



Ab initio studies of early stages of AlN growth process on the oxygen-terminated diamond (111) surface

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ABSTRACT

We discuss the early stages of AlN growth on the oxygenated diamond (111) surface based on first principles calculations in the framework of density functional theory. Some stable adsorption sites of Al and N atoms are found on the O/diamond (111) surface that in consequence allow formation of two AlN structures with distinct morphologies, which are characterized by different energetic structures. They reflect the way how strain present in the system is released in the relaxation process of deposited layers. Two essential charge carrier redistributions occur within the topmost carbon substrate layers, the first one is a result of oxygenation of the diamond (111) surface, and the second one is a consequence of deposition of 1st Al monolayer on O/diamond (111). Finally, it is demonstrated that passivation of the diamond (111) surface by a layer with mixed O and H atoms does not result in the formation of a stable AlN structure, due to considerably large buckling of the system's top layers.

1. Introduction

Diamond and wide-bandgap nitride materials are in focus of contemporary high power, high frequency, high temperature microelectronics and optoelectronics due to their unique properties. In particular, the hexagonal wurtzite structure of AlN exhibits a large forbidden energy bandgap ($E_g \sim 6.2$ eV), high-breakdown field, and high-piezoelectric properties [1,2]. Though diamond is an indirect bandgap material ($E_g \sim 5.5$ eV) it possesses high-breakdown field, high chemical and physical inertness, high carrier mobility [3], high saturation velocity [4], as well as the highest sound velocity and thermal conductivity among other known materials. Since AlN, among the III group nitrides has the closest thermal expansion coefficient to diamond, many attempts have been made to combine properties of these two materials into one structure, i.e. a heterojunction. Up to now, the AlN layer has been deposited on diamond substrates by various techniques, starting from chemical vapor deposition (CVD) [5], chemical beam epitaxy (CBE) [6], molecular beam epitaxy (MBE) [7], and metal-organic vapor phase epitaxy (MOVPE) [8–10]. The AlN/diamond heterojunction has been tested so far as deep ultraviolet light-emitting diode (DUV LED) [11,12], high-power and high-frequency field-effect transistor (FET) [13], as well as high-frequency surface acoustic wave device (SAW) [14]. Recently, Imura et al. demonstrated the single-crystal AlN/diamond heterojunction with high-density interface hole channel, grown by MOVPE on the hydrogenated diamond (111) surface [15]. However, the same growth method and treatment of the substrate

leading to the oxygen terminated diamond (111) surface [16] resulted in AlN layer of two-domain structure with poor crystalline quality [9], which was the origin of high-gate-leakage current of the fabricated FET [17], and hindered the practical use of AlN/diamond FET. Exploration of the passivation layer which does not degrade the two-dimensional hole gas is still an important issue for the AlN/diamond heterojunction FET performance.

It is of interest therefore to perform modelling of the early stages of AlN growth process on the oxygenated diamond (111) surface in order to find a morphology of the energetically preferred structure, as well as its energetical and electronic structures. This enables tracing changes in the spatial distribution of charge carriers across the AlN/O-diamond (111) interface at each stage of layer's growth, what extends our knowledge on microscopic details of interfaces' morphology and stability. Studies presented in this paper are based on *ab-initio* density functional theory calculations, and we focus on the [111] growth direction of the AlN/O-diamond(111) heterostructure.

2. Calculation method and model of diamond/(111) surface

Our first principle calculations are performed in the framework of the density functional theory (DFT) by means of SIESTA program [18]. 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 [19]. The electron ion-core interactions are represented by the Troullier-Martins

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type [20] pseudopotentials 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 integration is performed by means of the (11,11,11) and (7,7,1) k -points meshes for diamond bulk and supercell calculations, respectively. The above chosen numerical parameters ensure good convergence in calculations, in particular the resulting lattice constant of bulk diamond equals to 3.6584 Å (exp. value 3.56683(1) Å [21]).

The diamond (111) surface is represented by an isolated slab model that consists of 18 carbon monolayers in the growth direction [111]. A size of the lateral unit cell is chosen to be 2×2 , what in consequence leads to the total number of 72 carbon atoms in the system. All single dangling bonds of the lowermost carbon layer are saturated by hydrogen atoms. The slabs are separated from their periodic replicas in the [111] growth direction by 30 Å vacuum layer. The atoms belonging to six uppermost carbon monolayers, as well as four saturating hydrogen atoms undergo in computations full relaxation, until the forces acting on them are smaller than 0.02 eV/Å, while the remaining carbon atoms are kept frozen at their positions in order to mimic the bulk behaviour of diamond.

The model of diamond (111) surface is presented in Fig. 1 a), where some high-symmetry on-surface sites are indicated. These sites serve in our study as possible adsorption places for oxygen, aluminium, and nitrogen adsorbates. In particular, these are the position “on-top” of the carbon atom of the topmost surface layer, in H_3 or T_4 site, and in the “bridge” between two neighbouring topmost atoms.

3. Results and discussion

3.1. Formation of oxygen layer on the diamond (111) surface

In order to model the AlN growth process on oxygen-terminated diamond (111) substrate we start from the adsorption process of oxygen atoms on the diamond (111) surface, presented in Fig. 1 a). The chosen 2×2 lateral cell size enables taking into account possible interaction of adsorbates on the diamond surface. The following three coverages have been tested, 0.25 monolayer (ML), 0.5 ML, and 1.0 ML, which correspond to one, two, and four oxygen atoms placed above certain adsorption sites within the 2×2 lateral unit cell.

Fig. 2 a) presents the resulting adsorption energies of oxygen atoms calculated according to the formula:

$$E_{\text{ads}} = E_{\text{atom/surf.}} - E_{\text{surf.}} - n \times E_{\text{atom}}, \quad (1)$$

where $E_{\text{atom/surf.}}$ and $E_{\text{surf.}}$ represent the total energy of a slab with adsorbed atom (here O) and a clean diamond surface, respectively,

while E_{atom} stands for the total energy of a corresponding isolated adsorbed atom, and n denotes the number of the adsorbates.

Our studies show that, independently on the coverage, the most stable adsorption site for O atoms is the on-top one, i.e., oxygen atoms placed initially in all studied adsorption sites, at certain distances from the surface, adsorb finally in the on-top site (Fig. 2 b)). This behaviour is indicated in Fig. 2 a) by coinciding points corresponding to all studied sites, at most coverages. The difference in final E_{ads} values, at certain coverage, does not exceed then 0.0009 eV/atom. The average C–O distance increases with the coverage and it is equal to 1.3061 Å (for 0.25 ML, $E_{\text{ads}} = -7.4829$ eV/atom), 1.3242 Å (0.5 ML, $E_{\text{ads}} = -7.3679$ eV/atom), and 1.3275 Å (1 ML). At the same time the adsorption energies become less negative, what presents a typical behaviour of increased interaction between adsorbates with coverage. At the coverage 1 ML, the minimum adsorption energy $E_{\text{ads}} = -7.1280$ eV/atom. Our results are in a good agreement with the previous DFT calculations concerning oxygen adsorption on the diamond (111) surfaces [22,23].

Since the surface treatment applied by Imura et al. to the diamond (111) substrate prior to the AlN growth did not affect the crystalline structure of diamond (the absence of amorphous carbon, atomic steps, or reconstruction) [9,16,17] instead, it produced the oxygen-terminated diamond (111) surface, we apply in further studies the obtained simplest model of O/diamond (111) surface, shown in Fig. 2 b).

First, we analyse the effect of passivation on atomic relaxation process. As it is seen from Fig. 1 b), the relaxed diamond (111) clean surface is flattened with present sp^2 bonds. The average bond length between 1st and 2nd carbon layers is 1.4830 Å. Oxygen adsorption induces some changes in the atomic structure of this surface. They depend almost linearly on the O coverage with a tendency of reducing the relaxation (see Fig. 3 a)–c)). However, the relaxation of the distance between the uppermost layers is not completely suppressed by adsorption of 1 ML of oxygen, this concerns the first and third interlayer distances (Δz_{12} , Δz_{34}). Additionally, the diamond (111) surface experiences the buckling of the topmost layer. As a measure of this quantity we assume the maximal difference Δd_{max} between the z positions of the topmost carbon monolayer atoms. Fig. 3 d) shows changes of Δd_{max} as a function of coverage. As can be seen, the buckling is the most pronounced at the coverage 0.25 ML of oxygen, and it is absent when the surface is passivated by 1 ML of oxygen. Note however, that when the carbon topmost monolayer is covered by a mixed layer of O and H atoms (i.e., 3 atoms of O and 1 atom of H, or 3 atoms of H and 1 atom of O within 2×2 lateral unit cell) than the buckling is present again, what in consequence can hinder further AlN growth, as will be discussed below.

It is important to study further the energetic and electronic structure of the diamond (111) clean and O/diamond (111) surfaces. For this purpose we calculate the total density of states function (DOS) of the diamond slab with a clean surface, and then of the slab covered with oxygen layer, at various coverages. Fig. 4 a) presents a comparison of the total DOS of diamond bulk crystal (enlarged to account for the same number of atoms at both systems) with that of a clean slab. As it is seen, in the case of diamond slab with a clean surface non-zero surface states exist in the range of energy gap of diamond bulk crystal, triggered by broken bonds at the clean surface. When the surface undergoes passivation, these states diminish with the increasing oxygen coverage (see Fig. 4 b)), however, at 1 ML of O atoms, they are still present in the energy bandgap of diamond bulk crystal. Since oxygen can contribute up to six valence electrons to the tetrahedrally coordinated top carbon atom, there is an excess of valence electrons in the studied 2×2 lateral cell, and, as a consequence, the O/diamond (111) surface is charged. The edge of the valence band of O/diamond is created mainly by the p states of oxygen hybridized with p and d states of carbon four top layers (the share of oxygen electron states is dominant), while the edge of conduction band originates mainly from p and d carbon electron states.

Deposition of 1 ML of oxygen on diamond (111) surface induces a

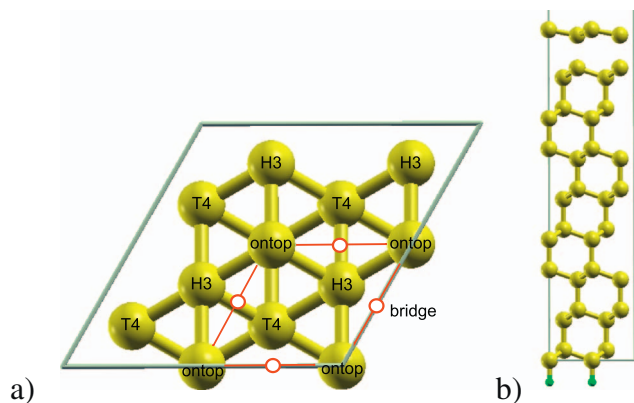


Fig. 1. a) 2×2 lateral unit cell representing the model of diamond (111) surface with indicated sites of adsorption. b) Side view on the relaxed diamond slab model with clean surface in the [111] growth direction. Small green balls represent terminating H atoms. (For interpretation of the references to colour in this figure legend, the reader is referred to the web version of this article.)

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