

# Semi-empirical modelling of the di-interstitial defect in silicon

C. A. Londos · T. Angeletos · A. Chroneos

Received: 4 September 2014 / Accepted: 14 September 2014 / Published online: 21 September 2014  
© Springer Science+Business Media New York 2014

**Abstract** Previous infrared spectroscopy studies of the defect spectrum of neutron irradiated Czochralski grown silicon (Cz-Si) revealed a band at  $533\text{ cm}^{-1}$ , which disappears from the spectra at  $\sim 170\text{ }^\circ\text{C}$  and exhibits a similar thermal stability with the Si-P6 Electron paramagnetic resonance (EPR) spectrum correlated with the di-interstitial defect. The proposed structural model for this defect consists of two self-interstitial atoms located symmetrically around a lattice site Si atom. The calculations reveal that the previously suggested structure of the Si-P6 defect has a vibrational frequency at about  $513\text{ cm}^{-1}$ , which is close to the experimental value of  $533\text{ cm}^{-1}$ . The modeling results indicate that the  $533\text{ cm}^{-1}$  infrared band originates from the same structure as that of the Si-P6 EPR spectrum.

## 1 Introduction

Defect processes in Si as in most semiconductor materials are greatly affected by point defects and/or doping in the lattice [1–11]. Small self-interstitial clusters in Si can have a fundamental role in many solid-state processes and this impacts its mechanical and electrical properties. In

particular, small interstitial clusters can cause or contribute [12, 13] to anomalous transient enhanced phenomena of dopants in Si. Additionally, the evolution of small interstitial clusters to {311} extended defects is not completely understood, however, it has been proposed that di-interstitial defects act as precursors for the formation of the {311} defects [14–18]. It is therefore necessary to control them as their formation can cause detrimental effects and impact technological application.

Electron paramagnetic resonance (EPR) measurements concluded [19] that an EPR center (called Si-P6) consists from two self-interstitials placed symmetrically ( $\{100\}$  symmetry) a substitutional atom. Its g-tensor exhibits a  $C_2$  (or  $C_{1h}$ ) symmetry with the symmetry axis along the  $\langle 100 \rangle$  direction at lower temperatures (200 K), becoming  $D_{2d}$  at 300 K. The Si-P6 signal corresponds [20] to the positive charge state of the defect, whereas ab initio total energy calculations [21] support this model for the Si-P6 defect and a transition between a  $C_{1h}$  and a  $C_{2v}$  symmetry. Density functional theory (DFT) calculations [22] indicated that the stress-tensor B of the suggested Si-P6 model of the defect is significantly different from that determined experimentally [19]. The DFT calculations have also shown that the di-interstitial defect exhibits considerable diffusion even at room temperature [22]. The implication is that it can be undetected for measurements at these temperatures supporting other theoretical results [23] for other di-interstitial structural forms. It was suggested therefore that the Si-P6 EPR cannot originate from a di-interstitial defect. Accordingly, it may originate either from a metastable version of it or from a larger interstitial complex [22]. So far a universally approved picture regarding the structure and geometry of the di-interstitial defect has not been established. Further investigations are necessary to bridge relative experimental and theoretical results in a

---

C. A. Londos · T. Angeletos  
Solid State Section, Physics Department, University of Athens,  
Panepistimiopolis, Zografos, 157 84 Athens, Greece  
e-mail: hlontos@phys.uoa.gr

A. Chroneos  
Faculty of Engineering and Computing, Coventry University,  
3 Gulson Street, Coventry CV1 2JH, UK

A. Chroneos (✉)  
Department of Materials, Imperial College London,  
London SW7 2BP, UK  
e-mail: alexander.chroneos@imperial.ac.uk

unified picture. In this line of thought, theoretical calculations of the vibrational frequency of the EPR Si-P<sub>6</sub> defect geometry suggested by Lee [19] and its correlation with the 533 cm<sup>-1</sup> infrared band it is expected to provide additional evidence in favor or against the correct structure of the di-interstitial defect.

The present study is focused on the investigation and modeling of the 533 cm<sup>-1</sup> infrared band in neutron irradiated Si. In particular semi-empirical calculations were employed to estimate a Localized Vibrational Mode (LVM) frequency of the Si-P6 defect model.

## 2 Modeling the di-interstitial defect

Experimental results concerning radiation defects can be gathered from electron irradiations and low fluence ion implantations as these produce native point defects. Neutron irradiation typically produces more complex defects with more complicated spectra. Neutron damage produces a higher concentration of native defects favouring the formation of larger clusters [24, 25].

The similarity of the thermal stability of the 533 cm<sup>-1</sup> band and the Si-P6 EPR center lead us to investigate the possibility whether the di-interstitial defect structure suggested [19] as the origin of the Si-P6 center can have a vibrational frequency in the range of 533 cm<sup>-1</sup>. In the model suggested [19] for Si-P6 EPR defect the di-interstitial complex comprises two interstitials I<sub>1</sub>, I<sub>2</sub> which are located symmetrically around a lattice site Si atom C. The I<sub>1</sub>, I<sub>2</sub> dumbbell is  $\phi = 17^\circ$  away from the [001] axis (refer to Fig. 1). The figure comprises the structure of the di-interstitial defect suggested by Lee [19] and some selected surrounding atoms for clarity. In what follows we shall calculate the vibrational frequency of the complex considering the defect as a triatomic linear molecule. In this respect considering the longitudinal atomic displacements, it can be shown [26] that the kinetic T and potential U energies of the molecule are given by the expressions:

$$T = \frac{1}{2}m_{I1}\dot{x}_{I1}^2 + \frac{1}{2}m_{I2}\dot{x}_{I2}^2 + \frac{1}{2}m_C\dot{x}_C^2,$$

$$U = \frac{1}{2}k_{C-I1}(x_C - x_{I1})^2 + \frac{1}{2}k_{C-I2}(x_C - x_{I2})^2$$

where  $m_C$ ,  $m_{I1}$  and  $m_{I2}$  are the respective masses of the atoms,  $x_C$ ,  $x_{I1}$  and  $x_{I2}$  are the respective displacements from the equilibrium sites and  $k_{C-I1}$ ,  $k_{C-I2}$ , are the interatomic force constants (IFC's) that bind atoms C and I<sub>1</sub>, and C and I<sub>2</sub> respectively. In our case:  $m_{I1} = m_{I2} = m_C \equiv m$ , where m is the mass of the Si atom, and due to symmetry of the structure:  $k_{C-I1} = k_{C-I2} \equiv k$ . Then the kinetic  $\hat{T}$  and the potential  $\hat{U}$  matrixes are respectively:

$$\hat{T} = \begin{pmatrix} m & 0 & 0 \\ 0 & m & 0 \\ 0 & 0 & m \end{pmatrix}, \quad \hat{U} = \begin{pmatrix} k & -k & 0 \\ -k & 2k & -k \\ 0 & -k & k \end{pmatrix} \quad (1)$$

Therefore the characteristic equation of the system is:

$$|\hat{U} - \omega^2\hat{T}| = 0 \quad (2)$$

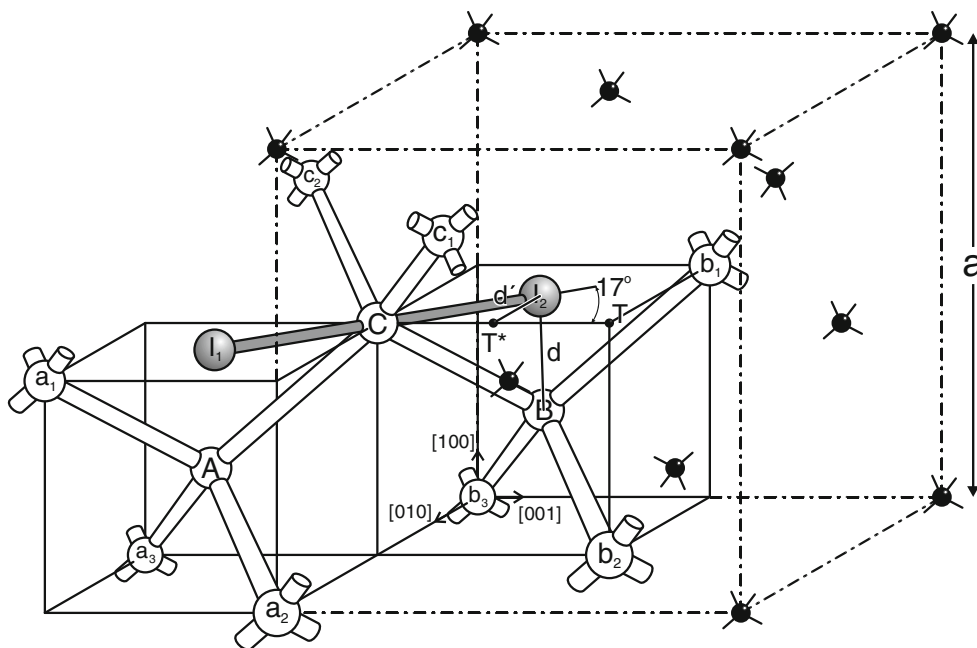
where  $\omega$  are its characteristic normal frequencies. There are three possible vibrational modes: the symmetric one with  $\omega_{sym.} = \sqrt{\frac{k}{m}}$ , the antisymmetric one with  $\omega_{antisym.} = \sqrt{\frac{k}{\mu}}$ , where  $\mu = m/3$ , the reduced mass of the molecule, and the collective one with a normal mode frequency  $\omega_{col}$  that corresponds to the state where the entire molecule oscillates collectively as a single structure. Notably, for a free triatomic molecule, this mode corresponds to the simple transitional motion, therefore  $\omega_{col.} = 0$ . Obviously, if the molecule is considered to be inside the silicon crystal, the collective mode would have a vibrational frequency different than zero ( $\omega_{col.} > 0$ ). However, the latter frequency has the lowest value among the frequencies of the three modes, whereas it is expected that the antisymmetric frequency  $\omega_{antisym}$  has the highest value.

We shall now calculate the frequency of the collective mode of oscillation of the defect structure. In studying this mode we shall consider that the three atoms oscillate as an entity in the field of their nearest neighbours, the latter considered immobile. This approximation allows the calculation of the distance d of the interstitial atoms of the structure from their nearest neighbours e.g. the distance between atoms I<sub>2</sub> and B (equivalently the distance between I<sub>1</sub> and A) and finally to estimate the frequency of the mode. The coordinates of some of the atoms are:  $b_3(0, 0, 0)$ ,  $C(a/2, a/2, 0)$ ,  $B(a/4, a/4, a/4)$ ,  $b_1(a/2, 0, a/2)$  and so on, where  $a = 5.43 \text{ \AA}$  is the lattice constant for Si.  $T(a/2, a/2, a/2)$ , is the tetrahedral interstitial site, at the center of the fcc cell depicted in Fig. 1 and  $T^*(a/2, a/2, a/4)$  is the site located halfway [19] down from the T site along the [001] axis.

Firstly we calculate the exact location of the atom I<sub>2</sub>. The I<sub>1</sub> – I<sub>2</sub> “dumbbell” is  $17^\circ$  away from the [001] direction and located about half-way down from the tetrahedral interstitial sites above the lattice site Si atoms A and B [19]. Thus, we assumed that the projections of I<sub>2</sub> in the axis CT is at T\* located at half-way CT (refer to Fig. 1). So the exact coordinates of the interstitial atom I<sub>2</sub> are  $(a/2, a/2 - d', a/4)$ , where:

$$d' = I_2T^* = CT^* \tan 17^\circ = \frac{a}{4} \tan 17^\circ = 0.415 \text{ \AA} \quad (3)$$

Thus the distance of I<sub>2</sub> atom from the nearest neighbour atom B is:



**Fig. 1** The model of the Si di-interstitial defect after Ref. [19]. A unit cell is also depicted, the c enter of which is the tetrahedral interstitial site T

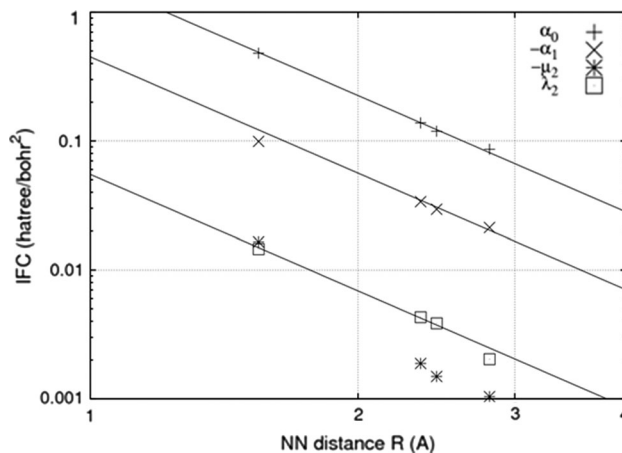
$$d = (I_2B) = \sqrt{\left(\frac{a}{2} - \frac{a}{4}\right)^2 + \left(\frac{a}{2} - d' - \frac{a}{4}\right)^2 + \left(\frac{a}{4} - \frac{a}{4}\right)^2} = \sqrt{\frac{a^2}{8} - \frac{ad'}{2} + d'^2} \cong 1.653 \text{ \AA} \tag{4}$$

The maximum frequency [27, 28]  $\omega$  of the phonon branch in Si is  $\sim 523 \text{ cm}^{-1}$ . At this frequency we assume that a single Si atom in the undistorted lattice vibrates with respect to its neighbors. This frequency can be written in the form of  $\omega = \sqrt{\frac{K}{m'}}$ , where K is a generalized force constant and  $m'$  refers to the mass of the respective mode. Following our assumption that the three Si atoms oscillate as an entity in the field of their nearest neighbours the latter considered immovable, we will make use of the results obtained by Aouissi et al. [29] on the interatomic force (IFC) constants of diamond structure lattices. In that work the real space IFC's of diamond, Si, Ge and  $\alpha$ -Sn were calculated by employing DFT (see Ref. [29] and references therein).

Analytical expressions for certain high symmetry points were obtained [29]; for example, the phonon frequency at the  $\Gamma$  point, which corresponds to the center of the brillouin zone, in terms of the IFC's  $\alpha_0, \alpha_1, \mu_1$  and  $\lambda_2$  is

$$\omega_0 = \sqrt{\frac{\alpha_0 - 4\alpha_1 + 8\mu_2 + 4\lambda_2}{m}} \tag{5}$$

These IFC's when plotted (see Fig. 2) versus the nearest neighbor distance R indicate a dominating  $1/R^3$  behavior. Thus, we may assume that K varies as  $K \propto (R/R_0)^{-a}$  where



**Fig. 2** Some IFC's versus the nearest neighbor distance R. The values have been obtained from Table 1 of Ref. [29]. The notation is according to Ref. [30]. The solid lines correspond to the  $1/R^3$  behavior and have been drawn as a guide to the eye. Only  $\mu_2$  deviates from the  $1/R^3$  behavior exhibiting a more pronounced behavior (i.e.  $1/R^{3.5}$ )

$a \approx 3$ , and  $R_0 = 2.35 \text{ \AA}$  is the nearest neighbor distance in the Si lattice. For the collective mode of the cluster described above, where the three Si atoms oscillate as an entity ( $m' = 3m$ , where  $m$  is the mass of the silicon atom) in the field of their 1st neighbors. It is reasonable to assume that the corresponding generalized constant  $K'$  also varies as  $K' \propto d^{-3}$ , where  $d = 1.65 \text{ \AA}$  is the distance between the Si atom of the vibrating cluster and the nearest neighbor. Thus we have:

$$\frac{\omega'}{\omega} = \sqrt{\frac{K' m}{K m'}} = \left(\frac{R}{d}\right)^{3/2} \sqrt{\frac{m}{3m}} = \left(\frac{2.35}{1.65}\right)^{3/2} \frac{1}{\sqrt{3}} \cong 0.98 \quad (6)$$

and  $\omega' = 0.98\omega = 0.98 \cdot 523 \text{ cm}^{-1} = 513 \text{ cm}^{-1}$ .

Additionally, by applying the above approach, the estimated frequency of the antisymmetric mode (where  $m' = m/3$ ) at the  $\Gamma$ -point, as received from formula (6) has a value of about  $1,540 \text{ cm}^{-1}$ . This value is much larger than that of our experimental value for the  $533 \text{ cm}^{-1}$  band, and reasonably the latter band does not correspond to the antisymmetric frequency of the di-interstitial defect. Regarding the symmetric mode of oscillation, following the same way ( $m' = m$ ), the calculated frequency at the  $\Gamma$ -point gives a value of about  $889 \text{ cm}^{-1}$ . Similarly, this value also cannot be associated with the  $533 \text{ cm}^{-1}$  band.

Notably, the calculation of the IFC's, drawn from first principles, is based [29] on the existence of covalent bonds between the Si atoms and was applied in the case of a perfect Si crystal. In particular, each Si atom is bonded with its nearest neighbors with  $sp^3$ -hybrid covalent bonds. However, in the structural model considered for the di-interstitial defect, the two extreme atoms are at interstitial sites. As a result, it is not possible for them to be connected with the central Si atom of the structure with a  $sp^3$ -covalent bond, due to its geometry. Apparently the central atom can be  $sp^3$ -covalently bonded only with neighboring lattice Si atoms. Furthermore, both of these interstitial atoms also interact with their local crystalline environment, of course with a much weaker force potential than that of a covalent bond. Importantly, the presence of interstitial atoms destroys the local symmetry of the perfect crystal. As a result the IFC's model, introduces substantial errors in the calculation of the vibrational frequency of the antisymmetric and the symmetric mode. On the other hand, the  $513 \text{ cm}^{-1}$  value derived for the collective mode of oscillation deviates  $<5 \%$ , actually  $3.7 \%$  from the experimental one, supporting the correlation of the  $533 \text{ cm}^{-1}$  band to the di-interstitial structure suggested by Lee [19]. Notably, in finding the oscillation frequency of the collective mode, the applying IFC's approach for the calculation [29] of  $k$  simulates more realistically the physical problem under consideration. The  $sp^3$ -orbitals approach is more representative for this kind of oscillation as compared with the other two cases. Indeed, in the case of the collective mode the three atoms are oscillating in phase as one entity, representing in essence one point of the silicon lattice which is physically connected with  $sp^3$ -orbitals with the other neighbor lattice points. Thus, the introduced errors by applying the IFC's approach are expected to be much smaller than the two other cases of symmetric and antisymmetric oscillation.

The small differences about  $20 \text{ cm}^{-1}$  between the theoretically calculated frequency of the collective mode and the experimentally measured frequency, may be due to (i) ignoring the existence of additional individual interactions of the two extreme interstitial atoms with their nearest neighbors and (ii) to the extended structure of the defect, which possibly create compressive stresses in the near crystalline environment. Both of these factors may increase the actual measured vibrational frequency ( $533 \text{ cm}^{-1}$ ) of the collective mode as compared to the calculated one ( $513 \text{ cm}^{-1}$ ).

After careful consideration we suggest that the  $533 \text{ cm}^{-1}$  IR band and the Si-P6 EPR spectrum in Si originate from the same center attributed to the di-interstitial defect. Our assignment was mainly based firstly on the similarity of the thermal stability of the two centers and the consistency between the extracted experimental values of the activation energies [31] and on the present theoretical calculations of the vibration frequency of the collective oscillation of the three atoms of the di-interstitial defect.

### 3 Conclusions

The present study was mainly focused on the modeling of the  $533 \text{ cm}^{-1}$  band that is observed in the IR spectra of neutron- irradiated Si. Calculations of the collective mode vibrational frequency of the suggested di-interstitial structure correlated with the Si-P6 defect, gave a value at about  $513 \text{ cm}^{-1}$  in good agreement with the reported experimental values of  $533 \text{ cm}^{-1}$ . This indicates that the  $533 \text{ cm}^{-1}$  IR band originates from the same defect as that of the Si-P6 EPR spectrum attributed to a di-interstitial structure. From a technological viewpoint the present study provides further information on a defect that is important for the agglomeration processes of self-interstitials in heat-treated Si leading to extended structural defects, thus impacting the Si material properties.

**Acknowledgments** We wish to thank Prof. N. V. Sarlis and Dr. D. Aliprantis for helpful discussions regarding calculations and explanations of the experimental results.

### References

1. S.G. Gloutier, P.A. Kossyrev, J. Xu, Nat. Mater. **4**, 887 (2005)
2. A. Chroneos, J. Appl. Phys. **105**, 056101 (2009)
3. E.N. Sgourou, D. Timerkaeva, C.A. Londos, D. Aliprantis, A. Chroneos, D. Caliste, P. Pochet, J. Appl. Phys. **113**, 113506 (2013)
4. R. Kube, H. Bracht, A. Chroneos, M. Posselt, B. Schmidt, J. Appl. Phys. **106**, 063534 (2009)
5. A. Chroneos, C.A. Londos, E.N. Sgourou, P. Pochet, Appl. Phys. Lett. **99**, 241901 (2011)

6. D.D. Berhanuddin, M.A. Lourenco, R.M. Gwilliam, K.P. Homewood, *Adv. Funct. Mater.* **22**, 2709 (2012)
7. C. Gao, X. Ma, J. Zhao, D. Yang, *J. Appl. Phys.* **113**, 093511 (2013)
8. C.A. Londos, E.N. Sgourou, A. Chroneos, *J. Mater. Sci.: Mater. Electron.* **24**, 1696 (2013)
9. C.A. Londos, G. Antonaras, A. Chroneos, *J. Appl. Phys.* **114**, 043502 (2013)
10. C.A. Londos, G. Antonaras, A. Chroneos, *J. Mater. Sci.: Mater. Electron.* **24**, 4328 (2013)
11. H. Wang, A. Chroneos, C.A. Londos, E.N. Sgourou, U. Schwingenschlögl, *Appl. Phys. Lett.* **103**, 052101 (2013)
12. P.A. Stolk, H.J. Gossmann, D.J. Eaglesham, J.M. Poate, *Appl. Phys. Lett.* **66**, 568 (1995)
13. L.H. Zhang, K.S. Jones, P.H. Chi, D.S. Simons, *Appl. Phys. Lett.* **67**, 2025 (1995)
14. S. Lee, R.J. Bondi, G.S. Hwang, *Mol. Simul.* **35**, 867 (2009)
15. S. Lee, G.S. Hwang, *Phys. Rev. B* **77**, 085210 (2008)
16. L.A. Marques, L. Pelaz, I. Santos, P. Lopez, M. Aboy, *Phys. Rev. B* **78**, 193201 (2008)
17. S.S. Kapur, T. Sinno, *Phys. Rev. B* **82**, 045205 (2010)
18. J. Kim, J.W. Wilkins, F.S. Khan, A. Canning, *Phys. Rev. B* **55**, 16186 (1997)
19. Y.H. Lee, *Appl. Phys. Lett.* **73**, 1119 (1998)
20. Y.H. Lee, N.N. Gerasimenko, J.W. Corbett, *Phys. Rev. B* **14**, 4506 (1976)
21. J. Kim, F. Kirchoff, W.G. Aulbur, J.W. Wilkins, F.S. Khan, G. Kresse, *Phys. Rev. Lett.* **83**, 1990 (1999)
22. R. Jones, T.A.G. Eberlein, N. Pinho, B.J. Coomer, J.P. Goss, P.R. Briddon, S. Berg, *Nucl. Instrum. Methods Phys. Res. B* **186**, 10 (2002)
23. S.K. Estreicher, M. Gharaibeh, P.A. Fedders, P. Ordejon, *Phys. Rev. Lett.* **86**, 1247 (2001)
24. K. Laithwaite, R.C. Newman, D.H.J. Totterdell, *J. Phys. C* **8**, 236 (1975)
25. N. Fukata, T. Odori, M. Seuzawa, H. Takahashi, *J. Appl. Phys.* **91**, 5831 (2002)
26. L.D. Landau, E.M. Lifshitz, *Mechanics*, Vol.1, (Pergamon Press, Ltd 1776), p.72
27. S.L. Altmann, A. Lapicciarella, K.W. Lodge, N. Tomassini, *J. Phys. C* **15**, 5581 (1982)
28. M. Holt, Z. Wu, H. Hong, P. Zschack, P. Jemian, J. Tischler, H. Chen, T.-C. Chiang, *Phys. Rev. Lett.* **83**, 3317 (1999)
29. M. Aouissi, I. Hamdi, N. Meskini, A. Qteish, *Phys. Rev. B* **74**, 054302 (2006)
30. F. Herman, *J. Phys. Chem. Solids* **8**, 405 (1959)
31. C.A. Londos, G. Antonaras, A. Chroneos, *J. Appl. Phys.* **114**, 193513 (2013)