I_4 IN SILICON: CORRELATION WITH EXPERIMENT

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Ab initio methods are employed in this study of the properties of the self-interstitial aggregate, I_4 in silicon. Our calculations show the defect to be electrically active and we identify it with the B3 EPR center. We also show that its properties are consistent with DLTS and optical spectra observed following implantation of silicon.

I. INTRODUCTION

Recently, evidence has emerged that the structure of small self-interstitial aggregates is markedly different from that of the {311} extended defect. The transient supersaturation of a system undergoing Ostwald ripening has been exploited to estimate the formation energies of small interstitial aggregates[9]. These experiments demonstrated that magic numbers exist for interstitial aggregates in the early annealing stage. I_4 and I_8 are found to be particularly stable with a transition at $n \gtrsim 10$ to a broad range of defects with the characteristic energy of {311} condensates. Furthermore, optical studies[10] confirm this picture, indicating that a structural transformation from I clusters to {311} defects occurs at ~ 600°C.

Deep level transient spectroscopy (DLTS) studies of Si ion implanted silicon has provided further information on the early stages of the ripening process[11]. Two donor (0/+) levels at $E_v + 0.29$ and $E_v + 0.48$ eV associated with small interstitial clusters are found to dominate the DLTS spectrum before the emergence of a different DLTS signal at $E_v + 0.50$ eV. The latter level exhibits carrier capture kinetics typical of extended defects and is associated with {311} condensates. The $E_v + 0.29$ eV level has been observed previously in carbon implanted silicon and is correlated with the B3 EPR center[12].

B3 is a prominent $S = 1/2$ center, observed in boron doped, neutron irradiated and heat-treated silicon[4,13]. It is first observed upon annealing at around 200°C and completely anneals out at 500°C[13,4]. B3 is one of only eight defect centers observed in irradiated silicon which have been reported to possess D_{2d} symmetry and its stability to high temperatures suggests a simple secondary irradiation product of particularly low formation energy. The lack of low temperature stress response for B3 indicates that the D_{2d} symmetry is not resultant from a Jahn-Teller distortion[4]. Analysis of the hyperfine structure reveals further information about the defect structure: (i) The defect center is probably vacant. (ii) Two equivalent Si atoms lie along the principal ⟨001⟩ axis. (iii) Only 9% of the unpaired electron is localized on each of these two atoms. (iv) The electronic wavefunction on these atoms is predominantly p-like with only 6% s character.

Due to the high concentration of the defect in the samples used compared to their impurity content, the defect is assumed to be intrinsic. Additionally, no hyperfine interaction with impurity atoms could be detected. The defect is not thought to be vacancy related for two key reasons. Only V_1 and V_5 amongst the small vacancy aggregates could possess D_{2d} symmetry, but in conflict with the observation, this could only result from a distortion from tetrahedral symmetry. Secondly, vacancy defects possess hyperfine splitting character which reflects the high electron localization on $\langle 111 \rangle$ dangling bonds whereas the B3 spectrum does not reflect this degree of localization.

The geometry of I_4 which we present here as a structural model for the B3 EPR center has been put forward previously[15–17]. The latter proposal for this structure in silicon lacked experimental backing and the authors suggested that the absence of data consistent with the defect was due to its inert nature. Here, we show that the structure is electrically active and relate the center to experiment.

We analyze the interstitial defects within local density-functional theory using both cluster-based (AIMPRO[18]) and supercell methods. In the cluster method the defect is positioned at the center of a cluster of crystalline silicon. The dangling bonds at the cluster surface are saturated using hydrogen atoms. The positions of all bulk atoms are optimized using a conjugate gradient method. Electrical levels are calculated using a method described elsewhere[19]. The I_4 defect structure is optimized in three clusters with configurations $Si_{88}H_{64}$, $Si_{188}H_{120}$ and $Si_{290}H_{144}$ and also in a Si_{100} supercell.

We now consider the calculated properties of the optimised defect separately and relate the results with experiment.

Structure: The I_4 defect is constructed by replacing four next-nearest neighbour atoms which lie in a common $\{001\}$ plane with four $\langle 001 \rangle$ split interstitial pairs. Optimisation of the structure demonstrates that each atom pair forms bonds with the nrighboring pair, resulting in full four-fold coordination. The defect possesses two perpendicular mirror planes and three orthogonal C_2 rotational axes and therefore belongs to the D_{2d} point group, consistent with the symmetry assignment of the B3 EPR center. We calculate that I_4^0 possesses bond lengths and bond angles close to their ideal values (2.35 Å and 109.47° respectively), in agreement with previous *ab initio* calculations[17]. In particular, the bond angle distortions in the defect core of I_4 relaxed in the $Si_{290}H_{144}$ cluster were found to be within the range -0.9 to -11.8% of the ideal bond angle compared with -1.3 to -13.2% found using a 196 atom supercell[17]. The bondlengths in the defect core, are found to be within $\sim 5\%$ of the bulk value.

Electronic levels: The positions of the electronic levels of I_4 were estimated using the $Si_{290}H_{144}$ cluster. A single deep donor $(0/+)$ level was calculated to lie in the lower half of the band gap at $E_v + 0.18$ eV. Given the errors involved, this results supports the correlation of the $E_v + 0.29$ eV hole trap with the B3[12] center. No other electronic levels are calculated to lie within the band gap. This determination of an electrical level associated with I_4 is in contradiction with previous results[17] and is probably resultant from the more reliable electronic level calculation method employed here. The association of a donor level with this fully-coordinated structure may be expected as a result of the compressive strain in the defect core. The compression of bonds leads to increased interaction between sp^3 orbitals, pushing states into the band-gap region. The donor activity then arises from these filled states displaced upwards from the valence band edge.

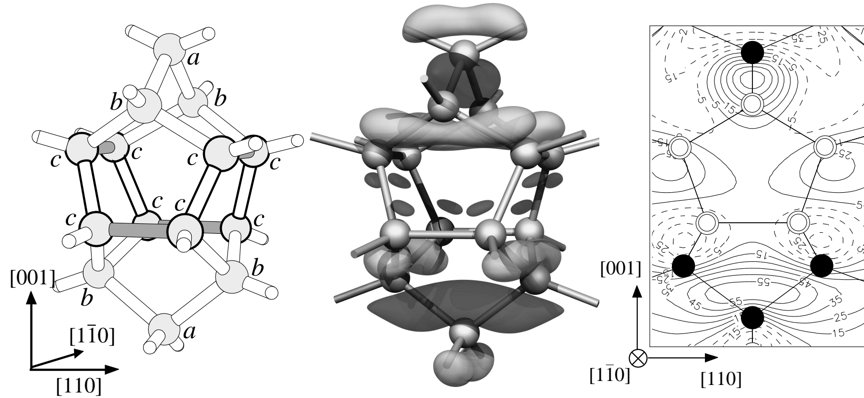

FIG. 1. Schematics showing the structure and unpaired wavefunction of I_4^+. Left: The fully optimized structure of I_4 in silicon. For clarity, the four [001] split interstitial pairs which make up the defect are shown in bold. The reconstructed bonds which link the interstitial pairs are shaded. Atoms which are equivalent by symmetry are labelled with the same letter. Center: A 3-dimensional schematic of an isosurface of the unpaired wavefunction. Dark (light) surfaces indicate positive (negative) regions of the wavefunction. Right: Contour plot of the unpaired wavefunction on the [110] plane. Contours representing positive (negative) regions are shown by solid (dashed) lines. Atoms lying in the plane are shown as black circles. Double circles indicate that two atoms lie equidistant from the plane along [110] and [$\bar{1}\bar{1}$0] .

Paramagnetic properties: The presence of a donor level shows that the defect exists in the positive charge state. Whilst, in principle, a defect with D_{2d} symmetry could undergo a Jahn-Teller distortion, no such distortion is expected from I_4^+ as the highest occupied orbital is non-degenerate with a_1 symmetry. I_4 was optimized in the positive charge state and the bondlengths in the defect core were found to differ by less than 1% from those of the neutral defect.

The defect structure is wholly consistent with the interpretation of the nuclear hyperfine interaction data on B3[4], having no atom present at the defect center and two equivalent atoms (labelled a in Fig. 1) lying along the principal $\langle 001 \rangle$ axis. The wavefunction occupied by the unpaired electron of I_4^+ is shown in Fig. 1. Clearly the unpaired wavefunction is spread over a number of atoms, whilst the largest amplitude lie near atom sites labelled a. Mulliken analysis shows that 6% of the unpaired wavefunction is localized near atom a in excellent agreement with the value obtained from ^{29}Si hyperfine measurements (9%). We also find that the unpaired electronic wavefunction is strongly p-like in character consistent with the 94% anisotropic component observed. Hyperfine splitting due to interaction with other nuclei is also observed in the B3 spectrum. These were not resolved and therefore no further detailed information regarding other nearby nuclei could be ascertained. The Mulliken analysis, however, shows that around 3% of the unpaired wavefunction is localized upon each site labelled b and another 3% is localized near the sites labelled c. It is probable that the unresolved hyperfine splitting is a result of interaction with nuclei at sites b or at c.

Energetics: The formation energy of the I_4 defect, $E_f(I_4)$, relative to four bulk atoms was calculated using the supercell method to be 8.7 eV. Experimental determination of this energy gives a value of around $E_f(I_1) + 3.4$ eV[9]. We calculate $E_f(I_1)$, the formation energy

of the isolated $\langle 110 \rangle$ orientated interstitial to be 3.9 eV. This brings the calculated formation energy of I_4 to $E_f(I_1) + 4.8$ eV, in agreement with experiment given the errors involved in both the theoretical and experimental determination of these values. The binding energy of I_4 relative to four separated [110] orientated interstitial atoms is calculated to be 6.9 eV.

The high thermal stability of B3 is explained by the low formation energy calculated for I_4. This result is expected from the I_4 model because of the near ideal bonding arrangements of all atoms. The I_4 model also explains the finding that I_8 also possesses remarkably low formation energy[9]. Clearly, eight [001] split-interstitial pairs can be sited on a (001) plane resulting in the formation of two neighboring I_4 defects. It is likely that this $(I_4)_2$ defect will posses a lower formation energy per interstitial than two separated I_4 units due to the mutual strain relief interaction between the units. The large increases observed in the formation energies of the defects I_5, I_6, I_7 relative to I_4 and I_8 is also consequent from this model as these intermediate defects are unable to achieve full coordination.

Optical properties: The correlation of I_4 to experimental spectra may possibly be extended to observations in photoluminescence and absorption. The 1039.8 meV zero phonon line (labelled I_3 or X) is produced by neutron, proton or ion implantation between 230 and 530°C independently of carbon or oxygen doping[20] and has been classified as an intrinsic center[21]. As for the B3 EPR center, the X-center is suggested to have inherent D_{2d} symmetry from stress measurements and consideration of the vibronic bandshape[20]. For the reasons discussed above this symmetry assignment is inconsistent with the defect being a small vacancy cluster.

Isochronal annealing experiments show the 1039.8 meV zero phonon line intensity appears to increase at the expense of another zero phonon line labelled W. The W-optical spectrum is also classified as an intrinsic center and experiments suggest that is an interstitial rather than a vacancy aggregate[6,14]. This supports the identification of the X-center with I_4 and suggests that the W-center is a smaller aggregate, I_2 or I_3 which is the precursor to the I_4 defect.

Calculation of the matrix elements for dipole transitions between the defect states in the band gap region was performed. A number of transitions are allowed between near band edge states with radiative lifetimes around 1-5μs. The fastest of these transitions occurs between states of b_2 and a_1 symmetry. Rescaling the energy difference between these states by a factor which brings the calculated band-gap into agreement with experiment gives a transition energy of around 1.0 eV in good agreement with the 1039.8 eV energy associated with the X-line.

In conclusion, we have identified I_4^+ with the B3 EPR center observed in irradiated p-type silicon. Its formation circumstances, symmetry, structure and electronic levels strongly support this assignment. The calculated electrical activity further supports the correlation of I_4 with the 0.29 eV DLTS signal. We have linked the X-optical center with the B3 EPR center and the optical properties of the I_4 defect are calculated to be in agreement with this assignment. We calculate the vibrational properties of I_4^0 and predict that the defect gives rise to a series of local modes lying close to the Raman edge. The structure of the I_4 center clearly excludes it as an embryo for aggregation of the {311} defects. This marked structural difference between small aggregates and extended interstitial defects, however, is supported by optical, DLTS and transient supersaturation experiments.

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