

## Glide dislocations in diamond: first-principles calculations of similarities with and differences from silicon and the effects of hydrogen

This article has been downloaded from IOPscience. Please scroll down to see the full text article.

2002 J. Phys.: Condens. Matter 14 12689

(<http://iopscience.iop.org/0953-8984/14/48/304>)

View [the table of contents for this issue](#), or go to the [journal homepage](#) for more

Download details:

IP Address: 171.66.16.97

The article was downloaded on 18/05/2010 at 19:12

Please note that [terms and conditions apply](#).

# Glide dislocations in diamond: first-principles calculations of similarities with and differences from silicon and the effects of hydrogen

M I Heggie<sup>1</sup>, C P Ewels<sup>1</sup>, N Martsinovich<sup>1</sup>, S Scarle<sup>1</sup>, R Jones<sup>2</sup>, J P Goss<sup>2</sup>,  
B Hourahine<sup>2</sup> and P R Briddon<sup>3</sup>

<sup>1</sup> CPES, University of Sussex, Falmer, Brighton BN1 9QJ, UK

<sup>2</sup> School of Physics, University of Exeter, Exeter EX4 4PY, UK

<sup>3</sup> Department of Physics, University of Newcastle, Newcastle upon Tyne NE1 7RU, UK

Received 1 October 2002

Published 22 November 2002

Online at [stacks.iop.org/JPhysCM/14/12689](http://stacks.iop.org/JPhysCM/14/12689)

## Abstract

We review first-principles calculations of dislocation core structure in diamond, and draw out similarities with and differences from silicon. Primary differences are in hybridization changes in carbon and in the different behaviour of H interacting with dislocations. In both materials, condensation of a homogeneous distribution of H atoms should result, first, in formation of small H aggregates with the appearance of a glide dislocation dipole and, second, in formation of larger platelets based on the half-stacking-fault model.

(Some figures in this article are in colour only in the electronic version)

## 1. Introduction

Carbon and silicon both condense into one of the simplest covalent crystal structures: the diamond structure, whose slip systems are derived from its parent fcc lattice [1]. Single slip is most often accommodated by 60° and screw dislocations lying along ⟨110⟩ directions in {111} slip planes. While dislocations in diamond are difficult to introduce and observe, what TEM observations have been made find {111}⟨110⟩ dislocations which are dissociated following the Burgers vector reaction

$$\frac{a}{2}[1\bar{1}0] \rightarrow \frac{a}{6}[1\bar{2}1] + \frac{a}{6}[2\bar{1}1] \quad (1)$$

with 25–42 Å of stacking fault ribbon [2], establishing clear parallels with silicon, where dissociation widths are typically 50–70 Å [3].

There are many excellent examples of first-principles calculations on dislocation cores in silicon from the earliest [4, 5] to the latest [6], but the subject has been reviewed often, e.g. [7], and this will not be duplicated here. Diamond studies are fewer and broadly shadow efforts in silicon, starting with cluster calculations of structure and mobility parameters [8]

and most recently including calculations of new core structures: the  $90^\circ$  partial in silicon was found to have a double-period (DP) core reconstruction [9, 10] which has been confirmed in diamond [11] dislocations and an alternative metastable core has also been found [12], which will be described in more detail later in this paper. One of the most comprehensive studies of dislocations in any material at a first-principles level has recently appeared for diamond [13], and confirmed that the DP reconstruction is the ground state and that the glide set of  $60^\circ$  dislocations are lower in energy than the shuffle set. It has also shown that shuffle partials formed by addition of vacancies to glide partials are lower in energy than those formed from addition of interstitials.

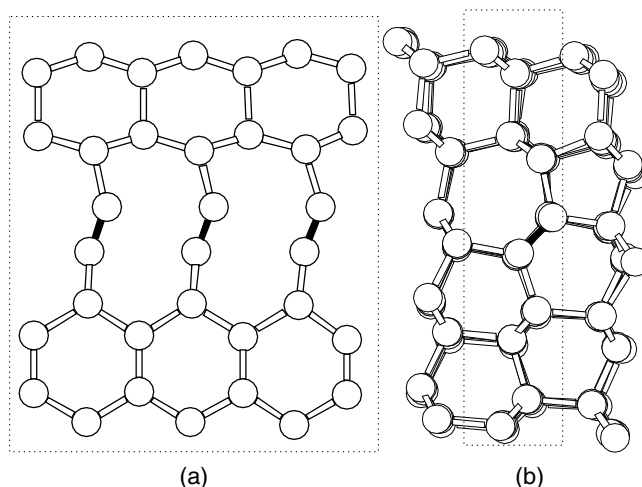
We can expect differences in chemistry between carbon and silicon, essentially because of carbon's position in the first row of the periodic table, with only a small  $1s^2$  core and a high electronegativity. This means that it forms short bonds and is able to compensate undercoordination by forming  $\pi$ -bonds when the geometry so allows. Its compact lattice is repulsive to interstitial hydrogen atoms and molecular hydrogen is not favoured, the preferred dimer being a bond-centred hydrogen accompanied by an antibonding hydrogen atom—the  $H_2^*$  defect [14].

The diffusion of H in these materials is not straightforward and recent experiments find anomalies in monocrystalline and polycrystalline CVD undoped diamond [15, 16] and in silicon [17], which might be attributable to substantial interaction with the lattice [18]. In particular, an accumulation layer of H in diamond, containing up to  $10^{22}$  H cm $^{-3}$ , has been found in plasma studies.

The interaction of H with dislocations in silicon is strong and causes the hydrogen-enhanced dislocation glide (HEDG) effect [19], reducing the activation energy for glide by 1 eV. It also causes hydrogen to recombine more efficiently into dihydrogen in the presence of dislocations [20]. First-principles calculations have reproduced the observed HEDG activation energy from examination of selected structures and reactions of H [21]. While the exact mechanism cannot yet be stated and the static relaxation procedure might not accurately reflect the dynamics of the proton, both H-catalysed processes treated did yield activation energies of the correct magnitude, indicative of a broad uniformity in the activation energy of such processes. In diamond, dislocations are effectively immobile, due to the high activation energy (3.3 eV) [8], but structural change does occur in amorphous forms of  $sp^3$  carbon in the presence of H, and this is possibly linked to processes similar to those in the core of a gliding dislocation in diamond. First-principles calculations confirm that the HEDG should operate in diamond and reduce the activation energy to 1.8 eV [22].

In detail, the steady-state concentration of H in the dislocation core is not known (the working assumption of [21] was that the concentration was low on the basis that the dislocation efficiently facilitates the recombination of H atoms to dihydrogen molecules [20]). There is also a mystery concerning the intermediate store of H—the HEDG effect relies on a pretreatment under the plasma and does not necessarily need the plasma to exist at the same time as the deformation [19]. Either H is being stored in the core of existing dislocations (which might imply a strain-hardening effect as the loops expand and linear concentration of H reduces) or there is a local bulk store in the neighbourhood of the dislocations (which also raises the possibility that the rate of emission of H from this intermediate store could be the rate-limiting step for HEDG).

Hydrogen in Si is technologically important because of the SmartCut process [23] for silicon-on-insulator technology, which allows almost atomically sharp (100) surfaces to be cut. Protons are implanted to a well defined depth and then heating or mechanical shock causes cleavage across platelets which are pressurized by molecular hydrogen. Most TEM observations of platelets [24–27] do not indicate a net displacement of the lattice and



**Figure 1.** The  $90^\circ$  partial in diamond with a  $sp^2$  SP structure. Double bonds linking  $sp^2$ -coordinated C atoms are marked in black. Plane (a) is a side view of the plane marked with the dotted line in (b).

suggested that platelets are not due to dislocation loops. However, some investigations [28–31] demonstrated the existence of features similar to a stacking fault and the presence of dislocation loops surrounding platelet-like defects. A model of the structure of these platelets proposed by Beaufort *et al* [31] is similar to the hydrogenated half-stacking fault considered by Zhang and Jackson [32]. The latter authors discarded this model because of the high activation energy of its formation in the absence of pre-existing defects such as dislocations. However, we show later that dislocation dipoles can form concomitantly with the aggregation of hydrogen. Also, investigations of the effect of hydrogen on dislocation mobilities showed that hydrogenation of dislocation cores reduces the activation energy of dislocation motion [22]; therefore the energy barrier of platelet nucleation and expansion is not so high as predicted by Zhang and Jackson [32].

Thus this paper will deal with the metastable core structure that is possible in diamond but not in silicon and then turn to the process of H precipitation in silicon and diamond, suggesting that it can lead to the creation of glide partials in both materials. We deal with defects and slip systems on (111) planes, and use a mix of cluster and supercell calculations as appropriate to the problem.

## 2. The ethene-like core of a $90^\circ$ partial in diamond

Two observations stimulated a search for an  $sp^2$ -containing core. Brown diamonds are known to contain dislocations [33] and colour might come from  $\pi-\pi^*$  or  $\pi-\sigma^*$  transitions between dispersive bands. Dislocation motion is almost impossible to observe in diamond unless the  $P$ ,  $T$  conditions are moved into the graphite stable regions.

In [12] a  $90^\circ$  partial dislocation with the conventional single-period (SP) core was constructed and converted to the ethene-like core (figure 1) by cutting alternate bonds in the  $\langle 110 \rangle$  zigzag chain neighbouring the reconstruction bonds. The result was a row of carbon-carbon double bonds stacked along the dislocation core.

Hydrogenated clusters  $C_{60}H_{60}$ ,  $C_{120}H_{92}$  and  $C_{180}H_{124}$  were extracted corresponding to one, two and three DPs (each of length 5.22 Å) and the AIMPRO cluster code [38] used to

deduce structure and energies per repeat period. The resulting ethene structure was 0.68 eV per repeat higher in energy than the ground state DP structure and exhibited C–C bond lengths of 1.33 Å close to that of ethene. The bond angles were close to 120°.

Two alternatives can also be imagined: one ethene-like core obtained from the DP structure and one butadiene-like core obtained by cutting alternate bonds in the  $\langle 110 \rangle$  zigzag chains either side of the reconstruction bonds. The first was found to be higher in energy than the SP ethene structure and here we report that the second was also higher in energy, but both were metastable.

The fascination of this model is that it is a concrete example of a structural motif around which speculations of hypothetical carbons have turned for many years—the stacking of double bonds with a separation of approximately 2.5 Å [34]. Graphites normally exhibit inter-layer spacings of 3.3–3.4 Å, rather than 2.61 Å, the second-nearest-neighbour distance in diamond. Such compressed stackings of  $\pi$ -systems have been observed in carbon onions [35].

The Kohn–Sham eigenvalues indicate that the ethene core structure introduces states into the gap (reducing the gap to 2.2 eV for three periods). A dispersive band or sections of ethene core of differing lengths could well give rise to a broad absorption band, making this one of a number of possible explanations for the brown coloration of certain diamonds—other explanations invoke various core structures with undercoordinated carbon atoms (see [39]).

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:

- (i) some low-frequency vibrational modes from the out-of-plane vibrations of the double bond should cause high vibrational entropy and drive the free energy in favour of the ethene core at high temperatures;
- (ii) when bounded in the core by entities which prefer threefold coordination or change phase of reconstruction (group III or V atoms, C–H groups, jogs or kinks), the ethene core can become the ground state;
- (iii) capture of electrons or holes should increase the stability because of the gap states.

In the case of (ii), we now report that two N atoms bounding either a SP or a DP section of the ethene core is more stable than their  $sp^3$  structures. Now we turn to the evolution of hydrogen.

### 3. H<sub>4</sub> structures: forming a faulted glide dipole loop

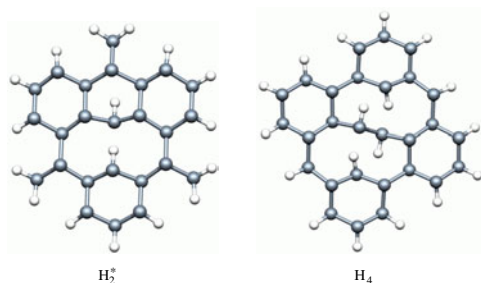
Here we concentrate on how H<sub>*n*</sub> clusters evolve from H<sub>BC</sub> beyond H<sub>2</sub>, making the assumption that at each stage the cluster is in local thermal equilibrium.

The theory of hydrogen in diamond has been reviewed and extensively studied with first-principles methods [14]. In diamond, H<sub>BC</sub> is unstable with respect to vacuum, and the H<sub>2</sub> molecule is unstable with respect to H<sub>2</sub><sup>\*</sup>. The reverse is true for silicon.

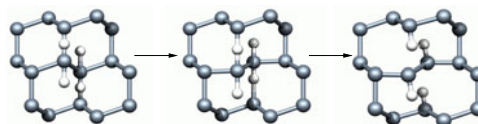
It is possible to hydrogenate a C–C bond [37] but this is 0.29 eV less stable than H<sub>2</sub><sup>\*</sup>.

When four H atoms cluster (figure 2), they spontaneously form a small glide dipole loop (an incipient dipole [36]). This process may be considered either as a result of single addition of H<sub>BC</sub> or as dimerization of H<sub>2</sub><sup>\*</sup> (shown diagrammatically in figure 3), but H<sub>2</sub><sup>\*</sup> is rather immobile in diamond (activation energy: 3.3 eV) [14].

This formation of an incipient dipole might be considered surprising, given that the energy required to form one in the perfect lattice is 5.1 eV. Nevertheless, it is spontaneous for H<sub>4</sub> and this structure has no electronic states in the gap. It is 0.49 eV lower in energy than hydrogenating two neighbouring  $\langle 111 \rangle$  bonds and 1.74 eV lower than hydrogenating two neighbouring  $\langle 110 \rangle$  bonds.



**Figure 2.** A glide plane view of AIMPRO cluster relaxed structures of  $H_2^*$  and  $H_4$  dipoles.



**Figure 3.** Diagrammatic representations of two neighbouring  $H_2^*$  defects transforming into a hydrogenated incipient dipole.

Removing H from this  $H_4$  structure gives  $H_{BC}$  on one side of the incipient dipole and this is the most stable neutral structure, although it does introduce levels into the gap. In the neutral charge state, this  $H_3$  structure is 0.6 eV more stable than  $H_2^*$  and  $H_{BC}$ , indicating that accretion of  $H_{BC}$  to  $H_2^*$  will tend to produce the incipient dipole. In the negative charge state of  $H_3$ ,  $H_{BC}$  adopts an antibonding site,  $H_{AB}$ .

Deconstructing this further to  $H_2$  at an incipient dipole produces a structure 1.26 eV higher in energy than  $H_2^*$ . Thus, in aggregating four H atoms together in diamond, an incipient dipole is nucleated.

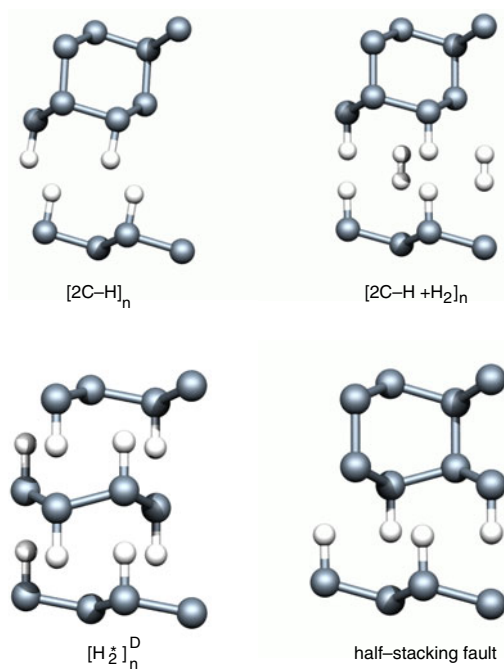
#### 4. Small platelets

Infinite platelets are depicted in figure 4. AIMPRO 12-atom supercell calculations used a Gaussian basis fitting the charge density to plane waves with an energy cut-off of 200 Ryd. The Brillouin zone was modelled using the Monkhorst–Pack sampling scheme with four  $k$ -points. Energies per H atom as a function of dilation perpendicular to the plane of the platelet are given in figure 5. One thing is abundantly clear: in the absence of dilation, the half-stacking-fault model is lowest in energy. For small platelets, dilation is difficult because of the interaction of the effective bounding dislocations of opposite sign. For large platelets, these dislocations interact weakly and large dilations are allowed, ultimately favouring the  $[H_2^*]_n^D$  model and models containing molecular hydrogen—these ‘mature’ platelets are the ones that are observed and are not the subject of this paper.

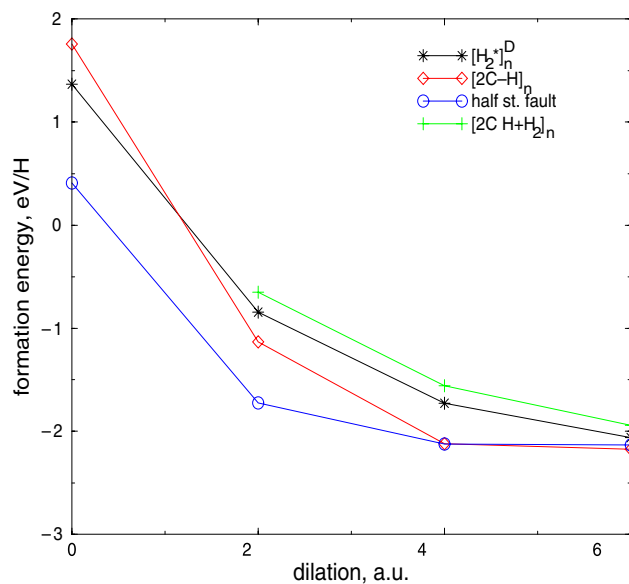
We can illustrate the early stages of platelet formation by considering a ribbon platelet with four columns of H atoms in a supercell of 96 atoms using eight  $k$ -points and an energy cut-off of 300 Ryd. Hydrogenating two parallel columns of  $\langle 111 \rangle$  bonds without shear leads to the high-energy structure of figure 6. This is unstable and relaxes by shear to give the dipole of glide dislocations on the shuffle plane (figure 7).

However, introducing a glide dipole of  $90^\circ$  partials and hydrogenating the core atoms yields the structure of figure 8 which, in general, is the lowest-energy state. For a 48-atom cell the energy difference is slightly basis set dependent and is 0.58–0.76 eV depending on the basis set used for carbon. The energy differences appear to be controlled by the elastic interactions of the effective bounding dislocations and, since these interactions are proportional to  $\log(r)$  ( $r$  is the separation between partials), the glide partials have a lower energy than the shuffle. This must be part of the reason that the finite  $H_4$  clusters preferred the incipient dipole structure to the twin hydrogenated  $\langle 111 \rangle$  bonds.

For larger cells, the energy differences reduce and we believe that this is due to the increase in dilation allowed for the shuffle platelet. For a 96-atom cell, the shuffle and glide platelets



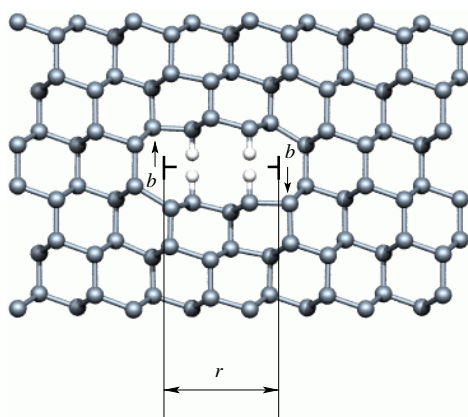
**Figure 4.** Structures of the infinite platelet in diamond obtained using an AIMPRO supercell.



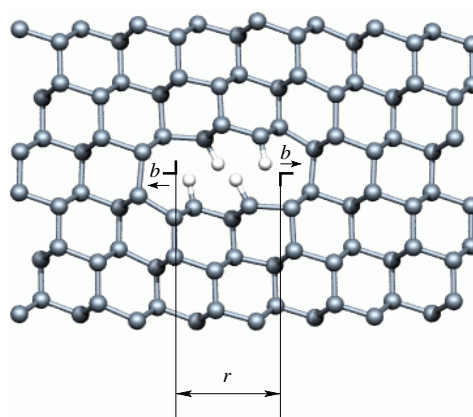
**Figure 5.** Energies of the platelets of the preceding figure as a function of dilation.

are effectively degenerate, but we note that the finite clusters still exhibit the preference for the glide structure.

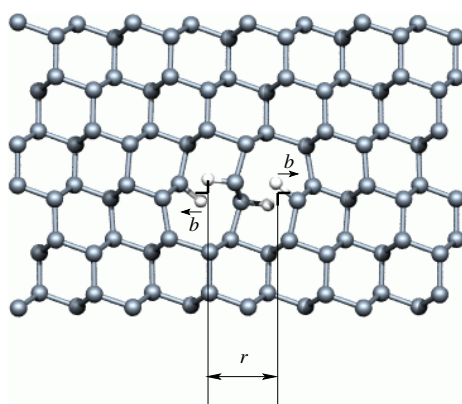
There is thus strong indication that in diamond, H could aggregate initially with shear relaxation (evolving into the half-stacking-fault model). Silicon behaves similarly in principle,



**Figure 6.** An AIMPRO supercell relaxed structure of a prismatic dipole before collapse. The Burgers vector,  $b$ , of the effective dislocation strain field is shown, as is the approximate core separation,  $r$ .



**Figure 7.** An AIMPRO supercell relaxed structure of a shuffle platelet. The Burgers vector,  $b$ , of the effective dislocation strain field is shown, as is the approximate core separation,  $r$ .



**Figure 8.** An AIMPRO supercell relaxed structure of a hydrogenated glide dipole. The Burgers vector,  $b$ , of the effective dislocation strain field is shown, as is the approximate core separation,  $r$ .

but observations that there is no shear involved in observed platelets (which are necessarily large) must either be explained by absence of quasi-equilibrium during growth, or by the dislocation character gliding out as platelet size increases.

## 5. Conclusions

We have reviewed some important differences as regards dislocations between diamond and silicon, showing that unsaturated bonding can occur as the ground state for the  $90^\circ$  partial in diamond in the presence of N at least. Then we followed the evolution of H platelets in diamond (in the context of experimental knowledge from Si) and found that they should, in principle, evolve initially with some glide dislocation character. These early stages in precipitation of H may explain the intermediate store of H in silicon postulated for the HEDG and the H accumulation layer in diamond.



## Acknowledgments

The authors would like to acknowledge the Sussex High Performance Computing Initiative and the e6 Consortium.

## References

- [1] Hirth J P and Lothe J 1982 *Theory of Dislocations* 2nd edn (New York: Wiley)
- [2] Pirouz P, Cockayne D J H, Sumida N, Hirsch P B and Lang A R 1983 *Proc. R. Soc. A* **386** 241
- [3] Ray I L F and Cockayne D J H 1970 *Phil. Mag.* **22** 853
- [4] Heggie M I, Jones R and Umerski A 1991 *Phil. Mag. A* **63** 571
- [5] Bigger J R K, McInnes D A, Sutton A P, Payne M C, Stich I, King-Smith R D, Bird D M and Clarke L J 1992 *Phys. Rev. Lett.* **69** 2224
- [6] Antonelli A, Justo J F and Fazzio A 2001 *Physica B* **308** 470
- [7] Lehto N and Heggie M I 1999 *Properties of Crystalline Silicon (EMIS Datareview Series No 20)* ed R Hull (London: IEE)
- [8] Sitch P K, Jones R, Öberg S and Heggie M I 1997 *J. Physique* **7** 1381
- [9] Nunes R W, Bennetto J and Vanderbilt D 1998 *Phys. Rev. B* **58** 12563
- [10] Lehto N and Öberg S 1998 *Phys. Rev. Lett.* **80** 5568
- [11] Blase X, Lin K, Canning A, Louie S G and Chrzan D C 2000 *Phys. Rev. Lett.* **84** 5780
- [12] Ewels C P, Wilson N T N T, Heggie M I, Jones R and Briddon P R 2001 *J. Phys.: Condens. Matter* **13** 8965
- [13] Blumenau A T, Heggie M I, Fall C J, Jones R and Frauenheim T 2002 *Phys. Rev. B* **65** 205205
- [14] Goss J P, Jones R, Heggie M I, Ewels C P, Briddon P R and Öberg S 2002 *Phys. Rev. B* **65** 115207
- [15] Chevallier J, Ballutaud D, Theys B, Jomard F, Deneuille A, Gheeraert E and Pruvost F 1999 *Phys. Status Solidi* **174** 73
- [16] Ballutaud D, Jomard F, Theys B, Mer C, Tromson D and Bergonzo P 2001 *Diamond Relat. Mater.* **10** 405
- [17] Beyer W and Zastrow U 2000 *J. Non-Cryst. Solids* **266–269** 206
- [18] Doremus R H 2000 *Mater. Res. Innov.* **4** 49
- [19] Yamashita Y, Jyobe F, Kamiura Y and Maeda K 1999 *Phys. Status Solidi a* **171** 27
- [20] Pizzini S 1999 *Phys. Status Solidi a* **171** 123
- [21] Ewels C P, Leoni S, Heggie M I, Jemmer P, Hernández E, Jones R and Briddon P R 2000 *Phys. Rev. Lett.* **84** 690
- [22] Heggie M I, Jenkins S, Ewels C P, Jemmer P, Jones R and Briddon P R 2000 *J. Phys.: Condens. Matter* **12** 10263
- [23] Bruel M 1995 *Nucl. Instrum. Methods B* **108** 313
- [24] Johnson N M, Ponce F, Street R A and Nemanich R J 1987 *Phys. Rev. B* **35** 4166
- [25] Muto S, Takeda S, Hirata S and Tanabe T 1991 *J. Appl. Phys.* **70** 3505
- [26] Muto S, Takeda S and Hirata S 1995 *Phil. Mag. A* **72** 1057
- [27] Weldon M K, Marsico V E and Chabal Y J *et al* 1997 *J. Vac. Sci. Technol. B* **15** 1065
- [28] Jeng S J and Oehrlein G S 1987 *Appl. Phys. Lett.* **50** 1912
- [29] Jeng S J, Oehrlein G S and Scilla G J 1988 *Appl. Phys. Lett.* **53** 1735
- [30] Beaufort M F, Garem H, Lepinoux J and Desoyer J C 1991 *Scr. Metall. Mater.* **25** 1187
- [31] Beaufort M F, Garem H and Lepinoux J 1994 *Phil. Mag. A* **69** 881
- [32] Zhang S B and Jackson W B 1991 *Phys. Rev. B* **43** 12142
- [33] Graham R J and Buseck P R 1994 *Phil. Mag. B* **70** 1177
- [34] Tamor M A and Hass K C 1990 *J. Mater. Res.* **5** 2273
- [35] Banhart F and Ajayan P M 1997 *Adv. Mater.* **9** 244
- [36] Heggie M I 1989 *Inst. Phys. Conf. Ser.* **104** 43
- [37] Deak P, Ortiz C R, Snyder L C and Corbett J W 1991 *Physica B* **170** 223
- [38] Jones R and Briddon P R 1998 *Semicond. Semimet. A* **51** 287
- [39] Fall C J, Blumenau A T, Jones R, Briddon P R, Frauenheim T, Gutierrez-Sosa A, Bangert U, Mora A E, Steeds J W and Butler J E 2002 *Phys. Rev. B* **65**