

## Interstitial hydrogen and enhanced dissociation of C-H complexes in GaAs

S. J. Breuer and R. Jones

*Department of Physics, The University of Exeter, Exeter EX4 4QL, United Kingdom*

P. R. Briddon

*Department of Physics, The University of Newcastle upon Tyne, Newcastle upon Tyne NE1 7RU, United Kingdom*

S. Öberg

*Department of Mathematics, University of Luleå, Luleå S95187, Sweden*

(Received 22 January 1996)

Local-density-functional-based *ab initio* calculations are used to investigate hydrogen and carbon-hydrogen defects in GaAs. The equilibrium structure for both the C-H and C-H<sup>-</sup> complexes are shown to be similar, with the hydrogen located at a C-Ga bond-centered site. The dissociation of these complexes is investigated and it is found that the energy barrier of 1.84 eV for the process C-H → C<sup>-</sup> + H<sup>+</sup> is substantially lowered to 0.88 eV in the presence of an electron resonantly bound to the defect. This is in good quantitative agreement with recent experiments. Isolated interstitial hydrogen is found to lie at a Ga-As bond-centered site for both H<sup>+</sup> and H<sup>0</sup> and at an antibonding site relative to a Ga atom for H<sup>-</sup>. It is also found that the stable form of the hydrogen dimer is a H<sub>2</sub> molecule, the dissociation energy of which is 1.64 eV, and that interstitial hydrogen is a negative-*U* defect. Finally, a mechanism for minority-carrier-induced device degradation is proposed. [S0163-1829(96)06724-0]

### I. INTRODUCTION

Currently, carbon is the preferred *p*-type dopant in GaAs and Al<sub>x</sub>Ga<sub>1-x</sub>As. This is due to its low diffusivity compared with other *p*-type dopants (Be and Zn) and to the fact that high concentrations, 10<sup>20</sup>–10<sup>21</sup> cm<sup>-3</sup>, can be incorporated into the material using metalorganic vapor-phase epitaxy (MOVPE) and metalorganic molecular-beam epitaxial (MOMBE) growth techniques. Recent experimental work on heterojunction bipolar transistors (HBT's) and *p-n* junction diodes containing GaAs:C as a *p*-type region has concentrated on investigating the degradation of the device during operation.<sup>1-3</sup> A catastrophic decrease in current gain and related increase in low bias leakage current occurs under normal operating conditions over a time scale short enough to be an obstacle to their wide-spread use, e.g., as high-speed switches in communications systems. These degradation effects could also prove to be significant in other devices using carbon-doped GaAs, such as vertical cavity surface emitting lasers. In this paper we carry out theoretical simulations of processes connected with this degradation, in order to clarify the mechanisms involved and compare with related experimental results.

Carbon in GaAs has been studied by both theoretical<sup>4-6</sup> and experimental techniques.<sup>7,8</sup> It has been established that the substitutional defect is not an amphoteric dopant, and is only observed to lie on the arsenic sublattice,<sup>9</sup> thus acting as an acceptor. An interstitial form, stable below 150 °C, is known<sup>10,11</sup> and has been investigated previously.<sup>12</sup> A dicarbon defect<sup>13,14</sup> that acts as a donor appears to have a low formation energy but has not been detected to date.

The current favored growth techniques introduce large amounts of hydrogen along with carbon into the material. This arises from the precursors, such as trimethyl gallium

(TMGa) and arsine (AsH<sub>3</sub>), which are used in MOVPE and MOMBE. The passivation of shallow impurities in semiconductors by the formation of defect complexes with hydrogen is well documented,<sup>15-17</sup> and experimental<sup>18-21</sup> and theoretical techniques<sup>4,5,13</sup> have already been used to investigate the C-H complex in GaAs and Al<sub>x</sub>Ga<sub>1-x</sub>As. The *ab initio* calculations have shown that the lowest-energy structure for the neutral C-H complex is one where H lies at a bond-centered (BC) site along a C-Ga bond. In addition to C-H complexes, secondary-ion-mass spectroscopy (SIMS) measurements have shown that the MOVPE material can contain interstitial H<sup>+</sup> donors. SIMS was used to monitor changes in the depth profiles of hydrogen during thermal annealing at 380 °C.<sup>22</sup> Infrared absorption measurements showed that the concentration of C-H complexes remained unchanged after the anneal, and the changes in depth profile were attributed to the movement of a rapidly diffusing hydrogen species. As the barrier to this hydrogen movement was determined to be only 0.4 eV, it was proposed that isolated hydrogen interstitials were present, probably as H<sup>+</sup>. The presence of free hydrogen seems related to the growth technique, as other workers report that almost all H is present as C-H complexes.<sup>3</sup>

Fushimi *et al.*<sup>1</sup> investigated the degradation of GaAs/Al<sub>x</sub>Ga<sub>1-x</sub>As diodes under a large current load. The diode provides a simpler system to investigate than HBT's with GaAs:C as the base region, but exhibits the same degradation effects. The degradation was correlated with the presence of free H in the device. The free hydrogen can be removed by thermal annealing at 450 °C, leaving only C-H defects. It was then demonstrated that, on heating the device up to typical operating temperatures of 200 °C, negligible dissociation of C-H occurred. However, on passing a large current through the device at this temperature, rapid disso-

ciation of the C-H complexes occurred, leading to further device degradation. It was therefore inferred that the energy barrier to C-H dissociation is lowered by the injection of minority carriers into the  $p$ -type region. It was also observed that the degradation rate was proportional to the injection current squared.<sup>1</sup> Enhanced dissociation of other H-passivated dopants has been reported and studied previously in, for example, boron-doped silicon.<sup>23,24</sup> In this case, the injection of electrons reduced the dissociation barrier of B-H complexes.

Two main experimental approaches have been used in order to determine the energy barrier to complex dissociation. First, straightforward thermal decomposition of X-H donor/acceptor-hydrogen complexes has been carried out by annealing. This technique should overestimate the energy barrier as the reaction is assumed to be first order and the reformation of the X-H complex is not taken into account. Second, X-H complex dissociation in reverse-biased Shottky diodes has been studied. Reformation of the complexes is now inhibited as the electric field sweeps the charged hydrogen atoms away from the ionized donors or acceptors. This technique is best suited to lightly doped material in which there is a low concentration of ionized donors. However, in this case the barrier energy should be underestimated, as the presence of the electric field lowers the barrier energy due to the Poole-Frenkel effect. In fact, it has been shown that the dissociation energy of Si-H complexes in GaAs can vary between 1.79 and 1.20 eV, depending on the applied bias voltage.<sup>25</sup> Experimental results for the barrier to the process  $C-H \rightarrow C^- + H^+$  are  $1.75 \pm 0.3$  eV by thermal dissociation<sup>22</sup> and  $1.35 \pm 0.05$  eV by field-assisted dissociation.<sup>26</sup> The experimental work described above implies that the source of the degradation in devices is closely related to defect formation involving hydrogen. It has recently been suggested that the degradation process is related to the formation of platelets.<sup>2</sup> One final experimental result is that the presence of small concentrations of In in the GaAs:C region has been shown to reduce the rate of device degradation.<sup>2</sup>

Information on the sites of isolated H interstitials has come from muon spin spectroscopy.<sup>27-31</sup> The muon remains as  $\mu^+$  in  $p$ -type GaAs but can form neutral muonium ( $Mu^0$ ) or negative muonium ( $Mu^-$ ) in high resistivity or  $n$ -type GaAs. This does not show that isolated H interstitials can exist in three stable charge states as the muon results refer to configurations limited by its lifetime. The values of the hyperfine parameters for anomalous muonium in GaAs imply that this center is  $Mu^0$  lying at a BC site.<sup>30</sup> Muon level-crossing resonance and muon-spin-rotation measurements<sup>31</sup> show that  $Mu^-$  is present either at the tetrahedral interstitial site surrounded by four Ga atoms,  $T_{Ga}$  in Fig. 1(a), or at the close-by antibonding site,  $AB_{Ga}$ . The  $Mu^-$ -Ga distance is estimated to be about 10% smaller than a GaAs bond. The activation energy for the diffusion of  $H^+$  has been estimated to be 0.66 eV using capacitance transient measurements.<sup>32</sup> It has been suggested that  $Mu^-$  has a lower diffusivity than  $Mu^0$  and  $Mu^+$  and a diffusion rate of at least  $10^{-2}$  times smaller than  $Mu^0$  at the  $T$  site has been deduced.<sup>29</sup> In relation to the charge state of interstitial atomic hydrogen, Clerjaud *et al.*<sup>18</sup> deduced an associated 0/+ or

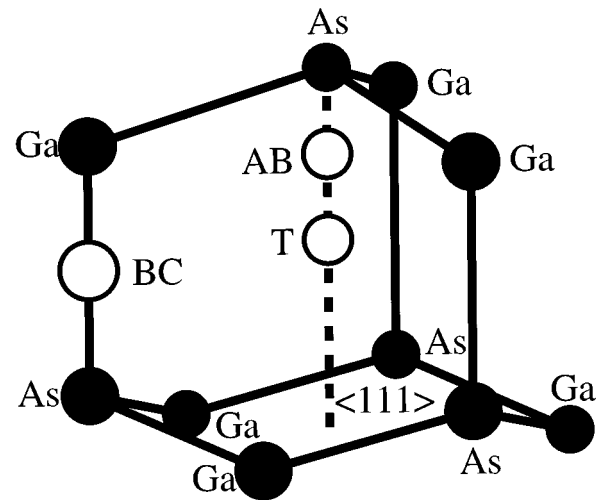


FIG. 1. Sites in the lattice referred to in the text in describing the location of hydrogen atoms and molecules.  $T$  is the tetrahedral interstitial site, BC is the bond-centered site, and AB is the antibonding site. Subscripts are used in the text to indicate the nearest atoms in the AB and  $T$  sites. In the figure, these would be  $T_{As}$  and  $AB_{As}$  sites. The  $\langle 111 \rangle$  axis is labeled.

−/+ level at around 0.5 eV above the valence band.

Interstitial hydrogen in GaAs has previously been investigated theoretically by *ab initio* methods. Cluster calculations<sup>33</sup> using 56-atom clusters found  $H^0$  to be stable at the  $T_{Ga}$  site. Neutral interstitial hydrogen at the BC site was modeled both by Hartree-Fock<sup>34</sup> and density-functional (LDF) methods,<sup>35,36</sup> yielding structural information and hyperfine parameters that compared favorably with those experimentally determined for anomalous muonium. Supercell-plane-wave LDF calculations have been used to investigate structures involving one and two interstitial hydrogen atoms.<sup>35</sup> These calculations found that  $H^0$  was stable at the As antibonding ( $AB_{As}$ ) site and  $H^+$  at the M site.  $H^-$  was found to be stable at the C site equidistant from two Ga atoms. However, the energy differences between sites was often very small. They also found that hydrogen in GaAs is a negative- $U$  system, so that, depending on the Fermi level,  $H^+$  or  $H^-$  should be the most energetically favorable charge state, but never  $H^0$ . The lowest-energy structure for two hydrogen atoms was shown to be a  $H_2$  molecule at the  $T_{Ga}$  site, and this possessed an energy 0.5 eV *higher* than a molecule outside the crystal. However, only small supercells of 16 and 32 atoms were used in these calculations. This would correspond to a hydrogen concentration of around 3% and might lead to strong defect-defect interactions.

In this paper, we present a comprehensive investigation of C-H complexes and interstitial hydrogen defects in GaAs, including C-H complex dissociation, in an attempt to explain certain aspects of the experimental results on the subject. In Sec. II we present details of our calculational formalism and its implementation. In Secs. III and IV we present the results of our investigations of the C-H complex and its dissociation, single interstitial hydrogen atoms, and structures involving two interstitial hydrogen atoms. Finally, in Sec. V we draw our conclusions.

## II. CALCULATIONAL METHOD

The modeling of defects presented in this paper was carried out using the AIMPRO code for atomic simulations. The formalism implemented by this code is based on LDF theory, and was originally presented by Jones<sup>37</sup> with modifications described by Briddon<sup>38</sup> and Breuer.<sup>39</sup> The approach used in modeling defects in solids is as follows. A cluster of bulk atoms is constructed, which is terminated with hydrogen in order to saturate the surface dangling bonds. GaAs clusters containing 86 atoms ( $\text{Ga}_{21}\text{As}_{21}\text{H}_{44}$ ), 176 atoms ( $\text{Ga}_{48}\text{As}_{48}\text{H}_{80}$ ), and 300 atoms ( $\text{Ga}_{95}\text{As}_{95}\text{H}_{110}$ ) were used for these calculations. These clusters are stoichiometric with  $C_{3v}$  symmetry and have the Ga and As atoms at the bulk GaAs positions (before the addition of defects and the subsequent relaxation of the atoms). The atomic cores are replaced by pseudopotentials as generated by Bachelet, Hamann, and Schlüter<sup>40</sup> and the valence electrons are dealt with under a LDF framework. The electron wave functions are expanded using a basis of localized modified Gaussian functions. These Gaussian orbitals are made  $s$  type or  $p$  type by multiplicative factors and are centered at atomic sites and on the centers of certain atomic bonds. For the largest clusters used in these calculations (302 atoms) this corresponds to a total wave function basis of 3500 functions. The defect is generally located near the center of the cluster and always as far from the cluster surface as possible. The rationale is that, at a central location, the defect is essentially in a bulk environment with only limited effects arising from the surface of the cluster. After the construction of a suitable cluster containing the defect, the atoms are then allowed to move in order to minimize the total energy and thus determine the equilibrium structure. A conjugate gradient algorithm is used to carry out this minimization. Constraints can be applied to the motion of the atoms during these structural optimizations in order to study effects such as diffusion or dissociation, as described in Sec. III B.

## III. C-H COMPLEX

### A. Equilibrium structure

The defect complex formed when hydrogen passivates substitutional  $C_{\text{As}}$  in GaAs has been extensively studied. Hydrogen has been found to lie at a BC site between C and Ga.<sup>4,5</sup> The symmetry and characteristic vibrational modes and frequencies of the neutral defect have been determined both experimentally and theoretically. An analysis of these aspects of the defect will not be presented here. The recent experimental work has implied that the C-H complex more readily dissociates in GaAs:C under minority-carrier injection. There are no defect levels in the gap associated with the neutral C-H complex, so that the charge state of the complex should be independent of the Fermi level. If, however, the defect captures an electron as a long-lived resonance then it might be possible for the complex to reorient to a lower-energy structure, or dissociate with a lower barrier energy.

The first steps in the investigation of dissociation were to determine the equilibrium structure of the  $\text{C-H}^-$  complex, where an additional electron is inserted into the cluster, and to find the site to which the hydrogen atom would move on the dissociation of both neutral C-H and charged  $\text{C-H}^-$  com-

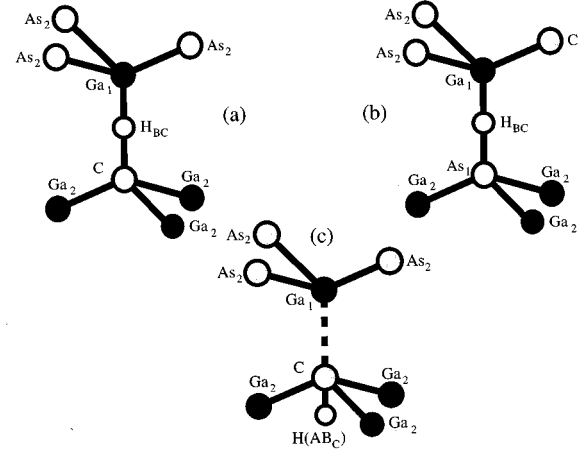


FIG. 2. The relaxed structures for a  $C_{\text{As}}$  and H atom in GaAs as referred to in the text and in Table II. The Ga and As atoms are numbered to facilitate quoting bond lengths in the table. The hydrogen atom is located at (a) a C-Ga BC site ( $\text{BC}_1$ ), (b) a Ga-As BC site with C as a nearest neighbor of the Ga ( $\text{BC}_2$ ), and (c) the  $\text{AB}_C$  site.

plexes. To these ends, the possible structures with hydrogen as a first or second nearest neighbor of the carbon were investigated. The 86-atom cluster described in Sec. II was used for these calculations. The As atom nearest to the center of the cluster was replaced by a C atom, and a H atom was added to the cluster in the appropriate position for each of the structures investigated. In the first case, the H atom was placed at a BC site between C and a neighboring Ga atom. This configuration is called  $\text{BC}_1$  and illustrated in Fig. 2(a). This is the stable configuration found previously for the neutral defect. The simplest dissociated complex, called  $\text{BC}_2$ , consisted of H placed at a bond center between As and a Ga neighbor of C as shown in Fig. 2(b). Three other possible positions for the H atom were considered. In the first, it was placed at the  $T_{\text{Ga}}$  site, nearest to C. In the second, it was placed at a  $T_{\text{As}}$  site, and at  $T_{\text{C}}$  in the third case. All the atoms in the corresponding structures in both the neutral and negative charge states were allowed to relax with no constraints placed on their movements.

The lowest-energy site for the H atom in both charge states was found to be  $\text{BC}_1$  [Fig. 2(a)]. Table I gives the energies of the other metastable sites. H is strongly bonded to C in the  $\text{BC}_1$  structure and the bond lengths are given in Table II, with reference to Fig. 2. The bond between H and Ga is very weak or broken and the presence of an additional electron located in the conduction band causes only a slight change to the equilibrium structure (Table II). The main effect is to weaken the  $\text{Ga}_1\text{-H}$  bond even further. The  $\text{BC}_1$  structure possesses a gap free from defect levels, but the

TABLE I. The energies in eV of the structures investigated for the C-H and  $\text{C-H}^-$  complexes. The zero of energy in each charge state is the stable structure for that charge state (uns=unstable).

Defect	$\text{BC}_1$	$\text{AB}_C$	$\text{BC}_2$	$T_{\text{Ga}}$
C-H	0.00	0.64	0.96	uns
$\text{C-H}^-$	0.00	0.11	0.44	1.67

TABLE II. The bond lengths in Å corresponding to the relaxed structures investigated for C-H and C-H<sup>-</sup> complexes, with reference to Fig. 2.

Bond Lengths	C-H	C-H <sup>-</sup>	
	BC <sub>1</sub>		
C-H	1.09	1.09	
Ga <sub>1</sub> -H	2.43	2.77	
C-Ga <sub>2</sub>	1.96	1.95	
Ga <sub>1</sub> -As <sub>2</sub>	2.31	2.40	
	BC <sub>2</sub>		
Ga <sub>1</sub> -H	2.31	1.55	
As <sub>1</sub> -H	1.51	2.25	
As <sub>1</sub> -Ga <sub>2</sub>	2.42	2.39	
Ga <sub>1</sub> -As <sub>2</sub>	2.34	2.42	
Ga <sub>1</sub> -C	1.93	2.05	
	AB <sub>C</sub>		
C-H	1.09	1.09	
C-Ga <sub>1</sub>	3.81	3.47	
C-Ga <sub>2</sub>	2.25	2.33	
Ga <sub>1</sub> -As <sub>2</sub>	2.31	2.4	2

wave function for the lowest empty state in the neutral defect is largely composed of a  $p$  orbital, parallel to C-H, on the threefold coordinated Ga atom nearest to H. This state is then a defect-induced resonance and could trap an additional electron.

The BC<sub>2</sub> configuration of Fig. 2(b) is the most stable structure corresponding to a C-H complex where H is no longer bonded to C but lies within a second-neighbor distance of C, for both charge states. Here, H is strongly bonded with the As atom in the neutral charge state and to the Ga atom in the negative charge state. We shall see below that the H-As and H-Ga bond lengths for the neutral BC<sub>2</sub> configuration are close to the corresponding bond lengths for isolated H<sup>+</sup> (Sec. IV). However, in the charged state, although the H-Ga length is close to that found in the isolated H<sup>0</sup> interstitial, the H-As length is longer. This probably arises from the polarization of the bond by C.

The energy difference between the BC<sub>1</sub> and BC<sub>2</sub> configurations is the approximate dissociation energy of the complex. This is 0.96 eV for C-H and 0.44 eV for C-H<sup>-</sup>. The dissociation energy of the neutral complex is considerably lower than the 1.85 eV found by a supercell calculation<sup>5</sup> for the reaction C-H → C<sup>0</sup> + H<sup>0</sup>. Presumably, this energy would be reduced by the difference in the H<sup>0</sup> donor and C acceptor levels, if charge transfer had been allowed. The dissociation energy of the neutral complex must be higher than 0.5 eV, as this is known to be the barrier for reorientation of the defect among the four equivalent BC<sub>1</sub> configurations.<sup>41</sup> The reorientation barrier is approximately the energy difference between the BC<sub>1</sub> and AB<sub>C</sub> configurations, i.e., 0.64 eV—close to the value of 0.67 eV found previously.<sup>4</sup> C-H<sup>-</sup> dissociates more easily than the neutral defect because the additional electron, initially trapped as a conduction-band resonance, occupies a lower-energy gap level in H<sup>0</sup>.

The  $T$  sites are not stable configurations. For both charge states, the H atom spontaneously moved from  $T_C$  to AB<sub>C</sub>, with H becoming strongly bonded to C. Similarly, for the

neutral defect, H at either  $T_{As}$  or  $T_{Ga}$  is unstable, and moves to the BC<sub>2</sub> site. For the negatively charged defect, the  $T_{As}$  site is also unstable, but  $T_{Ga}$  is metastable.

### B. The activation energy for C-H dissociation

The results obtained in Sec. III A show that the BC<sub>1</sub> structure of Fig. 2(a) has the lowest energy for both the C-H and C-H<sup>-</sup> complexes. Therefore, the trapping of an electron by C-H would not cause a spontaneous dissociation or reorientation of the defect structure, and so the dissociation of the complex should proceed from this structure for both charge states. Although the next-lowest-energy structure in Table I is AB<sub>C</sub> for both neutral and negatively charged defects, the hydrogen atom is still directly bonded to the carbon atom and a switch to this configuration would not result in a dissociation. On the other hand, the BC<sub>2</sub> site has the lowest energy for both charge states when H is not bonded directly to the C atom. Therefore, it is expected that the initial step in the dissociation of C-H → C<sup>-</sup> + H<sup>+</sup> and C-H<sup>-</sup> → C<sup>-</sup> + H<sup>0</sup> involves the movement of the atoms from the BC<sub>1</sub> to the BC<sub>2</sub> configurations. These are the start and end points of the primary dissociation event. We need then to determine the barrier between these sites. Merely displacing the H atom in a straight line trajectory, or interpolating between the initial and final coordinates, would not determine an accurate energy barrier because it ignores the relaxation that can take place near the barrier top. Moreover, it is not clear whether it is the breaking of the C-H bond or the breaking of the Ga<sub>1</sub>-As<sub>2</sub> bond in Fig. 2(a), or a combination of both, that determines this barrier. A better procedure is to place two constraints on the cluster that control the breaking of these bonds, and allow all the atoms to move to their lowest-energy sites consistent with these constraints. Two variables,  $c_1$  and  $c_2$ , are introduced. The first of these variables takes the H atom from the BC site between C and Ga<sub>1</sub>, in the undissociated BC<sub>1</sub> complex of Fig. 2(a), to the BC site between Ga<sub>1</sub> and As<sub>2</sub> in the dissociated BC<sub>2</sub> complex. The second variable,  $c_2$ , takes Ga<sub>1</sub> from its position in BC<sub>1</sub>, where it is bonded to As<sub>2</sub>, to its position in BC<sub>2</sub> in which it is bonded to C. Specifically,

$$c_1 = (\mathbf{R}_H - \mathbf{R}_C)^2 - (\mathbf{R}_H - \mathbf{R}_{As_2})^2, \quad (1)$$

$$c_2 = (\mathbf{R}_{Ga_1} - \mathbf{R}_{As_2})^2 - (\mathbf{R}_{Ga_1} - \mathbf{R}_C)^2. \quad (2)$$

Here  $\mathbf{R}_H$ ,  $\mathbf{R}_C$ ,  $\mathbf{R}_{Ga_1}$ , and  $\mathbf{R}_{As_2}$  are the positions of the atoms shown in Fig. 2(a) during the dissociation process. Clearly,  $c_1$  and  $c_2$  are negative for BC<sub>1</sub> and positive for BC<sub>2</sub>. The values of  $c_1$  and  $c_2$  for the start- and end-point structures have been determined in Sec. III A above. Other values of  $c_1$  and  $c_2$  were then chosen between these delimiters, and all the atoms in the clusters were relaxed, while maintaining  $c_1$  and  $c_2$  at their prescribed values. The relaxation of the clusters according to these constraints effectively maps out an energy surface in two-dimensional constraint space. The saddle point on the energy surface between the start and end points is then the energy barrier for dissociation of the complex. This approach has been used in several previous studies.<sup>42</sup>

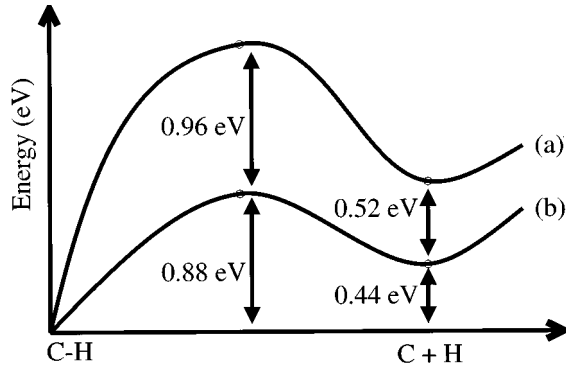


FIG. 3. Schematic energy configuration diagram of the dissociation of the C-H complex in the two charge states investigated. (a)  $C-H \rightarrow C^- + H^+$  and (b)  $C-H \rightarrow C^- + H^0$ . The two minima denote the initial and final configurations, which are separated by a barrier. The barrier is lower in case (b). Note that there are also barriers to the formation of the C-H complexes starting from free H and C.

The energy barrier was thereby found to be 1.84 eV for  $C-H \rightarrow C^- + H^+$  and 0.88 eV for  $C-H^- \rightarrow C^- + H^0$ . The saddle-point structure in the neutral case involves H forming a bond with  $As_2$  and C being threefold coordinated. The structure possesses a deep gap level that is empty for the neutral case and partially occupied for the  $C-H^-$  case. These results show that the addition of an electron to the C-H complex reduces the activation energy to dissociation of the C-H defect as well as its dissociation energy. The reductions in the dissociation energy and the barrier to dissociation are probably due to two effects. First, the additional electron initially present as a conduction-band resonance is lowered in energy as a result of dissociation, since it now occupies a gap level due to  $H_{BC}^0$ . Second, the electrostatic work done in separating  $H^+$  from  $C^-$  is absent in the second case, where H is neutral. A schematic figure of the processes is given in Fig. 3. We note also that there is an energy barrier to the recombination of  $C^-$  and  $H^+$  showing that free interstitial hydrogen can coexist with C acceptors. This would explain why, experimentally, even when the concentration of hydrogen atoms is of the order of the concentration of carbon atoms, only around half of the carbon atoms are passivated by hydrogen. There is also a barrier — although a smaller one — for the recombination of  $C^-$  and  $H^0$ .

#### IV. INTERSTITIAL HYDROGEN

##### A. Isolated hydrogen atoms

An 87-atom cluster,  $Ga_{21}As_{21}H_{45}$ , was used to investigate the stable sites for interstitial H. The cluster was al-

TABLE III. The energies in eV of the structures investigated for the single interstitial hydrogen atom in GaAs relative to the stable configuration for that charge state (uns=unstable).

Defect	BC	$AB_{As}$	$AB_{Ga}$	$T_{As}$	$T_{Ga}$
$H^+$	0.00	0.40	1.35	uns	uns
$H^0$	0.00	0.34	0.48	uns	uns
$H^-$	0.30	uns	0.00	0.52	uns

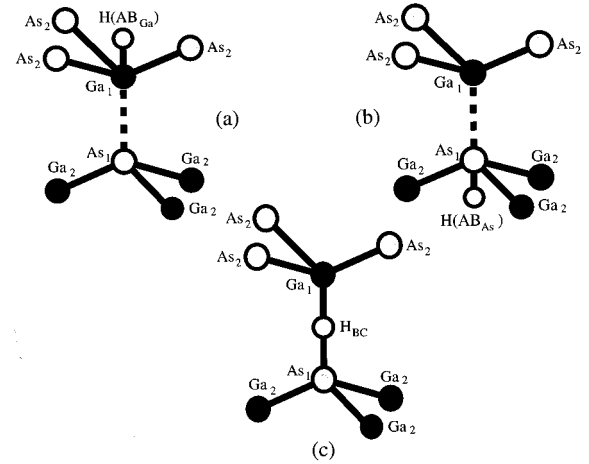


FIG. 4. The relaxed structures for a single interstitial hydrogen atom as referred to in the text and in Table IV. The Ga and As atoms are numbered to facilitate quoting bond lengths in the table. The hydrogen atom is located at (a) the  $AB_{Ga}$  site, (b) the  $AB_{As}$  site, and (c) the Ga-As bond-centered site.

lowed to relax without any constraint for each charge state. A single interstitial H atom was modeled in three charge states as  $H^+$ ,  $H^0$  and  $H^-$  and was initially located at the  $T_{As}$ ,  $T_{Ga}$ , and BC sites.

The BC site was found to be the stable one for both  $H^+$  and  $H^0$ , but  $H^-$  was stable at the  $AB_{Ga}$  site (Fig. 4). The relative energies of the metastable structures are given in Table III. These results differ from supercell calculations<sup>35</sup> as well as those using smaller clusters. The bond lengths of the stable and metastable structures are given in Table IV. The 43% expansion of the GaAs bond caused by  $H^0$  at a BC site is comparable with a 32(7)% expansion estimated<sup>30</sup> for  $Mu^0$ . The defect has a deep midgap level.

Except for  $H^-$  at  $T_{As}$ , the  $T$  sites are unstable. Upon relaxation, the H atom moved from the  $T_{As}$  and  $T_{Ga}$  sites to  $AB_{As}$  and  $AB_{Ga}$  (Fig. 4), respectively. For  $H^-$ ,  $T_{As}$  is a metastable site with energy 0.52 eV above the  $AB_{Ga}$  stable site. The H-Ga bond is 1.49 Å for the  $AB_{Ga}$  site, which is

TABLE IV. The bond lengths in Å corresponding to the relaxed structures investigated for isolated  $H^0$ ,  $H^+$ , and  $H^-$ , with reference to Fig. 4.

Bond lengths	$H^-$	$H^0$	$H^+$
BC			
$As_1$ -H	2.44	1.78	1.50
$Ga_1$ -H	1.48	1.66	2.14
$As_1$ - $Ga_2$	2.31	2.37	2.41
$Ga_1$ - $As_2$	2.39	2.36	2.31
$AB_{As}$			
$As_1$ -H		1.63	1.51
$As_1$ - $Ga_2$		2.42	2.45
$Ga_1$ - $As_2$		2.36	2.31
$AB_{Ga}$			
$Ga_1$ -H	1.49	1.57	1.58
$As_1$ - $Ga_2$	2.33	2.37	2.41
$Ga_1$ - $As_2$	2.39	2.40	2.44

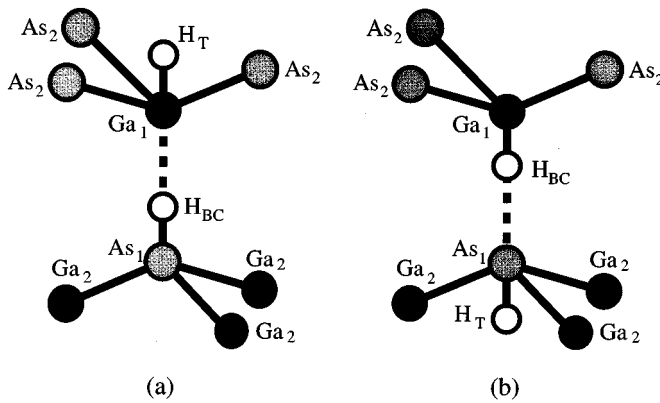


FIG. 5. The relaxed structures of the two possible  $H_2^*$  defect configurations in GaAs as referred to in the text and Table VI; (a)  $H_2^*(As)$ , (b)  $H_2^*(Ga)$ .

considerably less than the 2.19 Å deduced from the muon studies.<sup>31</sup> However, as the zero-point energy of  $Mu^-$  is about 0.3–0.4 eV, it is likely that a dynamic reorientation of  $Mu^-$  among the four  $AB_{Ga}$  occurs, leading to a longer average Ga-Mu bond length. This explanation is much more likely than  $Mu^-$  being located at the  $T_{Ga}$  site and pulling each of the four Ga atoms towards it by about 0.2 Å. The H atom remained on the bond axis in the BC structure for all charge states. However,  $H^-$  bonded most strongly with the Ga atom, whereas  $H^+$  lay closest to the As atom, and  $H^0$  remained roughly equidistant from the Ga and As atoms. In order to confirm the stability of the BC site,  $H^+$  and  $H^0$  were displaced from their equilibrium BC structures in a direction perpendicular to the bond axis by 0.5 Å and the clusters relaxed. In both cases, H returned to the BC site, showing that the BC site is a stable one.

In summary, we find  $H^0$  and  $H^+$  to be stable at a BC site and  $H^-$  to be stable at an  $AB_{Ga}$  site. These results are consistent with muon studies once its large zero-point motion is taken into account.

### B. The hydrogen dimer

Simulations of structures containing two hydrogen atoms in close proximity to each other were carried out. One expects that hydrogen molecules and  $H_2^*$  defects, i.e., defects where  $H_{BC}^+$  lies close to  $H_{AB}^-$  (Fig. 5) have particularly low energies. The structures investigated in a 178-atom cluster were a  $H_2$  molecule at the  $T_{As}$  and  $T_{Ga}$  sites, the two possible  $H_2^*$  defects in GaAs (Fig. 5) and two H atoms at nearest-neighbor Ga-As BC sites. The  $H_2$  molecule was located at both  $T$  sites with initial orientations along the  $\langle 111 \rangle$ ,  $\langle 110 \rangle$ , and  $\langle 100 \rangle$  directions. The  $H_2^*$  defects were constructed with one H atom at a BC site, and the other H atom at the appropriate  $T_{As}$  or  $T_{Ga}$  site. The clusters were relaxed without any constraints.

The stable dimer is a  $H_2$  molecule oriented along  $\langle 111 \rangle$  at the  $T_{Ga}$  site. The energies of the metastable structures relative to this are given in Table V. The  $H_2$  molecule initially oriented along  $\langle 110 \rangle$  spontaneously reorients along  $\langle 111 \rangle$  at both  $T$  sites. The H-H bond length for  $\langle 111 \rangle$  and  $\langle 100 \rangle$  orientations lay between 0.74 and 0.77 Å. There were no deep gap levels associated with the molecules. In the  $H_2^*$  defects,

TABLE V. The energies in eV of the structures investigated for the H dimer relative to the stable structure. The  $H_2$  molecule is oriented along either  $\langle 111 \rangle$  or  $\langle 100 \rangle$  at a  $T$  site.

Defect	Relative energy (eV)
$H_2 \langle 111 \rangle T_{Ga}$	0.00
$H_2 \langle 111 \rangle T_{As}$	0.09
$H_2 \langle 100 \rangle T_{Ga}$	0.02
$H_2 \langle 100 \rangle T_{As}$	0.06
$H_2^*(As)$	0.90
$H_2^*(Ga)$	0.42

the hydrogen atom initially at the  $T$  site spontaneously moved to the corresponding AB site and the BC-sited H atom moved away from the other H atom to bond more strongly with the host atom. The bond lengths are shown in Table VI. Again, the defect does not possess any deep levels. The dimer consisting of a neighboring pair of BC sited atoms is unstable and relaxed to  $H_2^*(Ga)$ .

### C. Larger cluster calculations

The lowest-energy form for the hydrogen dimer was shown in Sec. IV B to be a  $H_2$  molecule. In order to determine its dissociation energy, calculations were performed using a 302-atom cluster.

A  $H_2$  molecule was located near the center of the cluster at a  $T_{Ga}$  site and oriented along  $\langle 111 \rangle$ . We also considered two configurations for the separated pair of H atoms: one involving two neutral H atoms at BC sites separated by 12 Å and a  $H_{AB}^-$  and  $H_{BC}^+$  pair separated by 10 Å. All atoms were then relaxed in each of the three clusters.

The dissociation energy of  $H_2$ , producing a  $H^-$  and  $H^+$  pair, is 1.64 eV, and 2.38 eV if two  $H^0$  defects were produced. These values are comparable with those found in the supercell calculations<sup>35</sup> and demonstrate that isolated interstitial H atoms in GaAs behave as a negative- $U$  defect, i.e., the reaction  $2 H^0 \rightarrow H^+ + H^-$  is exothermic. The existence of  $Mu^0$  is not in contradiction with our demonstration for negative- $U$  behavior, for the muon experiment is carried out on GaAs containing a single muon with a limited lifetime.

## V. DISCUSSION

The calculations have shown that the dissociation energy for C-H and C- $H^-$  are 0.96 and 0.44 eV, respectively. The

TABLE VI. The bond lengths in Å corresponding to the relaxed  $H_2^*$  structures investigated, with reference to Fig. 5.

Bond lengths	$H_2^*(Ga)$	$H_2^*(As)$
$As_1-H_{BC}$	1.51	2.14
$Ga_1-H_{BC}$	2.13	1.46
$As_1-H_{AB}$		1.52
$Ga_1-H_{AB}$	1.52	
$As_1-Ga_2$	2.40	2.38
$Ga_1-As_2$	2.39	2.40

corresponding activation barriers to the dissociation are 1.84 and 0.88 eV, and the reorientation energy of the neutral C-H complex is estimated to be 0.64 eV. The experimentally determined activation barrier<sup>22</sup> and reorientation energies<sup>41</sup> are  $1.75 \pm 0.3$  eV and 0.5 eV, respectively, for the neutral C-H complex. Since the presentation of these results in a preliminary paper,<sup>46</sup> an experimental determination of the energy barrier of  $C-H^- \rightarrow C^- + H^0$  has been carried out<sup>47</sup> yielding 0.9 eV, in agreement with these calculations.

The activation barrier is lowered by a electron resonantly bound to the defect because the work done in separating  $H^0$  from  $C^-$  is less than that in separating  $H^+$  from  $C^-$ ; and the electron, initially present as a conduction-band resonance, now occupies a deep state in  $H^0$ . There is also a barrier of about 0.9 eV to the passivation process where free  $H^+$  complexes with  $C^-$  and a smaller barrier for the recombination of  $H^0$ . This means that a gas of free  $H^+$  can exist in the presence of ionized C acceptors, as indeed found.<sup>22</sup>

The stable site for  $H^0$  or  $H^+$  is a bond-centered one, whereas  $H^-$  is stable at the Ga anti-bonding site. For  $Mu^-$ , the large zero-point energy probably causes a dynamic reorientation among the four antibonding sites. Taking this into account, these results are consistent with muon studies and differ from earlier theoretical ones.

A hydrogen molecule is stable at the  $T_{Ga}$  site with a dissociation energy of 1.64 eV. The product of the dissociation consists of a  $H^+$  and  $H^-$  pair, rather than neutral atoms, showing that hydrogen is a negative- $U$  defect, in agreement with previous theoretical studies.<sup>35</sup>

We now discuss the degradation of devices caused by H aggregation. As hydrogen is a negative  $U$  defect, the  $H^0$  released in the process  $C-H + e^- \rightarrow C^- + H^0$  during minority carrier injection is unstable. It either loses an electron and becomes  $H^+$ , which would then have a high probability of recombining with  $C^-$  and reforming the passivated complex, or it captures a second electron, becoming  $H^-$ . This must then switch sites, but will not recombine with  $C^-$ . In fact, it is likely to migrate further away due to Coulomb repulsion, and could eventually form either a molecule by combining with an  $H^+$  or a larger H cluster or aggregate. In the latter case, the dissociation process results in the capture of two electrons, which implies a dependence on the square of the injection current, as observed experimentally. On the injection of electrons, the two-electron capture process and

subsequent molecule formation could also occur for any free hydrogen present in the material before electron injection. However, the effects of the degradation manifest themselves in the formation of recombination centers, i.e., defects possessing deep gap levels, but  $H_2$  molecules do not possess such levels. The degradation process must then involve further reactions associated with molecular hydrogen, which lead to the creation of very efficient recombination centers.

One possibility is that the molecules aggregate in the form of bubbles that plastically distort the surrounding lattice creating Ga and As interstitials, possibly in the form of a small dislocation loop. The driving forces for this process are a gain of about 0.5 eV for every hydrogen molecule ejected from the crystalline environment into vacuum, and the lowering in the tensile strain energy in the bulk. This strain energy is present as the volume occupied by the C acceptor is less than that of the As atom that it has replaced in the lattice. It is then implied that the barriers to the production of interstitials are less than the 0.96 eV calculated for enhanced C-H dissociation. The details of the process that leads to the creation of these interstitials is unclear. The bubbles may be related to platelets seen in degraded devices, although it is not clear that the platelets are associated with dislocations. It suggests that if hydrogen bubble formation was inhibited, then the degradation would disappear. This would correlate with the results indicating that the incorporation of a small concentration of In atoms into the material reduces the rate of degradation. The tensile strain energy of C acceptors will be reduced by the presence of the larger In atom reducing one of the driving forces for bubble growth. In addition, In is known to lock As dislocations, preventing their growth.<sup>48</sup> In this way, the effect of In on the degradation process could be explained. However, further experiments and calculations are necessary to confirm this model.

#### ACKNOWLEDGMENTS

We thank Kazumi Wada for helpful discussions and communication of his experimental results. We also thank the EPSRC for financial support for this work and the HPCI for an allocation of computer time on the Cray T3D at Edinburgh. S.J.B thanks the Edinburgh Parallel Computing Centre TRACS scheme for additional time on the T3D. S.Ö. thanks NFR and TFR in Sweden for financial support, and also PDC at KTH for computer time on the SP2.

<sup>1</sup>H. Fushimi and K. Wada, *Mater. Sci. Forum*, **196-201**, 957 (1995).

<sup>2</sup>H. Sugahara, J. Nagano, T. Nittono, and K. Ogawa (unpublished).

<sup>3</sup>F. Ren, C. R. Abernathy, S. N. G. Chu, J. R. Lothian, and S. J. Pearton, *Solid State Electron.* **38**, 1137 (1995).

<sup>4</sup>R. Jones and S. Öberg, *Phys. Rev. B*, **44**, 3673 (1991).

<sup>5</sup>A. Amore Bonapasta, *Phys. Rev. B* **48**, 8771 (1993).

<sup>6</sup>D. N. Talwar, *Phys. Rev. B* **52**, 8121 (1995).

<sup>7</sup>T. H. Chu, J. E. Cunningham, J. A. Ditzenberger, and W. Y. Jan, *J. Cryst. Growth* **111**, 274 (1991).

<sup>8</sup>R. C. Newman, *Infra-Red Studies of Crystal Defects* (Taylor and Francis, London 1973).

<sup>9</sup>M. J. Ashwin, B. R. Davidson, K. Woodhouse, R. C. Newman, T.

J. Bullough, T. B. Joyce, R. Nicklin, and R. R. Bradley, *Semicond. Sci. Technol.* **8**, 625 (1993).

<sup>10</sup>J. D. Collins, G. A. Gledhill, R. Murray, P. S. Nandra, and R. C. Newman, *Phys. Status Solidi B* **151**, 469 (1989).

<sup>11</sup>G. A. Gledhill, S. B. Upadhyay, M. J. L. Sangster, and R. C. Newman, *J. Mol. Struct.* **247**, 313 (1991).

<sup>12</sup>R. Jones, and S. Öberg, *Semicond. Sci. Technol.* **7**, 855 (1992).

<sup>13</sup>R. Jones and S. Öberg, *Mater. Sci. Forum*, **143-47**, 253 (1994); *Phys. Rev. B* **49**, 5306 (1994).

<sup>14</sup>B.-Ho Cheung, and K. J. Chang, *Phys. Rev. B* **49**, 17436 (1994).

<sup>15</sup>R. Jones, *Philos. Trans. R. Soc. London Sect. A* **350**, 189 (1995).

<sup>16</sup>S. K. Estreicher, *Mater. Sci. Rep.* **14**, 319 (1995).

<sup>17</sup>R. C. Newman, *Semicond. Semimet.* **38**, 117 (1995).

- <sup>18</sup>B. Clerjaud, F. Gendron, M. Krause, and W. Ulrici, *Phys. Rev. Lett.* **65**, 1800 (1990).
- <sup>19</sup>D. M. Kozuch, M. Stavola, S. J. Pearton, C. R. Abernathy, and W. S. Hobson, *J. Appl. Phys.*, **73** 3716 (1994).
- <sup>20</sup>B. R. Davidson, R. C. Newman, T. J. Bullough, and T. B. Joyce, *Semicond. Sci. Technol.* **8**, 1783 (1993).
- <sup>21</sup>B. R. Davidson, R. C. Newman, R. E. Pritchard, T. J. Bullough, T. B. Joyce, R. Jones, and S. Öberg, in *Physics and Applications of Defects in Advanced Semiconductors*, edited by M. O. Manasreh, H. J. von Bardeleben, G. S. Pomrenke, and M. Lannoo, MRS Symposia Proceedings No. 325 (Materials Research Society, Pittsburgh, 1994), p. 241.
- <sup>22</sup>H. Fushimi and K. Wada, *J. Cryst. Growth* **145**, 420 (1994).
- <sup>23</sup>C. H. Seager and R. A. Anderson, *Appl. Phys. Lett.* **59**, 585 (1991).
- <sup>24</sup>T. Zundel and J. Weber, *Phys. Rev. B* **39**, 13 549 (1989).
- <sup>25</sup>H. Y. Cho, S. Min, K. J. Chang, and C. Lee, *Phys. Rev. B* **44**, 13 779 (1991).
- <sup>26</sup>S. J. Pearton, C. R. Abernathy, and J. Lopata, *Appl. Phys. Lett.* **59**, 3571 (1991).
- <sup>27</sup>B. D. Patterson, *Rev. Mod. Phys.* **60**, 69 (1988).
- <sup>28</sup>J. W. Schneider, K. H. Chow, R. F. Kiefl, S. R. Kreitzman, A. MacFarlane, R. C. DuVarney, T. L. Estle, R. L. Lichti, and C. Schwab, *Phys. Rev. B* **47**, 10 193 (1993).
- <sup>29</sup>R. Kadano, A. Matsushita, K. Nagamine, K. Nishyama, K. H. Chow, R. F. Kiefl, A. MacFarlane, D. Schumann, S. Fujii, and S. Tanigawa, *Phys. Rev. B* **50**, 1999 (1994).
- <sup>30</sup>R. F. Kiefl, M. Celio, T. L. Estle, G. M. Luke, S. R. Kreitzman, J. H. Brewer, D. R. Noakes, E. J. Ansaldo, and K. Nishyama, *Phys. Rev. Lett.* **58**, 1780 (1987).
- <sup>31</sup>K. H. Chow, R. F. Kiefl, W. A. MacFarlane, J. W. Schneider, D. W. Cooke, M. Leon, M. Paciotti, T. L. Estle, B. Hitti, R. L. Lichti, S. F. J. Cox, C. Schwab, E. A. Davis, A. Morrobel-Sosa, and L. Zavieh, *Phys. Rev. B*, **51**, 14762 (1995).
- <sup>32</sup>N. M. Johnson, C. Herring and D. Bour, *Phys. Rev. B* **48**, 18 308 (1993).
- <sup>33</sup>P. Briddon and R. Jones, in *Shallow Defects in Semiconductors*, edited by B. Monemar, IOP Conf. Proc. No. 95 (Institute of Physics, London, 1988), pp. 459-64 (1988).
- <sup>34</sup>Dj. M. Maric, S. Vogel, P. F. Meier, and S. K. Estreicher, *Phys. Rev. B* **40**, 8545 (1989).
- <sup>35</sup>L. Pavesi and P. Gianozzi, *Phys. Rev. B* **43**, 2446 (1991).
- <sup>36</sup>C. G. Van de Walle and L. Pavesi, *Phys. Rev. B* **47**, 4256 (1993).
- <sup>37</sup>R. Jones, *J. Phys. C* **21**, 5735 (1988).
- <sup>38</sup>P. R. Briddon, Ph.D. thesis, University of Exeter, 1990.
- <sup>39</sup>S. J. Breuer, Ph.D. thesis, University of Newcastle upon Tyne, 1994.
- <sup>40</sup>G. B. Bachelet, D. R. Hamann, and M. Schlüter, *Phys. Rev. B* **26**, 4199 (1982).
- <sup>41</sup>B. Clerjaud, D. Cote, F. Gendron, W-S. Hahn, M. Krause, and C. Porte, *Mater. Sci. Forum*, **83-7**, 563 (1991).
- <sup>42</sup>S. Öberg, P. K. Sitch, R. Jones, and M. I. Heggie, *Phys. Rev. B*, **51**, 13 138 (1995).
- <sup>43</sup>P. R. Briddon, R. Jones, and G. M. S. Lister, *J. Phys. C* **21**, L1027 (1988).
- <sup>44</sup>K. J. Chang and D. J. Chadi, *Phys. Rev. B* **40**, 11 644 (1989).
- <sup>45</sup>J. D. Holbeck, B. Bech Nielsen, R. Jones, P. Sitch, and S. Öberg, *Phys. Rev. Lett.* **71**, 875 (1993).
- <sup>46</sup>S. J. Breuer, R. Jones, S. Öberg, and P. R. Briddon, *Mater. Sci. Forum*, **196-201**, 951 (1995).
- <sup>47</sup>H. Fushimi and K. Wada (private communication).
- <sup>48</sup>I. Yonenaga and K. Sumino, *J. Appl. Phys.* **65**, 85 (1989).