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POINT DEFECT POPULATIONS IN AMORPHOUS AND CRYSTALLINE SILICON

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Crystalline Si (*c*-Si) and relaxed amorphous Si (*a*-Si) have been ion-bombarded. The kinetics and temperature dependence of the heat released on annealing of these materials are found to be qualitatively similar for temperatures lower than epitaxial crystallization temperatures (550 °C). This behavior suggests a close similarity between the mechanisms of structural relaxation in *a*-Si and defect annihilation in *c*-Si. The heat release measurements imply that ion bombardment generates a variety of point defects in both *a*-Si and *c*-Si.

1. INTRODUCTION

Amorphous Si (*a*-Si) in its unhydrogenated form is the model system for the 'ideal' covalently bonded continuous random network (CRN) but the role of defects in this structure is not understood[1]. Many of the properties[1-4] of *a*-Si depend on its preparation and thermal history. This behaviour is considered to be an intrinsic property of *a*-Si, reflecting the fact that a CRN may exist in structurally different thermodynamic states[5]. The transition from a high internal free energy state to a low one is known as structural relaxation[6] and is accompanied by a heat release of about one third of the heat of crystallization[7,8] for *a*-Si. Structural relaxation is generally viewed as a process of local ordering, to which every atom in the CRN contributes. The heat of relaxation has been associated solely with a decrease in average bond angle distortion as a result of this local ordering process[5]. However, the contribution of defects to structural relaxation is not known.

The experiments described in this Communication show that large concentrations of point defect complexes, introduced by means of ion bombardment in either *a*-Si or crystalline Si (*c*-Si), exhibit strikingly similar annealing kinetics, indicating that the population of defects in both materials is similar. Furthermore, these kinetics are similar to those of structural relaxation[8,9], implying that defects play an important role in the structural relaxation of *a*-Si.

2. EXPERIMENTAL PROCEDURES

The amorphous layers, 2 μm in thickness, were prepared by bombarding small *c*-Si discs of 7.6 mm diameter and 100 μm thickness with $^{28}Si^+$ ions at energies of 0.5, 1 and 2 MeV to a dose of $5x10^{15}$ cm^{-2} for each energy. Instantaneous beam power was maintained at 10 W to ensure that target temperatures did not rise significantly above liquid nitrogen temperature. Subsequently, the discs were annealed in a vacuum furnace at 500 °C for 45 minutes. As a result of this treatment, the *a*-Si has become well-relaxed and in thermal quasi-equilibrium up to 500 °C[7,8]. To introduce defects, these *a*-Si layers as well as virgin *c*-Si discs were ion bombarded with He^+ ions at 50 keV, 120 keV and 200 keV, to fluences ranging from $5x10^{13}$ to $2x10^{16}$ ions/cm^2 using the same method as described above. Multiple implants were used to obtain a uniform damage profile to a depth of ≈1.2 μm. One set of the higher dose samples was implanted with 120 and 200 keV He^+ only. The number of collision-induced displacements per atom (dpa) in the target material was estimated using Monte Carlo simulations[10]. These simulations were performed assuming a threshold displacement energy of 15 eV, a lattice binding energy of 2 eV and included displacements by recoil Si atoms. The ion fluences used here are in the range of 0.003 to 1 dpa. The thermodynamic and structural properties of the bombarded samples were investigated by differential scanning calorimetry (DSC), Rutherford backscattering spectroscopy and channeling (RBS, *c*-Si only), transmission electron microscopy (TEM, *c*-Si only) and Raman spectroscopy[11].

The DSC measurements were taken on a Perkin-Elmer DSC-2 instrument using two bombarded discs for each measurement, so that the amount of damaged material in the calorimeter was ≈9 μmol. The samples were not in direct contact with the DSC furnace pans, but rested on graphite spacers. Two unimplanted *c*-Si discs of the same mass as the measured samples were loaded in the reference DSC pan. After loading of the samples but before each measurement, the calorimeter was allowed to equilibrate for several

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minutes. Scans ran from 50 to either 400 or 727 °C at 40 K/min; after cooling down from the first scan, a second scan was taken without touching the samples between scans. Subtraction of the second curve from the first gives the heat release from the damaged material during the first scan. For scans with a maximum temperature of 400 °C, the baseline stability, in terms of total integrated heat release, was better then 10 mJ.

3. RESULTS

Fig. 1 shows the heat release from *c*-Si (bottom trace) and *a*-Si (top trace) for samples irradiated with He^+ ions to a dose corresponding to 0.3 dpa ("0.3 dpa Si"). The top trace has been offset for clarity. In the low-temperature region, the zero-signal baseline for both curves is indicated with a dashed line. The trace for *a*-Si exhibits a sharp peak which corresponds to a heat release due to crystallization. This peak is clearly absent on the curve for *c*-Si. The shape of the peak is determined by the crystallization kinetics: crystallization occurs via solid phase epitaxial regrowth at the *a*-Si/*c*-Si interface which is a thermally activated process characterized by a single activation energy of 2.7 eV[8]. Therefore the heat flow increases exponentially with temperature until all *a*-Si has crystallized. At low temperatures both 0.3 dpa *a*-Si and 0.3 dpa *c*-Si show a heat release over a wide temperature range (hatched areas) without any peaks. This is attributed to removal of ion beam induced damage which evidently is not characterized by a single activation energy. The low-temperature heat release is investigated in more detail using DSC scans to a maximum temperature of 400 °C, thus ensuring a better baseline stability. This is necessary, because for scans over the full temperature range, the curvature in the baseline can exceed the signal due to heat release from relaxation at lower temperatures.

Fig. 2 shows the low-temperature DSC traces of (a) well-relaxed *a*-Si and (b) *c*-Si, both after irradiation with He^+ ions for a range of ion fluences. The curves for less than 0.03 dpa did not differ significantly from the zero-signal baseline and are not shown. The curves for 0.03 to 1 dpa *a*-Si (Fig. 2 (a)) deviate clearly from the baseline, and show a heat release similar to that observed when as-implanted *a*-Si is ramp heated for the first time[7,8]. It can be seen that saturation occurs between 0.03 and 0.1 dpa. Thus, bombardment with He^+ ions yielding 0.03 (or more) dpa in well-relaxed *a*-Si results in 'de-relaxation' of the *a*-Si, i.e. the *a*-Si returns to the unrelaxed state which cannot be distinguished from as-implanted *a*-Si. Raman analysis of light and heavy ion bombarded *a*-Si confirmed this finding[11].

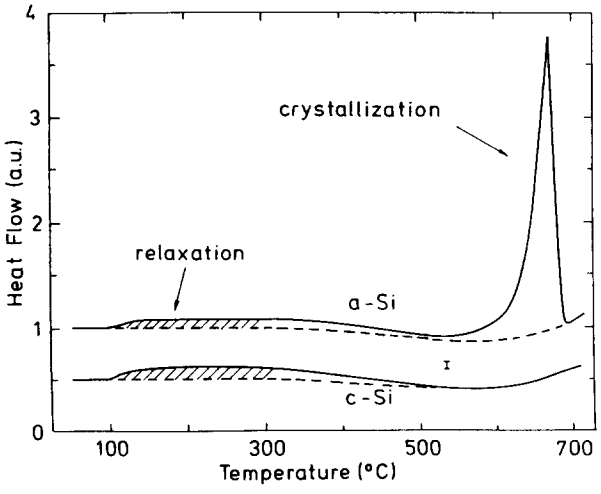

Fig. 1 - DSC difference traces for relaxed *a*-Si and *c*-Si, after irradiation with He^+ ions to a fluence resulting in 0.3 dpa.

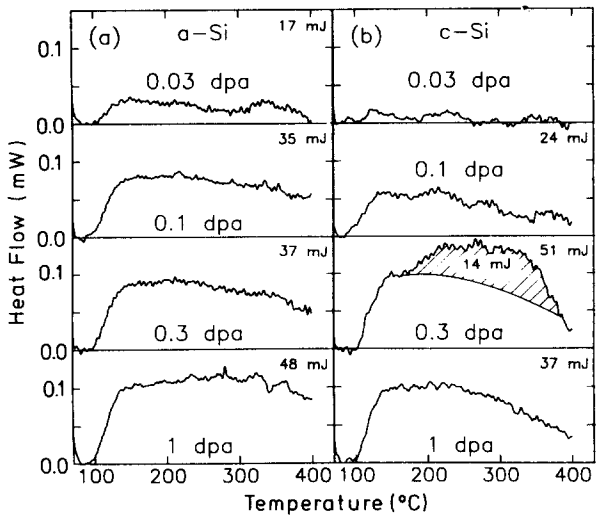

Fig. 2 - Low-temperature DSC difference traces for (a) well-relaxed *a*-Si and (b) *c*-Si, after irradiation with He^+ ions. The hatched area is discussed in the text. The values of the integrated heat release are shown.

Traces from He^+ bombarded *c*-Si are shown in Fig. 2 (b). The curve for 0.03 dpa is not significantly different from the baseline but the curve for 0.1 dpa indicates a heat release which is qualitatively similar to the signal from *a*-Si. The area under the curve corresponds to the total amount of heat released, this is 30 % less than from 0.1 dpa *a*-Si. For 1 dpa the signal from *c*-Si resembles that from *a*-Si, but with somewhat reduced magnitude. It is significant that the curve for 0.3 dpa *c*-Si differs from all other curves: a heat release can be seen which is larger than any other. Moreover, this curve is qualitatively different because above 180 °C an extra heat release begins (hatched area). In order to understand these results, it is instructive first to examine the RBS-channeling spectra taken on this material.

The RBS-channeling spectra of He^+ bombarded *c*-Si are shown in Fig. 3 (a), which shows spectra taken before DSC analysis and Fig. 3 (b), which shows spectra after DSC analysis. A random spectrum and a channeled spectrum of unimplanted *c*-Si (virgin) are shown for comparison. Four samples are shown, with ion fluences resulting in 0.03, 0.1, 0.3 (120 and 200 keV only) and 1 dpa. The spectrum for 0.01 dpa (not shown) cannot be distinguished from that of virgin *c*-Si. The spectrum for 0.03 dpa is only slightly different from that of virgin Si, but the other spectra all show an increased yield, the curve for 1 dpa being indistinguishable from that of completely amorphized Si. The number of

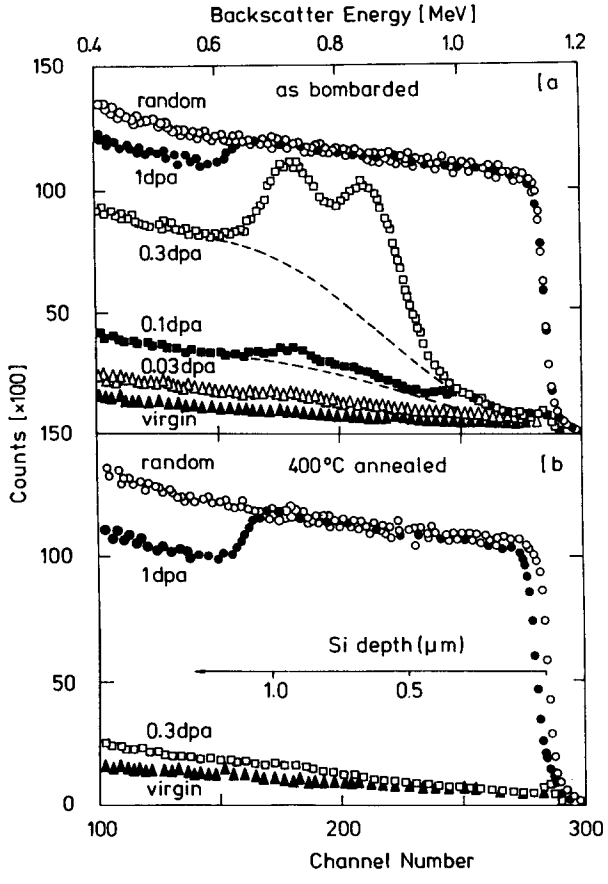

Fig. 3 - RBS-channeling spectra of *c*-Si bombarded with multiple energy He^+ ions, (a) before and (b) after DSC analysis to 400 °C. The dashed lines indicate yields due to dechanneling.

displaced atoms can be estimated from the spectra in Fig. 3 (a) by subtracting the contribution of dechanneling from the total yield. For 0.1 dpa this number is $\approx 3 \times 10^{17}$ cm^{-2}, and for 0.3 dpa, $\approx 1.3 \times 10^{18}$ cm^{-2}. These numbers should be compared with the Si areal density of a 1.2 μm thick layer which is 6×10^{18} cm^{-2} and thus correspond to 5% and 20% of displaced atoms, respectively. The TEM analysis revealed that the damage in 0.3 dpa *c*-Si is mostly in the form of a high density of small clusters. It is not possible to distinguish whether these clusters are amorphous zones or heavily defected *c*-Si. Most importantly, 0.1 dpa *c*-Si showed no clusters at all, but only a very slight contrast difference between the irradiated surface layer and the substrate. Apparently there is a critical density of displaced atoms, above which point defects accumulate to form clusters, visible in TEM. This view is consistent with the observation by Ruault *et al.* of a time delay in the formation of ion beam induced amorphous zones in heavy ion irradiated *c*-Si[12]. This threshold density of displaced atoms appears to be formed during irradiations (at 77 K) corresponding to 0.1 - 0.3 dpa.

4. DISCUSSION

The RBS-channeling spectra after (low-temperature) DSC to 400 °C are shown in Fig. 3 (b) (spectra for 0.03 and 0.1 dpa cannot be distinguished from the virgin spectrum and are not shown). The damage causing the increased yield in Fig 3 (a) has all disappeared except in case of the 1 dpa bombardment. Apparently 1 dpa suffices to amorphize Si completely[13]. It appears, therefore, that an ion fluence corresponding to 0.3 dpa gives the maximum amount of damage which is unstable under heating to 400 °C.

The 0.1 dpa implants in *c*-Si produce no extended defects observable in TEM, but give rise to a defect population which is visible in RBS and anneals out during DSC to 400 °C. We therefore conclude that while the heat release from *c*-Si at 0.3 dpa is due to the removal of both point defects and defect clusters or amorphous zones, the heat release from 0.1 dpa *c*-Si is due to annihilation of point defects alone (where we use the term point defect loosely, to include all defect clusters too small to be imaged in TEM). These point defects seem to anneal out continuously over a range of temperatures, as opposed to annealing kinetics dominated by only a few processes (which would give rise to peaks in the DSC trace). Such annealing behaviour implies a zoo of point defects in irradiated *c*-Si, with a large number of routes to annihilation.

The observations shed some light on the origin of the DSC curve for the structural relaxation of *a*-Si. The close similarity in the annealing behaviour of 0.1 dpa bombarded *a*-Si and *c*-Si (Fig. 1 (a) and (b)) suggests that the underlying mechanisms are very similar and presents persuasive evidence for the existence of point defects in *a*-Si similar to those in *c*-Si. Although this suggestion is at first sight surprising, one can define both vacancies and interstitials in a fully-connected *a*-Si network. The stability of vacancies and vacancy clusters in a fourfold coordinated covalently bonded CRN is in fact predicted in total-energy calculations based on the Keating potential[14]. It is interesting that more heat is released from the defects in *a*-Si than *c*-Si, compare 0.1 dpa *a*-Si with 0.1 dpa *c*-Si. This would imply, if the defect complexes were identical in both *a*-Si and *c*-Si, that defects are retained more effectively in *a*-Si than in *c*-Si. In other words, defect mobilities and annihilation rates during bombardment would be less in *a*-Si than in *c*-Si.

The DSC traces shown in Figs. 1 and 2 are obtained on He^+ bombarded material. Experiments with Si^+ and Ge^+ ion bombardments reproduced the results shown on Fig. 2 (a) and (b), as long as the ion fluences were scaled to dpa. Therefore, the ion beam induced damage, which gives rise to a heat release, is due to nuclear collisions rather than electronic energy loss mechanisms. This further supports the suggestion that the heat release in 0.1 dpa bombarded Si is due to point defect annihilation in both amorphous and crystalline Si.

Electron spin resonance (ESR) measurements of a decrease in the spin density in *a*-Si before and after a thermal anneal[2,15,16] have also been interpreted as defect annihilation. However, the maximum spin density in *a*-Si (5×10^{19} cm^{-3}) is a factor of 60 lower than the number of displaced atoms in 0.1 dpa Si (inferred from the channeling measurement in Fig. 3). It appears that the majority of defects can not be detected by ESR.

The low-temperature excess heat release (hatched area in Fig. 2) in the 0.3 dpa *c*-Si can now be understood in terms of recrystallization of amorphous zones at anomalously low temperatures. It is assumed that the heat release from the 0.1 dpa *c*-Si can be associated with the total

number of displaced atoms as determined by RBS ($3x10^{17}$ cm^{-2}), giving an energy of 0.56 eV per displaced atom. For the 0.3 dpa *c*-Si, the assumption is made that the heat release is a linear superposition of annihilation of point defects (i.e. 0.56 eV/displaced atom) and heat release from crystallization and relaxation of amorphous zones (0.12-0.16 eV/atom[7,8]). The heat release from point defects should have the same onset and form as the 0.1 dpa *c*-Si. The hatched area, therefore, corresponds to heat release from amorphous zones. From the measured heat release, the hatched area in Fig. 2 would then correspond to $8.2\text{-}6.2x10^{17}$ atoms/cm^2 and the remaining area to $4.6x10^{17}$ cm^{-2} displaced atoms, thus giving a total number of $1.3\text{-}1.1x10^{18}$ cm^{-2}. This number is in good agreement with the channeling estimate of $1.3x10^{18}$ cm^{-2}. This analysis shows in an *ad hoc* fashion that the amorphous fraction in the 0.1 dpa *c*-Si is effectively zero thus confirming the TEM and RBS analyses. It is remarkable that the onset of epitaxial recrystallization in the 0.3 dpa *c*-Si occurs at 180 °C. One possible reason for this phenomenon is that these small amorphous zones are embedded in a sea of defects which can enhance crystallization.

It is known that annealing of ion implanted *a*-Si produces a significant change in the Raman spectrum[5]. Moreover, recent X-ray diffraction[17] show a change in the average structure during annealing of as-implanted *a*-Si. These measurements might appear to conflict with a defect picture of structural relaxation in *a*-Si. However, in a covalently bonded network we would expect point defects to be accomodated by large local bond-angle distortions[18]. The defect concentrations in *a*-Si for 0.03 dpa, inferred from damage in *c*-Si are already so large that the average spacing between two neighbouring defects is estimated to be no more than 4-5 atomic distances.

5. CONCLUSIONS

In conclusion, ion bombardment has been used to introduce point defect complexes in *c*-Si and relaxed *a*-Si. Only 1 out of every 30 to 50 Si atoms needs to be displaced in order to return 500 °C relaxed *a*-Si to its unrelaxed state. The annealing characteristics of unrelaxed *a*-Si and defected *c*-Si are very similar, which indicates two important similarities: (1) the mechanisms of structural relaxation of *a*-Si and defect annihilation in heavily defected *c*-Si are closely related, and (2) point defect populations in *c*-Si and *a*-Si produced by ion bombardment are very similar. For very heavily defected *c*-Si, the annealing characteristics can be interpreted in terms of recrystallization of small amorphous zones at temperatures as low as 180 °C.

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