THE TRI-INTERSTITIAL DEFECT IN SI

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First principle supercell calculations are carried out on competitive models of tri-interstitial defects in Si. These models are distinguished by their symmetry and location within the lattice and consist of (a) a trigonal defect located in the open part of the lattice, (b) a compact form with C_{3v} symmetry, and (c) a compact form with T_d symmetry. It is found that (b) and (c) have the lowest energies in 64, 128 and 216 atom cells. However, these models have properties at variance with the W-photoluminescent centre, previously attributed to I_3, while those of the open form (a) are in general agreement.

I. INTRODUCTION

The properties of multi-interstitial defects in Si is a topic of considerable current interest. Work reported at this conference has identified the tetra-interstitial defect, I_4, with the B3 EPR centre[1] which has D_{2d} symmetry. This high symmetry is comparatively rare among defects. This defect has been detected in neutron irradiated p-Si annealed between 170 °C and 500 °C and has been correlated with a DLTS level at $E_v + 0.29$[2] found in p-type carbon implanted Si which is subsequently annealed around 350 °C. A level at $E_v + 0.40$ eV is detected immediately after irradiation in the carbon implanted material but not in boron implanted. This level anneals around 350 °C and two levels at $E_v + 0.29$ eV and $E_v + 0.46$ eV appear. The latter defects are annealed out completely after 5 hours anneal at 475 °C. The similarity in the annealing behaviour of the $E_v + 0.29$ eV level with the B3 EPR centre has suggested their connection. PL experiments on Cz- or Fz-Si into which ions have been implanted, and subsequently annealed beyond 200 °C, reveal two emission bands: W (or I1) at 1.018 eV and X (or I3) at 1.0398 eV. The intensities of these lines are anti-correlated[3,4] and the W and X line anneal out by 350 °C and 600 °C respectively. The symmetry of the X centre has been shown to be D_{2d}[5] and from this combined with the thermal stability and calculated electronic properties, we identify it with I_4.

The W centre has been suggested to arise from a self-interstitial defect[6–8] although other workers favour a vacancy related centre[9–11]. Assuming that it is interstitial related, then its anti-correlation with the X centre suggests that it originates from I_3 or I_2. The W-defect is known to be trigonal and insensitive to stress. The line is seen in absorption as well as photoluminescence and this is taken to imply that the transition occurs between two localised gap states. There is a wide vibronic band and a phonon replica L, separated from the zero phonon line by 70 meV. If this is a local vibrational mode then it rules out models for the defect based on vacancies. Satellite lines reflecting the isotopic abundance of ^{29}Si and ^{30}Si are seen on the high energy side of L. These are shifted from the phonon sideband by about 16 cm^{-1} in the case of ^{30}Si. This is a surprisingly large shift in a local vibrational mode. Replacing all the atoms in bulk Si with ^{30}Si would be expected to produce a shift in the Raman line of $523/28 \sim 18.6$ cm^{-1}. The conclusion must be that almost the whole amplitude of the vibrational mode is localised on a single Si atom which must lie on the trigonal axis. The last follows as otherwise the amplitude would be shared by several atoms. Any model then has to possess a unique Si atom located on the trigonal axis.

An acceptor $(-/0)$ level has been tentatively linked to the centre at $E_c - 0.075$ eV[12]. This suggests that the defect which gives rise to the W centre also has a level around about $E_v + 0.1$ eV to account for the energy of the 1.018 eV absorption band,

We have previously argued that a form of I_3 shown in Fig. 2(a) has properties consistent with the centre[13]. The evidence mainly rested on the finding of a local vibrational mode at 74 meV which could shift by up to 12 cm^{-1} upon replacing one atom with ^{29}Si. The frequency and shift are reasonably close to those observed suggesting that the defect could be identified with the W centre. However, several other candidate structures for the tri-interstitial defect have recently been proposed and it is now necessary to compare their properties.

The calculations of the energies of the defects were carried out in 64 atom supercells with a basis of s and p Gaussian functions with four independent exponents. An s and p Gaussian function with one exponent was placed at each bond centre. Further details of the method are given elsewhere[14]. The energy levels were investigated with large hydrogen terminated clusters using a transition state method[15].

II. RESULTS

Three forms of I_3 were investigated. The first shown in Fig. 2(a) is our previous model where three interstitials are added to a bond centred sites surrounding a T_d site in the open part of the lattice. The second[16] is a compact structure where the three interstitials form a necklace around a bond centred site as shown in Fig. 2(b), and the third[17] is where four atoms are added to the unoccupied vertices of a cube surrounding a vacancy as shown in Fig. 2(c). The first two defects are trigonal but the third has tetrahedral symmetry.

The lowest energy structures were the T_d and compact C_{3v} defects and the open trigonal one in Fig. 2(a) was about 1.4 eV higher. The energy difference between the lowest pair is not significant, and in the positive charge state, the ordering of energies is the same.

The calculations were repeated for 216 atom cells using only Γ-point sampling. The energies were unchanged.

We now describe in detail the properties of each structure.

(a) *Open C_{3v} I_3 structure:* This model has been investigated previously[13]. The presence of three bond centred Si interstitials as shown in Fig. 2(a) compresses the unique Si-Si bond along [111] giving a bond of length 2.19 Å compared with a bulk length of 2.35 Å. The three bond centred Si interstitials make bonds of length 2.16, 2.19 and 2.26 (2) Å with their neighbours. The compression of the bond on the trigonal axis causes a local vibrational mode to appear at 74 meV as discussed previously. The magnitude of the shift of this mode upon replacement of one of the atoms lying on the trigonal axis with ^{30}Si is found to be quite sensitive to calculation details. This sensitivity arises as the mode interacts with another nearby vibrational mode. The magnitude of their interaction depends critically on their energy separation. It is possible that the observed 16 cm^{-1} shift could be explained through this sort of interaction.

The Kohn-Sham levels in Fig. 1(b) show filled singlet and doublet levels near E_v and empty levels near E_c. These one-electron levels are not directly related to the DLTS levels and the latter can only be found from an analysis of the ionisation energies and electron affinities of the defects. Calculations of these using the method described in Ref.[15] gave levels within 0.1 eV of the band edges. The accuracy of these levels is around 0.2 eV. In summary, the properties of this defect are in line with those of the W centre. The large isotopic shift of the local mode is underestimated but could be explained through the coupling with another mode.

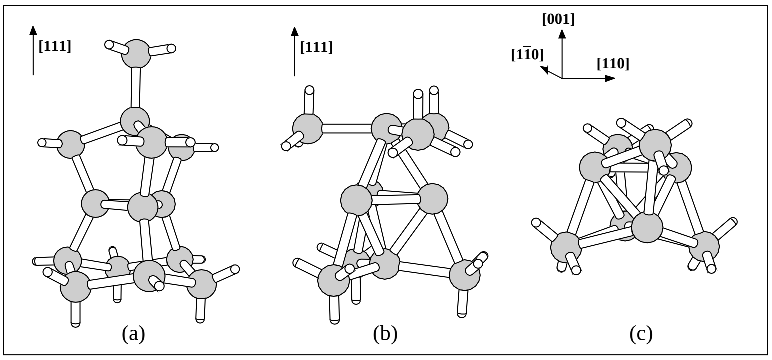

FIG. 1. Structures of three models for I_3. (a) The open C_{3v} model, (b) The compact C_{3v} model, and (c) the T_d model.

(b) *Compact C_{3v} I_3 structure:* This defect was suggested by Gharaibeh *et al.*[16] and consists of an equilateral triangle of three interstitials surrounding a bond centred site as shown in Fig. 2(b). The two atoms on the trigonal axis are severely over-coordinated and each has 6 bonds of lengths between 2.34 to 2.48 Å.

The bond lengths of the core atoms are not particularly compressed and we find no vibrational modes lying above the Raman. However, there are resonant modes at 263.27 and 320.37 cm^{-1} in the case of ^{28}Si. These shift to 259.19 and 319.94 cm^{-1} when one atom is replaced by ^{30}Si and 261.13 and 318.77 cm^{-1} when the other atom is replaced. If the L feature observed as a phonon replica to the W-line is interpreted as an overtone, then the maximum isotopic shift with ^{30}Si is about 8 $\mathrm{cm}^{-1}$and much less than that observed.

The Kohn-Sham levels (Fig. 1(c)) show two or three filled levels below mid-gap and an empty one above. A calculation of the energy states gave very shallow $(-/0)$ and $(0/+)$ levels within 0.1 eV of E_c and E_v respectively.

In conclusion, although this defect is energetically favourable, and possesses symmetry consistent with the W center, this model appears unable to account for the vibronic properties of the W-line.

(c) *Compact T_d I_3 structure* It is remarkable that the 8 atoms in the core of the defect adjust so that each possesses 6 bonds with lengths between 2.32 and 2.52 Å. The symmetry alone rules out this as a candidate for the W centre but in addition the lack of compressed bonds in the core of the defect implies the absence of modes around 70 meV.

The Kohn-Sham levels shown in Fig. 1(c) suggest electrical properties similar to the other I_3 models. The defect has few of the properties possessed by the W centre.

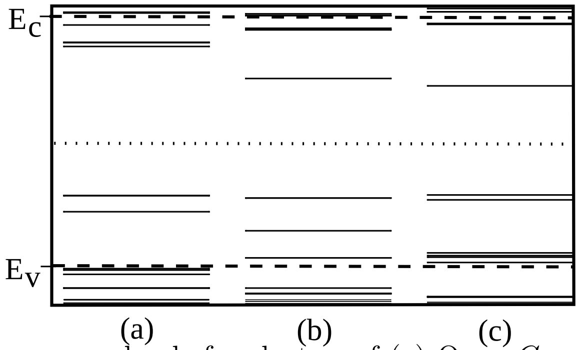

FIG. 2. The Kohn-Sham energy levels for clusters of (a) Open C_{3v}, (b) Compact C_{3v}, and (c) T_d I_3 models. The dashed line indicates the positions of the valence and conduction band edges calculated using a pure cluster. The dotted line shows the midgap level. All levels which lie below midgap are filled, all those above are empty.

III. CONCLUSION

The calculations of three models for I_3 show that the compact structures have lower energies than the open one shown in Fig. 2(a). The open defect discussed here is a small segment of a [110] chain of interstitials believed to grow into the {113} defect[18]. The compact models, in contrast with the open one, do not have properties which are closely related to the W centre.

The implication is that either the W centre is a different defect or the open I_3 structure is a metastable centre formed directly from the aggregation of self-interstitials. In this case, there must be a substantial energy barrier preventing the three interstitials from entering the same tetrahedral cage. We hope to determine the barrier for interconversion of the defects in a future publication. Another possibility, under consideration, is that the W centre is a di-interstitial.

It is of interest to enquire whether $I_3^{\pm}$ has been detected in EPR. Since the I_3 structures yield donor and/or acceptor levels within about 0.1 eV of the band edges they could only be observed in their paramagnetic charge state if the fermi level were close to a band edge. This suggests that the EPR active defect $I_3^{\pm}$ can only be formed in lightly irradiated annealed material where the Fermi-level is pinned to the shallow dopant levels.

In conclusion, a metastable form of I_3 has properties in reasonable agreement with those of the W centre. One of the lowest energy I_3 structures investigated possess symmetry consistent with the W centre but it difficult to reconcile with the observed vibronic character.

IV. ACKNOWLEDGEMENTS

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