Dislocation Related Photoluminescence in Silicon

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Dislocation related photoluminescence in Si and SiGe is attributed to stable interstitial clusters bound to 60° dislocations. Density functional based total energy calculations in Si give binding energies between 1.5 and 3.6 eV for I_3 and I_4 clusters with 90° and 30° partials. They possess donor levels around $E_v + 0.4$ eV which are consistent with deep level transient spectroscopic studies on p-Si. It is further suggested that the clusters would act as the obstacles to the movement of dislocations which may have been observed in recent transmission electron microscopy studies.

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The indirect band gap of Si leads to inefficient interband optical emission, but this could be altered by a modification of the band structure caused by defects trapped in a dislocation strain field. Accordingly, interest in the optical properties of dislocations in Si has increased following reports of efficient room-temperature light emitting Si devices whose operation is related to dislocations [1–3]. Plastic deformation of Si yields several photoluminescent (PL) bands which at low temperatures are labeled $D1$ to $D4$ and have emission peaks at 0.807, 0.870, 0.935, and 1.0 eV [4]. The intensities of the bands are affected by impurities such as oxygen, hydrogen, and Cu, but different groups report contrary results [5]. Spatially resolved cathodoluminescence measurements demonstrate that $D3$ and $D4$ originate from the dislocation cores, but $D1$ and $D2$ appear to arise from point defects, lying in a Cottrell atmosphere surrounding the dislocation core [5]. The same bands are found in CZ-Si which has been annealed to around 1000 °C producing oxygen related extended defects [6], and similar bands shifted downward by ~0.1 eV are detected in relaxed SiGe epilayers [7].

The temperature dependence of the emission is controversial. Microscopic PL studies of the luminescence generated by oxygen precipitates reveal that the $D1$ and $D2$ bands broaden and shift downwards with increasing temperature leading to a room temperature peak at 0.77 eV (D_b band) [8]. The same technique showed that this band originated from the dislocation core in contrast with the low temperature $D1/D2$ bands. Extrapolating the D_b band to cryogenic temperatures gives an emission at 0.83 eV which is close to $D1$.

The structures of common dislocations have been extensively investigated [9] and the prevailing view is that dangling bonds in the cores of 90° and 30° straight and kinked partials are reconstructed although there is uncertainty whether the core of the former partial has double periodicity [10–12]. Consistent with the result that these structures do not introduce deep levels into the band gap are recent electron energy loss spectroscopic experiments on $Ge_{0.35}Si_{0.65}$ [13], and electron beam induced current studies on clean dislocations [14]. Thus dislocations alone are unable to explain the D bands.

Deep level transient spectroscopic studies (DLTS) carried out on plastically deformed (700 °C) p-Si [15] reveal a band around $E_v + 0.47$ eV which has been correlated with the $D1$ to $D4$ optical bands. The density of levels, $\sim 1 \times 10^{12}$ cm^{-3}, corresponds to an upper limit of about one state per ten spacings along the dislocation line. This suggests that the DLTS and PL signals are to be interpreted as effects due to point defects, stable to 1000 °C, attached to the line. Their density would rule out jogs, with separation ~1 μm [16], as a source of the electrical activity. We show here that stable interstitial clusters bound to the dislocation could account for both the PL and DLTS signals.

A single interstitial trapped by the core is most unlikely to be a stable immobile defect surviving beyond 700 °C. Rather it will diffuse along the core until it meets a jog or another defect. If the density of interstitials is greater

than that of jogs, then it is likely to form a di-interstitial. However, the di-interstitial is also expected to be a mobile center as it is not a fully reconstructed defect. Centers which are stable and immobile will naturally be those that are fully bonded as there is then a large energy barrier to break bonds necessary for migration. The growth of these immobile clusters then competes with jog formation, diffusion, and subsequent dislocation climb. Two interstitial defects which are reconstructed are the trigonal tri-interstitial I_3 and tetrainterstitial I_4 shown in Figs. 1 and 2. Previous investigations [17–19] find that they possess levels in the lower half of the gap and that they are the origin of two interstitial related PL bands called the W (or $I1$)—line at 1.018 eV and the X (or $I3$)—line at 1.0398 eV. These defects are formed in irradiated Si and anneal out around 400 and 500 °C, respectively [20].

Here we have investigated their stability and electrical activity when bound to 90° and 30° partial dislocations. A minimal basis self-consistent charge density functional tight-binding method (SCC-DFTB) [21] is used on ~700 atom clusters containing the defects, but more reliable energy spectra were obtained using a self-consistent density functional cluster code (AIMPRO), with 16 Gaussian orbitals per atom, on the resulting structures [22]. The gap is scaled to bring that for the hydrogen terminated cluster into agreement with the experimental one. This procedure when applied to the isolated I_3 and I_4 defects gives optical transitions around 0.8–0.9 eV in fair agreement with the W and X transitions. Using a fully self-consistent density functional method (AIMPRO), we find the binding energy of four interstitials in I_4 to be 6.9 eV [19] in good agreement with 7.24 eV found by a plane wave code [23]. This energy is within about 20% of experimental estimates of the binding energy which lie between 6.5 and 8.3 eV [24] taking the formation energy of I_1 to be 3.3–3.9 eV [25]. The binding energies calculated by SCC-DFTB are within 0.1 eV of the AIMPRO values for the structures considered—a result which probably comes from the saturated bonding in all the defects investigated.

Figure 3 shows the resulting reconstructed core structure found for the single and double period 90° partial and the 30° partial. The SCC-DFTB method gave bond lengths at the dislocation cores within ±3% of the bulk value and identical with those found previously [11]. The energy difference between the double and single period structures, 2 meV/Å, was negligible and consistent with previous calculations [10,11]. Our calculations show that deep states do not arise from any of the partials. We now investigate the effect of adding interstitial clusters to the line.

Figures 1 and 2 show the tri- and tetrainterstitial. Although the defects are fully coordinated, the core compressive stress is sufficient to push occupied levels into the gap as demonstrated by the Kohn-Sham levels shown in Fig. 4. These levels suggest that the defects can bind excitons with a localized hole leading to optical lines around 1 eV.

Figure 3 shows the most stable sites, among 77 different models, of I_3 and I_4 bound to the three partials. These sites involved insertion into the widest $[01\bar{1}]$ channel, labeled A in Fig. 3, resulting in a 2% reconstructed bond elongation in the interstitials. The binding energies between I_3 and the single and double period 90° and 30° dislocations are 3.4, 3.6, and 1.7 eV, respectively (SCC-DFTB). For I_4 with the same partials we obtain 3.1, 2.6, and 1.4 eV. The defects are not strongly bound (~0.8 eV) to the stacking fault. The binding energies are consistent with the high thermal stability of the dislocation related PL.

The electronic structures of the defects are approximately described by the Kohn-Sham energy levels (Fig. 4). In most cases there are both filled and empty levels introduced into the gap by the defects. Although there are variations in the position of the empty level with structure, all the defects induce filled levels in the lower half of the

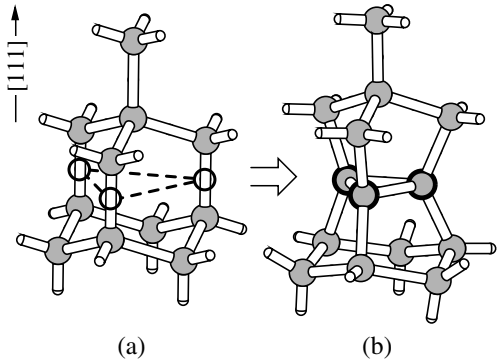

FIG. 1. Schematics showing the trigonal tri-interstitial structure. (a) A section of the ideal silicon lattice. To form I_3, bond centered interstitial atoms are placed on three parallel [111] bonds. The inserted atoms are drawn as circles connected by dashed lines. (b) The energetically optimized structure of I_3. The three additional atoms are outlined in bold. All atoms are fully fourfold coordinated.

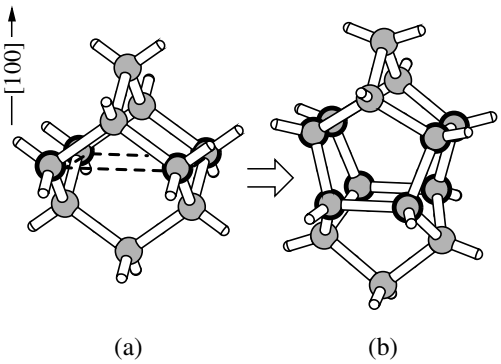

FIG. 2. Schematics showing the tetrainterstitial structure. (a) A section of the ideal silicon lattice. To form I_4, four next-nearest neighbor atoms (outlined in bold and connected by dashed lines) are each replaced by [100] orientated atom pairs. (b) The energetically optimized structure of I_4. The atoms of the resulting four split interstitial pairs are outlined in bold. All atoms are fully fourfold coordinated.

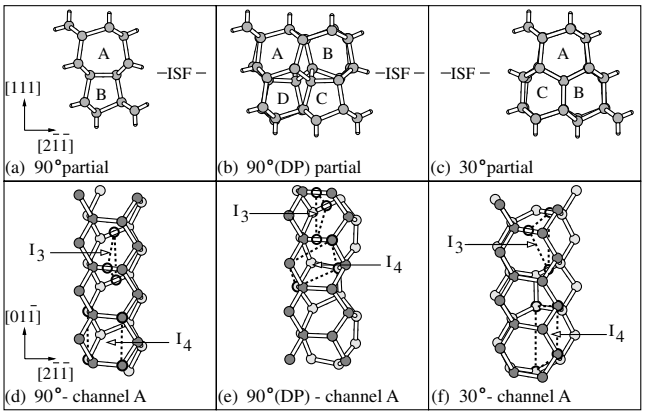

FIG. 3. Optimized core structures of the single period 90° partial dislocation, the double period (DP) 90° partial, and the 30° partial dislocation. (a),(b),(c) View of the three core structures projected onto the $\{01\bar{1}\}$ plane (view along the dislocation line). ISF marks the area where the intrinsic stacking fault extends into the $\{111\}$ plane. Different channels along the dislocation line are labeled A, B, C, and D. (d),(e),(f) View of channel A for the different cores with the lowest energy sites for I_3 and I_4 (compare with Figs. 1 and 2). Atoms in the top and bottom plane are drawn in dark and light grey, respectively.

band gap and in some cases an empty level in the upper. The filled levels lead to donor states around $E_v + 0.45$ eV. These levels suggest that the defects when bound to the core have similar optical properties as the isolated ones. The main differences are that the W- and X-optical transitions around 1 eV due to the I_3 and I_4 defects in the bulk are shifted downwards in energy by 0.1 to 0.3 eV bringing them into the region of the 0.8 eV D_b band.

In summary, the calculations demonstrate that I_3 and I_4 are bound to the dislocation line with energies between 1.5 and 3.6 eV. There is a strong perturbation to the electrical activity of the dislocation with the appearance of occupied states low in the gap, similar to those of the isolated I_3 and I_4 defects, and unoccupied levels in the upper quarter. These states could account for the broad band seen in DLTS studies [15] and the 0.83 eV D_b PL band linked with dislocations [8].

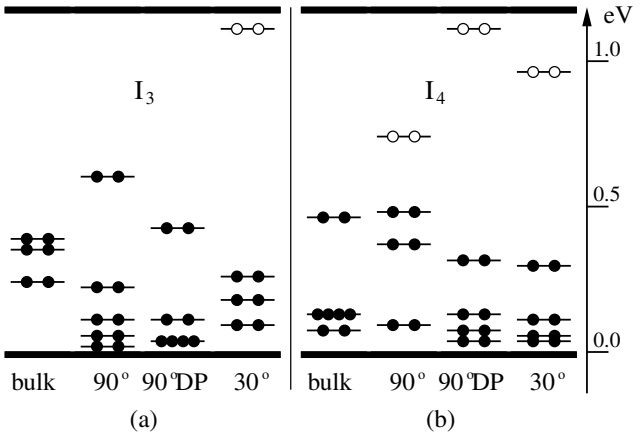

FIG. 4. Kohn-Sham levels of interstitial clusters in bulk Si and at lowest energy sites at the core of the single period 90° partial dislocation, the double period 90° partial (labeled 90°DP), and the 30° partial dislocation. Filled circles indicate electrons. Gap and levels have been scaled linearly so the gap fits the experimental value. (a) The gap levels induced by I_3. (b) The gap levels induced by I_4.

The interstitial aggregates may also be the obstacles which limit the dislocation velocity. There has been a long-standing dispute about whether dislocation glide in Si is due to the generation and propagation of kinks as described by the theory of Hirth and Lothe [26] or controlled by obstacles on the dislocation line [27,28].

According to the former, the mobility of a dislocation is governed by the creation, diffusion, and annihilation of kinks. The activation energy of the dislocation velocity for long segments is then the sum of the kink formation energy F_k and migration energy W. Experimental estimates of these in Si [29] are $0.4 < F_k < 0.7$ eV and $1.2 < W < 1.8$ eV. However, several calculations employing both first-principles and tight-binding methods have given F_k to be significantly lower: around 0.1 eV [30], 0.12 eV [10], or 0.04 eV [31], while W is found to be 1.8 eV [30], 1.62 eV [10], and 1.1 eV [31]. Clearly, the values of F_k are in conflict with experiment. Furthermore, there are difficulties with the Hirth-Lothe theory when the length L of a dislocation segment is less than the average separation between kinks. In this case the velocity is linear in L and its activation barrier controlled by the creation and propagation of a double kink, or $2F_k + W$. The activation energy should then switch from $F_k + W$ for long segments to $2F_k + W$ for short ones, but experiments show that this does not occur [16,32].

Further difficulties come from transmission electron microscopy (TEM) images allowing moving kinks to be observed [33]. Analysis of their movement along the 90° partial gave an activation energy of about 1.24 eV at 130 °C and 1.7 eV at 600 °C. However, in the latter case the kinks were observed to become pinned by obstacles separated by about 100 Å and were subsequently released with an activation barrier of 2.4 eV. The velocity of the dislocation segment is then controlled by kinks released by the obstacles and not by their generation rate.

Although further experiments ruling out radiation damage are required, it is noteworthy that the density of obstacles is of the same order as the density of DLTS levels suggesting that the obstacles could include interstitial clusters. The reorientation energy of I_4 is known to be 2.3 eV [34] and similar to the barrier for dislocation movement. The clusters are then able to follow a moving dislocation. Accordingly, upon release from the core, they will diffuse with every likelihood of reforming on the dislocation. Thus the dislocation maintains its straightness and would not zigzag as indeed observed. Their binding energies suggest they are stable to at least 1000 °C.

Finally, we note that the tetragonal symmetry of the point defects leading to the $D1$ and $D2$ PL bands [35] is

the *same* as the I_4 defect considered here. This suggests that I_4 defects released from the core are responsible for $D1$ and $D2$. The $\sim$0.2 eV lower energy for $D1$ and $D2$ over the X line arises from a transition to a shallow state associated with the dislocation.

In summary, the calculations have shown a strong binding energy of interstitial clusters with the dislocation line. The clusters possess donor levels in the lower half of the band gap and their presence will lead to DLTS levels around $E_v + 0.4$ eV and a PL around 0.8 eV. The latter we identify with the dislocation related D_b band. The clusters may also account for obstacles which control the dislocation velocity and are observed in TEM experiments.

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