Strain effects on the interface properties of nitride semiconductors

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An *ab initio* study of nitride-based heteroepitaxial interfaces that uses norm-conserving pseudopotentials and explicitly treats the strain due to lattice mismatch is presented. Strain effects on the band offsets range from 20% to 40%. The AlN/GaN/InN interfaces (with AlN in-plane lattice constant) are all of type I, while the $Al_{0.5}Ga_{0.5}N$/AlN zinc-blende (001) interface is of type II. Further, the bulk polarizations in wurtzite AlN and GaN are -1.2 and -0.45 $\mu C/cm^2$, respectively, and the interface contribution to the polarization in the GaN/AlN wurtzite multiquantum-well is small. [S0163-1829(97)52912-2]

With the recent demonstration of stimulated emission in the blue region of the spectrum from a nitride-based multiquantum-well structure,[1] interest in the nitride-based semiconductors has burgeoned. This discovery has served to underscore the very attractive properties of the nitride-based materials, which include a wide band gap and the ability to form a continuous range of solutions of GaN, AlN, and InN, materials that have very different band gaps. This latter property makes possible the engineering of band gaps that span the range from the deep ultraviolet to the visible.[2]

Not surprisingly the potential technological importance of these materials has elicited the interest of a number of theoretical groups.[3–7] In spite of this, the strained interfaces of these lattice mismatched materials have not been studied. We find that strain effects are significant, inducing changes of 20% to 40% in the value of the band offset and that these changes increase with decreasing in-plane lattice parameter. The AlN/GaN/InN interfaces are all of type I, while the $Al_{0.5}Ga_{0.5}N$/AlN zinc-blende (001) interface is found to be of type II. Finally, we studied the GaN/AlN wurtzite interface, where qualitatively new features, namely pyroelectric and piezoelectric effects, appear due to the low symmetry of the wurtzite lattice.

The standard *ab initio* plane-wave pseudopotential method[8–10] was employed in the calculations. The energy cutoff for the plane-wave expansion was 50 Ry to ensure convergence of the nitrogen pseudopotential. We used the equivalent of ten k points for bulk and superlattice calculations in the zinc-blende structure[11] and six k points for calculations of the wurtzite structure.[12] Convergence both in the size of the plane-wave basis and in the number of special points has been carefully checked. The Perdew-Zunger parametrization[13] of the Ceperley-Alder form[14] of the exchange-correlation energy was used. For interface calculations, we employed $4+4$ superlattices (16 atoms) along the (001) and (0001) directions. Nonlocal, norm-conserving pseudopotentials[15–17] were included using the Kleinman-Bylander approach.[18] For nitrogen, we used a neutral configuration as the atomic reference for all states.

In pseudopotentials where d electrons are treated as core electrons, experience with II-VI semiconductors[19] has shown that the inclusion of the nonlinear core correction[20] results in a substantial improvement of the bulk properties. As an early work demonstrated,[5] the reference atomic state plays a critical role in the generation of the pseudopotential. In order that the pseudopotential be consistently descreened, it is necessary, when using the nonlinear core correction, that the reference atomic state be the same for all angular-momentum channels. This is in contrast with the standard Bachelet, Hamann, and Schlüter prescription[15] in which the atomic ground state is used as a reference for each angular-momentum channel present in the ground state, while, to improve transferability, an appropriately ionized, excited-atom configuration is used as the reference state for the angular-momentum channels present only in the excited states. Dal Corso *et al.*[21] have dealt with the inconsistency between the restriction imposed by the use of the nonlinear core correction and the importance of different atomic reference configuations for different angular-momentum channels by simultaneously fitting the pseudopotential and the core charge to more than one configuration.

The approach introduced here resolves this inconsistency while maintaining the improved transferability obtained through the choice of different, atomic reference configurations. This is achieved by choosing as the initial reference configuration the neutral ground state and generating the angular-momenta channels for it together with the core charge. For angular momenta present only in the excited states, we use the appropriately ionized, excited-atom configuration of the frozen-core atom (with the core from the neutral ground state). We generated pseudopotentials for aluminum, gallium, and indium with this procedure using the standard reference configurations for the empty d channel,[16,22] namely $3s^{0.75}\ 3p^0\ 3d^{0.25}$ for aluminum, $4s^{0.75}\ 4p^0\ 4d^{0.25}$ for gallium, and $5s^1\ 5p^{0.75}\ 5d^{0.25}$ for indium.

The calculated bulk properties are presented in Table I. In general, agreement with experiment is excellent.[23,24] The theoretical lattice parameters of both the zinc-blende and wurtzite forms agree very well with experiment; a similar level of accuracy is expected for the interface calculations described below. We have also calculated the bulk properties of GaN treating the $3d$ electrons of gallium as valence electrons following Ref. 7. With a cutoff of 240 Ry, we find $a_0 = 4.46$ Å and $B_0 = 2.14$ Mbar, which reproduces the experimental values to the same degree as our calculations employing the present pseudopotentials with the d electrons in core.

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TABLE I. Calculated bulk properties of zinc-blende and wurtzite nitride semiconductors. The values of the gap at the Γ pt (E_Γ) and of the valence-band width (ΔE_{vbw}) are the LDA results. Note that the LDA indirect gap in zinc-blende AlN is 3.2 eV. Experimental values are in parentheses and follow Ref. 7.

	Zinc blende		
	AlN	GaN	InN
a_0 (Å)	4.37 (4.38)	4.52 (4.5)	5.01 (4.98)
B_0 (MBar)	2.02 (2.02)	1.70 (1.90)	1.58 (1.37)
E_Γ (eV)	4.09	2.24 (3.45)	0.16
ΔE_{vbw} (eV)	14.86	15.48	14.01
	Wurtzite		
a (Å)	3.09 (3.11)	3.20 (3.19)	3.55 (3.54)
c/a	1.62 (1.60)	1.63 (1.63)	1.63 (1.61)
u (units of c)	0.378 (0.382)	0.376 (0.377)	0.375
B_0 (MBar)	1.99 (2.02)	1.69 (1.95, 2.37)	1.62 (1.26, 1.39)
E_Γ (eV)	4.44 (6.28)	2.29 (3.50)	0.16 (1.89)
ΔE_{vbw} (eV)	14.89	15.60	14.00

The properties of nitride-based semiconductor devices are critically dependent upon their interface properties. Due to the lattice mismatch between AlN and GaN (3.5%) and between InN and AlN (12.8%), superlattices of these materials are expected to be strained.[25] We investigate first the (001) zinc-blende interface. The supercell for the strained superlattice was determined using macroscopic elasticity theory.[26] In this theory, each half of the heterojunction is treated as a strained bulk with a fixed in-plane lattice constant $a_\parallel$. The perpendicular lattice constant of the epilayer c is obtained by minimizing the strain energy of the system subject to the fixed in-plane constant. For AlN, GaN, and InN, the calculated elastic constants used to determine the strains are given in Table II. Using total energy calculations, we find that macroscopic elasticity theory predicts well the perpendicular lattice constant for the epilayer. The residual relaxation of the atoms at the interface is negligible (<0.05 Å) and does not affect the band offset of the interface.

For the (001) direction, the supercell contains two identical interfaces and the interface energy, which is the excess energy due to the presence of the interface, can be calculated in a straightforward manner. We considered three different interfaces, namely the biaxially strained GaN/AlN (with AlN in-plane lattice constant) and the biaxially strained AlN/GaN (with GaN in-plane lattice constant) interfaces together with the GaN/AlN interface with an in-plane lattice constant that is the average of the GaN and AlN equilibrium lattice constants and is therefore not under any biaxial strain. In each case, the interface energy was found to be extremely small, $\sim$ 1 meV/interface atom, which is of the order of the precision of the calculations. Therefore, all of the interfaces show similar bonding characteristics.

TABLE II. Elastic constants calculated for zinc-blende AlN, GaN, and InN (in units of Mbar). The experimental values in parentheses are from Ref. 42.

	AlN	GaN	InN
c_{11}	3.01	2.61 (2.64)	2.14
c_{12}	1.62	1.27 (1.53)	1.37

TABLE III. Electrostatic potential line up ΔV and valence-band offsets, VBO and $\mathrm{VBO}_{\mathrm{ave}}$. The $\mathrm{VBO}_{\mathrm{ave}}$ is computed using the averages of the split valence-band manifolds. All quantities are in eV and are quoted with respect to AlN.

	ΔV	VBO	$\mathrm{VBO}_{\mathrm{ave}}$
AlN lattice constant	1.05	−0.73	−0.55
Average lattice constant	0.33	−0.58	−0.53
GaN lattice constant	0.74	−0.44	−0.53

We have investigated the effects of strain on the band offsets of the (001) GaN/AlN heterojunctions following the procedure of Ref. 27. The valence-band offset is divided into a band-structure contribution that is the difference between the energies of the valence-band edges when the average electrostatic potentials of the epilayers are aligned and the difference in the value of the average electrostatic potential (ΔV) in the two epilayers of the heterostructure. Since the band edges of the individual materials comprising the heterostructure behave differently when the system is stressed, i.e., having different deformation potentials, strain is liable to have a significant effect on the band offsets. Further, in the case of a biaxial strain, degenerate states split. We find that the average valence-band offset ($\mathrm{VBO}_{\mathrm{ave}}$), defined using the averages of the split valence-band manifolds, depends only weakly on the strain. In contrast, the valence-band offset (VBO), defined using the valence-band maximum, strongly depends upon the in-plane lattice constant. This is consistent with the results in other lattice mismatched heterojunctions.[28] In particular, the valence-band offsets vary between 20% and 40% in biaxially strained GaN/AlN, biaxially strained AlN/GaN and GaN/AlN with the average lattice constant. The results are given in Table III.

Table IV shows the band offsets for the (001) GaN/AlN, InN/AlN, and InN/GaN strained heterojunctions with AlN in-plane lattice constant.[29] We find that each interface is of type I, with the InN band edges sandwiched by the band edges of the other materials, since the band gap in InN is the smallest. The transitivity rule is satisfied. We do not observe any interface states in the gap of the superlattice. As might be expected, states at the top of the valence band are mostly localized to the epilayer with the smaller gap. Similar behavior is observed for the conduction-band minimum; the degree of localization of the states at the conduction-band minimum increases with increasing band offset.

The case of the wurtzite (0001) GaN/AlN interface was also investigated. Strain effects were explicitly included using macroscopic elasticity theory[30] and a total energy opti-

TABLE IV. Calculated band offsets for the three interfaces described in the text for an AlN substrate.

	VBO	CBO
GaN/AlN	−0.73	0.75
InN/AlN	−1.37	1.95
InN/GaN	−0.70	1.13

mization. The calculated valence-band offset is estimated to be -0.57 eV, a value smaller than the result for the strained nonpolar (001) GaN/AlN interface.[31] The ratio of the conduction-band to valence-band offset is 65:20. Our results agree very well with the experimental measurements of the (0001) wurtzite interface.[32]

Spin-orbit effects in both AlN and GaN have been shown to be of the order of 20 meV so that their difference, which enters into the calculations of the band offsets, is of the order of a few one hundreths of an eV and is much smaller than other possible sources of systematic error.[33] These include the neglect of the anion p-state and cation d-state repulsion[34] and the well-known neglect of many-body effects in the local-density approximation (LDA). In GaN/AlN interfaces, the inclusion of the $3d$ electrons as valence electrons results in a constant shift of 0.2 eV, which is less than the experimental error,[32] and does not change the character of the interface. Incorporating this shift gives results in agreement with previous estimates using a d-valence pseudopotential[6] and an all-electron calculation.[4] The importance of many-body effects on the band offsets is not known and awaits a future GW calculation.

Because of its low symmetry, the wurtzite system may display pyroelectric and piezoelectric behavior.[35] These effects, if present, will manifest themselves macroscopically in multiquantum wells along those directions that do not have a perpendicular mirror plane.[36,37] Thus, for instance, macroscopic fields are not observed in the strained (001) interfaces in zinc-blende structure, while they are observed in strained (111) interfaces.[36] Indeed, a polarization will be induced only if off-diagonal components of the strain are present. In (0001) strained GaN/AlN, we observe a substantial electric field as has been previously noted by Satta and co-workers.[38] In order to distinguish the bulk pyroelectric and piezoelectric contributions to this field from that induced by the interface, we have calculated the spontaneous bulk polarization of unstrained AlN and the strain induced polarization for the GaN epilayer. A superlattice consisting of eight layers of wurtzite and six layers of lattice matched zinc blende was used.[39] As the bulk spontaneous polarization is rigorously zero in unstrained zinc blende and, further, no chemical or geometrical perturbations are introduced by the interface (due to the lattice match and the special nature of the zinc-blende-wurtzite interface), this construction permits the unambiguous determination of the spontaneous polarization present in the wurtzite structure from the slope of the macroscopic average of the electrostatic potential. The spontaneous polarization (P_3) of AlN and GaN in equilibrium are -1.227 μC/cm^2 and -0.448 μC/cm^2, respectively; the polarization of the strained GaN is -0.454 μC/cm^2. These values are comparable to the computed bulk polarization in BeO.[39] The effect of the interface dipole is small; the polarization in the GaN/AlN multiquantum well is well described by the superposition of the polarizations of the constituent epilayers of the multiquantum well. The estimated contribution of the interface dipole (which includes the response of one epilayer to the field of the other) is 0.057 μC/cm^2, which is of opposite sign and an order of magnitude smaller than the bulk polarizations. The computed value of the polarization in the superlattice agrees with that estimated from experiment by Martin *et al.*[32]

Alloying provides another way to tune band offsets through changes to the strain in the system and changes to the electronic structure. The virtual crystal approximation in which the pseudopotentials of the constituent species are averaged by their fractional composition has been shown to adequately describe band offsets in certain alloy interfaces.[40] We have studied the zinc-blende (001) $Al_{0.5}Ga_{0.5}N$/AlN interface in the virtual crystal approximation. First, we used the virtual crystal approximation to calculate the elastic properties of the zinc-blende alloy (with theoretical lattice constant of 4.44 Å), finding $c_{11}=2.79$ Mbar and $c_{12}=1.4$ Mbar, and used macroscopic elasticity theory to predict the strains. In contrast to the pure nitride interfaces, we found that this particular alloy interface is a staggered type II interface. The valence-band offset is -0.39 eV and the conduction-band offset -0.17 eV. In order to verify the accuracy of the approach, we compared the lineup of the virtual crystal approximation with a fully relaxed $(GaN)_1(AlN)_1$/AlN interface; the alloy was replaced by the 1×1 superlattice, an extreme example of an ordered alloy. The results are -0.37 eV and -0.09 eV for the valence-band and conduction-band offsets, respectively. Further, the character of the interface remains unchanged. The macroscopic average of the electrostatic potential is already well represented in a short period superlattice and this permits a comparison with the band offsets calculated using the virtual crystal approximation. The agreement is good.

The alloying effect that leads to the change of the interface character is easily understood by reference to the definition of the conduction-band offset, which is

$$\mathrm{CBO}=\mathrm{VBO}+\Delta E_{gap}, \tag{1}$$

where ΔE_{gap} is the difference between the gap (corrected with the scissors operator) in the two epilayers of the superlattice. In pure zinc-blende AlN, the gap is indirect ($\Gamma_1^v\rightarrow X_1^c$); in contrast, the gap in pure zinc-blende GaN is direct. For (001) superlattices, where X is folded into Γ, the gap is determined by the smaller of the two. In the alloy, the gap at Γ is much more strongly dependent upon the gallium composition than is the gap at X. Consequently, the dependence of the conduction-band offset on gallium concentration has two distinct regimes: (i) for small gallium concentrations ($\leqslant 50\%$), where the gap is at X, ΔE_{gap} is small, the valence-band offset dominates, and the interface is of type II; (ii) for large gallium concentrations, where the gap is at Γ, the larger difference in the gaps make the interface of type I. This behavior is common to other systems, like $Al_{1-x}Ga_xAs$ on AlAs, where the same effect has been experimentally observed.[43]

In summary, we have investigated the influence of strain and composition on the interface properties of nitride-based heterostructures. In these lattice mismatched heterojunctions, the in-plane lattice constant can be varied by changing the characteristics of the substrate and so tune the band offset. Strain effects on the band offsets in GaN/AlN range from 20% to 40%. The bulk spontaneous polarization of the constituent materials, which range from -1.227 to -0.448×10^{-2} C/m^2 for AlN and GaN, respectively, constitutes the preponderant contribution to the polarization

present in the low symmetry wurtzite GaN/AlN interface, i.e., the interface contribution to the polarization is small. Finally, the pure interfaces are all of type I, while the $Al_{0.5}Ga_{0.5}N$/AlN interface is of type II and a change of character is, thus, expected to be observed as the gallium composition of the alloy is increased.

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