle radiation field has been studied extensively, but the exact mechanism by which the c-to-a transition occurs remains controversial.[1-4] Si can be amorphized by energetic ions with a mass $\gtrsim 1$ amu.[2-4] The critical fluence [displacements per atom (dpa)] required to induce the c-to-a transition is a function of the temperature and the flux (dpa s^{-1}). Alternatively, e^- irradiations—in the range 15 K to room temperature—to fluences of several dpa *cannot* amorphize Si.[5,6] The point-defect mechanism(s) for the amorphization of ion-irradiated Si and the reasons why it is *not* possible to amorphize Si by energetic e^- irradiation have remained elusive. We present new results on the irradiation of Si with 1-MeV e^- and/or 1.0- and 1.5-MeV Kr^+ at < 10 K. The results are analyzed in terms of the properties of the primary state of damage and point defects in Si, and a detailed mechanism is proposed for the c-to-a transition.

The first experiment was the *in situ* irradiation of $\langle 100\rangle$ p-type Si with 1-MeV e^- at < 10 K and a flux of 3.6×10^{19} e^- cm^{-2} s^{-1} (2.6×10^{-3} dpa s^{-1}) to a fluence of 1.9×10^{23} e^- cm^{-2} (≈ 9 dpa). A second specimen of the same material was irradiated at < 10 K at a flux of 5.6×10^{19} e^- cm^{-2} s^{-1} (4×10^{-3} dpa s^{-1}) to 3×10^{23} e^- cm^{-2} (≈ 14 dpa). Selected area diffraction patterns (SADP's) and bend-extinction contours indicated that the above e^--irradiation conditions failed to amorphize Si. These are the lowest temperature (< 10 K) and the highest fluence (14 dpa) conditions to which Si has been subjected in an attempt to amorphize it by e^-. The e^- irradiation did produce dislocation loops. Similar results were obtained by Föll.[6]

A second experiment was performed which involved the simultaneous irradiation of Si with 1.0- or 1.5-MeV Kr^+ and 1-MeV e^- at < 10 K. A portion of the samples were irradiated with *only* Kr^+. The 1.0- or 1.5-MeV Kr^+ ions passed through the Si—thus *no* Kr^+ came to rest in the specimens. The results for this experiment are as follows: (1) The *dual-irradiated* area retained a degree of *crystallinity* throughout the irradiation, and (2) the Kr^+-irradiated region became *amorphous* early in the irradiation period. These results demonstrate that the spatial distribution of point defects in the primary state of damage plays a key role in the c-to-a transition. Figure 1 illustrates this for a dual irradiation, where the e^- flux was constant at 5.7×10^{19} e^- cm^{-2} s^{-1} (4.1×10^{-3} dpa s^{-1}) and the Kr^+ flux was increased in steps. The result was that the diameter of the region that retained a degree of crystallinity (D_c) *decreased* with increasing Kr^+ ion flux. The region D_c is indicated by a dashed circle. Note the presence of bend-extinction contours inside D_c. In Fig. 1(c) the bend-extinction contour is indicated by two black arrowheads. The corresponding SADP is of a region which had a smaller diameter than D_c. The SADP's and the bend-extinction contours demonstrate that the dual-irradiated volume retained a degree of crystallinity, while the region outside D_c became amorphous. That is, the SADP's that did *not* include D_c indicated *mainly* diffuse scattering rings, and the region outside D_c exhibited *no* bend-extinction contours—after a fluence of <0.4 dpa—indicating that it was amorphous. In Figs. 1(a)-1(c) the Kr^+ ion fluxes are 4.1×10^{11}, 8.4×10^{11}, and 1.7×10^{12} ions cm^{-2} s^{-1} (1.1×10^{-3}, 2.2×10^{-3}, and 4.5×10^{-3} dpa s^{-1}), respectively. The accumulated Kr^+ fluences are 2.9×10^{14}, 4.4×10^{14}, and 5.8×10^{14} ions cm^{-2} (0.75, 1.1, and 1.5 dpa), respectively. A subsequent 1-MeV e^- irradiation, at < 10 K, of partially a-Si *failed* to crystallize the a-Si.

Figure 2 exhibits a plot of D_c (left-hand ordinate) versus the Kr^+ ion flux and also the *critical* e^- flux I_e^c (right-hand ordinate) versus the ion flux. The value of I_e^c was calculated under the assumption that the e^- current distribution is Gaussian[7]; i.e., $I_e(r)=I_0\exp[-(r/r_0)^2]$, where I_0 is the e^- flux at $r=0$ (3.63×10^{19} e^- cm^{-2} s^{-1}), and $r_0=(I_T/\pi I_0)^{1/2}$ where I_T is the total e^- current (168.5 nA). The effective beam diameter was 1.92 μm for the irradiations. The value of D_c was measured from each micrograph—it is the diameter of the region that retains a degree of crystallinity as determined from the bend contours—and I_e^c was then calculated from the calibrated Gaussian expression. Note that the slope (R) of the I_e^c versus ion flux curve is a con-

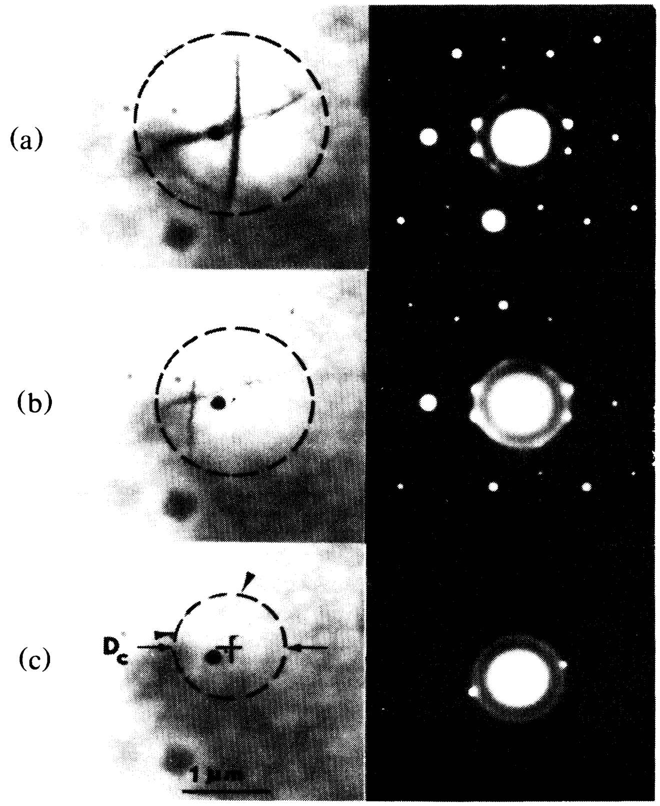

FIG. 1. Effect of a dual irradiation on the degree of crystallinity. The 1.0-MeV e^- flux was 5.67×10^{19} e^- cm^{-2} s^{-1} (4.1×10^{-3} dpa s^{-1}) and the 1.0-MeV Kr^+ ion flux was increased in steps. The effective diameter of the dual-irradiated region was 1.92 μm. (a)-(c) Accumulated Kr^+ ion flux 0.75, 1.1, and 1.5 dpa, respectively. In each micrograph the dashed circle (D_c) indicates the region that retained a degree of crystallinity; note the presence of bend-extinction contours within D_c. The ratio of the e^- to ion displacement rates at D_c is ≈ 0.5. The corresponding SADP's of a region smaller than D_c demonstrate that the dual-irradiated region retains a degree of crystallinity up to 1.5 dpa. The surrounding material, which had been irradiated by only 1.0-MeV Kr^+ ions, became amorphous at a fluence of ≈ 0.4 dpa.

stant (≈ 0.5). The conversions from e^- or ion currents to dpa s^{-1} were made employing e^- cross sections[8] and the TRIM program[9] with a modified Kinchin-Pease expression and a displacement threshold of 15 eV.[10] To demonstrate that the observed effects were not influenced by beam heating of the specimen, we repeated the experiments employing a Si specimen with a thickness of 2000–4000 Å, which was similar to others, but that had a 300-Å-thick layer of Cu deposited on its bottom surface. The Cu layer provided a high–thermal-conductivity path, which prevented any significant temperature rise in the specimen.

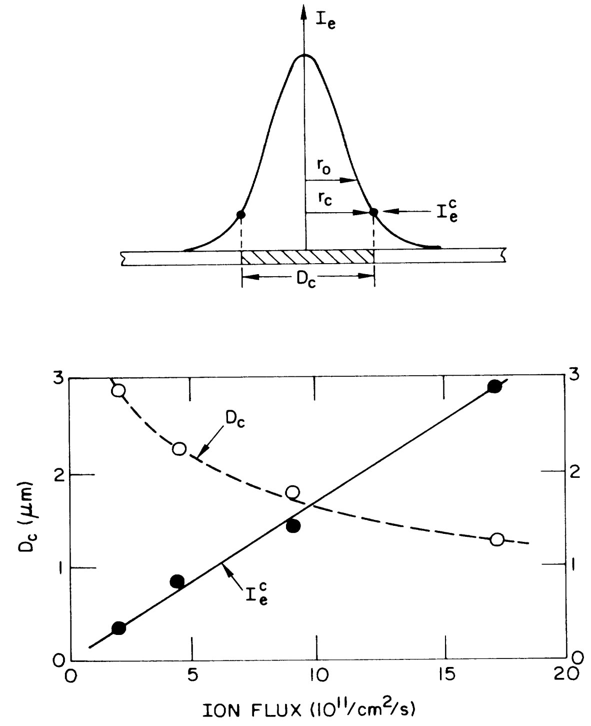

FIG. 2. Plot of D_c (open circles, left-hand scale) in micrometers vs the Kr^+ ion flux and the critical e^- current I_e^c (filled circles, right-hand scale) vs the ion flux.

The dislocation loops observed for the e^- irradiations are presumably interstitial in character.[4] The neutral vacancy (v) becomes mobile at ≈ 70 K and the v^{--} at ≈ 160 K.[4] *No* experimental evidence has been obtained for the stimulated athermal migration of v's in Si by the e^- beam via, for example, the Bourgoin-Corbett mechanism.[4,11] Thus, the only possible origin of the loops observed by Föll and ourselves is from reactions between highly mobile self-interstitial atoms (SIA's) which lead to SIA clusters that convert into small dislocation loops once a SIA cluster exceeds a critical size. In the e^--irradiation case the existence of highly mobile SIA's at 10 K which cluster, as a result of random-walk encounters, and then convert to dislocation loops prevents *a*-Si from forming. Our result that the 1.0- or 1.5-MeV Kr^+ irradiations produced *a*-Si is not surprising, as there is ample prior evidence which indicates that under cascade-producing conditions Si becomes amorphous.[4] The new and surprising result in the present work, is that under the *dual* irradiation conditions employed, Si retained a degree of *crystallinity*. The value of R for 1-MeV e^- to 1.0-MeV Kr^+ to retain a degree of crystallinity is ≈ 0.5 at < 10 K. For larger values of R, the *c*-to-*a* transition can be strongly retarded or suppressed. To understand this result we first emphasize that 1.0-MeV e^- irradiation produces a random array of v's and SIA's [Frenkel pairs (FP's)],[12] while the 1.0- or 1.5-

MeV Kr$^+$ ion irradiation produces cascades. Qualitatively, one can visualize each cascade as consisting of a *v*-rich core surrounded by a distribution of SIA's.[12,13] The local concentration of SIA's on the periphery of each cascade is several atomic percent.[13] The SIA distribution is determined by the range of replacement-collision sequences plus the *v*-SIA recombination events that occur in the high-*v*-concentration core of the cascade. The degree of dispersion of the *v*'s depends on the mass of the projectile ion relative to the mass of the target atoms.[14,15] Hence, the spatial distribution of *v*'s and SIA's in the primary state of damage is *radically* different for the two irradiation conditions. In the case of the dual irradiation we are dealing with an open thermodynamic system for which R is the control variable. The value of R to maintain a given degree of crystallinity is a function of temperature and the mass of the projectile ion, that is, the degree of dispersion of the cascade.

On the basis of the above we suggest a new mechanism for the amorphization of Si under cascade-producing conditions. Since the local concentration of SIA's on the periphery of a cascade is high (>1 at.%),[13] the number of thermally activated jumps for one SIA to reach a second SIA is <10. The value of ten jumps is an upper bound since the reaction radii for SIA-SIA interactions are large[16] and the local SIA concentrations are >1 at.%. Hence, the clustering most likely takes place with little or no thermally activated migration of SIA's, i.e., the clusters form dynamically and not as the result of long-range random-walk events as was shown for cascades in Al.[17] Hence, on the periphery of the cascades the SIA's can form three-dimensional clusters and bypass conversion into dislocation loops. The clustering of SIA's, moreover, results in a local lowering of the symmetry of the diamond cubic lattice. We suggest that these SIA clusters are *a*-Si embryos. In the diamond cubic lattice each atom has four first nearest neighbors sitting at the vertices of a tetrahedron, which has a basic building block of six-membered rings.[4] Amorphous Si preserves the fourfold coordination of the atoms, and incorporates five- and seven-membered rings.[18] The three-dimensional clustering of SIA's introduces these five- and seven-membered rings and creates embryos of *a*-Si on the periphery of each cascade. For example, two split-$\langle 100\rangle$ SIA's along a $\langle 100\rangle$ direction produce a five-membered planar ring of atoms in the diamond cubic lattice.[4] To estimate if the above atomistic model is energetically plausible we consider the difference in Gibbs free energies for *c*-Si containing point defects and *a*-Si at 0 K. The free-energy difference between *c*-Si without FP's and *a*-Si is <0.1 eV atom^{-1}.[19] An assumed FP formation energy of 5 eV atom^{-1} and a SIA concentration of 2 at.% yields 0.1 eV atom^{-1}.

We remark on the question of whether the *c*-to-*a* transition is the result of a continuous buildup of damage or if it can occur in a single cascade event. From the above model we expect that the *c*-to-*a* transition can take place in a single cascade event if the concentration of *a* embryos is sufficiently high. Alternatively, for more dispersed cascades the *c*-to-*a* transition is a gradual process that requires the interaction of *a* embryos from different cascade events. The high-resolution TEM observations[20] that bismuth-irradiated Si contains amorphous zones at low fluences represents a dense cascade condition, whereas the observation of crystalline zones in Si irradiated at 323 K with fast neutrons—equivalent to a self-ion irradiation—is an example of a dispersed cascade condition.[21]

The above physics can be used to explain the results of the dual irradiations which involve an interaction of the two radically different types of primary states of damage, 1.0-MeV e^- and 1.0- or 1.5-MeV Kr$^+$ damage. To understand how 1.0-MeV e^- irradiation can retard the *c*-to-*a* transition it is essential to understand the detailed point-defect distributions. One cannot make the assumption of randomizing the primary state of damage, produced by the ions, into a uniform sea of *v*'s and SIA's and then assume steady-state conditions. For if this is done then the effect of the 1.0-MeV e^- irradiation can only be additive.

We start by considering the situation where a Si specimen is irradiated simultaneously by megaelectronvolt e^- and ions, where the displacement rate for e^- is greater than for ions, and where within a specified volume there is a single cascade. The cascade described previously consists of a *v*-rich core surrounded by a halo of *a* embryos (SIA clusters). Diffuse x-ray scattering studies[17] on neutron-irradiated Al at 8 K show that the mean size of an SIA cluster is 3.

We are concerned here with how the SIA distribution—i.e., *a* embryos—changes with e^- fluence. Hence we superimpose on this specified volume a random distribution of FP's with the number of FP's greater than that produced in a single cascade. Those FP's that are produced within the *v*-rich core leave the number of *v*'s in the core unchanged, as each SIA that is annihilated by a *v* is simply replaced by the *v* of the FP. In the remainder of the specified volume the following point-defect reactions can take place: (a) correlated or uncorrelated recombination of FP's, (b) the annihilation of mobile SIA's on the "surface" of the vacancy-rich core, (c) the reaction of the immobile *v*'s with the *a* embryos, (d) the addition of the mobile SIA's to the immobile *a* embryos (SIA clusters), and (e) the reaction of mobile SIA's with one another to produce immobile di-SIA's.[4] Reaction (a) produces no change in the SIA distribution. Reaction (b) reduces the number of SIA's produced by the e^- irradiation but leaves the SIA cluster distribution unchanged. Reaction (c) helps to shrink *a* embryos and hence returns the system back to the *c* phase. It is postulated that the minimum stable *a* embryo consists of di-SIA's so that the addition of a vacancy to an *a* embryo consisting of a di-SIA produces a mobile SIA. The SIA either is then annihilated at the v-rich core or it reacts with an a embryo. Thus, the net result is a decrease in the number of SIA's in the a embryo by one or possibly two. Reaction (d) increases the size of a embryos by one. Reaction (e) leads to a decrease in the number of SIA's. The *net* effect of reactions (c)-(e) is to change the distribution of a embryos—that is, the number of embryos as a function of their size. The net results are (i) a decrease in the number of small a embryos, (ii) an increase in the number of large a embryos, and (iii) a net reduction in the volume fraction of embryos. Note that since the SIA is mobile, the addition of one v to a di-SIA can eliminate two SIA's. When the size of an a embryo exceeds a critical value, it becomes an a nucleus, i.e., a certain amount of material has become a-Si. A 1-MeV e^- irradiation does not crystallize partially a-Si at < 10 K. This is in contrast to a 1-MeV e^- irradiation of partially a-Si at room temperature which induces crystallization.[22] With an increasing number of displacements in the same volume, the volume fraction of a-Si is a function of R at a given temperature. The value of R determines how the a-embryo distribution evolves with time. A high value of R implies that it takes a long time before the dual-irradiated region becomes amorphous, while for a small value of R the time to achieve a-Si approaches that for the ion irradiation alone. The evolution of the a-embryo distribution with time is an example of a one-dimensional random walk with absorbing boundaries, i.e., the "Gambler's Ruin" problem.

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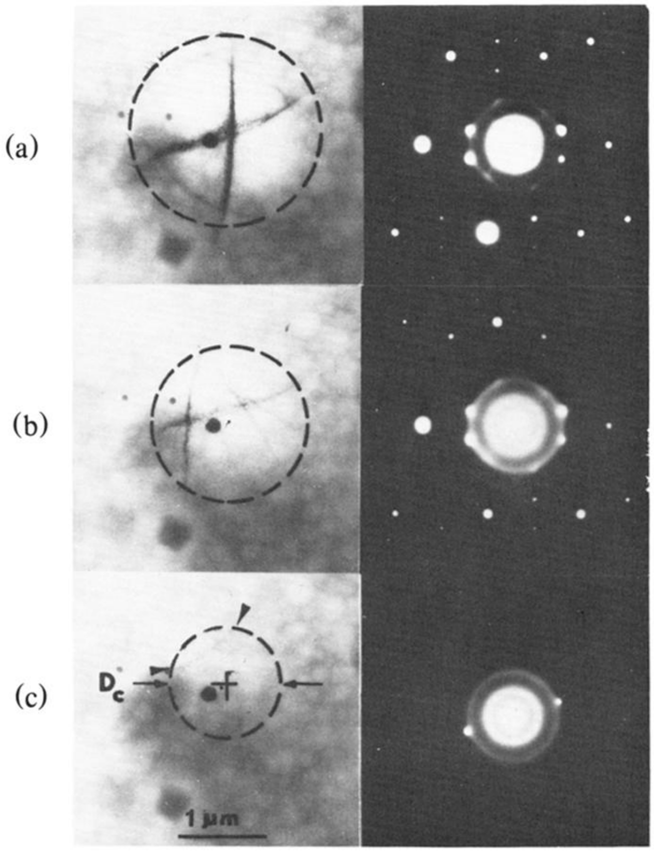

FIG. 1. Effect of a dual irradiation on the degree of crystallinity. The 1.0-MeV e^- flux was 5.67×10^{19} e^- cm^{-2} s^{-1} (4.1×10^{-3} dpa s^{-1}) and the 1.0-MeV Kr$^+$ ion flux was increased in steps. The effective diameter of the dual-irradiated region was 1.92 μm. (a)–(c) Accumulated Kr$^+$ ion flux 0.75, 1.1, and 1.5 dpa, respectively. In each micrograph the dashed circle (D_c) indicates the region that retained a degree of crystallinity; note the presence of bend-extinction contours within D_c. The ratio of the e^- to ion displacement rates at D_c is ≈ 0.5. The corresponding SADP's of a region smaller than D_c demonstrate that the dual-irradiated region retains a degree of crystallinity up to 1.5 dpa. The surrounding material, which had been irradiated by only 1.0-MeV Kr$^+$ ions, became amorphous at a fluence of ≈ 0.4 dpa.