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 ≥ 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—influence 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 (100) p-type Si with 1-MeV e⁻ at < 10 K and a flux of 3.6 x 10¹⁹ e⁻ cm⁻² s⁻¹ (2.6 x 10⁻¹⁰ dpa s⁻¹) to a fluence of 1.9 x 10²³ e⁻ cm⁻² (= 9 dpa). A second specimen of the same material was irradiated at < 10 K at a flux of 5.6 x 10¹⁹ e⁻ cm⁻² s⁻¹ (4 x 10⁻¹⁰ dpa s⁻¹) to 3 x 10²³ e⁻ cm⁻² (≈ 14 dpa). Selected area diffraction patterns (SADPs) 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 region retained a degree of crystallinity throughout the irradiation, and (2) the Kr⁺-irradiated region became amor-
FIG. 1. Effect of a dual irradiation on the degree of crystallinity. The 1.0-MeV $e^-$ flux was $5.67 \times 10^{19}$ $e^-$ cm$^{-2}$ s$^{-1}$ ($4.1 \times 10^{-3}$ 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 $\mu$m. (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 $\approx 0.5$. 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 Kr$^+$ ions, became amorphous at a fluence of $\approx 0.4$ dpa.

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.

are presumably interstitial in character. The neutral vacancy ($v$) becomes mobile at $\approx 70$ K and the $e^-$ at $\approx 160$ K. 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. 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. 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 $\approx 0.5$ 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)], 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 surrounding by a distribution of SIA's.\textsuperscript{12,13} The local concentration of SIA's on the periphery of each cascade is several atomic percent.\textsuperscript{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.\textsuperscript{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.%),\textsuperscript{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\textsuperscript{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.\textsuperscript{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.\textsuperscript{4} Amorphous Si preserves the fourfold coordination of the atoms, and incorporates five- and seven-membered rings.\textsuperscript{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-($100$) SIA's along a ($100$) direction produce a five-membered planar ring of atoms in the diamond cubic lattice.\textsuperscript{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$^{-1}$.\textsuperscript{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\textsuperscript{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.\textsuperscript{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 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\textsuperscript{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.\textsuperscript{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 \( \gamma \)-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 \( \nu \) 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 \( \gamma \)-Si at room temperature which induces crystallization. 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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\(^{(a)}\)Permanent address: Department of Materials Science, Northwestern University, Evanston, IL 60201.

\(^{(b)}\)Now at Department of Materials Science, University of Illinois, Urbana, IL 61801.
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