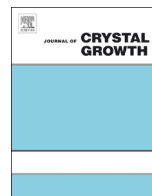




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Ab initio studies of early stages of nitride growth process on silicon carbide

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ABSTRACT

We present results of our studies dealing with the early stages of growth of Ga–N and Al–N monolayers on the 4H-SiC {0001} substrates. These studies are based on first principles calculation in the framework of density functional theory. Some stable adsorption sites are found for Ga, N, and Al atoms on the 4H-SiC {0001} surfaces. These are in particular T_4 for Ga and N atoms adsorbed on the (0001) surface and on top of the topmost surface atom for Al at the 1 ML coverage. In the case of (000 $\bar{1}$) surface, it is the 'on-top' position for Ga and Al, as well as T_4 for N atoms, at the same coverage. Further, the energetics of the GaN and AlN monolayers formation on the SiC substrate is investigated. It can be stated that the best 4H-SiC substrate termination allowing the single unreconstructed GaN bilayer growth is the (0001) one. Possible charge compensation patterns of interfaces are proposed together with the discussion on their stability. They involve the mixed Ga–C/SiC{0001} or Ga–Si/SiC{0001} layers that in consequence lead to the adsorption energy gain for nitrogen.

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1. Introduction

The deposition and formation of interfaces between III–V compounds and silicon interfaces have been the subject of studies since the 90s of the last century. The considerable potential of the nitrides for high power, high frequency, and high temperature microelectronics (see e.g. [1]) has resulted in numerous studies on the growth of GaN, AlN on both silicon and silicon carbide substrates. Both theoretical and experimental investigations have shown that the substrate plays a major role in determining the quality of the optoelectronic material deposited on it, and that the important feature of the substrate influencing this quality is the lattice-mismatch or strain. However, in the case of GaN and SiC which are partly ionic and partly covalent bonded materials with different degrees of ionicity, the interfacial polarity plays also an important role for understanding of the growth process in these materials, and it affects the quality of GaN deposited films, as first experimentally recognized by Sasaki and Matsuoka [2]. The heterostructures 4H-SiC/wz-GaN, 6H-SiC/wz-GaN exhibit imbedded macroscopic electric fields that originate both from the heterovalent character of the interface, and from piezo- and pyroelectric characters

of the constituent bulk materials [3,4]. The issue of interface charge in such systems is still discussed in the literature. In particular, Capaz et al. while studying the epitaxial growth of double bilayer GaN on hexagonal (0001) 6H-SiC by *ab initio* methods and supercell approach came to the conclusion that the polarity matching at the interface determines the lower-energy structures, yielding strong binding for Si–N and C–Ga unreconstructed interfaces and very weak binding for Si–Ga and C–N ones [5]. Later on, Ren and Dow, studying the growth of GaN and AlN films on (0001) 6H-SiC substrates [6], have argued that a polar interface with a large positive interfacial charge, which is achieved on a Si-terminated surface, leads to stronger attraction of GaN's nitrogen to the substrate, and hence to better epitaxial growth and better quality GaN or AlN films. Next, Städele et al. [7] have investigated the stability of reconstructed polar interfaces between cubic SiC(001) substrate and strained zinc blende GaN and AlN. By means of first-principle calculations and supercell approach, they found that the preferred bonding configurations at the interfaces are Si–N and Ga–C and that the most stable ones are the interfaces with a single mixed layer.

The purpose of this study is to investigate the early growth stages of Ga–N, Al–N monolayers on the 4H-SiC{0001} substrates in the process of adsorption of Ga, Al, N elements by means of *ab initio* approach. Additionally, some possible surface reconstructions are examined which are connected with the interface charge

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compensation at the 4H-SiC{0001}/wz-GaN interfaces. We show that a certain surface reconstruction can lead to a better energetic stability of the considered systems.

2. Calculation method and model of 4H-SiC surface

We have performed *ab initio* calculations in the framework of the density functional theory (DFT) as implemented in SIESTA program package [8]. The electron exchange–correlation effects are treated within the generalized gradient approximation (GGA) using the PBE form of the exchange–correlation functional [9]. The electron ion–core interactions are represented by pseudopotentials of the Troullier–Martins type [10] and the electron wavefunctions are expanded into the atomic-orbital basis set using the double- ζ polarized set. The cutoff of 120 Ry is used for the real space mesh. The Brillouin zone integrations are performed by means of the (8,8,2) and (8,8,1) k -point meshes for bulk and surface calculations, respectively. The calculated lattice parameters for 4H-SiC polytype ($a=3.113$ Å, $c=10.205$ Å) are in a good agreement with experimental data ($a=3.073$ Å, $c=10.053$ Å [11]). The determined lattice parameters are applied to construct slabs of 24 Si–C layers representing the (0001) and (000 $\bar{1}$) substrate surfaces of the wurtzite 4H-SiC crystal, terminated with Si and C atoms, respectively. All dangling bonds on the bottom atom layer of the slabs are saturated by hydrogen atoms. Altogether, the slabs with the lateral unit cell 2×2 consist of 100 atoms. The resulting slabs of thickness about 60 Å are separated from their periodic replicas in neighbouring cells by a vacuum region of 20 Å. Positions of the atoms belonging to 16 bottom layers of the substrate are kept fixed in order to mimic the behaviour of bulk material, while the terminating H atoms, the atoms of uppermost eight SiC surface and those adsorbed on the surface have a possibility for relaxation until forces acting on them converge to less than 0.02 eV/Å.

The model of 4H-SiC substrate seen from above is presented in Fig. 1. Red rhombus shows the smallest 1×1 lateral unit cell, where a few high-symmetry on-surface sites are indicated. These sites served as possible adsorption places. In particular, these are the position “on-top” of the Si (C) atom of the topmost surface layer, in the H_3 or in T_4 site, or in the “bridge” between two neighbouring topmost atoms. We have investigated the adsorption of Ga, Al, and N atoms on both surface terminations, i.e. SiC(0001) and SiC(000 $\bar{1}$).

3. Energetics of the single GaN and AlN layers formation on the 4H-SiC{0001} surfaces

We start our investigations by studying different surface coverages, i.e., one monolayer (ML), 1/2, 1/4, and 1/9 ML of adsorbate

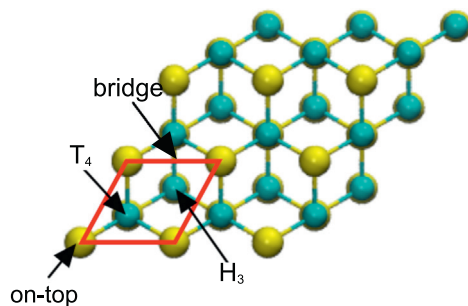


Fig. 1. The model of 4H-SiC/{0001} surfaces with sites of adsorption. Blue/yellow balls represent Si or C atoms depending on the termination of the surface. (For interpretation of the references to color in this figure caption, the reader is referred to the web version of this paper.)

atoms. Studies of 1/2 and 1 ML are performed in a 2×2 lateral supercell in order to take into account possible interaction of adsorbates on the surfaces. In this case two or four adsorbate atoms are placed in different inequivalent high-symmetry sites of the surface.

The adsorption energy E_{ads} of adsorbed atoms reads

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

where $E_{\text{atom/SiC}}$ and E_{SiC} are the total energies of a slab with an adsorbed atom and of a clean 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 all the considered models foresee the possibility of Ga, Al, and N adsorption on the SiC surface. The dependence of the adsorption energy versus Ga and Al coverage is presented in Fig. 2. From this figure it follows that the adsorption energy is the smallest for the small concentration of adsorbates, both for Si- and C-terminated 4H-SiC surfaces. Moreover, for the coverages below 0.5 ML, both metals prefer adsorption in T_4 position on the Si-terminated surface, and in H_3 position on the C-terminated one. Aluminium binds stronger to the SiC surface than gallium at both terminations and for all coverages. For this metal, the adsorption on the C-terminated SiC surface is more favourable than that on Si-terminated one by ~ 1 eV. In the case of gallium, this difference is smaller and it amounts maximally ~ 0.4 eV at the coverage 1 ML. The adsorption on SiC(000 $\bar{1}$) is preferred by both metals at all coverages. Our investigations show that at the coverage 1 ML aluminium atoms, on both surface terminations, adsorb on the top of the topmost surface atoms forming a stable monolayer with the adsorption energy of -4.75 eV/atom at SiC(0001) surface and -5.4 eV/atom at the SiC(000 $\bar{1}$) one. On the contrary, gallium atoms adsorb on the top of the topmost surface atoms only at the SiC(000 $\bar{1}$) surface with the adsorption energy -4.34 eV/atom. In the case of SiC(0001) surface, the adsorption takes place at the site which is slightly shifted from T_4 towards the H_3 site and the adsorption energy equals -3.97 eV/atom. As a result, both metals are uniformly spread over the 4H-SiC{0001} surfaces forming a stable, flat monolayer. Other details of investigations concerning orientation of both adsorbents adsorbates with respect to the 4H-SiC surface, bond lengths between adsorbates and substrate, charge density distribution, etc., for various coverages on the 4H-SiC{0001} surfaces can be found in [12].

In the case of nitrogen adsorption on the SiC{0001} surfaces, we can state that this process is more favourable on the SiC(0001) surface than on the SiC(000 $\bar{1}$) one by about 1.7 eV/atom, below the 1/2 ML coverages. At 1/2 ML this energy difference decreases down to ~ 0.7 eV/atom. However, at 1 ML the situation is opposite, E_{ads} is by 0.3 eV/atom more negative on the SiC(000 $\bar{1}$) surface than on the SiC(0001) one. At this coverage nitrogen atoms are partially mixed with surface C atoms, which is consistent with the experiment [13]. On both surfaces, the most stable adsorption site is T_4 .

The above-obtained preadsorbed Ga and Al monolayers served us further to investigate the subsequent process of nitrogen adsorption on the Ga/SiC{0001} and Al/SiC{0001} surfaces.

However, first we have checked whether it is energetically more favourable when Ga (Al) atom migrates into 4H-SiC substrate and substitutes one of the substrate atoms, by analogy to the results of [7] obtained for the cubic SiC(001) substrate and strained zinc blende GaN and AlN. In the last study, the most stable interfaces exhibited a single layer of deposited GaN (AlN) with Ga atoms mixed with Si (C) surface atoms. Our calculations show that it is not the case for wurtzite GaN. For both metals, the resulting adsorption energies are positive, e.g., at 1/4 ML $E_{\text{ads}} = 3.28$ eV for Ga adsorbed on the SiC(0001) surface, while in the case of Al atom E_{ads} are 1.03 eV and 5.00 eV for the SiC(0001)

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