Random-cluster calculation of bond lengths in strained-semiconductor alloys

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The bond lengths in tetragonally distorted, pseudobinary $Ga_{1-x}In_xAs$ alloys on GaAs(001) and GaAs(111) have been calculated within a random-cluster approximation utilizing a valence-force field. For growth on the (001) substrate, the In-As and Ga-As bond lengths are uniformally contracted from their bulk-alloy values by an amount that increases monotonically with x. For growth on the (111) substrate, strain splits the bonds: bonds along [111] are less contracted than bonds along $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}1]$; however, their average behavior is similar to the (001) case. [S0163-1829(98)00211-2]

When a thin semiconductor film is grown coherently on a substrate that differs in lattice constant, the lattice constant of the film perpendicular to the interface responds to the distortion of its lattice constant parallel to the interface. Although macroscopic-elastic theory[1] has been known to accurately describe the *macroscopic* distortions of epitaxial films,[2] the *microscopic* distortions, from which the macroscopic distortions follow, have remained elusive despite numerous studies aimed at determining the exact local atomic geometry within these technologically relevant materials: In some cases, the strain has been reported to have ''remarkable'' effects on bond lengths,[3,4] while others have found little or no effect.[5–10] Even the counterintuitive result that bonds are longer in layers under compression has been reported.[11]

In order to address the issue of bond-length strain theoretically, we have performed a random-cluster calculation of the In-As and Ga-As bond lengths in tetragonally distorted, pseudobinary $Ga_{1-x}In_xAs$ alloys grown on GaAs(001) and GaAs(111). This model-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, the In-As and Ga-As bond lengths in bulk $Ga_{1-x}In_xAs$ alloys have been studied in detail,[12] and their compositional dependence is the best quantified of all semiconductor alloys. Second, the lattice constants of InAs and GaAs differ by a full 7%; therefore, effects that may arise due to the different natural-bond lengths of InAs (2.623 Å) and GaAs (2.448 Å) should be more evident in $Ga_{1-x}In_xAs$ than in other alloy systems that are more closely lattice matched.

Our random-cluster calculation is a simplification of the quasichemical approach developed in Ref. 13. The bond lengths in 16-bond $Ga_{4-j}In_jAs$ clusters ($j=0,1,2,3,4$) are calculated separately as a function of composition x, and then statistically averaged to determine the In-As and Ga-As bond lengths. Fluctuations in cluster population due to chemical effects are ignored. We believe that this approximation is valid for the calculation of the bond lengths because chemical effects are small at elevated growth temperatures,[13] and because extended x-ray absorption fine structure has found no evidence to the contrary.[12]

Figure 1 shows the 16 bond cluster used in our calculation. The central atom is As, which occupies the anion sites, and the j In atoms and the $4-j$ Ga atoms randomly occupy the cation sites. In order to treat the clusters statistically, the clusters must be weakly interacting with their external medium.[14] This is achieved by bonding the 12 peripheral As atoms of the cluster to 24 external virtual-crystal atoms (not shown) that are fixed at their virtual-crystal sites.

The Keating valence-force field,[15] generalized for the pseudobinary alloy, was chosen to model the interactions within the clusters:

$$\Delta E=\sum_s \tfrac{3}{8}\alpha_s\frac{(\mathbf{r}_s^2-r_{s,0}^2)^2}{r_{s,0}^2}+\sum_{s<t}\sum_t \tfrac{3}{8}\beta_{s,t}\frac{(\mathbf{r}_s\cdot\mathbf{r}_t-\mathbf{r}_{s,0}\cdot\mathbf{r}_{t,0})^2}{r_{s,0}r_{t,0}}. \tag{1}$$

The α_s's are the two-body radial-force constants, and the $\beta_{s,t}$'s are the three-body angular-force constants. The $\mathbf{r}_s$'s are the bond vectors between atoms with equilibrium distance $r_{s,0}$; i.e., the natural-bond lengths. The sums run over all of the bonds within the cluster. α and β for InAs and GaAs were taken from Ref. 16. For cases where the bond angle links a Ga and an In atom, β was taken to be the average of the InAs and GaAs values. In order to reduce the excess rigidity imposed by the statistical constraint, β was set equal to zero for interactions that link an internal-cluster atom with an external-medium atom.

Input to the program was handled in the following manner. A dimensionless position matrix of the diamond structure, $D_{n,i}$, was written in the Cartesian coordinates $\mathbf{x}_1=[100]$, $\mathbf{x}_2=[010]$, and $\mathbf{x}_3=[001]$ for the 17 cluster atoms

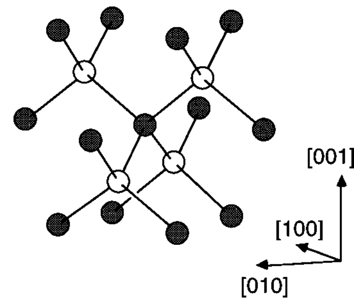

FIG. 1. Sixteen-bond pseudobinary $Ga_{4-j}In_jAs$ cluster with a central As atom. The 12 peripheral As atoms are more weakly bonded to 24 external virtual-crystal atoms (not shown) that are fixed at their virtual-crystal sites. Relaxation of the atoms within the cluster produces the cluster bond lengths.

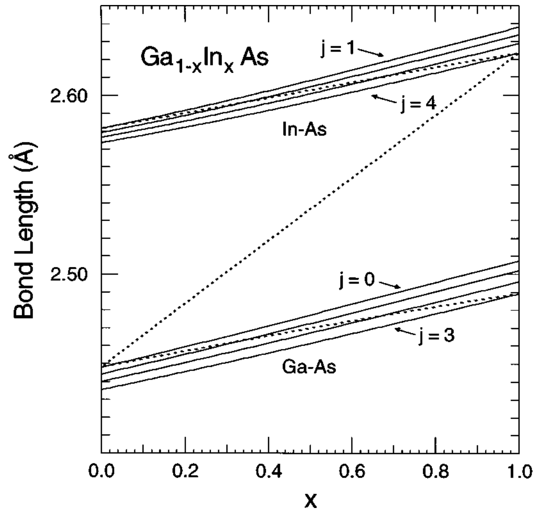

FIG. 2. In-As and Ga-As bond lengths in $Ga_{4-j}In_jAs$ clusters as a function of medium composition x. j is the number of In atoms per cluster. The In-As and Ga-As bond lengths in cubic $Ga_{1-x}In_xAs$ (dashed lines) are obtained by statistically averaging the cluster-bond lengths. Also shown is their virtual-crystal average.

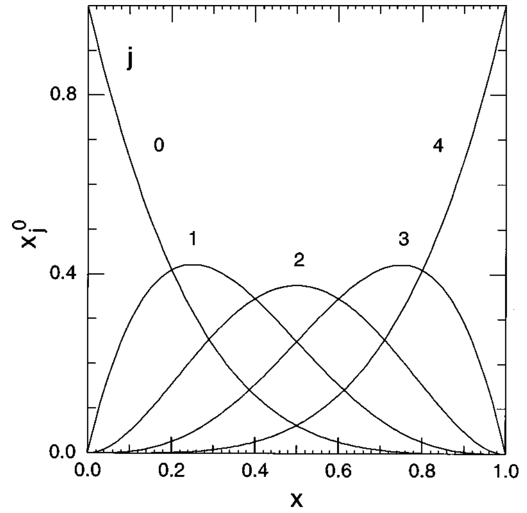

FIG. 3. Random-cluster population x_j^0.

and the 24 medium atoms. The 41 rows of D were taken to be the dimensionless position vectors, $\mathbf{p}_n$, of each atom. $\mathbf{p}_1 = [000]$, $\mathbf{p}_2 = [111]$, etc. The initial virtual-crystal position matrix was then calculated for each composition from

$$P_{n,i} = D_{n,i} a_i / 4. \tag{2}$$

$\mathbf{a}$ is the [111] lattice vector in the Cartesian basis: $\mathbf{a} = [a_x a_y a_z]$. For bulk (cubic) $Ga_{1-x}In_xAs$, $a_x = a_y = a_z = a_{\mathrm{VCA}}$; a_{VCA} is given by Vegard's law:

$$a_{\mathrm{VCA}} = x\, a_{\mathrm{InAs}} + (1-x) a_{\mathrm{GaAs}}. \tag{3}$$

After the initial input was constructed, the 17 atoms within the cluster were allowed to relax until an energy minimum, as determined by Eq. (1), was found. (No 1×10^{-6} Å step of any of the 51 independent coordinates resulted in a lower energy.)

Figure 2 shows the resulting cluster-bond lengths plotted as a function of medium composition x. Note that for a given cluster, the addition of an In atom into the cluster from the medium reduces both the In-As and Ga-As bond lengths. It may therefore be surmised that it is the external influence of the medium on the clusters that dominates the net bond-length behavior.

Once the bond lengths within the individual clusters have been calculated, they must be statistically averaged. Because our clusters are assumed random, their population for a given x is determined by the Bernoulli distribution

$$x_j^0 = g_j x^j (1-x)^{4-j}. \tag{4}$$

$g_j = \binom{4}{j}$ is the cluster degeneracy equal to 1,4,6,4,1 for $j = 0,1,2,3,4$ In atoms. x_j^0 is plotted in Fig. 3. Note that the most probable cluster for a given In content is the one that most closely matches the concentration of the medium.

The In-As and Ga-As bond lengths are then calculated from

$$\langle r \rangle = \sum_j r_j x_j^0 n_j \Bigg/ \sum_j x_j^0 n_j. \tag{5}$$

n_j is the corresponding number of cations in each cluster.

The statistically averaged bond lengths are plotted in Fig. 2 (dashed lines) along with their virtual-crystal average. The statistical weighting is evident. Excellent agreement is found with experiment;[12] the largest deviation from the measurement occurs in the dilute $x = 0$ limit of the In-As bond length (2.582 Å theoretical; 2.588 ± 0.005 Å experimental).

Having demonstrated that our approach accurately produces the cubic bond lengths, we turn our focus to the strained alloys. Because we have written the initial virtual-crystal position matrix in terms of the basis vectors of the diamond lattice, it is a straightforward exercise to extend our computational method to the strained alloys. All that is necessary is to tetragonally distort the basis vectors of the diamond lattice in compliance with macroscopic-elastic theory.[17]

For growth on the (001) substrate,[2] the fractional strain perpendicular to the interface, $\varepsilon_\perp = (a_\perp - a_f)/a_f$, is determined by the fractional strain parallel to the interface, $\varepsilon_\parallel = (a_\parallel - a_f)/a_f$:

$$\varepsilon_\perp = -2(c_{12}/c_{11})\varepsilon_\parallel. \tag{6}$$

a_f is the bulk lattice constant of cubic $Ga_{1-x}In_xAs$ given by Vegard's law, c_{11} and c_{12} are the concentration-weighted averages of the macroscopic-elastic constants of InAs and GaAs,[2] and $a_\parallel = a_{\mathrm{GaAs}}$ is the coherency condition. The perpendicular lattice constant of the film, $a_\perp$, is then determined. Consequently, the bond lengths in the tetragonally distorted alloy may be obtained by changing the basis vector $\mathbf{a}$ from $a_x = a_y = a_z = a_{\mathrm{VCA}}$ to $a_x = a_y = a_\parallel$, and $a_z = a_\perp$. Additionally, strain reduces the degeneracy of the $j = 2$ cluster. [The energy is slightly lower if the two In atoms reside in the same (004) plane.]

The results of the (001) calculation are shown in Fig. 4. For comparison, we also plot (dashed lines) the bulk-alloy bond lengths. Relative to their bulk-alloy values, the strained In-As and Ga-As bond lengths are contracted by nearly the same amount for a given composition x despite the inequivalent In-As and Ga-As bond lengths. The slight upturn or

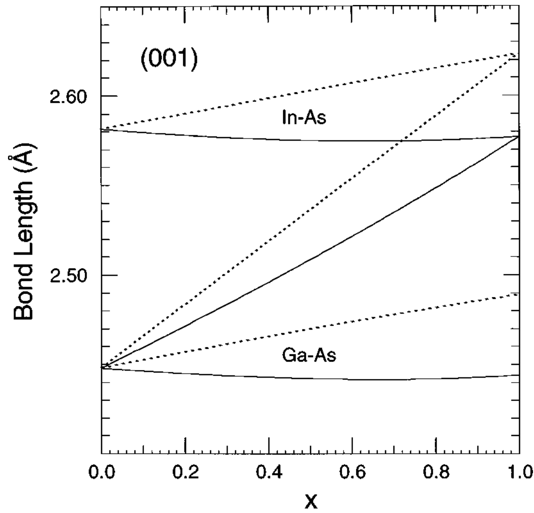

FIG. 4. In-As and Ga-As bond lengths in tetragonally distorted $Ga_{1-x}In_xAs$ on GaAs(001) and their virtual-crystal average. Also shown are the cubic bond lengths (dashed lines) from Fig. 2.

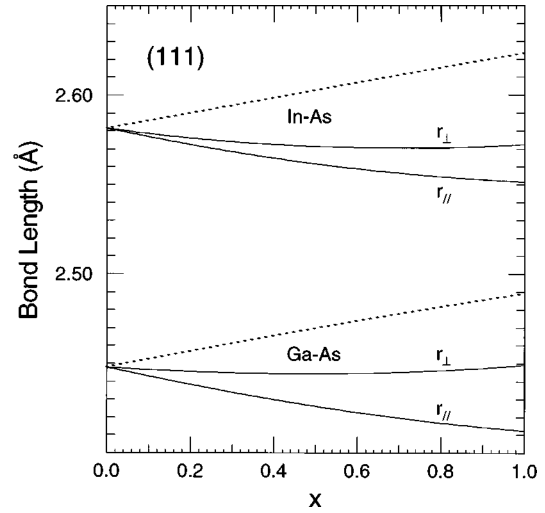

FIG. 5. In-As and Ga-As bond lengths in tetragonally distorted $Ga_{1-x}In_xAs$ on GaAs(111). $r_\perp$ denotes bonds along [111], and $r_\parallel$ denotes bonds along $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}1]$. Also shown are the cubic bond lengths (dashed lines) from Fig. 2.

bowing of the bond lengths with increasing x is due to the larger c_{12}/c_{11} value of InAs relative to GaAs; i.e., it is harder to compress In-As bonds than it is to compress Ga-As bonds.

To our knowledge, there has been only one previous theoretical calculation of the bond lengths in strained-$Ga_{1-x}In_xAs$ alloys. By performing *ab initio* total-energy and Hellmann-Feynman force calculations within the local-density approximation, it was concluded that the bond-length strain in $Ga_{1-x}In_xAs$ ($x \sim 0.25$) grown on GaAs(001) was accommodated primarily by a contraction of the *longer* In-As rather than the *shorter* Ga-As bond.[18] Because these calculations were performed for selected, periodic structures, the random nature of the alloy was explicitly neglected. As the uniform nature of the bond-length distortion has recently been established by experiment,[19] it would be interesting to compare the present random-cluster calculation based on the *semiempirical* valence-force field, which predicts equal contractions of the In-As and Ga-As bond lengths, to an *ab initio* calculation that properly accounts for the randomness of the alloy.

The calculation for the (111) growth is nearly as straightforward; however, the dimensionless position matrix must first be rewritten in a [111] basis. This is achieved through the transformation

$$\mathbf{p}_n' = \sum_i (\mathbf{p}_n \cdot \mathbf{x}_i')\mathbf{x}_i', \tag{7}$$

where we have chosen the new basis $\mathbf{x}_1' = [1\bar{1}0]/\sqrt{2}$, $\mathbf{x}_2' = [\bar{1}12]/\sqrt{6}$, and $\mathbf{x}_3' = [111]/\sqrt{3}$. Equation (6) is modified for the (111) growth as well[2] ($C = 2c_{44} - c_{11} + c_{12}$):

$$\varepsilon_\perp = -2(c_{12} - C/3)/(c_{11} + 2C/3)\varepsilon_\parallel. \tag{8}$$

As in the (001) case, the degeneracy of the $j=2$ cluster is reduced, but now so are the degeneracies of the $j=1$ and $j=3$ clusters. Additionally, because the crystal is uniaxially expanded along the [111] bond direction, strain splits the bonds: Those along [111] are less contracted than those along $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}1]$.

The results of the (111) calculation are shown in Fig. 5. We have indicated bonds along [111] by $r_\perp$ and those along $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}1]$ by $r_\parallel$. Note that the average In-As and Ga-As bond lengths,

$$r' = (r_\perp + 3r_\parallel)/4, \tag{9}$$

are similar to the (001) case, but they are more contracted due to the modification of Eq. (6).

In conclusion, we have performed a random-cluster calculation of the bond lengths in strained $Ga_{1-x}In_xAs$ alloys grown on GaAs(001) and GaAs(111). The calculation was adapted from the calculation of the bulk (cubic) bond lengths by tetragonally distorting the basis vectors of the diamond lattice in compliance with macroscopic-elastic theory. For growth on the (001) substrate, the In-As and Ga-As bond lengths exhibit a uniform contraction which increases monotonically with x despite the inequivalent In-As and Ga-As bond lengths. Bowing is attributed to the larger c_{12}/c_{11} value of InAs relative to GaAs. For growth on the (111) substrate, strain is found to split the bonds: Those along [111] are less contracted than those along $[\bar{1}1\bar{1}]$, $[1\bar{1}\bar{1}]$, and $[\bar{1}\bar{1}1]$; however, their average behavior is similar to the (001) case.

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