

## Graphitization at diamond dislocation cores

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### Abstract

We examine possible mechanisms for graphitization at dislocation cores in diamond, both as an explanation for brown coloration in natural brown diamond and as a model for annealing in amorphous carbon materials. We find a metastable structure for the 90° partial dislocation core where bonds are broken in both single- and double-period structures leading to a row of paired sp<sup>2</sup> C atoms. We examine the effect of hydrogen and other impurities on this core structure both through direct interaction and potential charging effects. We also investigate a mechanism for progressive aromatization through the migration and aggregation of 30° partial dislocations.

### 1. Introduction

Tetrahedral amorphous carbon films have attracted considerable interest because they can be used as an inexpensive and easily produced wide-band-gap semiconductor (2.0–2.7 eV) in the fabrication of heterojunction devices, thin-film transistors and large-area flat-emitter display materials [1].

Diamond films possess extremely useful material properties including extreme hardness, high thermal conductivity and chemical inertness, which makes them suitable for a variety of applications including as abrasives, and in coatings, optics and corrosion protection [2].

Relaxation processes via post-growth annealing are vital for useful diamond or diamond-like films, which usually have large grown-in stresses. Stress relief reduces the chances of delamination. Diamond thin films generally consist of columnar structures containing high concentrations of dislocation loops and stacking faults, as well as varying concentrations of amorphous or graphitic carbon [3].

Post-growth annealing also changes the band gap. There is a supposition for diamond-like films that the reduction in band gap with post-growth annealing can be attributed to the encroachment on the gap by aromatic  $\pi$ - $\pi^*$  states. It is argued that the  $\pi$ - $\pi^*$  gap in DLC decreases as the degree of sp<sup>2</sup> clustering increases, in the same way as it does for polyaromatic molecules [4–9]. It seems that such clustering need not necessarily be aromatic [4].

All sp<sup>3</sup> systems eventually graphitize with temperature (sp<sup>3</sup>-to-sp<sup>2</sup> conversion), but there is evidence that sp<sup>2</sup> carbon atoms can effectively aggregate during annealing, without further conversion of sp<sup>3</sup> atoms [10].

We have used dislocations in crystalline diamond as models for some of the environments and processes occurring within diamond-like carbon and tetrahedral amorphous carbon. Our justification is that a dislocation core shares some of the features of the amorphous state (i.e. non-crystalline ring statistics) and that structural changes are easily identified with dislocation motion. Clearly, the model has most applicability for films with a density approaching that of diamond.

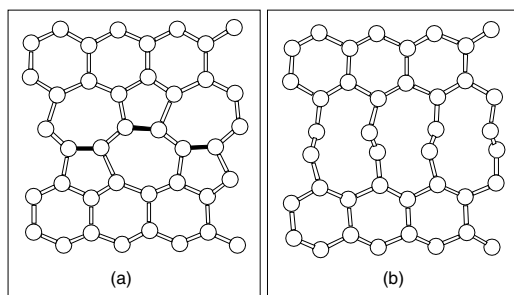
There is also direct interest in the structures that we have found in terms of brown diamonds which are known to contain dislocations [11]. The possibility exists that the sub-band-gap absorptions arise from the  $\pi$ - $\pi^*$  or  $\pi$ - $\sigma$  band transitions in the  $sp^2$  core. We have investigated the possibilities that the cores of dislocations in diamond are graphitized, and/or that dislocations can glide together to form climb dipoles which nucleate graphitic regions.

## 2. Methodology

The dislocations were modelled with both cluster-based (for the  $90^\circ$  partial problem) and supercell *ab initio* local density functional theory with the AIMPRO [13] package which uses norm-conserving pseudopotentials [14] and a basis of s- and p-Gaussian orbitals for the pseudo-wavefunction with four independently varied exponents for C and four for H. The charge density was fitted with s-Gaussians (four for C, three for H). The cluster method places the dislocation in a cluster of carbon atoms whose external dangling bonds are saturated with hydrogen. The energy is then minimized with respect to the atomic coordinates using a conjugate gradient method.

These calculations were performed on  $90^\circ$  partial dislocation cores in diamond. Previous density functional supercell calculations have shown the double-period (DP) structure to be lower in energy than the single-period (SP) structure for the  $90^\circ$  partial in diamond by  $\sim 0.172$  eV  $\text{\AA}^{-1}$  [15] and  $0.069$ – $0.198$  eV  $\text{\AA}^{-1}$  depending on applied stress [16]. For this reason we started with the DP structure.

We examined both the standard DP core model (figure 1(a)), and a modified model where bonds along the core have been broken (see figure 1(b)), allowing core C atoms to pair up into pairs of  $sp^2$ -coordinated atoms. Hereafter we will refer to this structure as the DP  $sp^2$  structure (see figure 1(b)).

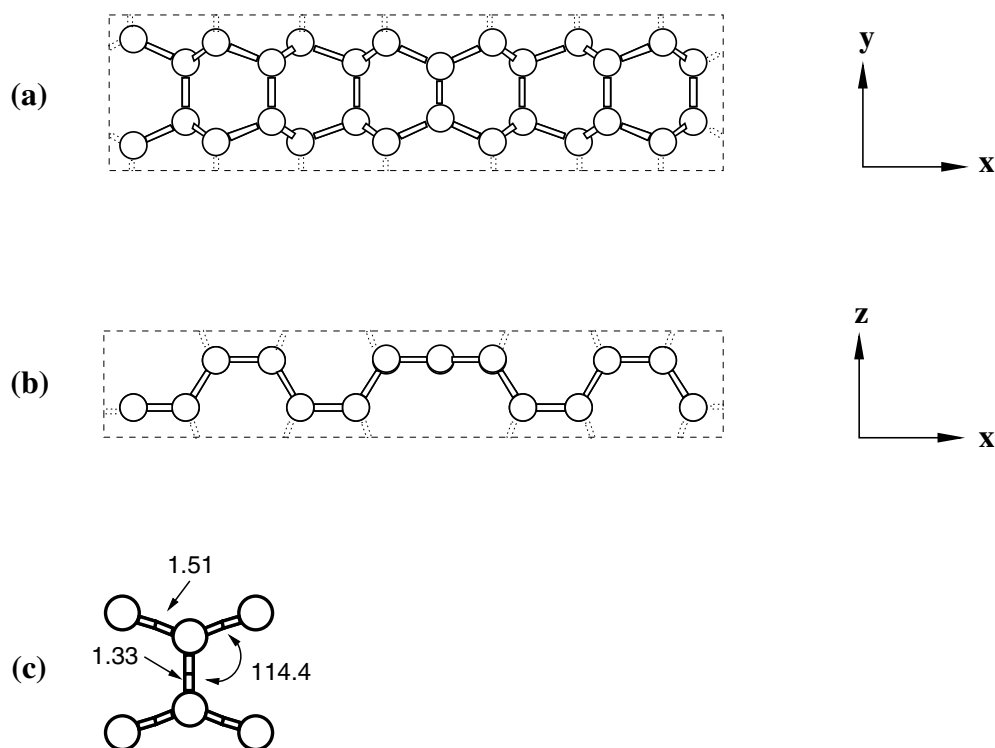


**Figure 1.** The  $90^\circ$  partial dislocation core in diamond; (a) the double-period (DP) structure; (b) the alternative  $sp^2$  paired structure. The black bonds along the dislocation core are broken to create (b).

Calculations used three different cluster sizes, featuring one, two and three repeat units of length  $5.22$   $\text{\AA}$ . Each repeat unit consists of two pairs of  $sp^2$  C atoms, i.e. four carbon atoms along the dislocation core. The cluster sizes were respectively  $C_{60}H_{60}$ ,  $C_{120}H_{92}$  and  $C_{180}H_{124}$ . Since we are using finite hydrogen-terminated clusters, it is necessary to handle the ends of the

dislocation core caused by the cluster surface. For the DP  $sp^2$  structure there are no dangling-bond states at the cluster end, but for the standard DP model it was necessary to terminate both ends with H atoms.

Supercell calculations were performed on a unit cell of diamond containing four  $30^\circ$  partial dislocations. Each unreconstructed partial has an isolated  $sp^2$  atom per repeat. When the  $30^\circ$  partials glide together on neighbouring (111) planes, the result, in our small supercell, is two regions of hexagonal diamond, separated from each other by mirror twin boundaries. Thus the cell contains two pairs of  $30^\circ$  partial dislocations. The unit cell consists of 28 atoms with two pairs of  $sp^2$  carbon atoms and is shown in figures 2(a) and 2(b). The supercell calculations used a Gaussian basis but the charge density was fitted to plane waves with an energy cut-off of 120 Ryd. The Brillouin zone was modelled using the Monkhorst–Pack [17] sampling scheme with two  $k$ -points in the  $x$ -direction and four in each of the  $y$ - and  $z$ -directions which when folding using the symmetry of the supercell gave eight unique sampling points.



**Figure 2.** A side view (a) and a top view (b) of a twin boundary formed from two  $30^\circ$  partial dislocations in diamond on neighbouring (111) glide planes. (c) Bond lengths ( $\text{\AA}$ ) and angles (degrees) for an  $sp^2$  carbon pair in this structure.

### 3. Results

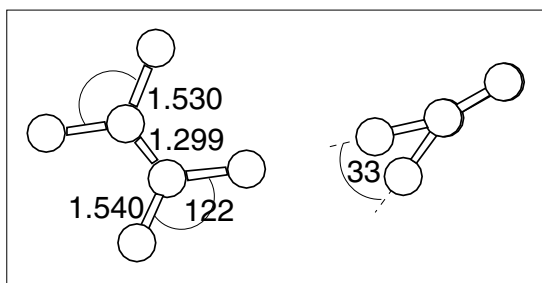
#### 3.1. The $90^\circ$ partial core

The core structure for the DP  $sp^2$  structure is shown in figure 1(b), and is metastable. By comparing the energies of pairs of clusters (either 1 + 2 or 2 + 3 repeat units) in table 1 we find that on average the standard DP structure is 2.28 eV more stable per repeat unit than the

**Table 1.** Relative energies per unit length ( $\text{eV \AA}^{-1}$ ) of the DP,  $\text{sp}^2$  DP and  $\text{sp}^2$  SP structures for the  $90^\circ$  partial dislocation core in diamond. Note that the DP structures are averaged from three cluster sizes (see the text).

Structure	Energy ( $\text{eV/C at core}$ )	Energy ( $\text{eV \AA}^{-1}$ )
$\text{sp}^3$ DP	0.00	0.00
$\text{sp}^2$ SP	0.34	0.26
$\text{sp}^2$ DP	0.57	0.44
$\text{sp}^3$ SP		0.07–0.20 [16]

DP  $\text{sp}^2$  structure, i.e.  $0.57 \text{ eV}$  per C atom along the core. Details of bond lengths and angles are given in figure 3 from which it can be seen that the bond angles are close to  $120^\circ$  and the bond length is close to the value for ethene calculated with the same basis sets of  $1.33 \text{ \AA}$  (experimental value:  $1.339 \text{ \AA}$ ).



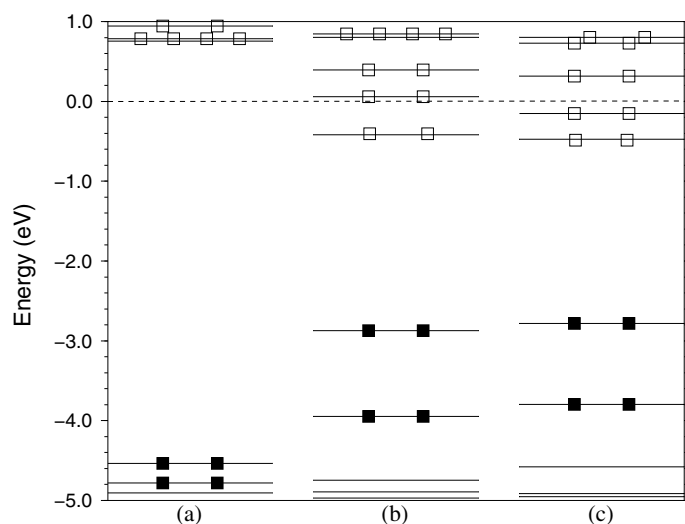
**Figure 3.** Bond lengths ( $\text{\AA}$ ) and angles (degrees) for the  $\text{sp}^2$  carbon pair at the diamond  $90^\circ$  partial dislocation core.

The elevated energy of the  $\text{sp}^2$  structure comes from the close spacing between the  $\text{sp}^2$  pairs which are highly compressed along the core. Hexagonal graphite has an inter-layer spacing of  $3.35 \text{ \AA}$ ; however, the  $\text{sp}^2$  pairs along the core have an average inter-layer spacing of only  $2.61 \text{ \AA}$ , the second-nearest-neighbour distance in diamond.

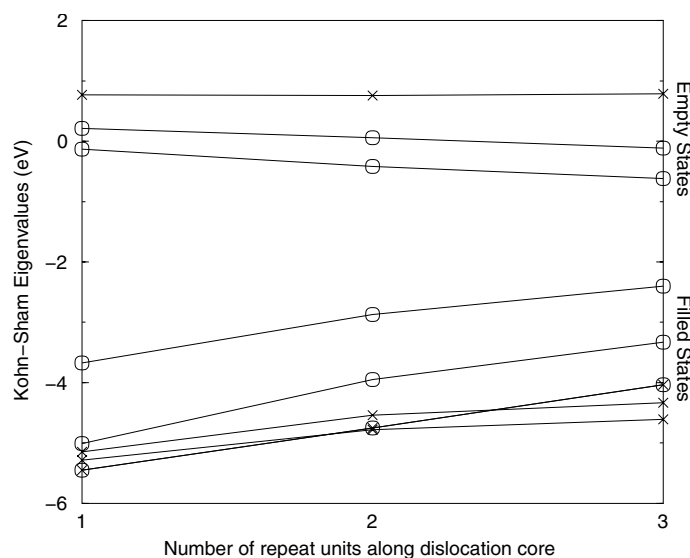
It can be seen from the Kohn–Sham eigenvalues that the  $\text{sp}^2$  core structure introduces various electronic states into the gap (see figure 4, and the variation with cluster size is shown in figure 5), reducing the gap to  $2.2 \text{ eV}$  for three repeat units. The progression in band-gap reduction as the number of repeat units in the cluster is increased is indicative of a strong interaction between  $\pi$ -states along the dislocation and hence of highly dispersive  $\pi$ - and  $\pi^*$ -bands which could cause brown coloration as the number of units increases.

Just as the standard SP and DP structures are linked by a  $90^\circ$  rotation of every other reconstructed bond along the SP core [15], so it is possible to rotate every other reconstructed  $\text{sp}^2$  pair along the  $\text{sp}^2$  DP core to produce an equivalent  $\text{sp}^2$  SP structure. The result is shown in figure 6. Unlike other structural defects in the SP core such as solitons, the bonds affected here are not only the reconstructed bonds lying along the core, but also their neighbours along the side of the dislocation. These form a  $\langle 110 \rangle$  zigzag chain normally, but in the  $\text{sp}^2$  structure alternate zigzag bonds have been broken. Unlike in the DP structure all  $\text{sp}^2$  pairs are aligned. Interestingly this structure is lower in energy than its  $\text{sp}^2$  DP equivalent by  $0.45 \text{ eV}$  per  $\text{sp}^2$  pair, i.e. it is only  $0.34 \text{ eV}$  higher in energy than the standard  $\text{sp}^3$  DP structure per C atom.

This structure could in principle be extended since the dislocation has two sets of these zigzag bonds, one each side of the reconstructed core bonds. Hence another  $\text{sp}^2$  core structure



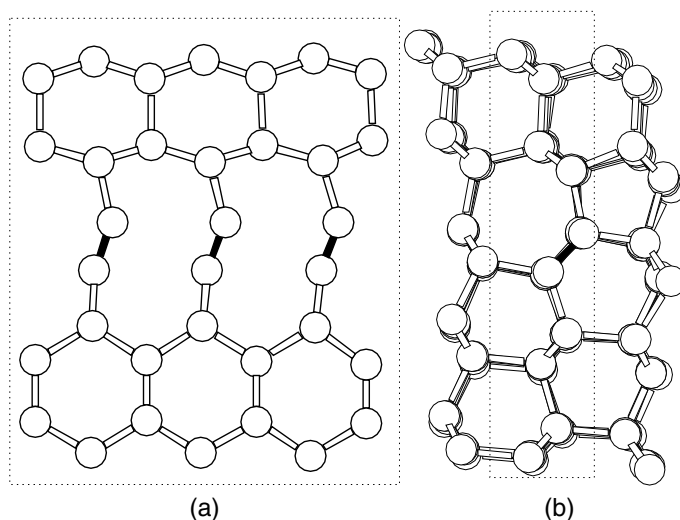
**Figure 4.** Kohn-Sham eigenvalues for  $90^\circ$  partial dislocation in diamond in the (a)  $sp^3$  double-period, (b)  $sp^2$  double-period, (c)  $sp^2$  single-period structure. Levels close to the gap are marked with filled (empty) squares denoting electron occupancy (empty state).



**Figure 5.** Kohn-Sham eigenvalues for  $90^\circ$  partial dislocation for varying cluster sizes: (a) one, (b) two and (c) three repeat units along the core. Note how the gap closes with increasing dislocation length. Circles denote the  $sp^2$  DP structure, crosses the standard  $sp^3$  DP structure.

is one where bonds are broken in this alternate way on *both* sides of the core reconstruction, resulting in chains of four  $sp^2$  C atoms running across the core of the dislocation. We are currently investigating these extended  $sp^2$  cores.

Our standard  $sp^3$  DP core is in reasonable agreement with those in the literature (compared to bulk diamond, minimum C length  $-4.3\%$  ( $-4.4\%$ ), maximum C length  $+10.5\%$  ( $+6.5\%$ ), rms C length  $1.6\%$  ( $2.8\%$ ); bracketed values from reference [15]).



**Figure 6.** A  $90^\circ$  partial dislocation in diamond with a  $sp^2$  single-period (SP) structure. Double bonds linking  $sp^2$ -coordinated C atoms are marked in black. Plane (a) is side view of the plane marked with dotted lines in (b).

### 3.2. Aggregation of $30^\circ$ partials

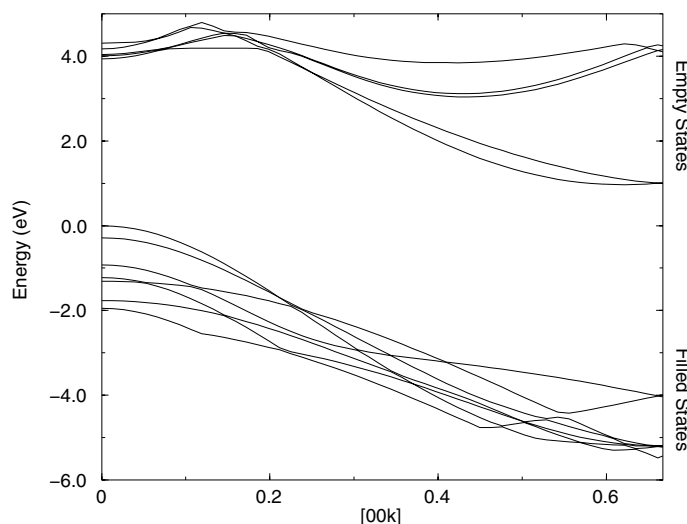
In an effort to understand how  $sp^2$  C atoms might aggregate (and so reduce the  $\pi-\pi^*$  gap) without increasing their number, we studied the means by which the single-period,  $30^\circ$  partial, which has one  $sp^2$  carbon at its core, might begin to form aggregates of adjacent  $sp^2$  carbons. In most dislocation core processes, movement of undercoordinated atoms (e.g. soliton motion) leads to annihilation. Other processes, such as graphitization in the previous section, lead to an increase of  $sp^2$  carbons. Here we have constructed a small model (28 atoms) from cubic diamond in which a  $30^\circ$  partial has migrated from the right cell boundary to the centre along the upper glide plane and another has been migrated from the left along the lower glide plane. The result, in this small supercell, is two regions of hexagonal diamond (corresponding to stacking faults introduced by partial dislocation glide), separated from each other by two boundaries made from the cores of  $30^\circ$  partials. The  $sp^2$  atoms bond to give a column of double bonds (C–C = 1.33 Å) separated by 2.61 Å. Figure 1 shows the relaxed supercell.

The structure is metastable, and higher in energy than the perfect diamond lattice by 1.49 eV per  $sp^2$  carbon atom. The Kohn–Sham band structure around the band gap is shown in figure 7. The  $sp^2$  atoms introduce levels into the gap which reduce the band gap to 3.89 eV at the gamma point compared to 5.57 eV in diamond and 5.85 eV in ethene as calculated using the same methodology.

## 4. Discussion

Although these  $sp^2$  paired structures are metastable and higher in energy than the fully reconstructed  $sp^3$  core structures, it is possible that they will form locally for any combination of the following reasons:

- (a) *Vibrational entropy, assisting graphite formation at raised temperatures.* It is highly likely that they will act as nucleation points for graphitization from within bulk diamond as the temperature is raised.



**Figure 7.** The top section of the Kohn-Sham band structure for the periodic  $(2\bar{1}\bar{1})$  mirror twin boundary; the abscissa shows the distance along the  $z$ -axis of the unit cell in cartesian space (atomic units); see figure 2.

- (b) *Charging.* The  $\pi$ -states in the gap will trap charge carriers and the  $sp^2$  formation energy will thus reduce.
- (c) *Impurity effects.* It is known that H has a profound effect on the structure and mobility of dislocations in silicon [18, 19]. Recent calculations for H in diamond show that 2H atoms are more stable at a  $90^\circ$  partial dislocation core than in the bulk [12]. CVD diamond shows higher H concentrations in regions of brown coloration in diamond, so it is not unreasonable to speculate that H will be present in dislocation cores in diamond. In this case H can act to terminate lengths of  $sp^3$  reconstructed core and it is possible that short core regions between H atoms will reconstruct pairwise as  $sp^2$ , as shown here. Other impurities such as N, B and point defects such as V may well have similar effects, preferring reduced coordination which thus terminates  $sp^3$  segments.

Note that previous studies of H in  $90^\circ$  partial dislocation cores have concentrated on the single-period structure [12], and the role and behaviour of H in DP cores is not yet clear.

- (d) *Intrinsic point defects.* Vacancies will also play an important role in the graphitization of dislocation cores. All structures discussed here are based around  $sp^2$  pairs whose spacing is determined by the diamond next-neighbour distance, i.e.  $2.61 \text{ \AA}$ . This is considerably closer packing than the inter-layer spacing of graphite ( $3.35 \text{ \AA}$ ). V pairs at the dislocation core could substitute for alternate pairs of  $sp^2$  C atoms, increasing their spacing to  $5.22 \text{ \AA}$  and hence reducing inter-layer compression (presumably also increasing the  $\pi-\pi^*$  gap).

During annealing at  $1700^\circ\text{C}$ , vacancies are known to be mobile, since in N-containing diamond, vacancies are trapped to form N-V-N centres [20]. At the same time the  $2.526 \text{ eV}$  zero-phonon line (ZPL) associated with dislocations reduces in intensity [20]. A possible interpretation is that vacancies previously trapped at the dislocation core are released and trapped by the N. This reduces the  $sp^2$  spacing at the core to  $2.61 \text{ \AA}$  once again, which is unstable, and hence the core restructures to  $sp^3$  and the ZPL associated with  $sp^2$  material disappears.

## 5. Conclusions

These calculations have modelled structures and processes which could occur in dislocated diamond and could be representative of structural processes in the formation and annealing of diamond-like carbon. The formation of  $sp^2$  carbon pairs is a likely first step in the process of graphitization and we have suggested ways in which these pairs could lead on to further graphitization at dislocation cores. In both situations modelled here, sub-band-gap excitations become possible and hence also optical absorptions, from  $\pi-\pi^*$  transitions which can give rise to brown coloration when the gap is small.

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