

# Morphology and Stability of the Diamond/BN (001) and (111) Interfaces Based on *Ab Initio* Studies

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The morphology, charge distribution and energetic stability of interfaces in the diamond/c-BN heteropolar junctions grown along [001] and [111] crystallographic directions are obtained from first principles calculations in the framework of density functional theory. It turns out that there exist reconstructions of the abrupt interfaces of the C and N adjacent layers (C–N type) that induce charge compensation and lead to the stabilization of the interfaces. On the contrary, our studies strongly suggest that analogous reconstructions of the abrupt interfaces of C and B adjacent layers (C–B type) are not energetically favorable and do not stabilize abrupt interfaces.

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## 1. Introduction

Interesting properties of cubic boron nitride (c-BN), like wide band gap, extreme hardness, good transmittance over a large spectral range, and high thermal conductivity [1] enable its application in micro-, nano-, and optoelectronics. Another important form of this compound is hexagonal boron nitride (h-BN), which is proved to be one of the best substrate for graphene layers and, in general, for 2D electronic devices, where operation of both vertically stacked and in-plane graphene/h-BN hybrid structures have been demonstrated [2–4].

The application of such structures requires good understanding of interface properties, in particular its morphology and stability. Herein, we continue our *ab initio* density functional theory (DFT) based studies of diamond/BN heterostructure junctions, being a prototype of the interfaces between carbon/boron and carbon/nitrogen atomic layers [5]. Due to different valency of the atoms constituting the adjacent layers of these junctions, one deals with the problem of “oversaturated” or “undersaturated” bonds present at these interfaces, and at the same time, with the energetic stability of the interface. Investigations on such system types e.g., X-ray absorption fine structure (XAFS) spectroscopy of thin GaN films grown by MBE on 6H-SiC substrates led to the conclusion that the experimental data matched best with a mixed N/C plane at the interface [6]. Additionally, high resolution electron microscopy (HREM) examination of the atomic arrangements in the GaN/SiC heterostructure identified some intermixing of atoms at the interface that protected from charge accumulation [7]. We have demonstrated that there exist some reconstruction patterns which improve the energetical stability of the (001)-diamond/BN interface [5]. The proposed reconstructions took place in the BN first monolayer, i.e., in the grown

material and they led to similar values of the formation enthalpies of the heterostructure (0.906–1.415 eV/cell) in the [001] direction. The diamond/BN heterostructure has been represented by the non-stoichiometric superlattice model with lateral  $2\sqrt{2} \times 2\sqrt{2}$  unit cell. In the present work we analyze reconstructions occurring both in the substrate interface layer and in the interface layer of the material grown in [001] and [111] directions. To enable a comparison of our results with those presented already for other nitrides grown on carbon or silicon carbon substrate [8, 9], we decrease the lateral unit cell to  $2 \times 2$  size and utilize both the non-stoichiometric superlattice and isolated slab models.

## 2. Calculation method and models of diamond/c-BN heterostructure

We perform the DFT-based *ab initio* calculations by means of SIESTA program [10]. The electron exchange-correlation effects are treated within the generalized gradient approximation (GGA) using the Perdew–Burke–Ernzerhof (PBE) form of the exchange-correlation functional [11]. The electron ion–core interactions are represented by pseudopotentials of the Troullier–Martins type [12] and the electron wave-functions are expanded into the atomic-orbital basis set using the double- $\zeta$  polarized set. The cut-off 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 above chosen numerical parameters lead to a good agreement between numerical and experimental values of lattice constants for the bulk diamond  $a_0 = 3.5864 \text{ \AA}$ , and bulk c-BN  $a_0 = 3.6150 \text{ \AA}$  (experimental values diamond: 3.5668  $\text{\AA}$  and c-BN: 3.615  $\text{\AA}$  [13]).

The interfaces between diamond and c-BN layers are represented by the non-stoichiometric superlattice model (in the growth directions [001] and [111]). As it is explained below, the non-stoichiometric superlattice model

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possesses two interfaces and, in particular, in the [111] direction the reconstruction in lower and upper interfaces comprises different number of atoms of given chemical sort. Meanwhile, in [001] the considered reconstruction of lower and upper interfaces leads to the exchange of the same number of atoms of given chemical sort. At the same time, this reconstruction restores the stoichiometry of the system. These circumstances can influence the energetic stability of the whole system.

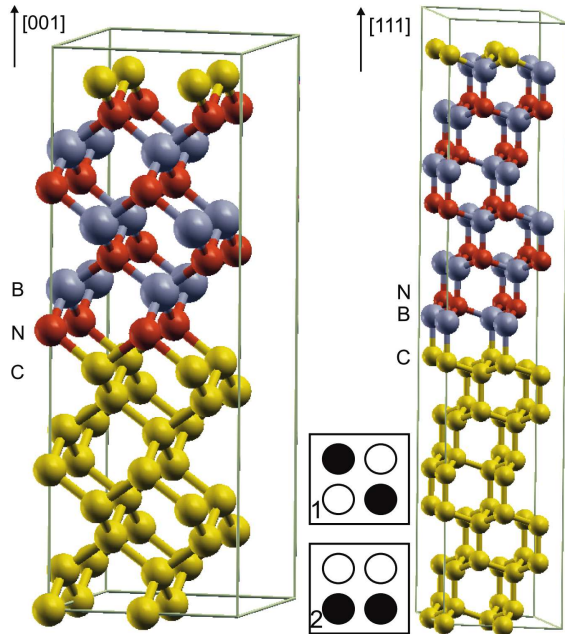


Fig. 1. Left: non-stoichiometric diamond/c-BN superlattice with the abrupt C–N interface in the growth direction [001]. Middle: parts 1, 2: reconstruction patterns for the (001) interface planes. Right: non-stoichiometric diamond/c-BN superlattice with the abrupt C–B interface in the growth direction [111].

Two models of the abrupt diamond/c-BN interfaces are presented in Fig. 1. The non-stoichiometric superlattice model in Fig. 1 (left) consists of 9C monolayers with  $2 \times 2$  lateral unit cell stacked along the [001] axis, above which there are 4N(B) and 3B(N) alternating layers creating zinc-blende structure of BN. There are two chemically equivalent interfaces in the superlattice of the C–B or C–N type, and the interface formation energy can be calculated unambiguously. The geometry of this 64 atom system is fully relaxed, until forces acting on the atoms are smaller than  $0.02 \text{ eV}/\text{\AA}$ . The right part of Fig. 1 shows the non-stoichiometric superlattice model of diamond/c-BN heterostructure in the [111] direction that consists of 13C, 6B(N), and 5N(B) monolayers. There are 2 interfaces: at the first one, one long bond joins group IV atom with group III(V) atom, and in the second one, each III(V) group atom creates 3 short bonds with 3 carbon atoms. All 96 atoms in the unit cell undergo relaxation. Such a choice of unit cell size enables comparison of the

calculation results obtained for diamond/c-BN [111] and 3C-SiC/GaN studied by us independently.

Note that in zinc-blende structure each of (001) and (111) planes contains atoms of one type. Therefore, at the abrupt interfaces in Fig. 1 the plane containing only group IV elements (C) has the adjacent plane which contains solely group III (B) or group V (N) elements. This leads to under- or oversaturated bonds and accumulation of charge at the interface as described below. The reconstruction of the interface can prevent this pileup of charge and increase the stability of the interface [8].

In the case of abrupt C–N interface with 4N atoms in the  $2 \times 2$  lateral unit cell (Fig. 1, left) there is an excess of  $1/2$  electron per each N atom, leading to the total abundance of 2 electrons in the cell. In turn, the abrupt C–B interfaces exhibit the total deficiency of 2 electrons per such cell. Hence, the reconstruction in the first BN monolayer analogous to that of studied in Ref. [5] can be as follows: 2N(B) atoms present in the adjacent layer to carbon one in the  $2 \times 2$  lateral unit cell should be replaced by 2B(N) ones, respectively. In this way, the reconstructed cell layer possesses  $2N+2B$  atoms. The other possible reconstruction concerns diamond interface layer and it is following:  $2C+2B$  in the case of C–N type interface or,  $2C+2N$  in the case of C–B one. The choice of atoms in the corresponding (001) plane can be done according to 1st or 2nd reconstruction pattern shown in the middle part of Fig. 1.

The reconstruction pattern that is valid for long tetrahedral bonds joining interface atoms of diamond/c-BN [111] in the right part of Fig. 1 has been presented in [9] for the 4H-SiC/GaN heterostructure with analogous wurtzite structure. On this basis it can be concluded that in the case of abrupt C–B interface 1 out of 4B atoms in the lateral  $2 \times 2$  unit cell should be replaced by 1C atom, whereas in the case of abrupt C–N interface the substitution involves 1N atom in the first nitrogen layer. Hence, the reconstruction patterns are:  $3B+1C$  or,  $3N+1C$ . The model of non-stoichiometric superlattice in Fig. 1 (right) exhibits additionally the upper interface with short tetrahedral bonds. As for C–B upper interface, there is a total lack of  $3/4 e$  near each B interface atom sharing its bonds with 3 carbon atoms. However, when one carbon atom replaces one B atom in this configuration, there is an excess of  $1/4 e$  in its neighborhood. This observation enables to propose the following reconstruction pattern in the considered boron layer: 3C atoms are introduced into the  $2 \times 2$  lateral unit cell in order to replace 3B atoms, which leads to  $1B+3C$ . By analogy, the reconstructed C–N upper interface layer with short tetrahedral bonds possesses  $1N+3C$  atoms.

### 3. Results

In order to check the energetic stability of the reconstructed interfaces we compute the energy gain per one primitive lateral cell of the studied system according to the formula [14]:

$$\Delta H = \frac{1}{2} \frac{1}{2 \times 2} (E_{\text{tot}}^{\text{sup. abr.}} - E_{\text{tot}}^{\text{sup. comp.}} + \mu_{\text{comp. atom}} - \mu_{\text{orig. atom}}), \quad (1)$$

where  $\frac{1}{2 \times 2}$  is the surface of the chosen lateral unit cell, ratio  $\frac{1}{2}$  takes into account two equivalent interfaces in the superlattice,  $E_{\text{tot}}^{\text{sup. abr.}}$  and  $E_{\text{tot}}^{\text{sup. comp.}}$  denote total energy of the abrupt and compensated superlattices, respectively,  $\mu_{\text{comp. atom}}$  denotes the chemical potential of each compensating atom that replaces an original atom with chemical potential  $\mu_{\text{orig. atom}}$ .

Table I presents the resulting values of  $\Delta H$  for the diamond/BN superlattices in the growth directions [001] and [111]. For the calculations of  $\Delta H$ , values of the chemical potentials are adapted from the bulk materials, as in [5].

TABLE I

Formation enthalpies for reconstructed interfaces in the diamond/c-BN superlattice in the growth directions [001] and [111]. Patterns 1 and 2 are shown in the middle part of Fig. 1. Upper and lower interfaces are reconstructed either by 1st or 2nd pattern, simultaneously. #1 — reconstruction by, #2 — reconstructed layer.

Direction	Type	#1	#2	Pattern	$\Delta H$ [eV/cell]
[001]	C-N	B	N layer	1	1.605
				2	1.709
	C-N	B	C layer	1	2.568
				2	2.483
	C-B	N	B layer	1	-3.417
				2	-3.476
	C-B	N	C layer	1	-0.594
				2	-0.697
[111]	C-N	C	N layer	3N+1C	2.304
				1N+3C	
	C-B	C	B layer	3B+1C	-0.257
				1B+3C	

It follows from Table I that the reconstruction of the C-N type interface is energetically favorable in both growth directions. Moreover, this reconstruction leading to valence charge compensation in unit cell is preferred in the diamond substrate layer than in the material BN deposited on the substrate. At the same time the reconstructed C-B interfaces studied in both crystallographic directions are less stable than the abrupt ones.

From the picture of the spatial valence electron density distribution follows that the energetically best reconstruction concerning C-N interface ( $\Delta H = 2.568$  eV/cell) is connected with relatively large charge transfer. It starts from the nitrogen plane and proceeds towards 1st and 2nd diamond layers. Not only the compensated diamond layer gains some electron charge, but also bonds joining this layer with nearest layers, especially bonds with 2nd diamond layer. In the case of C-B interface with the most negative formation enthalpy, the accumulation of electron charge is observed only around N

compensating atoms in first boron layer and on bonds joining these atoms with lower neighbors. In comparison with the former situation electron charge is not smeared out within a large volume. Finally, charge transfer at C-N reconstructed interfaces in diamond/BN stacked along [111] lies at most in the increase in electron charge at the bonds joining the compensating C atom with the nearest neighbours, as well as in the increase in electron charge present in the boron and second substrate carbon monolayers. The results obtained for reconstructed interfaces of the (111)-C-N type, common in diamond/c-BN, 4H-SiC/GaN [9], 3C-SiC/GaN (not presented here), show that the charge compensation by means of C atoms is always energetically favorable in the nitride layer (with  $\Delta H > 0$ ), opposed to the reconstructed interfaces (111)-C-B and (111)-C-Ga. In our opinion it is a consequence of different charge transfer picture within atomic layers. In the case of direction [001] and C-N type interface, the energetically most stable reconstruction occurs in the substrate diamond layer.

#### 4. Conclusions

Performed *ab initio* studies of the diamond/c-BN heteropolar junctions reveal interface reconstruction patterns that lead to the charge compensation of the “oversaturated” bonds at the abrupt interfaces of the C-N type and are energetically more stable than the abrupt interfaces. Unexpectedly, it is not so in the case of C-B type of abrupt interfaces. None of the considered reconstructed interfaces is more stable than the abrupt one. We ascribe this behavior to the different charge transfer patterns for the C-N and C-B types of abrupt interfaces. However, further studies to shed light on the physical mechanisms of this phenomenon are under way.

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