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Morphology and Stability of the C/BN Interfaces: *Ab Initio* Studies

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We investigate the morphology and charge distribution at the (001)-diamond/BN heteropolar junctions of the cubic materials. Our investigations are based on the first principles calculations in the framework of the density functional theory. These studies reveal that reconstruction of the interface leads to possible charge compensation at the interface and increases also the stability of the junction in comparison to the abrupt interfaces.

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1. Introduction

Recently one observes increasing interest in various crystallographic forms of boron nitride. This material possesses many properties similar to that of diamond, such as wide band gap, extreme hardness, high thermal conductivity, and good transmittance over a large spectral range [1]. These unique physical properties make it be an appropriate material for technological development of micro-, and/or nanoelectronic devices and also of optoelectronic ones operating in the visible/ultra-violet regions of electromagnetic spectrum. Physical and chemical properties of BN have been studied in great detail, both theoretically and experimentally [2]. It turns out that hexagonal boron nitride (h-BN) is the best substrate for graphene layers, so the interface between BN and C is of importance for 2D electronics. It has been also demonstrated experimentally [3] that not only vertically stacked graphene/h-BN hybrid structures can be grown [4, 5] but also in-plane graphene/h-BN atomic layer can be integrated into a lateral heterostructure with randomly distributed domains by CVD method.

However, the employment of such structures in potential applications requires deep understanding of interface properties and, therefore, a physical insight into microscopic details of interfaces’ morphology. In this work, we present *ab initio* density functional theory (DFT) based studies of (001)-diamond/BN heterostructure junctions as a prototype of the interfaces between boron/carbon and nitrogen/carbon atomic layers. We consider the c-BN stacked on the (001) diamond surface employing superlattice approach. The chosen superlattices contain two chemically equivalent B/C (or N/C) interfaces. It is commonly known that, owing to the different valency of the atoms constituting the adjacent layers of the junction, the abrupt B/C and N/C interfaces contain “oversaturated” or “undersaturated” tetrahedral bonds [6]. This *bond heteropolarity* leads to macroscopically charged interfaces that are generally energetically unstable and undergo various reconstructions. We propose various interface reconstruction patterns, which involve one mixed layer of B and N in proportion one-half adjacent to C layer, and then search for the preferred bonding configurations. To describe various mixing patterns, we use $2\sqrt{2}\times 2\sqrt{2}$ lateral unit cell (eight primitive lateral cells) in the superlattice, which results into systems with up to 128 atoms in the unit cell.

2. Calculation method and model of C/c-BN heterostructure

Our *ab initio* calculations are performed in the framework of the DFT as implemented in Siesta program package [7]. The electron exchange-correlation effects are treated within the generalized gradient approximation (GGA) using the PBE form of the exchange-correlation functional [8]. The electron ion-core interactions are represented by pseudopotentials of the Troullier-Martins type [9] and the electron wave functions are expanded into the atomic-orbital basis set using the double-ζ polarized set. The cutoff of 400 Ry is used for the real space mesh. The Brillouin zone integrations are performed by means of the (11,11,11) and (9,9,9) k-points meshes for bulk diamond and boron nitride crystals, respectively, as well as the (5,5,1) one for superlattice calculations. The diamond and zinc-blende (c-BN) nitride crystals are represented by cubic supercells that are repeated periodically in space. The above chosen numerical parameters lead to the following lattice constants for the bulk crystals: diamond $a_0 = 3.5864$ Å, and c-BN $a_0 = 3.6150$ Å, in fairly good agreement with experimental values (3.5668 Å and 3.615 Å, for diamond and c-BN, respectively [10]).

The interfaces between diamond and c-BN surfaces are represented in our model by means of the non-stoichiometric diamond/c-BN superlattice. The system consists of 9 C monolayers with $2\sqrt{2}\times 2\sqrt{2}$ diamond lateral unit cell stacked along the [001] axis, above which there are 4 B(N) and 3 N(B) alternating layers creating zinc-blende structure (note that such cell contains

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8 atoms). This guarantees that there are two chemically equivalent interfaces in the superlattice (however, note that due to non-stoichiometric amount of different monolayers in the system, atoms in the lower and upper interfaces exhibit different configurations of the nearest neighbors in space) and that the interface formation energy can be calculated unambiguously. The geometry of this 128 atom system is fully relaxed, until forces acting on the atoms are smaller than 0.02 eV/Å, and the heterostructure interface is created between C–B(N) atoms. The considered, abrupt and reconstructed interfaces of diamond/c-BN junction are presented in Fig. 1. Note that in zinc-blende structure each (001) plane contains atoms of one type. Therefore, at the abrupt interfaces diamond/c-BN we have the following sequence of planes: ...–C–**C**–**B**–N–..., or ...–C–**C**–**N**–B–..., i.e., the plane containing only group IV elements (C) has the adjacent plane which contains solely group III (N) or group V (B) elements. This leads to under- or oversaturated bonds and accumulation of charge at the interface as described below. As it turns out the reconstruction of the interface can prevent this pileup of charge and increase the stability of the interface [6]. Here, as the reconstructed interface we consider the structure, where the crystallographic (001) plane adjacent to the carbon plane contains both atoms of group III and atoms of group V in suitable proportion, and distributed in a lateral unit cell according to a certain pattern.

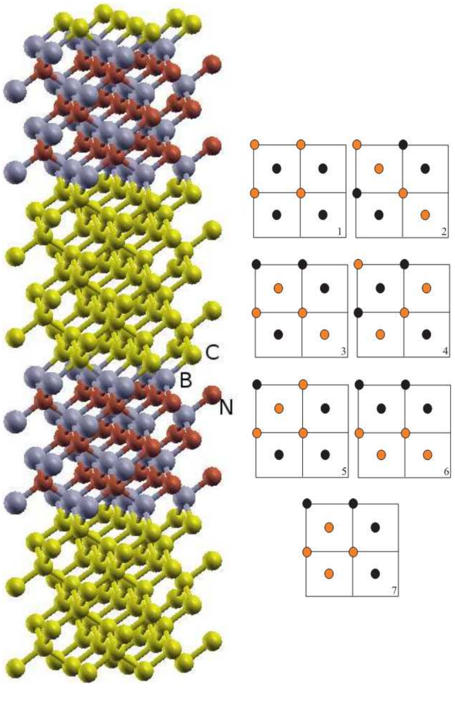

Fig. 1. Left: Non-stoichiometric diamond/c-BN superlattice with the abrupt C–B interface. Right (parts 1–7): Compensation patterns for diamond/c-BN interfaces involving four B and four N atoms present in the adjacent layer to carbon one in $2\sqrt{2} \times 2\sqrt{2}$ lateral unit cell. Boron and nitrogen atoms are distinguished by colors.

The discussed abrupt systems possess under- or oversaturated tetrahedral bonds at the interface due to different valency of the neighboring atoms. In the case of abrupt C–B interface with 8 B atoms in the $2\sqrt{2} \times 2\sqrt{2}$ lateral unit cell, shown in the left part of Fig. 1, there is a lack of 1/2 electron per each B atom, leading to the total deficiency of 4 electrons in the lateral unit cell. In turn, the abrupt C–N interfaces exhibit the total abundance of 4 electrons per such cell. This enables one to propose the following compensation pattern: 4 B(N) atoms present in the adjacent layer to carbon one in the $2\sqrt{2} \times 2\sqrt{2}$ lateral unit cell should be replaced by 4 N(B) ones, respectively. Hence, we study the following arrangements of the B and N atoms shown in right part of Fig. 1, which lead to the charge compensated interfaces. In our case, they represent systems with a mixed N:B layer in proportion 1/2, which is adjacent to the pure carbon layer. Note that due to the periodic boundary conditions and symmetry of the system, other atomic arrangements of four B and four N atoms in the $2\sqrt{2} \times 2\sqrt{2}$ lateral unit cell become equivalent. Moreover, a given sequence of the reconstructing atoms in e.g., [110] direction in the lower interface of non-stoichiometric superlattice leads to the analogous sequence of atoms in the upper interface, however, in the direction $[\bar{1}10]$. We consider here much richer variety of reconstructions that were previously considered for the (001)-3C-SiC/GaN cubic heterostructures [6].

3. Results

For the systems studied, we have computed the total energies of the abrupt and compensated superlattices, distributions of the probability density of valence electrons n, as well as the laterally averaged distributions of the total potential $\langle V_{\text{tot}} \rangle$ and charge $\langle Q_{\text{tot}} \rangle$. The resulting total energies of the superlattices with abrupt interfaces are $E_{\text{tot}} = -171.01$ eV/atom for C–B interface, and $E_{\text{tot}} = -181.70$ eV/atom for the C–N interface. It should be noted that this huge difference in energy is due to some distortions in five elementary tetrahedrons in the C–N interface type. In particular, in the central one, the bond angle of a N atom in the nitrogen layer to two B atoms in the adjacent layer is nearly perfect tetrahedral angle of 114°, whereas the bond angle of the same N atom to two C atoms from the adjacent C layer is strongly distorted and equal to 63°. This change in shape causes further distortions consisting in broken single C–N bond in each of the neighboring four tetrahedrons. The angles inside them differ less from the perfect one and are in the range of 107° to 112°. These distortions, in our opinion, lead to the above differences in the total energy of the both interface types and, moreover, they have been observed in a slab model of the abrupt C–N interface, studied by us independently. It suggests that this kind of abrupt interface is not stable, and the interface undergoes strong deformation to guarantee binding of the two materials, simultaneously making plausible all kinds of reconstruction. In further discussion we focus on C–N interfaces, which can be also compared to C–N interfaces in 3C-SiC/GaN heterostructures studied previously [6].

We have analyzed the relative energetic stability, distributions of the valence charge, as well as the profiles of $\langle Q_{\rm tot}\rangle$ and $\langle V_{\rm tot}\rangle$ of all 7 reconstruction patterns leading to the charge compensation, shown in Fig. 1. Note that for these systems comparison of total energies is equivalent to the comparison of the formation enthalpies defined in Eq. (1). It turns out that the structures with reconstructed interfaces are always energetically preferable in comparison to ones with abrupt interfaces. Among reconstructed interfaces, the most favorable energetically is configuration No. 2. In this configuration, the compensating B atoms are situated in one row along the [110] direction, while in the $[\bar{1}10]$ one a periodic, alternating sequence of B and N atoms is observed. An essential redistribution of the electron charge on the B–C bond is to be noticed in the picture of $\Delta n = n - n_{\rm at}$ ($n_{\rm at}$ is the superposition of probability distributions for free atoms (pseudoatoms) creating the superlattice) span by the $[\bar{1}10]$ and [001] directions, shown in Fig. 2. The electron charge density is shifted towards carbon atom, which plays the role of anion. In turn, an electron pair is located on the bond between the interface IV-valency C and V-valency N atoms. The profiles of laterally averaged $\langle Q_{\rm tot}\rangle$ and $\langle V_{\rm tot}\rangle$ exhibit a smaller difference in oscillation amplitude in the range of the compensated interface, as compared to the non-compensated one. This most favorable energetically compensation pattern 2 leads to such configuration of the nearest neighbors in which each C interface atom creates bonds with different species: B and N. The least energetically favorable configuration is the one No. 4.

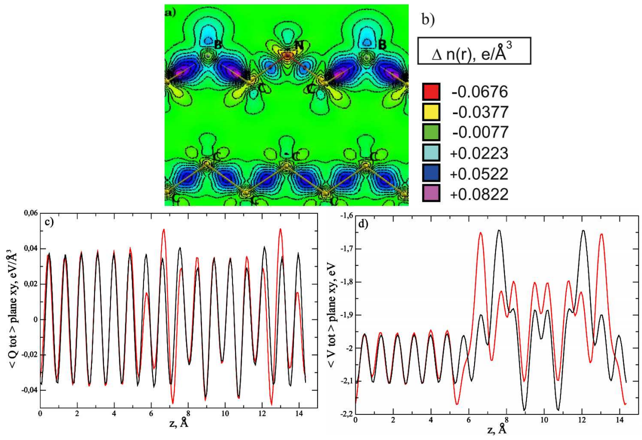

Fig. 2. (a) Valence electron density distribution (colour key in legend (b)) in compensated C/c-BN superlattice (pattern No. 2) and the resulting profiles of laterally averaged (c) $\langle Q_{\rm tot}\rangle$ and (d) $\langle V_{\rm tot}\rangle$. Dashed red and solid black lines represent profiles of the abrupt and compensated interfaces, respectively.

Next, we compute the energy gain per one primitive lateral cell (of the surface area $a^2/2$, where a is a standard cubic lattice constant) connected to the formation of the reconstructed interface considered in the present paper as

$$\Delta H = \frac{1}{2}\frac{1}{2\sqrt{2}\times 2\sqrt{2}}\left(E_{\rm tot}^{\rm sup.abr.} - E_{\rm tot}^{\rm sup.comp.}\right.$$
$$\left. + N_{\rm change}\mu_{\rm N} - N_{\rm change}\mu_{\rm B}\right), \qquad (1)$$

where $\frac{1}{2\sqrt{2}\times 2\sqrt{2}}$ is the surface of the chosen lateral unit cell in terms of the area of primitive lateral unit cell, $\frac{1}{2}$ comes from the fact that we have two equivalent interfaces in the superlattice, $E_{\rm tot}^{\rm sup.abr.}$ and $E_{\rm tot}^{\rm sup.comp.}$ denote total energy of the abrupt and compensated superlattices, respectively, $N_{\rm change} = 8$ denotes the number of nitrogen atoms that have been substituted by B atoms in the two reconstructed planes constituting the interfaces in the superlattice, and $\mu_{\rm N}$ and $\mu_{\rm B}$ are chemical potentials of N and B, respectively.

Table I presents the resulting values of ΔH for the diamond/c-BN superlattices with the reconstructed C–(N:B) interfaces (see Fig. 1). For the calculations of ΔH, the value of the chemical potential for B was taken as the total energy of boron bulk crystal per atom ($\mu_{\rm B} = -106.94$ eV/atom), next, the chemical potential of cubic BN crystal has been found per BN molecule ($\mu_{\rm BN} = -389.72$ eV/molecule), and finally the chemical potential of N atom has been calculated from the relation $\mu_{\rm N} = \mu_{\rm BN} - \mu_{\rm B}$ that holds in thermodynamic equilibrium (leading to $\mu_{\rm N} = -282.78$ eV/atom). This procedure would correspond to the case of boron rich conditions during the interface growth.

TABLE I

Formation entalphies for zinc-blende diamond/c-BN reconstructed interfaces.

Comp. pattern	ΔH, [eV/cell]
1	0.906
2	1.415
3	1.016
4	0.801
5	0.997
6	1.249
7	1.245

4. Conclusions

We have studied possible reconstructions on the (001)-diamond/c-BN junctions. The obtained values of formation enthalpies confirm that the proposed interface reconstruction patterns Nos. 1–7 involving an appropriate exchange of 50% of N(B) atoms in the N(B) layer of the N(B)–C interface by B(N) atoms in the diamond/c-BN junction leads to stable, charge compensated interfaces. Our studies confirms general trend observed in heterovalent junctions (e.g., 4H-SiC/wz-GaN [11, 12]) that charge compensating reconstruction of the interface is a prerequisite of its energetic stability.

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