CONF-851217--40

THE CRYSTALLINE-TO-AMORPHOUS PHASE TRANSITION IN IRRADIATED SILICON*

D. N. Seidman,** R. S. Averback, P. R. Okamoto and A. C. Baily**
Materials Science and Technology Division
Argonne National Laboratory
Argonne, Illinois 60439
**Northwestern University, Materials Science Dept.
Evanston, IL 60201

CONF-851217--40

DE86 006170

FINAL

MASTER

January 1986

The submitted manuscript has been authored by a contractor of the U. S. Government under contract No. W-31-109-ENG-38. Accordingly, the U. S. Government retains a nonexclusive, royalty-free license to publish or reproduce the published form of this contribution, or allow others to do so, for U. S. Government purposes.

DISCLAIMER

This report was prepared as an account of work sponsored by an agency of the United States Government. Neither the United States Government nor any agency thereof, nor any of their employees, makes any warranty, express or implied, or assumes any legal liability or responsibility for the accuracy, completeness, or usefulness of any information, apparatus, product, or process disclosed, or represents that its use would not infringe privately owned rights. Reference herein to any specific commercial product, process, or service by trade name, trademark, manufacturer, or otherwise does not necessarily constitute or imply its endorsement, recommendation, or favoring by the United States Government or any agency thereof. The views and opinions of authors expressed herein do not necessarily state or reflect those of the United States Government or any agency thereof.

Submitted to the Materials Research Society (MRS) 1985 Fall Meeting, December 2-7, 1985, Boston, MA.

*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

DISTRIBUTION OF THIS DOCUMENT IS UNLIMITED

THE CRYSTALLINE-TO-AMORPHOUS PHASE TRANSITION IN IRRADIATED SILICON*

D. N. Seidman,** R. S. Averback, P. R. Okamoto and A. C. Baily**
Materials Science and Technology Division
Argonne National Laboratory
Argonne, Illinois 60439
**Northwestern University, Materials Science Dept.
Evanston, IL 60201

FINAL

January 1986

Submitted to the Materials Research Society (MRS) 1985 Fall Meeting, December 2-7, 1985, Boston, MA.
*Work supported by the U. S. Department of Energy, BES-Materials Sciences, under Contract W-31-109-Eng-38.

THE CRYSTALLINE-TO-AMORPHOUS PHASE TRANSITION IN IRRADIATED SILICON

D.N. SEIDMAN*,**, R.S. AVERBACK**, P.R. OKAMOTO** AND A.C. BAILY*,**
*Northwestern University, Materials Science Dept., Evanston, IL 60201
**Argonne National Laboratory, Materials Science and Technology Division, Argonne, IL 60439

ABSTRACT

The amorphous(a)-to-crystalline (c) phase transition has been studied in electron(e^-) and/or ion irradiated silicon (Si). The irradiations were performed in situ in the Argonne High Voltage Microscope-Tandem Facility The irradiation of Si, at <10 K, with 1-MeV e^- to a fluence of 14 dpa failed to induce the c-to-a transition. Whereas an irradiation, at <10 K, with 1.0 or 1.5-MeV Kr^+ ions induced the c-to-a transition by a fluence of ≈0.37 dpa. Alternatively a dual irradiation, at 10 K, with 1.0-MeV e^- and 1.0 or 1.5-MeV Kr^+ to a Kr^+ fluence of 1.5 dpa -- where the ratio of the displacement rates for e^- to ions was ≈0.5--resulted in the Si specimen retaining a degree of crystallinity. These results are discussed in terms of the degree of dispersion of point defects in the primary state of radiation damage and the mobilities of point defects.

INTRODUCTION

The amorphization of silicon (Si) as a result of irradiation by energetic particles has been studied for over two decades, but the exact mechanism(s) by which the transition from the crystalline(c)-to-amorphous(a) phase takes place has remained unresolved[1-12]. In this paper we present new experimental results on the c-to-a phase transition for electron (1- MeV e^-) and/or ion-irradiated Si (1.0 or 1.5-MeV Kr^+ions). The experiments were performed employing the unique capabilities of the Argonne National Laboratory High Voltage Electron Microscope-Tandem Facility. The experimental results show directly that the c-to-a phase transition depends on the degree of dispersion of the point defect distribution in the primary state of radiation damage. That is, a 1 MeV e^- irradiation--which produces a random distribution of Frenkel pairs[13]--to a fluence of 14 dpa failed to induce the c-to-a transition. Whereas, an irradiation with 1.0 or 1.5-MeV Kr^+ ions--which produces dense displacement cascades[14]-- to a fluence of 0.37 dpa induces the c-to-a transition. Moreover, it has been shown for the first time that suprisingly the dual irradiation of a region with 1-MeV e^- and 1.0 or 1.5-MeV Kr^+ ions can strongly retard the c-to-a transition, if the ratio (R) of the displacement rates (dpa s^{-1}) for electrons-to-ions exceeds ≈0.5. Atomistic models are presented for the observations.

EXPERIMENTAL PROCEDURE

The experiments consisted of irradiating <100>-p-type Si specimens in the 1-MeV transmission e^- microscope (TEM) with 1-MeV e^- and/or 1.0 or 1.5-MeV Kr^+ions at a specimen temperature of <10 K. The first experiment consisted of irradiating a small region-- ≈2 µm diam.-- of the Si specimen with 1.0-MeV e^- to a high fluence, at ≤10 K, to see if it could be amorphized under these extreme conditions. The thermal conductivity of c-Si is similiar to that of pure metals and therefore c-Si presents no special beam heating problems. The second experiment involved irradiating Si with 1.0 or 1.5-MeV Kr^+ions, at <10 K, to determine the fluence at which the c-to-a phase transition occurs. And the third experiment consisted of a simultaneous irradiation, of a small region, with 1.0-MeV e^- and 1.0 or 1.5-MeV Kr^+ions at a fixed value of R. The last experiment was used to study directly the effect of the spatial distribution of point defects on the c-to-a transition.

Electron Current Density Profile and Electron Irradiations

The electron current density as a function of position in the specimen has been shown to be given by a Gaussian expression [15]. The expression has the form:

$$I_e(r)=I_0\exp[-(r/r_0)^2];$$

where I_0 is the value of the electron flux at r=0 and r_0 is given by

$$r_0=(I_T/\pi I_0)^{1/2};$$

where I_T is the total electron current. The values of I_0 and I_T employed were

3.63×10^{19} $e^-cm^{-2}s^{-1}$and 168.5 nA, respectively. The value of r_0 was first determined by measuring I_T and I_0 with the aid of a Faraday cup. The quantity $2r_0$ is the effective beam diameter (D_0) and this value was 1.92 μm for all the e^- irradiations.

The e^- irradiations were performed by continuously irradiating the specimen and intermittently monitoring the state of the irradiated volume by observing bend extinction contours in bright-field transmission electron micrographs and selected area diffraction patterns (SADPs). The SADPs were taken employing an aperture whose diameter was smaller than the diameter of the e^- irradiated area.

Kr^+ Ion Irradiations and the Dual Irradiations

All the 1.0 or 1.5-MeV Kr^+ irradiations were performed *in situ* employing the tandem accelerator. The dual irradiations were performed by irradiating a small region--D_0= 1.92 μm--of the specimen with e^- and a much larger region which included this small region with the 1.0 or 1.5-MeV Kr^+ion beam. At the latter energies no Kr^+ ions were deposited in the specimen. The e^- flux was maintained at a constant value and the Kr^+ ion flux was systematically increased in steps. The state of the dual irradiated region was also monitored intermittently as described above.

EXPERIMENTAL RESULTS

1.0-MeV Electron Irradiation

Figure 1 shows the effect of the1-MeV e^- irradiation of a specimen maintained at <10 K. The bright field transmission electron micrographs are on the left-hand side and their corresponding SADPs are on the right-hand side Figures 1(a) and 1(b) are for fluences of zero and 14 dpa, respectively. The displacement of the bend extinction contour in the e$^-$-irradiated area demonstrates that there are stresses associated with this region. Note the absence of diffuse scattering rings in the SADP even after 14 dpa had been accumulated. Small secondary point-defect clusters--≈50 Å diameter-- were found in the e$^-$-irradiated area.

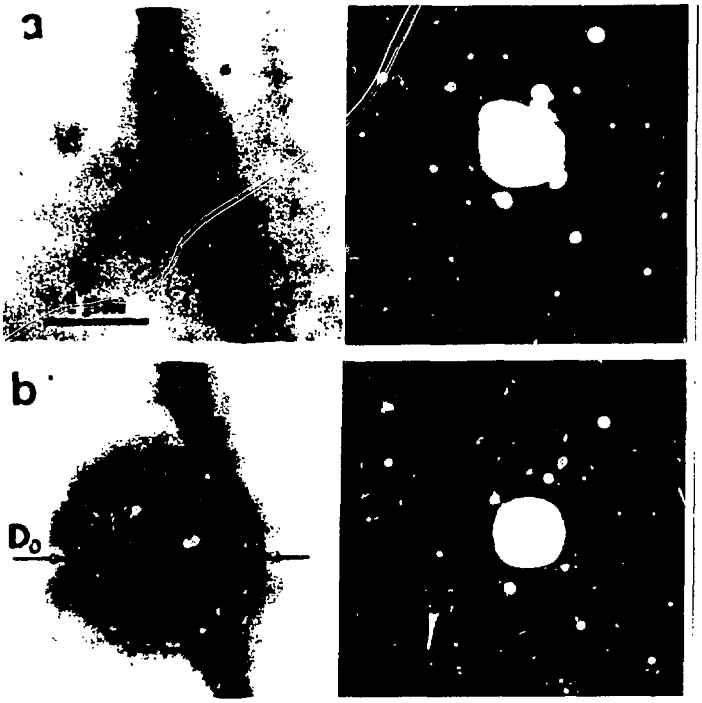

Figure 1: The effects of 1 MeV e$^-$ irradiation of a Si speciman at <10 K. In (a) the specimen had received zero dpa and in (b) 14 dpa. The irradiated area is denoted by D_0. The corresponding SADPs are on the right-hand side.

1.0 or 1.5-MeV Kr$^+$ Ion Irradiation

Silicon specimens irradiated at <10 K with either 1.0 or 1.5-MeV Kr$^+$ became amorphous at <0.4 dpa. The lack of crystallinity was determined from the absence of bend extinction contours, and the absence of sharp diffraction spots and the presence of diffuse scattering rings in the SADPs.

Dual Electron and Ion Irradiations

Figure 2 demonstrates the effects of the dual irradiation, at <10 K, on the degree of crystallinity of the irradiated volume of material. The accumulated fluences due to the 1.0-MeV Kr$^+$ion irradiation in Figs. 1(a), 1(b) and 1(c) are 8.57×10^{12} cm^{-2}, 4.26×10^{13} and 1.45×10^{14} cm^{-2} (0.02, 0.11 and 0.37 dpa), respectively. The value of the e$^-$ flux was 3.63×10^{19}cm^{-2}s^{-1}(2.64×10^{-3} dpa s^{-1}).

The displacement of the bend extinction contour in going from Fig.2(a) to 2(c) is quite clear. This displacement is due to the stresses associated with the dual irradiated region. The presence of the bend extinction contours after 0.37 dpa of 1.0-MeV Kr^+ had been accumulated demonstrates that the Si retains a large degree of crystallinity. The corresponding SADP [Fig. 2(c)] exhibits sharp diffraction spots as well as some diffuse scattering. The latter is indicative of a-Si in this region. It is important to note that by 0.37 dpa of 1.0-MeV Kr^+ the surrounding Si is essentially completely amorphous. The dashed circle in Fig. 2(c) is denoted the critical diameter (D_C) and is defined by the displaced bend extinction contour(s). The value of R at D_C is ≈ 0.5. Physically this is the minimum value of R necessary to maintain a degree of crystallinity. The same silicon specimen was irradiated to an accumulated Kr^+ fluence of 1.5 dpa by increasing the Kr^+ ion flux in discrete steps to a value of 4.5×10^{-3} dpa s^{-1}. The value of D_C decreased but the value of R at D_C was constant at ≈0.5. A 1-MeV e^- irradiation of a partially a-Si region, at <10 K, failed to induce crystallization of the a-Si.

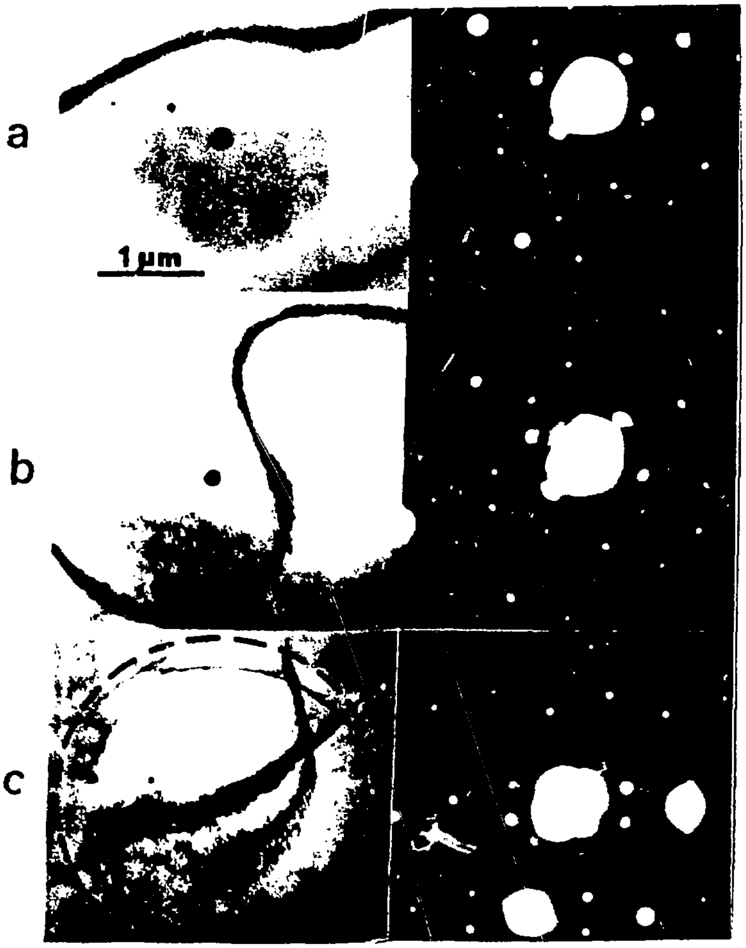

Figure 2: This figure shows the effect of a dual irradiation--1.0-MeV e^- and 1.0-MeV Kr^+ --on a small (D_0=1.92 µm) area. Figures 1(a),1(b) and1(c) were irradiated to fluences of 0.02, 0.11 and 0.37 dpa, respectively. The e^- flux was 2.64×10^{-3} dpa s^{-1}. The SADPs (right hand side) were taken with an aperture whose diameter was <1.92 µm. Note the bend extinction contours in the irradiated area.

DISCUSSION

1 MeV Electron Irradiation

The irradiation, at <10 K, to a fluence of 14 dpa with 1 MeV e^- demonstrates that even under these extreme conditions Si can not be amorphized. The only other low-temperature in situ e^- irradiation experiment is due to Foell[16]. Foell e^--irradiated Si specimens between 15 and 60 K, employing a beam voltage between 400 and 650-keV; the maximum value of the fluence was ≈10.8 dpa ($5x10^{23}$ cm^{-2}). Foell also found no evidence of a-Si. However, he observed small dislocation loops. These loops are presumably interstitial in character, as some form of the self-interstitial atom (SIA) is known to be mobile in Si at these low temperatures[12]. The existence of a highly-mobile SIA at <10 K implies that this temperature is in the so-called Stage II regime. The neutral vacancy (v) becomes mobile at ≈70 K and the negatively doubly-charged v at ≈160 K[12]; hence all charge states of the v are immobile at <10 K. To date 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[17,18]. Hence, the only possible origin of the dislocation loops observed by Foell and ourselves is due to the clustering of highly mobile SIAs--as a result of random-walk encounters--which convert into dislocation loops when the clusters exceed a critical size. The formation of dislocation loops from the clustered SIAs suppresses the c-to-a transition in the case of the e^- irradiation. Thus, the conditions for the suppression of the c-to-a transition appear to be: (a) a random distribution of Frenkel pairs; (b) a highly mobile SIA; and (c) an immobile v.

It should be noted that measurements of the production rate of damage in e^--irradiated metals, in Stages I and II, are consistent with the preceeding ideas. Electron irradiation, below Stage I, produces a random distribution of immobile Frenkel pairs. In Stage II--where SIAs are highly mobile--clustering of SIAs and trapping of SIAs at impurities are very important reactions. The net result is that the production rate of radiation damage--caused by MeV e^- irradiation-- in Stage II is very low compared to that in Stage I and therefore the supersaturation of Frenkel pairs in Stage II is small compared to the value in Stage I--this reduces the the tendency towards amorphization. In Stage II the concentration of isolated v's is greater than that of SIAs, since the clustering of SIAs as a result of long-range thermally activated migration reduces the concentration of isolated SIAs.

Dual Electron and Kr^+ Ion Irradiations

The retardation of the c-to-a transition, at <10 K, as a result of a dual irradiation can be understood qualitatively employing the following argument. The 1.0-MeV Kr^+ produce displacement cascades with a v-rich core[19,20], surrounded by a mantle of SIAs whose local concentration is several at.%[21]. Embryos of a-Si form in this region as a result of essentially dynamic SIA-SIA reactions--that is, little or no thermally-activated long-range migration. This is analogous to small Stage I recovery in metals which had been irradiated with heavy ions. The 1.0-MeV e^--irradiation in Stage II produces a state of damage, as described above, which has a strong surplus of isolated v's over SIAs. Hence, the v's dynamically shrink and/or destroy the a-Si embryos around the displacement cascades--this retards the c-to-a transition. With increasing fluence the volume fraction of the a-Si phase increases as a result of the conversion of the a-Si embryos to the a-Si phase. Once the latter conversion has occurred it can not be converted back to the c-Si phase at <10 K, as we have observed that a 1-MeV e^- irradiation of a partially a-Si region, at <10 K, failed to induce crystallization of the a-Si. The growth and shrinkage of the a-embryos is essentially the random walk problem with absorbing barriers. The effect of the e^--irradiation is a strong one, as in the presence of only the Kr^+ flux the c-to-a transition takes place at <0.4 dpa, while for the dual irradiation Si retains crystallinity at a Kr^+ fluence of 1.5 dpa. The ratio R is the control variable and for larger values of R the value of the ion fluence to which Si retains crystallinity is increased. [The details of this model will be published elsewhere.]

ACKNOWLEDGEMENTS

This research was supported by the U.S. Department of Energy. Dr. Hartmut Wiedersich is thanked for kind support and encouragement. DNS wishes to thank Dr. Georges Martin for stimulating his interest in the c-to-a phase transition problem and for useful discussions during a most pleasant stay at Saclay.

References

1. F.L. Vook and H.J. Stein, Radiat. Effects 2, 23 (1969).
2. F. F. Morehead, Jr. and B.L. Crowder, Radiat. Effects 6,27 (1970).
3. L.T. Chadderton, Radiat. Effects 8, 77 (1971).
4. M.L. Swanson, J.R. Parsons and C.W. Hoelke, Radiat. Effects 9, 249 (1971).
5. J.F. Gibbons, Proc. IEEE, 60,1062 (1972).
6. J.R. Dennis and E.B. Hale, Radiat. Effects 30, 219 (1976); J. Appl. Phys 49,1119 (1978).
7. R.S. Nelson, Radiat. Effects 32, 19 (1977).
8. F. Cembali, L. Dori, R. Galloni, M. Servidori and F. Zignani, Radiat. Effects 36, 111 (1978).
9. N.A. Sobolev, G. Götz, W. Karthe and B. Schnabel, Radiat. Effects 42, 23 (1979).
10. R. Kalish, T. Bernstein, B. Shapiro and A. Talmi, Radiat. Effects 52, 153 (1980).
11. R.P. Webb and G. Carter, Radiat. Effects 59, 69 (1981).
12. J.W. Corbett, J.P. Karins and T.Y. Tan, Nucl. Instum. & Meth. 182/183, 457 (1981).
13. J.W. Corbett, Solid State Physics:Suppl.7 (Academic Press, New York,1966),Chapt. 1, pp.1-5; M.W. Thompson,Defects and Radiation Damage in Metals (Cambridge Press, England, 1969),Chapt. 4, pp.

89-142.

14. J.A. Brinkman, Am. J. Phys. 24, 246 (1956).
15. P.R. Okamoto and N.Q. Lam, Mat. Res. Soc. Sympos. Proc. 41,241 (1985).
16. H. Föll, Inst. Phys. Conf. Ser. 23,233 (1975).
17. J.W. Corbett and J.C. Bourgoin, Trans. IEEE NS-18, 11 (1971).
18. J.C. Bourgoin and J.W. Corbett, Phys. Lett. 38A, 135 (1972).
19. C.-Y. Wei and D.N. Seidman, Appl. Phys. Lett. 34, 622 (1979); C.-Y. Wei,M.I. Current and D.N. Seidman, Philos. Mag. A, 44, 459 (1981); M.I. Current, C.-Y. Wei and D.N. Seidman, Philos. Mag. A, 47, 407 (1983).
20. R.S. Averback, R. Bendek, K.L. Merkle, J. Sprinkle and L.J. Thompson, J. Nucl. Mater. 113, 211 (1983).
21. L.A. Beaven, R.M. Scanlan and D.N. Seidman, Acta Metall. 19, 1339 (1971); C.-Y. Wei and D.N. Seidman, Philos. Mag. A, 43, 1419 (1981).