CHANGING THE STRUCTURAL STATE OF AMORPHOUS SILICON BY ION IRRADIATION

S. Roorda[1], W.C. Sinke[1], J.M. Poate[2], D.C. Jacobson[2], S. Dierker[2], B.S. Dennis[2], D.J. Eaglesham[2] and F. Spaepen[3].
1) FOM-Institute for Atomic and Molecular Physics, Kruislaan 407, 1089 SJ Amsterdam, The Netherlands.
2) AT&T Bell Laboratories, Murray Hill, NJ 07974, USA.
3) Harvard University, Cambridge, MA 02138, USA

ABSTRACT

Ion beams of keV and MeV energies have been used to bombard amorphous Si (a-Si), which had previously been annealed ('relaxed'). Analysis by Raman spectroscopy and differential scanning calorimetry shows that when 1 out of every 20 Si atoms is displaced by a nuclear collision, the a-Si returns to its unrelaxed state and cannot be distinguished from as implanted a-Si. Moreover, the kinetics of the heat release on annealing of similarly bombarded crystalline Si (c-Si) are qualitatively identical to those of structural relaxation in a-Si. This implies that the population of ion beam induced defects in a-Si is very similar to that in c-Si. It also shows that defect annihilation is an important ingredient in the mechanism of structural relaxation of a-Si.

INTRODUCTION

Many properties of a-Si are not uniquely determined but are variable and depend on the thermal history of the material [1-3]. From Raman spectroscopy it has been observed that local order increases when freshly prepared a-Si is annealed [2,4,5]. This has been inferred from a decrease in the width of the TO-like peak in the Raman spectrum of a-Si. This width has been argued to be roughly linearly dependent on the width of the distribution of bond angle distortions [2]. The ordering process is accompanied by a considerable heat release of about one third of the heat of crystallization [6,7]. This process is named 'structural relaxation'. It is generally viewed as a process to which every atom in the solid contributes, decreasing the average bond angle distortion $\Delta\Theta$ between tetrahedral covalent bonds. The heat release upon structural relaxation has been related to a decrease in strain energy due to a decrease in $\Delta\Theta$ [8].

This view of structural relaxation assumes a fully connected continuous random network (CRN) both before and after annealing. This is not unreasonable, since electron spin resonance (ESR) measurements of pure a-Si [3] before relaxation show only a small number of unpaired electrons (dangling bonds), namely $\approx 1 \times 10^{19}$ cm^{-3}. This number decreases upon annealing to $\approx 5 \times 10^{18}$ cm^{-3}. This would indicate a dangling bond density change of less than 0.02 %. However, ESR is not sensitive to paired electrons in charged dangling bonds and at reconstructed internal surfaces. Therefore, the majority of the unsaturated bonds may be hidden to ESR.

In this study, ion beams have been used to intentially damage a-Si, which has previously been annealed. The resulting structure has been examined with Raman spectroscopy and differential scanning calorimetry (DSC). In addition, c-Si which received similar irradiations has been analyzed [9] with DSC, Rutherford Backscattering/channeling (RBS) and Transmission Electron Microscopy (TEM). The density of both a-Si and c-Si after ion bombardment has been determined. The results from these measurements are discussed elsewhere in these proceedings [10]. In addition, a-Si was prepared in different intermediate states of relaxation. These different states were characterized by Raman, DSC, infrared optical properties, X-ray diffraction and density measurements. Some results of this work are also reported in these proceedings [11].

SAMPLE PREPARATION AND EXPERIMENTAL METHODS

Amorphous Si layers of 2 μm thickness were prepared by $^{28}Si^+$ ion implantation into c-Si substrates.Multiple implants of 0.5, 1 and 2 MeV, 5×10^{15} ions/cm^2 each, were performed while the targets were held at liquid nitrogen temperature. As a result of the implantation, the top 2 μm of the c-Si targets have turned amorphous. These a-Si layers were then annealed under vacuum at 500 °C for 45 minutes. This results in a-Si which is thermally stable up to 500 °C. In order to introduce damage in this 'well-relaxed' a-Si, it was then bombarded with He^+, C^+, Si^+ or Ge^+

TABLE I Post-anneal bombardment conditions (normalized to 1 dpa).

Raman or DSC	ion species	E_1 (MeV)	$dose_1$ (10^{15}/cm^2)	E_2 (MeV)	$dose_2$ (10^{15}/cm^2)	E_3 (MeV)	$dose_3$ (10^{15}/cm^2)
Raman	C^+	4.5	125	-	-	-	-
Raman	Si^+	5.5	16	-	-	-	-
Raman	Ge^+	8.3	2.5	-	-	-	-
DSC	He^+	0.05	12	0.12	7	0.2	7
DSC	Si^+	0.5	0.5	1.5	1	-	-
DSC	Ge^+	0.7	0.2	2.2	0.4	-	-

ions. Ion energies were varied from 50 keV to 8 MeV and the ion fluence ranged from 10^{11} to 10^{16} ions/cm^2 (see Table I). Simultaneously, c-Si targets were bombarded with the same ion beams. During the bombardments the targets were again held at liquid nitrogen temperature. The number of target atoms displaced by the ion irradiation was estimated using Monte Carlo calculations [12], assuming a threshold displacement energy of 15 eV and a lattice binding energy of 2 eV per bond. The ion dose was multiplied by the calculated number of displaced atoms per incident ion to give the ion damage dose in displacements per atom (dpa).

To prepare samples for Raman analysis, high ion energy irradiation was used (Table I) because this results in a uniform damage profile in a 0.1 μm thick surface layer. This corresponds roughly to the probe depth of the Raman measurements. Raman spectra were recorded using the 488 nm line from an Ar ion laser. Spectra were characterized by the position and half-width (at the high wavenumber side) of the TO-like peak. These parameters may be used as an indicator for the state of relaxation of a-Si. A peak position at high frequency (≈479 cm^{-1}), and narrow peak width (≈35 cm^{-1}) indicate anneal-stable a-Si, whereas a lower frequency peak position (≈471 cm^{-1}) and a broad peak (≈43 cm^{-1}) are indicative of 'unrelaxed' or 'as implanted' a-Si [4,6,8].

Ion beam damaged a-Si for DSC was prepared using multiple energy bombardments, such that all radiation damage was confined in the a-Si layer and resulted in a reasonably uniform damage profile (Table I). Simultaneously, c-Si discs were subjected to the same bombardments. DSC scans were taken with two bombarded samples of 7.6 mm diameter in one of the DSC pans and two untreated c-Si discs in the other. This balances the thermal load on the DSC pans. Scans were taken at a scan rate of 40 K/min from 50 to 400 °C. After cooling down and stabilizing, every scan was followed by a second measurement on the same set of samples in order to obtain the baseline. If the sample releases heat when it is first brought to an elevated temperature, this shows up as a difference between the signals of the first and the second run.

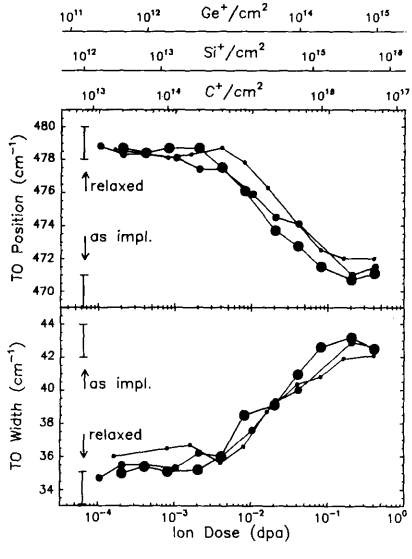

Figure 1. TO-like peak width (bottom) and position (top) of the Raman spectra of ion (C^+, Si^+, Ge^+) bombarded a-Si as a function of ion dose. Symbol size corresponds to projectile mass. The ion dose is expressed in terms of dpa in a 0.1 μm thick surface layer.

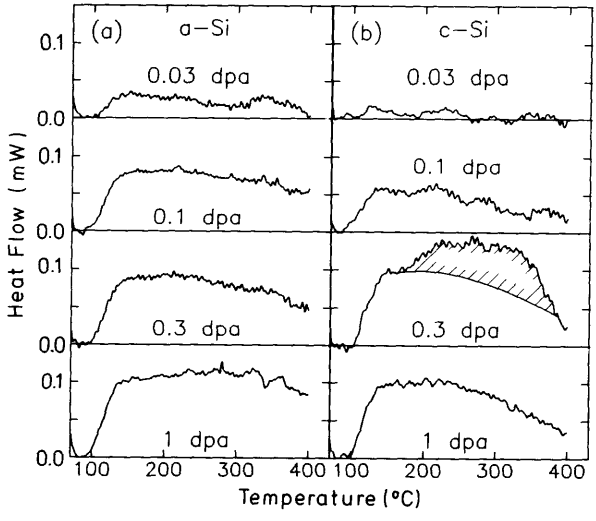

Figure 2. Differential Scanning Calorimetry difference traces for (a) well-relaxed a-Si and (b) c-Si, after bombardment with He^+ ions to fluences resulting in 0.03 to 1 dpa.

RESULTS AND DISCUSSION

Raman results are summarized in Fig. 1, which shows the TO-like peak width (open circles, left scale) and position (solid circles, right scale) of a-Si as a function of post-anneal C^+, Si^+ or Ge^+ ion bombardment dose. Increasing symbol size corresponds to increasing projectile mass. For ion doses leading to less than 0.01 dpa, both the peak width and position are the same as those of well-relaxed a-Si, within the experimental error. From ≈0.01 to 0.1 dpa, a peak shift and broadening occurs which indicate that the annealed a-Si is gradually brought back to its unrelaxed or as-implanted state. For ion doses of more than 0.1 dpa, the peak width and position saturate at the position of as-implanted a-Si. The major part of the transition from relaxed to unrelaxed has already occurred for the 0.05 dpa bombardments, which means that only one out of every 20 Si atoms needs to be displaced in order to de-relax the a-Si. This is substantially less than the damage dose to amorphize c-Si, which is close to 1 dpa. From the fact that the de-relaxation occurs at the same damage dose (in terms of dpa) for all three projectiles, it is concluded that de-relaxation is a result of nuclear collisions of the implanted projectiles rather than of electronic energy loss mechanisms. Thus, according to Raman, relaxed a-Si which has been ion bombarded to a dose of 0.05 dpa cannot be distinguished from as-implanted a-Si. In the following, we will see whether this still holds when ion-irradiated a-Si is investigated with DSC.

DSC traces of 0.03 to 1 dpa Si are shown in Fig. 2 (a) for a-Si and (b) for c-Si. Traces for less than 0.03 dpa Si were not significantly different from the zero-signal baseline and are not shown. Ion bombarded a-Si in all cases shows a clear heat release, similar to the heat release from as-implanted a-Si [6,7], but for 0.03 dpa the heat release is smaller than for the higher dose implants. This indicates that between 0.03 and 0.1 dpa, a-Si is completely brought back to its unrelaxed state. This confirms the conclusion on the basis of the Raman results (Fig. 1). For c-Si the situation is somewhat different, as can be seen in Fig. 2 (b). For 0.03 dpa c-Si hardly any deviations from the baseline are observed. For 0.1 and 1 dpa c-Si a heat release is observed which is qualitatively the same as that from a-Si, but for 0.1 dpa the total amount of heat released from c-Si is substantially smaller than that from a-Si. For 0.3 dpa c-Si, a heat release is observed which is larger than any other heat release. Moreover, for 0.3 dpa c-Si the shape of the trace is qualitatively different from all the other traces; at 180 °C an 'extra' heat release sets in (hatched area) which seems to come on top of the 'normal' trace. In order to understand the mechanisms underlying this behaviour, both RBS/channeling [9] and TEM analysis of 0.03 to 1 dpa c-Si were performed.

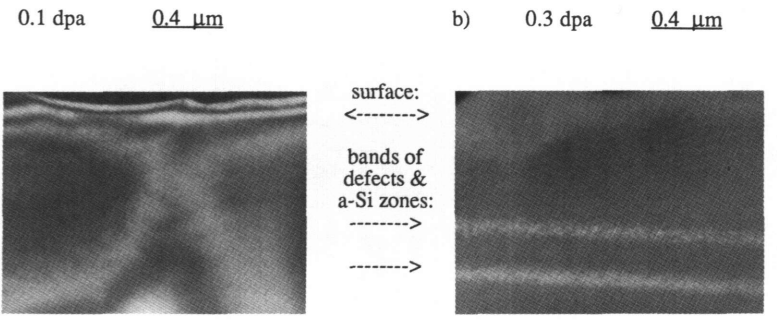

Figure 3. TEM micrographs of (a) 0.1 dpa and (b) 0.3 dpa He^+ bombarded c-Si, before DSC measurements. Arrows indicate the surface, bands of defects and the interface between the damaged layer and the substrate.

TEM-micrographs of 0.1 and 0.3 dpa c-Si, prepared by He^+ implantation, are shown in Fig. 3 (a) and (b). The 0.3 dpa c-Si, which was implanted with 120 and 200 keV He^+, exhibits two bands of extended defects or small amorphous zones at a depth corresponding to the maximum in the damage profile of both implants, as were also observed in RBS/channeling [9]. No such bands are observed in the 0.1 dpa c-Si (50, 120 and 200 keV He^+), which shows only a very small contrast difference between a ≈1 μm thick surface layer and the substrate. Examination of this material at higher magnification showed no evidence for amorphous zones or defect clusters large enough to be observable in TEM. On the other hand, RBS/channeling analysis of 0.1 dpa c-Si revealed a ≈6 at% density of direct scattering centers in a ≈1 μm thick surface layer. It is concluded that these scattering centers are point defects that remain after recombination of the vacancies and interstitials, formed during the bombardment. Here, the term "point defect" is meant to include every cluster of point defects that is too small to be observed in TEM. It was found that after DSC, all damage in the 0.1 dpa and most of the damage in the 0.3 dpa c-Si had disappeared. RBS/channeling analysis of 1 dpa c-Si (He^+ bombarded) showed that an amorphous layer of ≈1 μm thickness had formed.

On the basis of the RBS and TEM results, we can now establish the origin of the heat release from ion beam damaged c-Si (Fig. 2 (b)). Bombardment to 1 dpa leads to the formation of a ≈1μm thick a-Si layer (not shown, see [9]), therefore the heat release from 1 dpa c-Si is due to structural relaxation of the a-Si layer. Ion bombardment to a dose of 0.1 dpa leads to the formation of a distribution of point defects, but no amorphous clusters, therefore the heat release from 0.1 dpa c-Si is due to point defect annihilation alone. It is noted that the temperature dependence of this heat release is similar to that of structural relaxation [5-7]; it exhibits a broad signal over a large temperature range. This indicates that there is a large population of different point defects with a large number of different routes to annihilation. The heat release from 0.3 dpa c-Si can now be understood as being due to both annihilation of point defects (area under curve in Fig. 2 (b)) and recrystallization of small amorphous zones or removal of large defect clusters (hatched area in Fig 2 (b)).

Now we are able to provide a more detailed interpretation of 'structural relaxation' of a-Si. The similarity of the traces for 0.1 dpa a-Si and c-Si (Fig. 2 (a) and (b)) suggests a common mechanism for annihilation of a large population of point defects and structural relaxation. We therefore conclude that point defect annihilation plays an important role in structural relaxation of a-Si. At first sight this may seem to contradict the initial interpretation in terms of average properties such as a decrease in the average bond angle distortion [5]. However, a point defect concentration as low as 3 at% corresponds already to an average distance between defects of less than four interatomic spacings. Because a point defect leads to small local rearrangements in its immediate vicinity, involving bond angle distortions [13], it follows that these defect concentrations lead to a distortion of the majority of the bond angles.

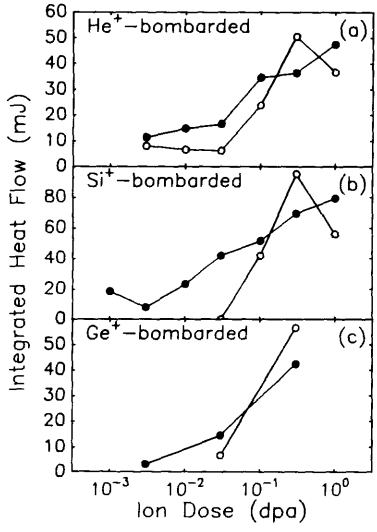

Figure 4. Integrated heat release from (a) He^+, (b) Si^+ and (c) Ge^+ bombarded a-Si (solid circles) and c-Si (open circles) as a fuction of the ion fluence. The amount of defected material in the DSC was ≈9.1 μmol (a) resp. 15.1 μmol (b), (c).

This interpretation not only provides a more detailed picture of structural relaxation of a-Si, it also implies that the population of point defects in a-Si is similar to that in c-Si. This also may seem surprising at first sight. However, both single vacancies and interstitials as well as small clusters of defects can easily be defined in a fully connected a-Si network without any need for translational or rotational symmetry as exhibited by the c-Si lattice. In fact, the possible existence of stable single vacancies and small vacancy clusters in a fourfold covalently bonded CRN has been predicted from total energy calculations based on the Keating potential [14].

DSC results similar to those shown in Fig. 2 are obtained for Si^+ and Ge^+ bombarded Si. This is shown in Fig. 4, which shows the integrated heat release in the temperature range from 50 to 400 °C, as a function of ion beam damage for three different projectiles (He^+, Si^+, Ge^+) and two different targets (c-Si and well-relaxed a-Si). It can be seen that in all cases 0.03 dpa is the minimum damage necessary to induce a heat release, and that in all cases the heat release from a-Si is larger than that from c-Si except for the 0.3 dpa bombardments. The shape of the DSC traces obtained from Si^+ and Ge^+ bombarded Si were similar to that of structural relaxation, except for the 0.3 dpa c-Si traces, which showed a similar signal as observed for He^+ bombarded c-Si. Thus, the results shown in Fig. 2 (a) and (b) can be reproduced using not He^+, but Si^+ or Ge^+ bombardment, as long as the ion doses are scaled to the ion beam induced damage. This confirms the conclusion from the Raman measurements, namely that ion beam induced de-relaxation of a-Si is due to nuclear energy loss processes rather than of electronic energy loss mechanisms.

CONCLUSIONS

Bombardment of relaxed a-Si with a minimum dose of energetic ions returns it to a state which can not be distinguished from the as-implanted state. This occurs as a result of nuclear collisions of the impinging projectiles at a dose which is substantially less than is necessary for amorphization of c-Si. From the similarity of the temperature dependence of defect annihilation in heavily damaged c-Si and structural relaxation of a-Si, it is inferred that annihilation of point defects plays an important role in the process of structural relaxation of a-Si. It also implies that the population of point defects in ion bombarded a-Si is similar to that in ion bombarded c-Si.

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REFERENCES

1 G.K. Hubler, E.P. Donovan, K.W. Wang and W.G. Spitzer, Soc. Photo-Optical Instr. Eng. Vol. **530**, 222 (1985), and E.P. Donovan, G.K. Hubler and C.N. Waddell, Nucl. Instrum. and Meth. **B19/20**, 590 (1987).
2 R. Alben, D. Weaire, J.E. Smith, Jr. and M.H. Brodsky, Phys. Rev. **B11**, 2271 (1975).
3 W.G. Spitzer, G.K. Hubler and T.A. Kennedy, Nucl. Instrum. and Meth. **209/210**, 309 (1983).
4 R. Tsu, J.G. Hernandez and F.H. Pollak, Sol. State. Commun. **54**, 447 (1985).
5 W.C. Sinke, T. Warabisako, M. Miyao, T. Tokuyama, S. Roorda and F.W. Saris, J. Non-Cryst. Solids **99**, 308 (1988).
6 S. Roorda, S. Doorn, W.C. Sinke, P.M.L.O. Scholte and E. van Loenen, Phys. Rev. Lett. **62**, 1880 (1989).
7 E.P. Donovan, F. Spaepen, J.M. Poate and D.C. Jacobson, Appl. Phys. Lett. **55**, 1516 (1989)
8 W.C. Sinke, S. Roorda and F.W. Saris, J. Mater. Res. **3**, 120 (1988).
9 S. Roorda, J.M. Poate, D.C. Jacobson, D.J. Eaglesham, B.S. Dennis, W.C. Sinke and F. Spaepen, submitted, and: S. Roorda, J.M. Poate, D.C. Jacobson, B.S. Dennis, S. Dierker and W.C. Sinke, submitted.
10 J.S. Custer, M.O. Thompson, J.M. Poate, D.C. Jacobson, S. Roorda, W.C. Sinke and F. Spaepen, *These Proceedings*.
11 S. Roorda, J.M Poate, D.C. Jacobson, P. Fuoss, B.S. Dennis, S. Dierker, W.C. Sinke and F. Spaepen, *These Proceedings*.
12 J.P. Biersack and L.J. Haggmark, Nucl. Instrum. and Meth. **174**, 257 (1980).
13 *Point Defects in Solids*, edited by J.H. Crawford and L.M. Slifkin (Plenum, New York, 1975) Vol. 2, p 4.
14 C.H. Bennett, P. Chaudhari, V. Moruzzi and P. Steinhardt, Phil. Mag. **A40**, 485 (1979).