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Band discontinuities in zinc-blende and wurtzite AlN/SiC heterostructures

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The AlN/SiC band discontinuities in zinc-blende (110), (111), and wurtzite (0001) heterostructures were examined using the *ab initio* pseudopotential approach. At the nonpolar AlN/SiC(110) junction, we find a valence-band offset of 1.7 eV. At the polar heterojunctions the band alignment depends on the interface composition, and valence-band offsets as high as 2.5 eV are obtained for neutral interfaces with an Al/Si mixed plane and as low as 1.3 eV with a N/C mixed plane. Atomic relaxation plays a major role in determining the offset. The structural change from cubic (111) to hexagonal (0001) heterojunctions affects predominantly the conduction-band offset, and has only a minor influence on the valence discontinuity. [S0163-1829(97)50612-6]

The group-III nitrides and SiC are of considerable interest for device applications in blue-violet optoelectronics and high-temperature electronics. The ideal lattice match of SiC and AlN, and the relatively low misfit with GaN, make SiC a suitable substrate and AlN an adequate buffer layer for GaN-based light-emitting devices.[1] The main parameters which determine carrier injection and confinement in the resulting heterostructures are the valence- and conduction-band offsets. Presently, very few experimental[2] or theoretical results[3–5] are available on the band offsets of heterovalent nitride heterojunctions, and little is known of their dependence on orientation, heterovalency, and polytype. Here we present a first-principles study of these properties for the prototype lattice-matched AlN/SiC system.

Heterovalent quaternary systems such as AlN/SiC give rise to complex interface configurations. Two types of abrupt AlN/SiC interfaces may be distinguished: those containing only cation-anion bonds (Si-N,C-Al) and those involving cation-cation and/or anion-anion bonds (C-N,Si-Al). Previous theoretical studies[3,4] showed that the former are more stable than the latter, consistent with a recent transmission-electron microscopy analysis of the 2H-AlN/6H-SiC(0001) interface.[6] We thus focus here on the cubic (110), (111), and hexagonal (0001) interfaces with Si-N and C-Al bonds. Furthermore, since the formation energy of the AlN/SiC interfaces is positive, we only consider AlN/SiC(111) and (0001) junctions with the ‘‘long-bond’’ interface geometry, which has the lower density of interface bonds.

The abrupt polar AlN/SiC (111) and (0001) interfaces are charged, and therefore thermodynamically unstable. Charge neutrality can be restored in these systems by atomic intermixing at the interface.[7] The simplest atomic arrangements giving rise to neutral interfaces are those with one mixed N/C plane (or Al/Si plane). The corresponding neutral configurations, schematically represented in Figs. 1(b) and 1(c) (see also Fig. 2, upper panel), are obtained by replacing 25% of N by C in the N plane at the abrupt N-Si interface or 25% of C by N in the C plane at the Al-C interface (configurations A and A', respectively), or similarly by replacing 25% of Si by Al in the Si plane at the N-Si interface or 25% of Al by Si in the Al plane at the Al-C interface (configurations B and B', respectively).[8] This intermixing neutralizes the junction leaving interface dipoles (which are opposite for the N/C and Al/Si mixed layers) in the macroscopic average[9] of the ion point-charge distribution of the junctions (see Fig. 1).

The interface charge may also be neutralized by two mixed planes, e.g., by replacing 12.5% of N by C in the N plane and 12.5% of Si by Al in the Si plane at the abrupt Si-N interface, or 12.5% of C by N in the C plane and 12.5% of Al by Si in the Al plane at the C-Al interface (configurations C and C', respectively). The latter atomic arrangements are intermediate between the A and B configurations (C) or A' and B' configurations (C') given in Fig. 1, and

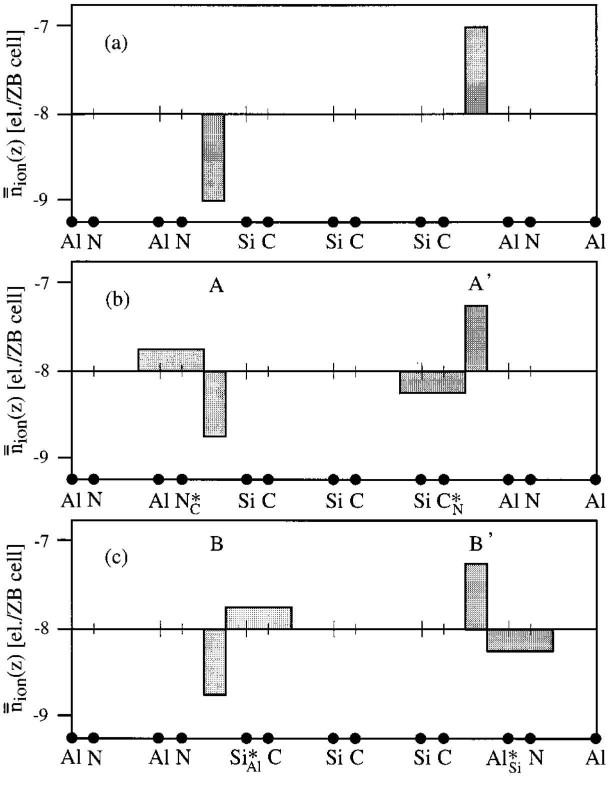

FIG. 1. Macroscopic average of the ion point-charge distribution in the zinc-blende AlN/SiC (111) heterostructures with charged, abrupt interfaces (a), neutral interfaces with one mixed C/N plane (b), and one mixed Al/Si plane (c). The symbol A^*_B indicates a mixed plane containing 75% A atoms and 25% B atoms.

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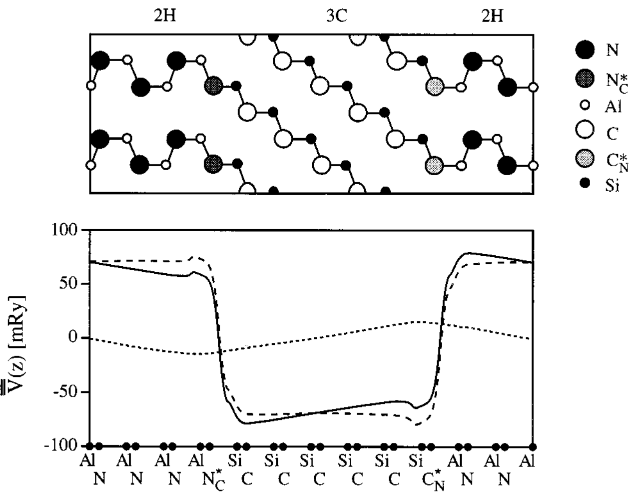

FIG. 2. Upper panel: atomic configuration at the 3C-SiC/2H-AlN(0001) interfaces with mixed N/C layers, in the plane through the Al-N and Si-C bonds. Lower panel: macroscopic average of the electrostatic potentials in the 3C-SiC/2H-AlN(0001) (solid line) and 3C-SiC/3C-AlN(111) (dashed line) heterostructures. The difference between the two macroscopic averages is also shown (dotted line).

give rise only to quadrupoles and higher order multipoles in the macroscopically averaged ion point-charge distribution. We studied the band alignment at these six neutral A, A', B, B', C and C' (111) junctions with one or two mixed layers at the interface.

The first-principles calculations were carried out within the local-density approximation (LDA) to density-functional theory, using the Ceperley-Alder functional,[10] and the pseudopotential plane-wave method. The pseudopotentials were generated with the method of Troullier-Martins and cast into the Kleinman-Bylander nonlocal form.[11] The heterojunctions were modeled with supercells containing up to 24 atoms, i.e., 12 monolayers for the cubic (110) and 24 monolayers for the cubic (111) and hexagonal (0001) interfaces. The supercell calculations were performed with an energy cutoff of 60 Ry, and using for the **k**-space integrations the (4,2,1) Monkhorst-Pack grid for the (110) junction and the (3,3,1) grid for the (111) and (0001) junctions.[12] The mixed layers at the (111) and (0001) interfaces were dealt with using the virtual crystal approximation.[9] All calculations were performed using the theoretical equilibrium lattice constant of cubic SiC (a = 4.32 Å), which is almost identical to that calculated for AlN (4.33 Å); the experimental values are 4.36 and 4.37 Å, respectively.

To evaluate the valence-band offset (VBO), we separated it into two contributions:[9] $\Delta E_{\rm VBO}=\Delta E_v+\Delta V$. The band-structure term ΔE_v is the difference between the valence-band edges of the two semiconductors forming the junction, each measured with respect to the average electrostatic potential of the corresponding crystal. This term does not depend on the interface, and was determined from standard bulk band-structure calculations for the two crystals using an energy cutoff of 70 Ry and a (4,4,4) Monkhorst-Pack mesh. The electrostatic potential lineup ΔV across the interface may depend on interface-specific features, and was obtained from the supercell calculations using the macroscopic-average technique.[9,13]

TABLE I. AlN/SiC valence-band offsets (in eV) at the zinc-blende (110) and (111) heterojunctions. The (111) offsets are given for neutral interfaces with a C/N mixed plane (A,A'), an Al/Si mixed plane (B,B'), or a C/N and an Al/Si mixed plane (C,C') (see text).

	VBO(110)	VBO(111)					
		A	A'	B	B'	C	C'
Unrelaxed	1.59	0.65	0.67	2.37	2.72	1.47	1.74
Relaxed	1.71	1.33	1.31	2.26	2.54	1.78	1.97

In Table I, we present our results for the VBO at the zinc-blende (110) and (111) junctions, with and without atomic relaxation at the interface. Using the experimental band-gap value[14] of 2.4 eV and the estimated value[15] of 4.9 eV for cubic SiC and AlN, respectively, we obtain for the relaxed interfaces a type-I band alignment in all cases. Many-body corrections on the SiC and AlN band-structure terms could affect the absolute value of the VBO by a few tenths of an eV.[16] Such corrections, however, are expected to decrease the AlN/SiC VBO, and are therefore unlikely to change the type of band alignment. The VBO values we find for the (110) junction agree within 0.1 eV with the results of an existing LMTO calculation for the unrelaxed interface,[3] and a recent pseudopotential calculation for the relaxed junction.[4]

In contrast to the case of the conventional, smaller gap, semiconductor heterojunctions,[9,17] we find here that lattice relaxation has a drastic effect on the band offsets of the polar (111) junctions, and a non-negligible influence on the offset of the (110) junction. In the case of the (110) interface, lattice relaxation increases the VBO by 0.12 eV. In the (111) junctions, the relaxation changes the offsets by as much as 0.7 eV at the interfaces A and A'. Although relaxation effects are somewhat smaller at the other (111) interfaces, they change the band alignment from type II to type I at the interface B'.

In the (110) junction, the anion sublayers in the two planes closest to the interface are found to relax towards SiC, and the cation sublayers in the opposite direction. The resulting anion-cation relative displacement is about $\Delta u_z=-0.025$ a.u. Within a linear-response theory approach,[17] the displacement u_z of each interfacial atomic layer produces a shift $\Delta V_{\rm rel}=4\pi Z^* e^2 u_z/S\epsilon_\infty$ in the potential lineup, where Z^* is the effective charge of the ions, S the surface per ion in the layer, and ϵ_∞ the geometric average of the dielectric constants of the two crystals forming the junction. Using $\epsilon_\infty^{\rm AlN}=4.61$, $\epsilon_\infty^{\rm SiC}=6.95$,[18] and $Z^*_{\rm cation}=-Z^*_{\rm anion}\approx 2.7$ in these materials,[19] we obtained a total relaxation contribution to the VBO of 0.18 eV, in reasonable agreement with the *ab initio* result.

We also evaluated the potential lineup at the unrelaxed (110) interface from linear-response-theory calculations. In these calculations, the junction is treated as a perturbation with respect to a virtual crystal composed of $\langle {\rm Ga}_{1/2}{\rm Si}_{1/2}\rangle$ and $\langle {\rm C}_{1/2}{\rm N}_{1/2}\rangle$ pseudoions.[9] From such calculations we obtain a VBO of 1.59 eV, identical to the *ab initio* result. Within the linear-response approach, the offset at the (111) interfaces C and C' with the quadrupoles should be equal to that of the

(110) interface, whereas at the interfaces A, A' and B, B' with the dipoles the VBO should differ by $\Delta V_{\rm dip}=\pm\pi e^2/2a\epsilon_\infty$ from the (110) VBO. The average of the VBO for the unrelaxed interfaces C and C' in Table I agrees within 20 meV with the (110) value. The estimated corrections $\Delta V_{\rm dip}$ for the interfaces A, A' and B, B' are ± 0.94 eV. Using the average of the *ab initio* values for the unrelaxed A and A' interfaces and for the B and B' interfaces, we obtain corrections of -0.93, $+0.96$ eV, close to the linear-response estimates. We note, however, that due to the high ionicity of the heterovalent wide-gap systems, deviations from the average value predicted by linear-response theory can be as large as $\sim$0.2 eV (interfaces B and B'), at variance with the situation in the conventional semiconductor heterojunctions such as GaAs/Ge or GaAs/ZnSe.[20] These deviations are related to the presence of important second-order terms (intersite interactions) in the response to the atomic substitutions transforming the virtual crystal into the real AlN/SiC junctions.[21] Such quadratic terms cancel each other out by symmetry in the (110) junction, but not in the case of the (111) junctions.

In the A and A' junctions, the mixed anion plane is found to relax toward SiC by about 0.07 a.u., and the cation plane closest to the interface relaxes by about the same amount in the opposite direction. Both displacements tend to increase the VBO, and the total effect evaluated from linear-response theory is $\Delta V_{\rm rel}=$ 0.8 eV, which compares well with the *ab initio* results. The displacements of the planes closest to the interface are about two times smaller for the B and B' junctions, and the cation and anion planes both relax towards SiC. The cation- and anion-relaxation effects thus tend to cancel each other, and the impact of the relaxation on the VBO is much smaller in these junctions. The relaxation at the polar A, A' and B, B' interfaces is mainly driven by electrostatic forces,[22] which tend to decrease the ionic interface dipole $\Delta V_{\rm dip}$. The larger relaxation observed at the interfaces A and A' as compared to the interfaces B and B' is attributed to the larger electrostatic potential discontinuity ΔV and resulting electric field at the A and A' junctions.

The zinc-blende and hexagonal polytypes such as the wurtzite (2H) form consist of identical atomic layers with different stacking sequences (see Fig. 2), and are characterized by very different band gaps. The 2H-SiC and 2H-AlN band gaps are 3.3 eV and 6.3 eV, respectively,[14,15] i.e., 0.9 eV and 1.4 eV larger than those of the corresponding cubic (3C) phase. To assess the effect of the crystal structure on the band offsets, we evaluated the VBO at the ideal wurtzite AlN/SiC(0001) heterojunctions with the atomic volume of the zinc-blende form, and the ideal lattice ratio $c/a=\sqrt{8/3}$ and internal parameter $u=3/8$ reproducing the interplanar separations of the (111) junctions. Such values of the structural parameters describe within 0.5 % the *ab initio* values for the 2H-SiC structure and within 2% those for the 2H-AlN structure.[23] The VBO we obtain for the unrelaxed AlN/SiC(0001) junctions are 0.70, 0.70, 2.38, and 2.71 eV for the interfaces A, A', B, and B', respectively. Notwithstanding the very large difference in the band gap of the cubic and hexagonal structures, the VBO and also the ΔV of the two phases differ by less than 0.1 eV. The 0.5 eV change in the band-gap discontinuity associated with the structural transformation from the cubic to the hexagonal form is thus predominantly absorbed by the conduction-band offset. Using the same lattice parameters, we also performed calculations for the relaxed wurtzite junctions, and the VBO were found to reproduce within 0.1 eV the values of the corresponding relaxed zinc-blende junctions.

In order to understand and generalize these results, we investigated the effect of the 3C/2H stacking faults on the potential lineup in the transformation 3C-AlN/3C-SiC → 2H-AlN/3C-SiC → 2H-AlN/2H-SiC, and the impact of the structural transformation from cubic to hexagonal on the band-structure terms of the AlN and SiC crystals. In Fig. 2 we display the electrostatic potentials in the 2H-AlN/3C-SiC and 3C-AlN/3C-SiC heterostructures with A and A' interfaces, and their difference. In supercells including a ferroelectric (2H) and nonferroelectric (3C) structure, two opposite electronic charges are induced at the interfaces.[24] As a result, two different electric fields are present in the bulk materials forming the 2H/3C heterostructure. The difference between the 2H/3C and 3C/3C electrostatic potentials, in Fig. 2, exhibits the typical sawtooth profile produced by interface charges. However, virtually no potential discontinuity can be distinguished which could be related to an interface dipole. The ΔV in the 2H/3C junction is identical, within $\sim$50 meV, to those of the 2H/2H and 3C/3C heterojunctions. Such results are consistent with the very small potential discontinuities observed in BeO, SiC, and AlN 2H/3C homojunctions, in recent *ab initio* studies of the spontaneous polarization of the wurtzite materials.[23,24] For the 2H-AlN/3C-AlN and 2H-SiC/3C-SiC junctions, we find ΔV of the order of 10^{-2} eV. All these results indicate that, in general, stacking faults have a very small impact on ΔV, both in homojunctions and in heterojunctions.

In Fig. 3 we show the alignment of the zinc-blende and

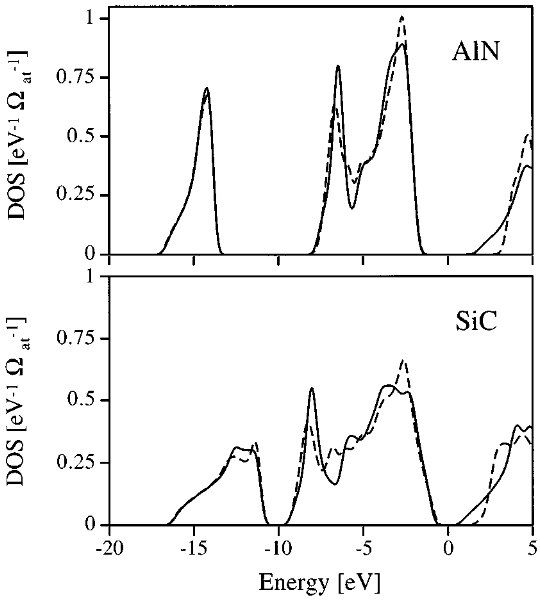

FIG. 3. Upper panel: electron density of states of the 3C-AlN (solid line) and 2H-AlN (dashed line) bulk crystals aligned according to the self-consistent potential lineup calculated for the 3C-AlN/2H-AlN(0001) junction. The zero of energy has been chosen at the midgap value of the 3C polytype. Lower panel: same data as in upper panel, but for SiC.

wurtzite LDA densities of states at the 2H-AlN/3C-AlN and 2H-SiC/3C-SiC homojunctions, as obtained from the lineups $\Delta V \sim 0$. For both materials, the matching of the 2H and 3C density of states features and band-edge positions in the valence band is quite striking, and in contrast with the situation of the conduction band. This is because the environment of each atom in the cubic and hexagonal structures differs only beyond the first neighbors, and unlike the bonding orbitals, which are highly localized on the anions, the more delocalized conduction states are quite sensitive to the bonding geometry of the neighboring atoms. The results in Fig. 3 for the band-structure terms together with the very small impact of stacking faults on ΔV indicate that the change in the band-gap discontinuity associated with a cubic to hexagonal structural modification in heterojunctions will be selectively found in the conduction-band offset, leaving the VBO essentially unchanged.

In conclusion, our results showed that lattice relaxation plays a major role in determining the band offset trends in the heterovalent nitride heterojunctions. This is in contrast to the case of the conventional semiconductor heterojunctions, and follows from the high ionicity of the heterovalent nitride systems. We found, however, that even in such highly ionic heterojunctions, when lattice relaxation is taken into account, the band offset dependence on orientation and heterovalency can still be qualitatively explained using linear-response-theory schemes. Finally, we showed that the cubic versus hexagonal crystal structure selectively affects the conduction-band offset, and has only a minor impact on the valence-band offset.

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