Preferential Amorphization at Extended Defects of Self-Ion-Irradiated Silicon

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Nucleation of an amorphous Si layer is shown to occur preferentially at a thin band of dislocations during self-ion-irradiation of silicon at elevated temperatures. This process occurs even when the defect band is well separated from the peak of the ion damage distribution. Without such a nucleation site, amorphization does not occur under identical bombardment conditions. These results suggest that amorphization can be nucleation limited under conditions where significant defect annealing occurs during irradiation. This process can be understood if mobile, implantation-induced defects are trapped at preexisting damage and raise the local free energy above that of the amorphous phase. [S0031-9007(98)08308-2]

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The disordering and amorphization of silicon under ion irradiation has been under investigation for over 30 years. Early models of the amorphization process [1,2] and more recent refinements [3,4] have generally been successful in explaining the accumulation of disorder with fluence and the ultimate formation of continuous amorphous layers in cases where the damage produced after quenching of the collision cascades is relatively stable. The critical density models [2,3] are particularly applicable to dilute collision cascades (e.g., light ion irradiation), where defects accumulate homogeneously with increasing fluence until a critical density is reached and the lattice collapses to an amorphous phase. For low energy heavy ions, amorphization occurs heterogeneously via damage accumulation, dominated by the overlap of individual collision cascades [1,4] and, in come cases, directly amorphized zones [5].

In higher irradiation temperature regimes, where the point defects remaining (following quenching of the collision cascades) are mobile, significant dynamic annealing can occur, and the nature and extent of residual damage can change dramatically. When the rate of dynamic annealing balances or exceeds the rate of damage production, perfect annihilation of point defects rarely occurs and secondary defects can accumulate with fluence and ultimately lead to amorphization [6]. Such an amorphization process is not accounted for by previous models which did not adequately consider defect migration and agglomeration on the time scale of several seconds following cascade quenching.

In such an irradiation regime, the residual damage and the onset of amorphization depend critically on the ion fluence, flux, and substrate temperature [6,7]. Furthermore, amorphization can take place preferentially at preexisting amorphous-crystalline interfaces [8,9], surfaces [10], and within bands of secondary defects which form during implantation [7]. For example, for Si self-irradiated at elevated temperatures, a band of interstitially based complexes and loops can form at depths substantially exceeding the maximum in the nuclear energy deposition distribution [6]. Indeed, such a band has been shown to provide a favored site for the initiation of amorphization at higher fluences [7]. These situations, where amorphization is mediated by secondary defects built up in the early stages of bombardment, suggest that amorphization is nucleation limited in these cases. Indeed, recently we reported amorphization results [11] which suggested that preexisting crystalline defects could provide favorable nucleation sites for amorphization. In this Letter, we provide conclusive evidence for nucleation of amorphous silicon on a preexisting band of extended defects during elevated temperature bombardment. This process is shown to involve substantial diffusion and gettering of mobile, irradiation-induced defects.

A single (100) Si wafer was irradiated with 80-keV Si ions at various elevated temperatures between 50 and 90 °C, using the 1.7 MV NEC 5SDH tandem accelerator at the Australian National University. Each irradiation was carried out in separate 0.5-cm-diameter regions of the wafer to a fluence of 1×10^{15} ions cm^{-2} at a constant flux of 1.3×10^{12} ions $\mathrm{cm}^{-2}\,\mathrm{s}^{-1}$ ($0.2\ \mu\mathrm{A\,cm}^{-2}$). Samples were tilted by 7° relative to the incident ion beam to avoid channeling. The irradiation temperature was monitored using a chromel-alumel thermocouple mounted in the target block and is estimated to be accurate to ±2 °C. The highest temperature irradiation was carried out first and the temperature lowered for subsequent irradiations. These samples were routinely analyzed by Rutherford backscattering and channeling (RBS-C) using 2 MeV He^{+} ions. RBS-C results of the typical residual damage structures, observed in samples maintained at 60 and 70 °C, are shown in Fig. 1. From the spectra it is clear that the lower temperature irradiation has produced a buried amorphous layer, centered around a depth of ~95 nm. Elevating the temperature by only 10 °C, to 70 °C, results in only moderate levels of (preamorphous) disorder. Such disorder can be characterized by an aligned yield in RBS-C spectra which only reaches a peak of about 10% of the random value at a depth close

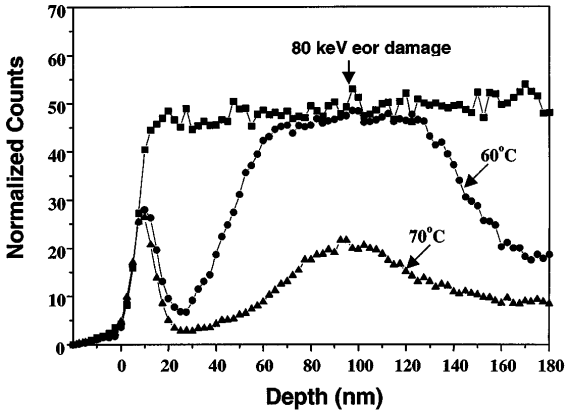

FIG. 1. RBS-C spectra of the damage structures in (100) Si after bombardment with 1×10^{15} 80-keV Si ions per cm^2, delivered at 1.3×10^{12} ions $cm^{-2}\,s^{-1}$. The samples were maintained at 60 °C (●) and 70 °C (▲) during the irradiation. A random spectrum (■) is shown for comparison and indicates that a buried amorphous layer has formed at a depth of ~95 nm in the low temperature sample. The end of range defects (eor) are indicated.

to the maximum in the energy deposition distribution for 80-keV Si ions. This dramatic change in residual damage with implantation temperature is indicative of a critical regime in which small changes in temperature can result in substantial changes in defect mobility and enhanced dynamic annealing. Under these conditions, the rate of dynamic annealing closely balances or exceeds the damage production rate, and small changes in implant temperature, fluence, and flux can dramatically alter the level and nature of residual disorder. It is worth mentioning that, even for the 60 °C case in Fig. 1, significant dynamic annealing has reduced the observed level of disorder. For example, a similar irradiation at liquid nitrogen temperatures would have resulted in an amorphous layer continuous to the surface for a fluence of $\sim 4 \times 10^{14}$ ions cm^{-2} [12]. Furthermore, the amorphous layer formed at 60 °C (Fig. 1) is found to nucleate much deeper than the peak in the nuclear energy deposition distribution (shown in Fig. 3 below), at a band of interstitial-based complexes and loops, as indicated earlier [6].

Preexisting defect structures were introduced into another (100) Si wafer by irradiating it with 33-keV B ions to a fluence of 1×10^{15} ions cm^{-2}. The irradiation was performed at −180 °C. Subsequent annealing of the sample, in a nitrogen atmosphere at 600 °C for 35 min, resulted in the formation of a thin band of residual defects within the material as shown by the RBS-C spectrum in Fig. 2(a). Cross-sectional transmission electron microscopy (XTEM) on the same material, taken using a Joel 2000 FX microscope, is displayed in Fig. 2(b) and indicates the existence of a thin defect band consisting mainly of long interstitial loops, centered at ~45 nm, surrounded by otherwise good crystal. The formation of these secondary defects resulted from imperfect annealing of a buried amorphous layer produced by the B implant. The resultant "clam shell" defects can form when two advancing amorphous-crystalline interfaces meet during annealing [13]. When the boron implanted and annealed sample is reirradiated at 70 °C, under identical conditions to those of Fig. 1, a buried amorphous layer is observed at the location of the preexisting defect structure [see Fig. 2(a)]. Cross-sectional transmission electron microscopy micrographs confirm this result for a sample

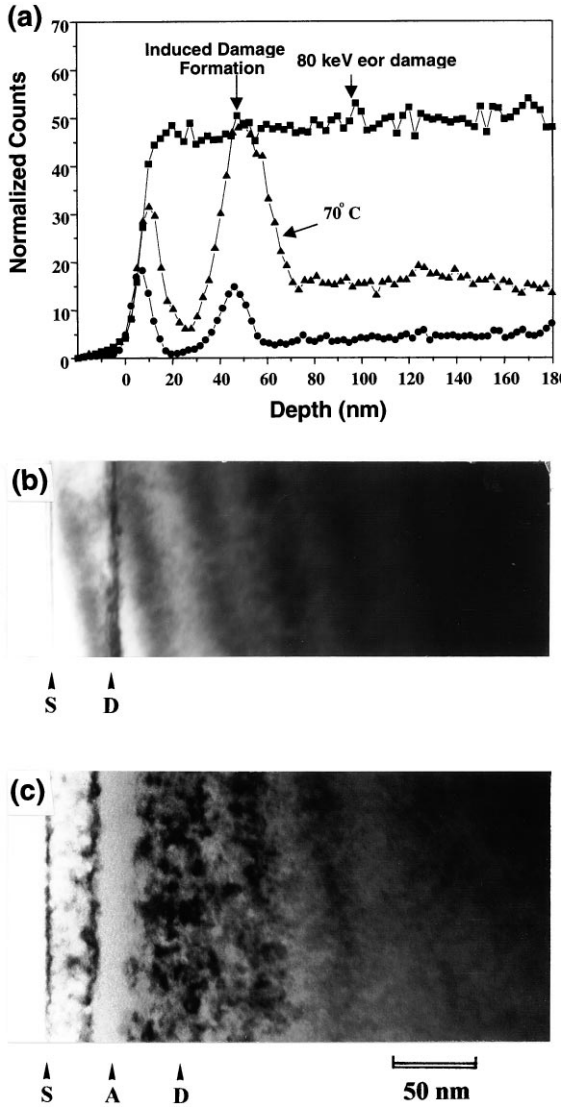

FIG. 2. (a) RBS-C spectra showing the predamage created by a 1×10^{15} 33-keV B ions per cm^2 irradiation at −180 °C and a subsequent anneal at 600 °C for 35 min (●). On subsequent irradiation at 70 °C with a 80-keV Si beam, under conditions similar to Fig. 1, an amorphous layer is observed to nucleate on these defects (▲). A random spectrum (■) is shown for comparison. XTEM micrographs show (b) the predamage and (c) the amorphous layer that appears during a subsequent 6.2×10^{12} ions $cm^{-2}\,s^{-1}$ Si irradiation at 88 °C. The surface is labeled as *S* and the amorphous layer as *A*. The preexisting defects in (b) and the deeper, end of range, loops in (c) are labeled as *D*. End of range (eor) defects are indicated.

irradiated under similar conditions to those in Fig. 2(a). In Fig. 2(c) we show the XTEM micrograph of a sample irradiated at a slightly higher flux and temperature, which clearly illustrates preferential amorphization at a preexisting dislocation band. The B concentration is estimated to be $\sim$0.2 at. % at the peak of the distribution. Such concentrations are not expected to cause metallurgical stabilization of the amorphous phase, as observed for metals with impurity concentrations of 10–20 at. %. Indeed, heavily boron-doped Si without a dislocation band has previously been shown to be harder to amorphize due to the increased fraction of highly mobile charged defects [9]. Together, the data in Fig. 2 show that a preexisting defect band is a suitable nucleation site for amorphization over a range of implant conditions. These results indicate the difficulty in nucleating an amorphous phase when the rate of dynamic annealing dominates the defect production rate. However, if irradiation-induced defects can be trapped at preexisting defects then an amorphous phase can be nucleated, presumably when the local free energy of this defective crystalline region exceeds that of the amorphous phase. In this sense, amorphization can be viewed as being nucleation limited in situations where dynamic annealing is dominant. If a suitable nucleation site exists, such as a preexisting amorphous-crystalline interface [8,9], a surface [10], or a band of dislocations as in the current study, an amorphous phase can form in a region well separated from the peak of the ion energy deposition distribution.

Figure 3 displays the distribution of residual displacements in both the virgin and predamaged wafers following irradiation at 70 °C. Also shown is the preexisting boron-induced damage prior to the silicon irradiation and the nuclear energy deposition distribution of the implanted Si ions, as calculated by TRIM95 [14]. The displacement profiles, extracted from the RBS-C spectra of Figs. 1 and 2 using the N_d code [15], were normalized so that amorphous material corresponds to a damage level of 1. Despite displacing each atom more than 10 times at the peak of the nuclear energy distribution, 1×10^{15} Si ions per cm^2 do not produce amorphization in the virgin material. Residual defects accumulate at the surface and significantly beyond the maximum in the nuclear energy deposition distribution. Irradiation of the predamaged sample results in a completely different distribution of damage. Despite the buried amorphous layer, which has nucleated around the preexisting dislocation band, the level of deep disorder is much lower than for the corresponding irradiation of virgin material. This result strongly suggests that the preexisting dislocation band not only provides local trapping sites for defects generated close to the maximum in the nuclear energy deposition distribution but also constitutes a favored gettering site for mobile interstitial-based defects which normally coalesce deeper in the material. It is interesting to note that the degree of defect accumulation at the surface is similar in both cases. At much higher doses ($\sim 10^{16}$ Si cm^{-2}) than used in this study, a continuous amorphous layer is obtained [7,9]. In this case, as well as nucleation of the amorphous layer at the defect band, nucleation also eventually occurs at the surface and these amorphous layers extend and overlap as the dose increases.

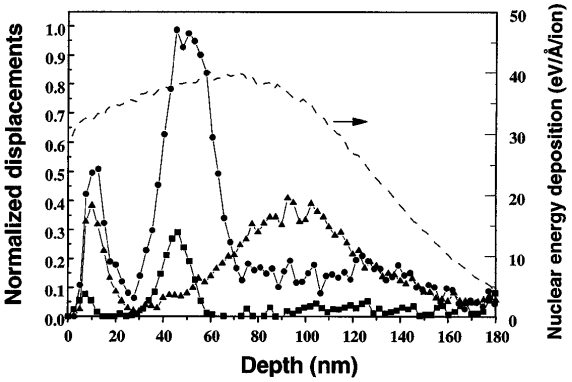

FIG. 3. Displacement profiles extracted from the RBS-C data in Figs. 1 and 2 for 1×10^{15} 80-keV ions per cm^2 Si irradiation at 70 °C of both virgin Si (▲) and a sample containing a preexisting dislocation band (●). Also shown is the disorder distribution of the preexisting defects (■) and the nuclear energy deposition distribution (dashed line) for 80-keV ions obtained from TRIM95 [14]. The projected range of an 80-keV Si ion is 120 nm.

Several studies have attempted to identify the defects responsible for annealing, damage accumulation, and eventual amorphization in the temperature range of interest. For temperatures above $\sim$150 °C, the Si divacancy has previously been suggested to be the controlling defect for amorphization [8]. However, the measured activation energy for defect-mediated processes which control amorphization appears to vary with ion mass [9]. This suggests that several defect-mediated processes may contribute to defect accumulation and amorphization, depending on the temperature of irradiation.

In conclusion, we have demonstrated an intriguing nucleation-limited amorphization process in self-ion-irradiated Si at elevated temperature. Under conditions where the rate of dynamic annealing of mobile, irradiation-induced defects balances or exceeds the damage production rate, amorphization is mediated by the accumulation of (interstitial-based) secondary defects at the tail of the ion damage distribution. Such a defect band and the surface appear to provide gettering sites for mobile defects generated elsewhere in the cascade. Indeed, under favorable irradiation conditions, preexisting defects, such as a dislocation band, can also getter defects and ultimately lead to local amorphization. Once the local free energy of the defective region of the crystal exceeds that of the amorphous phase, amorphization occurs. Such an amorphization process is not well described by traditional models but is controlled by defect mobility and the accumulation of secondary defects.

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[1] F. F. Morehead, Jr., and B. L. Crowder, Radiat. Eff. **6**, 27 (1970).
[2] H. J. Stein, F. L. Vook, D. K. Brice, J. A. Borders, and S. T. Picraux, in *Proceedings of the 1st International Conference on Ion Implantation*, edited by L. T. Chadderton and F. H. Eisen (Gordon and Breach, New York, 1971), p. 17.
[3] L. A. Christel, J. F. Gibbons, and T. W. Sigmon, J. Appl. Phys. **52**, 7143 (1981).
[4] J. R. Dennis and E. B. Hale, J. Appl. Phys. **49**, 1119 (1978).
[5] L. M. Howe and M. H. Rainville, Nucl. Instrum. Methods Phys. Res., Sect. B **19/20**, 61 (1987).
[6] R. D. Goldberg, J. S. Williams, and R. G. Elliman, Mater. Res. Soc. Symp. Proc. **316**, 259 (1994).
[7] R. D. Goldberg, J. S. Williams, and R. G. Elliman, Nucl. Instrum. Methods Phys. Res., Sect. B **106**, 242 (1995).
[8] J. Linnros, R. G. Elliman, and W. L. Brown, J. Mater. Res. **3**, 1208 (1988).
[9] R. D. Goldberg, R. G. Elliman, and J. S. Williams, Nucl. Instrum. Methods Phys. Res., Sect. B **80/81**, 596 (1993).
[10] J. S. Williams, H. H. Tan, R. D. Goldberg, R. A. Brown, and C. Jagadish, Mater. Res. Soc. Symp. Proc. **316**, 15 (1994).
[11] J. S. Williams, R. D. Goldberg, M. Petravic, and Z. Rao, Nucl. Instrum. Methods Phys. Res., Sect. B **84**, 199 (1994).
[12] W. P. Maszara and G. A. Rozgonyi, J. Appl. Phys. **60**, 2310 (1986).
[13] K. S. Jones, S. Prussin, and E. R. Weber, Appl. Phys. A **45**, 1 (1988).
[14] J. F. Ziegler, J. P. Biersack, and U. Littmark, *The Stopping and Range of Ions in Solids* (Pergamon Press, New York, 1985).
[15] A computer program which extracts displaced atom profiles from RBS-C data. The program was written by R. A. Brown and is based on the technique described by J. F. Ziegler [J. Appl. Phys. **43**, 2973 (1972)].