

## 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  $\approx 14$  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  $\approx 0.5$ . 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.<sup>1-4</sup> Si can be amorphized by energetic ions with a mass  $\geq 1$  amu.<sup>2-4</sup> 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.<sup>5,6</sup> 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  $3.6 \times 10^{19} e^- cm^{-2} s^{-1}$  ( $2.6 \times 10^{-3}$  dpa  $s^{-1}$ ) to a fluence of  $1.9 \times 10^{23} e^- cm^{-2}$  ( $\approx 9$  dpa). A second specimen of the same material was irradiated at  $< 10$  K at a flux of  $5.6 \times 10^{19} e^- cm^{-2} s^{-1}$  ( $4 \times 10^{-3}$  dpa  $s^{-1}$ ) to  $3 \times 10^{23} e^- cm^{-2}$  ( $\approx 14$  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.<sup>6</sup>

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 *amor-*

*phous* 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  $5.7 \times 10^{19} e^- cm^{-2} s^{-1}$  ( $4.1 \times 10^{-3}$  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  $4.1 \times 10^{11}$ ,  $8.4 \times 10^{11}$ , and  $1.7 \times 10^{12}$  ions  $cm^{-2} s^{-1}$  ( $1.1 \times 10^{-3}$ ,  $2.2 \times 10^{-3}$ , and  $4.5 \times 10^{-3}$  dpa  $s^{-1}$ ), respectively. The accumulated  $Kr^+$  fluences are  $2.9 \times 10^{14}$ ,  $4.4 \times 10^{14}$ , and  $5.8 \times 10^{14}$  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  $I_c^e$  (right-hand ordinate) versus the ion flux. The value of  $I_c^e$  was calculated under the assumption that the  $e^-$  current distribution is Gaussian<sup>7</sup>; i.e.,  $I_e(r) = I_0 \exp[-(r/r_0)^2]$ , where  $I_0$  is the  $e^-$  flux at  $r=0$  ( $3.63 \times 10^{19} e^- cm^{-2} s^{-1}$ ), 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  $\mu m$  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  $I_c^e$  was then calculated from the calibrated Gaussian expression. Note that the slope ( $R$ ) of the  $I_c^e$  versus ion flux curve is a con-

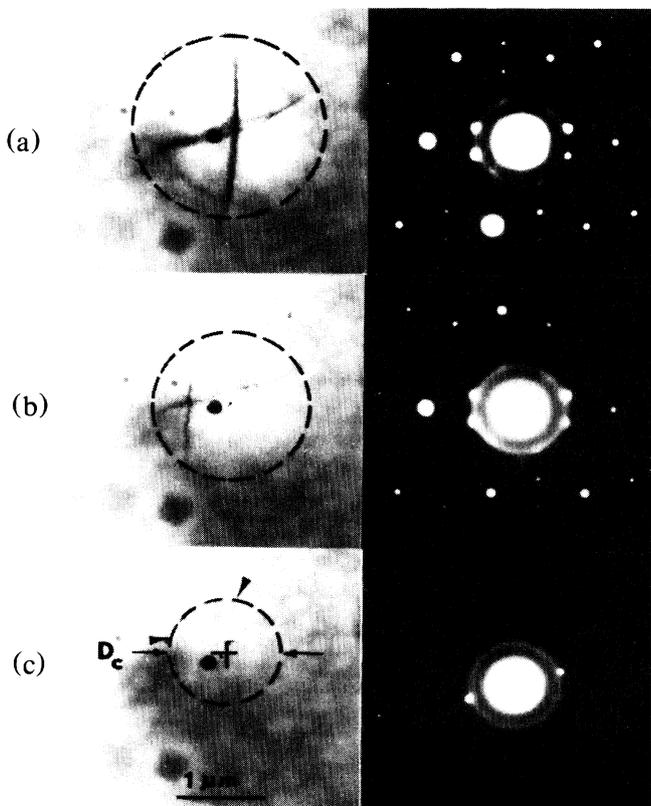


FIG. 1. Effect of a dual irradiation on the degree of crystallinity. The 1.0-MeV  $e^-$  flux was  $5.67 \times 10^{19} e^- \text{ cm}^{-2} \text{ s}^{-1}$  ( $4.1 \times 10^{-3} \text{ dpa s}^{-1}$ ) and the 1.0-MeV  $\text{Kr}^+$  ion flux was increased in steps. The effective diameter of the dual-irradiated region was  $1.92 \mu\text{m}$ . (a)–(c) Accumulated  $\text{Kr}^+$  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  $\approx 0.5$ . The corresponding SADPs 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  $\text{Kr}^+$  ions, became amorphous at a fluence of  $\approx 0.4 \text{ dpa}$ .

stant ( $\approx 0.5$ ). The conversions from  $e^-$  or ion currents to  $\text{dpa s}^{-1}$  were made employing  $e^-$  cross sections<sup>8</sup> and the TRIM program<sup>9</sup> with a modified Kinchin-Pease expression and a displacement threshold of 15 eV.<sup>10</sup> 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.

The dislocation loops observed for the  $e^-$  irradiations

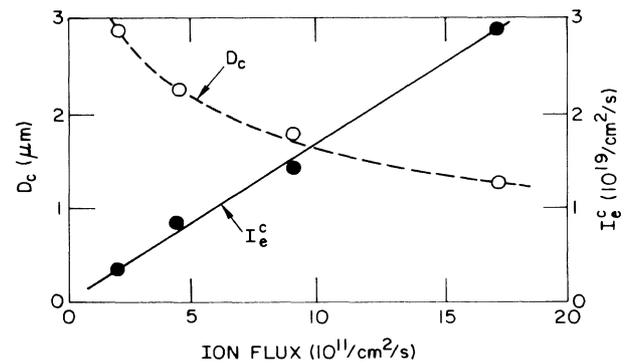
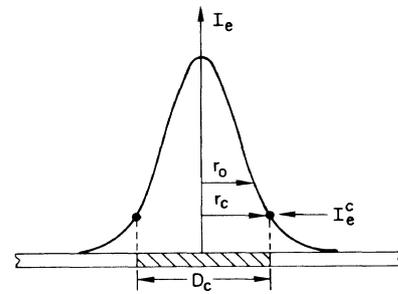


FIG. 2. Plot of  $D_c$  (open circles, left-hand scale) in micrometers vs the  $\text{Kr}^+$  ion flux and the critical  $e^-$  current  $I_e^c$  (filled circles, right-hand scale) vs the ion flux.

are presumably interstitial in character.<sup>4</sup> The neutral vacancy ( $v$ ) becomes mobile at  $\approx 70 \text{ K}$  and the  $v^{--}$  at  $\approx 160 \text{ K}$ .<sup>4</sup> 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.<sup>4,11</sup> 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  $\text{Kr}^+$  irradiations produced  $a$ -Si is not surprising, as there is ample prior evidence which indicates that under cascade-producing conditions Si becomes amorphous.<sup>4</sup> 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  $\text{Kr}^+$  to retain a degree of crystallinity is  $\approx 0.5$  at  $< 10 \text{ K}$ . 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)],<sup>12</sup> while the 1.0- or 1.5-

MeV  $\text{Kr}^+$  ion irradiation produces cascades. Qualitatively, one can visualize each cascade as consisting of a  $v$ -rich core surrounded by a distribution of SIA's.<sup>12,13</sup> The local concentration of SIA's on the periphery of each cascade is several atomic percent.<sup>13</sup> 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.<sup>14,15</sup> 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.%),<sup>13</sup> 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<sup>16</sup> 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.<sup>17</sup> 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.<sup>4</sup> Amorphous Si preserves the fourfold coordination of the atoms, and incorporates five- and seven-membered rings.<sup>18</sup> 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.<sup>4</sup> 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<sup>-1</sup>.<sup>19</sup> An assumed FP formation energy of 5 eV atom<sup>-1</sup> and a SIA concentration of 2 at.% yields 0.1 eV atom<sup>-1</sup>.

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<sup>20</sup> 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.<sup>21</sup>

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  $\text{Kr}^+$  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<sup>17</sup> 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.<sup>4</sup> 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.<sup>22</sup> 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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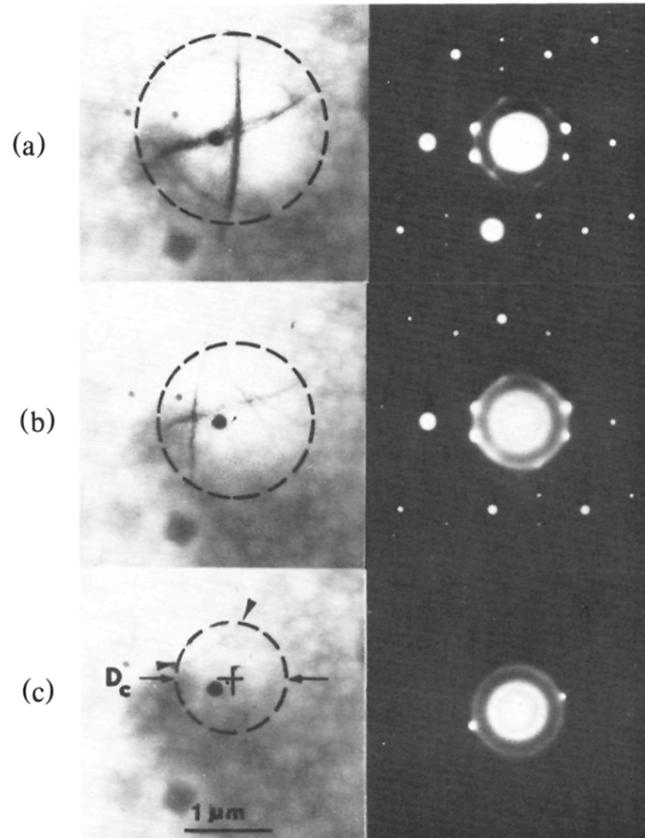


FIG. 1. Effect of a dual irradiation on the degree of crystallinity. The 1.0-MeV  $e^-$  flux was  $5.67 \times 10^{19} e^- \text{ cm}^{-2} \text{ s}^{-1}$  ( $4.1 \times 10^{-3} \text{ dpa s}^{-1}$ ) and the 1.0-MeV  $\text{Kr}^+$  ion flux was increased in steps. The effective diameter of the dual-irradiated region was  $1.92 \mu\text{m}$ . (a)–(c) Accumulated  $\text{Kr}^+$  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  $\approx 0.5$ . 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  $\text{Kr}^+$  ions, became amorphous at a fluence of  $\approx 0.4 \text{ dpa}$ .