AIP | Applied Physics Letters

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

James E. Bernard and Alex Zunger

Citation: Applied Physics Letters **65**, 165 (1994); doi: 10.1063/1.112660
View online: http://dx.doi.org/10.1063/1.112660
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/65/2?ver=pdfcov
Published by the AIP Publishing

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

Alex Zunger
National Renewable Energy Laboratory, Golden, Colorado 80401

(Received 20 December 1993; accepted for publication 21 April 1994)

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. In particular, they found for a single monolayer of InAs a lattice distortion that corresponds to $\epsilon_\perp = 12.5\%$. 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 $a_h \neq a_0$, the buried layer undergoes a distortion of its lattice parameter c perpendicular to the plane of the layer in response to the distortion of its lattice parameter 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 $\epsilon_\parallel = (a_h - a_0)/a_0$ 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 microscopic (HREM) analysis. For a single layer of InAs they found a lattice distortion corresponding to $\epsilon_\perp = 12.46\%$, much greater than the prediction of Eq. (1). In contrast, the same measurement technique, 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 any dependence of the perpendicular strain on the thickness of the embedded layer. Regarding (1), we can expect the harmonic approximation to break down for sufficiently large strains; however, the lattice mismatch between GaAs and InAs ($\approx 7\%$) 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. But for (001)-oriented interfaces the allowed relaxations all lie parallel to [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 two interfaces becomes small, interaction between them might substantially alter the relaxations, invalidating the results of continuum elasticity 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 of the system as a function of its structural parameters.

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,[6–8] 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 circumvents objections regarding behavior in the atomically thin limit. Second, we include all major contributions to the total energy, not just the elastic contribution, using 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

 0003-6951/94/65(2)/165/3/$6.00

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 for the relaxed geometry of the system.

In the first step, we applied the VFF model, with the elastic parameters of Martin[7] and experimental equilibrium bond lengths,[2] 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 prediction of Eq. (1) and shows no evidence of anomalously 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 than predicted by elasticity theory. They cited this as being in good agreement with the experiment of Brandt *et al.*[3] However, 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 anomaly cited by Brandt *et al.* led us to extend the theory to include electronic effects as well. Our total-energy calculations were performed using the LDA in the form of the scalar-relativistic self-consistent pseudopotential plane-wave method.[11] Pseudopotentials were generated by the method of Troullier and Martins,[12] with the core correction of Louie *et al.*[13] for In and Ga. The basis set kinetic energy cutoff was 20 Ry, and the Brillouin zone (BZ) was sampled using the 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 value deduced from the experiment of Brandt *et al.*[3] and the prediction of Eq. (1). The theoretical equilibrium lattice constants 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 given in parentheses. The 1% error in the calculated lattice 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 thin layers of InAs buried in a GaAs host we used as model structures (001) superlattices (SLs) with a period of eight 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 using a VFF model have shown this total thickness to be 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_h was used to find the equilibrium c/a_h 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.

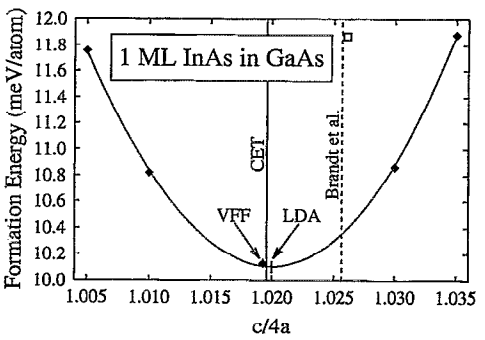

FIG. 1. Formation energy of the atomically relaxed eight-layer structure containing 1 monolayer of InAs vs its $c/4a$ ratio. Filled diamonds denote direct first-principles LDA results; the curve is a cubic fit to those points. The minimum of the fit curve is marked by a vertical tick, labeled "LDA." 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 continuum elasticity theory, and the dashed line marks the $c/4a$ value corresponding to the experimental result of Ref. 3. The open square denotes the first-principles- calculated formation energy of the structure distorted so that the InAs layer has $\epsilon_\perp = 12.5\%$, illustrating the large energy penalty incurred if the strain is concentrated in the InAs layer.

Our results are illustrated for the single-monolayer case in Fig. 1, where the rather different result of Brandt *et al.*[3] is also shown. The equilibrium c/a_h ratios for the three methods correspond to $\epsilon_\perp = 7.73\%$ (first-principles LDA), 7.38% (VFF with LDA-determined equilibrium bond lengths), and 7.58% (continuum elasticity theory with LDA-determined 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 three calculations was found in the two and three monolayer cases. Our results may appear to differ from the results of a 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 $\epsilon_\perp$ is the presence of excess In in the GaAs overlayer. This is 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 to investigate the effects of excess In. This showed that the 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 12.46% observed by Brandt *et al.*[3] However, subsequent refinement[18,19] 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 ways depending on whether the sample is imaged along [110] or along [$\bar{1}$10]—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 knowledge, this has not been done.

In a recent paper, Giannini *et al.*[21] have studied the composition profile of samples similar to those used in the study of Brandt *et al.*[3] They estimated the total of 1.08 monolayers of InAs to be distributed among three layers, with 75% in the first layer, 25% in the second, and 5% in the third. Unfortunately, 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 perpendicular distortion of an isolated InAs monolayer in GaAs, in order to determine whether such a layer would exhibit an anomalously large distortion. We find no such anomaly in our calculations and have suggested an experiment 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 distortion, our results stand in distinct contrast to the experimental findings, and further work to attempt to resolve the discrepancy is warranted.

One of us (J.E.B.) acknowledges support for this work received under Subcontract No. XR-1-11236-1 from the National Renewable Energy Laboratory. Work at NREL was done under Contract No. DE-AC02-CH10093. Correspondence with O. Brandt, M. Hohenstein, and K. Shiraishi is gratefully acknowledged. We thank the reviewer for pointing out the references cited in Ref. 5.

[1] D. M. Wood and A. Zunger, Phys. Rev. B **40**, 4062 (1989); A. Zunger and D. M. Wood, J. Cryst. Growth **98**, 1 (1989).

[2] *Physics of Group IV Elements and III-V Compounds,* edited by O. Madelung, Landolt–Börnstein, New Series (Springer, Berlin, 1982), Group III, Vol. 17, Pt. A.

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

[4] R. G. Dandrea, J. E. Bernard, S.-H. Wei, and A. Zunger, Phys. Rev. Lett. **64**, 36 (1990).

[5] For metal films the thickness dependence has been studied, e.g., by D. Wolf, Surf. Sci. **225**, 117 (1990); Appl. Phys. Lett. **58**, 2081 (1991); B. M. Clemens and G. L. Eesley, Phys. Rev. Lett. **61**, 2356 (1988).

[6] P. N. Keating, Phys. Rev. **145**, 637 (1966).

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

[8] J. L. Martins and A. Zunger, Phys. Rev. B **30**, 6217 (1984).

[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).

[10] J. Massies and N. Grandjean, Phys. Rev. Lett. **71**, 1411 (1993).

[11] J. Ihm, A. Zunger, and M. L. Cohen, J. Phys. C **12**, 4409 (1979).

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

[13] S. G. Louie, S. Froyen, and M. L. Cohen, Phys. Rev. B **26**, 1738 (1982).

[14] S. Froyen, Phys. Rev. B **39**, 3168 (1989).

[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 an elastic anomaly in the monolayer limit. Specifically cited are the InAs bond lengths for the cubic zinc-blende structure (2.56 Å) and for 1 ML of InAs in GaAs (2.55 Å). However, Dr. Shiraishi has informed us that the quoted bond length for the embedded InAs layer was scaled by the ratio of the experimental zinc-blende GaAs bond length to their calculated zinc-blende GaAs bond length. Their calculated bond length for the embedded layer is 2.49 Å, corresponding to $\epsilon_\perp$=4.6%.

[18] O. Brandt (unpublished).

[19] M. Hohenstein (unpublished).

[20] With the refined analysis, the sum of the individual spacings agrees well with the overall shift. Further, application of the method (Ref. 19) to simulated data containing the three excess In percentages we suggested, showed the two largest to be above the threshold of detectability.

[21] C. Giannini, L. Tapfer, S. Lagomarsino, J. C. Boulliard, A. Taccoen, B. Capelle, M. Ilg, O. Brandt, and K. H. Ploog, Phys. Rev. B **48**, 11496 (1993).