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

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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.
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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

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 6 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^{22} 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.

direction whose strength must therefore be 216 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]