Self interstitial defects in silicon

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Defects in Si & SiGe

Abstract

We investigate theoretically recent experimental work that has assigned the self-interstitial to the AA12 EPR centre in silicon. We also discuss the assignments of the tri-interstitial and tetra-interstitial to the W optical centre and the B3 EPR centre respectively. Difficulties in the assignment of the di-interstitial with the P6 EPR centre are noted.

AA12 EPR centre (I_1)

- The spectrum is found when *p*-Si is irradiated with 30 MeV protons (or 4.7 MeV α-particles) between 77 and 270 K, and subsequently the sample is illuminated with band gap light. It is not seen in *n*-type Si.
- AA12 is an isotropic centre with a resolved 45 MHz hyperfine interaction with a single Si atom.
- Unresolved hyperfine interactions with shells of 4–6 Si atoms are also detected.
- The small value of the hyperfine tensor suggests that only 1.5 % of the spin density is localised in an *s*-orbital on the interstitial.
- The defect has been correlated with an MCTS (minority carrier transient spectroscopic) level at $E_c - 0.39$ eV
- It anneals at 350 K in the dark or at 77 K under minority carrier injection. The growth of other interstitial defects such as C_i, Al_i, and Si_i-O_i is detected after the anneal.

P6 EPR centre

- The P6 EPR centre is formed in neutron, ion or MeV proton irradiated intrinsic Si.
- Its *g*-tensor reveals a C_2 axis along [100] at 200 K, but at 300 K, the symmetry becomes D_2 or D_{2d}. The activation energy for this change is only 0.2 eV and represents a thermally activated reorientation between equivalent sites.
- P6 anneals at 170°C.
- It has been correlated with a DLTS donor level at $E_v+0.4$ eV.
- Uniaxial stress studies showed that the defect could reorientate at 100°C with an activation energy of 0.6 eV and with a low pre-exponential factor of 10^8 s^{-1}. This activation energy is similar to the anneal of the 0.4 eV DLTS level found in irradiated *p*-Si.

W optical centre (I_3)

- The W-optical centre is seen in both *n*- and *p*- type silicon following Si implantation and subsequent annealing.
- The centre is characterised by a sharp peak at 1.0182 eV and an associated phonon sideband due to a local vibrational mode (LVM) with an energy of 70.0 meV.
- Uniaxial stress measurements reveal the symmetry of the defect to be trigonal.

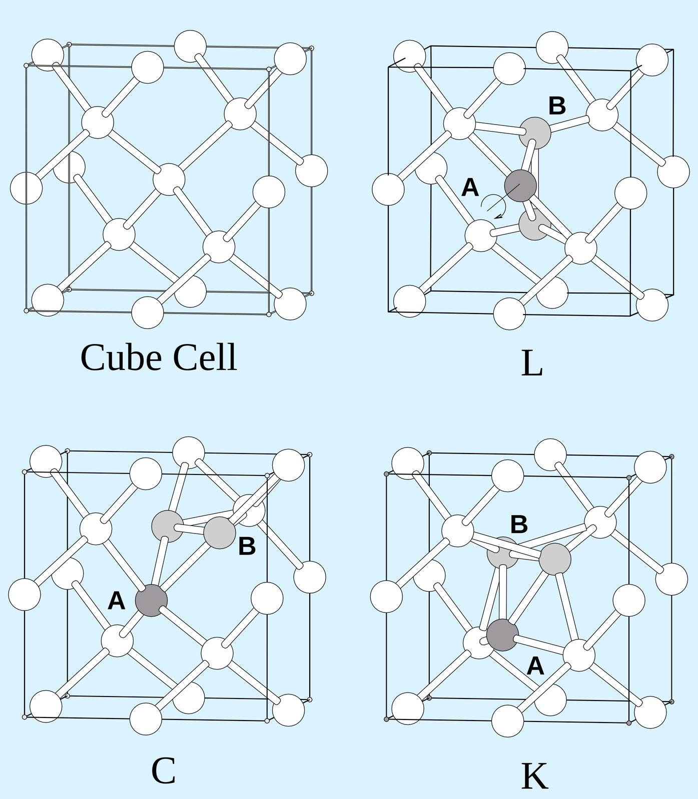
B3 EPR centre (I_4)

- B3 is formed in neutron irradiated *p*-Si heated between $\sim$ 200–500 °C. It is one of only eight defect centres 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 indicates that the D_{2d} symmetry does not result from a Jahn-Teller distortion.
- Analysis of the hyperfine structure reveals further information:
  - The defect centre is probably vacant.
  - Two equivalent Si atoms lie along the principal $\langle 001\rangle$ axis.
  - Only 9% of the unpaired electron is localised on each of these two atoms.
  - The electronic wavefunction on these atoms is predominantly *p*-like with only 6% *s* character.
- A hole trap at $E_v + 0.29$ eV is correlated to the B3 centre.

Conclusions

- The single interstitial is stable at the T-site in the positive and double positive charge state, and it has a symmetry, spin-density and diffusion barrier consistent with the AA12 EPR centre. However, the (+/++) calculated level is much more shallow than the $E_c-0.39$ eV reported for AA12. Furthermore it is unclear how it can be created since during irradiation the number of electron-hole pairs should exceed the number if I_1. Therefore the interstitial should trap electrons and be subject to diffusion.
- The lowest energy configuration for I_2 found by Kim *et al.* is not the P6 EPR centre since its symmetry is inconsistent with the one of P6. Further, the Lee *et al.* model for I_2 is only metastable and has a *B*-tensor at variance with P6. The calculated diffusion barrier for I_2 is only 0.5 eV. The therefrom resulting rapid mobility of I_2 at room temperature explains the absence of a dominant EPR centre that can be assigned to the defect.
- We linked a high energy form of I_3 with the W photoluminescent centre. We expect I_4 defects to be formed at the same time as I_3. I_4 has been linked with the B3 EPR centre which is known to be stable to around 500 °C. An intriguing suggestion is that it may be the X optical centre which appears when the W-line diminishes.

I_2



Cube Cell L

C K

- Relative total energies in eV.

State	L (C_2)	C (C_{1h})	K (C_{1h})
-1	1.07	0.00	0.04
0	1.05	0.00	0.07
+1	1.12	0.00	0.01

- The formation energies of the neutral C, K, L forms of I_2 are 5.12, 5.19 and 6.17 eV.
- The (0/+) levels of the stable C form of I_2 lies at $E_v + 0.3$ eV.
- The net migration barrier is about 0.5 eV. This shows that I_2 is likely to diffuse *faster* than I_1^{++}.
- The calculated values for the B tensor are very different from the experimental ones of I_2 whereas they are quite close to the ones of I_4. This suggests that the structure of P6 is somewhat close to that of I_4.

Calculations

Supercell and cluster based, spin-polarised–LDF calculations using the AIMPRO code.

- The calculations for the energies have been carried out in supercells of 64 atoms but the electrical levels have been calculated from the ionisation energies of the defects when embedded in large H-terminated clusters.
- Cartesian Gaussian *s*, *p* & *d* basis in the supercell.
- Perdew–Zunger based correlation and SLDA exchange
- BHS pseudopotentials
- All atoms allowed to relax by conjugate gradient

I_1

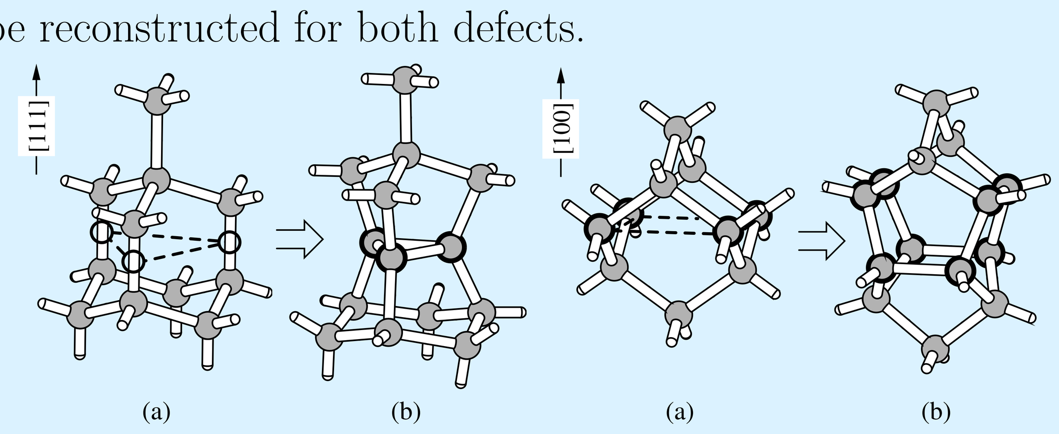
- Relative total energies in eV for I_1 at the T site, the H site and the $\langle 110\rangle$-split configuration.

State	T (T_d)	$\langle 110\rangle$-split (C_{2v})	H (D_{3d})
-1	0.15	0.00	0.40
0	0.00	0.05	0.16
+1	0.00	0.60	0.54
+2	0.00	1.19	1.02

- The formation energy for the interstitial at the T site in the neutral charge state is found to be 3.4 eV.
- The T-interstitial possesses a t_2-level in the upper part of the gap which is occupied by two electrons when neutral.
- The single donor level of I_1 at the T site is above the conduction band and thus the interstitial is always ionised at the T-site. On the other hand, the [110] split interstitial has a donor level close to E_v and thus is only neutral in this site. Hole trapping of the neutral defect must then lead to a switch to the T-site and subsequent electron trapping would reverse this site change. In this way rapid athermal diffusion could occur at low temperatures in the presence of irradiation.
- We find the second donor level of I_1 at the T-site to lie at $E_c - 0.08$ eV and about 0.31 eV above the level attributed to AA12. This is at the very upper limit of the error expected in the method.
- In the positive charge state, the isotropic hyperfine interaction with the nucleus of the unique Si atom is almost zero consistent with the 1.5 % low value seen experimentally for AA12.
- The H-site is a saddle point on the diffusion path of I_1^{++}. The barrier in this charge state is found to be about 1 eV which corresponds to an annealing temperature of around 350 K consistent with the anneal of the AA12 centre. In the metastable neutral charge state the diffusion barrier for T-H-T path is found to be below 0.2 eV which is also consistent with the measured annealing of AA12 around 80 K under minority carrier injection.

I_3 and I_4

- Recent work has found that another than the here presented form of I_3 has lower formation energy but is much more mobile. The suggestion is then that both forms arise in irradiated material but the immobile form of I_3 described here persists to 300 °C while the mobile one is rapidly lost.
- A trigonal I_3 centre is obtained by placing three interstitial atoms at the centres of adjacent [111] bonds (left figure). I_4 is constructed by replacing four atoms by dumbbells orientated along [100] (right figure). The bonds of the interstitials can all be reconstructed for both defects.



- Although the defects are fully coordinated, a gap level is induced by the compressive stress for both structures. The I_3 defect can bind excitons with a localised hole leading to optical lines around 1 eV whereas I_4 has a donor level between $E_v + 0.16$ and $E_v + 0.27$ eV. This result is consistent with the correlation of the $E_v + 0.29$ eV hole trap with the B3 centre. No other electronic levels are calculated to lie within the band gap.
- Calculations show that vacancy defects possess weak reconstructed Si–Si bonds therefore such defects could not give rise to local modes lying above the Raman frequency. For I_3 we calculate a symmetric LVM lying just above the Raman frequency at 74 meV consistent with a strengthened Si–Si bond. This suggests that the W defect is interstitial related and its trigonal symmetry indicates I_3 as a likely candidate.