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Stability of the strained-layer superlattice $(\mathrm{GaP})_1/(\mathrm{InP})_1$ (001)

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First-principles total-energy methods have been used to study the stability of the strained monolayer superlattice $(\mathrm{GaP})_1/(\mathrm{InP})_1$ (001). We find a value of 4 mRy for the heat of formation, suggesting that this superlattice is unstable to disproportionation into its bulk constituent compounds. Upon formation of the superlattice, a small charge transfer from GaP to the more ionic InP is found. The Ga—P and In—P bond lengths in $(\mathrm{GaP})_1/(\mathrm{InP})_1$ are within 1% of their bulk theoretical values.

I. INTRODUCTION

The stability and ordering in semiconductor superlattices and semiconductor alloys have recently received much attention. Kuan *et al.*[1] were the first to observe long-range ordering in the semiconductor III-V ternary alloy $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$. They found that the equilibrium state of $\mathrm{Al}_x\mathrm{Ga}_{1-x}\mathrm{As}$ below 800 °C takes the form of a monolayer superlattice, $(\mathrm{GaAs})_1/(\mathrm{AlAs})_1$. Ourmazd and Bean[2] also observed long-range ordering in the alloy region of the strained-layer superlattice (SLS) GeSi/Si. Srivastava *et al.*[3] theoretically predicted (based on first-principles total-energy calculations) similar long-range ordering in other semiconductor alloys (e.g., $\mathrm{Ga}_n\mathrm{In}_{4-n}\mathrm{P}_4$, for $n=1,2,3$).

Because of the added flexibility allowed by SLS's for band-gap engineering, it is of interest to study stability- and ordering-related phenomena in these systems. The stability of the SLS will depend on the relative energetics of the positive-definite strain contribution to the energy and the possible negative contributions due to enhanced chemical binding effects at the interface. One particular SLS of current interest is the GaP-InP system. The experimental lattice mismatch in this case is about 7%. It has been found,[4,5] under certain experimental conditions, that metalorganic vapor-phase epitaxially (MOVPE) grown $\mathrm{Ga}_{0.5}\mathrm{In}_{0.5}\mathrm{P}$ can have a band gap 50 meV lower (1.85 eV) than the same alloy grown using liquid-phase epitaxy (LPE) (1.90 eV). Gomyo *et al.*[5] correlated the smaller- (larger-) band-gap material with an ordered (random) alloy. Their diffraction measurements[5] suggested that the ordered alloy is a (111) monolayer superlattice, $(\mathrm{GaP})_1/(\mathrm{InP})_1$. The sensitivity of the band gap to the ordering of the group-III cation (Ga,In) atomic arrangement is reasonable since the lowest-conduction-band states in III-V compound semiconductors are predominantly associated with the cations sites.

Using a first-principles pseudopotential method, Srivastava *et al.*[3] and Mbaye *et al.*[6] found that the ordered GaInP_2 phase [(001) monolayer superlattice] is more stable than either the disordered phase, or the bulk constituent compounds. The chalcopyrite GaInP_2 phase (two-layer superlattice in the [210] direction) was found to be only about 0.3 mRy lower in energy than the monolayer superlattice. Their results[3,6] suggest that the chemical binding effects at the interface dominate the positive contribution to the energy imposed by the 7% lattice mismatch between GaP and InP. These results have recently been commented upon by Podgorny and Czyzyk.[7] They suggest,[7] from a quasichemical approach (QCA), that the ordered GaInP_2 phase is unstable to disproportionation into constituent compounds. The stability of the ordered phase of GaInP_2 is somewhat unexpected, since it has been found[8] that the ordered phase of GaAlAs_2 [(001) monolayer superlattice], which is almost perfectly lattice matched, is inherently unstable against disproportionation into constituent compounds. Srivastava *et al.*[3] have recognized that their calculations possibly overestimated the (negative) formation enthalpies (too stable) of the ordered phases and have suggested empirical scaling of these results to reproduce the enthalpy of the disordered phase.[6,9] In view of these considerations, it is important to further investigate this system to help resolve the discrepancy.

In this paper, we have carried out first-principles self-consistent total-energy pseudopotential calculations to determine the stability (heat of formation) of the monolayer superlattice, $(\mathrm{GaP})_1/(\mathrm{InP})_1$ (001). The norm-conserved *ab initio* nonlocal ionic pseudopotential[10] used in our work should give a better description of the energetics as compared to the smoothed local ionic potentials used in Refs. 3, 6, and 9. The rest of the paper is organized as follows: in Sec. II the method is presented and in Sec. III the results and discussion are given.

II. METHOD

The calculations are performed within the momentum-space formalism of the self-consistent pseudopotential method,[11] using *ab initio* nonlocal pseudopotentials,[10] and the Wigner form of the exchange-correlation potential.[12] To obtain a value for the heat of formation of the monolayer superlattice,

$$\Delta H = E_T((\mathrm{GaP})_1/(\mathrm{InP})_1) - E_T((\mathrm{GaP}),\mathrm{bulk}) - E_T((\mathrm{InP}),\mathrm{bulk}) ,$$

one must have consistent values for the bulk GaP and InP total energies so that these total energies can be compared with the superlattice total energy. To minimize errors associated with k-point sampling and plane-wave expansions, the bulk calculations are performed in the superlattice geometry. The tetragonal unit cell used for all three (001) superlattices, $(\mathrm{GaP})_1/(\mathrm{GaP})_1$, $(\mathrm{InP})_1/(\mathrm{InP})_1$, and $(\mathrm{GaP})_1/(\mathrm{InP})_1$ is depicted in Fig. 1. The unit cell has a volume of $\Omega = a^2c$, where c is the cubic lattice constant (A_{cubic}) and a is equal to $A_{\mathrm{cubic}}/\sqrt{2}$. For each unit cell the total energy is minimized with respect to A_{cubic}, keeping c/a fixed at $\sqrt{2}$. For the $(\mathrm{GaP})_1/(\mathrm{InP})_1$ structure the total energy is minimized with respect to A_{cubic} and the internal positions of the P atoms. By allowing the P atoms to move, the Ga—P and In—P bond lengths can change to minimize the energy for a given volume deformation. This procedure determines the GaP and InP perpendicular lattice constants ($a_\perp$) for a given strain in the x-y plane. We have also performed calculation which allow c/a to change from $\sqrt{2}$.

The wave functions are expanded in plane waves with kinetic energy up to $|\mathbf{k}+\mathbf{G}|^2 = 10$ Ry. This amounts to about 300 plane waves for the four-atom unit cells considered here. The charge density was sampled at 48 k points in the superlattice Brillouin zone. Self-consistency iterations were terminated when input and output screening potentials differed by less than 1×10^{-5} Ry.

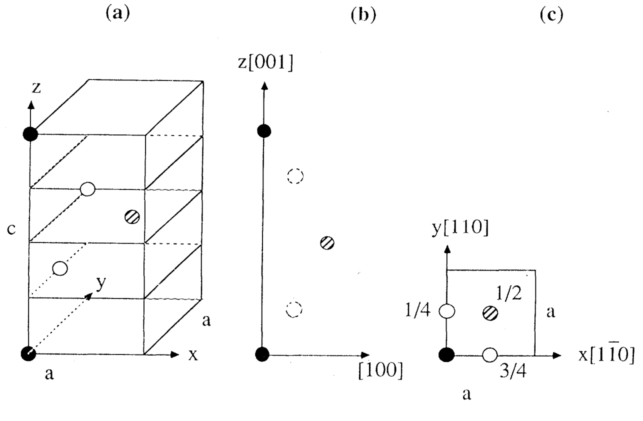

FIG. 1. Schematic drawing of (a) the superlattice $(\mathrm{GaP})_1/(\mathrm{InP})_1$ and (b) and (c) its projection on two different planes. Solid circles are Ga atoms, open circles are P atoms, and hatched circles are In atoms. Dashed open circles in (b) are P atoms not in the plane. The fractions in (c) denote the heights of the atoms along the [001] direction in units of c. This figure has been reproduced from I. P. Batra *et al.*, J. Vac. Sci. Technol. B **5**, 1300 (1987).

III. RESULTS AND DISCUSSION

The variations of the total energy with respect to the cubic lattice constant for the bulk superlattices, $(\mathrm{GaP})_1/(\mathrm{GaP})_1$ and $(\mathrm{InP})_1/(\mathrm{InP})_1$, are given in Fig. 2. The calculations give a GaP and InP equilibrium lattice constant of 5.31 and 5.60 Å and total energies of −35.3701 and −34.5735 Ry, respectively. The theoretical equilibrium lattice constants differ from the experimental values by 2.6% for GaP and 4.6% for InP. A more important quantity to compare with the experiment is the theoretical lattice mismatch. Experimentally the lattice mismatch is 7%, while the theory predicts a smaller value of 5%. Assuming that any enhanced chemical stabilization energy at the interface is roughly independent of lattice mismatch, our 5% lattice mismatch will be a lower estimate of the heat of formation, since strain is a positive contribution to the energy. In Refs. 6 and 9, the authors used the experimental values of the bulk GaP and InP lattice constants to determine the bulk energies. By doing so, the bulk structures are in a state of "artificial" strain. The authors of Refs. 6 and 9 then minimized the $(\mathrm{GaP})_1/(\mathrm{InP})_1$ (001) superlattice structure, which places the bulk and superlattice total energies on different footings. We feel the minimized bulk superlattice energies should provide a more realistic comparison. This is perhaps the reason the authors[3,9] introduced the empirical scaling.

The total-energy minimization with respect to the A_{cubic} (keeping c/a fixed at $\sqrt{2}$), for $(\mathrm{GaP})_1/(\mathrm{InP})_1$, is shown in Fig. 3. The calculations give a minimum energy of −34.9571 Ry at a cubic lattice constant of 5.45 Å. At

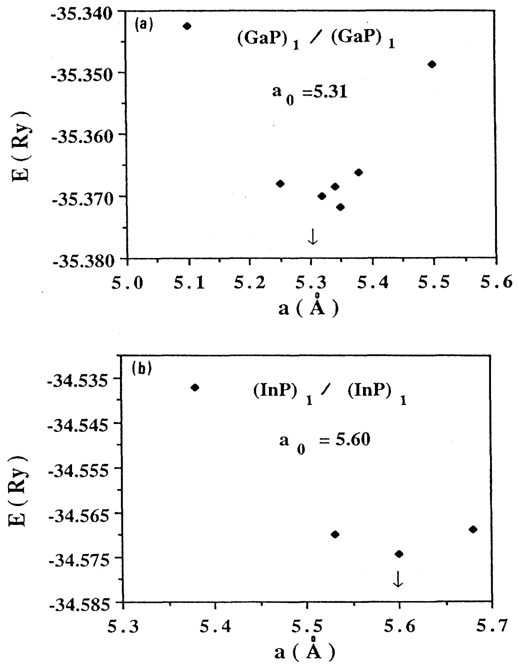

FIG. 2. Total energy vs cubic lattice constant for (a) $(\mathrm{GaP})_1/(\mathrm{GaP})_1$ and (b) $(\mathrm{InP})_1$-$(\mathrm{InP})_1$. The equilibrium lattice constant a_0 of GaP and InP are 5.31 and 5.60 Å, respectively.

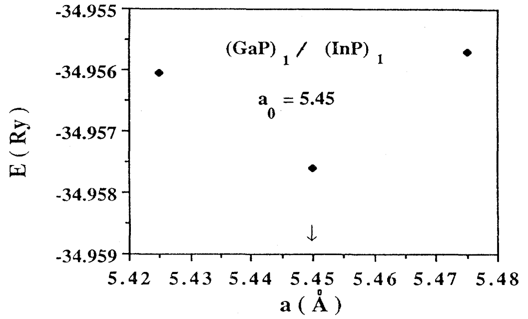

FIG. 3. Total energy vs cubic lattice constant for $(\mathrm{GaP})_1/(\mathrm{InP})_1$. The equilibrium lattice constant a_0 is 5.45 Å.

this lattice constant, the Ga—P bond length is expanded by 2.6%, while the In—P bond length is contracted by 2.8% from their bulk values. By minimizing the Ga—P and In—P bond lengths (or equivalently the $a_\perp$ of GaP and InP) with respect to the energy, we obtain a value of -34.9678 Ry for the fully minimized monolayer superlattice, $(\mathrm{GaP})_1/(\mathrm{InP})_1$. This value is still 4 mRy higher in energy than the sum of the bulk energies of $(\mathrm{GaP})_1$ and $(\mathrm{InP})_1$, suggesting that this structure is unstable with respect to disproportionation into constituent compounds. Since this is a small energy, we have performed additional calculations similar to the ones presented above to check the convergence of our total-energy differences. With a plane-wave cutoff of 8 Ry (about 220 plane waves) and the Wigner exchange-correlation potential,[12] we found a value of 5 mRy for the heat of formation. Using a plane-wave cutoff of 10 Ry and a different exchange-correlation potential (Ceperley and Alder[13]) we obtained a value of 4 mRy for the heat of formation. Thus, we are confident that our total-energy differences have converged. In addition, at the minimum-energy configuration found above, we have allowed the c/a ratio to change by $\pm 1\%$, and find that in both cases the energy increases by about 1 mRy with these deformations; a c/a ratio of $\sqrt{2}$ is the lowest-energy configuration.

The Ga—P and In—P bond lengths in the fully optimized $(\mathrm{GaP})_1/(\mathrm{InP})_1$ superlattice are within about 1% of the theoretical bulk values. The calculations also give perpendicular GaP and InP lattice constants of 5.07 and 5.87 Å, respectively. These findings are consistent with the earlier results.[3,6,9] Therefore, we feel the discrepancy between our value of the heat of formation (4 mRy) and the one found in Refs. 6 and 9 (-1.85 mRy) is due to an inconsistent use of the bulk experimental lattice constants of GaP and InP and a theoretically minimized superlattice structure. Their bulk constituent energies are less negative due to excess positive strain energy. Therefore, it is not surprising that they found the superlattice to be stable. The value of -9.4 mRy found in Ref. 3 obviously overestimates the stability. Our results are consistent with recent first-principles linear augmented-plane-wave (LAPW) calculations by Wei *et al.*,[14] showing that for large-lattice-mismatched constituents, the stability energy is dictated by the positive-definite strain energy, indicating a tendency for disproportionation into bulk constituent compounds.

Another interesting quantity reflecting the stability of the superlattice is the change in charge distributions in the Ga—P and In—P bonds when the interface is formed. These changes can be seen in Fig. 4. For the bulk structures, GaP and InP, we found charge density maximums of 0.115 and 0.112 a.u., respectively. The position of the maximum charge density is closer to the P atom in InP. These results indicate that the GaP bond is stronger (also reflected by the lower total energy) and less ionic than the InP bond.[15] Phillips[16] ionocity values are 0.33 and 0.42 for GaP and InP, respectively. Our results are consistent with these trends. From Fig. 4, we can see that when the interface is formed the InP charge-density maximum increases to 0.114 a.u., while the GaP maximum decreases to 0.113 a.u., indicating a small charge transfer from GaP to the more ionic InP. The positions of the maximums are virtually unchanged. This charge transfer (i.e., chemical stabilization energy) does not seem large enough to stabilize the $(\mathrm{GaP})_1/(\mathrm{InP})_1$ (001) superlattice.

In summary, we have found that the enhanced chemical binding energy at the interface between GaP and InP is not large enough to stabilize the monolayer superlattice, resulting in a tendency for disproportionation into bulk constituent compounds. Our results suggest that larger-layer $(\mathrm{GaP})_n/(\mathrm{InP})_n$ (001) superlattices are meta-

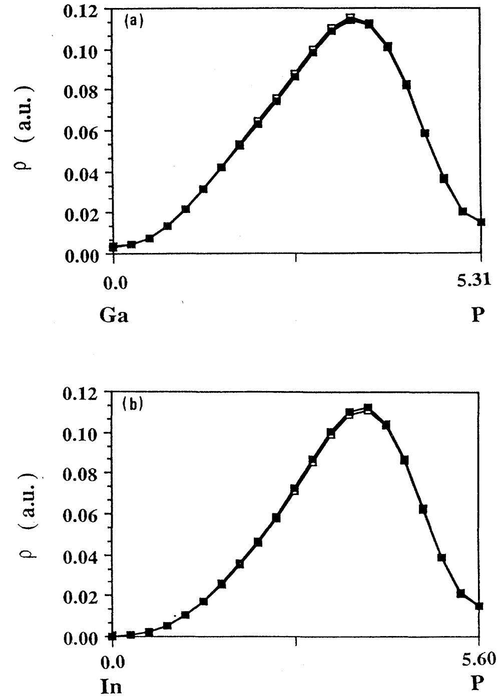

FIG. 4. Comparison of bulk and superlattice charge density along the (a) Ga—P and (b) In—P bonds. The charge-density maximums are 0.115 and 0.112 a.u. for bulk GaP and InP, respectively. When the superlattice is formed the GaP charge density decreases by 0.002 a.u. while the InP charge density along the bond increases by about 0.002 a.u.

stable at best, since even at $n=1$ we find that the chemical contribution to the stability energy is not large enough to cancel out the positive-definite strain contribution imposed by the large lattice mismatch, assuming the strain energy is proportional to n.

Note added in proof. Recently, several calculations of the heat of formation of the $(\mathrm{GaP})_1$-$(\mathrm{InP})_1$ (001) superlattice have appeared: (1) Ref. 16 of James E. Bernard *et al.*, Phys. Rev. B **38**, 6338 (1988), $\Delta H=+6.7$ mRy/4-atoms, and (2) P. Boguslawski and A. Baldereschi, Proceedings of the 19th International Conference on the Physics of Semiconductors, Warsaw, 1988 (unpublished), $\Delta H=+8.5$ mRy/4-atoms. These values are in good agreement with our calculations.

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