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Electronic structures of hexagonal ZnO/GaN interfaces

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Abstract

By the *ab initio* calculation using the superlattice geometry with neutral interfaces and the repeated-slab geometry with virtual-hydrogen-terminated surfaces, the electronic structures of hexagonal ZnO/GaN(0001) interfaces are investigated. The ZnO/GaN system has type-II band alignment, where both the valence-band top and the conduction-band bottom of ZnO are located below those of GaN. The calculated valence-band offset is around 1.6 eV on average, but it varies from 1.0 to 2.2 eV depending on the interface growth treatment. It is shown that the excess charges originating from the heterovalent bondings are strongly localized at the interface. © 2000 Elsevier Science B.V. All rights reserved.

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1. Introduction

Both ZnO and GaN are noble wide-gap semiconductors for optoelectronic usage and have been studied intensively. Since ZnO and GaN have the same wurtzite crystal structures and nearly the same lattice constants of 3.25 and 3.16 Å, respectively, GaN is often grown on ZnO substrate, and vice versa [1]. These growth processes naturally produce ZnO/GaN interfaces and the crystalline nature of grown layers depends on the electronic properties of ZnO/GaN interfaces. This is because due to the difference of valence electron number between ZnO and GaN, i.e. the valency mismatch, the Ga–O donor and Zn–N acceptor bonds appear

at the interface, which often produces charged defects such as vacancy. ZnSe/GaAs and Ge/GaAs(001) zincblende interfaces are typical examples of such heterovalent interfaces [2,3], while ZnO/GaN is a wurtzite-structure (0001) interface having different symmetry and bondings. To our knowledge, however, there is no theoretical investigation for the ZnO/GaN interface.

The purpose of the present work is to clarify the fundamental electronic structures of hexagonal ZnO/GaN interfaces, by using the *ab initio* calculation and adopting the invented geometry. Especially, we elucidate the band offset and discuss the potential profiles of the charged interfaces at initial growth.

2. Methodology

Electronic structures are calculated by using the first principles pseudopotential method in a local

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density approximation, where d electrons of Zn atoms and spin-orbit interaction are not included. This is a standard method and the details are described in Refs. [3,4]. In the first approximation, we assume the unstrained ZnO/GaN interface with an observed lattice constant of 3.2 Å. Moreover, we concentrate not on the detailed atom configuration [5,6] but on the average feature, assume that only anion or cation atoms are randomly distributed at the interface monolayer, and adopt the virtual crystal approximation for such an alloying layer as O_xN_{1-x} or Zn_xGa_{1-x} .

To simulate the hexagonal heterovalent interface, we employ two geometries; (1) superlattice geometry having neutral interface to elucidate band offset and (2) repeated-slab geometry having vacuum layers and hydrogen-terminated back surface to investigate the neutral and charged interfaces at initial growth. For the latter case, we will discuss the details in a subsequent section. On the other hand, in the former case, the alloying layers, $A = O_{1/4}N_{3/4}$ and $A' = O_{3/4}N_{1/4}$, are adopted for the anion monolayer at the interface, and the alloying layers, $B = Zn_{3/4}Ga_{1/4}$ and $B' = Zn_{1/4}Ga_{3/4}$, are adopted for the cation monolayer at the interface. Apparently, such fractional alloying composition is due to the bond-number asymmetry at the hexagonal interface.

Fig. 1(a) shows the calculated potential and total-charge-density profiles along the (0001) direction for $(ZnO)_4(GaN)_4$ superlattice with interface alloying layers, $A = O_{1/4}N_{3/4}$ and $A' = O_{3/4}N_{1/4}$. Apart from the interface, the potential is flat on average and has the same shape as those in bulks, ZnO and GaN. This result indicates that the neutral interface is useful to elucidate the band offset and the average feature of hexagonal heterovalent interface. In fact, if we adopt interface anion layers of $A = A' = O_{1/2}N_{1/2}$, the interface A (A') has one excess (deficit) electron on average and a definite charge transfer occurs from A to A' interface. This transfer induces a potential slope between A and A' interfaces as seen in Fig. 1(b), which is physically unreasonable for the isolated interface [3] and from which one cannot elucidate the band offset without adopting other assumptions [7,8].

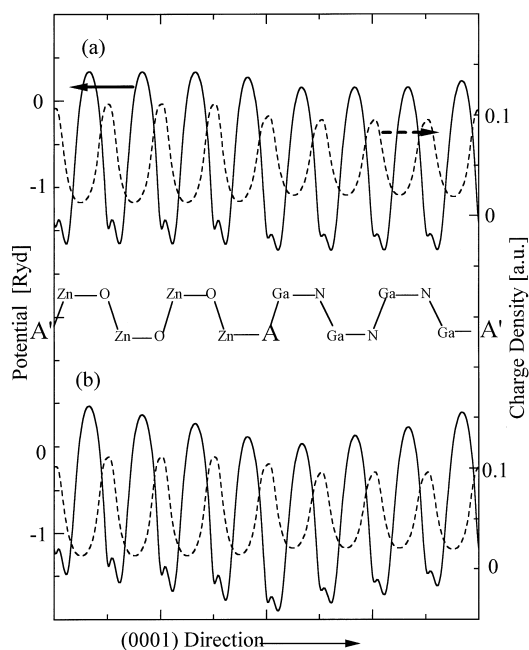


Fig. 1. Calculated potential (solid lines) and total-charge-density (dashed lines) profiles along the (0001) direction for $(ZnO)_4(GaN)_4$ superlattices with anion-alloying interface monolayers. Interface anion layers have compositions (a) $A = O_{1/4}N_{3/4}$ and $A' = O_{3/4}N_{1/4}$, and (b) $A = O_{1/2}N_{1/2}$ and $A' = O_{1/2}N_{1/2}$.

3. Band offset

For all systems studied, ZnO/GaN interface shows the type-II band alignment, where both the valence-band top and the conduction-band bottom of ZnO are located below those of GaN as shown in Fig. 2. To check its validity, the charge-density profiles of the top and second-top valence-band states are shown in Fig. 3. It is clearly seen that both states are strongly localized in GaN layers. The method used to calculate the band-offset value is described in Ref. [3]. The average value of calculated valence-band offset is about 1.6 eV, as shown in Fig. 2. This value is in good agreement with the values estimated using the empirical sp^3 -hybrid energies [9]. It was observed that Zn produces deep acceptor-like states in GaN [10], which is consistent with the profile in Fig. 2. On the other hand, the calculated band offset of cubic ZnO/GaN interface has a value similar to that of hexagonal

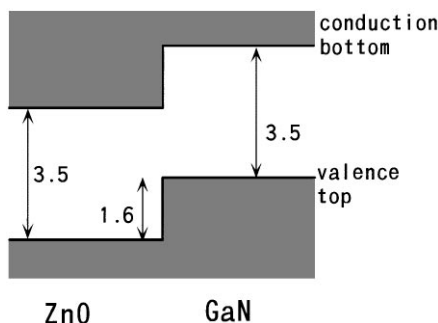


Fig. 2. Calculated band alignment at hexagonal (0001)ZnO/GaN interface. Values are in eV units.

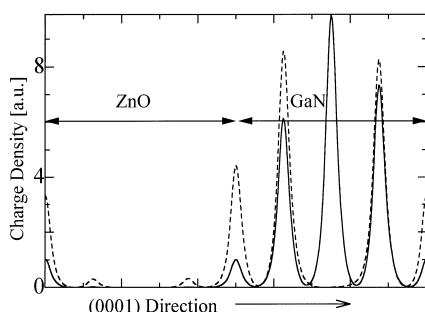


Fig. 3. Calculated charge density along the (0001) direction for the top (solid line) and second top (dashed line) valence-band states in $(\text{ZnO})_4/(\text{GaN})_4$ superlattice.

ZnO/GaN. This indicates that ZnO/GaN interface has a highly ionic nature and the offset depends on not the crystal structures but the average atom density [11].

In the case of heterovalent interface, the band offset strongly depends on the growth process, i.e. the atom configuration at the interface [2,3]. With varying the interface, the calculated valence-band offset ranges from 1.0 eV for the (0001)A interface having the anion–atom-mixed layers to 2.2 eV for the (0001)B interface with the cation–atom mixing. This is because the direction of charge transfer between ZnO and GaN is different between the two interfaces [3]. In the case of (0001)A interface in Fig. 1(a), for example, the interface atom is $A = \text{O}_{1/4}\text{N}_{3/4}$ and has 5.25 valence electrons on average, thus three Zn–A and one Ga–A interface bonds, respectively, becoming acceptor and donor bonds. As a result, the charge transfers from Ga–A

to Zn–A sides, which produces the dipole field at the interface. As seen in Fig. 1(a), this charge transfer is localized at the interface and increases the average potential height in ZnO. On the other hand, for the (0001)B interface, the charge transfer occurs from ZnO to GaN side and decreases the average potential in ZnO layers.

4. Charged interface and initial growth

Next we consider the charged interface and the surface at initial growth. In this case, we use the repeated-slab geometry; when the GaN growth on ZnO(0001)A is considered, we first prepare a $(\text{ZnO})_2\text{ZnA}$ slab and terminate the back Zn surface with virtual hydrogens, H^* . H^* has 0.5 electron, is located straight along the (0001) direction from Zn, and has a Zn– H^* bond length about half that of Zn–O. A is the front-surface virtual-crystal atom, O_xN_{1-x} . The GaN adatoms are put on this surface at their ideal wurtzite positions. Fig. 4 shows the calculated potential profile of ZnO/GaN interface. Solid lines correspond to neutral interface in Fig. 1(a) with $A = \text{O}_{1/4}\text{N}_{3/4}$, while dashed lines to negatively charged interface in Fig. 1(b) with $A = \text{O}_{1/2}\text{N}_{1/2}$. The potentials are numbered according to the number of Ga and N adatom layers and shifted in energy to coincide with each other in inner ZnO layers. It is seen that, compared to the case of charged superlattice geometry in Fig. 1(b), the potentials in inner ZnO layers are very flat regardless of whether the interface is neutral or charged. This result justifies the use of repeated-slab geometry for heterovalent interfaces.

First, the neutral interfaces at initial growth are considered. As seen in Fig. 4, when the surface is terminated with anion atoms, A ($n = 0$) or N ($n = 2$), the potential in vacuum region is higher by about 1.5 eV compared to the cation terminations, Ga ($n = 1$ and 3). This indicates that the electron work function is large for the former terminations. The most remarkable feature in Fig. 4 is that the potential in ZnO layers does not change with varying the number of adatom layers, n . This result indicates that when GaN is grown on ZnO there is little band bending ($< 10 \text{ meV/\AA}$) in ZnO layers.

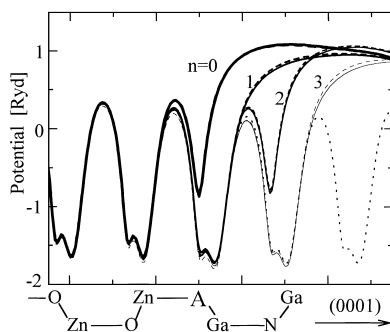


Fig. 4. Calculated potential profile for GaN-adsorbed ZnO surfaces. The interface is made of $A = O_{1/4}N_{3/4}$ (solid lines) or $A = O_{1/2}N_{1/2}$ (dashed lines) anion layer, which, respectively, corresponds to the neutral and charged interfaces. n denotes the number of GaN-adatom atomic layers. The dotted line corresponds to the profile in ZnO/GaN superlattices.

Next, the charged interfaces at initial growth are considered. As seen in Fig. 4, the potential in a vacuum region is about 0.5 eV higher for the charged interface than the neutral interface, while that in ZnO layers is almost the same between both interfaces. The difference of potential height in vacuum region can be explained by observing the charge density in Fig. 5. Since the charged interface has excess electrons, the charge density is seen to be larger for the charged interface than for the neutral interface. As shown by the arrow in Fig. 5, however, we note that the charge density is also larger in the N-adatom layers in the case of the charged interface. This result indicates that a little charge flows from the interface to GaN layers to increase the potential and induces band bending ($\sim 10^2$ meV/Å) in GaN layers. One of the reasons for such a charge transfer is the existence of the surface states. The GaN surface states have lower energy than the conduction-band states in ZnO and are partially occupied by the charge transfer from the charged interface. According to this interpretation, when the grown layers are increased and the GaN surface states have no overlap to the charged interface, such a charge transfer is expected to be suppressed and the excess charge is strongly localized about one or two layers around the charged interface. In this view, we can say that the excess or deficit charge at the hetero-

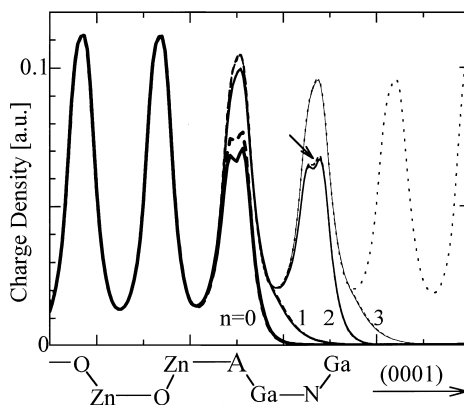


Fig. 5. Calculated total-charge-density profile for GaN-adsorbed ZnO surfaces. The meanings of lines and symbols are the same as in Fig. 4.

valent interface affects only the initial few-mono-layer growth.

5. Conclusion

By the ab initio calculation using pseudopotentials, the electronic structures of hexagonal ZnO/GaN(0001) interfaces were investigated. It was shown that the ZnO/GaN system has type-II band alignment with an average valence-band offset of 1.6 eV, where both valence-band top and the conduction-band bottom of ZnO are located below those of GaN. However, the valence-band offset varies from 1.0 to 2.2 eV depending on the interface growth treatment. When the interface is charged, the excess charge originating from the heterovalent bondings is strongly localized at the interface.

Acknowledgements

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