# Electronic structure of GaAs with an InAs (001) monolayer

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The effect on the electronic structure of an InAs monomolecular plane inserted in bulk GaAs is investigated theoretically. The $(\mathrm{InAs})_1(\mathrm{GaAs})_n$ (001) strained superlattice is studied via *ab initio* self-consistent pseudopotential calculations. Both electrons and holes are localized nearby the inserted InAs monolayer, which therefore acts as a quantum well for all the charge carriers. The small thickness of the inserted InAs slab is responsible for high confinement energies of the charge carriers, and therefore the interband electron–heavy-hole transition energy is close to the energy gap of the bulk GaAs, in agreement with recent experimental data.

Strained superlattices (SSL's) offer a great flexibility for tuning the properties of microelectronic devices, yielding different combinations of band gaps and band discontinuities according to the thickness and the composition of wells and barriers. Samples of GaAs with very well localized one-monolayer (ML) thick InAs intralayers have been recently synthesized using the flow-rate modulation epitaxy technique[1] and molecular-beam epitaxy technique.[2] The inserted InAs plane is found to play the role of a quantum well (QW), strongly localizing both electrons and holes. Such heterostructures are now attracting a great interest in optoelectronic technology, and their electronic and optical properties have been the subject of several recent experimental and theoretical works.[1–6]

In this paper, we present a theoretical study of the electronic structure of GaAs with 1 ML InAs inserted, grown on (001) GaAs substrates. Our calculations are based on the density functional theory[7] within the local density approximation. We use norm-conserving pseudopotentials,[8] plane wave basis sets corresponding to a kinetic energy cutoff of 20 Ry, and a special point technique for Brillouin zone integration [basically the (333) Monkhorst-Pack[9] cubic mesh appropriately folded for cells with various shapes and sizes]. Periodically repeated tetragonal supercells containing 12 atoms are used to simulate the InAs/GaAs dopant-ML/host-crystal system, which, therefore, in our description is a $(\mathrm{GaAs})_5\mathrm{InAs}$ (001) SSL.

The equilibrium lattice parameters calculated at full convergence are 10.65 a.u. and 11.25 a.u. for bulk GaAs and InAs, respectively, to be compared with the experimental values 10.68 a.u. and 11.44 a.u.. The theoretical values give a lattice mismatch of about 5.5%, only slightly below the experimental value. It has been recently experimentally observed[10] that for InAs inserted in GaAs, the macroscopic theory of elasticity (MTE) breaks down in the ML limit; in particular, the measured strain is much higher than expected according to MTE, and it rather corresponds to bulk bond length conservation (BLC). This observation is supported by the theoretical calculations of Ref. 3, whereas different findings are conversely reported in Ref. 11. We found that, with respect to our numerical accuracy, the supercells describing the inserted InAs ML in the two different strain states (MTE or BLC) are very similar in total energy, also after additional internal relaxations, which make the atomic forces vanish. In the final optimized structures, the interplanar In-As distance is intermediate between the MTE and BLC predictions, and a small compressive strain affects the GaAs plane adjacent to the inserted InAs, as similarly found in other SSL's,[12,13] in the region close to the interface. More accurate calculations (e.g., improving cell size, kinetic energy cutoff, number of special points) would be required to definitely establish the true equilibrium structure. Since this is not the main purpose of the present work, in the following, we consider the strain state of the InAs ML as predicted by BLC, according to the experimental observations.

The calculated energy gaps of bulk GaAs, bulk and strained InAs, are 1.07 eV [the experimental value is 1.52 eV (Ref. 14)], 0.58 eV [experimental 0.42 eV (Ref. 14)], and 0.19 eV, respectively, taking properly into account strain splitting effects for InAs. We have previously found[15] that the nonrelativistic valence band offset (VBO) at GaAs/InAs interface amounts to 0.26 eV, almost independent of the local strain in the interface region, with GaAs valence band top edge lower in energy. The corresponding conduction band offset (CBO) is CBO=$\Delta E_g$−VBO=0.62 eV, where $\Delta E_g$=0.88 eV is the band gap difference between bulk GaAs and strained InAs. The inserted InAs layer acts, therefore, as a QW for electrons and holes, giving a so called type-I heterostructure. Spin-orbit (s.o.) effects can be taken into account and added *a posteriori* to our calculations (see Ref. 13), using the experimental data[14] $\Delta_0$=0.34 eV for GaAs and 0.38 eV for InAs. The corrected band gaps of bulk GaAs and strained InAs are 0.96 eV and 0.06 eV, respectively; the VBO and the band gap difference $\Delta E_g$ increase by about 0.02 eV, whereas the CBO is unchanged.

The calculated band structure of the $(\mathrm{GaAs})_5\mathrm{InAs}$

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(001) SSL is shown in Fig. 1 together with the one of pure bulk GaAs, which is also considered in a 12-atom supercell in order to facilitate the comparison with the SSL. Figure 2 gives the corresponding density of states (DOS), $N_0(E)$ and $N(E)$ for pure GaAs and $(GaAs)_5InAs$ (001) SSL, respectively; panel (c) reports the difference $\Delta N(E) = N(E) - N_0(E)$ in order to make evident the effects of the inserted InAs ML. From Fig. 1, we see that the group of the six lowest valence bands is not significantly affected by the insertion of InAs ML: this is because such bands are related to the *s* states of anions, which are not changed (except a small variation of the bond length from the Ga-As to In-As bond). Higher in energy there is the group of bands coming from the *s* cationic states and from all the *p* states. It is evident from Fig. 1 a splitting (i.e., a reduction of the degeneracy) of the lowest band of this group, due to one substitution Ga→In; in correspondence to this, we see a broadening in the DOS (Fig. 2). The other relevant effect of the insertion of the InAs ML is a reduction of the forbidden energy gap between valence and conduction bands with respect to the pure GaAs: in the $(GaAs)_5InAs$ (001) SSL, the calculated energy gap is intermediate between those of strained InAs and of bulk GaAs, i.e., 0.76 (0.87) eV including (neglecting) s.o. effects.

An estimate of the SSL gap can be derived from a much simpler one-dimensional finite square-well model,[16] which —once tested on the present configuration— could be easily extended to SSL characterized by other barrier and well thicknesses, for which the *ab-initio* approach can be unfeasible. We are interested in states confined in the InAs well ($w$) and evanescent in the GaAs barrier ($b$).

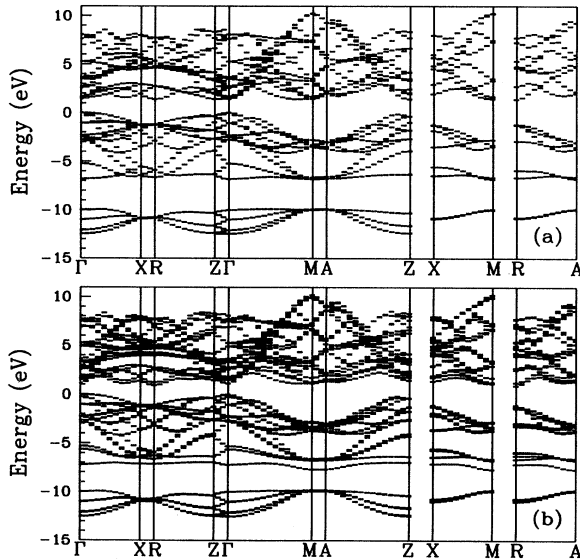


FIG. 1. Calculated nonrelativistic band structure for a 12-atom tetragonal supercell, describing (001) SSL corresponding to (a) pure bulk GaAs and (b) $(GaAs)_5InAs$ SSL, where the In-As bond length is taken equal to its bulk equilibrium value. We choose to represent pure GaAs in the supercell in order to facilitate the comparison with the SSL. The origin of the energy scale is the valence band top edge.

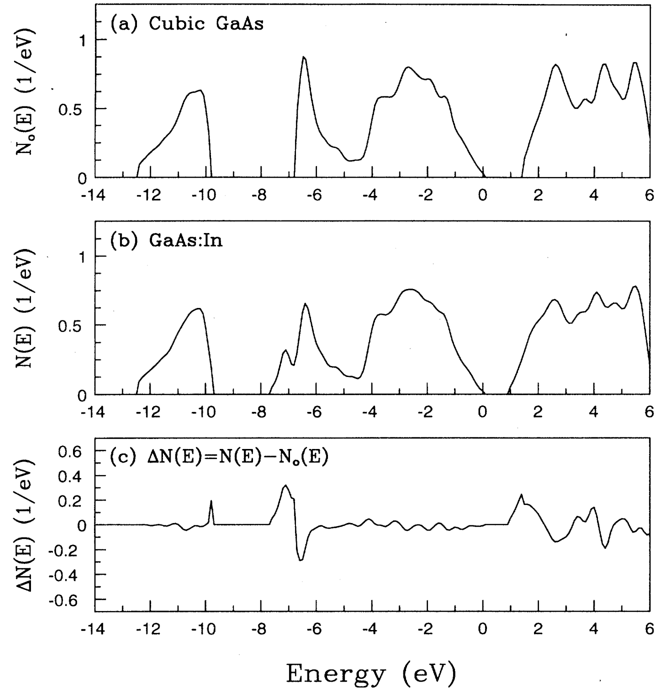


FIG. 2. Calculated density of states $N_0(E)$ and $N(E)$ corresponding to the band structures shown in Fig. 1 for pure bulk GaAs (a) and $(GaAs)_5InAs$ SSL (b), respectively. The difference $\Delta N(E) = N(E) - N_0(E)$ is displayed in (c) to better illustrate the effects of the inserted InAs ML.

The VBO and CBO (with s.o. effects included) give the barrier height $V_b$ for holes and electrons; the well and barrier thicknesses are, respectively, $L_w=0.5a_\perp(\mathrm{InAs})=3.27$ Å and $L_b=2.5a_\perp(\mathrm{GaAs})=14.10$ Å, where $a_\perp(\mathrm{XAs})$ is the lattice parameter of the material XAs along the growth direction of the superlattice. The other parameters involved are the effective masses for heavy holes (HH) and electrons in the well and in the barrier: $m_w^{\mathrm{HH}}=0.41$, $m_b^{\mathrm{HH}}=0.45$, $m_w^{\mathrm{el}}=0.023$, and $m_b^{\mathrm{el}}=0.0665$ in free electronic mass units.[16]

In Fig. 3, we show the predictions of the model for our system. All the parameters are fixed at the values given before, except the barrier thickness $L_b$, whose effect on the confinement charge carrier energy $E_{\mathrm{conf}}$ (defined positive, measured from the bottom of the well) is studied and reported in the figure. In the upper panel, we have plotted the ratio $E_{\mathrm{conf}}/V_b$, so that the plot is general, independent of the barrier height. In the lower panel, we report the absolute value of $E_{\mathrm{conf}}$ and we magnify the length scale in a range around the value $L_b=14.1$ Å (shown by the arrow) corresponding to our supercell geometry. In this particular case, it is evident that (i) the very small well thickness makes the confinement energies very high, and this explains that the SSL energy gap is closer to the one of bulk GaAs rather than to the one of strained InAs; (ii) the small barrier thickness used in our supercell corresponds to a quite large bandwidth that, combined with the high superlattice band bottom edge, is responsible of the fact that only the first bottom band edge falls below the barrier, and only one confined HH

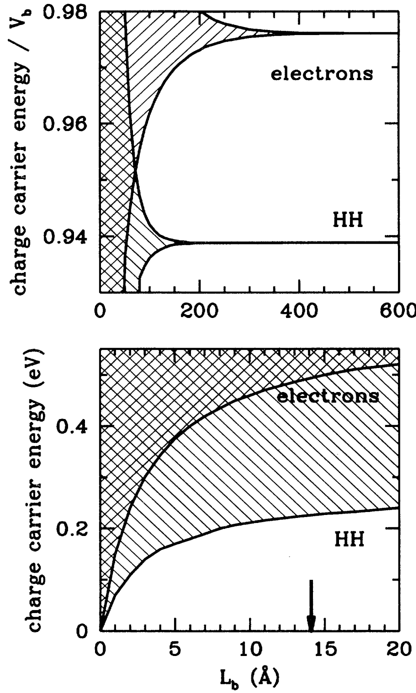


FIG. 3. Evolution of the lowest allowed band for electrons and HH in InAs-GaAs dopant-ML/host-crystal SSL when the barrier thickness $L_b$ is increased. The allowed energy regions are hatched. Upper panel reports the ratio between the charge carrier energy (calculated from the bottom of the well) and the barrier height $V_b$, so that the plot is valid for any given barrier height. In the lower panel, the absolute value of the charge carrier energy is reported, corresponding to a barrier height of 0.62 eV for electrons and 0.28 eV for HH; the length scale is magnified in a range around the value $L_b$=14.1 Å (shown by the arrow) used in the supercell calculation.

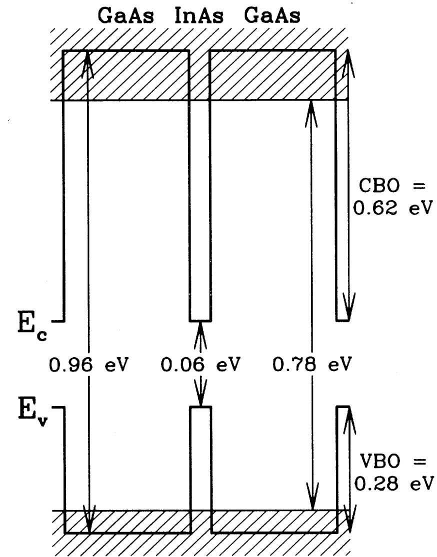


FIG. 4. Schematic energy band profile for $(GaAs)_5InAs$ (001) SSL. The values reported include s.o. effects. The bottom edge of the lowest allowed bands for electrons and HH are indicated, and the allowed energy regions are hatched.

and electronic state exist. More precisely, we obtain that the confinement energies for electrons and HH are 0.50 eV and 0.22 eV, respectively, so that the SSL energy gap derived from the model is $E_g(\mathrm{SSL}) = E_g(\mathrm{InAs}) + E^{\mathrm{HH}}_{\mathrm{conf}} + E^{\mathrm{el}}_{\mathrm{conf}}$=0.78 eV, in good agreement with the value 0.76 eV obtained from the *ab initio* calculations. In Fig. 4, we show the schematic energy band profile for the system studied.

By inspection of Fig. 3, we see that by increasing the barrier thickness, the confinement energies for electrons and HH increase, and the bandwidth reduces up to reach the limit of isolated energy levels (the QW regime). In that case, i.e., for $L_b$ larger than about 400 Å, the interband transition energy $E(e\text{-HH})$ is about 0.04 eV smaller than the calculated band gap of the host GaAs crystal, in reasonable agreement with the values 0.04–0.07 eV from recent photoluminescence experiments[17] reported in Refs. 2–6. We stress that the inaccuracies of our calculations for the band gaps tend to cancel out when comparing similar quantities; it is, therefore, more reasonable to compare with the experiments the differential quantity $\Delta E = E_g(\mathrm{GaAs}) - E(e\text{-HH})$ rather than the absolute value $E(e\text{-HH})$.

It is useful to estimate the sensitivity of our predictions with respect to the parameters involved, mainly to those affected by bigger uncertainty, i.e., the strain state of the inserted InAs, the VBO and CBO. Setting the strain state of InAs ML as predicted by MTE, and using the corresponding theoretical values for $L_w$ and the band energies, we get $\Delta E$=0.02 eV. But it seems more reasonable, because of our poor description of conduction bands, to make use of some experimental values in our model, e.g., the widely accepted value $\Delta E_g$=1.0 eV; correcting, consequently, the CBO, we get again $\Delta E$=0.04 eV. Varying CBO/VBO from 0.7/0.3 to 0.85/0.15 (i.e., according to the different ratios proposed in literature), the final result again does not change significantly. Last, the simple model explains the spreading of the experimental data in terms of possible variations of the nominal InAs coverage: our estimated $\Delta E$ varies from 0.03 eV to 0.05 eV if the InAs coverage varies from 0.8 to 1.2 ML.

Finally, we have estimated the corrections due to many-body effects from the data available in literature,[18,19] for the two bulks constituting the SSL, and added *a posteriori* to our results. We found that such corrections do not change our main conclusions.

In summary, we have discussed the electronic properties of the InAs/GaAs dopant-ML/host-crystal system. We found that it is a type-I heterostructure, where the InAs acts as a QW for both electrons and holes. The very small thickness of the inserted InAs strained slab makes the superlattice band gap close to the one of pure GaAs. We have calculated accurately the relevant energy parameters (band alignments, charge carrier confinement energies, superlattice band gap) performing *ab initio* pseudopotential supercell calculations. The evolution of the superlattice band structure when the GaAs slab thickness increases is predicted on the basis of a simple one-dimensional model, giving in the QW limit an interband transition energy $E(e\text{-HH})$ about 0.04 eV smaller

than the host GaAs band gap, in reasonable agreement with recent photoluminescence measurements.

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