Raman study of de-relaxation and defects in amorphous silicon induced by MeV ion beams

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Raman spectroscopy is used as a probe of the state of amorphous Si (*a*-Si) and damaged crystalline Si. MeV ion beams have been used to irradiate structurally relaxed *a*-Si. When the density of Si atoms displaced by nuclear collisions exceeds 5%, the *a*-Si is "de-relaxed", and thus returns to its as-implanted state. This behavior is an indication that point defect complexes exist in *a*-Si and play an important role in the process of structural relaxation.

The structure of pure amorphous Si[1] (*a*-Si) depends on its thermal history as evidenced by the fact that ion-implanted *a*-Si, when heated in a differential scanning calorimeter (DSC), shows a considerable heat release at temperatures well below the crystallization temperature.[2,3] Such a heat release does not occur when *a*-Si has already been thermally annealed. The Raman spectrum of *a*-Si, and especially the TO-like peak, exhibits large changes upon thermal annealing of *a*-Si at temperatures in the same temperature range.[4,5] Thus Raman is a sensitive probe of the state of *a*-Si. These changes in the state of *a*-Si are associated with a phenomenon known as structural relaxation. It has been previously suggested that structural relaxation can be associated solely with a decrease in the average bond angle distortion $\Delta\theta$ in the continuous random network (CRN). The width of the TO-like peak in the Raman spectrum of *a*-Si has been related to $\Delta\theta$,[4,6] and indeed has been found to decrease upon annealing. The role of isolated defects, such as small vacancy and interstitial complexes in structural relaxation, has not previously been established. In this letter, we show, through the use of Raman spectroscopy, that relaxation is intimately related to the removal of defects from *a*-Si. The defects are originally introduced by light and heavy ion irradiation of relaxed *a*-Si. We also show that the damage, produced in single-crystal Si (*c*-Si) by equivalent irradiations, can be probed by Raman spectroscopy.

Ion implantation of $^{28}Si^+$ ions of 0.5, 1.0, and 2.0 MeV into *c*-Si substrates held at 77 K was used to prepare thick layers of *a*-Si. These samples were than annealed for 45 min at a temperature of 500 °C in vacuum. This results in *a*-Si layers which are structurally well relaxed.[2,3] The samples were then irradiated with either 4.5 MeV C^+, 5.5 MeV Si^+, or 8.3 MeV Ge^+ ions to fluences ranging from 10^{11} to 10^{17} ions/cm^2. In addition, *c*-Si was irradiated with 120 and 200 keV He^+ ions to a dose of either 2×10^{15} or 7×10^{15} cm^{-2} each. The high dose sample was also irradiated with 50 keV He^+ to a dose of 1.2×10^{16} cm^{-2}. During all irradiations the samples were held at 77 K. The spot size of the ion beam was defocused to $\approx$1 cm in diameter and was rastered electrostatically over the target. The instantaneous beam power was maintained lower than 10 W to avoid beam heating. Monte Carlo simulations of all irradiations were performed,[7] assuming a displacement threshold energy in *a*-Si of 15 eV (a lattice binding energy of 2 eV per bond) and including displacements by recoiled target atoms. The calculated number of displaced atoms per incident ion in a 0.1 μm surface layer (corresponding to the probe depth of the Raman measurement) increases from 4 for the C^+ to 203 for the Ge^+ irradiations, whereas the electronic energy loss varies only by a factor of 4. In the figures the ion dose is expressed in terms of displacements per target atom (dpa). (The ion fluence has been multiplied by the calculated number of displacements in the probed surface layer per incident ion and divided by the number of Si atoms in the same layer. The probe depth depends on the absorption coefficient and is $\approx$0.1 μm *a*-Si and $\approx$0.7 μm in *c*-Si[8]). The damage in He^+-irradiated *c*-Si was investigated[9] with channeled ion scattering measurements as well as transmission electron microscopy. These results are not shown here but can be summarized as follows. The low dose (0.3 dpa) irradiated sample showed two bands of extended defects and/or small amorphous clusters at a depth of $\approx$1 μm and an increased ion scattering yield, presumably due to small point defect complexes, at shallower depths. The high dose (1 dpa) irradiated sample showed an amorphous layer extending almost completely to the surface. After irradiation all samples were characterized by Raman spectroscopy using the 488 nm line from an Ar ion laser. The laser beam was focused to a spot of $\approx50\times200$ μm and the total power was 150 mW. A triple monochromator was used to disperse the spectrum on a CCD camera.

Figures 1 and 2 show the complete gamut of Raman spectra from virgin single *c*-Si through damaged single *c*-Si to amorphized Si (Fig. 1) in different stages of relaxation (Fig. 2). The spectrum for virgin *c*-Si (bottom) shows a sharp 1st order peak at 521 cm^{-1}, 2nd order peaks near 300 and 440 cm^{-1}, and no signal below 200 cm^{1}. The spectrum for ion-irradiated *c*-Si (middle) shows a broadening of the 1st order peak as well as the appearance of

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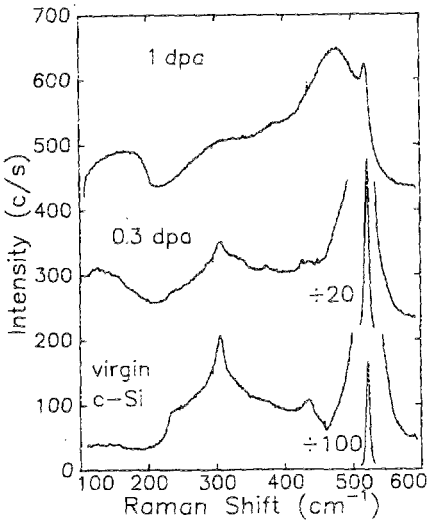

FIG. 1. Raman spectra of virgin *c*-Si (bottom) and *c*-Si after irradiation with keV He^+ ions to a dose which results in small defect complexes (middle) or in an amorphized surface layer (top).

signal at low wave numbers. These changes are indicative of distortions in the crystal lattice. The intensity of the 1st order peak has decreased which is most likely due to a higher absorption in the damaged *c*-Si and to broadening of the peak. The spectrum for amorphized Si (top) shows broad peaks near 150 and 470 cm^{-1} and weak features around 300 and 380 cm^{-1}. The presence of the small peak near 521 cm^{-1} shows the existence of *c*-Si at the surface. Note that the signal below 200 cm^{-1} is qualitatively different for *a*-Si than for damaged *c*-Si.[10]

The effect of annealing (i.e., relaxing) and subsequent ion irradiation (i.e., de-relaxing) on *a*-Si is shown in Fig. 2. The position (λ_0) and half-width ($\Gamma/2$) of the TO-like peaks are indicated. It can be seen that λ_0 shifts to higher

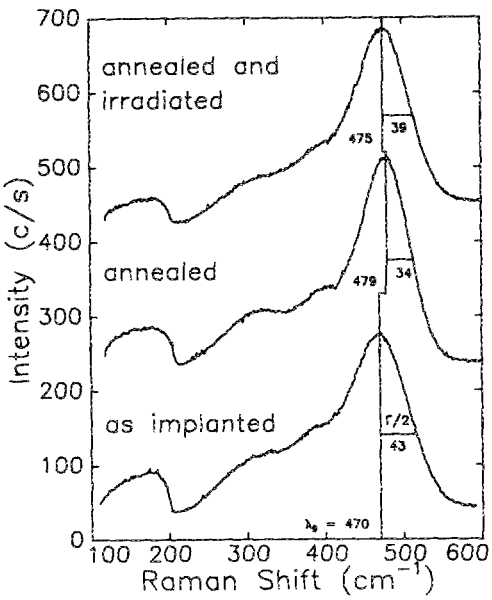

FIG. 2. Raman spectra of *a*-Si as implanted (bottom), 500 °C annealed (middle), and annealed and irradiated (5×10^{15} C^+/cm^2, top). Indicated are the position and half-width of the TO-like peak.

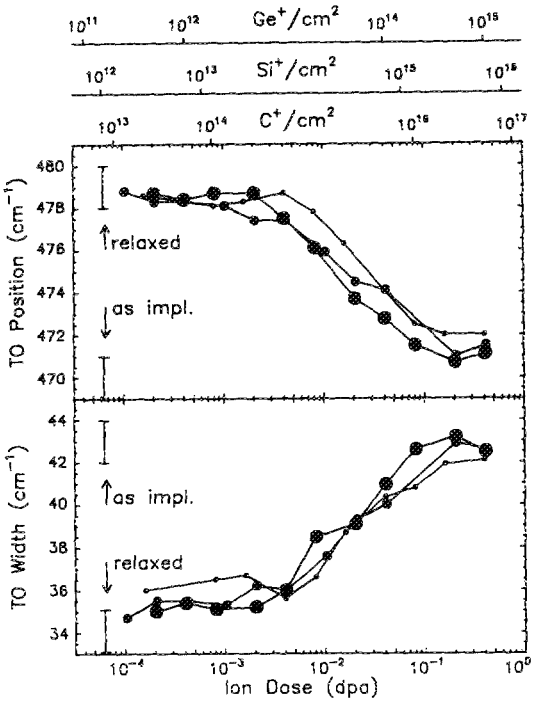

FIG. 3. Half-width (bottom) and position (top) of the TO-like Raman peak from annealed *a*-Si as a function of post-anneal ion irradion dose. Increasing symbol size corresponds to increasing projectile mass for C^+, Si^+, and Ge^+ ions. Indicated are typical values for as-implanted and relaxed *a*-Si.

wave numbers and that $\Gamma/2$ decreases as a result of the anneal ($\Gamma/2$ rather than the full width is used because on the low wave number side the TO-like peak overlaps with LO- and LA-like features in the spectrum). The top spectrum is that of relaxed *a*-Si which has been irradiated with 4.5 MeV, 5×10^{15} C^+/cm^2. This spectrum resembles that of as-implanted *a*-Si (bottom) indicating that the effect of the ion irradiation on relaxed *a*-Si is to return it to its unrelaxed state. In itself, this is not surprising because the *a*-Si was made by ion implantation in the first place. What is surprising is the ion dose at which this occurs: the dose used here is namely much smaller than that needed for amorphization of *c*-Si, i.e., (5×10^{16} C^+/cm^2).

Figure 3 shows $\Gamma/2$ and λ_0 for C^+, Si^+, and Ge^+ irradiations as a function of ion dose. For comparison, the values for as-implanted and well-relaxed *a*-Si are indicated. The ion dose is expressed in dpa as well as in ions/cm^2. It can be seen that for low ion doses, $\Gamma/2$ and λ_0 resemble the values characteristic for well-relaxed *a*-Si, while for high doses $\Gamma/2$ and λ_0 resemble values as as-implanted *a*-Si. The transition from relaxed to unrelaxed spectra occurs for ion doses on the order of $\approx$0.02 dpa, irrespective of the mass of the projectile. This is the critical dose for de-relaxation. When the three projectiles are compared on an equivalent dpa base, the amount of energy deposited in *a*-Si due to electronic stopping changes over several orders of magnitude. Therefore, it can be concluded that the phenomenon of de-relaxation by ion beams is due to nuclear collisions. Since the major part of the transition has occurred for a dose of 0.05 dpa, it appears that only one out of every 20 Si

atoms needs to be displaced by a violent collision in order to almost completely de-relax the *a*-Si. This may be compared with the damage that is necessary to completely amorphize *c*-Si, which is between 0.3 and 1 dpa.[9]

An explanation of these observations is that the ion beam introduces stable (at room temperature) defects in the *a*-Si layer as a result of nuclear collisions. In a fully connected CRN, it is to be expected that the configuration of small defect clusters will be similar to that in the crystal. Moreover, it has been predicted that vacancies as well as small vacancy clusters are stable in a CRN.[11] Since a defect has a strain field extending over several atomic distances,[12] it is to be fully expected that at the high defect densities in these experiments, every atom in the network feels the presence of a defect. It should be emphasized that the relaxed or unrelaxed states of *a*-Si do not necessarily represent different phases of *a*-Si but rather differences in the densities of point defect complexes. Additional confirmation for this point comes from our calorimetry experiments.[9] We have not, however, resolved from these experiments the interesting question of the number of defects remaining in the *a*-Si after the 500 °C relaxation anneal.

In summary, MeV ion beams have been used to irradiate *a*-Si which was previously relaxed. When the density of displaced Si atoms exceeds 5%, the *a*-Si has returned to its as-implanted state; it has been de-relaxed. This phenomenon has been correlated with the nuclear collisions of the projectiles (or recoils) with Si atoms in the solid. The data suggest that stable defects are introduced by nuclear collisions in *a*-Si thus causing the de-relaxation of the network. Conversely, it would appear that relaxation of the network involves annihilation of these defects. We emphasize that the presence of large concentrations of defects in the structure implies a large average bond angle distortion.

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[1] D. E. Polk and D. S. Boudreaux, Phys. Rev. Lett. **31**, 92 (1973).
[2] S. Roorda, S. Doorn, W. C. Sinke, P. M. L. O. Scholte, and E. van Loenen, Phys. Rev. Lett. **62**, 1880 (1989).
[3] E. P. Donovan, F. Spaepen, J. M. Poate, and D. C. Jacobson, Appl. Phys. Lett. **55**, 1516 (1989).
[4] R. Tsu, J. Gonzalez-Hernandez, and F. H. Pollack, J. Non-Cryst. Solids **66**, 109 (1984); Solid 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] D. Beeman, R. Tsu, and M. F. Thorpe, Phys. Rev. B **32**, 874 (1985).
[7] J. P. Biersack and L. J. Haggmark, Nucl. Instrum. Methods **174**, 257 (1980).
[8] *Properties of Silicon* (INSPEC, The Institution of Electrical Engineering, London and New York, 1988).
[9] S. Roorda, J. M. Poate, D. C. Jacobson, D. J. Eaglesham, B. S. Dennis, S. Dierker, W. C. Sinke, and F. Spaepen (unpublished).
[10] T. Shimada, Y. Katayama, K. Nakagawa, H. Matsubara, M. Migitaki, and E. Maruyama, J. Non-Cryst. Solids **59/60**, 783 (1983).
[11] C. H. Bennet, P. Chaudhari, V. Moruzzi, and P. Steinhardt, Philos. Mag. A **40**, 485 (1979).
[12] J. W. Corbett and J. C. Bourgoin, in *Point Defects in Solids*, edited by J. H. Crawford and L. M. Slifkin (Plenum, New York, 1975), Vol. 2, p. 407.