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Divacancies in proton irradiated silicon: characterization and annealing mechanisms

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Abstract

Annealing of divacancies produced by ion bombardment of crystalline silicon has been characterized using differential scanning calorimetry (DSC) and Fourier transform infrared absorption (FTIR). DSC at a rate of 40°C/min shows two clear peaks in the heat release, one at 140°C and the other at 240°C. The activation energies of these peaks were calculated assuming first order kinetics and found to be approximately 1.2 and 1.5 eV. The remaining fraction of divacancies with respect to annealing temperature was measured by FTIR and compared to the remaining fraction of defects calculated from the heat released in DSC. Annealing measurements are in agreement with previous work on electron and neutron irradiation of Si despite much higher defect concentrations.

Keywords: Silicon; Divacancy; Ion implantation; Calorimetry; Annealing

1. Introduction

Despite more than three decades of work on vacancies and divacancies in crystalline silicon, some important aspects of these point defects are not completely known and understood. In particular, the formation energy of divacancies has yet to be measured experimentally. Our aim is to measure that formation energy. Several studies were conducted on electron irradiated Si [1]; however, defect concentrations were always much lower than in ion irradiated Si. In this paper we describe the preparation and characterization of Si samples with divacancy concentrations high enough to be used for such a measurement.

Divacancies are produced by bombardment with 8 MeV protons which have enough energy to completely go through the samples and produce defects without leaving residual hydrogen which would react very effectively with vacancy-type defects to produce unwanted point defects in our material [2,3]. The total amount of divacancies in an irradiated sample can be measured using infrared absorption [1,4], electron spin resonance (ESR) [5], positron annihilation study (PAS) [6] and deep level transient spectroscopy (DLTS). However, a quantitative evaluation of the divacancy count in a sample is very difficult to achieve. We plan to eventually do this by establishing a correlation between these different methods. The heat released during a thermal anneal measured using differential scanning calorimetry (DSC) clearly indicates two annealing mechanisms of different activation energies. This raises questions about the annealing behaviour of divacancies that must be answered before we can evaluate their formation energy by simply taking the ratio of the heat released to the total number of divacancies in the sample.

2. Sample preparation and analysis techniques

The samples were cut from three types of ⟨1 1 1⟩ float-zone crystalline silicon manufactured by Wacker: nominally undoped Si which is in fact a high resistivity (> 7000 Ω cm) N-type crystal, N-type Si with a resistivity of about 60 cm and P-type Si with a resistivity of about

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100 Ω cm. The dopant concentrations in the N-type and P-type samples are lower than $1 \times 10^{14}\,\mathrm{cm}^{-3}$ while oxygen and carbon impurities concentrations are lower than 1×10^{16} and $2 \times 10^{16}\,\mathrm{cm}^{-3}$, respectively. These are two orders of magnitude lower than the divacancy concentration in irradiated sample as measured by Fourier transform infrared absorption (FTIR).

High energy proton bombardment of silicon is used to create vacancies in the crystalline structure by displacing atoms. Vacancies have a high diffusivity at room temperature and can coalesce into divacancies [7]. To limit emitted radiation during and after the experiment, early bombardments were made with 3.5 MeV protons and the samples were thinned by mechanical polishing to 100 μm using SiC grinding disks to allow the protons to go through them. Reproducibility was difficult to obtain by this method and the thinning process was abandonned. We now rather use 8 MeV protons which have sufficient energy to go through 300 μm of Si while losing approximately 3.5 MeV in the sample. Samples are irradiated to a fluence of $5 \times 10^{16}\,\mathrm{ion/cm}^2$ with a beam current below 750 nA rastered over an area of $9\,\mathrm{cm}^2$, thus keeping the areal power density below $0.3\,\mathrm{W/cm}^2$. Furthermore, the samples are kept at liquid nitrogen temperature (77 K) during bombardment to avoid dynamical annealing of vacancies. After bombardment the samples are allowed to warm to room temperature and cut in pieces of approximately $5 \times 5\,\mathrm{mm}^2$.

The irradiation damage was characterized with a Bomem DA3 Fourier transform infrared spectrometer with a CaF_2 beamsplitter and liquid-nitrogen-cooled MCT detector. A broad absorption peak around 1.8 μm associated with the divacancy [1,4] was observed in all irradiated samples. The absorbance (αd) of the 1.8 μm band, defined as the logarithm of the ratio of the sample intensity and of a reference intensity of an unirradiated sample measured under identical conditions, can be related to the areal density of divacancies (N_{vv}) in our sample using the criterion developed by Stein and co-workers [4] by the equation $N_{\mathrm{vv}} = (\alpha d)7.7 \times 10^{16}$ divacancies/cm^2.

The heat released during annealing of the radiation damage was monitored with a Perkin-Elmer DSC7 differential scanning calorimeter flushed with dry argon gas [8,9]. Two or three pieces of bombarded Si were stacked together in the sample pan of the DSC while the same number of unirradiated Si were loaded in the reference pan. Three identical scans from 20°C to 400°C at a rate of 40°C/min were made for each measurement, preceded and followed by an isotherm of several minutes to allow the calorimeter to stabilize. The difference between the first and second scan represents the heat released by defect annealing in the sample, while the third scan allowed us to ensure that the baseline remained constant between consecutive scans.

3. Results and discussion

Fig. 1 presents a DSC scan of two irradiated samples at a rate of 40°C/min. Two peaks are clearly observable, one at 140°C and the other at 240°C, thus identifying two distinct annealing mechanisms for divacancies in c-Si. Assuming first order kinetics and a constant prefactor of 15 THz, a typical phonon frequency in silicon, the activation energies of these processes are found to be approximately 1.2 and 1.5 eV. The positions of the peaks varies with scanning rate but the calculated activation energies remain constant. The values of these activation energies are bound to change depending on the validity of our assumptions which remain to be checked through isothermal annealing. Nevertheless, the activation energy of 1.2 eV agrees closely with values obtained from neutron and electron irradiation of silicon and is associated with the onset of divacancy migration [1,10]. The second mechanism remains to be identified, however it could be due to divacancy dissociation. The heat released may be integrated to yield the evolution of the divacancy concentration as shown in Fig. 2. Of course, by doing so we assume that the heat released is only due to divacancies, and that there is no contributions from simultaneoulsy annealing interstitials, for example.

The divacancy concentration in ion irradiated samples, as measured by FTIR, is approximately $10^{18}\,\mathrm{cm}^{-3}$, while it was about $10^{15}\,\mathrm{cm}^{-3}$ for electron irradiated Si with similar fluences [5]. Fig. 2 shows the fraction of remaining divacancies as measured by FTIR and calculated from the DSC curve from Fig. 1. The samples in the first set (open symbols) were thinned to 100 μm

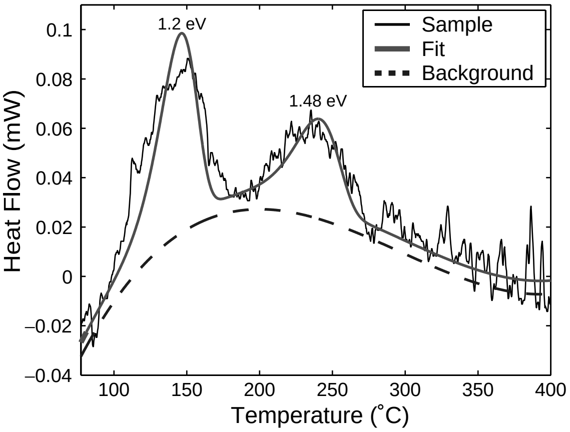

Fig. 1. DSC scan of two irradiated samples at a rate of 40°C/min. Two peaks are clearly observable, one at 140°C and the other at 240°C. Activation energies of 1.2 and 1.5 eV for the two processes respectively are obtained by fitting the peaks using first order kinetics and a constant prefactor of 15 THz.

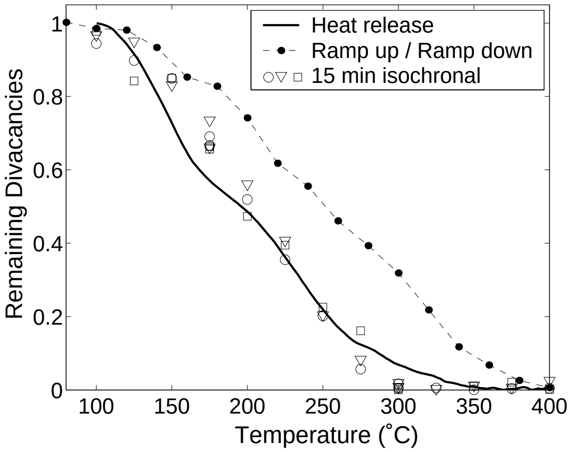

Fig. 2. Remaining fraction of divacancies as measured by FTIR and calculated from the DSC curve from Fig. 1. (A) Open symbols: 100 μm samples bombarded with 3.5 MeV protons annealed 15 min at the indicated temperature. (B) Solid circles: 300 μm samples bombarded with 8 MeV protons scanned from 20°C to the temperature *T* and back at a rate of 80°C/min. The dotted line is only a guide for the eye. (C) Solid line: remaining fraction of divacancies calculated by integrating the DSC curve in Fig. 1, assuming that the heat released is entirely due to divancy annihilation.

and bombarded with 3.5 MeV protons before being annealed 15 min at the indicated temperature. No discernable difference between the three types of silicon can be observed. This either indicate that dopants concentration ($<10^{14}\,\mathrm{cm}^{-3}$) is too low to have an influence on the annealing mechanism or that they do not play a significant role in divacancy annihilation behaviour. This curve is comparable to the annihilation curve of neutron damage in silicon [10] even though defect concentrations were several orders of magnitudes higher in this study.

For the second set of data (filled circles), the samples were scanned in temperature from 20°C to the temperature *T* and immediately cooled at a rate of 80°C/min. The sample therefore received an equivalent thermal treatment and the results could then be directly compared to the third set of data (solid line) calculated by integrating the DSC curve in Fig. 1. If the heat released during annealing is entirely due to divacancies and if the 80°C/min scan and DSC are equivalent, the second and third data set would coincide. Since they do not, either the kinetics are different or another process is emitting heat in the irradiated samples. This heat release could be associated with the background shown by the dotted line in Fig. 1 and must be related to annihilation of defects not visible by FTIR.

4. Conclusions

DSC measurements clearly show two distinct peaks in the heat released during annealing of proton irradiated silicon. The activation energies of these peaks were calculated assuming first order kinetics and found to be approximately 1.2 and 1.5 eV. The remaining fraction of divacancies with respect to annealing temperature was measured by FTIR and compared to the remaining fraction of defects calculated from the heat released in DSC. This comparison appears to indicate that the heat released during annealing is in part due to defects other than the divacancy. Our annealing measurements are in agreement with previous work on electron and neutron irradiation of Si in spite of much higher defect concentrations.

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