

Bond-Length Distortions in Strained Semiconductor Alloys

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Extended x-ray absorption fine structure measurements performed at In-*K* edge have resolved the outstanding issue of bond-length strain in semiconductor-alloy heterostructures. We determine the In-As bond length to be 2.581 ± 0.004 Å in a buried, 213 Å thick Ga_{0.78}In_{0.22}As layer grown coherently on GaAs(001). This bond length corresponds to a strain-induced contraction of 0.015 ± 0.004 Å relative to the In-As bond length in bulk Ga_{1-x}In_xAs of the same composition; it is consistent with a simple model which assumes a uniform bond-length distortion in the epilayer despite the inequivalent In-As and Ga-As bond lengths. [S0031-9007(97)04857-6]

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When a macroscopic body is acted upon by small external forces, its deformations are accurately described by the theory of elasticity [1]. Despite the maturity of this branch of theoretical physics, the microscopic distortions—bond length and bond angle—which govern the macroscopic behavior of the body are, in general, not well understood, particularly from an experimental point of view. Additionally, although in principle it is possible to calculate the normal modes of a crystal from its electronic structure, in practice it is impossible, for a crystal typically possesses as many independent force constants as it does atoms. Consequently, the atomistic description of choice used to model these distortions is based on the fitting of the microscopic-force constants from the macroscopic-elastic constants via a two-parameter valance-force field which neglects long-range forces [2].

A technologically relevant application of the theory of elasticity lies with the study of pseudomorphic growth. When a thin film with lattice constant a_f is grown coherently ($a_{\parallel} = a_s$) on a substrate with a different lattice constant a_s , the lattice constant a_{\perp} of the layer perpendicular to the interface is either Poisson expanded or contracted in response to the distortion of its lattice constant a_{\parallel} parallel to the interface. For an isotropic cubic layer grown on a (001) substrate, macroscopic-elastic theory [3] accurately relates the fractional strains of the layer relative to the interface, $\varepsilon_{\parallel} = (a_{\parallel} - a_f)/a_f$ and $\varepsilon_{\perp} = (a_{\perp} - a_f)/a_f$, through its elastic constants c_{11} and c_{12} :

$$\varepsilon_{\perp} = -2(c_{12}/c_{11})\varepsilon_{\parallel}. \quad (1)$$

Because the macroscopic-strain state of semiconductor layers can be accurately determined by bulk-sensitive techniques such as x-ray diffraction, strained-layer semiconductors offer a unique vehicle with which to study the

microscopic distortions quantitatively in the anticipation of improving both first-principles and phenomenological modeling. It is therefore disappointing that the numerous studies performed to date, designed to decipher the local atomic geometry within such films, have failed to reach a consensus concerning the exact nature of these distortions: In some studies, the strain has been reported to have “remarkable” effects on bond lengths [4,5], while other studies have found little or no effect [6]. Still, others have reported the counterintuitive result that bonds are actually longer in layers under compression [7].

In order to resolve the issue of bond-length strain, we have performed high-resolution extended x-ray absorption fine structure (EXAFS) measurements at the In-*K* absorption edge (27 940 eV) on a well-characterized, buried Ga_{1-x}In_xAs layer grown coherently on GaAs(001). This layer/substrate system was chosen for several reasons beyond its technological relevance. (Strained Ga_{1-x}In_xAs is used as the channel material in pseudomorphic high-electron mobility transistors.) First, both the In-As and the Ga-As bond lengths in bulk Ga_{1-x}In_xAs alloys have been studied in detail by EXAFS [8], and their compositional dependence is the best quantified of all semiconductor alloys. Second, Ga_{1-x}In_xAs/GaAs(001) is one of the only strained-layer systems for which a first-principles theoretical calculation [9] exists with which to compare our EXAFS results. Third, and perhaps most importantly, because Ga_{1-x}In_xAs is a pseudobinary alloy, unlike the true binary alloy Ge_{1-x}Si_x, it possesses an ideal phase and amplitude standard, namely, bulk InAs, with which to analyze the In-As bond length. Similar careful measurements and data analysis of bulk Ga_{1-x}In_xAs alloys [8] have determined bond lengths with an accuracy better than ± 0.005 Å. Additionally, because the lattice constants of InAs and GaAs differ by a full 7%, effects which may arise due to the inequivalent lengths of In-As

and Ga-As bonds should be more readily detected in this model-alloy/substrate system than in other systems which possess a smaller natural mismatch.

The sample studied consisted of a GaAs(001) substrate, a 1000 Å GaAs buffer layer, a nominally 200 Å thick $\text{Ga}_{0.8}\text{In}_{0.2}\text{As}$ layer, and a 50 Å GaAs cap. The layer was capped with GaAs to protect it from oxidation and to provide a bulk termination of its structure. Growth rates were estimated from the oscillatory period of the 00 reflection high-energy electron diffraction (RHEED) spot from a calibration wafer prior to growth of the heterostructure. Growth temperatures were 580 °C for the buffer layer and 480 °C for the $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer and cap.

X-ray topographs taken at the National Institute of Standards and Technology beamline X23-A3 of the National Synchrotron Light Source in the (004) Bragg geometry found the layer and substrate to be free of misfit dislocations, proving that the layer thickness is below the critical thickness for pseudomorphic growth at this In concentration.

In order to establish the macroscopic-strain state of the layer, and to more accurately determine its In content and thickness, high-resolution specular (004) x-ray diffraction was performed in the vicinity of the GaAs(004) Bragg reflection at the University of Washington using a Cu target, rotating-anode source. Figure 1 shows the diffraction data. The very sharp, intense peak near 33° is the (004) Bragg reflection from the GaAs substrate. The scattering from the pseudomorphic $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer consists of a central primary maximum, centered at approximately 32°, surrounded by subsidiary maxima that decrease in intensity away from the central primary maximum.

From the position of the primary maximum relative to the Bragg peak from the GaAs substrate, the perpendicular lattice constant of the $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer may be determined quite accurately: $a_{\perp} = 5.8216 \pm 0.002$ Å. Because we know that the layer is coherent with the GaAs

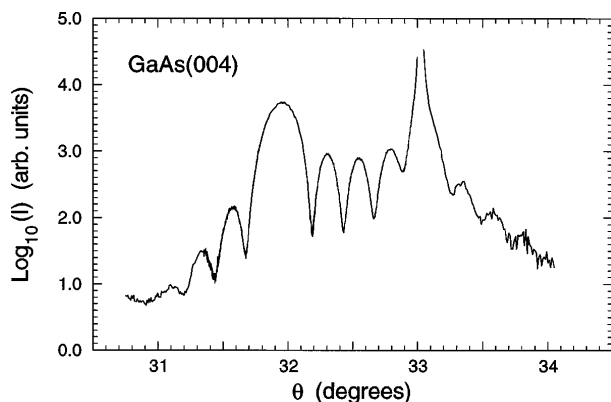


FIG. 1. Scattered intensity versus angle in the vicinity of the GaAs(004) Bragg reflection. The primary maximum near $\theta = 33^\circ$ is the GaAs(004) Bragg reflection, and the primary maximum near 32° is the scattering from the pseudomorphic $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer.

substrate, as discussed by Hornstra and Bartels [3], we may use Eq. (1), together with Vegard's law,

$$a_f = (1 - x)a_{\text{GaAs}} + (x)a_{\text{InAs}}, \quad (2)$$

and the bulk lattice constants of InAs (6.0584 Å) and GaAs (5.65321 Å) to calculate the concentration of the layer from a_{\perp} . The result is $x = 21.5 \pm 0.5\%$, which corresponds to a perpendicular strain $\epsilon_{\perp} = 1.41\%$ relative to unstrained $\text{Ga}_{1-x}\text{In}_x\text{As}$ of the same composition. In addition, because the widths of the primary maximum and the subsidiary maxima are direct consequences of the finite thickness of the film, its thickness t can be calculated from the observed periodicity, ΔQ , of the minima. Using $t = 2\pi/\Delta Q$, we find $t = 213 \pm 3$ Å. This value is consistent with a slightly higher In growth rate than that estimated from RHEED. Consequently, the In content will be taken at 21.5% in all subsequent calculations.

Figure 2 shows our In- K edge EXAFS data from the strained $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer. These data were recorded at beamline X18-B of the National Synchrotron Light Source using a Si(111) channel-cut monochromator and a 13 element Ge solid-state detector set to monitor the In- K_{α} fluorescence yield. The figure also shows the EXAFS from bulk InAs, recorded in transmission. Both are plotted with their Fourier-filtered first-shell contributions, which correspond to the In-As bond lengths.

It is immediately evident from the raw EXAFS data that the first-neighbor In-As bond length in the strained $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer, which is proportional to the frequency of the EXAFS oscillations, is compressed relative to the In-As bond length in bulk InAs. This is clear because the

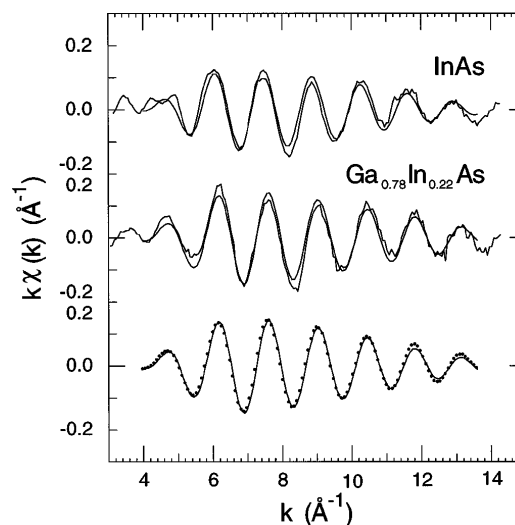


FIG. 2. k -weighted In- K -edge EXAFS, $k\chi(k)$, from the pseudomorphic $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer on GaAs(001) (middle) and the bulk InAs standard (upper). Superimposed on the data are the Fourier-filtered first-shell contributions, which correspond to the In-As bond lengths. Note the lower frequency of the EXAFS oscillations from the strained layer. The lower portion of the figure shows the fit (solid line) to the filtered data from the layer.

nodes of the spectrum from the layer are shifted towards higher- k values. To obtain quantitative information, these data were fit by the function $k\chi(k)$, where

$$\chi(k) = N|f(k)| \sin[2kr + \phi(k)], \quad (3)$$

using the phase, $\phi(k)$, and amplitude, $|f(k)|$, functions derived from the bulk InAs standard. In the fit, only the two parameters N (the In-As coordination number) and r (the In-As bond length) were varied. The measured In-As bond length in the film is $r'_{\text{InAs}} = 2.581 \pm 0.004 \text{ \AA}$ [10]. Because the bond length in bulk InAs is 2.623 \AA , the In-As bond length in the strained $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer is contracted $0.042 \pm 0.004 \text{ \AA}$ relative to the In-As bond length in bulk InAs. Note that the extended k range (to $k = 14 \text{ \AA}^{-1}$) and the use of the ideal, bulk InAs model compound in the EXAFS data analysis allow us to make this accurate structural determination [8,11].

In their pioneering study, Mikkelson and Boyce [8] used EXAFS to measure the bond lengths in bulk $\text{Ga}_{1-x}\text{In}_x\text{As}$ alloys. They found that, instead of following the virtual-crystal approximation (VCA), the In-As and Ga-As bond lengths maintain two chemically distinct values. Although these distinct values do vary linearly with the alloy composition, this variation is only about one-fourth ($\sim 0.04 \text{ \AA}$) of the natural bond-length difference between bulk InAs ($r_{\text{InAs}}^0 = 2.623 \text{ \AA}$) and bulk GaAs ($r_{\text{GaAs}}^0 = 2.448 \text{ \AA}$):

$$\begin{aligned} r_{\text{InAs}} &= r_{\text{InAs}}^0 + \delta(r_{\text{VCA}} - r_{\text{InAs}}^0), \\ r_{\text{GaAs}} &= r_{\text{GaAs}}^0 + \delta(r_{\text{VCA}} - r_{\text{GaAs}}^0), \end{aligned} \quad (4)$$

where $\delta \sim 1/4$.

This behavior was later explained theoretically by Martins and Zunger [12] using a valence-force field. In the Pauling limit, two chemically distinct bond lengths exist that are equal to the sum of their covalent radii. In the VCA limit, only one bond length exists that varies linearly with alloy composition,

$$r_{\text{VCA}} = (1-x)r_{\text{GaAs}}^0 + (x)r_{\text{InAs}}^0. \quad (5)$$

Because of the higher energy cost of bond stretching versus bond bending, the behavior is found to be closer to the Pauling rather than the VCA limit.

We may now interpret our EXAFS data relative to the bond lengths in bulk (unstrained) $\text{Ga}_{1-x}\text{In}_x\text{As}$. Using an accurate value of δ [13], the In-As and Ga-As bond lengths in a bulk alloy with In content 21.5% are $r_{\text{InAs}} = 2.596 \text{ \AA}$ and $r_{\text{GaAs}} = 2.455 \text{ \AA}$, respectively. The In-As bond length in the strained layer, $r'_{\text{InAs}} = 2.581 \pm 0.004 \text{ \AA}$, is significantly shorter than this value. In fact, it is even shorter than the In-As bond length measured by Mikkelson and Boyce [8] in the dilute-alloy limit, $r_{\text{InAs}} = 2.588 \text{ \AA}$ for $x \rightarrow 0$; therefore, it must reflect the external compressive strain imposed on the layer by the substrate: $\Delta r = -0.015 \pm 0.004 \text{ \AA}$.

Although EXAFS has been used previously to measure the bond lengths in strained $\text{Ga}_{1-x}\text{In}_x\text{As}/\text{GaAs}(001)$ for

$x \leq 0.25$ [4], this study has been questioned by a total-energy and Hellmann-Feynman force calculation that found In-As and Ga-As bond lengths equal to 2.54 and 2.44 \AA , respectively, in strained alloys of similar composition. Based on their calculations, the authors of the theoretical study [9] concluded that the bond-length strain is accommodated primarily by a contraction of the longer In-As rather than the shorter Ga-As bond. No striking, stretched bond lengths as reported in Ref. [4] were found, and the experimental findings were therefore presumed to be artifact related. Because the previous EXAFS studies [4,7] were performed at the Ga- K and As- K edges, the EXAFS unavoidably sampled bonds that were not only in the alloy film but also in the oxidized surface region, as well as in the GaAs substrate and cap. Because our measurements were performed at the In- K edge, our data sample bonds that are located only within the buried $\text{Ga}_{1-x}\text{In}_x\text{As}$ layer and are thus free from such artifacts.

We shall now estimate the amount of bond-length distortion expected in such a layer based on the virtual-crystal approximation. Because the lattice constant of InAs is 7% larger than the lattice constant of GaAs, pseudomorphic growth of a $\text{Ga}_{1-x}\text{In}_x\text{As}$ alloy on GaAs(001) results in a layer that is compressed bilaterally within the (001) plane of the substrate and Poisson expanded uniaxially along the [001] growth direction. Because of this tetragonal distortion, the average bond length in the layer is no longer equal to $\frac{\sqrt{3}}{4}a_f$; however, it may be computed from

$$r' = \frac{1}{4} \left(2a_{\parallel}^2 + a_{\perp}^2 \right)^{1/2}. \quad (6)$$

Using $a_{\parallel} = a_f + \Delta a_{\parallel}$ and $a_{\perp} = a_f + \Delta a_{\perp}$, it is easily shown that, to first order in ε ,

$$r' = \frac{\sqrt{3}}{4} a_f \left[1 + \frac{1}{3} (2\varepsilon_{\parallel} + \varepsilon_{\perp}) \right]. \quad (7)$$

As in Eq. (1), $\varepsilon_{\perp} = \Delta a_{\perp}/a_f$ and $\varepsilon_{\parallel} = \Delta a_{\parallel}/a_f$.

Equation (7) may be further simplified by using the macroscopic-elastic theory result [Eq. (1)] and the fact that $\varepsilon_{\parallel} = (r_{\text{GaAs}}^0 - r_{\text{VCA}})/r_{\text{VCA}}$:

$$r' = r_{\text{VCA}} - \gamma(r_{\text{VCA}} - r_{\text{GaAs}}^0), \quad (8)$$

where $\gamma = \frac{2}{3}(1 - c_{12}/c_{11})$. Note that γ depends only on the elastic constants c_{11} and c_{12} , and that it is approximately equal to $\frac{1}{3}$ [3].

Because Eq. (8) describes the distortion of the *average* bond length in the layer, a further assumption about the *relative* distortions is needed before the bond lengths can be calculated. If we assume that the In-As and Ga-As bond lengths change by the same amount, it follows from Eq. (8) that

$$\begin{aligned} r'_{\text{InAs}} &= r_{\text{InAs}} - \gamma(r_{\text{VCA}} - r_{\text{GaAs}}^0), \\ r'_{\text{GaAs}} &= r_{\text{GaAs}} - \gamma(r_{\text{VCA}} - r_{\text{GaAs}}^0). \end{aligned} \quad (9)$$

These equations render $r'_{\text{InAs}} = 2.582 \text{ \AA}$ and $r'_{\text{GaAs}} = 2.442 \text{ \AA}$, which is indistinguishable from our experimental value: $r'_{\text{InAs}} = 2.581 \pm 0.004 \text{ \AA}$.

Although this uniform distortion reproduces our experiment accurately, it lacks a key ingredient proposed in the theoretical study, namely, that pseudomorphic growth of a larger $\text{Ga}_{1-x}\text{In}_x\text{As}$ alloy on a smaller $\text{GaAs}(001)$ substrate may result in a bond-length strain that is accommodated primarily by the distortion of the longer In-As rather than the shorter Ga-As bond. If we instead let the In-As and Ga-As bond lengths reflect their individual (rather than average) mismatch with the GaAs substrate, then it follows from Eq. (8) that

$$\begin{aligned} r'_{\text{InAs}} &= r_{\text{InAs}} - \gamma(r_{\text{InAs}} - r_{\text{GaAs}}^0), \\ r'_{\text{GaAs}} &= r_{\text{GaAs}} - \gamma(r_{\text{GaAs}} - r_{\text{GaAs}}^0). \end{aligned} \quad (10)$$

These equations render $r'_{\text{InAs}} = 2.543 \text{ \AA}$ and $r'_{\text{GaAs}} = 2.453 \text{ \AA}$. Although this mismatched distortion severely overestimates the actual In-As bond-length contraction determined by our experiment, these predictions are practically identical to the In-As and Ga-As bond lengths calculated from first principles: 2.54 and 2.44 \AA , respectively [9]. Despite this apparent agreement, our experiment shows that equal distortions of the In-As and Ga-As bond lengths are energetically favored.

Let us now test this conclusion within the context of our simple model. Because we have used Eq. (1) in the derivation of Eq. (8), the lowest energy solution may be obtained by minimizing the approximate expression [14]

$$E = E_0 + \frac{1}{2} k[(1-x)(\Delta r_{\text{GaAs}})^2 + (x)(\Delta r_{\text{InAs}})^2] \quad (11)$$

subject to the geometric constraint imposed by Eq. (8),

$$(1-x)\Delta r_{\text{GaAs}} + (x)\Delta r_{\text{InAs}} = -\gamma(r_{\text{VCA}} - r_{\text{GaAs}}^0). \quad (12)$$

This minimization renders the uniform distortion identically:

$$\begin{aligned} \Delta r_{\text{InAs}} &= -\gamma(r_{\text{VCA}} - r_{\text{GaAs}}^0), \\ \Delta r_{\text{GaAs}} &= -\gamma(r_{\text{VCA}} - r_{\text{GaAs}}^0). \end{aligned} \quad (13)$$

In conclusion, we have performed a high-resolution extended x-ray absorption fine-structure measurement at the In- K edge on a well-characterized, buried $\text{Ga}_{0.78}\text{In}_{0.22}\text{As}$ alloy film grown coherently on $\text{GaAs}(001)$. Counter to previous theory and experiment, we find that the In-As

bond length is contracted by $0.015 \pm 0.004 \text{ \AA}$ relative to the In-As bond length in bulk $\text{Ga}_{1-x}\text{In}_x\text{As}$ of the same composition. This contraction is shown to be consistent with a simple model based on the virtual-crystal approximation and macroscopic-elastic theory in which the In-As and Ga-As bond lengths are uniformly distorted.

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- [1] L.D. Landau and E.M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Oxford, 1970).
 [2] P.N. Keating, Phys. Rev. **145**, 637 (1966).
 [3] J. Hornstra and W.J. Bartels, J. Cryst. Growth **44**, 513 (1978).
 [4] M.G. Proietti, F. Martelli, S. Turchini, L. Alagna, M.R. Bruni, T. Prosperi, M.G. Simeone, and J. Garcia, J. Cryst. Growth **127**, 592 (1993).
 [5] H. Oyanagi, Y. Takeda, T. Matsushita, T. Ishiguro, T. Yao, and A. Sasaki, Superlattices Microstruct. **4**, 413 (1988).
 [6] J.C. Woicik, C.E. Bouldin, M.I. Bell, J.O. Cross, D.J. Tweet, B.D. Swanson, T.M. Zhang, L.B. Sorensen, C.A. King, J.L. Hoyt, P. Pianetta, and J.F. Gibbons, Phys. Rev. B **43**, 2419 (1991); M. Matsuura, J.M. Tonnerre, and G.S. Cargill III, Phys. Rev. B **44**, 3842 (1991); E. Canova, A.I. Goldman, S.C. Woronick, Y.H. Kao, and L.L. Chang, Phys. Rev. B **31**, 8308 (1985); C. Lamberti, S. Bordiga, F. Boscherini, S. Pascarelli, G.M. Schiavini, C. Ferrari, L. Lazzarini, and G. Salviati, Appl. Phys. Lett. **64**, 1430 (1994).
 [7] M.G. Proietti, S. Turchini, J. Garcia, G. Lambelle, F. Martelli, and T. Prosperi, J. Appl. Phys. **78**, 6574 (1995).
 [8] J.C. Mikkelsen, Jr. and J.B. Boyce, Phys. Rev. Lett. **49**, 1412 (1982).
 [9] A.A. Bonapasta and G. Scavia, Phys. Rev. B **50**, 2671 (1994).
 [10] $\pm 0.004 \text{ \AA}$ corresponds to the spread of bond lengths which doubles the residual squared error while the coordination number is allowed to vary.
 [11] See, e.g., *X-Ray Absorption: Principles, Applications, Techniques of EXAFS, SEXAFS, and XANES*, edited by D.C. Koningsberger and R. Prins (Wiley, New York, 1988).
 [12] J.L. Martins and A. Zunger, Phys. Rev. B **30**, 6217 (1984).
 [13] Y. Cai and M.F. Thorpe, Phys. Rev. B **46**, 15 879 (1992).
 [14] C.K. Shih, W.E. Spicer, W.A. Harrison, and A. Sher, Phys. Rev. B **31**, 1139 (1985).