

Infrared signals correlated with self-interstitial clusters in neutron-irradiated silicon

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Abstract Using infrared spectroscopy we have investigated the defect spectrum of neutron-irradiated Czochralski–silicon (Cz–Si). The study was focused on three weak signals, mainly on a band at 533 cm^{-1} , as well as on two other bands at 582 and 592 cm^{-1} . The band at 533 cm^{-1} disappears from the spectra at $\sim 170\text{ }^\circ\text{C}$ exhibiting similar thermal stability with the Si-P₆ electron paramagnetic resonance spectrum, previously correlated with a di-interstitial defect. The suggested model for the latter defect, comprising two self-interstitials placed symmetrically a lattice site Si atom, is very similar with that of the allene molecule. This allowed the calculation of the vibrational frequency of the suggested di-interstitial structure giving a value close to the 533 cm^{-1} , in further support of the above assignment. The band at 582 cm^{-1} is stable up to $550\text{ }^\circ\text{C}$. The possible correlation of its origin to large self-interstitial clusters is examined. Also, the origin of the 592 cm^{-1} band, which is stable up to $200\text{ }^\circ\text{C}$ is discussed, with indications tentatively pointing to a CV pair.

1 Introduction

The properties of semiconductor materials are affected by the processes induced by the defects in the lattice and their interactions [1–9]. The investigation of small self-interstitial clusters in Si is technologically important. It is required to control them as their formation during material processing can cause detrimental effects. It is important to understand their properties, behaviour and evolution to larger self-interstitial clusters and {311} defects.

The processes involving self-interstitials are not completely understood. For instance, the mechanisms that govern their aggregation to form large clusters have not been definitely established and understood [10–12]. It has been proposed [13] that di-interstitial complexes (I₂) act as “building blocks” which can serve as precursor structures for the {311} defects and larger defect clusters. Interestingly, other reports consider the tri-interstitial (I₃) or/and the tetra-interstitial (I₄) as playing this role [14, 15].

Upon irradiation self-interstitials and vacancies form. The self-interstitials are extremely mobile and those avoiding annihilation by vacancies tend to form pairs, the di-interstitial defects (I₂). This defect has been studied by electron paramagnetic resonance (EPR) and a Si-P₆ EPR signal has been correlated to its structure [16, 17]. The defect is stable up to $\sim 170\text{ }^\circ\text{C}$, where its signal begins to disappear from the spectra. It has been suggested that the defect comprises three Si atoms, one at its lattice site and two interstitials sharing a lattice site. Notably, the model proposed [17] for the structure of the I₂ defect is not consistent with the results of some theoretical calculations [18, 19]. In this respect other structures for the Di-interstitial defect were proposed. The experimental data available in the literature is not adequate to support a structural model among the various ones that have been suggested.

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Additionally, the exact mechanisms governing the migration of the defect, its evolution and its role in the formation of extended defects can not be established [17–25]. Here we present additional experimental evidence by infrared spectroscopy (IR) that the Si-P₆ EPR signal and an IR band at 533 cm⁻¹ may originate from the same di-interstitial defect. Furthermore, semiempirical calculations support the Si-P₆ proposed model for the I₂ structure where two self-interstitial atoms are placed symmetrically with respect to a Si lattice site atom [17].

2 Experimental methodology

Pre-polished silicon samples of 2 mm thickness were used in this study. Their initial oxygen and carbon concentration were [O]_i = 8.7 × 10¹⁷ cm⁻³ and [C]_s = 4 × 10¹⁶ cm⁻³, respectively. The samples were irradiated with 5 MeV neutrons at a dose of 1 × 10¹⁷ n/cm². The temperature of irradiation was T_{irr} ≤ 50 °C. During the irradiation the samples were covered by Cd to avoid the effect of thermal neutrons. Afterwards, 20 min isochronal anneals were carried out, in steps of ΔT ≈ 10 °C. After each annealing step, the IR spectra were recorded at room temperature and the amplitudes of the peaks were monitored up to 600 °C. The two phonon intrinsic absorption was always removed by subtracted the spectrum of a Float-Zone sample of equal thickness. We focused on the spectral range 500–600 cm⁻¹ where some very weak IR peaks were detected. Due to the weakness of the bands under investigation, we recorded the spectra repeatedly. Thereafter, we derived an average spectrum, to obtain the best signal to noise ratio and improve the appearance of the peaks.

3 Results and discussion

Figure 1 shows the IR spectra in the range 500–600 cm⁻¹. The 544 cm⁻¹ band has contributions from the C_iC_s and the C_iO_i defects [26]. We shall focus our study to the 533, 582 and 592 cm⁻¹ bands. Figure 2 shows the thermal evolution of the latter three bands in the course of the isochronal anneal sequence.

Concerning the 533 cm⁻¹ band we see that it is stable up to ~170 °C showing similar thermal stability as that of the Si-P₆ EPR defect [17]. This is an indication that the two signals may originate from the same structure. To further support such a correlation it will be interesting to calculate the vibrational frequency of the structure suggested for the Si-P₆ EPR defect. In this structure, the two self-interstitial (di-interstitial) atoms are placed symmetrically around a Si lattice site atom (Fig. 3a).

A way to estimate the vibrational frequencies of a defect is in principle, by comparing molecules of similar

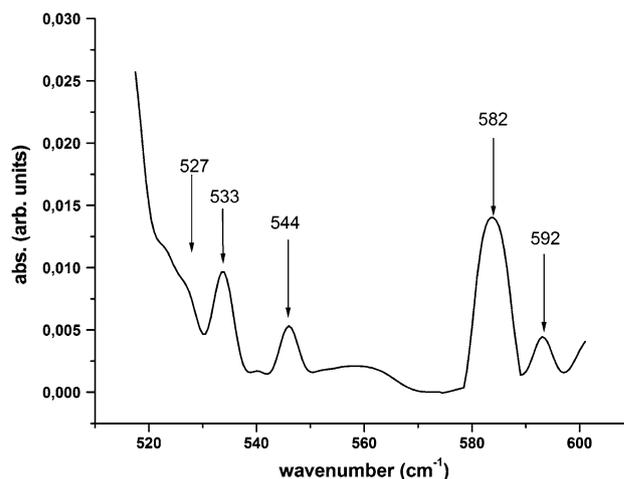


Fig. 1 Fragment of the IR spectra in neutron irradiated Cz-Si

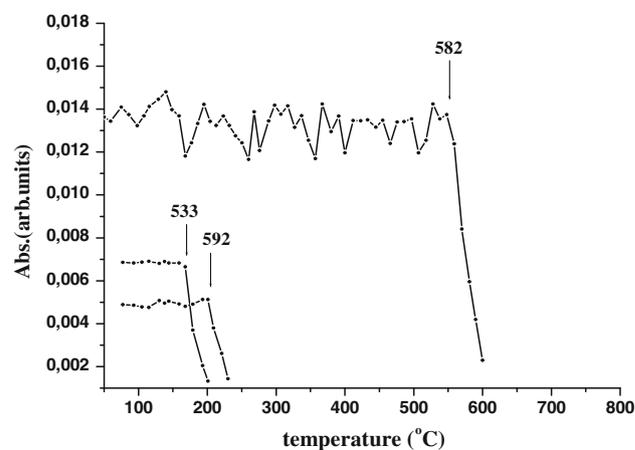


Fig. 2 Isochronal anneals of the 533, 582, 592 cm⁻¹ bands in Cz-Si

structure. According to the model of the di-interstitial defect [17], its structure is very similar (with the same hybrid orbitals) with that of the allene [27, 28] molecule (H₂C = C = CH₂). In Fig. 3b the geometry of the allene molecule is depicted together with the corresponding bonds of the carbon atoms. The allene structure contains four hydrogen atoms. The distance between the hydrogen atoms labeled 1, 2 in Fig. 3b is around 3.87 Å [28]. This is very close to the second nearest neighbor (2NN) distance of two atoms in the Si crystal, e.g. atoms A and B in Fig. 3a. Actually the latter distance is $a/\sqrt{2} = 5.43/\sqrt{2} = 3.84$ Å. Then, the LVM's of the di-interstitial can be related with those of allene by taking into account only the increased atomic weight of Si in the di-interstitial geometry with respect to that of carbon in the allene geometry. It is expected that the vibrating frequency of the bending mode of allene, as well as of the di-interstitial geometry (Fig. 3), will mainly depend on the binding orbitals of the central C and Si atoms. Due to the similarity in the two geometries

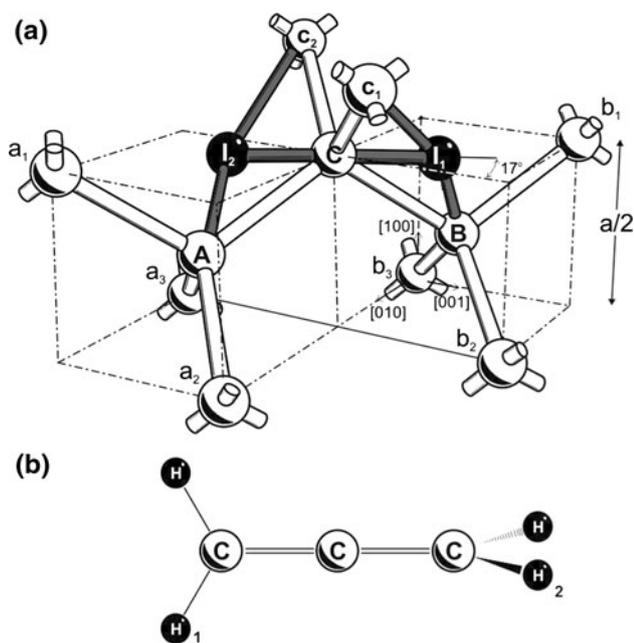


Fig. 3 Defect model of the di-interstitial defect (a) and the allene structure (b)

(compare Fig. 3a, b), the binding orbitals of the corresponding structures have the same symmetry. Therefore we may assume that the force constant for the bending mode is approximately the same in both structures. Thus,

$$\omega_{di-int.} = \sqrt{m_C/m_{Si}} \omega_{allene} \quad (1)$$

where $m_C = 12$ and $m_{Si} = 28$. The IR active bands of allene are those with symmetry species B_2 and E [29]. More specifically, the bending mode [30] of the C–C–C unit of the allene structure has a strong LVM frequency at 841 cm^{-1} [31]. Substituting these values in formula (1) we can obtain: $\omega_{di-int.} = 550.6 \text{ cm}^{-1}$

Remarkably well, this value compares favorably with the experimental value of 533 cm^{-1} (estimated error 3.3 %). This is a further supporting element besides the similarity of the thermal stability that the 533 cm^{-1} band could possibly originate from a di-interstitial structure, as that giving rise to the Si–P₆ EPR spectrum. Furthermore, the data of the annealing of the defect follow a first order kinetics which is described by the equation $dN/dt = -KN$, where N is the concentration of the defect and K the rate constant. By integrating we receive the expression $K\Delta t = \ln(N_t/N_{t+\Delta t})$ where N_t is the concentration of the defect after annealing time t and $N_{t+\Delta t}$ the concentration after annealing time $t + \Delta t$. By plotting $\ln(K\Delta t)$ versus $1/T$ (Fig. 4) we find that $K\Delta t$ exhibits an Arrhenius behavior that is $K \propto \exp(-E/kT)$ where E is the activation energy of the process and k is Boltzmann's constant. The calculated activation energy is $0.83(3) \text{ eV}$. This value does not deviate substantially from the value 0.6 eV obtained by EPR

measurement. Notably, molecular dynamics simulations have predicted migration energy of 0.89 eV for the I_2 defect [23]. Importantly, oxygen and carbon impurities in Si, due to their tendencies to interact strongly [32–36] with intrinsic defects may affect their behavior significantly. In relation with this, it is worth noting that the 533 cm^{-1} band appears also in float-zone Si samples with carbon concentration $[C_s] < 1 \times 10^{16} \text{ cm}^{-3}$. This indicates that its presence in the spectra is not particularly related with the oxygen and carbon impurities.

Regarding the 582 cm^{-1} band we notice that it disappears from the spectra in the range $550\text{--}600 \text{ }^\circ\text{C}$. Its thermal stability is similar to that of two bands at 530 and 550 cm^{-1} previously reported [37] in neutron irradiated Si and attributed to interstitial-related clusters. The 582 cm^{-1} band may be tentatively correlated with the tetra-interstitial (I_4) cluster which also disappears from the spectra in approximately the same temperature range [38]. Such an assignment certainly merits further verification.

Regarding the 592 cm^{-1} band which disappears from the spectra around $200 \text{ }^\circ\text{C}$ the present results are insufficient to lead to a definite correlation with a defect. In previous density functional theory calculations [39, 40] it was predicted that carbon–vacancy (C–V) complexes can form in Si. In this regard, an electronic band at $1.28 \mu\text{m}$ which anneals out at $220 \text{ }^\circ\text{C}$ may be tentatively associated with a C–V defect [41]. Obviously, the band is expected to form in samples with relatively low oxygen content, since the latter impurity is a selective trap for vacancies. Also a C–V defect should have a vibrating frequency lower than that of the C_s impurity due to the larger available volume available for the carbon atom in a C–V structure. Although there is circumstantial evidence reinforcing a view of possible correlation of the 592 cm^{-1} band with a C–V structure we feel that additional experimental evidence is

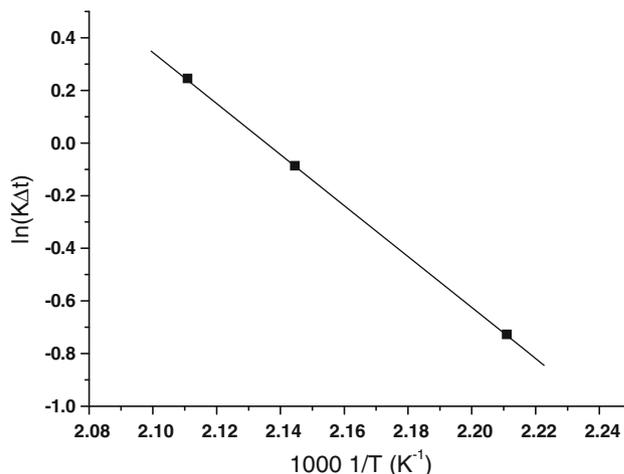


Fig. 4 Arrhenius plot of the annealing of the 533 cm^{-1} band

necessary to establish a positive identification of the origin of the band.

4 Conclusions

By means of IR spectroscopy we have studied three weak bands at 533, 582 and 592 cm^{-1} appearing in the spectra of neutron-irradiated Si, at room temperature. Based on the similarity in the thermal stability, the 533 cm^{-1} band was suggested to have the same origin as the Si-P₆ EPR signal associated with the di-interstitial defect (I₂). Further support was provided by the results of semi-empirical calculations indicating that the structure of the di-interstitial cluster, comprising two interstitial Si atoms located symmetrically around a substitutional atom. This is similar to that of the Allene molecule having a vibrational frequency close to that of the 533 cm^{-1} band. Regarding the 582 cm^{-1} band, our measurements determined that its thermal stability is similar to that of larger self-interstitial clusters reported in the literature. A tentative correlation with the tetra-interstitial (I₄) cluster is considered, although further verification is needed. Regarding the 592 cm^{-1} band, there are indications that its origin may be related with a C–V structure.

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