ELSEVIER

Available online at www.sciencedirect.com
SCIENCE DIRECT®

Nuclear Instruments and Methods in Physics Research B 206 (2003) 85–89

NIM B
Beam Interactions with Materials & Atoms

www.elsevier.com/locate/nimb

Divacancies in proton irradiated silicon: Comparison of annealing mechanisms studied with infrared spectroscopy and positron annihilation

R. Poirier [a,*], V. Avalos [b], S. Dannefaer [b], F. Schiettekatte [a], S. Roorda [a]

[a] *Groupe de Recherche en Physique et Technologie des Couches Minces, Département de Physique, Université de Montréal, C.P. 6128 Succ. Centre-Ville, Montréal, Que., Canada H3C 3J7*

[b] *Physics Department, University of Winnipeg, 515 Portage Avenue, Winnipeg, Man., Canada R3B 2E9*

Abstract

Defects produced in 8 MeV proton irradiated silicon were studied using Fourier transform infrared spectroscopy (FTIR) and positron annihilation measurements (PAS). Isothermal annealing of the divacancy absorption band monitored using FTIR, has been compared with PAS on similar samples. The two methods agree perfectly during isothermal annealing at 150 °C, but at 250 °C the 1.8 μm absorption band disappears after annealing for 60 min, whereas positron lifetime and trapping rate remain constant, and annealing to 500 °C is required to remove the divacancy response. Since divacancies are not mobile at 150 °C their annealing can be ascribed to recombination with mobile interstitials. The discrepancy observed during annealing at 250 °C is suggested to be a consequence of some sort of divacancy agglomeration.
© 2003 Elsevier Science B.V. All rights reserved.

PACS: 61.72.Cc; 61.72.Ji; 61.80.Jh
Keywords: Silicon; Defects; Divacancy; Ion implantation; Infrared absorption; Positron annihilation

1. Introduction

Electron paramagnetic resonance (EPR) has identified the divacancy in electron irradiated silicon [1]. That led to the association of the 1.8 μm absorption band with the divacancy [2]. There is still doubt however as to the charge state that gives rise to this band [2–5]. None of the EPR or IR based data give a clue to how the divacancy disappears. Sinks of unknown nature were suggested [6], but no evidence of such sinks was reported.

DSC measurements reported in a previous article [7], clearly show two peaks in the heat released during a 40 °C/min temperature scan, one at 140 °C and the other at 240 °C. This suggests the presence of at least two distinct annealing mechanisms for divacancies in c-Si. These peaks had been fitted using first order kinetics to evaluate their activation energy and were found to be 1.2 and 1.5 eV, respectively. However, isothermal annealing of irradiated samples at temperature ranging from 100 to 300 °C monitored using the

* Corresponding author. Fax: +1-514-343-6215.
E-mail address: remi@poirier.com (R. Poirier).

0168-583X/03/$ - see front matter © 2003 Elsevier Science B.V. All rights reserved.
doi:10.1016/S0168-583X(03)00686-4

1.8 μm absorption band are not consistent with such a simple process. Evidently this situation demanded further investigation, therefore IR absorption and positron annihilation studies of these samples were undertaken in order to identify these mechanisms. Since both methods yield the same results for isothermal annealing of defects at 150 °C, they present unexplained discrepancies for annealing at 250 °C. In order to tentatively explain these discrepancies, it is suggested that the divacancies disappear by two mechanisms, one at 150 °C related to the diffusion of self-interstitials created during irradiation and the other at 250 °C by divacancy agglomeration, which of course entails migration of divacancies.

2. Experiment

High purity n-type $\langle 111 \rangle$ Float-zone silicon wafers with a resistivity greater than 7000 Ωcm and a thickness of 300 μm were irradiated with 8 MeV protons in a Tandem Van de Graaf 6 MV accelerator to a fluence of $\approx 5 \times 10^{16}$ ions/cm^2. Protons of such energies penetrate the wafer, creating vacancies through atomic collisions without leaving residual hydrogen in the silicon crystal. The protons lose $\approx$3.5 MeV in electronic and atomic collisions in the crystal and to avoid dynamical annealing of the vacancies during irradiation, the samples were maintained at liquid nitrogen temperature (77 K). After irradiation, the wafers were heated to room temperature (RT), at which vacancies in silicon are mobile and diffuse through the crystal to form divacancies.

The broad 1.8 μm infrared absorption band, observed in all irradiated samples and presumably associated with neutral divacancies [2,8] was monitored using a Fourier transform infrared spectrometer equipped with a CaF_2 beamsplitter, a liquid nitrogen cooled mercury–cadmium–tellurium detector and a tungsten–halogen lamp as a light source. Absorbance of the irradiated samples at 1.8 μm was measured by comparing the absorption spectra of an irradiated sample to an unirradiated reference sample. Using the calibration developed by Stein et al. [8], the divacancy concentration is evaluated from these measurements to be of the order of 10^{18} cm^{-3}, much larger than the oxygen, carbon and phosphorous impurity concentrations (1×10^{16}, 2×10^{16} and 6×10^{12} cm^{-3}, respectively) in this type of silicon.

Annealing of the irradiated samples was performed using a Perkin–Elmer DSC7 calorimeter used as a programmable furnace. For these annealings, the samples were heated from 20 °C to the annealing temperature at a rate of 500 °C/min for anneals at 140 and 160 °C and 200 °C/min for the other annealing temperatures. Sample preparation and FTIR analysis methods were described in greater detail in [7]. Positron annihilation measurements were performed at the University of Winnipeg using a ^{22}Na source sandwiched between two similar samples.

3. Results and discussion

Fig. 1 shows the comparison between IR absorption at 1.8 μm (a), the positron lifetime (b) and associated positron trapping rate (c) for isothermal annealing at 150 °C. The positron lifetime is related to the type of defect present in the sample, a higher lifetime being an indication of larger vacancy-type defects. The trapping rate on the other hand is an indication of the concentration of defects in the sample [9]. The positron lifetime of 280 ps is compatible with the presence of divacancies even though it is somewhat shorter than that in electron irradiated materials (310 ps) [10]. This lifetime component remains constant and indicates that the divacancies do not undergo structural changes during annealing at this temperature. Both the trapping rate associated with this lifetime component and the intensity of the IR absorption band decrease with increasing annealing time by 54%. Since the divacancy is not yet mobile at this temperature, this annealing must be the result of interstitial diffusion. Interstitials "evaporating" from clusters diffuse through the crystal and recombine with a vacancy in a divacancy or form stable complexes with other wandering interstitials or already existing stable interstitial clusters. Thus the 54% decrease in divacancy concentration is only the balance between these processes. No discrepancy between IR

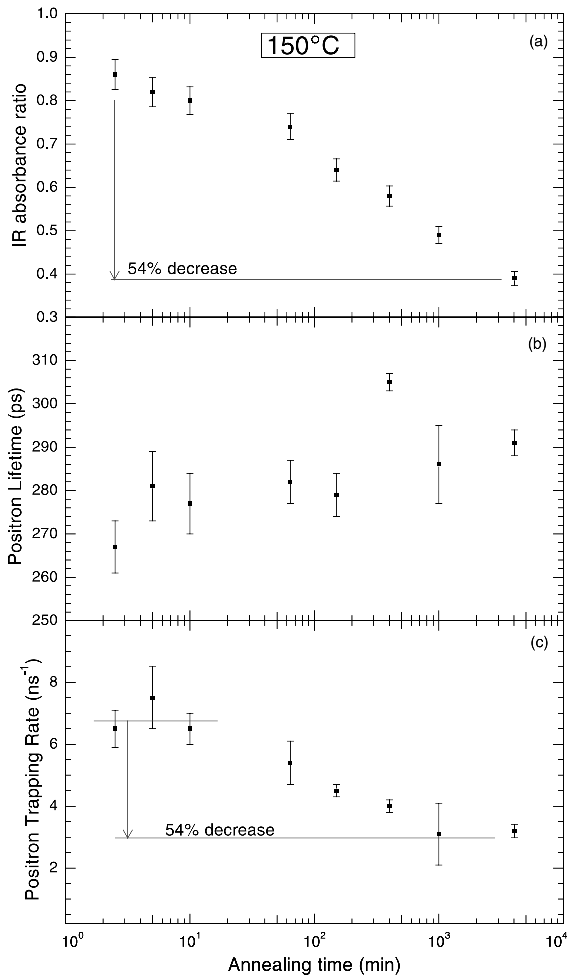

Fig. 1. Isothermal annealing at 150 °C. The data from both methods agree closely. Both IR absorbance at 1.8 μm (a) and trapping rate of positrons (c) decrease by 54%. The positron lifetime (b) of ≈280 ps is consistent with the presence of divacancies and remains constant throughout the annealing stage.

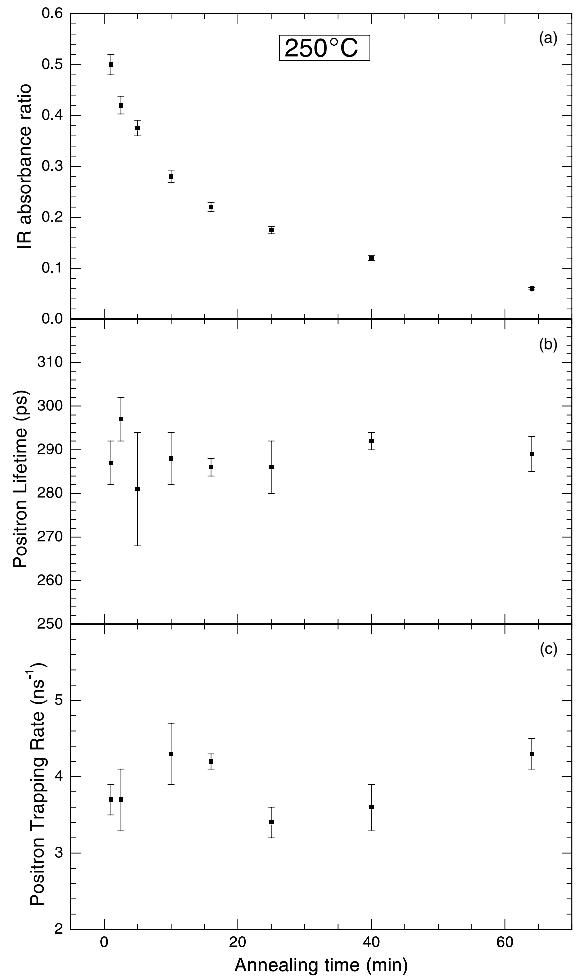

Fig. 2. Isothermal annealing at 250 °C. IR data (a) show a complete disappearance of the 1.8 μm absorption line after isothermal annealing for about 60 min, while positron lifetime (b) and trapping rate (c) remain constant no matter how long the annealing, suggesting that the divacancy concentration remains constant in the sample.

and PAS is expected from this annealing mechanism.

Fig. 2 shows again the comparison between IR absorption at 1.8 μm (a), the positron lifetime (b) and associated positron trapping rate (c), but this time for isothermal annealing at 250 °C. FTIR presents a rapid decrease of the 1.8 μm absorption band intensity, reaching zero in a little more than an hour. On the other hand, positron lifetime as well as trapping rate remain constant no matter how long the annealing time and despite the fact that the IR signal has completely disappeared.

Fig. 3 presents isochronal annealing of the defects above 250 °C. The positron lifetime (a) indicate that a temperature of 500 °C was necessary to remove the divacancy signal. The dramatic increase in lifetime after 500 °C indicates a clustering into defects consisting of more than two vacancies.The decrease in positron trapping rate (b) indicate that the concentration of divacancy-type

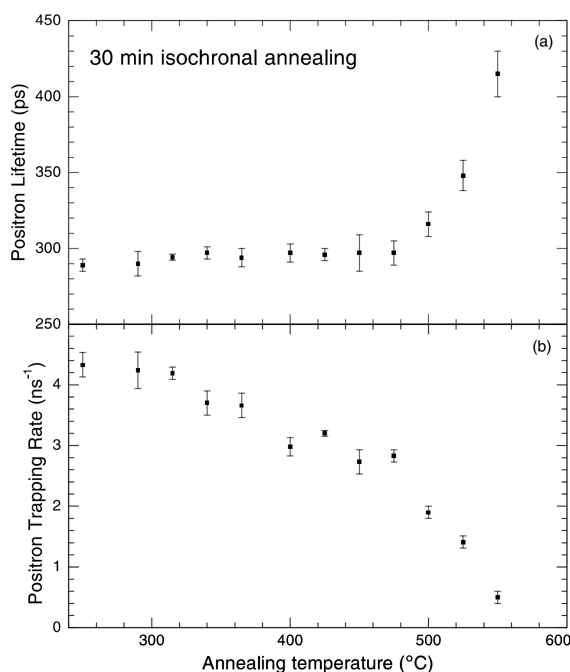

Fig. 3. Thirty minutes isochronal anneals above 250 °C. The increase in positron lifetime (a) above 500 °C indicates the formation of larger vacancy-type defects while the trapping rate (b) decreases to zero.

defects is rapidly decreasing, having annealed completely after 30 min at 575 °C.

The IR isothermal annealing data for temperatures of 250 °C and lower cannot be fitted using neither first nor second order kinetics, probably since more than one annealing mechanisms are at play simultaneously at those temperatures. The annealing of the divacancy 1.8 μm absorption band data for 275 and 300 °C can be fitted using a bimolecular mechanism $(N/N_0 = 1/(1 + \tau t))$, where N/N_0 is the remaining fraction of divacancies as measured by FTIR, τ the 2nd order annealing parameter and t the annealing time. If the annealing parameters for this 2nd order annealing follow Arrhenius law, they are consistent with an activation energy of 1.2 eV which was previously associated with the onset of divacancy migration [2,6,11].

FTIR data at temperatures around 250 °C seem to indicate that the divacancies are mobile in the crystal. If it is indeed so, they could loosely associate with one another, without yet forming larger defects. The electronic structure of the defects would be perturbed, thus removing the 1.8 μm absorption band. This perturbation does not have a significant effect on positrons which continue to monitor the presence of divacancies in the crystal. Only at temperatures higher than 500 °C can the associated divacancies agglomerate into larger defects.

4. Conclusion

IR absorption and positron annihilation measurements are in complete agreement for isothermal annealing at temperatures around 150 °C. It is suggested since divacancies are not yet mobile, that interstitals are responsible for this annealing stage. For higher temperatures annealing however, the 1.8 μm IR absorption band disappears while the positron response remains constant indicating the presence of divacancies up to 500 °C. This discrepancy is tentatively explained using a model where the divacancies are becoming mobile and loosely associating with each other.

Further measurements such as EPR and low-temperature measurements of the 3.6 μm IR absorption band associated with the singly negatively charged divacancy [4] are necessary to investigate the possibillity that the discrepancy between IR and positron annihilation results may be due to a change in the charge state of the divacancy.

Acknowledgements

Many thanks to Réal Gosselin and Louis Godbout for their help with the accelerator, Marc Lalancette and Janik Zikovsky for their help in acquiring some of the FTIR data. This work was made possible by grants from the Natural Sciences and Engineering Research Council of Canada (NSERC) and Le Fond pour la Formation de Chercheurs et l'Aide à la Recherche du Québec (FCAR).

References

[1] G.D. Watkins, J.W. Corbett, Phys. Rev. 138 (1965) A543.
[2] L.J. Cheng, J.C. Corelli, J.W. Corbett, G.D. Watkins, Phys. Rev. 152 (1966) 761.
[3] L.J. Cheng, P. Vajda, Phys. Rev. 186 (1969) 816.
[4] F. Carton-Merlet, B. Pajot, P. Vajda, J. Phys. Lett. 39 (1978) L113.
[5] J.-H. Svensson, B.G. Svensson, B. Monemar, Phys. Rev. B 38 (1988) 4192.
[6] P. Pellegrino, P. Lévêque, J. Lalita, A. Hallén, C. Jagadish, B.G. Svensson, Phys. Rev. B 64 (2001).
[7] R. Poirier, S. Roorda, F. Schiettekatte, M. Lalancette, J. Zikovsky, Physica B 308–310 (2001) 462.
[8] H.J. Stein, F.L. Vook, D.K. Brice, J.A. Borders, S.T. Picraux, Radiat. Eff. 6 (1970) 19.
[9] R. Krause-Rehberg, H.S. Leipner, Positron annihilation in semiconductors: Defect studies, Springer Series in Solid-state Sciences, Berlin, 1999.
[10] A. Polity, F. Börner, S. Huth, S. Eichler, R. Krause-Rehberg, Phys. Rev. B 58 (1998) 10363.
[11] L.J. Cheng, J. Lori, Phys. Rev. 171 (1968) 856.