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Divacancies in proton irradiated silicon: variation of ESR signal with annealing time

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Abstract

Annealing of divacancies in 8 MeV proton-irradiated silicon was investigated using electron paramagnetic resonance (EPR). This paper presents the results for annealing at 160°C for up to 600 min and for one sample annealed at 250°C. The EPR signal shows a clear evolution with annealing time for annealing at 160°C. Annealing for 40 min at 250°C, yields almost the same EPR signal as for a 600 min anneal at 160°C, but with a lowered intensity. In the light of previous results, the EPR behaviour substantiate the presence of two distinct annealing stages for defects in proton-irradiated silicon.

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Keywords: Divacancies; Annealing; Positron annihilation; Electron spin resonance

1. Introduction

Electron paramagnetic resonance (EPR) is amongst the first experimental techniques used to study radiation damage in silicon, and in particular was essential in the identification of the divacancy in silicon and in determination of its structure [1]. The comparison of EPR with Fourier transform infrared spectroscopy (FTIR) has led to the association of the 1.8 μm absorption band with the divacancy [2]. Since most techniques are only sensitive to specific charge states of the defects, only a conjunction of those techniques can lead to a complete picture of the divacancy in irradiated silicon. In view of the foregoing, it was attempted in previous work [3–5], to gain a better understanding of the annealing mechanisms of divacancies produced in crystalline silicon by proton irradiation, using differential scanning calorimetry (DSC), infrared spectroscopy (FTIR) and positron annihilation spectroscopy (PAS), on samples having the same thermal history. These studies have identified three different annealing stages for the divacancy in proton-irradiated silicon.

A first stage, around 150°C, corresponding to the recombination of divacancies with migrating interstitial defects (activation energy of ~1.0 eV). A second stage at higher temperature (~250°C), due to divacancy migration (activation energy of

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$\sim$1.2 eV) and association in chain-like defects. And finally, a third stage occurring at 500°C, where string-like vacancies agglomerate into large 3D vacancy clusters.

In this paper, we present the first EPR results for our samples. EPR measurements are required for a direct comparison between defects created in proton irradiated Si, and most of the early studies on electron irradiated Si. Moreover, precise determination of the absolute number of divacancies in irradiated samples, can only be done with EPR, since FTIR and PAS both rely on this technique for calibration [6,7]. Our hope is to further understand the annealing mechanisms of divacancies in proton irradiated silicon, and eventually measure the amount of energy released by each divacancy.

2. Experiment

High purity n-type $\langle 1\,1\,1 \rangle$ float-zone silicon wafers, with a resistivity greater than 7000 Ω cm and a thickness of 300 μm, were irradiated with 8 MeV protons in a 6 MV Tandem accelerator, to a fluence of $\sim 4 \times 10^{16}$ ions/cm^2. The samples were irradiated at liquid nitrogen temperature to avoid dynamical annealing of the defects during irradiation. The beam current was $\sim$750 nA, rastered over an area of 9 cm^2. A Monte Carlo simulation of the irradiation process estimates that 27 vacancies are created for each incoming ion. After irradiation, the samples were allowed to warm-up to 300 K, at which temperature about 1% of the vacancies created during irradiation agglomerate into divacancies. The expected divacancy concentration in the sample, after irradiation and warm-up, is therefore of the order of 10^{18} divacancies/cm^3 (20 ppm).

Annealing of the irradiated samples was performed in a Perkin-Elmer DSC7 calorimeter, used as a programmable furnace, to insure that every sample had the same thermal history. The samples were heated from 20°C to the annealing temperature, at a rate of 500°C/min. The annealing time quoted in the following figures relates to the time the sample spent at the annealing temperature, and does not include heating/cooling time.

The EPR signal was recorded in a Bruker ER 200 D-SRC spectrometer with an ER 301M Field Controller in a TE104 double rectangular cavity using a frequency of $\sim$9.60 GHz (X-band) and a field ranging from 3000 to 4000 G. The samples were mounted such that the $\langle 1\,1\,1 \rangle$ orientation, normal to the sample's surface, was parallel to $\pm 1°$ to the magnetic field in the cavity. The spectra were acquired in the dark with no illumination of the samples at a temperature of 10 K in a continuous flow crysostat ESR9 from Oxford Instruments.

3. Results

The main differences between this set of samples and most of the early EPR studies of radiation induced defects in silicon [1,8] are: (1) the crystallographic orientation of the samples is $\langle 1\,1\,1 \rangle$ instead of $\langle 1\,0\,0 \rangle$ or $\langle 1\,1\,0 \rangle$; (2) The samples were irradiated with high doses of high energy protons, which have enough energy to create damage cascades involving several primary and secondary recoiling atoms. Interstitial clusters are surely more important in these samples than in the electron irradiated samples.

Fig. 1 shows the evolution of EPR signal with annealing time at 160°C up to 600 min as well as one sample annealed at 250°C for 40 min. All spectra were collected with the same sample orientation and temperature. The foremost feature of this set of data is the disappearance of a resonance peak (labelled A) at a g factor of 2.017, while another peak (labelled B) at 2.011 is increasing in intensity, as the annealing time at 160°C is increased.

A comparison of the intensity of these two peaks with respect to the annealing time is presented in Fig. 2. The absolute number of spins was measured by comparing the intensity of the resonance peak to the intensity of a reference sample made of polycrystalline silicon doped with 4×10^{15} phosphorus atoms in polyethylene, 0.6 mm thick. The fairly low number of resonating spins, compared to the expected number of defects in the sample, is due to the fact that the EPR spectra were acquired in the dark, and that most

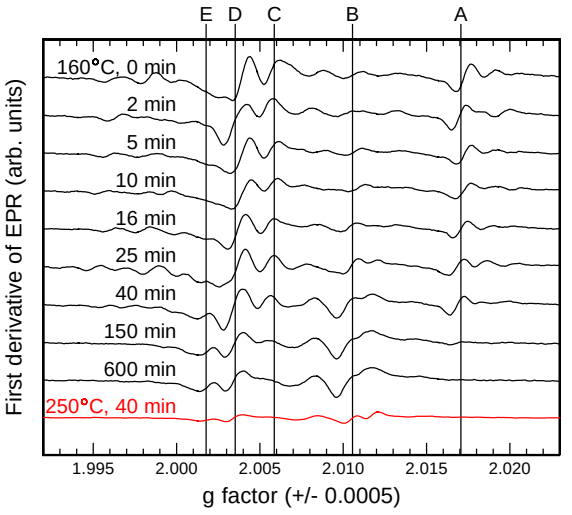

Fig. 1. EPR spectra of irradiated samples annealed at 160°C and 250°C. The signal shows a clear evolution with increasing annealing time at 160°C up to 600 min. Labels A–E, indicate the position of principal resonance peaks. Note the resonance at 2.017 (A) disappearance while correspondingly a resonance at 2.011 (B) is increasing in intensity. Peak C at $g = 2.002$ has the same behaviour as resonance A and most probably comes from the same centre. Intensity of peak D decreases with no discernable trend, and peak E appears after 25 min and increases slightly afterward.

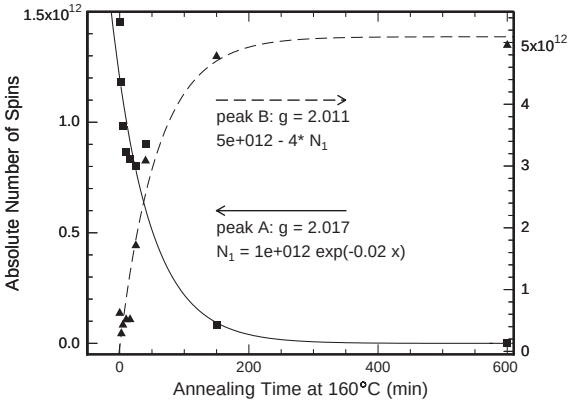

Fig. 2. Intensity (in absolute number of spins) with respect to annealing time (in minutes) at 160°C for the peaks A at $g = 2.011$ (left scale) and B at $g = 2.017$ (right scale). Resonance A decreases with an exponential trend, while resonance B increases with the same exponential behaviour but with a factor of 4 in the intensity.

defects were diamagnetic as neutral divacancies. This fact is corroborated, by positron measurements [4,5] showing that a very small fraction of the divacancies are negatively charged at low temperature in the dark. The intensity of peak A decreases with an exponential trend of $1 \times 10^{12} \exp(-0.02t)$, where t is the annealing time in minutes. Correspondingly, the intensity of peak B increases with the same exponential trend, but approximately 4 (± 0.5) times faster. This last peak (B) is most likely the Si–P1 spectrum identified as a dominant paramagnetic centre in ion irradiated silicon [8]. This P1 spectrum was observed to appear at $g = 2.011$ for the $\langle 1\,1\,1 \rangle$ orientation after 170°C annealing, and was modeled in the aforementioned article to be a five-vacancy cluster. However, positron annihilation measurements [4,5] taken on our samples, do not show any increase in positron lifetime below 500°C, which would indicate the presence of larger vacancy clusters such as the pentavacancy.

Resonance peak C identified in Fig. 1, follows very closely the behaviour of resonance peak A discussed previously. Both are thus most likely to arise from the same defect centre. Although peak D shows a tendency to decrease with annealing time, and peak E appears after 25–40 min annealing and increases slightly in intensity, their behaviour could not be established as accurately as for the other peaks.

Fig. 3 shows the comparison of the EPR signal of a sample annealed at 160°C for 600 min and another sample annealed at 250°C for 40 min. Both signals are very similar, but for one peak at $g = 2.012$ that is significantly larger after the 250°C anneal. The intensity ratio between the two signals is a factor of 3.5 ± 0.5. We may compare this EPR intensity decrease with the ratio of remaining divacancy concentration between the two samples. This was obtained by measuring the 1.8 μm FTIR absorption for both samples, before and after their respective anneal. This concentration ratio yields a factor of 4.3 ± 0.2. The discrepancy in the reduction of signal intensity for EPR and FTIR, can be due to either that the EPR signal is not due to the divacancy, or that negatively charged vacancies (observed with EPR) do not anneal as quickly as neutral ones (observed with FTIR) during the first

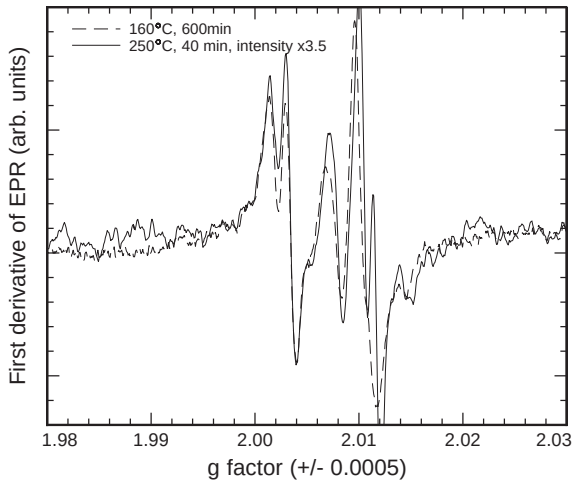

Fig. 3. Comparison of the EPR signals for samples annealed at 160°C for 600 min (dashed line) and 250°C for 40 min (solid line). The intensity of the 250°C signal was multiplied by a factor of 3.5 to help the comparison of both spectra. The signals are very similar, despite the increase in intensity of a single resonance peak at $g = 2.012$ in the 250°C signal.

stage of the anneal. Another fact to consider is that as defects anneal in the sample, the Fermi level position can change in the silicon band gap, resulting in a change in the charge state population distribution of the defects.

4. Conclusions

The EPR signal defects produced with 8 MeV proton irradiation of silicon, shows a clear evolution in the first 600 min of annealing at 160°C. Annealing of a sample to 250°C for 40 min, essentially leads to the same signal with a lowered intensity. This substantiate the presence of a first defect annealing stage at temperatures around 160°C, before complete annealing of the divacancies, and that differs significantly from annealing at higher temperatures ($\sim$250°C).

Of course further EPR spectra, including angular dependant measurements and illumination of the samples, are necessary in order to associate the different resonance peaks with specific defects. This identification is necessary before any more conclusions can be reached regarding the comparison of EPR results with FTIR and PAS in proton irradiated Si.

Nevertheless, the results presented here show that direct comparison of EPR data with other spectroscopic techniques such as FTIR and PAS, on the same samples, is necessary to gain a complete picture of divacancy annealing behaviour in ion implanted silicon.

Acknowledgements

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