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STABILITY AND BAND OFFSETS OF HETEROVALENT SiC/GaN INTERFACES

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We present first-principles calculations of structural and electronic properties of heterovalent SiC/GaN [001] interfaces. We have investigated interfaces consisting of one and two mixed layers with lateral $c(2 \times 2)$, 2×1 , 1×2 , 2×2 arrangements. Abrupt polar [001] interfaces are energetically unstable with respect to reconstruction. The preferred bonding configurations are found to be Si-N and Ga-C, which correspond to cation-anion bonding. The valence band offsets of the energetically most favorable structures are 1.39 eV for the interface with a mixed Ga/Si layer and 0.45 eV with a mixed C/N layer, with the top of the valence band lying higher in SiC.

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Thin films of GaN are currently attracting much interest because of their applications in light emitting devices ranging from the green to the ultraviolet region. Recently, devices that consist of GaN films grown on sapphire substrates have been reported. In order to overcome the poor interface quality and the high concentration of dislocations that are induced by the large lattice mismatch between GaN and sapphire (that is larger than 12%), alternative substrate materials are being explored. A promising candidate for future device applications seems to be SiC [1]. The present work predicts the relative stability of several SiC/GaN [001] reconstructed interfaces and the resulting band offsets.

Our calculations are based on the first-principles total-energy pseudopotential method within the local-density-functional formalism [2]. We have used norm-conserving separable pseudopotentials [3] and a preconditioned conjugate gradient algorithm [4] for minimizing the total crystal energy, with respect to electronic as well as ionic degrees of freedom. The semicore Ga $3d$ -electrons are treated as part of the frozen core, but their considerable overlap with the valence electrons is accounted for by including the nonlinear core exchange-correlation correction [5]. This procedure increases the transferability of the pseudopotentials and yields lattice constants that agree very well with experiment (the computed lattice constants for GaN in the zinc blende and wurtzite phase, respectively, are $a_{zb} = 4.49 \text{ \AA}$ (4.52 \AA), and $a_{wz} = 3.182 \text{ \AA}$ (3.189 \AA), $c_{wz} = 5.171 \text{ \AA}$ (5.185 \AA), with the experimental values [6] given in parenthesis).

An "ideal" abrupt SiC/GaN [001] interface contains bonds that are not filled with 2 electrons. There are four such possibilities, namely the two acceptor bonds Si-Ga and C-Ga, and the two donor bonds Si-N and C-N. This lack of local charge neutrality implies local charge accumulation which is energetically unstable [7]. By replacing some interface atoms and taking into account the bonds adjacent to the interface layer as well, local charge neutrality can be restored. Simple possibilities are the replacement of every other group-III element at the abrupt Si-Ga or C-Ga interface by a group-IV element, or the replacement of every other group-IV element in a Si-N or C-N interface by a group-III element. In this way one neutralizes half of the acceptor (donor) bonds at the interface but simultaneously produces the same number of donor (acceptor) bonds in the adjacent layer, thus replacing the charge pile-up by a dipole.

In this work, we have calculated reconstructed interfaces that are charge compensated and consist of one or a maximum of two mixed interface layers. In the case of a single mixed layer at the interface, we considered three lateral atomic arrangements $c(2 \times 2)$, 2×1 , 1×2 , as depicted in Fig. 1. For a Si-Ga interface, for example, this amounts to replacing 50% of the Si atoms by N atoms or, alternatively, 50% of the Ga atoms by C. Altogether, 12 different types of interfaces were analyzed.

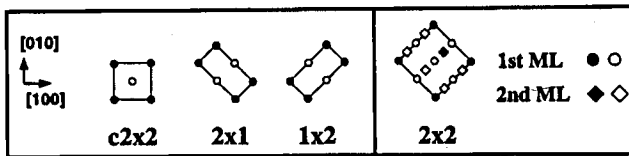


Fig. 1. Lateral atomic arrangements for interfaces consisting of one [$c(2 \times 2)$, 2×1 , 1×2] and two mixed layers [2×2].

For the case of two mixed layers forming the interface, each layer contains two types of atoms in the ratio of 1:3 (or 3:1) with a 2×2 lateral reconstruction (see Fig. 1). Out of the 32 different interface structures that we have studied in detail, the energetically most favorable ones contain all cations (Ga and Si) within one layer and all anions (C and N) in the adjacent layer.

We consider GaN films that are pseudomorphically grown on a SiC substrate. The reconstructed SiC/GaN [001] interfaces are modeled by supercells with up to 16 monolayers. Typically, we find supercells already with 12 monolayers to yield well converged values of the interface formation energies and valence band offsets (VBOs). Since cubic GaN and SiC have a lattice mismatch of 3.6%, the lattice constant of the superlattice in the growth direction was determined by minimization of the total energy, and all atomic relaxations were determined by Hellmann-Feynman force calculations. They play a crucial role in establishing the detailed interface formation enthalpies and VBOs.

As a measure of the stability of different interface structures, we use the formation enthalpy δH_{int} normalized to a 1×1 unit cell area

$$\delta H_{\text{int}} = \frac{1}{2pq} (E_{\text{tot}}^{\text{SiC}} - n_{\text{GaN}} E_{\text{tot}}^{\text{GaN}} - n_{\text{SiC}} E_{\text{tot}}^{\text{SiC}}),$$

where $E_{\text{tot}}^{\text{SiC}}$ denotes the total energy of the supercell that contains n_{GaN} and n_{SiC} units of GaN and SiC, respectively, with bulk total energies $E_{\text{tot}}^{\text{GaN}}$ and $E_{\text{tot}}^{\text{SiC}}$ per unit. Here, pq is the area of the lateral unit cell of the reconstructed interface, in units of the ideal one.

All interfaces that we have studied have positive formation enthalpies, indicating that the underlying structures represent metastable configurations. First, we discuss the results for interfaces with a single mixed layer. Our calculations predict a formation enthalpy of 0.17, 0.23, and 0.24 eV for the $c(2 \times 2)$, 2×1 , and 1×2 structures with a Ga/Si interface layer, respectively. The C/N interfaces yield 0.20 eV for the $c(2 \times 2)$, and 0.24 and 0.25 eV for the 2×1 and 1×2 reconstructions, respectively. For the Ga/C and Si/N interfaces, the enthalpy δH_{int} is larger by at least an order of magnitude. This can easily be understood by noting that the latter cases contain predominantly cation-cation or anion-anion (Ga-Si or C-N) bonds, whereas the more stable Ga/Si and C/N interfaces contain only cation-anion bonds.

For interfaces with two mixed layers, we also found only those interfaces to possess low formation enthalpies that contain solely cation-anion bonds. The theory gives δH_{int} equal to 0.23 and 0.24 eV for the $\text{C}_{0.25}/\text{N}_{0.75}\text{-Ga}_{0.25}/\text{Si}_{0.75}$ and $\text{Ga}_{0.75}/\text{Si}_{0.25}\text{-C}_{0.75}/\text{N}_{0.25}$ interface, respectively. Thus, we finally conclude that the $c(2 \times 2)$ structure with a single Ga/Si interface layer is the most favorable interface reconstruction.

We now turn to the VBOs and consider only those interfaces that we found to be energetically favorable. The VBO is conventionally split up into two contributions [8], $\Delta E_v = \Delta E_v^{\text{BS}} + \Delta V$. The first contribution is the energy difference between the two valence-band edges, measured with respect to the average electrostatic potential in each of the two bulk materials. Thus, ΔE_v^{BS} is a property of the two bulks and is independent of the detailed interface structure. The second term ΔV is the difference between the electrostatic potential energies in the two materials far from the interface. It depends on the charge distribution at the interface and is related to the interface dipole moment. The electronic charge distributions associated with three reconstructed interfaces are depicted in Fig. 2a.

The present calculations show that those mixed interfaces that differ only by the lateral atomic arrangement (such as shown in Fig. 1) have very similar dipole moments. Consequently, we find the corresponding offsets to be almost identical (Fig. 2b). Indeed, this figure exhibits three groups of VBOs for SiC/GaN [001] heterostructures. One group corresponds to an interface layer with C/N atoms, another one to Ga/Si atoms and a third one to the two mixed monolayer structures discussed above. The respective VBO values are 0.42–0.45, 1.31–1.41, and 0.85 eV. This reveals that the top of the valence band lies higher in SiC than in GaN for all kinds of interfaces investigated. Since the energy gaps of the cubic modifications of SiC and GaN are 2.39 and about 3.3 eV, respectively, this implies either a type-I or a type-II heterostructure, depending on the chemical type of interface. Thus, the type of chemical bonding at the interface has a drastic effect on the band offsets. Since both the Ga/Si and C/N interfaces have low formation enthalpies, one may

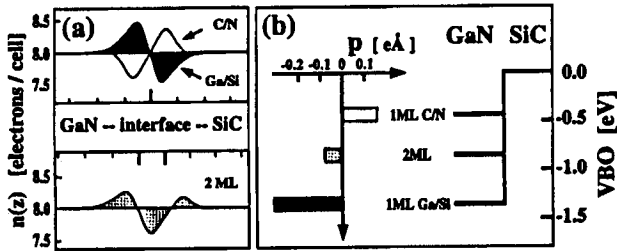


Fig. 2. (a) Macroscopically averaged electronic charge distribution $n(z)$ for interfaces with C/N and Ga/Si mixed layer (top) and two (one Ga/Si, the second C/N) mixed monolayers (bottom). The shorter and longer ticks along the horizontal axis indicate the positions of the bulk monolayers and mixed layers, respectively. (b) Dipole moments p (left panel) and valence band offsets (right panel) for the three types of interfaces described above in SiC/GaN [001] heterostructures.

be able to utilize these results for VBO engineering.

In conclusion, we have shown that the interfaces between GaN and SiC containing single mixed Ga/Si or C/N layers are the energetically most favorable ones. The corresponding valence band offsets are 1.39 and 0.45 eV, respectively, with the top of the valence band lying higher in SiC.

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