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Accommodation of strain in ultrathin InAs/GaAs films

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X-ray standing-wave and extended x-ray-absorption fine-structure measurements have determined the strain and bond distortions in a buried InAs monolayer grown epitaxially on GaAs(001). The In atoms are found to reside 1.64±0.03 Å above the last-As plane of the GaAs substrate with an In-As bond length of 2.57±0.02 Å. Relative to bulk InAs, this corresponds to an 8% expansion in the In-As planar distance perpendicular to the interface and a 0.05-Å compression in the In-As bond length. This experiment indicates that macroscopic-elastic theory describes the distortions in InAs/GaAs(001) films even in the monolayer limit.

Unlike conventional homojunctions, which are fabricated by differential doping of the same semiconductor, heterojunctions rely on compositional variation across an interface. The performance of heterojunction-based devices therefore depends on the ability to grow lattice-mismatched materials epitaxially without defects. In this strained-layer growth, the layer undergoes a tetragonal distortion due to the infinite extent of the substrate: $a_{\parallel}$, the lattice parameter of the layer parallel to the interface, becomes equal to that of the substrate (coherency condition), and $a_{\perp}$, the lattice parameter of the layer perpendicular to the interface, responds by becoming equal to that determined by the strain tensor.[1]

Although much research has been devoted to understanding the electronic consequences of strained-layer growth, relatively little work has been performed to understand the geometric aspects. In particular, the strain and bond distortions in ultrathin layers remain an open issue, for typical experimental techniques devoted to the study of these systems, such as x-ray diffraction, lose their sensitivity when the thickness of the film is less than a few lattice constants. In addition, diffraction does not measure bond lengths directly, and these films are often buried and thus inaccessible to many other common microscopies and spectroscopies.

An issue that has become of particular importance lately is whether or not macroscopic-elastic theory describes the tetragonal distortions in ultrathin films. Although it had been demonstrated as early as the 1970s to accurately predict the distortions in thick films,[1] it is evident that this may not be the case for thin films, because interactions among the substrate and cap of a buried layer may affect the equilibrium value of these bond distortions much in the same way that relaxations occur at surfaces, which are vacuum-bulk interfaces.

Using high-resolution electron microscopy (HREM), Brandt *et al.*[2] found a strain of 13%—nearly twice that predicted by macroscopic-elastic theory—for a 1-monolayer (ML) film of InAs grown on GaAs(001). They attributed this anomaly to the conservation of the In-As bond length at the interface, despite the large compressive strain imposed on the layer by the substrate. The same authors found no anomaly for a 3-ML film and therefore concluded that macroscopic theory breaks down in the monolayer limit. This experiment was not unfounded, for an earlier *ab initio* total-energy calculation by Shiraishi and Yamaguchi[3] predicted that the In-As bond length at the InAs/GaAs interface was only slightly shorter than in bulk InAs. Massies and Grandjean[4] later used a one-dimensional valence-force field (VFF) model to calculate the strain in a monolayer InAs film grown on GaAs(001). They also found the same anomaly determined experimentally by Brandt *et al.*[2]

More recently, however, Bernard and Zunger[5] applied density-functional theory in the local-density approximation (LDA) to calculate the strain of a 1-ML InAs film imbedded in GaAs(001). They found remarkable agreement between their calculations and harmonic-elastic theory, disagreeing with both the HREM experiment and the above-cited theories.

In this work, we apply two independent atomic-scale probes: x-ray standing waves (XSW's), which accurately measures the perpendicular distance of foreign or impurity atoms relative to the diffraction planes of a host crystal, and extended x-ray-absorption fine structure (EXAFS), which accurately measures near-neighbor bond lengths, to obtain the *microscopic* structure of the buried 1-ML InAs/GaAs(001) interface. Only by understanding these distortions on a microscopic scale is it possible to explain deviations from macroscopic theory. In addition to answering this question, the InAs/GaAs system is among the most highly strained of the typical III-V combinations; it possesses over a 7% lattice mismatch. Therefore, it poses a critical challenge to macroscopic theory itself while making the microscopic consequences of strain large enough to be measurable.

The InAs monolayer sample was grown by molecular-beam epitaxy (MBE) at the National Institute of Standards and Technology. Conventional solid sources of gallium, indium, and arsenic were used with effusion cell technology. Electronic-grade semi-insulating GaAs(001) substrates were chemically cleaned and then etched using a conventional sulfuric acid–hydrogen peroxide–deionized (D.I.) H_2O solution. The surface oxide layer was desorbed in the MBE growth chamber at a temperature of 580 °C in the presence of an arsenic flux. The sample layer arrangement consisted of

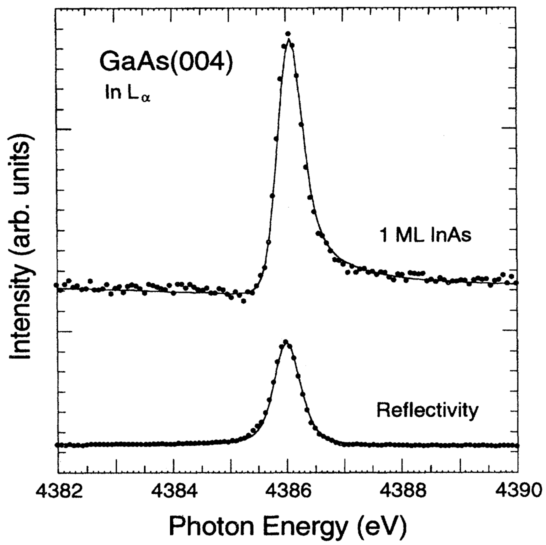

FIG. 1. Photon-energy dependence of the reflectivity (lower) and the In-L_α fluorescence yield (upper) near the GaAs(004) Bragg backreflection condition. The solid lines are the best fits to the data points (see text).

a 0.5-μm gallium arsenide buffer layer, 1 ML of indium arsenide, and then a 25-Å GaAs cap layer to inhibit oxidation of the buried interface. Throughout the growth the arsenic shutter was left open, and the gallium and indium cells were shuttered. A 3-s pause step was used before the growth of the successive layers (only the arsenic was left opened) in order to improve the interface. During the growth of the buffer layer, the sample temperature was linearly ramped from 580 to 480 °C, whereupon the Ga shutter was closed, and the In shutter was opened after a 3-s pause. The remainder of the growth took place at 480 °C. After the GaAs cap layer was grown, the sample temperature was ramped to 25 °C. The arsenic flux was left "on" until the sample temperature fell below 400 °C. The growth rates were 23.5 and 1.16 s/ML for the InAs and GaAs, respectively, and the III/V beam equivalent pressure ratio was 15. Growth rates and sample quality were determined by reflection high-energy electron diffraction (RHEED) prior to and during the growth sequence.

Our measurements were performed at the National Institute of Standards and Technology beamline X24A at the National Synchrotron Light Source, Brookhaven National Laboratory. XSW data were collected in a fixed-angle normal-incidence diffraction geometry by scanning a pair of Si(220) monochromator crystals through the GaAs(004) Bragg backreflection condition, which occurs near 4386 eV. In a single XSW scan, the backreflected photon intensity and the In-L_α fluorescence yield are recorded simultaneously.

Figure 1 shows the GaAs(004) reflectivity along with the best fit to the data points using the dynamical theory of x-ray diffraction.[6] The fit is the result of convolving the theoretical reflectivity with a Voigt function of width 0.38 eV and adjusting it for a small energy offset. Also shown is the In standing-wave pattern compared to its best fit to the function

$$Y = 1 + R + 2\sqrt{R}F\cos(\phi - 2\pi D),$$

using the energy offset and width obtained from the fit to the reflectivity. The pertinent fitting parameters here are D, the interlayer-substrate distance in units of the reflecting-plane spacing ($d_{\mathrm{GaAs(004)}} = 1.4133$ Å), and F, the coherent fraction of atoms at D. These values are determined to be 0.16 ± 0.02 and 0.73 ± 0.1, respectively, which locate the In atoms 1.64 ± 0.03 Å above the last-As plane of the GaAs(001) substrate.[7] An earlier investigation[8] found a much lower coherent fraction and attributed it to In segregation to the second and third layers of the GaAs structure. Because the inherent thermal vibrations of GaAs would lower F to ~ 0.9 for a structurally perfect layer,[9] our data indicate that $\sim 15\%$ of the In atoms were not in their ideal-monolayer sites.

TABLE I. The calculated-In position above the last-As layer of the GaAs substrate from macroscopic-elastic theory, the local-density approximation, and bond-length conservation. Also shown is the result of the HREM experiment, our standing-wave result, and the position of the In layer had it not been strained.

Theory or experiment	In-As planar distance (Å)
Unstrained	1.51
Macroscopic-elastic theory	1.62
Local-density approximation	1.63
Bond-length conservation	1.70
HREM	1.71
XSW	1.64 ± 0.03

Having measured the exact atomic position of the In layer relative to the GaAs planes, we can compare directly with theory. Because InAs is larger than GaAs, InAs growth on GaAs(001) results in a layer that is compressed bilaterally in the (001) plane and expanded uniaxially along the [001] direction. From macroscopic-elastic theory,[1] the InAs lattice strains parallel, $\varepsilon_\parallel$, and perpendicular, $\varepsilon_\perp$, to the InAs/GaAs(001) interface are related through the elastic constants C_{12} and C_{11} by $\varepsilon_\perp = -2(C_{12}/C_{11})\varepsilon_\parallel$. These strains are given in terms of the strained lattice constants $a_\parallel$ and $a_\perp$ and the lattice constant a of unstrained InAs ($a_{\mathrm{InAs}} = 6.0584$ Å) by $\varepsilon_\perp = (a_\perp - a)/a$ and $\varepsilon_\parallel = (a_\parallel - a)/a$.

Because the InAs layer is laterally epitaxial with the GaAs substrate,[10] the coherency condition is $a_\parallel = a_{\mathrm{GaAs}} = 5.6532$ Å. The elastic constants from Hornstra and Bartels[1] render a perpendicular strain of 7.27%, which translates to a perpendicular lattice constant of 6.4988 Å. Consequently, the indium layer would reside $6.4988/4 = 1.62$ Å above the last-As layer of the GaAs substrate.

Table I compares the D calculated from macroscopic-elastic theory, the local-density approximation,[5] our XSW result,[12] and the result from the HREM experiment.[2] We have also included the position had the In-As bond length been conserved, i.e., only a bond-angle distortion, and the position had the layer not been strained, i.e., $D = a_{\mathrm{InAs}}/4$. Mutual agreement is found between our standing-wave data, the LDA, and the macroscopic theory. Conversely, the bond-length-conserving distortion replicates the HREM experiment, but it overestimates the standing-wave result signifi-

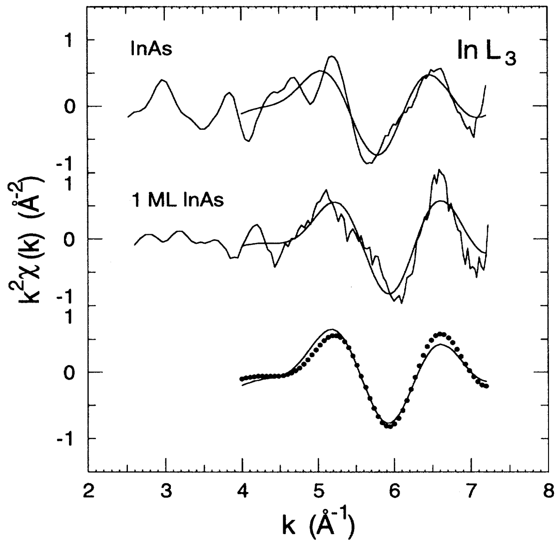

FIG. 2. k^2-weighted In-L_3 EXAFS, $k^2\chi(k)$, from the InAs monolayer (middle) and the bulk InAs standard (upper). Superimposed on the data are the Fourier-filtered first-shell contributions, which correspond to the In-As near-neighbor bond. The lower portion of the figure shows the fit (solid line) to the filtered data from the InAs monolayer (see text).

cantly. Therefore, the In-As bond length must be measured in order to resolve which of the two groups of results correctly describes this distortion.

To evaluate the In-As bond length, we turn to Fig. 2, which shows our EXAFS data from the InAs monolayer. These data were collected by scanning two Si(111) monochromator crystals through the In-L_3 absorption edge and monitoring the In-L_α fluorescence yield. Similar data are shown for bulk InAs recorded by monitoring the total-electron yield. Both are plotted with their Fourier-filtered first-shell contributions, which correspond to the In-As bond lengths. The raw EXAFS data show that the first-neighbor bond in the strained InAs, which is proportional to the lowest frequency of the EXAFS oscillations, is compressed relative to that in bulk InAs, because the nodes of the spectrum are shifted to higher k values. Therefore, these data directly support the results in Table I which do not predict an anomaly.

To obtain quantitative information, following standard EXAFS procedures, first-shell phase, $\phi(k)$, and amplitude, $|f(k)|$, functions were extracted from the bulk InAs standard. The lower portion of the figure compares the Fourier-filtered first-shell EXAFS data from the InAs monolayer to its best fit to the function $k^2\chi(k)$, where

$$\chi(k)=N|f(k)|\sin[2kr+\phi(k)],$$

using the phase and amplitude functions derived from the InAs standard. In the fit, only the linear parameter N, the In-As coordination number, and the nonlinear parameter r, the In-As bond length, were varied. The best fit was obtained with $N=4.1\pm0.4$ and $r=2.57\pm0.02$ Å.[7] Because the bulk In-As bond length is 2.62 Å, we find the bond length in the strained layer to be compressed 0.05 ± 0.02 Å.

To appreciate the origin of these distortions microscopically, Fig. 3 shows an InAs tetrahedron under compressive

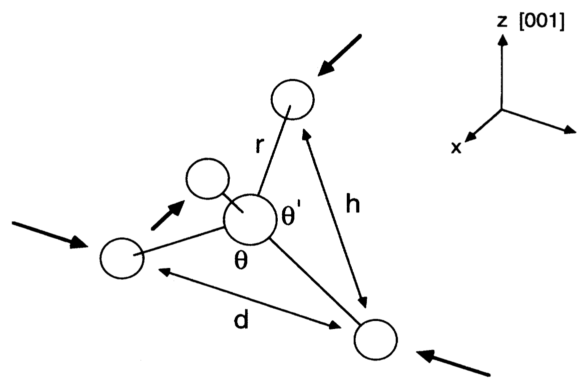

FIG. 3. An InAs tetrahedron under compressive strain in the x-y plane with equivalent near-neighbor bond lengths r. Here z is the [001] direction. The in-plane and out-of-plane second-neighbor distances are $d=2r\sin(\theta/2)$ and $h=2r\sin(\theta'/2)$.

strain in the x-y plane. Following a simple VFF model[13] for such a layer,[14] we may write the energy of this strain-induced distortion as

$$E(\Delta r/r,\Delta\theta)=-E_0+4[\tfrac{1}{2}k_r(\Delta r/r)^2]+3[\tfrac{1}{2}k_\theta(\Delta\theta)^2].$$

Here k_r is the bond-stretching force constant and k_θ is the bond-bending force constant. Δr and $\Delta\theta$ are the bond stretch and bond bend, respectively. The second-neighbor distance d in the two in-plane directions is given in terms of the first-neighbor distance r and the bond angle θ by $d=2r\sin(\theta/2)$. So, to first order in the distortions: $(\Delta d/r)=2(\Delta r/r)\sin(\theta/2)+(\Delta\theta)\cos(\theta/2)$. Minimizing the above energy subject to this geometric constraint yields the ratio of the radial to angular distortions in terms of the force constants:

$$(\Delta r/r)/(\Delta\theta)=(3\sqrt{2}/2)k_\theta/k_r.$$

From the radial and angular force constants for InAs tabulated by Harrison,[13] this ratio is 0.076. Since the strained layer is laterally epitaxial, Δd is known and the distortions can be calculated. The compression of the first-neighbor bond length is $\Delta r\sim-0.03$ Å, and the bond angles are shifted anisotropically with respect to the interface, $\Delta\theta\sim-9°$ and $\Delta\theta'\sim4.5°$. These calculated changes are consistent with our measured bond-length change of -0.05 ± 0.02 Å; they are a direct consequence of the compressive force imposed on the InAs layer by the GaAs substrate. The perpendicular expansion of the In layer resulting from this strain-induced bond bending may also be calculated from this simple model. The final result for the In position is $D=1.66$ Å, which slightly overestimates the standing-wave result because second-order and higher-neighbor interactions have been neglected. For completeness, our EXAFS determination of the In-As bond length and the coherency condition give $D=1.62\pm0.03$ Å.

In their work, Brandt *et al.*[2] reasoned that the discovery of a noncompressed In-As bond was a direct consequence of the small k_θ/k_r ratio of InAs. Although it is smaller for InAs than most other III-V combinations,[15] our simple VFF model still predicts a bond-length compression large enough to be consistent with both the In position measured by XSW and the In-As bond length measured by EXAFS. In an earlier EXAFS study of strained Ge_xSi_{1-x}/Si(001) alloys, no bond-length deviations from those in bulk alloys were found even though x-ray diffraction measured a significant perpendicular-lattice strain.[16] In this case the strain was only 1.4%, which gives an estimated bond-length compression of only 0.007 Å by the same model. Such a small distortion is below the EXAFS detectability limit of $\sim$0.01 Å.[17]

In conclusion, we have combined the synchrotron-based techniques of x-ray standing waves and extended x-ray-absorption fine structure to determine the strain and bond distortions in a monolayer InAs film grown on GaAs(001). Our data give direct experimental support that macroscopic-elastic theory describes the distortions in ultrathin InAs/GaAs(001) films.

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[7] Our uncertainties for D and r are estimated from the spread of values which double the residual χ^2.

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[10] Because the 1-ML film is below the critical thickness for epitaxial growth, $T_c \sim 2-3$ ML (Ref. 11), and because it possesses such a high degree of structural order as measured by standing waves, it is fair to assume that the layer is pseudomorphic.

[11] L. Tapfer, O. Brandt, K. Ploog, M. Ospelt, and H. von Kanel, in *Proceedings of the 20th International Conference on the Physics of Semiconductors, Thessaloniki, Greece, 1990*, edited by E. M. Anastassakis and J. D. Joannopoulos (World Scientific, Singapore, 1990), p. 949.

[12] It is straightforward to estimate the effect of a graded InAs/GaAs interface on the XSW determination of D. For example, our measurement of the coherent fraction indicates that $\sim$15% of the indium atoms reside in other than ideal-monolayer sites. If we place all of this indium in the second layer and calculate the position standing waves would measure assuming both layers to be ideally elastic, the result is $D = 0.18$. As segregation therefore tends to increase the standing-wave result, this suggests that the position of the first layer is even closer in reality to that given by macroscopic theory. Note that a graded interface would not affect the EXAFS result because EXAFS measures bond lengths and not position.

[13] W. A. Harrison, *Electronic Structure and the Properties of Solids* (Freeman, San Francisco, 1980).

[14] In general, this sum is taken over the four r's and six θ's of the tetrahedron. However, for the special symmetric case studied here, Δr is equal for all four bonds, and the in-plane $\Delta\theta$ and out-of-plane $\Delta\theta'$ are related by $\Delta\theta' = -\frac{1}{2}\Delta\theta$. Hence the factors of 4 and 3 in the total energy.

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