

Band offset of InGaAs(N)/GaAs interfaces from first principles

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Valence-band offsets of the InGaAs/GaAs(001) and InGaAsN/GaAs(001) interfaces are calculated from first principles. For InGaAs, we study the concentrations up to 25% of indium and for InGaAsN up to 12.5% of indium with 3% of nitrogen. Even though the band offset of the InGaAs/GaAs interface has a nearly linear dependence on the indium concentration, band offset of the InGaAsN/GaAs interface is strongly influenced by the amount of In–N bonds. Even a type-II band offset is found in the case of all indium located near to nitrogen and low strain of the InGaAsN layer. © 2008 American Institute of Physics. [DOI: 10.1063/1.2936074]

Since InGaAsN is one of the most important materials for the optoelectronic applications at the telecommunication wavelengths, it is important to have control and understanding of the band offset for efficient band engineering. Generally band offset can be quite straightforward to calculate, but InGaAsN band gap is known to fluctuate strongly depending on the nitrogen nearest neighbor configuration. This raises the question: how does the band offset change as a function of the nitrogen local geometry?

Short-range ordering in InGaAsN has been studied extensively. First computationally,¹ then experimentally,² and recently, a few studies with both experimental and computational methods have appeared.^{3,4} From these results relatively trustworthy concentrations of different bonding configurations at a certain composition and temperature can be estimated. In summary, as-grown samples tend to have indium atoms rather randomly distributed and annealing increases the number of In–N bonds. Changes in the short-range ordering induce bandgap changes and blueshift in photon emission spectra. This blueshift upon annealing is also widely reported experimentally.^{5–7} On the other hand, for InGaAs alloys such a strong band gap fluctuations have not been found, although the CuPt ordering, which has been found, is known to decrease the band gap.

Moreover, it is known that the N concentration does not affect the valence-band offset (VBO) much, while the In concentration does.⁸ We would expect only small changes in the VBO, because the blueshift is related to nitrogen bonding configuration, and from the electronic structure studies on GaAsN we know that it mostly affects the lowest conduction band.

In order to see how the concentrations, bonding configurations, and strain interplay on the final result, a computational approach is required. So far, there are no first-principles studies of band offsets on these material systems. Description of the band offset calculation scheme can be found in our previous article,⁹ and we will also follow the same notation here. All calculations are performed within the density functional theory (DFT) framework using a plane-wave basis and local density approximation (LDA) as implemented in the code VASP (Vienna *ab initio* simulation package).¹⁰ The atomic cores are described using projector-

augmented waves with the 3d electrons of gallium and indium explicitly included in the calculation. Spin-orbit coupling (SOC) is not used in the band-offset calculations, as its effect was earlier seen to be vanishingly small,⁹ but it is used for a few bulk cases to check the extent of the valence-band splitting.

All bulk calculations are done using 64-atom supercells and $2 \times 2 \times 2$ k -point mesh. InGaAs(N) supercells are laterally lattice matched to GaAs and the longitudinal lattice constant is allowed to relax. For the interface calculation, we have simply stacked two of these 64-atom InGaAs(N) supercells and two 64-atom GaAs supercells to form a 256-atom superlattice supercell, and finally relaxed the internal atomic positions. In this case, a $2 \times 2 \times 1$ k -point mesh was used.

Choice of the DFT with the LDA brings along the notorious band gap problem. As a result, only VBOs can be estimated reliably and the conduction-band offsets have to be estimated by using the experimental band gaps. Moreover, we are unable to go further than about 13% indium concentration with 3% nitrogen because higher concentration closes the band gap.

First, we check how the InGaAs/GaAs VBO behaves as a function of indium concentration and atomic configurations. Results are shown in Table I. Here, all the In_k configurations (with k atoms in the computational supercell) have segregated indium, i.e., all indium atoms are surrounding the same arsenic site. This reduces the spurious interactions from periodic atomic ordering, is geometrically well defined, and makes the comparison to InGaAsN configurations straightforward. The $\text{In}_8(\text{rand})$ configuration has one In atom at the same site in each eight-atom unit cell. In the $\text{In}_8(\text{CuPt})$ configuration, we start from the ideal CuPt crystal structure with 50% indium concentration and randomly replace half of the indium atoms by gallium atoms to achieve the CuPt-like random structure with 25% indium.

The results are shown in Fig. 1. We can immediately notice that the VBO depends linearly on the indium concentration (for $x < 0.125$), with about 5.4 meV/%In. Using experimental values for the band gap^{11,12} $E_g(x) = 1.43 - 1.11x + 0.45x^2$ (eV), we get the VBO ratio $Q_v = \Delta E_v / \Delta E_g = 0.5$, where $\Delta E_g = |E_g(\text{In}_x\text{Ga}_{1-x}\text{As}) - E_g(\text{GaAs})|$, at low ($< 12.5\%$) indium concentration and 0.4–0.45 at the 25% concentration, depending on the atomic ordering. We emphasize that our results are for 0 K and also without the zero-point motion.

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TABLE I. Longitudinal lattice constant (in Å), band gap, and shift in VBM ΔE_v^b from the bulk calculations, the shift in the electrostatic potential from the interface calculations ΔV_c^i , and finally the VBO ΔE_v . All energies are in the units of meV.

Configuration	a	E_g	ΔE_v^b	ΔV_c^i	ΔE_v
GaAs	5.605	529	...	...	...
In ₁	5.641	469	74	-57	17
In ₂	5.666	427	164	-130	34
In ₃	5.693	381	253	-201	52
In ₄	5.717	344	338	-271	67
In ₈ (rand)	5.844	195	632	-535	97
In ₈ (CuPt)	5.844	130	676	-537	139
GaAsN	5.542	51	31	4	35
In ₁ N ₁ /In ₁ N ₁ ⁽¹⁾	5.570	111/33	76/85	-67/-63	11/22
In ₂ N ₁ /In ₂ N ₁ ⁽²⁾	5.597	153/57	134/145	-140/-139	-6/6
In ₃ N ₁ /In ₃ N ₁ ⁽³⁾	5.622	185/15	207/227	-216/-209	-10/18
In ₄ N ₁ /In ₄ N ₁ ⁽⁴⁾	5.648	213/-143	284/342	-287/-269	-3/-73
In ₄ N ₁ ⁽¹⁾	5.648	143	291	-286	5
In ₄ N ₁ ⁽²⁾	5.648	53	308	-282	26
In ₄ N ₁ ⁽³⁾	5.648	-41	321	-276	45

However, even though the band gap depends strongly on temperature, the band offset ratio does not, and therefore, we believe that our results for Q_v are reliable at least at low temperatures. We obtain further confidence on our computational results from comparison to experimental VBO results, which cover quite a large range of values as has been collected in Refs. 11 and 13. Our results are in good agreement with the more recent and careful experiments of Ref. 13, where Q_v decreased linearly from about 0.55 at very low indium concentration to below 0.4 at 20% concentration, and also with Ref. 14.

The total energies show that indium would indeed like to segregate, as is known to take place, but the effect on the band offset is very small. It is difficult to model a random configuration on a 64-atom supercell, but tests on a few different configurations show band-offset fluctuations of about 10 meV. Compared to the random configuration, In₈(CuPt) is energetically only about 20 meV lower, whereas In segregation is clearly energetically favored. It is known experi-

mentally that the CuPt formation is driven by processes at the surface during growth. Even so, it is interesting to note how this results in a significantly, almost 40 meV, higher VBO, and also seems to follow better the linear dependence obtained at lower concentrations. This might explain some of the scattering on the experimental results.

Another interesting question is whether the light-hole (LH) band is energetically confined into the InGaAs layer or not. Li¹⁵ reported that the LH band is confined to the InGaAs layer. We performed a few bulk calculations with SOC and found the LH/heavy-hole (HH) splits of about 24, 68, and 109 meV for In₁, In₄, and In₈(rand) cases, respectively. Our results suggest that the LH band is not energetically confined to the InGaAs layer in segregated or random phases, and the quantum well confinement should push it further below the GaAs valence-band maximum (VBM). However, CuPt-like phase has larger band offset, but the VBM splitting is still 109 meV, meaning that the LH band is confined by 30 meV. Therefore, the results of Ref. 15, where band offset of 80 meV and split of 60 meV were found with 20% indium concentration, could be well explained with at least partial CuPt-like atomic ordering.

Next, we proceed on adding nitrogen in to the calculation. In Table I, In_kN_l represent configurations with all k indium atoms nearest neighbor to the l nitrogen atoms and In_kN_l^(m) represent configurations, where m out of k indium atoms have been removed away from the nitrogen nearest neighbor sites such that their mutual distances are also maximized. With three indium atoms the longitudinal lattice constant is seen to be just slightly above that of GaAs, meaning that the strain is smallest in this case. The indium to nitrogen concentration ratio for zero strain is experimentally known to be around 2.8, close to our 3:1 ratio. Interestingly, in the cluster configuration (In_kN_l) the band gap increases with the increasing indium concentration. Indium alleviates the strain, but does not contribute to the band gap decrease when clustered with nitrogen. A somewhat opposite result is found for the “far-away” indium cases (In_kN_l^(m)).

Our calculated total energies for the supercells follow the same trend as observed in the previous studies.^{5,7} In other

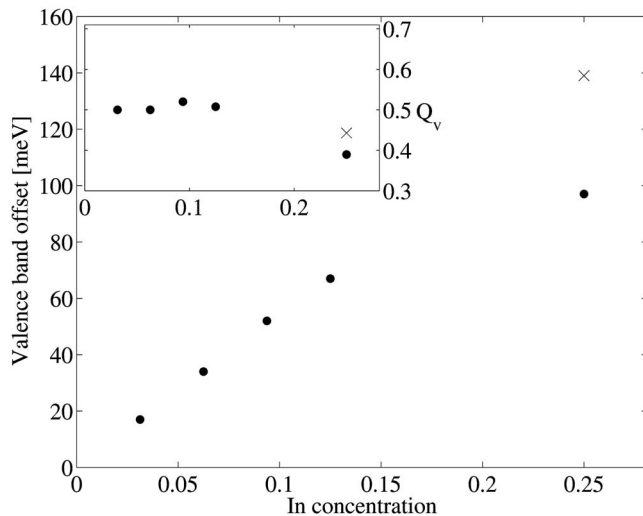


FIG. 1. VBO for the InGaAs/GaAs interface. The dots and the cross denote the segregated In configurations and the CuPt-like configuration, respectively. The VBO ratio $Q_v = \Delta E_v / \Delta E_g$ is shown in the inset.

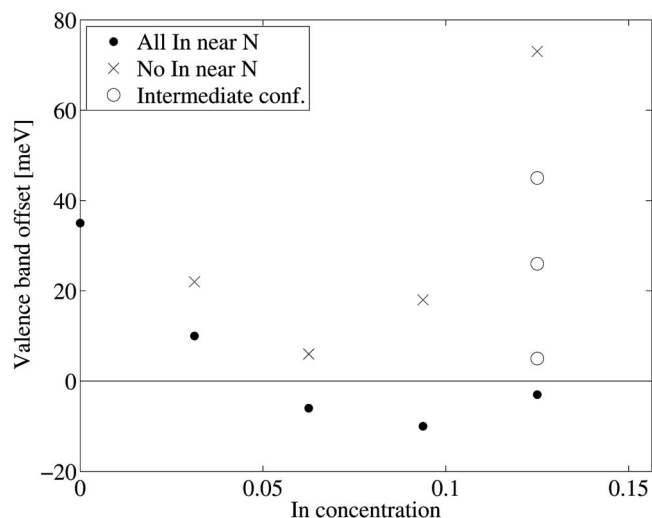


FIG. 2. Band offset for InGaAsN/GaAs interfaces. The dots denote the cases where all indium is nearest neighbor to nitrogen, crosses where indium is randomly distributed and far away from nitrogen, and circles present the intermediate structures between these two extrema.

words, In–N bonds are favored such that In_4N_1 is 1.2 eV below the far-away $\text{In}_4\text{N}_1^{(4)}$ case, while further segregation of indium away from the nitrogen atoms is favored by some 360 meV.

In Fig. 2, the results from the cluster and far-away calculations are shown. A clear difference can be seen: In the former case, it turns out that the bending of the VBO curve is completely caused by the splitting of the VBM due to strain, and the effect of indium concentration on the VBM energy is very small. Therefore, the splitting of the VBM, and consequently the VBO, achieves their minimum at the position of minimum strain. Interestingly, it would seem to be possible to achieve even a type-II band lineup in the case of the low strain. In the latter case, there is a larger contribution to the VBO from the change of the VBM energy as can be seen from the ΔE_v values of Table I for $\text{In}_k\text{N}_1^{(k)}$ and In_kN_1 configurations. This is more similar to the behavior of the In_k cases on the InGaAs/GaAs interface. Also due to this, the VBO minimum in the latter case is located at a somewhat lower concentration.

The conduction-band minimum wavefunction is known to be strongly localized on the nitrogen and its four nearest neighbor atoms in dilute nitrides. In this sense, it is possible to understand how the effect of indium has large impact only on the conduction-band offset when it is coordinated with nitrogen. However, it is still surprising to see how radically the VBO changes as indium and nitrogen coordination changes. This is quite problematic for the device engineering. Annealing is used to remove point defects, but from our

calculations we can infer that annealing, through increasing the number of the clusters, also decreases the VBO, subsequently decreasing the hole confinement. However, often in practice, the ratio of indium to nitrogen concentrations is much larger, and therefore the amount of the In–N bonds is smaller. Also, in order to go to high In–N coordination amounts, the sample has to be annealed quite aggressively.^{3,16} Our bulk calculation with the SOC shows that the LH/HH split with the In_4N_1 cluster is about 28 meV, which is close to that of the In_1 configuration with a similar strain. Therefore, in the as-grown samples, both valence bands should energetically be confined in the InGaAsN layer.

In Fig. 2, also the band offset transition from the cluster configuration to the “far-away” configuration is shown. The change in the band offset is seen to be relatively constant between the intermediate configuration steps. Moreover, indium or nitrogen “richness” at the interface did not have any effect on the band offset (not shown in this paper), rather expectedly.

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