Nuclear Instruments and Methods in Physics Research B 90 (1994) 412–414
North-Holland

NIM B
Beam Interactions with Materials & Atoms

Calorimetry of ion beam damage in silicon

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Annealing of ion-beam damage in crystalline Si has been characterized by differential scanning calorimetry and infrared absorption spectroscopy. Si discs of 100 μm thickness have been bombarded with 3.4 MeV protons. Scanning calorimetry reveals a sharp peak riding on a broad background signal. From infrared absorption, this peak is tentatively identified as heat release associated with divacancy annihilation.

1. Introduction

Crystal defects in Si and their annealing behaviour have been studied extensively and several specific defects have been identified by spectroscopic techniques [1]. In spite of their obvious importance, the thermodynamic properties of defects have escaped most of this attention. Specifically, the formation energies of most simple defects in c-Si have never been measured. The only formation energy that is known is that of the mono-vacancy; it has been deduced from differences in positron lifetimes as c-Si approaches its melting point [2]. In GaAs, only the energy stored by a vacancy-interstitial pair has been measured [3].

Differential scanning calorimetry (DSC) has been used earlier to characterize structural relaxation in amorphous Si, and the annealing behaviour of ion-beam-damaged crystalline and amorphous Si [4]. It was found that the kinetics and temperature dependence of relaxation and defect removal were very similar. A somewhat surprising finding was that the heat release upon defect annealing in c-Si showed a broad, featureless temperature dependence, instead of a series of well-defined peaks. This was tentatively attributed to extensive defect–defect interaction and the formation of a wide spectrum of defect clusters. In order to avoid such defect–defect interaction, lower defect concentrations are required while maintaining the sensitivity of the DSC.

We have now started a study of the thermodynamic properties of simple defects in Si, with an emphasis on the non-equilibrium character associated with ion implantation damage. We have used high-energy proton bombardment to generate low concentrations of simple defects in c-Si, but spread over a volume roughly 100 times that of the earlier samples. It was expected that the detection limit of the calorimeter should permit direct observation of the defect annealing and here we present our first results.

2. Sample preparation and analysis techniques

Nominally undoped float-zone c-Si discs of 100 μm thickness were bombarded with 3.4 MeV H^+ ions to a dose of $(1-12)\times 10^{16}$ ions/cm^2. Since more than 99% of the ions are transmitted for this combination of ion energy and Si thickness, the discs were clamped between two rings which held them at the edge only. During the bombardment, the sample holder was held at liquid nitrogen temperature. Furthermore, the ion beam current was kept below 1 μA and rastered over a large 10 cm^2 area, thus limiting the areal power density to less than 0.34 W/cm^2. Nevertheless, the cooling efficiency of the Si itself was erratic. About one in ten discs did not retain any bombardment damage, indicating that these particular samples reached such high temperatures that all defects produced were mobile and annealed out immediately.

After the ion bombardment, the samples were allowed to warm to room temperature, and the bombardment damage was characterized by infrared absorption spectroscopy using a Bomem DA3 Fourier transform infrared spectrometer (FTIR), with a quartz-halogen white-light source, CaF_2 beamsplitter and liquid-nitrogen cooled InSb detector. The low resolution used – just under 1 meV – was more than adequate for the broad peaks being investigated here. Absorption coefficients were calculated with respect to

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SSDI 0168-583X(93)E0627-S

the spectrum of an untreated Si sample, measured under identical conditions. Absorption features due to water vapour were observable at 0.47 and 0.77 eV and have been removed from more recent measurements by evacuating the instrument. A broad absorption peak centered around 0.7 eV (1.8 μm), indicating the presence of divacancies [5], was clearly evident in most samples.

Differential scanning calorimetry (DSC) was carried out using a Perkin–Elmer DSC2 apparatus. The scanning rate was 40 K/min and during the scans the sample pans were flushed with dry Ar gas. The samples rested not directly on the sample pans but on graphite spacers. For each measurement, four samples were stacked in one sample pan and four identical but non-implanted discs were loaded in the reference pan. Two scans were taken between 50 and 400°C; the difference between the first and second scan represents the heat released by the implanted discs during the first heating run. After DSC, all discs were again characterized by FTIR to verify that the absorption peak corresponding to divacancies had disappeared.

3. Results and discussion

Some examples of infrared absorption spectra are shown in Fig. 1, where the absorption coefficient is measured relative to an undamaged c-Si disc. Four spectra are shown, namely those of unbombarded c-Si, two proton-bombarded discs *before* DSC (3.6×10^{16} ions/cm^2 and 1.2×10^{17} ions/cm^2), and one bombarded disc *after* DSC. Ion bombardment leads to a change in the absorption spectrum consisting of a broad peak centered at a wavelength of 0.7 eV and an increase in near-edge absorption. The peak is known to be specific for divacancies, whereas the edge absorption has been attributed to ion-induced defect clusters [5]. The intensity of the absorption peak in Fig. 1 is proportional to the ion dose. This was found to be true for all implanted discs (except for those that got hot and did not retain any damage at all). After DSC, the divacancy peak and the absorption edge disappear and the spectrum is essentially identical to that of unbombarded c-Si.

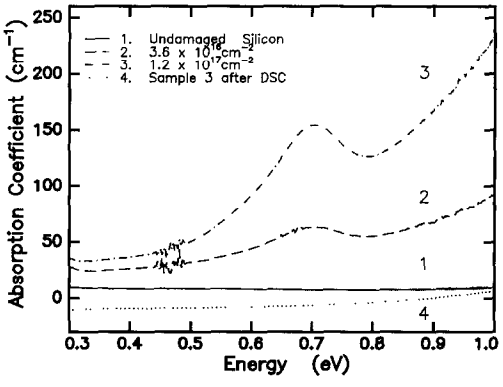

Fig. 1. FTIR absorption spectra of (1): untreated Si (full curve), (2): Si bombarded with 3.6×10^{16} H$^+$/cm^2 (dashed curve), (3) Si bombarded with 1.2×10^{17} H$^+$/cm^2 (dash-dotted curve) and (4): same sample as curve (3) but after DSC.

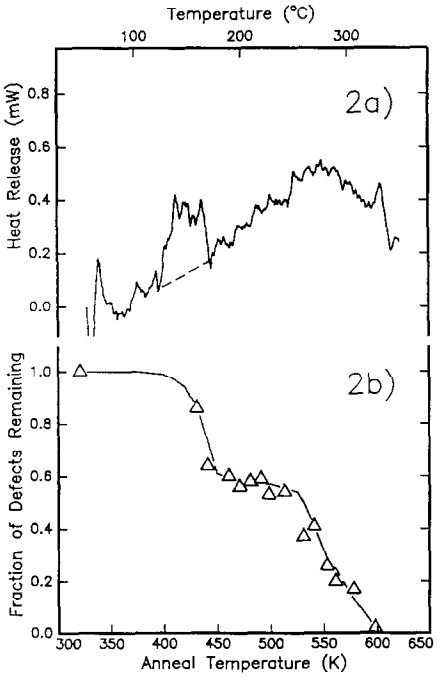

Fig. 2. (a) DSC curve measured on a stack of four Si discs bombarded with 1.2×10^{17} H$^+$/cm^2. An exothermic signal is plotted as positive. (b) Intensity of the FTIR 0.7 eV absorption peak after 15 min isochronal anneal, normalized to the initial intensity. After Cheng et al. [6].

In Fig. 2a we show a result from DSC. A well-defined peak can be seen, centered near 150°C and riding on a broad background signal. A less well-defined peak may be present near 280°C. At this point it is not clear whether the background signal corresponds to a heat release or not. Isothermal calorimetry is required to resolve these issues. In order to facilitate the interpretation of this DSC curve, the intensity of the 0.7 eV absorption peak, as measured by FTIR [6] has been plotted in Fig. 2b as a function of anneal temperature. Two anneal stages can be clearly identified. The first anneal stage shows a steep decline which corresponds to the sharp DSC peak near 150°C. The more gentle slope of the second anneal stage indicates that any corresponding heat release would be washed out over a wide temperature range, and indeed it is difficult to separate the signal from the background in the corresponding DSC curve. The first anneal stage has been

associated with removal of divacancies by other mobile defects but without the divacancies themselves being mobile [6] and is observed only in float-zone Si. The second anneal stage is attributed to normal divacancy annealing. It occurs at a somewhat higher temperature than divacancy annealing in Czochralski grown Si. On the basis of these results, we tentatively identify the sharp peak in the calorimetry as being due to heat release associated with divacancy annihilation.

Earlier calorimetry of ion beam damage in c-Si showed a broad signal over a wide temperature range with no sharp peaks. Here we observe a well-defined peak in the DSC measurements of proton-bombarded c-Si. Moreover, it can be identified with divacancy annealing. In both cases, the primary damage generated by the incident ions consists principally of vacancies and interstitials. However, after the samples have been allowed to warm to room temperature, the defect structure appears to be different. We think that this can be explained as follows: In the earlier work, a He ion beam of 50 to 200 keV was used. All the damage was confined in a 1 μm thick surface layer and the sensitivity of the DSC allowed the heat release associated with defect annealing to be detected only for the very high damage doses approaching the amorphization threshold. In these cases, the defect concentration amounted to several atomic percent, equivalent to a defect–defect separation of less than three atomic distances. Under these circumstances, extensive defect–complex formation is expected.

In the material studied in the present work, the defect concentrations are much lower. The 3.4 MeV protons are fully transmitted by the 100 μm Si discs; therefore, the thickness of the damaged layers is increased by a factor of 100 relative to those that were used for the earlier measurements. This allows much lower defect concentrations to be detected by DSC. The defect concentration after ion bombardment is not precisely known but can be estimated from the known cross section for atomic displacement by high energy protons and from the intensity of the infrared absorption at 0.7 eV. Based on such estimates, we expect that the defect concentration in none of the present samples exceeded 10 ppm. In this case, very few defect complexes are formed. Therefore, the anneal behaviour is expected to consist of well defined peaks, which is exactly what has been observed.

4. Conclusion

The heat released upon annealing of ion-bombarded crystalline silicon, measured by differential scanning calorimetry, shows a well-defined peak at 150°C, and possibly a second, broad feature near 280°C. By combining the calorimetry with infrared absorption measurements as a function of anneal temperature, the peak has been identified as heat release associated with the removal of divacancies.

Acknowledgments

It is a pleasure to acknowledge the expert assistance of P. Bérichon and R. Gosselin with the operation of the tandem accelerator and the help of L. Cliche and M. Verhaegen with the ion bombardments. We are grateful to Z. Altounian (McGill University) for allowing us to use the DSC. This work is financially supported by the Natural Science and Engineering Research Council of Canada (NSERC) and the Fonds pour la Formation de Chercheurs et l'Aide à la Recherche (FCAR).

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