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Structure and Charge Compensation of Heteropolar SiC/GaN Interfaces

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We present studies of the morphology and charge distribution at the 4H-SiC/wz-GaN heteropolar junctions. Our investigations are based on the first principles calculations in the framework of the density functional theory where the interfaces between the SiC substrate and GaN layers are represented by means of a slab. These studies reveal possible charge compensation patterns at the interfaces that lead to charge redistribution from monopole to dipole character and increase the stability of the junctions. It turns out that the interfaces with C–Ga and Si–Ga bonds across the junction and reconstructions involving substitution of group IV elements into Ga layer are the most favorable energetically.

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1. Introduction

Intriguing heterovalent interfaces between III-V and group-IV materials have been studied since the 90's of the last century. These studies have been motivated by the desire to integrate silicon microelectronics and III–V compounds based optoelectronics, as well as to take advantage of the higher electron mobilities in the latter materials. The considerable potential of the nitrides for high power, high frequency, and high temperature microelectronics (see e.g. [1]) has resulted in numerous studies of GaN and AlN layers grown onto 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 influencing this quality is the strain resulting from lattice--mismatch. However, in the case of GaN and SiC which are partly ionic and partly covalent materials, the interfacial polarity also plays an important role in the growth process and it affects the quality of GaN deposited films, as first experimentally recognized by Sasaki and Matsuoka [2]. The 4H-SiC/wz-GaN and 6H-SiC/wz-GaN heterostructures exhibit imbedded macroscopic electric fields that originate both from the heterovalent character of the interface, and from piezo- and pyroelectric character of the constituent bulk materials [3, 4]. Hence, the charge present at the interface of these materials originates from the abrupt change of the electric polarization on passing from the SiC to the GaN material and from different valency of the atoms on both sides of the interface.

The issue of interface charge in such systems is a long standing problem, still not solved yet. In particular, Capaz et al. [5] while studying the epitaxial growth of double bilayer GaN on hexagonal (0001) 6H-SiC by ab initio methods and supercell approach have come 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. Later on, Ren studying the growth of GaN and AlN films on (0001) 6H-SiC substrates [6] has 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 nitrogen atoms to the substrate, and hence to better epitaxial growth and better quality of 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 have found that the preferred bonding configurations at the interfaces is Si-N and Ga–C and that the most stable interfaces contain a single mixed layer consisting of group III (or V) atoms mixed with group-IV ones.

The purpose of this study is to investigate a role of interfacial charge density distribution on the stability of both abrupt and reconstructed 4H-SiC/wz-GaN interfaces with hexagonal symmetry. Possibilities for the interface charge compensation are discussed together with the interface reconstruction. In our approach we utilize a slab geometry and consider up to 32 Si–C–Ga–N monolayers.

2. Calculation method

Our *ab initio* calculations are performed using 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 Perdew–Burke–Ernzerhof (PBE) form of the exchange-correlation functional [9]. The electron ion-core interactions are represented by pseudopotentials of the Troullier–Martins type [10]

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casted into separable form, and the electron wave--functions are expanded into basis of the double- ζ polarized set of atomic orbitals. The cutoff of 120 Ry is used for the real space mesh. The Brillouin zone integrations is performed by means of the (8, 8, 2) and (8, 8, 1)k-points meshes for bulk and surface calculations, respectively. For consistency with heterostructure calculations, the 4H-SiC bulk crystal is represented by a hexagonal supercell containing eight atoms. 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 theoretical lattice parameters of 4H-SiC bulk are applied to construct slabs consisting of 16 Si-C layers, which represent the (0001) and $(000\overline{1})$ surfaces of the 4H-SiC crystal substrate, terminated with Si and C atoms, respectively. On the SiC substrate there are placed 16 GaN layers with wurtzite symmetry, terminated by either N or Ga. Then, all the dangling bonds on the bottom and the uppermost layers of the slabs are saturated by hydrogen atoms. Altogether, the slabs consist of 136 atoms. The resulting slabs of thickness about ≈ 40 Å are separated from their periodic replicas in neighbouring cells by a vacuum region of 30 Å. According to a common practice, the positions of the atoms belonging to eight bottom layers of the substrate and to the uppermost eight GaN layers are kept fixed in order to mimic the behavior of bulk material, while the atoms of eight middle layers of each material are relaxed until forces acting on them converge to less than 0.02 eV/Å. We consider four types of interfaces, namely, C-Ga, C-N, Si-Ga, and Si-N, as characterized by the long bonds across the interface, and depicted schematically in Fig. 1.



Fig. 1. The exemplary C–Ga interface (out of four possible ones) in the 4H-SiC/wz-GaN heteropolar junction. The tetrahedral coordination of the nearest-neighbor atoms is also indicated symbolically.

3. Results and discussion

As it can be seen in Fig. 1, the abrupt interfaces of the type C–Ga and Si–Ga possess undersaturated long bonds between C (or Si) and Ga atoms. Indeed, a tetrahedrally coordinated Ga atom shares four bonds with its nearest neighbors, having, however, only three valence electrons to form four bonds, whereas, the C atom (of valency IV) contributes four electrons to all four bonds it forms with the nearest neighbors. As a result, one quarter of electron lacks per one long bond that joins C and Ga interface atoms. In the case when there are four bonds of this type in the lateral unit cell, there is a total shortage of one electron per one lateral unit cell of the interface. Similarly, the abrupt C–N and Si–N interfaces possess oversaturated long bond joining C (or Si) and N interface atoms, i.e., there is an excess of one quarter of electron per one long bond. This leads to the total excess of one electron in the before mentioned lateral unit cell with four bonds. In both cases, there is an uncompensated electronic charge distribution (induced by the different valency of the interface atoms) at the interface of monopole character. However, this monopole character of charge distribution can be compensated in the following manner.

Note that replacement of an atom with valency V (N) by C or Si (of valency IV) would lead to a deficiency of three quarters of electron per one bond type presented in Fig. 1. Similarly, replacement of an atom with valency III (i.e., Ga) by C or Si (both with valency IV) would lead to an access of 3/4 electrons per bond. Hence, in the case of C–N (Si–N) interfaces, one (out of four) N atoms in the lateral 2×2 unit cell should be replaced by one Si (or C) atom. By analogy, the Si–Ga (C–Ga) interfaces can be compensated by the replacement of one Ga atom by one Si (or C) atom in the 2×2 lateral unit cell. Therefore, the electronic charge distribution at the compensated interfaces resembles a dipole.

Having determined the possible charge compensation patterns based on intuitive arguments presented above, we are in the position to calculate the total energies of the charge compensated (i.e., reconstructed) and abrupt interfaces, and further to compute the difference in the formation enthalpies according to the expression

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

where $E_{\text{tot}}^{\text{slab,abr.}}$ and $E_{\text{tot}}^{\text{slab,comp.}}$ are the total energies of the slab with an abrupt and charge compensated interface, respectively. The values of chemical potentials $\mu_{\rm comp.atom}$ and $\mu_{\rm orig.atom}$, of the compensating and original interface atoms, respectively, are adapted from the bulk materials in this study. The differences in formation entalphies ΔH have been calculated for all kinds of the reconstructed and the abrupt interfaces and are presented in Table. In the applied convention positive values of ΔH correspond to the energetically stable systems. However, ΔH contains the term that is connected with the supply of the compensating atom (C, Si) from an external reservoir to the system and its exchange with the host atom (Ga, N). It suggests that the chemical potential of the reservoir can influence the energetical stability of the charge compensated interfaces. Nevertheless, for the chemical potentials chosen in this study (we have used following values: $\mu_{\rm C} = -154.87 \text{ eV}, \ \mu_{\rm Si} = -106.94 \text{ eV},$ $\mu_{\rm Ga} = -58.52$ eV, $\mu_{\rm N} = -271.93$ eV) the most stable interfaces are of the type Si–Ga (C–Ga) with Ga layer compensated with Si atoms in proportion one to three.



Fig. 2. Front view of the valence electron distribution plots ($\delta \rho$ in units of electron/Å³) for the abrupt (left part) and compensated by Si (middle part) Si–Ga interfaces. In the right part the color scale of valence density distribution is depicted.

Formation entalphies.

TABLE

Interface type	Compensating atom	ΔH [eV]	
C–Ga	C	-0.502	
	Si	0.440	
Si–Ga	C	-0.475	
	Si	0.371	
C-N	C	0.231	
	Si	-0.685	
Si–N	C	0.055	
	Si	-1.299	

In order to gain some understanding of these results, we have computed the distribution of probability density of valence electrons ρ on abrupt and compensated interfaces. Note that the electronic charge density is then equal to $-e\rho$. We compare the probability density distribution of the valence electrons in the corresponding interface planes (Si, (C), Ga, (N)), as well as in their nearest neighbor planes. As a result, it can be stated that the energetically unfavorable compensated interfaces C–N and Si–N exhibit small changes of the electron probability distribution at the interface, which means that the charge density distributions of the abrupt and reconstructed interfaces do not differ significantly. The situation is different in the case of energetically favorable reconstructed interfaces Si-Ga and C-Ga. This is illustrated in Fig. 2, where the quantity $\delta \rho = \rho - \rho_{\rm at}$ ($\rho_{\rm at}$ is the superposition of probability distributions for free atoms (pseudoatoms) constituting the slab). The front view of $\delta \rho$ for the abrupt Si-Ga interface is presented in the left part in Fig. 2. As can be seen, the interface reconstruction really changes the valence electrons distribution, strongly suggesting that the transfer from monopole to dipole type of the electron distribution can really be induced by interface reconstruction (compensation). The similar behavior of the valence electron distribution is observed for the reconstructed C–Ga interface.

4. Conclusions

Our studies of the 4H-SiC/wz-GaN heterovalent junctions clearly demonstrate that the charge compensation is energetically favorable in the case of C–Ga (anion– cation) and Si–Ga (cation–cation) interfaces. This energy gain is associated with the charge density redistribution within the interface area of the 4H-SiC/wz-GaN junctions, from a monopole form to the dipole one. The charge compensation is energetically unfavorable in the case of the C–N (anion–anion) and Si–N (cation–anion) interfaces, for which no essential charge redistribution can be observed and the interfacial non-compensated charge remains in the form of a monopole.

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