Diffraction anomalous fine-structure study of strained $Ga_{1-x}In_xAs$ on GaAs(001)

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Diffraction anomalous fine-structure measurements performed at both the Ga and As K edges have determined the Ga-As bond length to be 2.442 ± 0.005 Å in a buried, 213-Å-thick $Ga_{0.785}In_{0.215}As$ layer grown coherently on GaAs(001). This bond length corresponds to a strain-induced contraction of 0.013 ± 0.005 Å relative to the Ga-As bond length in bulk $Ga_{1-x}In_xAs$ of the same composition. Together with recent extended x-ray-absorption fine-structure measurements performed at the In K edge [Woicik *et al.*, Phys. Rev. Lett. **79**, 5026 (1997)], excellent agreement is found with the uniform bond-length distortion model for strained-layer semiconductors on (001) substrates. [S0163-1829(98)52232-1]

When a thin semiconductor film is grown coherently on a substrate that differs in lattice constant, the lattice constant of the layer perpendicular to the film/substrate interface is either expanded or contracted in response to the distortion of its lattice constant parallel to the interface. Although the theory of elasticity[1] accurately describes the *macroscopic* distortions of the film, a consensus between experiment and theory concerning its *microscopic* distortions has only recently begun to form.[2,3] The ambiguity of previous experimental studies that have reported both strained[4–6] and unstrained[7–12] bond lengths in strained, quasibulk, thin-alloy films may be traced to the inherent rigidity of semiconductor bonds: strain effects often lie within the typical extended x-ray-absorption fine-structure (EXAFS) bond-length accuracy of ~0.02 Å.[7] Additionally, only a few theoretical studies[13,14] of the bond lengths within strained-layer semiconductors have existed with which to compare the varying experimental results, and these calculations have either been in conflict with experiment[2,4,14] or they have been performed for alloy/substrate systems for which little or no experimental data exist.[13] Furthermore, strained epitaxial films are often buried, and the same chemical elements exist in both the bulk substrate and capping layers of the heterostructure. Consequently, previous high-resolution EXAFS studies have provided structural information pertaining to only one type, the minority species, of heterostructure bond.[2]

In this work, we employ the relatively new technique of diffraction anomalous fine-structure[15] (DAFS) to accurately determine the *majority* Ga-As bond length in a strained, buried $Ga_{1-x}In_xAs$ thin-alloy film grown coherently on GaAs(001). DAFS combines the usual chemical specificity of EXAFS with the reciprocal-space specificity of diffraction. Use of DAFS circumvents the film/substrate common-element problem that makes film-specific measurements impossible with EXAFS because the strained-layer Bragg peaks of the film are separated in reciprocal space from the substrate peaks. Previous measurements have failed to obtain unambiguous structural information on the Ga-As bond length in similar heterostructures through surface-sensitive variants of the EXAFS technique.[4,6,14] Our experiment together with a recent high-resolution EXAFS study performed at the In K edge[2] establishes the uniform bond-length distortion model for strained-layer semiconductors on (001) substrates.

The DAFS technique[15] is based on the premise that information contained in absorption spectra can also be extracted from resonant, energy-dependent diffraction measurements through the causal relationship between the real and imaginary parts of the atomic-scattering amplitude f.[16] The integrated intensity I of an x-ray Bragg reflection from a weakly scattering crystal is proportional to the square of the crystallographic structure factor[17]

$$I(\mathbf{q}) \propto \left| \sum_j f_j e^{i\mathbf{q} \cdot \mathbf{r}_j} \right|^2. \tag{1}$$

The crystallographic-structure factor accounts for scattering at photon wave-vector-transfer $\mathbf{q} = \mathbf{k}_f - \mathbf{k}_i$ from each of the j

atoms in the unit cell according to their positions $\mathbf{r}_j$ and their atomic-scattering amplitudes f_j. The atomic-scattering amplitude f from a single atom[18] is the sum of the Thomson scattering amplitude f_0, which is independent of the photon energy, and an energy-dependent resonant correction Δf, which changes dramatically in the vicinity of a core-level excitation energy. Δf is the sum of a real part f', and an imaginary part f''.

In the standard EXAFS description of the absorption coefficient $\mu(E)$,[19] $\mu = \mu_0(1 + \chi'')$, μ_0 is the bare-atom, background absorption, and χ'' is the oscillatory part of the x-ray-absorption coefficient that arises from the local backscattering from nearby atoms. Analogously, the real and imaginary parts of Δf are also separable into their atomic and oscillatory terms,

$$\Delta f = f'_a + i f''_a + f''_0 (\chi' + i\chi''). \qquad (2)$$

The subscript a denotes the smooth, atomiclike contribution to the response function, and $\chi = \chi' + i\chi''$ is the generalized, energy-dependent fine-structure function. Because f' and f'' are linked by causality, f'' may be determined[20,21] either directly by measuring the total absorption cross section $\sigma_{\text{tot}}(E)$,

$$f''(E) = (E/2hc)\sigma_{\text{tot}}(E), \qquad (3)$$

or by measuring the photon-energy-dependent intensity of a Bragg reflection and then applying the Kramers-Kronig (principal value) dispersion relations,

$$f'(E) = \frac{2}{\pi} P \int_0^\infty dE' E' f''(E')/(E'^2 - E^2),$$
$$\qquad\qquad\qquad\qquad (4)$$
$$f''(E) = -\frac{2E}{\pi} P \int_0^\infty dE' f'(E')/(E'^2 - E^2),$$

to iteratively solve Eq. (1) for f''.[21]

The sample chosen for our Ga and As K-edge DAFS investigation was previously investigated by In K-edge EXAFS.[2] It consisted of a GaAs(001) substrate, a 1000-Å GaAs buffer layer, a 213-Å $Ga_{0.785}In_{0.215}As$ layer, and a 50-Å GaAs cap. Growth temperatures were 580 °C for the buffer layer and 480 °C for the $Ga_{1-x}In_xAs$ layer and cap. The layer was capped with GaAs to protect it from oxidation and to provide a bulklike 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. The actual concentration, thickness, and strain state ($\varepsilon_{\parallel} = -1.52\%$) of the film were determined by specular (004) x-ray diffraction.[2]

X-ray topographs taken at the National Institute of Standards and Technology beamline X23A3 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 (or, that it is in a metastable state).

DAFS data were collected at the National Institute of Standards and Technology beamline X23A2 of the National Synchrotron Light Source using a fixed-exit double-crystal monochromator operating with Si(311) crystals. The data
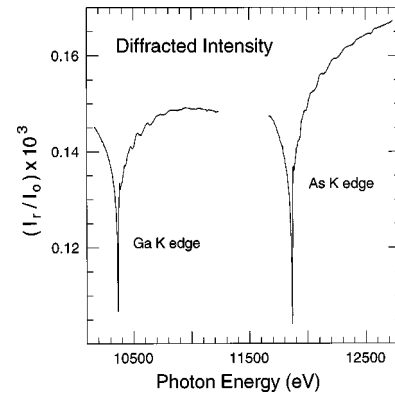

FIG. 1. Normalized intensity of the (004) strained-layer Bragg peak from the pseudomorphic $Ga_{1-x}In_xAs$ alloy on GaAs(001) as a function of photon energy around the Ga and As K edges. The data have been corrected for the background flourescence from the substrate.

were acquired by scanning the photon energy around the vicinity of the Ga (10367 eV) and As (11867 eV) K edges and recording the peak intensity of the (004) strained-layer Bragg reflection from the pseudomorphically grown layer with an Ar filled ionization chamber attached to the 2θ boom of a compact, θ-2θ diffractometer which was operated in the vertical-scattering plane. In order to accurately maintain the diffraction peak at its maximum intensity over the large scan-energy range, the sample angle was slightly oscillated, and a continuous, closed feed-back loop maintained the on-Bragg condition. To correct for the background signal originating from the substrate Ga and As fluorescence emission (which was $\sim 10\%$ of the magnitude of the diffracted peak intensity), background absorption scans were collected with the sample θ set 0.5° below the strained-layer Bragg peak; this background signal was subtracted from the on-peak data. The data were normalized to the incident flux as measured with an N_2 filled ionization chamber upstream of the diffractometer. To account for the different ionization cross sections of Ar and N_2, a bare transmission scan (no sample) was recorded after the DAFS data were collected; the data were then normalized by the measured energy-dependent ratio of Ar and N_2. Because the film is so thin, 213 Å, no absorption correction was applied to the data. EXAFS from InAs and GaAs powders (the empirical EXAFS phase and amplitude standards used in the data analysis) were recorded in transmission.

Figure 1 shows the resulting DAFS data from the $Ga_{1-x}In_xAs$ strained layer in the vicinity of the Ga and As K edges. Note the relatively small reflectivity of the layer ($I_r/I_0 \sim 10^{-4}$). The cusps in the intensity which occur at the Ga and As K edges are due primarily to the real part of the resonant correction to the Ga and As scattering factors.

In order to obtain the Ga and As K-edge fine structure from the strained layer, Eq. (1) was iteratively solved for f'' using initial values provided by theoretical Cromer-Liberman functions,[22] and the Kramers-Kronig transform. Once the absorption curves were generated, standard EXAFS analysis; i.e., spline-background subtraction and normalization to the edge step, resulted in the k-weighted fine structure that is shown in Fig. 2 (Ga K edge) and Fig. 3 (As K edge). These data are compared to the EXAFS recorded from crystalline GaAs (Fig. 2), and crystalline GaAs and InAs (Fig. 3),
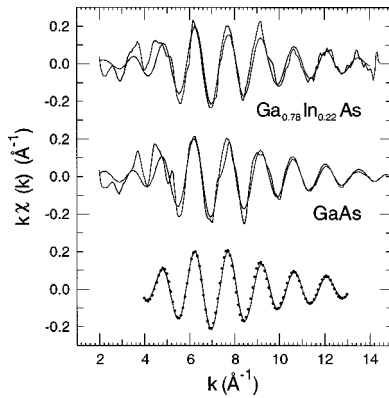
FIG. 2. k-weighted Ga K-edge fine structure from the pseudomorphic $Ga_{1-x}In_xAs$ alloy on GaAs(001) deduced from the DAFS data shown in Fig. 1. The data are compared to their Fourier-filtered first-shell contributions which contain only Ga-As bonds. Also shown is the Ga K-edge EXAFS of the GaAs standard. The lower portion of the figure compares the best fit to the filtered data from the layer (see text).

together with their Fourier-filtered first-shell contributions. The lower portions of each figure show the best fits to the strained-layer data by the EXAFS model function $k\chi(k)$, where

$$k\chi(k) = N|f(k)|\sin[2kr + \phi(k)], \quad (5)$$

using the appropriate phase, $\phi(k)$, and amplitude, $|f(k)|$, functions derived from the bulk GaAs and InAs standards. In the fits, only N, the coordination number(s), and r, the bond length(s), were varied. For the Ga K-edge data, the fits were performed using Ga-As bonds, whereas the fits to the As K-edge data were performed using both In-As and Ga-As bonds. The mixed coordination around the As atoms is due to alloying that occurs on the cation sublattice rather than on the anion sublattice for this pseudobinary, zinc-blende alloy. Table I shows the bond lengths determined from the fits.[23,24] We have also included the strained-layer In-As bond length determined by the In K-edge EXAFS study;[2] the resulting statistically averaged bond lengths are also shown. The strained-layer Ga-As bond lengths determined *independently*
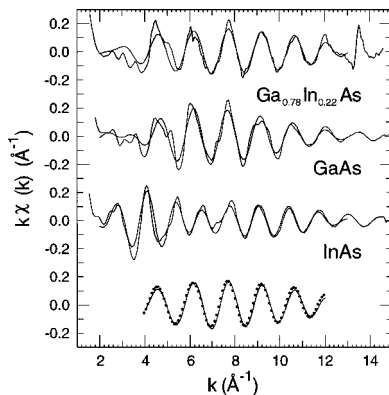
TABLE I. DAFS determination of the Ga-As and In-As bond lengths in the pseudomorphic $Ga_{1-x}In_xAs$ alloy on GaAs(001) together with the EXAFS determination (Ref. 2) of the In-As bond length. Also shown are the statistically averaged bond lengths resulting from both studies.

Ga K-edge DAFS	
Ga-As (Å)	2.440 ± 0.007
As K-edge DAFS	
Ga-As (Å)	2.444 ± 0.006
In-As (Å)	2.529 ± 0.024
In K-edge EXAFS	
In-As (Å)	2.581 ± 0.004
Averaged bond lengths	
In-As (Å)	2.580 ± 0.004
Ga-As (Å)	2.442 ± 0.005

from the Ga and As K-edge DAFS data closely coincide, lending additional credence to our accurate ($k = 14 \text{ Å}^{-1}$) structural determination.

It should be mentioned that while the two Ga-As bond-length measurements are nearly identical, the DAFS determination of the In-As bond length differs significantly from the EXAFS determination.[2] As the concentration of In is relatively low in this sample, the DAFS data recorded at the As K edge is dominated by Ga-As bonds rather than by In-As bonds. (The Ga K-edge DAFS data sample only the Ga-As bonds within the strained layer, and the In K-edge EXAFS data sample only the In-As bonds within the strained layer). Large uncertainties associated with the EXAFS determination of the dilute bond-length component in multishell systems are frequently observed;[25,26] it is also more likely subject to any additional systematic errors introduced by the iterative Kramers-Kronig extraction.[27] In order to evaluate the DAFS sensitivity to this uncertainty, fits to the As K-edge DAFS data were performed with the In-As bond length frozen at the value determined by the EXAFS measurement.[2] The resulting As K-edge DAFS determination of the Ga-As bond length with the In-As bond length frozen
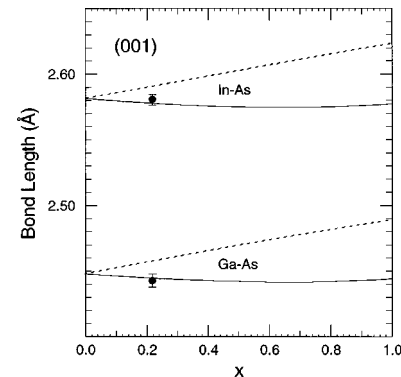

FIG. 3. k-weighted As K-edge fine structure from the pseudomorphic $Ga_{1-x}In_xAs$ alloy on GaAs(001) deduced from the DAFS data shown in Fig. 1. The data are compared to their Fourier-filtered first-shell contributions which contain both Ga-As and In-As bonds. Also shown are the As K-edge EXAFS of the GaAs and InAs standards. The lower portion of the figure compares the best fit to the filtered data from the layer (see text).

FIG. 4. Comparison of the experimentally determined [DAFS and EX-AFS (Ref. 2)] In-As and Ga-As bond lengths in the pseudomorphic $Ga_{1-x}In_xAs$ alloy on GaAs(001) with the results of a recent theoretical random-cluster calculation (Ref. 3). The dashed lines are the calculated cubic (bulk) bond lengths, and the solid lines are the calculated tetragonal (strained) bond lengths. The separation between the bulk and strained bond lengths is the same for In-As and Ga-As bonds; i.e., they are uniformly distorted.

was only 0.004 Å shorter than the value determined when both the In-As and Ga-As bond lengths were floated. Consequently, the primary objective of the DAFS investigation; i.e., the accurate determination of the strained-layer Ga-As bond length, is insensitive to this uncertainty.

In their pioneering study, Mikkelson and Boyce[28] used EXAFS to measure the bond lengths in bulk $Ga_{1-x}In_xAs$ 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 the In-As and Ga-As bond lengths vary linearly with alloy composition, this variation is only about a quarter (~ 0.04 Å) of the natural bond-length difference between bulk InAs ($r_{InAs}^0 = 2.623$ Å) and bulk GaAs ($r_{GaAs}^0 = 2.448$ Å).

Using the accurate fitted data of Mikkelson and Boyce,[28,29] the In-As and Ga-As bond lengths in a bulk (cubic) $Ga_{1-x}In_xAs$ alloy with In content 21.5% are $r_{InAs} = 2.596$ Å and $r_{GaAs} = 2.455$ Å, respectively. The In-As bond length measured in the strained layer, $r'_{InAs} = 2.580 \pm 0.004$ Å, is significantly shorter ($\Delta r_{InAs} = -0.016 \pm 0.004$ Å) than its bulk-alloy value. In fact, it is even shorter than the In-As bond length measured by Mikkelson and Boyce[28] in the dilute-alloy limit: $r_{InAs} = 2.588$ Å for $x = 0$. Similarly, the Ga-As bond length measured in the strained layer, $r'_{GaAs} = 2.442 \pm 0.005$ Å, is also significantly shorter ($\Delta r_{GaAs} = -0.013 \pm 0.005$ Å) than its bulk-alloy value. In fact, it is even shorter than the Ga-As bond length in bulk GaAs: $r_{GaAs}^0 = 2.448$ Å. Consequently, we conclude that both the In-As and Ga-As strained-layer bond lengths are compressed ($\Delta r = -0.015 \pm 0.003$ Å) from their bulk alloy values due to the external in-plane compressive strain imposed on the layer by the substrate. (Note that the corresponding *bond-length* strain is approximately one third of the external in-plane *epitaxial* strain: $\Delta r/r \sim 1/3\varepsilon_\parallel$.)

To compare these experimental results with theory, Fig. 4 shows the results of a recent random-cluster calculation of the bond lengths in strained $Ga_{1-x}In_xAs$ alloys grown coherently on GaAs(001).[3] The results of the calculation for both bulk-alloy (cubic) bond lengths and strained-alloy (tetragonal) bond lengths are shown. The calculated cubic bond lengths closely follow the bulk-alloy bond-length measurement of Mikkelson and Boyce;[28] the largest deviation from the bulk measurement occurs in the dilute $x = 0$ limit of the In-As bond length: 2.582 Å theoretical versus 2.588 ± 0.005 Å experimental. Likewise, the calculated tetragonally distorted bond lengths intercept the experimentally determined strained-layer bond lengths which differ significantly from their bulk values.

Clearly, the external strain imposed on the layer by the substrate opposes the natural bond-length distortions due to alloying (the positive slope of the nearly perfectly parallel bulk lines). In fact, the tetragonally distorted In-As and Ga-As bond lengths are uniformly contracted from their bulk-alloy values by an amount that increases monotonically with In composition. As in the case of the bulk bond lengths, the strained-alloy bond lengths follow nearly perfectly parallel curves despite the different lengths and force constants of In-As and Ga-As bonds.[30] The nonlinear behavior (bowing) of the strained-bond lengths has been attributed to the different elastic constants of InAs and GaAs.[3] (The bulk bond lengths appear as linear, parallel functions of composition due to Vegard's law and the fact that the radial-force constants of InAs and GaAs do not deviate by a large amount.) Consequently, this experiment demonstrates that the bond lengths in strained-layer semiconductors deviate significantly from their bulk-alloy values, and the deviations are uniform functions of the epitaxially induced strain.

In conclusion, we have performed a diffraction anomalous fine-structure study of the bond lengths in a strained $Ga_{1-x}In_xAs$ alloy grown coherently on GaAs(001). Excellent agreement is found with a random-cluster calculation that predicts equal, compositionally dependent distortions of the In-As and Ga-As bond lengths from their bulk-alloy values.

[1] L. D. Landau and E. M. Lifshitz, *Theory of Elasticity* (Pergamon Press, Oxford, 1970).
[2] J. C. Woick *et al.*, Phys. Rev. Lett. **79**, 5026 (1997).
[3] J. C. Woicik, Phys. Rev. B **57**, 6266 (1998).
[4] M. G. Proietti *et al.*, J. Cryst. Growth **127**, 592 (1993).
[5] M. Tabuchi *et al.*, J. Appl. Phys. **77**, 143 (1995).
[6] M. G. Proietti *et al.*, J. Appl. Phys. **78**, 6574 (1995).
[7] J. C. Woicik *et al.*, Phys. Rev. B **43**, 2419 (1991).
[8] M. Matsuura *et al.*, Phys. Rev. B **44**, 3842 (1991).
[9] C. Lamberti *et al.*, Appl. Phys. Lett. **64**, 1430 (1994).
[10] J. C. Woicik *et al.*, Phys. Rev. B **55**, 15 386 (1997).
[11] S. Pascarelli *et al.*, Phys. Rev. B **56**, 1936 (1997).
[12] C. Lamberti *et al.*, J. Appl. Phys. **83**, 1058 (1998).
[13] A. A. Mbaye *et al.*, Phys. Rev. B **37**, 3008 (1988).
[14] A. Amore Bonapasta and G. Scavia, Phys. Rev. B **50**, 2671 (1994).
[15] H. Stragier *et al.*, Phys. Rev. Lett. **69**, 3064 (1992).
[16] J. D. Jackson, *Classical Electrodynamics* (Wiley, New York, 1975).
[17] B. E. Warren, *X-ray Diffraction* (Dover, New York, 1990).
[18] R. W. James, *The Optical Principles of the Diffraction of X-rays* (G. Bells and Sons, London, England, 1950).
[19] S. I. Zabinsky *et al.*, Phys. Rev. B **52**, 2995 (1995).
[20] D. H. Templeton *et al.*, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr. **36**, 436 (1980).
[21] I. J. Pickering *et al.*, J. Am. Chem. Soc. **115**, 6302 (1993).
[22] D. T. Cromer and D. Liberman, J. Chem. Phys. **53**, 1891 (1970).
[23] Error bars on bond lengths correspond to the spread of distances that doubles the residual squared error while the coordination number(s) were allowed to float.
[24] The Ga *K*-edge DAFS data found $N(\text{Ga-As}) = 3.93$. This value is close to the expected value of 4. The As *K*-edge DAFS data found $N(\text{As-Ga}) = 3.71$ and $N(\text{As-In}) = 1.10$. Although the sum of the As coordination numbers, $N(\text{As-Ga}) + N(\text{As-In}) = 4.80$, exceeds 4, the ratio of the coordination numbers, $N(\text{As-Ga})/N(\text{As-In}) = 3.38$, is much closer to the expected value of 3.65 for this alloy composition. Note that the composition of the alloy as estimated from the As *K*-edge DAFS data, $x = N(\text{As-In})/[N(\text{As-In}) + N(\text{As-Ga})] = 0.228$, is also close to the actual composition of the alloy, $x = 0.215$.
[25] D. B. Aldrich *et al.*, Phys. Rev. B **50**, 15 026 (1994).
[26] J. C. Woicik *et al.*, Phys. Rev. B **57**, 14 592 (1998).
[27] A complete *ab initio* calculation of the DAFS spectra using FEFF (Ref. 19) is currently being performed. If successful, this analysis will not rely on the use of the Kramers-Kronig iterative solution, for the real and imaginary parts of the scattering amplitude can be calculated explicitly as functions of the alloy composition and of the In-As and Ga-As bond lengths.
[28] J. C. Mikkelson, Jr. and J. B. Boyce, Phys. Rev. Lett. **49**, 1412 (1982).
[29] Y. Cai and M. F. Thorpe, Phys. Rev. B **46**, 15 879 (1992).
[30] The radial-force constant of InAs is only $\sim 15\%$ softer than the radial-force constant of GaAs, whereas the angular-force constant of InAs is $\sim 39\%$ softer than the angular-force constant of GaAs.