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

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### 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.

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### 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 gives a clue to how the divacancy dis-

appears. 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

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42 1.8  $\mu\text{m}$  absorption band are not consistent with  
 43 such a simple process. Evidently this situation  
 44 demanded further investigation, therefore IR ab-  
 45 sorption and positron annihilation studies of these  
 46 samples were undertaken in order to identify these  
 47 mechanisms. If both methods yield the same re-  
 48 sults for isothermal annealing of defects at 150  $^{\circ}\text{C}$ ,  
 49 they present unexplained discrepancies for an-  
 50 nealing at 250  $^{\circ}\text{C}$ . In order to tentatively explain  
 51 these discrepancies, it is suggested that the diva-  
 52 cancies disappear by two mechanisms, one at 150  
 53  $^{\circ}\text{C}$  related to the diffusion of self-interstitials cre-  
 54 ated during irradiation and the other at 250  $^{\circ}\text{C}$  by  
 55 divacancy agglomeration, which of course entails  
 56 migration of divacancies.

## 57 2. Experiment

58 High purity n-type  $\langle 111 \rangle$  Float-zone silicon  
 59 wafers with a resistivity greater than 7000  $\Omega\text{cm}$   
 60 and a thickness of 300  $\mu\text{m}$  were irradiated with 8  
 61 MeV protons in a Tandem Van de Graaf 6 MV  
 62 accelerator to a fluence of  $\approx 5 \times 10^{16}$  ions/ $\text{cm}^2$ .  
 63 Protons of such energies penetrate the wafer, cre-  
 64 ating vacancies through atomic collisions without  
 65 leaving residual hydrogen in the silicon crystal.  
 66 The protons lose  $\approx 3.5$  MeV in electronic and  
 67 atomic collisions in the crystal and to avoid dy-  
 68 namical annealing of the vacancies during irradi-  
 69 ation, the samples were maintained at liquid  
 70 nitrogen temperature (77 K). After irradiation, the  
 71 wafers were heated to room temperature (RT), at  
 72 which vacancies in silicon are mobile and diffuse  
 73 through the crystal to form divacancies.

74 The broad 1.8  $\mu\text{m}$  infrared absorption band,  
 75 observed in all irradiated samples and presumably  
 76 associated with neutral divacancies [2,8] was  
 77 monitored using a Fourier transform infrared  
 78 spectrometer equipped with a  $\text{CaF}_2$  beamsplitter, a  
 79 liquid nitrogen cooled mercury–cadmium–telluri-  
 80 um detector and a tungsten–halogen lamp as a  
 81 light source. Absorbance of the irradiated samples  
 82 at 1.8  $\mu\text{m}$  was measured by comparing the ab-  
 83 sorption spectra of an irradiated sample to an  
 84 unirradiated reference sample. Using the criterion  
 85 developed by Stein et al. [8], the divacancy con-  
 86 centration is evaluated from these measurements

to be of the order of  $10^{18}$   $\text{cm}^{-3}$ , much larger than  
 the oxygen, carbon and phosphorous impurity  
 concentrations ( $1 \times 10^{16}$ ,  $2 \times 10^{16}$  and  $6 \times 10^{12}$   
 $\text{cm}^{-3}$ , respectively) in this type of silicon.

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

## 3. Results and discussion

Fig. 1 shows the comparison between IR ab-  
 sorption at 1.8  $\mu\text{m}$  (a), the positron lifetime (b) and  
 associated positron trapping rate (c) for defects  
 isothermal annealing at 150  $^{\circ}\text{C}$ . 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 concentra-  
 tion 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 tem-  
 perature. Both the trapping rate associated with  
 this lifetime component and the intensity of the IR  
 absorption band decrease with increasing anneal-  
 ing 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 diva-  
 cancy or form stable complexes with other wan-  
 dering interstitials or already existing stable  
 interstitial clusters. Thus the 54% decrease in di-  
 vacancy concentration is only the balance between

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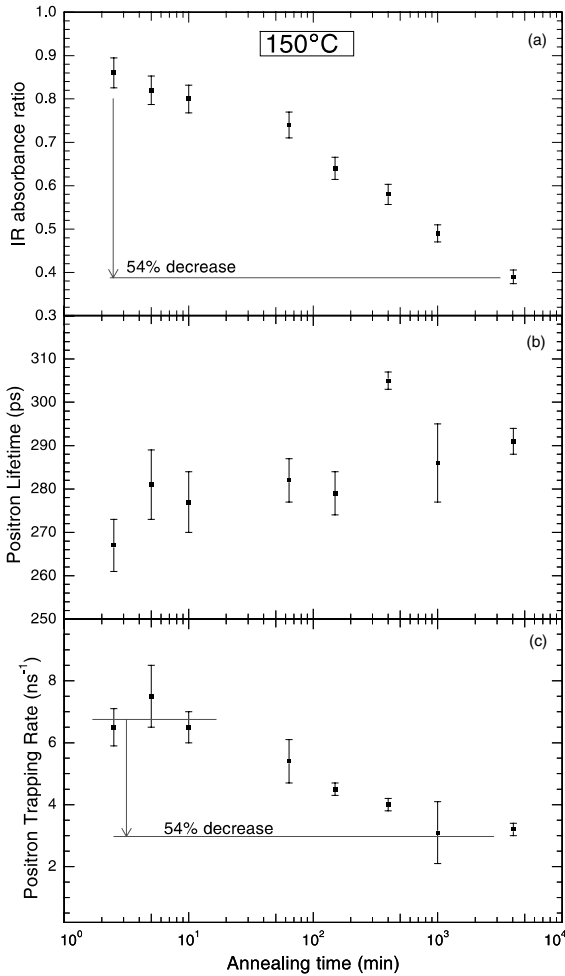


Fig. 1. Isothermal annealing at 150 °C. The data from both methods agree closely. Both IR absorbance at 1.8  $\mu\text{m}$  (a) and trapping rate of positrons (c) decrease by 54%. The positron lifetime (b) of  $\approx 280$  ps is consistent with the presence of divacancies and remains constant throughout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

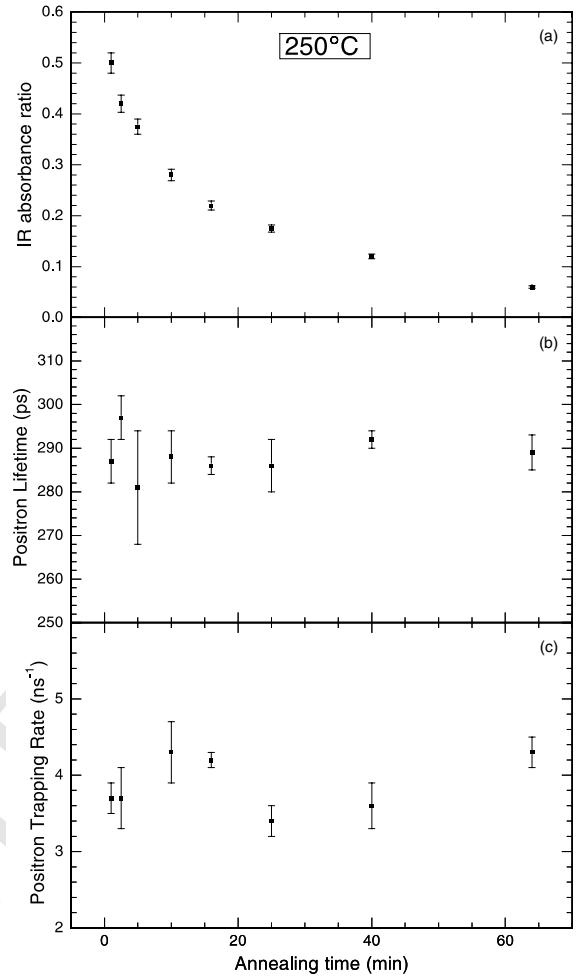


Fig. 2. Isothermal annealing at 250 °C. IR data (a) show a complete disappearance of the 1.8  $\mu\text{m}$  absorption line after isothermal annealing for about 60 min, while positron lifetime (b) and trapping rate (c) remain constant no matter how long the annealing, suggesting that the divacancy concentration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

131 these processes. No discrepancy between IR and  
132 PAS is expected from this annealing mechanism.

133 Fig. 2 shows again the comparison between IR  
134 absorption at 1.8  $\mu\text{m}$  (a), the positron lifetime (b)  
135 and associated positron trapping rate (c), but this  
136 time for isothermal annealing at 250 °C. FTIR  
137 presents a rapid decrease of the 1.8  $\mu\text{m}$  absorption  
138 band intensity, reaching zero in a little more than  
139 an hour. On the other hand, positrons lifetime as  
140 well as trapping rate remain constant no matter

141 how long the annealing time and despite the fact  
142 that the IR signal has completely disappeared.

143 Fig. 3 presents isochronal annealing of the de-  
144 fects above 250 °C. The positron lifetime (a) in-  
145 dicate that a temperature of 500 °C was necessary  
146 to remove the divacancy signal. The dramatic in-  
147 crease in lifetime after 500 °C indicates a clustering  
148 into defects consisting of more than two vacan-  
149 cies. The decrease in positron trapping rate (b) in-  
150 dicate that the concentration of divacancy-type

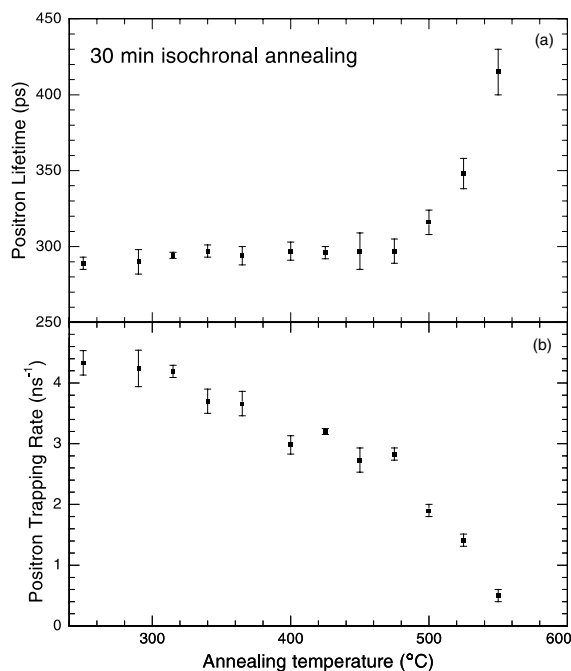


Fig. 3. Thirty minutes isochronal anneals above 250 °C. The increase in positron lifetime (a) above 500 °C indicates the formation of larger vacancy-type defects while the trapping rate (b) decreases to zero.

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

153 The IR isothermal annealing data for tempera-  
154 tures of 250 °C and lower cannot be fitted using  
155 neither first nor second order kinetics, probably  
156 since more than one annealing mechanisms are at  
157 play simultaneously at those temperatures. The  
158 annealing of the divacancy 1.8 μm absorption  
159 band data for 275 and 300 °C can be fitted using a  
160 bimolecular mechanism ( $N/N_0 = 1/(1 + \tau t)$ ),  
161 where  $N/N_0$  is the remaining fraction of divacancies  
162 as measured by FTIR,  $\tau$  the 2nd order anneal-  
163 ing parameter and  $t$  the annealing time. If the  
164 annealing parameters for this 2nd order annealing  
165 follow Arrhenius law, they are consistent with an  
166 activation energy of 1.2 eV which was previously  
167 associated with the onset of divacancy migration  
168 [2,6].

169 FTIR data at temperatures around 250 °C seem  
170 to indicate that the divacancies are mobile in the  
171 crystal. If it is indeed so, they could loosely asso-

ciate with one another, without yet forming larger  
172 defects. The electronic structure of the defects  
173 would be perturbed, thus removing the 1.8 μm  
174 absorption band. This perturbation does not have  
175 a significant effect on positrons which continue to  
176 monitor the presence of divacancies in the crystal.  
177 Only at temperatures higher than 500 °C can the  
178 associated divacancies agglomerate into larger  
179 defects.  
180

#### 4. Conclusion

181

IR absorption and positron annihilation mea-  
182 surements are in complete agreement for isother-  
183 mal annealing at temperatures around 150 °C. It is  
184 suggested since divacancies are not yet mobile,  
185 that interstitials are responsible for this annealing  
186 stage. For higher temperatures annealing however,  
187 the 1.8 μm IR absorption band disappears while  
188 the positron response remains constant indicating  
189 the presence of divacancies up to 500 °C. This  
190 discrepancy is tentatively explained using a model  
191 where the divacancies are becoming mobile and  
192 loosely associating with each other.  
193

Further measurements such as EPR and low-  
194 temperature measurements of the 3.6 μm IR ab-  
195 sorption band associated with the singly negatively  
196 charged divacancy [4] are necessary to investigate  
197 the possibility that the discrepancy between IR  
198 and positron annihilation results may be due to a  
199 change in the charge state of the divacancy.  
200

#### 5. Uncited reference

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[11]

202

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203

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