Interstitial aggregates and a new model for the I_1/W optical centre in silicon

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(August 3, 1999)

Abstract

First principles local-density-functional (LDF) theory is employed to investigate the properties of di-interstitial (I_2), tri-interstitial (I_3) and tetra-interstitial (I_4) structures in silicon. We show that a tri-interstitial defect can account for many of the fundamental properties of the I_1/W-optical centre which is observed in irradiated, annealed silicon.

Keywords: silicon, *W*-line, interstitial, aggregation

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It is well known that following the annealing of electron or ion irradiation of silicon or germanium, extended structures are generated that are observable with transmission-electron-microscopy (TEM). These 'rod-like' defects lie along [110] on a {311} habit-plane. The proposed model [1] is that of a [110] chain of self-interstitials which is inserted down a [110] channel. The TEM results are well matched by this model if a bonding rearrangement on both sides of the chain is included. This 'bond-switching' process has been shown to significantly lower the energy of the extended structure [2].

In contrast to the wealth of information on the extended defects, there is little published data concerning the first stages of the aggregation process of self-interstitials. One assignment has been made of a di-interstitial structure to the electron paramagnetic resonance (EPR) spectrum, P6 [3]. However, this model is not universally accepted.

The I_1/W-optical centre is observed in silicon which has been exposed to lattice damaging treatments with subsequent annealing at around 500 K. It is seen in both n- and p-type silicon following self-ion irradiation [4]. The centre is characterised by a sharp peak at 1018.2 eV and an associated phonon sideband, containing local vibrational modes (LVMs). Uniaxial stress measurements reveal the defect symmetry to be trigonal. Although this intriguing centre has received much attention by both experimentalists and theorists, a definitive model is still lacking.

It is generally accepted that the W-centre arises from the agglomeration of an intrinsic species. Much work in the past has concentrated on the defect being vacancy related [5–7] but more recent experiments [4,8,9] have supported the interstitial nature of the W-centre. We review this information now:

1. The LVM detected in luminescence, with energy 70.0 meV is consistent with a strengthened Si–Si bond. Calculations [10] have shown that the optimisation of vacancy defects leads to the lengthening of Si–Si bonds and such defects could not give rise to local modes lying above the Raman frequency [8].

2. The stress response of the *W*-optical line is two orders of magnitude smaller than that of the 1039 meV line in silicon which is believed to be a vacancy aggregate [8]. Also the shift of the *W*-luminescence line with stress is very much smaller than that of V_6(the B_{80}^4 luminescence centre) [11,12]. Analysis of the *W*-vibronic sideband suggests that the *W*-defect is less compressible than bulk Si [8]. Such a low stress response would be expected for an interstitial defect where bonds are compressed.

3. The release of interstitials from irradiation damage regions during annealing has been tentatively correlated with the growth of the *W*-centre [13].

4. Although the existence of the *W*-centre is not dependent on the presence of any impurity, the effect of carbon and oxygen impurities on the defect concentration has also been used to argue that the defect is interstitial related [9].

Following annealing at around 500 K of He, Ne, Ar or Kr ion-bombarded silicon, a new family of trigonal centres are observed. Although the new zero-phonon lines and associated LVM sideband structures are qualitatively the same as the *W*-centre, the system is red-shifted by between 1–10 meV, depending upon the identity of the noble-gas atom. The one-phonon replicas of the noble-gas related defects are also shifted slightly relative to the *W*-centre one-phonon replica. Davies *et al* [8] claims that this effect is consistent with a strain interaction between the noble-gas atom and the *W*-centre, i.e., the noble-gas atom lies close to the *W*-centre and, although no *chemical* bonding takes place, the presence of the noble-gas atom perturbs the electronic and geometric structure of the *W*-centre.

Comprehensive studies of Ar ion-beam etched silicon [14] have indicated that an unexpected and enhanced diffusion process takes place before the *W*-like defect forms. The observed depth profile of the noble-gas related centres suggests that the argon atoms are penetrating deeper into the sample than expected – up to 1 μm. The diffusion co-efficient was estimated to be $D = 5 \times 10^{-14}$ cm^{2}s^{-1}. Using $D = \nu a^2 e^{E_b/kT}$ where ν is the attempt frequency ($\sim 10^{13}$ Hz) and a is the diffusion length (~ 3.0 Å), this leads to a barrier height of E_b=0.65 eV. Implantation [15] and permeation [16] studies show that helium diffuses with an activation energy between 0.8 and 1.3 eV. Since the argon atom has almost twice the covalent radius of He, one would expect the diffusion barrier of Ar to be significantly greater than 0.65 eV.

Although it is thought that the thermal migration barrier for the self-interstitial is greater than 1 eV, the interstitial has been observed to undergo an enhanced diffusion at cryogenic temperatures [17]. Recent studies of irradiated silicon [18] have obtained a value of 0.065 ± 0.015 eV for the migration energy of the silicon self-interstitial under ionising conditions. Therefore, the anomalous diffusion of Ar could be explained by an interstitial mechanism if:

(a) A binding energy exists between the isolated self-interstitial and the noble-gas atom.

(b) The presence of the self-interstitial significantly reduces the energy required for the noble-gas atom to move through the lattice.

It has also been suggested [7] that the enhanced diffusion of the noble-gas atom could be due to repulsion from a wave of vacancies released during implantation. However, a microscopic model for this process has not been put forward.

We present the results of state-of-the-art calculations investigating the structures and electronic properties of interstitial defects. The properties of the lowest energy tri-interstitial are compared with the *W*-optical centre.

A local density-functional (LDF) code (AIMPRO [19]) is used. Large, hydrogen terminated clusters are used with composition $Si_{181+n}H_{116}$ ($n = 2, 3, 4$) to investigate the interstitial defects. Several models for I_2 and I_3 are compared in energy. For I_4, the structure proposed by Aria *et al* [20] is optimised. The total energy of the structure is compared with a [110] interstitial-chain element. The positions of all the Si atoms were optimised using a conjugate gradient method. Electrical levels were calculated using a transition-state method described elsewhere [21].

Several structures were considered for I_2. Two similar structures [22,23] were found lowest in energy and both consist of three Si atoms sharing a single substitutional site. The lowest energy form of this type of I_2 defect was found to possess C_{1h} symmetry (see Fig. 1). In this case the two interstitial atoms lie along [110] [23]. Two other structures were found to lie around 0.4 eV higher in energy. The first is formed by placing two parallel [100] split-interstitials at next-nearest-neighbour sites. The second is formed by placing the additional atoms in opposing bond-centred sites either side of a hexagonal ring. Both structures include two atoms which are 3-fold coordinated, all other atoms being fully coordinated. The model assigned by Lee [3] to the P6 EPR centre was calculated to lie $\sim$ 3.0 eV higher in energy with the symmetry constrained to D_{2d}. Removal of symmetry constraints results in a new structure and an energy lowering of 1.1 eV. However, the resultant defect has little in common with the ground state structure proposed by Lee.

The lowest energy tri-interstitial investigated possesses C_{3v} symmetry. The structure is formed by placing each additional Si atom at the centre of three parallel bonds which surround a tetrahedral interstitial site (see Fig. 2). Structural optimisation of this structure involves the formation of a three-atom ring resulting in full four-fold coordination of all atoms. The optimisation was repeated from an asymmetric starting configuration resulting in the same relaxed structure. It is interesting to note that this structure is a three atom section of a [110] interstitial-chain which is a basic element of the {311} planar defects observed following high temperature annealing of irradiated silicon [1].

The electrical levels of the tri-interstitial were calculated. The defect does not appear to possess an $(-/0)$ acceptor level but a possible $(0/+)$ donor level was calculated to lie close to the valence band edge ($\sim E_v + 0.1$ eV).

The I_3 defect possesses a number of LVMs. A symmetric vibrational mode lies at 74 meV, consistent with experiment (70.0 eV). This mode is localised upon unique atoms lying on the principal [111] axis of the defect. The mode shifts by 12 cm^{-1} when one atom is replaced by

^{30}Si, which is in reasonable agreement with the experimentally observed shift of 16 cm^{-1} [8].

A slightly enlarged interstitial cage lies along the principal [111] axis of the tri-interstitial, providing a possible site for noble-gas atoms. The effect of placing an argon atom at this site is to perturb the electronic structure of the tri-interstitial and enlarge the cage surrounding the argon atom. The bond which gives rise to the 74 meV symmetric mode is only slightly perturbed by the presence of the argon. To show that the trigonal symmetry structure was a local minimum, the argon was displaced from its optimised trigonal axis site by ~ 1.0 Å. In the subsequent optimisation the Ar relaxed back to the high symmetry site.

Two I_4 models were optimised. The model suggested by Aria *et al* [20] was found to be significantly lower in energy than a 4-atom [110] interstitial chain element. The optimised structure (Fig. 3) compares well with that calculated by Aria *et al.* All atoms are 4-fold coordinated with bond lengths and bond angles distorted from their ideal values by no more than ∼10%. The calculations suggest that the (-/0) and (0/+) levels lie within 0.1 eV of E_c and E_v respectively.

In conclusion, we propose a new model for the tri-interstitial in silicon. Its calculated properties agree well with experimental information on the *W*-optical centre. The structure is closely related to the {311} defect structure proposed by Takeda *et al* [1]. We propose a suitable site for a noble-gas atom nearby the tri-interstitial. This structure gives rise to the correct symmetry and the inert-gas atom is expected to perturb the *W*-centre as observed.

Energy comparisons between di-interstitial defects reveal four low energy structures within 0.5 eV of each other. Optimisation of the [100] oriented I_4 structure results in a geometry close to that reported in the previous theoretical calculations of Aria *et al.* Electrical level calculations show that the defect is unlikely to introduce deep levels into the band-gap.

ACKNOWLEDGMENTS

S. Ö. thanks NFR and TFR for financial support. We also thank the ENDEASD network.

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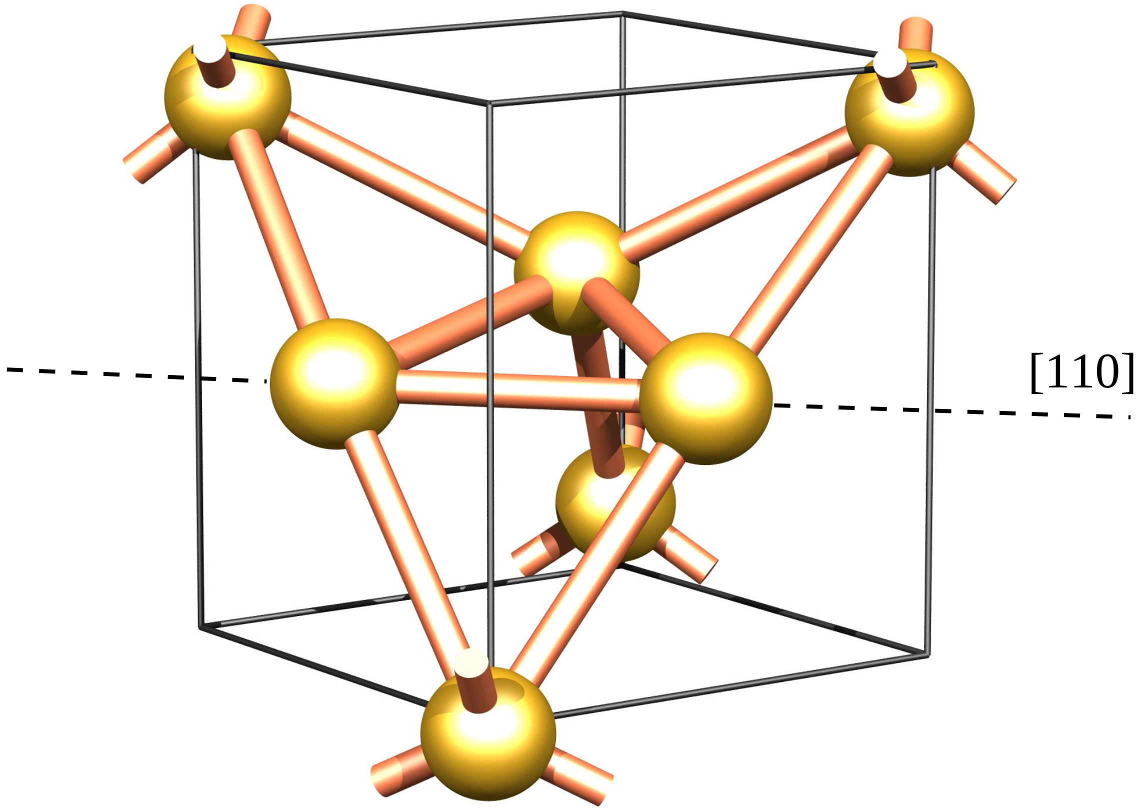
FIGURES

FIG. 1. Optimised structure of the lowest energy form of I_2 investigated. Three Si atoms share a single substiutional site. The two interstitial atoms lie along [110] as indicated.

FIG. 2. (a) A section taken from the ideal diamond structure. To form the tri-interstitial, additional atoms are placed at the bond-centred sites indicated by the black circles. The bond reconstruction that results from the structural optimisation is indicated by the dashed lines (b) The fully optimised structure. A possible site for a noble-gas atom is along $[\bar{1}\bar{1}\bar{1}]$ in the cage adjacent the 3-atom ring

FIG. 3. Optimised structure of I_4. Distortions from the ideal bond lengths and angles are shown.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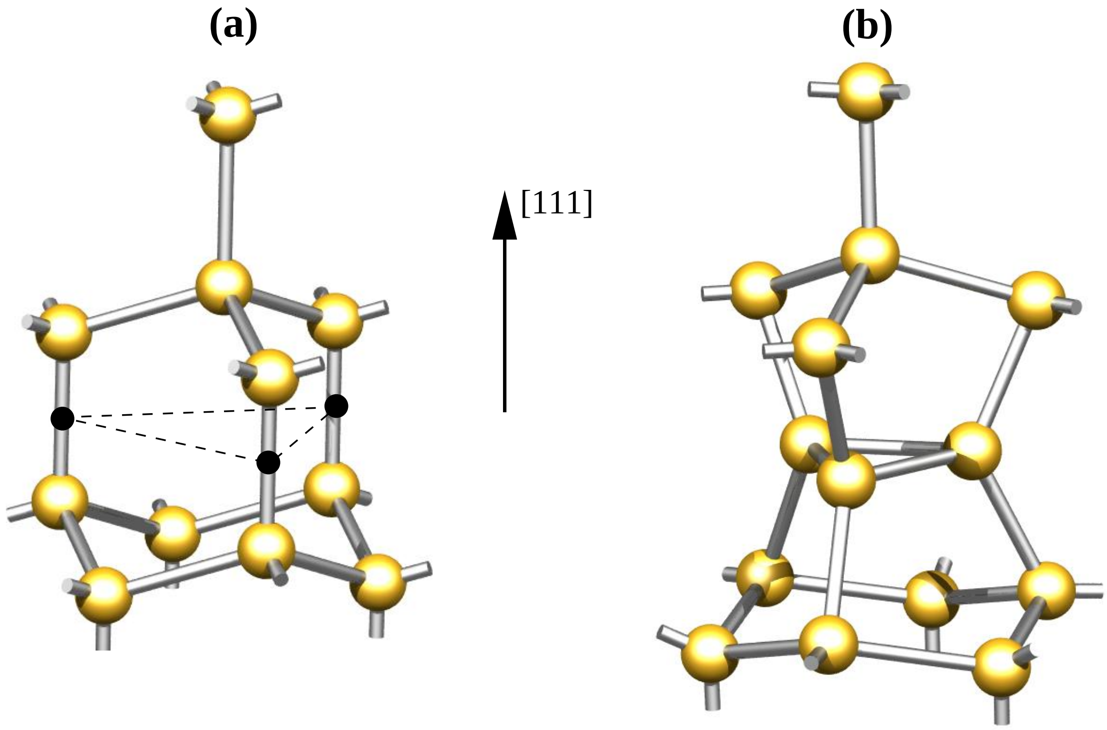
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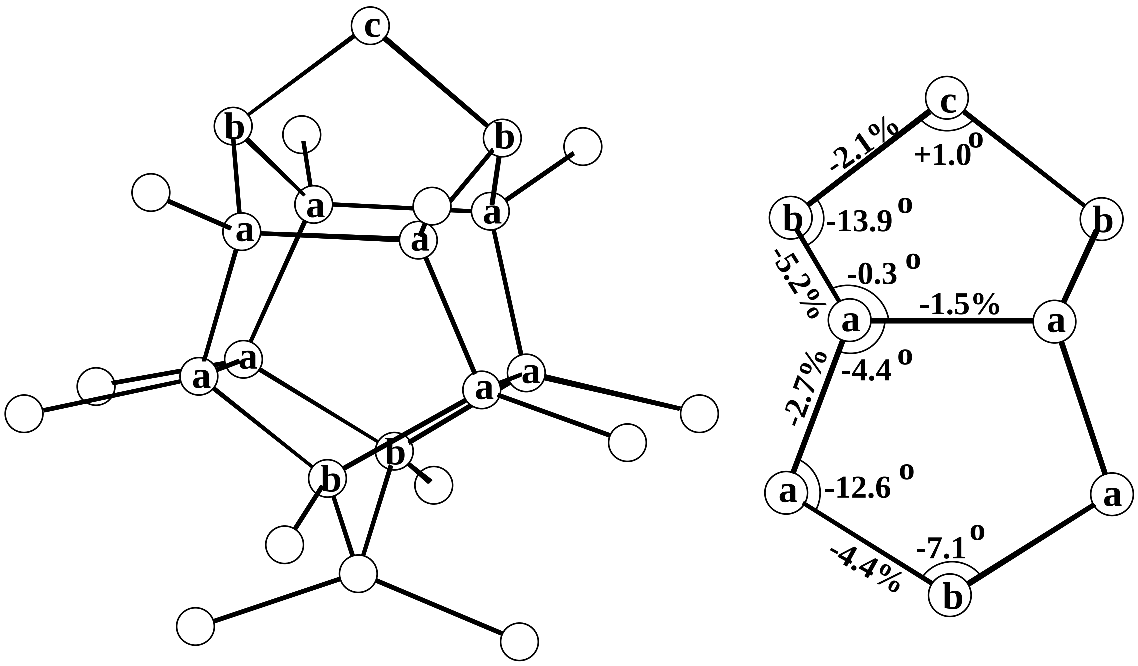
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