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Is there an elastic anomaly for a (001) monolayer of InAs embedded in GaAs?

James E. Bernard
Department of Physics, Colorado School of Mines, Golden, Colorado 80401

National Renewable Energy Laboratory, Golden, Colorado 80401

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When a coherently grown (001)-oriented layer of InAs is embedded in a GaAs host, the coherency strain induces a perpendicular distortion of the embedded layer, predicted by continuum elasticity theory to be $\epsilon_\perp = 7.3\%$. Brandt, Ploog, Bierwolf, and Hohenstein, [Phys. Rev. Lett. **68**, 1339 (1992)] have described a high-resolution electron-microscopic analysis of such buried layers that appears to reveal a breakdown of continuum elasticity theory in the limit of monolayer films. Here we report on an investigation into whether a first-principles local-density total energy minimization shows such an elastic anomaly in the monolayer limit. We find that it does not.

When a layer of material with cubic lattice parameter a_0 is grown coherently in a host with cubic lattice parameter $a_s \neq a_0$, the buried layer undergoes a distortion of its lattice parallel to the plane. Since surface effects are absent, the amount of the distortion can be accurately calculated by minimizing the bulk energy as a function of all the structural degrees of freedom. The simplest way to approximate this is to use harmonic continuum elasticity theory (see, e.g., Ref. 1). For example, for cubic materials with a layer orientation parallel to (001), the perpendicular strain $\epsilon_\perp = (c - a_0)/a_0$ is related[1] to the parallel strain $\epsilon_\parallel = (a_s - a_0)/a_0$ by

$$\epsilon_\perp = -2\,\frac{C_{12}}{C_{11}}\,\epsilon_\parallel, \tag{1}$$

where the C_{ij} are elastic constants of the embedded material. For example, with the measured[2] $C_{11} = 0.8329$ and $C_{12} = 0.4526$ (Tdyn/cm^2) for InAs, Eq. (1) predicts $\epsilon_\perp = 7.27\%$ for a layer of InAs buried in GaAs.

Recently, Brandt *et al.*[3] examined the strain of buried (001) layers of InAs in GaAs experimentally, via a high-resolution electron microscopy (HREM) technique. For sponding to $\epsilon_\perp = 12.46\%$, much greater than the prediction of Eq. (1). In contrast, their measurement, applied to a *three* monolayer film of InAs revealed a lattice distortion corresponding to $\epsilon_\perp = 6.96\%$, in good agreement with Eq. (1). Thus, they concluded that the widely used harmonic-elasticity theory breaks down in the extreme limit of a single monolayer.

Equation (1) involves several approximations: (1) the harmonic approximation, (2) neglect of any additional relaxations beyond a uniform uniaxial distortion, and (3) neglect of finiteness of the embedded layer. Regarding (1), we can expect the strains, however, the lattice mismatch between GaAs and InAs (≈7%) is not sufficient to cause a substantial departure from harmonicity. Regarding (2), it was previously shown[4] that for certain interface orientations nonuniform atomic relaxations near an interface can be large. For (001) [001], and the nonuniformity of these interplanar relaxations near the interfaces is quite small. We will see below that these do not substantially alter the applicability of the simple picture provided by continuum elasticity theory. Regarding (3), the question of thickness dependence has, until recently, been untested in semiconductor layers.[5] One might imagine, e.g., that as the separation between interfaces becomes small, interaction between them might substantially alter the theory.

In view of the unprecedented result of Brandt *et al.*,[3] we tested the validity of Eq. (1) via an atomistic, nonharmonic, first-principles theory of the relaxations of such a system to determine whether it would reveal the breakdown ostensibly demonstrated in the experiment. Our first-principles results in no way depend upon Eq. (1) or the approximations on which it is based. We found good agreement with Eq. (1) and no theoretical evidence for such a breakdown, in spite of using state-of-the-art techniques for relaxing the total energy.

Our tests improve on harmonic continuum elasticity theory in two steps. First, we replace the continuum approach by a discrete atomistic approach, still limited to purely elastic energies. This is done with the Keating valence-force-field (VFF) model, which uses a description in terms of microscopic quantities, the two-body bond stretching and three-body bond bending elastic energies. The strain energy is minimized as a function of *all* the structural degrees of freedom, not just the distortion of the embedded layer. This is accomplished by applying density-functional theory in the local-density approximation (LDA). With the total energy represented as a functional of the electron density of the system, all contributions to the total energy, not just the elastic contribution

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to it are treated on the same quantum-mechanical footing. This avoids all the potential pitfalls discussed above, and can be regarded as giving the best available theoretical estimate

In the first step, we applied the VFF model, with the [redacted] bond lengths,[7] to the calculation of the relaxed geometry of a structure containing an embedded (001)-oriented layer of InAs in a GaAs host, all confined to the GaAs lattice constant in the (001) plane. We found values ranging from $\epsilon_\perp = 7.09\%$ with 1 monolayer (ML) of InAs, to $\epsilon_\perp = 7.17\%$ with 10 ML.[9] This demonstrates good agreement with the large distortion in the ultrathin limit.

We note that in a recent paper Massies and Grandjean[10] used a one-dimensional variant of the VFF model to investigate the behavior of monolayer-height InAs surface islands on GaAs, finding a relaxation away from the surface larger [redacted] ever, the clear agreement of our bulk three-dimensional VFF calculations with continuum elasticity theory demonstrates that this comparison of a one-dimensional model of surface relaxation with bulk strain is inappropriate.

The inability of the VFF model to reproduce the [redacted] include electronic effects as well. Our total-energy calculations were performed using the LDA in the form of the [redacted] method.[11] Pseudopotentials were generated by the method of [redacted] equivalent of 10 special points[14] in the irreducible zinc-blende BZ. We estimate convergence errors in $\epsilon_\perp$ to be below 5%, far less than the more than 70% difference between the [redacted] stants of zinc-blende GaAs and InAs were determined by fitting to a Birch equation of state[15] the total energies from seven calculations with differing lattice constants. The fit gives the values (Å) 5.60±0.005 (5.65) for GaAs and 6.02 ±0.005 (6.06) for InAs, where experimental values[2] are [redacted] constants induces only about a 4% (0.3 percentage points) overestimation in our calculated $\epsilon_\perp$.

For the first-principles calculations of the properties of [redacted] layers, containing one to three layers of InAs. The in-plane lattice constant is constrained to be that of bulk GaAs, so as to obtain the structural effect of a thick GaAs substrate. Tests [redacted] more than adequate to converge the structural features of the interface and the GaAs layer to match those with much thicker layers. We minimized the SL total energy with respect to all structural degrees of freedom, subject to the coherency constraint. Quantum-mechanical forces[11] were used to relax the atomic positions, and a fit of total energy vs c/a,

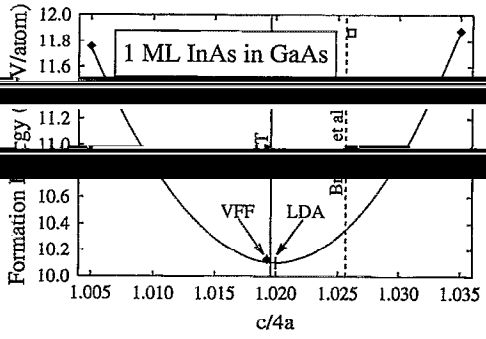

FIG. 1. Formation energy of the atomically relaxed eight-layer structure containing 1 monolayer of InAs vs its $c/4a$ ratio. Filled diamonds denote direct first-principles LDA results; the curve is a cubic fit to those points. The minimum of the fit curve is marked by a vertical tick, labeled "LDA." The diamond symbol labeled "VFF" lies at the $c/4a$ value predicted by the VFF model. The solid vertical line, labeled "CET," marks the prediction of [redacted] the InAs layer has $\epsilon_\perp = 12.5\%$, illustrating the large energy penalty incurred if the strain is concentrated in the InAs layer.

was used to find the equilibrium $c/a_{\parallel}$ ratio. While the symmetry of the structure permits additional relaxations beyond the relaxation of merely the InAs bond length, the effect of these was found to be rather small.

Our results are illustrated for the single-monolayer case [redacted] also shown. The equilibrium c/a ratios for the three meth[redacted] lattice constants). We estimate the error in the LDA value resulting from the fit used to determine the equilibrium c/a ratio to be about 1%. Similarly good agreement among the [redacted] recent pseudopotential calculation by Shiraishi and Yamaguchi.[16] However, correspondence with one of the authors[17] has clarified that their results do not, in fact, show evidence of an elastic anomaly in the monolayer limit.

One situation that could increase the apparent measured [redacted] so because the determination of $\epsilon_\perp$ is based on the overall measured shift in the lattice.[9] Because the VFF model provides a sufficiently accurate reproduction of the structural parameters obtained from the LDA calculations, we used it [redacted] substitution of In for Ga in the three GaAs layers grown after the InAs layer in the amounts 31.5%, 12.5%, and 6.25%, respectively, can raise $\epsilon_\perp$ to 13.05%, comparable to the [redacted] refinement [redacted] of the analysis of the HREM data of Ref. 3, permitting more precise determination of the individual spacings, suggests that they should be able to detect excess In, at least in the two larger amounts we have suggested.[20]

It is interesting that the effect of substitutional In in the first subsequently grown GaAs layer would be to change the

ratio of the two expanded spot-row spacings in different

[redacted]

[1̄10] or along [110]—in one case increasing the ratio, and in the other case decreasing it. Thus it would be possible to compare such images as another test for excess In. To our

[redacted]

of InAs to be distributed among three layers, with 75% in the

[redacted]

nately, the samples used for this study were not characterized by HREM, so it is not clear whether they would exhibit the apparent elastic anomaly seen by Brandt *et al.*[3]

In conclusion, we have applied well-converged first-principles total-energy methods to the determination of the

[redacted]

ment to help determine whether the experimental results of Brandt *et al.*[3] could be a consequence of excess In in the GaAs overlayer. If excess In is not responsible for the large

[redacted]

mental findings, and further work to attempt to resolve the

[redacted]

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[redacted]

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[redacted]

[redacted]

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[3]O. Brandt, K. Ploog, R. Bierwolf, and M. Hohenstein, Phys. Rev. Lett. **68**, 1339 (1992).

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[redacted]

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[7]R. M. Martin, Phys. Rev. B **1**, 4005 (1970).

[redacted]

[9]For consistency with Ref. 3, we calculate $\epsilon_\perp$ from the theoretical c/a ratio of the unit cell, attributing all of the c-axis expansion to the InAs layer. With actual layer spacings, $\epsilon_\perp$ increases by less than 0.5 percentage points locally at the interface, because of a slight expansion of InAs bonds there (accompanied by a similar contraction of GaAs bonds). This effect is seen generally at bulk semiconductor interfaces (Ref. 4).

[redacted]

[12]N. Troullier and J. L. Martins, Phys. Rev. B **43**, 1993 (1991).

[redacted]

[15]F. Birch, Phys. Rev. **71**, 809 (1947); J. Geophys. Res. **57**, 227 (1952).

[16]K. Shiraishi and E. Yamaguchi, Phys. Rev. B **42**, 3064 (1990).

[17]Reference 3 cites results of Ref. 16 as evidence of theoretical support for

[redacted]

InAs in GaAs (2.55 Å). However, Dr. Shiraishi has informed us that the

[redacted]

blende GaAs bond length. Their calculated bond length for the embedded layer is 2.49 Å, corresponding to $\epsilon_\perp = 4.6\%$.

[redacted]

with the overall shift. Further, application of the method (Ref. 19) to

[redacted]

[21]C. Giannini, L. Tapfer, S. Lagomarsino, J. C. Boulliard, A. Taccoen, B.

[redacted]