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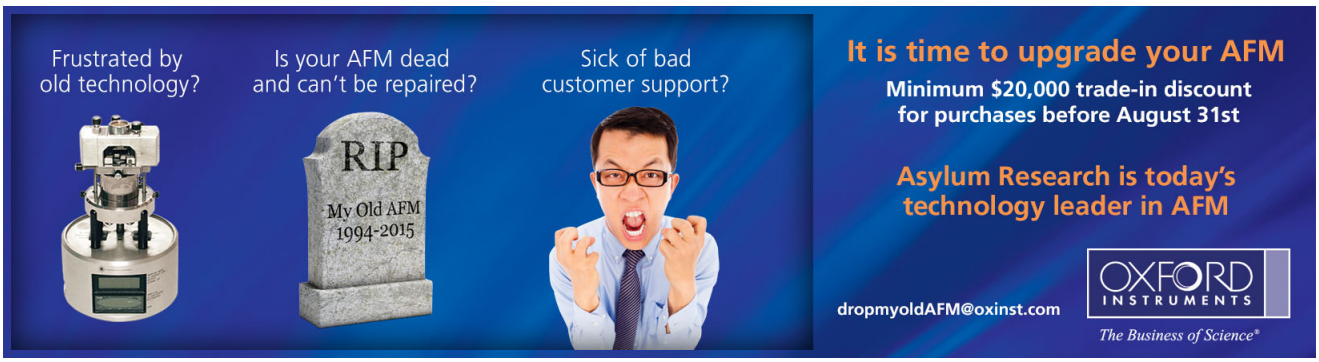

Polarization fields and band offsets in GaInP/GaAs and ordered/disordered GaInP superlattices

Sverre Froyen, Alex Zunger, and A. Mascarenhas
National Renewable Energy Laboratory, Golden, Colorado 80401

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Using the first-principles pseudopotential method we have calculated band offsets between ordered and disordered $Ga_{0.5}In_{0.5}P$ and between ordered $GaInP_2$ and GaAs. We find valence band offsets of 0.10 and 0.27 eV for the two interfaces with the valence band maximum on ordered $GaInP_2$ and GaAs, respectively. Using experimental band gaps these offsets indicate that the ordered/disordered $Ga_{0.5}In_{0.5}P$ interface has type I band alignment and that the ordered $GaInP_2$/GaAs interface has type II alignment. Assuming transitivity of the band offsets, these results suggest a type I alignment between disordered $Ga_{0.5}In_{0.5}P$ and GaAs and a transition from type I to type II as the GaInP side becomes more ordered. Our calculations also show that ordered $GaInP_2$ has a strong macroscopic electric polarization. This polarization will generate electric fields in inhomogeneous samples, strongly affecting the electronic properties of the material. © *1996 American Institute of Physics.* [S0003-6951(96)01620-8]

Spontaneous long-range order has been observed in many III–V pseudobinary alloys.[1] The most common is the CuPt type ordering that was first observed in $GaInP_2$ by Gomyo *et al.*[2] In ordered $GaInP_2$, the Ga and In atoms are located on alternating layers along a (111) direction. This cell doubling reduces the size of the Brillouin zone in the (111) direction and causes the zinc-blende L point to fold to Γ. Interactions between the folded-in L states and Γ states shift the conduction band minimum downwards[3] and split the heavy-hole light-hole degeneracy at the valence band maximum. These features combine to reduce the band gap of the ordered material. They are easily observed by experiment and are used to measure the degree of order in the sample.

Certain samples, usually multidomain with small domain size, do not fit this simple picture. At low temperature, a low energy photoluminescence (PL) peak is frequently observed 10–20 meV below the onset of absorption as observed by photoluminescence excitation (PLE). The exact value for the shift is sample dependent and the peak shows a strong blue shift with increasing excitation power.[4] Time-resolved studies of the low energy PL peak show long nonexponential decay times indicating spatial separation of the electrons and holes.[4,5] Furthermore, experiments performed in high magnetic fields[6] indicate that the PL arises from band-to-band recombination and not from excitonic transitions. Based on these observations, it has been proposed that the samples are not uniformly ordered but exhibit domains of varying degree of order[7] and that the interface between ordered and disordered GaInP has a type II alignment[6,8,9] with the valence band maximum in the disordered and the conduction band minimum in the ordered region. The type II band alignment is difficult, however, to reconcile with theoretical arguments, which suggest a type I offset.[3]

A separate class of experiments has measured the offset between GaInP and GaAs. GaAs is lattice matched to $Ga_{0.48}In_{0.52}P$ and is commonly used as a substrate. For many device applications it is therefore important to know the band alignment between the two materials. Various experiments have produced values for the conduction band offset ranging from 0.03 to 0.39 eV (type I).[10] There is even evidence for type II band alignment.[11]

In this letter, we present calculated values for the offset between fully ordered and disordered $Ga_{0.5}In_{0.5}P$ and between ordered $GaInP_2$ and GaAs. We find that the band alignment in the former case is type I. This is in accord with previous theoretical arguments but in disagreement with the accepted interpretation of experimental results. We find a type II band alignment between ordered $GaInP_2$ and GaAs but that the alignment changes to type I as the GaInP layer becomes disordered. This explains, in part, the large scatter in the measured GaAs/GaInP offsets.

In our calculations we observe a strong (-16 mV/Å) internal electric field in fully ordered $GaInP_2$. We suggest that this field can explain the experimental observations without a type II band alignment. The field is consistent with the observed pyroelectricity[12] and it is related to the internal electric fields that have been predicted for strained-layer (111) superlattices.[13] These fields are piezoelectric fields caused by the strain in the individual layers that make up the superlattice. Our calculations show that the fields remain even for layers of monolayer thickness.

We use the first-principles pseudopotential method within the local density approximation to calculate the superlattice offsets and the electric fields. The wave functions were expanded in plane waves using a kinetic-energy-cutoff of 20 Ry. Semirelativistic pseudopotentials generated using Kerker's method and the nonlinear core correction were used to improve the transferability of the Ga and In potentials. For the binaries, we calculate lattice constant of 5.40, 5.83, 5.60, and 5.62 Å for GaP, InP, GaAs, and ordered $GaInP_2$, respectively. These are within 1% of the experimental $T=0$ values and, more importantly, have the right relative ratios. We have assumed that ordered $GaInP_2$ retains its cubic cell dimensions. The band offsets were computed from the calculated potential offsets in (001) superlattices with periods of 8 and 16 bilayers and from the calculated band energies of the superlattice constituents. Our pseudopotentials do not include spin-orbit interaction. The spin-orbit splitting in

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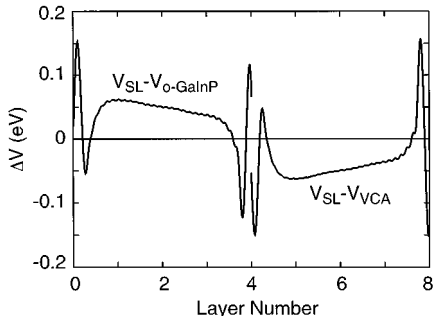

FIG. 1. Planar averaged superlattice potential measured with respect to the constituents as indicated for an ordered GaInP/VCA GaInP superlattice. Layers 0–4 are CuPt-ordered GaInP and 4–8 are disordered GaInP modeled using a VAC alloy.

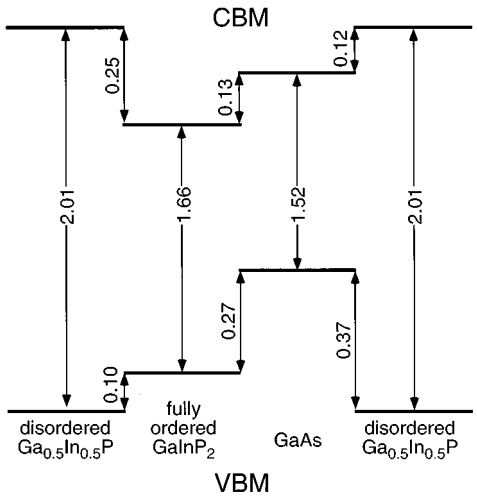

FIG. 2. Band alignment for VAC disordered GaInP, ordered GaInP, and GaAs. All energies are in eV.

the valence band was therefore added using experimental values for the spin-orbit splitting and the quasiparticle approximation.[14] Disordered $Ga_{0.5}In_{0.5}P$ was modeled in two ways. The more elaborate model employed a 32 atom cell in which the 16 Ga and In atoms were distributed according to a special quasirandom structure (SQS) construction.[15] The other, simpler model, used the virtual crystal approximation (VCA) in which the Ga and In pseudopotentials were replaced with a single average potential. The bandgap of the SQS structure was 0.35 eV larger (0.50 eV for VCA) than that of the fully ordered structure. Previous calculations range from 0.32 to 0.49 eV.[3,16] In estimating the conduction band offsets, we will use our calculated value of 0.35—which is in good agreement with a value of 0.38 ± 0.04 eV recently proposed by Wei *et al.* as the best estimate for the band-gap change.[17]

The superlattice interfaces were relaxed as follows. The various superlattice unit cell contains four (or eight) bilayers of the first material followed by four (eight) bilayers of the second material in the (001) direction. Except as noted below, the lattice parameters remained ideal. The interface anions were relaxed using atomic forces, while the positions of the remaining atoms (with the exception of a uniform translation of all the atoms within a superlattice layer) were kept fixed. For the GaInP/GaAs superlattices, we first formed a superlattice with one P interface and one As interface. We relaxed this superlattice as described above. The resulting structure gave us cation-anion distances across the P and As interfaces. These interface distances were then used to calculate the appropriate lattice parameters for superlattices with two P and two As interfaces. Residual forces on the interface atoms as well as the residual force acting on a layer (per interface atom) were in all cases smaller than 10^{-2} Ry/a.u. For the GaAs/GaInP superlattice with two P interfaces, we also allowed the cations adjacent to the interface layer to relax. The change in band offset was less than 2 meV and the change in the electric field was zero.

The result for the ordered $GaInP_2$/VCA superlattice is shown in Fig. 1. The figure demonstrates two important characteristics. First, the potential perturbation caused by the interface extends only a couple of monolayers around the interface. Second, the smooth part in the interior of each layer is not constant but has a uniform slope. The latter indicates a nonzero electric field in each layer. Such a field can arise in three ways. If the two interfaces are not identical, the offset at the *A/B* interface may not equal the negative of the offset at the *B/A* interface. Because the potential must be periodic over the superlattice unit cell, a compensating field would arise and create a potential drop equal to the offset difference. Such a compensation field would, however, be the same (assuming similar dielectric constants) in the two halves of the superlattice. A second possibility is a field caused by free-electric charges at the interfaces. This type of field can occur for instance in Ge/GaAs (001) superlattices,[18] where charged donor and acceptor states are created by the non-octet bonds at the interfaces. The homopolar III–V superlattices discussed here do not, however, have non-octet bonds and a careful examination of the superlattice states does not show any indication of donor or acceptor states. We are therefore left with a third alternative which is a macroscopic electric polarization in one or both superlattice regions. By symmetry there can be no polarization in the GaAs of the VCA GaInP. The polarization must therefore originate in the ordered $GaInP_2$ region.

We calculate a valence band offset of 0.10 eV for the ordered/disordered GaInP interface using the SQS to model the disordered structure (0.13 eV using VCA) with the valence band maximum (VBM) on ordered GaInP. For the GaAs/ordered GaInP interface the offset is 0.27 eV with VBM on GaAs. We find that the type of interface atoms (P or As) at the GaAs/ordered GaInP interface changes the offset by less than 0.02 eV. Using the calculated valence band offsets and experimental gaps, we obtain the band alignment shown in Fig. 2. That is, ordered GaInP and disordered GaInP have type I, ordered GaInP and GaAs have type II, and if we assume transitivity, disordered GaInP and GaAs have type I band alignment. Assuming a quadratic dependence of the conduction band offset on the ordering parameter,[3] we estimate that a transition from type I to type II band alignment between partially ordered GaInP and GaAs takes place at an ordering parameter of 0.7.

We calculate an electric field in the ordered GaInP region of -9 mV/A in the (001) direction. By symmetry, the (001) field must be a projection of a field along the (111)

direction whose strength must therefore be -16 mV/Å. In our calculation we chose the ordering vector along the (111) direction and assumed that the positive (111) direction goes from the cation to the anion.

The origin of the electric field is similar to that predicted[13] and later confirmed[19,20] to exist in artificially grown (111) strained-layer superlattices. Piezoelectric fields generated by the strain in each layer produce a total electric field that has an oscillating component that varies from layer to layer and an average component. For a macroscopic superlattice, the average component must be cancelled by surface charges. For a thin slice of a superlattice embedded in another material, however, the average field may be nonzero. We can calculate the piezoelectric fields in ordered $GaInP_2$. Using Eqs. (5) and (9) from Ref. 20, experimental elastic and dielectric constants, the calculated lattice parameters, and the values -0.1 and 0.04 C/m^2 (Ref. 21) for the piezoelectric constants e_{14} of GaP and InP, respectively, we calculate fields of -3.5 mV/Å for GaP and -2.6 mV/Å for InP. The fields point in the same direction because both the strain and the piezoelectric constants have opposite sign in the two materials. The average field along the (111) direction is therefore -3.1 mV/Å or about five times smaller than the value derived from the first principles calculation. The agreement is perhaps reasonable given that we have used bulk material parameters for layers as thin as two atomic monolayers.

In real samples, the ordering is not perfect and this will decrease the field strength. By symmetry, the field is unchanged under an interchange of Ga and In. To the lowest order, the field must therefore be quadratic in the ordering parameter.[3] A highly ordered sample can have an order parameter of 0.5, which would reduce the field by a factor of four. The electric field is still very large and would have important consequences for many experiments probing the electronic properties of a sample.

Consider for instance an ordered domain in a matrix of less ordered material. We assume undoped material. Even with zero potential drop across the sample, the field in the ordered domain could be sizable. For small domain sizes it could be as large as the intrinsic field (-4 mV/Å along the ordering vector for an ordering parameter of 0.5) and for larger domains it would be limited by the band gap divided by the domain size. For small electron/hole concentrations, the field would separate the electrons and holes spatially and the recombination rate would be very slow. The recombination energy would be below band gap. For higher electron/hole concentration, the larger number of electrons and holes would screen the field, the recombination rate and energy would both increase. This naturally explains the moving peak with the long lifetime that has been observed in PL on ordered GaInP. Such a moving peak has also been observed in the artificially grown strained-layer AlAs/AlInAs (111) superlattices.[20]

Similar effects would exist in ordered samples containing domains with ordering vectors along the (111) and the (111) directions. Frequently, such crystals grow with domain boundaries in the (110) planes which means that the (110) of the fields are oriented in opposite directions. This will again lead to fluctuating band edges and PL behavior very much like that described in the previous paragraph.

Finally, we note that an interface between a large domain of ordered GaInP and a cubic material such as GaAs will very likely have the Fermi level pinned at one of the band edges. If experiments such as those on band offsets fail to take this fact into account, the results may be misinterpreted. Note also that the excess electrons or holes at the interface may significantly modify the offset.

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