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Bond lengths in strained semiconductor alloys

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The bond lengths in a series of strained, buried $Ga_{1-x}In_xAs$ thin-alloy films grown coherently on GaAs(001) and InP(001) substrates have been determined by high-resolution extended x-ray absorption fine-structure and diffraction anomalous fine-structure measurements. Comparisons with random-cluster, valence-force field calculations demonstrate that the external in-plane epitaxial strain imposed by pseudomorphic growth opposes the natural bond-length distortions due to alloying.

Keywords: Bond Length, Strain.

1. Introduction

When a macroscopic body is acted upon by external forces, its deformations are accurately described by the theory of elasticity (Landau & Lifshitz, 1970). Implicit to the macroscopic theory of elasticity are the microscopic, atomic-scale structural distortions that cooperatively form the macroscopic response of the body (Harrison, 1980). Strained-layer semiconductor alloys offer a unique opportunity to study these microscopic distortions quantitatively because the coherent growth condition between the substrate and lattice-mismatched layer imposes an external in-plane biaxial strain on the layer that can be accurately characterized by bulk sensitive techniques such as x-ray diffraction (Woicik et al., 1991).

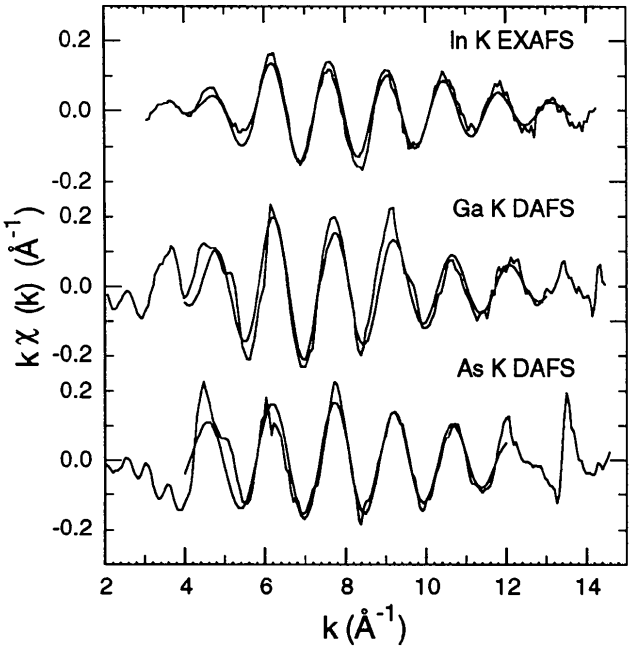

Figure 1
k-weighted In K-edge EXAFS, Ga K-edge DAFS, and As K-edge DAFS from the pseudomorphic $Ga_{1-x}In_xAs$ alloy on GaAs(001). The *raw* data are plotted with best fits to their Fourier-filtered first-shell contributions.

2. Experiment

In order to determine the effect that strain has on bond lengths, we have performed high-resolution extended x-ray absorption-fine structure (EXAFS) and diffraction anamolous-fine structure (DAFS) measurements on a well-characterized, buried 213 Å thick $Ga_{0.785}In_{0.215}As$ thin-alloy film grown coherently on GaAs(001). Figure 1 shows the *raw* k-weighted In K-edge EXAFS data (Woicik et al., 1997) together with the Ga and As K-edge DAFS data (Woicik et al., 1998). Because the lattice constant of InAs (6.0584 Å) is larger than the lattice constant of GaAs (5.6532 Å), this layer possesses an in-plane, bilateral epitaxial strain $\varepsilon_{//}$ = -1.52 %, as determined by x-ray diffraction. The layer was capped with GaAs to protect it from oxidation and to provide a bulk termination of its structure.

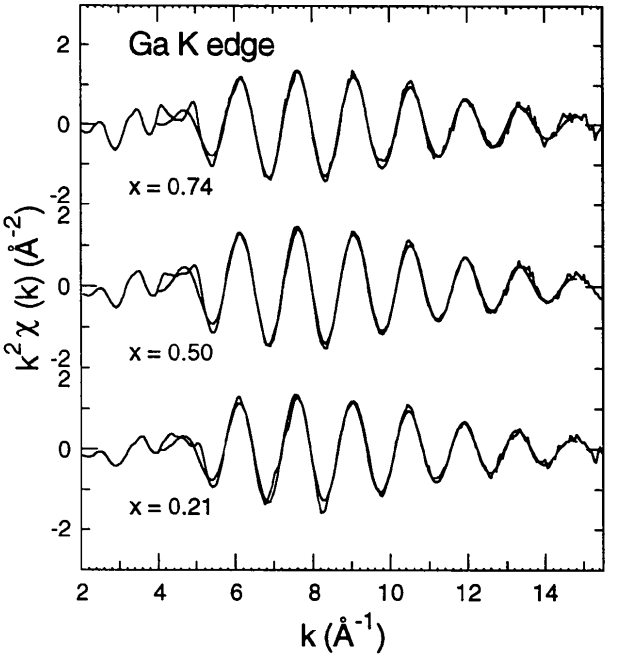

Figure 2
k^2-weighted Ga K-edge EXAFS from the pseudomorphic series of $Ga_{1-x}In_xAs$ alloys on InP(001). The *raw* data are plotted with best fits to their Fourier-filtered first-shell contributions which contain Ga-As bonds.

The DAFS data have been extracted from resonant, energy-dependent diffraction intensity measurements of the (004) strained-layer Bragg peak by an iterative Kramers-Kronig algorithm. The use of DAFS to measure the Ga-As bond length within the buried heterostructure circumvents the film/substrate common-element problem because the strained-layer Bragg peak is separated in reciprocal space from the substrate peak. These data are plotted with best fits to their Fourier-filtered first-shell contributions which contain In-As (In K-edge EXAFS), Ga-As (Ga K-edge DAFS), and both In-As and Ga-As (As K-edge DAFS) bonds using the empirical phase and amplitude standards deduced from the EXAFS of pure crystalline InAs and GaAs powders.

Also performed were high-resolution Ga and As K-edge EXAFS measaurements of the bond lengths within

pseudomorphically strained, buried $Ga_{1-x}In_xAs$ thin-alloy films grown coherently on InP(001) (Woicik et al., 1998). This alloy/substrate system is uniquely suited to the issue of bond-length strain because $Ga_{1-x}In_xAs$ is lattice matched to InP for x = 0.53. Consequently, the effects of both tensile and compressive strain may be studied for the same alloy/substrate system by varying only the alloy composition: $\varepsilon_{//}$ = +3.8 % for x = 0 and $\varepsilon_{//}$ = -3.1 % for x = 1. Figures 2 and 3 show the *raw* k^2-weighted Ga and As K-edge EXAFS from the pseudomorphic series plotted with best fits to their Fourier-filtered first-shell contributions again using the empirical phase and amplitude standards deduced from the EXAFS of pure crystalline InAs and GaAs powders.

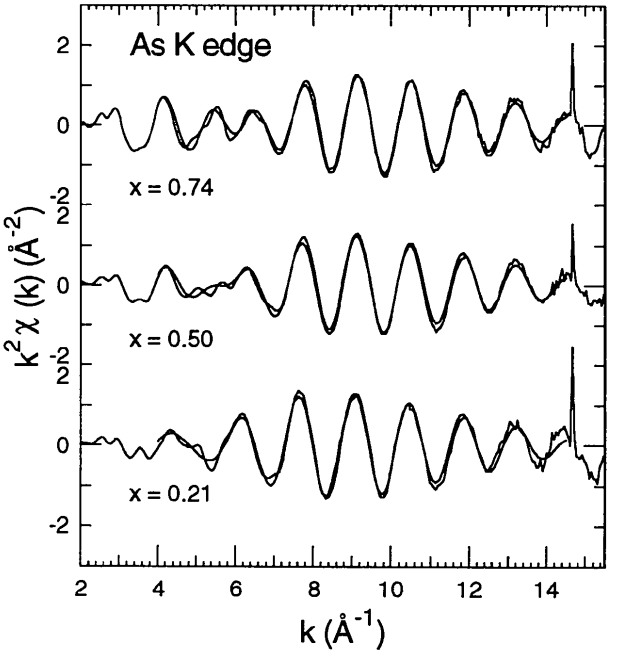

Figure 3
k^2-weighted As K-edge EXAFS from the pseudomorphic series of $Ga_{1-x}In_xAs$ alloys on InP(001). The *raw* data are plotted with best fits to their Fourier-filtered first-shell contributions which contain In-As and Ga-As bonds.

3. Theory

To compare our bond-length measurements with theory, we have performed theoretical, random-cluster calculations of the bond lengths in pseudomorphically strained $Ga_{1-x}In_xAs$ layers grown coherently on GaAs(001) (Woicik, 1998) and InP(001) (Woicik et al., 1998). In short, the calculations were performed by relaxing the atoms within sixteen-bond $Ga_{4-j}In_jAs$ clusters (j=0,1,2,3,4) embedded in virtual-crystal media. The bond lengths were calculated as functions of media composition x, and then they were statistically averaged according to the Bernoulli distribution. The Keating, 1966 valence-force field, generalized for the pseudobinary alloy, was used to model the interactions within the clusters:

$$\Delta E = \Sigma_s \, 3/8 \, \alpha_s \, (r_s^2 - r_{s,o}^2)^2 / r_{s,o}^2$$

$$+ \Sigma_{s<t} \Sigma_t \, 3/8 \, \beta_{s,t} \, (r_s \cdot r_t - r_{s,o} \cdot r_{t,o})^2 / r_{s,o} \cdot r_{t,o} .$$

The α_s's are the two-body radial-force constants and the $\beta_{s,t}$'s are the three-body angular-force constants, taken from (Martins & Zunger, 1984). The r_s's are the bond vectors between atoms with equilibrium distance $r_{s,o}$; i.e., the natural In-As and Ga-As bond lengths. The sums run over all bonds within the clusters.

4. Results

Figure 4 shows the resulting theoretical In-As and Ga-As bond lengths calculated for cubic clusters (dashed lines) and for clusters that have been tetragonally distorted in compliance with macroscopic-elastic theory (Hornstra & Bartels, 1978) for pseudomorphic growth on GaAs(001) and InP(001) substrates (solid lines). The calculated cubic bond lengths closely follow the bulk bond-length measurements of Mikkelson & Boyce, 1982. Likewise, the tetragonally distorted bond lengths accurately predict the strained bond-length determinations of the present EXAFS and DAFS studies (error bars were estimated by doubling the residual chi-squared error). The calculation for growth on the InP(001) substrate is also consistent with recent measurements by Romanato et al., 1998. Note that the calculated bulk and strained bond lengths coincide for the lattice-matched, zero-strain compositions.

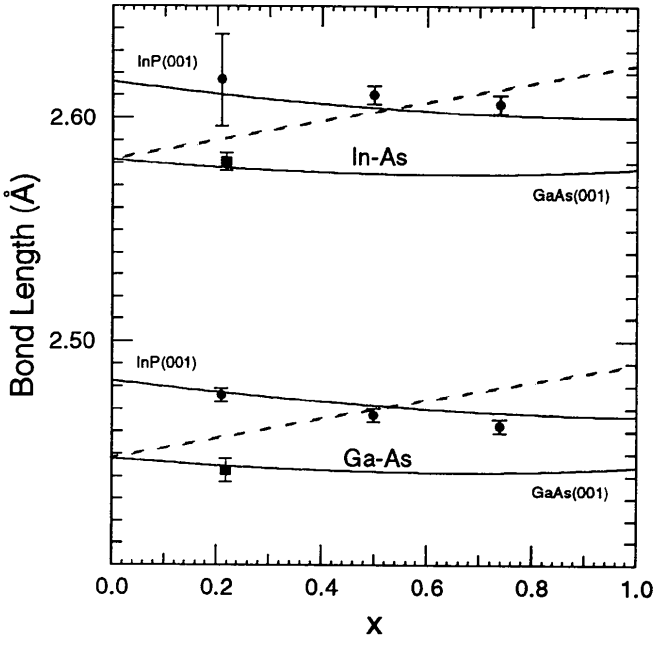

Figure 4
Comparison of the experimentally determined EXAFS and DAFS In-As and Ga-As bond lengths in pseudomorphic $Ga_{1-x}In_xAs$ alloys grown on GaAs(001) (squares) and InP(001) (circles) with the results of the theoretical, random-cluster calculations. The dashed lines are the calculated cubic (bulk) bond lengths, and the solid lines are the calculated tetragonal (strained) bond lengths. Results for the different substrates are as indicated. Note that the bulk and strained bond lengths coincide for the lattice-matched, zero-strain compositions.

5. Discussion

Clearly, the external strains imposed on the layers by the substrates oppose the natural bond-length distortions due to alloying (the positive slope of the parallel bulk lines). The nonlinear behavior (bowing) of the strained bond lengths (theoretically evaluated) is due to the different elastic constants of InAs and GaAs, which gives a nonlinear dependence to the $Ga_{1-x}In_xAs$ lattice spacing perpendicular to the alloy/substrate interface. Additionally, as for the case of the bulk bond lengths, the strained bond lengths are found to follow nearly perfectly parallel curves (for the same substrate) despite the different lengths and force constants of In-As and Ga-As bonds. Consequently, the bond lengths in strained-layer semiconductor alloys deviate significantly from their bulk-alloy values, and the deviations are found to be uniform functions of the epitaxially induced strain.

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