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Optical bands related to dislocations in Si

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Abstract. First-principles calculations are used to investigate the interaction of self-interstitial aggregates with the 90° partial dislocation in Si. We find that I_4 is bound to the line with an energy of around 3 eV. The defect causes deep levels to appear in the band gap and optical transitions between these levels may account for the luminescent bands relating to plastically deformed Si.

1. Introduction

The origin of the D1 to D4 photoluminescent bands at 0.807, 0.870, 0.935 and 1.0 eV detected [1] in plastically deformed Si is unknown. The intensities of the bands are affected by impurities like oxygen and Cu but their exact effects are unclear [2–4]. The bands are correlated with dislocations and are stable to around 1000 °C. It has been inferred from cathodoluminescence measurements that D1 and D2 originate from Lomer–Cottrell dislocations while D3 and D4 come from straight 60° dislocations [5]. Similar luminescent bands are seen in SiGe epilayers, up to at least 800 °C, although their energies are red-shifted by about 0.1 eV [6]. Suezawa and Sumino [2] find that the D1 band is polarized along the principal dislocation line direction ($\langle 110 \rangle$) and that D1 and D2 split into two components on application of $\langle 100 \rangle$ and $\langle 110 \rangle$ stress while D3 and D4 are split for $\langle 111 \rangle$ stress into components with different polarization characteristics. Other studies dispute the polarization properties, finding D1 and D2 to be polarized with the $\boldsymbol{E}$-field perpendicular to the glide plane [7, 8]. Fukatsu *et al* [9] show that the radiative lifetimes vary between 0.20 and 1.52 μs for D1 and D2 and 37 and 46 ns for D3 and D4.

The prevalence of the bands—seen in FZ and CZ n-Si and p-Si as well as SiGe—leads one to doubt whether impurities are *primarily* responsible while kink and jog densities are sensitive to annealing conditions. Spatially resolved cathodoluminescence measurements demonstrate that D3 and D4 originate from dislocations, but D1 and D2 appear mainly to arise from point defects lying in a Cottrell atmosphere surrounding the dislocation core [10]. This is surprising given that the bands are stable to around 1000 °C. At room temperature the D1 to D4 bands are quenched and a new luminescence band at 0.77 eV emerges which is localized to the dislocation core [11]. Its polarization properties are however unknown.

It does seem likely that the reconstructed cores for the 90° and 30° partials favoured by theory [12] cannot lead to optical transitions as low as around 0.8 eV. The prevalence of the bands—seen in FZ and CZ n-Si and p-Si as well as SiGe—lead one to doubt whether impurities

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are *primarily* responsible while kink and jog densities are sensitive to annealing conditions. We have recently suggested that interstitial or vacancy clusters bound to the dislocation line might be responsible for the optical activity [13] and here we report on initial calculations aimed at testing this idea.

The rationale for this suggestion stems from studies [14, 15] which have linked tri- and tetra-self-interstitial defects (I_3 and I_4) with prominent optical lines. These are, respectively, the W (or I1) line at 1.018 eV and the X (or I3) line at 1.0398 eV. These defects anneal out around 200 and 500 °C respectively. Since the dislocation is a sink for interstitials, we anticipate that interstitial clusters will accumulate at the core in a stable form. Smaller clusters with low binding energies will dissolve and larger ones grow. If I_4 is stable at the core, then we expect it to be associated with an optical line in the vicinity of 1 eV. It seems then important to investigate the optical properties of the defect when bound to the dislocation.

We applied two distinct computational methods for our calculations: *scc-DFTB* (**s**elf-**c**onsistent **c**harge **d**ensity-**f**unctional-based **t**ight-**b**inding method) [17] and *AIMPRO* (***ab i**nitio* **m**odelling **pro**gram) [18]. This means that the geometrical optimization is solely done with the more approximate *scc-DFTB*. The so-gained atomic positions are kept fixed for *AIMPRO*. Thus, in this work *AIMPRO* is used for the calculation of electronic properties only.

2. Results

2.1. The isolated tri- and tetra-self-interstitial defect in silicon

We modelled I_3 and I_4 following Coomer *et al* [14, 15]. As can be seen in figure 1, the trigonal I_3 centre is obtained by placing bond-centred atoms on three adjacent [111] bonds. Those three atoms lie in the {111} plane and their dangling bonds reconstruct, so all atoms are fourfold coordinated.

To form I_4, four next-nearest-neighbour atoms lying on a (100) plane are each replaced by [100]-oriented atom pairs. The dangling bonds of the four split interstitials can reconstruct and be eliminated as shown in figure 1. Just as in the case of I_3, all atoms are then

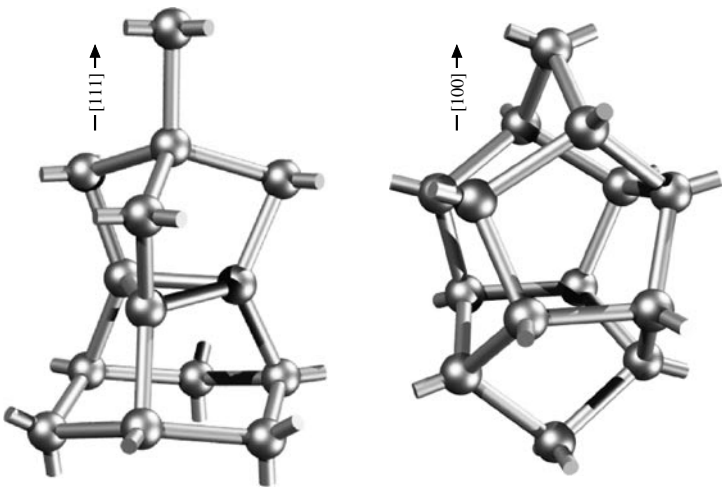

Figure 1. Schematic diagrams showing the structure of I_3 and I_4 according to previous work [14,15]. Left: the structure of the trigonal I_3. All bonds are reconstructed, thus leaving no dangling bonds. Right: the lowest-energy structure of I_4. Like for I_3, all atoms are fourfold coordinated.

fourfold coordinated. For further details on both interstitial complexes, we refer the reader to Coomer *et al* [14, 15].

2.2. The isolated 90° partial dislocation in silicon

One of the most common dislocations in silicon is the 60° dislocation. It lies on {111} planes and is dissociated into 30° and 90° partials separated by an intrinsic stacking fault [19–21]. The dislocation line lies along $[01\bar{1}]$. The energetically favoured partials are of the glide type [22] which means that their dangling bonds lie almost in the {111} glide plane allowing bond reconstruction.

We modelled the 90° partial in a 710-atom cluster where the outside dangling bonds were saturated with hydrogen. Figure 2 shows the reconstructed core structure that we found. The length of the strongly reconstructed bonds is 2.44 Å, very close to the ideal bulk value of 2.35 Å.

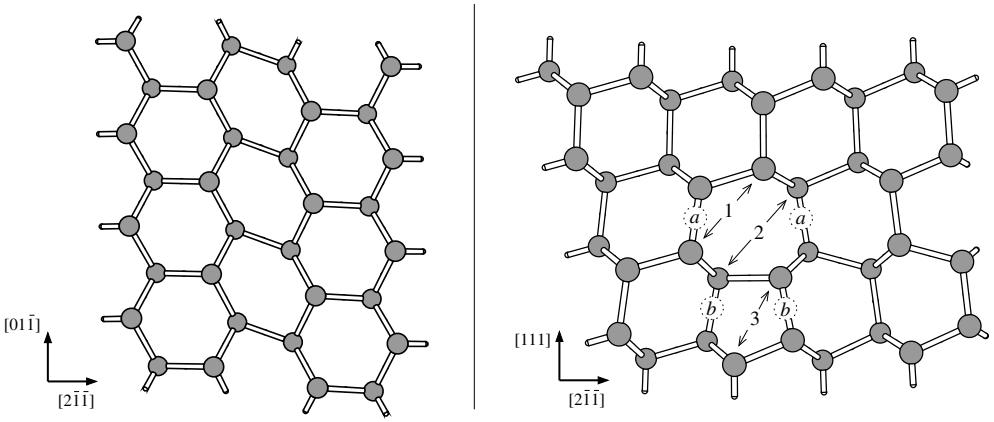

Figure 2. The reconstructed core of the 90° partial dislocation. Left: a view of the core projected onto the {111} glide plane. The dislocation line lies vertical ($[01\bar{1}]$). The two innermost vertical columns of atoms are the core atoms with the reconstructed bonds between them. Right: possible sites for the I_3 and I_4 self-interstitials at the dislocation core. 1, 2 and 3 each refer to a site for I_4 next to the dislocation core. The corresponding arrows point to those atoms, that are replaced by [100]-oriented atom pairs. To construct an I_4, this has to be done in the plane shown and the underlying plane. a and b refer to I_3 sites. The corresponding dashed circles show the positions of the bond-centred atoms. To construct an I_3, an additional bond-centred atom has to be placed in the underlying plane at the right-hand position for a and for b.

Since the core has no dangling bonds and the reconstructed bonds are almost bulk-like, it can be expected to be electrically inactive. Indeed, we find no deep states in the gap. A change in the density of states at the conduction band edge, however, indicates shallow states that might act as electron traps. Such states are observed experimentally at misfit dislocations near the GeSi/Si interface by Batson [23].

All results on the isolated 90° partial are in good agreement with previous work [24].

2.3. Interaction of self-interstitials with the dislocation core

Figure 2 shows possible sites for the I_3 and I_4 self-interstitials at the dislocation core. To obtain the energy difference between these structures and the respective I_n defect in ideal bulk material, these centres were also placed at sites several lattice constants away from the core.

Table 1 gives the differences in energy for all of the defects. Sites 1 and 2 in the sevenfold ring are lower in energy by more than 3 eV than site 3 where I_n is placed in the much smaller fivefold ring. The energy of the binding of I_4 to the dislocation core is 3.1 eV (site 1), while I_3 is bound by 1.8 eV (site b); thus the stability of I_3 within the core is considerably weaker than that of I_4. I_3 is also bound weakly to the stacking fault, by 0.8 eV. Several other sites for I_3 and I_4 have been investigated, but these all lead to negligible binding energies.

Table 1. Differences in total energy $\Delta E = E - E_{\text{bulk}}$ between the sites examined for the I_3 and I_4 self-interstitial and a site in the bulk-like region. Negative numbers mean that the site is preferred to the bulk site. 1, 2, 3, a and b refer to the sites shown in figure 2, and s to a stacking fault site for I_3.

	I_4			I_3		
	1	2	3	a	b	s
ΔE	−3.10 eV	−2.75 eV	+0.60 eV	−1.83 eV	−0.80 eV	−0.80 eV

We now describe the properties of the lowest-energy structure for I_4 at the dislocation core at site 1. Figure 3 reveals its structure which is very similar to the that of the isolated defect. There is, however, a slight twist due to the dislocation core and the D_{2d} symmetry of the defect is lost.

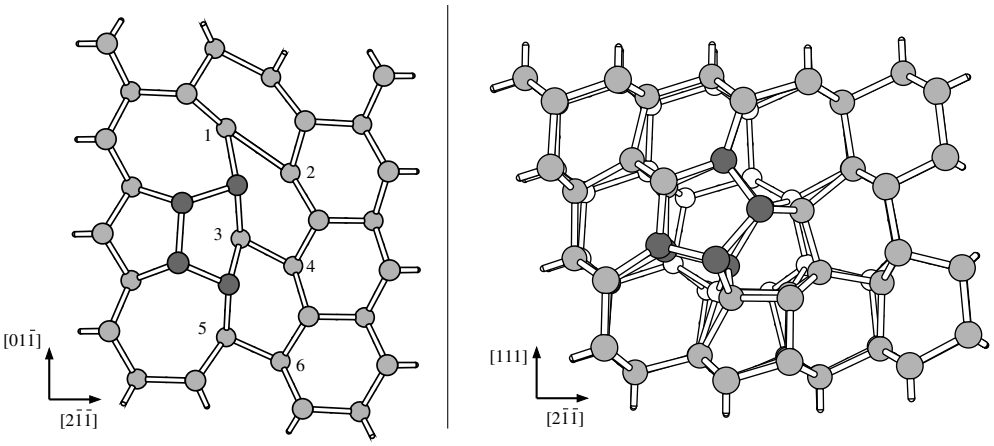

Figure 3. The lowest-energy structure of I_4 at the dislocation core (site 1; see figure 2). Left: all atoms are projected onto the {111} glide plane. The two I_4 atom pairs approximately in the plane are shown dark grey. Right: all atoms are projected onto the {01$\bar{1}$} plane. The four I_4 atom pairs are shown dark grey, atoms in the same {01$\bar{1}$} planes light grey, those in the underlying planes white.

In contrast with the modest change to I_4, the dislocation structure is heavily distorted. Comparing figure 3 with figure 2 reveals that the bond between atoms 1 and 2 is considerably stretched and attains a bond length of $b_{1,2} = 3.13$ Å. The other two dislocation core bonds near I_4 possess almost bulk-like lengths similar to those of the undisturbed core ($b_{3,4} = 2.37$ Å, $b_{5,6} = 2.38$ Å). The bond angles at atoms 1 and 2 (figure 3) range from 155° to 49°. Once again these atoms show the largest distortion. It may be that this large distortion arises from unfavourable starting coordinates and further calculations are in progress to test this.

Nevertheless, placing the tetra-interstitial at the dislocation core causes significant changes to the electronic structure. As shown in figure 4, the isolated I_4 (I_4 in bulk Si) induces several Kohn–Sham levels in the gap: a singlet and a doublet near the valence band edge and a second

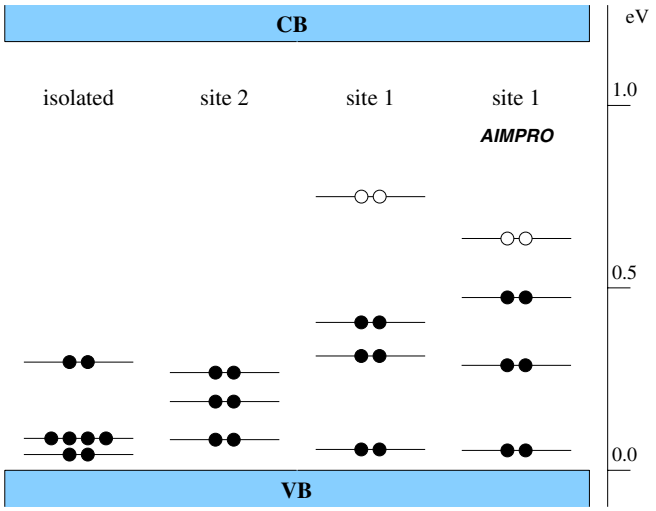

Figure 4. Kohn–Sham levels of I_4 in bulk Si (isolated) and at the two energetically favoured sites at the core of the 90° partial dislocation. The band gap has been scaled to the experimental value of ∼1.2 eV. All levels in the gap have been scaled accordingly. The level positions are based on the *scc-DFTB* results. For the lowest-energy configuration (site 1) the more accurate *AIMPRO* result is given as well.

singlet further up in the gap. As described above, the symmetry of I_4 is disturbed at the dislocation core. Thus we expect the doublet to split into two singlets for site 1 and 2 and this can displace occupied levels upwards towards the mid-gap. Indeed we find three occupied singlet states in the band gap for I_4 at both sites. One singlet has been pushed down into the valence band. The strong distortion of the dislocation core for site 1 gives rise to an empty level in the upper half of the band gap. For both sites there are further unoccupied levels at the conduction band edge, which are not shown in figure 4.

The lowest energy structure found by *scc-DFTB*, where I_4 is bound to the core of the 90° partial at site 1, has been investigated using *AIMPRO*. Figure 4 shows the energy levels in the vicinity of the band gap. In a H-terminated cluster, the energy gap of 2.9 eV exceeds the bulk value by a significant factor, and in the following, we have scaled the levels to bring the gap for the ideal cluster into agreement with the bulk value. This procedure when applied to the isolated I_4 defect gives an optical transition around 0.9–1.0 eV in fair agreement with the X line (1.0398 eV).

For the I_4 defect bound to the partial dislocation, filled levels are found at $E_v + 0.0$, 0.08, 0.30 and 0.41 eV, and empty levels occur at $E_v + 0.66$ and $E_v + 1.18$ eV. The dipole matrix elements for the 0.77 eV transition between the $E_v + 0.41$ and $E_v + 1.18$ eV levels have been evaluated and yield a radiative lifetime of about 1 μs and a polarization parallel to the dislocation line.

Thus the transition could account for the 0.707 eV dislocation-related band.

3. Discussion

Our calculations suggest the following:

(a) Straight 90° partials have no deep gap states and cannot explain the 0.707 eV dislocation-related band.

(b) The correlation of I_4 with the optical centre, stable to 500 °C, associated with the 1.098 eV X line, the B3 EPR centre and possibly with the $E_v + 0.29$ eV DLTS level, suggests that interstitial defects can be efficient optical centres. These defects are strongly bound to the dislocation core and could account for the optical band.

(c) An important consequence of our model is that there should be a correlation between the optical bands with donor levels around $E_v + 0.4$ eV. Feklisova *et al* [26] studied deformed FZ and CZ p-Si. No PL bands were detected in FZ-Si, except after Cu contamination, but the bands were present in CZ-Si. However, their intensities decreased upon extended annealing and could not be regenerated by Cu doping. A DLTS band around $E_v + 0.47$ eV, possibly a donor band, was detected in CZ-Si while distinct shallower states were found in FZ-Si. The deep $E_v + 0.47$ eV band disappeared with annealing in a similar way to how the optical bands disappeared, although there was little change to the EBIC signal. There is then evidence for such a correlation.

(d) Our calculations also find a deep acceptor level around $E_c - 0.5$ eV. Although DLTS levels are detected in the upper half of the gap, they do not appear to be correlated with the optical bands. Staiger *et al* [27] found that as-deformed n-Si has a dominant electron trap (probably an acceptor) at $E_c - 0.32$ eV. This was shifted by Cu doping to $E_c - 0.59$ eV, and eliminated by hydrogenation. Confusingly, the D1 to D4 bands were found to be *suppressed* by Cu doping, while D1 and D4 are strongly changed after hydrogenation but not apparently eliminated. Thus there does not appear to be a simple correlation between this acceptor level and the PL bands.

(e) We found a strong binding energy of around 3 eV for I_4 with the 90° partial. Now the binding energy of four neutral interstitials in I_4 itself is 6.9 eV and hence the energy of dissociation of I_4 into four isolated self-interstitials, I_1, is $B = 9.9$ eV.

Consider now the dissolution of I_4 bound to one of the N_{dis} dislocation sites into the $N \sim 5 \times 10^{22}$ cm^{-3} lattice sites of the bulk lattice. Assuming equilibrium between the free I_1 and bound I_4 we have

$$\frac{N_{\mathrm{I_4}}}{N_{\mathrm{dis}}} = \left(\frac{N_{\mathrm{I_1}}}{N}\right)^4 \mathrm{e}^{B/kT}. \tag{1}$$

We take a dislocation density of 5×10^5 cm^{-2} and suppose that at low temperatures there is an I_4 defect about every ten spacings of $b = 3.8$ Å along the partial, corresponding to a volume density of about 1.3×10^{12} cm^{-3}. This is comparable with the measured density of hole traps around $E_v + 0.47$ eV found in DLTS studies on p-Si [26]. Then the concentration of dissolved I_1 is negligible at temperatures up to T_c where

$$\frac{B}{kT_c} = \ln\left\{\frac{N}{N_{\mathrm{dis}}}\left(\frac{N}{N_{\mathrm{I_4}}}\right)^3\right\}. \tag{2}$$

Using $B = 9.9$ eV gives $T_c \sim 950$ °C which is clearly compatible with the experimental stability.

(f) The I_4 defects are electrically active at the core of the partial and the $E_v + 0.4$ eV donor level could account for the dislocation-related 0.707 eV band.

(g) The absence of the bands in deformed FZ-Si, and their elimination by extended annealing in CZ-Si, suggests that oxygen, or Cu, contamination is needed to create the I_4 defect. To explain the reduction of the bands with larger concentrations, and/or extended annealing treatments, we suppose that larger concentrations of interstitials promote dislocation climb or lead to larger interstitial aggregates which can become detached from the dislocation. Eremenko and Fedorov [28] report that arrays of microdefects lie on the slip plane of a moving dislocation and that these microdefects inhabit (113) slip planes similar to those of

the (113) self-interstitial aggregate [25]. We are not aware, however, of any reports that the 903 meV PL band associated with (113) defects [29] is detected in plastically deformed Si. This observation seems important as it suggests a direct link between interstitial aggregates and dislocations.

(h) Perhaps a direct test of our model would be to neutron or proton irradiate plastically deformed FZ-Si to create interstitials. Annealing should lead to their accumulation on the dislocation in the same way as for those generated by, say, oxygen precipitation. The optical bands should then appear and disappear in a similar way to those for annealed CZ-Si.

(i) Finally, we note that the I_4 defects bound to dislocations are candidates for the strong obstacles whose separation is $\sim$26 spacings that limit the dislocation velocity [30].

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