Role of Interface Strain in a Lattice-Matched Heterostructure

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(Received 6 November 1989)

First-principles total-energy-minimization calculations show that the interface bonds are significantly strained in nominally lattice-matched $In_{0.53}Ga_{0.47}As/InP(001)$ heterostructures, in agreement with recent x-ray measurements. Anion intermixing at the interface reduces this strain. The calculated valence-band offset is sensitive to interface bond lengths so an energetically (meta)stable interface structure must be used. Then the calculated valence-band offset is independent of intermixing (hence measured strain) and in quantitative agreement with experiment.

PACS numbers: 68.65.+g, 71.25.Tn, 73.40.Kp

Measurement, prediction, and control of semiconductor heterojunction band offsets continue to be challenging problems with important technological implications.[1] Despite extensive effort, it remains unclear whether the band offsets are determined by bulk properties of the constituent materials or by interface specific dipoles. This is a fascinating fundamental problem with important implications for the possibility of "tuning" the band offsets between a given pair of materials through manipulation of the interface structure or chemistry. Theories based on alignment of bulk derived "midgap" levels[2-4] naturally imply that such tuning is virtually impossible. It has recently been shown that for isovalent, lattice-matched heterojunctions, the band offset is independent of the chemical abruptness of the interface (e.g., Ga/Al interdiffusion for the GaAs/AlAs case).[5] Artificial order (e.g., ultrathin superlattices) in the heterostructure alters band offsets, but these must be regarded as offsets to a new constituent material.[6,7] More general manipulations of the interface structure and chemistry have influenced the band offset in some cases,[8] but not for device quality materials and well characterized interfaces.

The technologically important $In_xGa_{1-x}As/InP(001)$ system offers a heretofore unexplored parameter which may influence the band offsets: the interface bond lengths or interface strains. This is possible because there is neither common anion nor common cation. In this paper, the lattice-matched case ($x=0.53$) is examined in detail. The interface structure and band offset are studied for abrupt as well as chemically intermixed interfaces.

Figure 1(a) illustrates a sequence of planes for the $In_{0.53}Ga_{0.47}As/InP(001)$ heterostructure. Two chemically distinct interfaces result requiring In-As bonds on the left and M-P bonds on the right ($M=In_{0.53}Ga_{0.47}$). Bulk bond lengths[9] suggest that $d_{\text{In-As}} > d_{\text{In-P}} = d_{M\text{-As}} > d_{M\text{-P}}$ giving a positive interface strain on the left side of the barrier (InP) with a very nearly compensating negative strain on the right side. This naturally yields interfaces that are structurally as well as chemically different, and an intrinsic asymmetry. It is also evident that anion intermixing at the interfaces may alter the local strain. For example, $As_{0.5}P_{0.5}$ (denoted A) at each interface [Fig. 1(b)] reduces the strain at the interfaces to essentially zero, and the symmetry between left and right sides of the barrier is restored. (Since $d_{A\text{-In}} > d_{A\text{-}M}$, there is an internal strain coordinate to ϵ'.) These elementary considerations show that local strains are to be expected at the interfaces with the magnitude "tunable" from zero to several percent depending on interface composition. X-ray-diffraction scans of samples grown with the intention of exhibiting the asymmetric interfaces illustrated in Fig. 1(a) have been analyzed to obtain the first experimental evidence of significant strains near the interfaces.[10]

The calculations reported here show that this ideal heterojunction [Fig. 1(a)] has a large (6%) interface strain. Chemical intermixing [Fig. 1(b)] is shown to relieve the interface strain from which it follows that the measured strain is a sensitive test of the chemical abruptness of the interface. The calculated valence-band offset at the abrupt interface varies by 150 meV for $\epsilon=(0-8)\%$. Despite the chemical and structural asymmetry between the left and right sides of the barrier, the

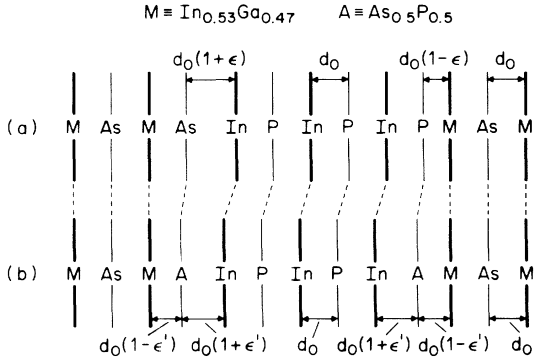

FIG. 1. (a) A sequence of planes in the $In_{0.53}Ga_{0.47}As/InP(001)$ heterojunction system illustrating local interface strains. (b) Chemical intermixing which relieves the net local strain in the interface molecular layer.

offset is well defined and the same for either side. The present first-principles calculation yields $\Delta E_v = 410 \pm 50$ meV, in very good agreement with experiment.[11-13] Furthermore, this value is well defined provided the interface structure is relaxed to a (local) total-energy minimum subject to constraints of composition: The abrupt case ($\epsilon = 0.06$) and the intermixed case ($\epsilon' = 0.03$) have the *same* valence-band offset. The present results demonstrate the importance of including the (local) minimum-energy interface structure in the calculation of the heterojunction band offsets. Different interface structures, and hence interface strains, may result depending on constraints imposed by growth conditions. However, the interface strain is not an independent parameter controlling the band offsets.

The local-density-functional approach[14] (LDA) is used to calculate the self-consistent ground-state charge density and total energy for a series of MAs/InP(001) superlattices with different interface configurations. The pseudopotential technique[15] is used with the core correction for the exchange-correlation potential.[16] The alloy (M) is treated with the virtual-crystal approximation, as applied to the bare ionic pseudopotentials. A plane-wave basis set is used[17] with a 9-Ry energy cutoff for the superlattice calculations. (Increasing this to 11 Ry does not change the results reported here.) For a given interface configuration, the valence-band offset is calculated from

$$\Delta E_v = (E_v - \langle V_{\mathrm{loc}} \rangle)^{\mathrm{bulk}}_{M\text{-As}} - (E_v - \langle V_{\mathrm{loc}} \rangle)^{\mathrm{bulk}}_{\mathrm{In\text{-}P}} - \Delta \langle V_{\mathrm{loc}} \rangle^{\mathrm{int}} . \qquad (1)$$

The position of the bulk valence-band edge E_v is required relative to the average local potential $\langle V_{\mathrm{loc}} \rangle$ in the bulk separately for each constituent material, taken from highly converged (24-Ry cutoff) self-consistent calculations.[18] The change in potential across the interface, $\Delta \langle V_{\mathrm{loc}} \rangle^{\mathrm{int}}$, requires a self-consistent interface calculation for each configuration. The relevant band diagram for Eq. (1) is well known[19] and sketched in the inset to Fig. 3. There is a further correction due to the fact that the LDA valence-band edge is not rigorously the electron removal energy. Proper quasiparticle energies require a self-energy calculation, which is outside the scope of the usual LDA total-energy calculations.[20] The resultant band offset can be written[21]

$$\Delta E_v = \Delta E_v^{\mathrm{LDA}} + \delta_v , \qquad (2)$$

where δ_v is a self-energy correction which derives from proper treatment of the many-body interaction effects in the constituent materials. For the GaAs/AlAs valence-band offset, δ_v is essential,[21] contributing 120 ± 20 meV. It is estimated that $\delta v \approx 110 \pm 40$ meV for the MAs/InP system.[22] This δ_v is included in the valence-band offsets reported here.

The bulk structural properties for the constituent materials are reproduced within the standard accuracy for the LDA total-energy scheme; e.g., the bulk lattice constant agrees with experiment to within about 1%. Furthermore, the theoretical lattice constant for $In_{0.35}Ga_{0.47}As$ is just 0.5% larger than that for InP, in close agreement with the lattice-matching situation found experimentally. (The theoretical mismatch is small compared to the interface strains of interest in the present study.) The interface calculations are done using the theoretical lattice constant of InP (d_0) and a $(M\mathrm{As})_3(\mathrm{InP})_3$ superlattice.

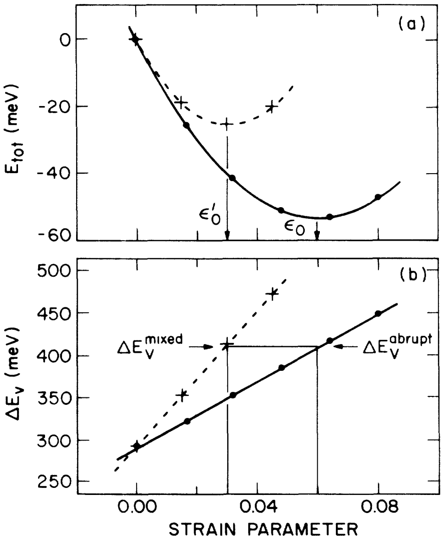

FIG. 2. (a) Superlattice total energy as a function of the local interface strain parameter. (b) Calculated valence-band offset as a function of local strain parameter. Solid line: abrupt case [Fig. 1(a)]; dashed line: chemically intermixed case [Fig. 1(b)].

The interface strain is studied with the one-parameter model illustrated in Fig. 1. The total energy as a function of interface strain parameter ϵ is shown in Fig. 2(a). The minimum-energy configuration corresponds to $\epsilon = 0.06$. Consideration of bulk bond lengths[9] would suggest $\epsilon \approx 0.03$. However, InAs (for example) is biaxially compressed on InP, so the perpendicular lattice parameter should be altered according to elastic compliance coefficients. Thus, if the elastic prediction for the d spacing of InAs on InP is taken to this extreme, one would suggest $\epsilon \approx 0.065$. This naive estimate is in good agreement with the full calculation and gives strong support to the notion that bond lengths are a very local property.

The interface dipole is a strongly varying function of ϵ. A running average of the local potential[5,23] is plotted for the superlattice in Fig. 3 for ϵ near the total-energy minimum. The values at the center of each region yield $\Delta \langle V_{\mathrm{loc}} \rangle^{\mathrm{int}}$. A more detailed discussion of the form of the dipole will be given elsewhere.[24] The strong dependence on local (e.g., InAs) bond length reflects the reduced

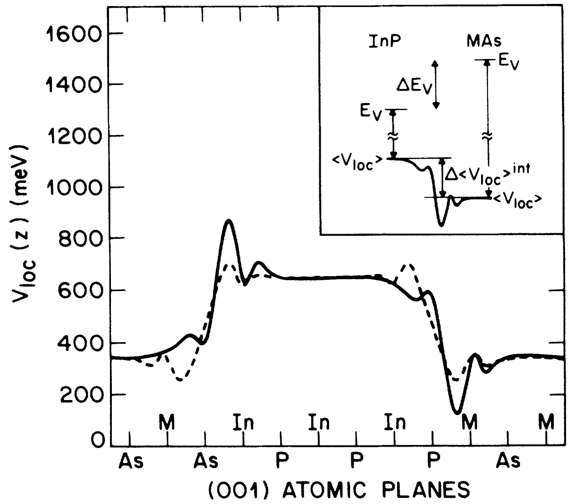

FIG. 3. Averaged local potential through the superlattice. Solid line: abrupt case with $\epsilon=0.064$; dashed line: chemically intermixed case with $\epsilon'=0.03$. Inset: Band diagram for calculation of the valence-band offset.

charge transfer between anion and cation with increasing separation. Despite the chemical and structural *asymmetry* between the left and right interfaces, there are no internal fields and the net dipoles are the same. The variation of the dipole with local bond length translates to a significant increase of the valence-band offset with ϵ, illustrated in Fig. 2(b). The minimum-energy value of $\epsilon=0.06$ yields $\Delta E_v=410$ meV, 120 meV larger than would be found under the assumption of unstrained interface bonds.

It is important to consider whether variations in interface composition might relieve the interface strain and hence alter the valence-band offset. The particular change in interface stoichiometry illustrated in Fig. 1(b) almost completely relieves the interface strain: The molecular layer spacing is uniform ($2d_0$). However, there is the internal structural coordinate ϵ' which describes the relative position of the anion layer *A*, here modeled with the virtual-crystal approximation. The total energy is minimized for a value of $\epsilon'=0.03$ [Fig. 2(a)]. As shown in Fig. 2(b), the offset increases strongly with ϵ', the slope being twice as large as for the abrupt case. However, the band offset for the minimum-energy $\epsilon'=0.03$, intermixed interface is essentially the *same* as for the abrupt case with $\epsilon=0.06$ (Fig. 2). This is further illustrated in Fig. 3. The details of the dipole are different, but the net dipole shift is the same. These qualitative features can be captured by a simple model.[24]

Another important question concerns the validity of the simple one-parameter structural models illustrated in Fig. 1 and the treatment of the As/P layer as an effective (virtual-crystal) anion plane. These points have been carefully examined. For the abrupt interface, all planar separations have been allowed to relax, minimizing the total energy with the help of the calculated forces on the ions.[17] Changes from the simple model ($\epsilon=0.06$) are very small: The total energy is further reduced by 4 meV per superlattice unit cell and the interplanar separations change by less than 0.4%. The interface strains are well described by the model in Fig. 1(a). The changes largely occur in the bulk regions driven by the small (0.5%) theoretical lattice mismatch between *M*As and InP. Taking this into account, the full planar relaxation does not significantly alter the calculated band offset. For the As/P interface, a $\sqrt{2}\times\sqrt{2}$ interface unit cell was examined and all internal coordinates relaxed. (A 5-Ry cutoff was used here.) The results were again in excellent agreement with the simple model of Fig. 1(b). In particular, the As/P plane showed almost no buckling and the calculated valence-band offset was unchanged. It is interesting to note that the formation of the intermixed interface requires approximately 50 meV more than the abrupt interface (per pair of interfaces). This is comparable to the growth temperature making some degree of intermixing plausible.

The interface structure for the $In_{0.53}Ga_{0.47}As$/InP(001) system has been accurately probed with x-ray-diffraction techniques.[10] The x-ray scan was fitted including possible interface strains modeled over a molecular layer ($2d_0$). Clear evidence of interface strain was obtained which translates into $\epsilon=+0.038$ (In-As interface) and $\epsilon=-0.034$ (*M*-P interface). This supports the simple model in Fig. 1(a) and is in reasonable agreement with the present microscopic calculations. Since strain over a range of $2d_0$ was considered, the x-ray experiments are insensitive to interdiffusion at the scale illustrated in Fig. 1(b). Furthermore, the beam sequence in the growth of the sample is consistent with having As/P mixture at the interface. This may have altered the measured strain from the value calculated here. In fact, the present calculations show that the strain may have any value from 0 to 0.06 depending on interface composition (chemical abruptness). The relatively large measured strain is testimony to the apparent precision with which the interface abruptness was controlled during sample preparation.

The most precise measurements for the band offsets at the $In_{0.53}Ga_{0.47}As$/InP(001) heterojunctions are based on transport[11,12] and internal photoemission.[13] The zero-temperature results for the valence-band offset range from 340 to 400 meV. These are based on the measured ΔE_c, extrapolated as necessary to $T=0$, and combined with the measured $\Delta E_g(T\rightarrow 0)=613$ meV. The precision of individual measurements is 10–30 meV while the extrapolation using data from Ref. 13 introduces a further 30-meV uncertainty. The experimental data are to be compared to the theoretical result of 410 ± 50 meV. If the interface strain had been neglected, the theory would have given 290 meV, considerably smaller than the experimental range. Also recent optical measurements[25] on $In_xGa_{1-x}As$/Inp(001) quantum wells could be accurately accounted for using $\Delta E_v=380$ meV for $x=0.53$. The analysis is more accurate than that used for earlier optical measurements[26] where $\Delta E_v=250$ meV was inferred. Recent photoemission measurements[27] were interpreted to imply $\Delta E_v=250$ meV for $In_{0.53}Ga_{0.47}As/InP(001)$ also. However, this result is indirect, being based on interpolation between end-point interface (e.g., GaAs/InP) measurements where large lattice mismatch is involved. Overall, the weight of experimental evidence together with the present calculations strongly support a value of $\Delta E_v=350\text{–}400$ meV for $In_{0.53}Ga_{0.47}As/InP(001)$.

First-principles theoretical work on this system[5] has previously neglected the interface strains emphasized here. The neutrality levels of Tersoff[3] (interpolated for $In_{0.53}Ga_{0.47}As$ and corrected for spin-orbit contributions) yield 240 meV, while the dielectric midgap levels of Cardona and Christensen[4] similarly give 260 meV. A "model-solid" theory[28] yielded 350 meV, in good agreement with the present results and experiment. However, this approach, like the midgap theories, is independent of details of the interface structure. It is also amusing to note that the (110) surface work functions (data from Ref. 9, averaged for the MAs case) may be combined to yield a valence-band offset of 360 meV.

Interface strains at the nominally lattice-matched $In_{0.53}Ga_{0.47}As/InP(001)$ heterointerfaces can be tuned over a significant range (0%–6%) by controlling the anion composition at the interface. Significantly, the calculated offset is *independent* of changes of interface strain induced by chemical intermixing, although it is crucial to use a minimum-energy interface structure for a given composition. This lends support to theories of band offsets on bulk derived levels, provided one understands them to apply to a (meta)stable interface. A more general proof of this speculation remains an open problem, although there must be obvious limitations to such a theorem. Nonetheless, this suggests that tunable band offsets at device-quality heterointerfaces may be more elusive than previously hoped.

It is a pleasure to acknowledge stimulating discussions with several colleagues at AT&T Bell Laboratories regarding experiments on the $In_xGa_{1-x}As/InP(001)$ system as well as the authors of Ref. 5. I thank R. C. Fulton for programming assistance and X.-J. Zhu and Professor S. G. Louie for making unpublished calculations available.

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