Indium-Indium Pair Correlation and Surface Segregation in InGaAs Alloys

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In-In pair correlations and In surface segregation in $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys are studied by first-principles total-energy calculations. By calculating the substitution energy of a single In atom, we find that the near-surface energetics explains the observed In segregation on InGaAs(001)-$\beta 2(2 \times 4)$ surfaces. Indium surface segregation further enhances the In site selectivity, thus the long-range ordering. We find that the [110] and [001] In-In pair correlations are repulsive and nearly isotropic in bulk but are highly anisotropic near the (001) surface. The sign of the [110] In-In interaction energies vs the distance from the surface is oscillatory. These findings explain the recent puzzling cross-sectional ×-STM results.

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Interest in spontaneous ordering [1], composition modulation [2,3], and segregation [4,5]in III-V alloys raised the question of the type of atom-atom interactions that exist at the surface of such alloys. Attractive (repulsive) effective interactions would lead to correlation (anticorrelation) in the association of like atoms. A number of recent cross-sectional scanning-tunneling-microscopy (×-STM) experiments [6–8] have attempted to measure such In-In atomic correlations in (001)-orientation molecular-beam epitaxy (MBE)-grown $\mathrm{In}_x\mathrm{Ga}_{1-x}\mathrm{As}$ alloys. In these experiments one images and then counts the number of consecutive atoms of a given type along the principal directions [001], [110], and $[\bar{1}10]$. Zheng *et al.* [6] reported a strong tendency of two to three In atoms to cluster along the [001] direction in $\mathrm{In}_{0.2}\mathrm{Ga}_{0.8}\mathrm{As}$ alloys MBE grown at $T = 813$ K on the GaAs(001) substrate. One may attempt to understand this correlation tendency by evaluating the difference in total energy of a nearest-neighbor (nn) pair relative to a well-separated pair

$$J_{\mathrm{nn}} = E(\text{In-In}; R = \text{nn}) - E(\text{In-In}; R = \infty). \quad (1)$$

To estimate the interaction energy one might first ignore chemical effects (e.g., charge transfer) and evaluate E from atomistic elasticity, e.g., using the valence-force-field (VFF) [9] method. Table I shows J_{nn} for the In-In pair inside bulk GaAs and near the (unreconstructed) surface. We see that elasticity predicts that two nearest-neighbor In atoms placed along the [001] direction will indeed attract each other: by -3.8 meV/pair if they are in the bulk, and by -7.4 meV/pair if they are near the unreconstructed GaAs(001) surface. This suggests that In-In nn pairs could form along the [001] direction as observed by Zheng *et al.* [6]. More recent experiments [7,8] considering more dilute InGaAs alloys also grown on (001) GaAs, via MBE, however, disagree with Ref. [6]: In the first experiment, Pfister *et al.* [7]reported a complete lack of [001] In-In correlation in $\mathrm{In}_{0.12}\mathrm{Ga}_{0.88}\mathrm{As}$ alloys grown at $T = 813$ K. In the second experiment, Chao *et al.* [8] found a total absence of the [001] nn correlation in $\mathrm{In}_{0.05}\mathrm{Ga}_{0.95}\mathrm{As}$ alloy grown at $T = 798$ K, and a strong anticorrelation for the [110] direction, i.e., there are *fewer* In-In pairs in this direction than would be granted by random distribution [10]. This anticorrelation implies $J_{\mathrm{nn}}^{[110]} > 0$, which contradicts the elasticity calculation for the unreconstructed surface yielding $J_{\mathrm{nn}}^{[110]} < 0$. Thus, there are contradictions (i) between elasticity theory and experiments, regarding the direction ([001] vs [110]) and sign (attractive vs repulsive) of In-In correlations, and (ii) among different experiments, even though the only noticeable difference among them is the In concentration. Since simple elastic models (such as the VFF) do not consider atomic-scale chemical effects or surface reconstruction, we will next treat the problem using the first-principles approach, which includes both effects.

We calculate the substitution energy of an In atom in GaAs and the In-In nn pair interaction energy in various near-surface positions. The "In substitution energy" $E_{\mathrm{sub}}(h\alpha)$ is the energy required to take an In atom from its bulk reservoir (having the energy μ_{In}), replacing a Ga atom at site $h\alpha$ in GaAs, and moving the replaced Ga atom to its bulk reservoir (having the energy μ_{Ga}):

$$E_{\mathrm{sub}}(h\alpha) = E_{\mathrm{tot}}(\mathrm{GaAs{:}In}_{h\alpha}) - E_{\mathrm{tot}}(\mathrm{GaAs}) - \mu_{\mathrm{In}} + \mu_{\mathrm{Ga}}, \quad (2)$$

where E_{tot} is the local-density-approximation (LDA) [11,12]total energy, h is the layer index, and α is the atomic site index within a layer (Fig. 1). The "In-In nn pair interaction energy" J_{nn} is the difference in energy of placing one In atom at site $h\alpha$ and another at site $h'\beta$, relative to the well-separated limit:

$$J_{\mathrm{nn}}(h\alpha, h'\beta) = [E_{\mathrm{tot}}(\mathrm{GaAs{:}In}_{h\alpha}\mathrm{In}_{h'\beta}) + E_{\mathrm{tot}}(\mathrm{GaAs})] - [E_{\mathrm{tot}}(\mathrm{GaAs{:}In}_{h\alpha}) + E_{\mathrm{tot}}(\mathrm{GaAs{:}In}_{h'\beta})], \quad (3)$$

where each total-energy term is relaxed separately with respect to the unit cell volume and the cell-internal atomic coordinates. We find a number of unexpected effects in the In-In pair interaction energy due both to the chemical nature of the atomic interaction and to the reconstruction and dimerization of the (001) surface (Table I): (i) In

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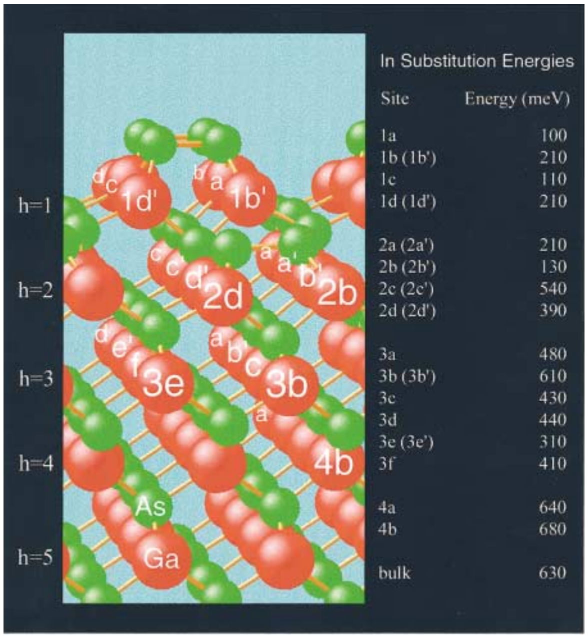
TABLE I. Calculated In-In nearest-neighbor interaction energies J_{nn} (meV/atom pair) using pure elasticity theory (via VFF [9]in a 1728-atom supercell), and first-principles LDA (which includes both elastic and chemical effects and is denoted "Total"). Surface calculations are done both for the 1×1 unreconstructed ("UR") model, as well as for the $\beta 2(2 \times 4)$ reconstructed ("R") structure. If $J_{\mathrm{nn}} < 0$ we expect clustering of In-In ("correlation"), while if $J_{\mathrm{nn}} > 0$ we expect anticorrelation (i.e., fewer pairs than random statistics). $J_{\mathrm{nn}} \approx 0$ implies randomness. We also indicate the sign of J_{nn} from experiments [6–8].

	Theory						
	Bulk		Surface		Experiment		
	Elastic	Total	Elastic (UR)	Total (R)	Ref. [8]	Ref. [7]	Ref. [6]
$J_{\mathrm{nn}}^{[001]}$	-3.8	$+27$	-7.4	~ 0	0	0	⋯
$J_{\mathrm{nn}}^{[110]}$	$+6.2$	$+34$	-10.3	$h = 1; -49$ $h = 3; +59$ $h \geq 5; +34$	+		

bulk GaAs, the LDA calculated J_{nn} is largely repulsive, irrespective of direction. (ii) Near the reconstructed surface, the In-In interaction energy $J_{\mathrm{nn}}^{[001]}$ ("out of plane") is vanishingly small, implying an absence of In-In correlation (i.e., randomness) in this direction, in agreement with Refs. [7,8]. (iii) The In-In interaction energy $J_{\mathrm{nn}}^{[110]}$ ("in plane") for the [110] nn pair is strongly layer dependent: In the first $h = 1$ surface layer, $J_{\mathrm{nn}}^{[110]}$ is attractive ($\sim$4 times larger than the elasticity value in Table I). This predicts an $h = 1$ In-In clustering which awaits for experimental testing. In contrast, in the third $h = 3$ subsurface layer, $J_{\mathrm{nn}}^{[110]}$ is repulsive (an order of magnitude larger than that given by the elasticity theory for bulk), in agreement with the In-In anticorrelation observed by Ref. [8]. We thus predict a highly anisotropic, subsurface In-In interaction. This anisotropy is a consequence of surface reconstruction. We will also explain the (001) In-In clustering reported in Ref. [6] as a combined effect of the anisotropy of the J_{nn}'s and the high In concentration used in Ref. [6]: Once the In concentration exceeds the percolation threshold (which places a fraction of the In atoms as mutual nn pairs), the strong repulsiveness along [110] leads to the depletion of In-In pairs from the [110] direction at the expense of increasing the number of such pairs along the "soft" directions, such as the [001].



In Substitution Energies

Site	Energy (meV)
1a	100
1b (1b')	210
1c	110
1d (1d')	210
2a (2a')	210
2b (2b')	130
2c (2c')	540
2d (2d')	390
3a	480
3b (3b')	610
3c	430
3d	440
3e (3e')	310
3f	410
4a	640
4b	680
bulk	630

FIG. 1 (color). A perspective of the GaAs(001)-$\beta 2(2 \times 4)$ surface indicating the layer index h and the site index α, along with the absolute indium substitution energy E_{sub} relative to the reservoirs of bulk metals.

Our total-energy calculations of Eqs. (2) and (3) use the plane-wave-basis pseudopotential method within the LDA [11,12]. Nonlocal pseudopotentials are generated by the scheme of Troullier and Martins [13]in the separable form of Kleinman and Bylander [14]. We use the Ceperley-Alder exchange-correlation functional [15], as parametrized by Perdew and Zunger [16], a kinetic energy cutoff of 10 Ry, and a single point in the surface Brillouin zone, $\mathbf{k} = (0, 0, 0)$. An artificial, periodic slab geometry is used to mimic isolated surfaces: It includes a 2×4 surface cell and nine atomic GaAs(001) layers normal to the surface and a vacuum region equivalent to seven atomic layers. The bottom of the slab is passivated by Li atoms so that the back surface will be electrically inactive with a minimum strain due to atomic relaxations at the back surface. The equilibrium atomic positions are obtained by relaxing all atoms (except the bottom-most As and the passivation layers) until the Hellmann-Feynman forces are smaller than 3 mRy/bohr. The lattice constant of the substrate used in the calculation is that of GaAs ($= 5.64$ Å [17]). Calculations of the In-In pair interaction in bulk GaAs are done using a 96 atom cell, relaxing all the atoms. Unit cell volume changes corresponding to the Vegard's rule have negligible effect on E_{sub} and J_{nn} (e.g., $J_{\mathrm{nn}}^{[001]}$ changes from 27 to 23 meV and $J_{\mathrm{nn}}^{[110]}$ changes from 34 to 42 meV). The above calculation parameters are found to give well-converged results for the atomic positions, the substitution, and the In-In nn-interaction energies along [001] and [110]. Numerical accuracies of the calculations are ± 0.05 eV for absolute substitution energy E_{sub} and ± 0.01 eV for $J_{\mathrm{nn}}(h\alpha, h'\beta)$. The relatively large error in E_{sub} is due mainly to the inequivalent k-point sampling for the bulk and the surface.

Figure 1 shows the GaAs(001)-$\beta 2(2 \times 4)$ surface, predicted by LDA calculations [18] and subsequently confirmed by experiment under MBE conditions [19]. On the top surface layer, there are two As-As dimers along the $[\bar{1}10]$ direction and two missing dimers. We label the cation sites according to their layer index h and the intralayer site index α. For $h = 1$, there are two missing Ga atoms. The remaining six atoms are labeled as a, $b(b')$, c, and $d(d')$, where b and b' and d and d' are equivalent due to mirror symmetry centered in the $(1a\text{-}1c)$ plane. For $h \geq 2$, there are no missing atoms. For $h = 2$, there are four inequivalent sites (i.e., $2a$ to $2d$). For $h = 3$, there are six inequivalent sites labeled from $3a$ to $3f$. For $h = 4$, three relevant sites ($4a$, $4b$, and $4c$) are labeled.

Single In substitution.—The calculated absolute substitution energies $E_{\mathrm{sub}}(h\alpha)$ are given in Fig. 1. We calculate $E_{\mathrm{sub}}(h\alpha)$ by assuming μ_{Ga} and μ_{In} in Eq. (2) at their respective upper bounds, i.e., at the energies of orthorhombic Ga and tetragonal In. In thermal equilibrium, metallic precipitates would form should μ_{Ga} or μ_{In} exceed these values. We see that replacing Ga of GaAs by In and moving away the replaced Ga at this set of chemical potentials *costs* energy. The cost is large (0.63 eV per In substitution) in the bulk (= the deep interior of a surface) but diminishes as one gets closer to the surface (smaller h). This implies *surface enhanced solubility* of indium in GaAs: For $h = 1$ on the average, E_{sub} is 0.47 eV lower than $E_{\mathrm{sub}}^{\mathrm{bulk}} = 0.63$ eV. However, E_{sub} quickly reaches the bulk value with increasing distance h from the surface. It is interesting to note that E_{sub} is also sensitive to the site index α: e.g., the variance of E_{sub} for the different sites α within $h = 2$ is almost 0.4 eV but is reduced to less than 0.1 eV for $h = 4$. The exceptionally large variance for $h = 2$ is a consequence of As-As surface dimerization which creates alternative tensile and compressive site strains [5]: The In atom is larger than the Ga atom and thus the In atom favors the sites $2a(2a')$ and $2b(2b')$ that are *in between* dimer rows (tensile strain) over the sites $2c(2c')$ and $2d(2d')$ that are *under* dimer rows (compressive strain). This site selectivity promotes atomic ordering near the surface and is consistent with the observation of the CuPt structure in GaInAs alloys, as suggested by previous theoretical studies [5,20].

The differences of the calculated substitution energies of the various In sites in Fig. 1 can be used to estimate the relative In occupation probabilities (σ_i) via a Boltzmann distribution function. At $T = 300$ K, 96% of the In atoms occupy only the $1a$, $1c$, $2b$, and $2b'$ sites: $\sigma_{1a} = 38.8\%$, $\sigma_{1c} = 29.7\%$, and $\sigma_{2b} = \sigma_{2b'} = 27.5\%$. As T increases, other sites in the $h = 1$ and 2 layers become populated. However, indium population in the compressive-strain sites $2c(2c')$ and $2d(2d')$ is rare and all the $h \geq 3$ sites are largely unpopulated. For example, at $T = 798$ K, the amount of In atoms below the second layer is less than 3%. Thus, In atoms are strongly surface segregated as noted in photoemission experiments [4]. The site occupation discussed here refers only to the relative site preference. Once all the low-energy sites are occupied, additional In atoms will have no low-energy sites to go but diffuse into bulk GaAs. The time scale of the bulk diffusion is, however, orders of magnitude longer than the surface and subsurface diffusions. So this may not happen during actual MBE growth [21]. On the other hand, In is completely miscible in GaAs during melt growth at $T > 650$ K [22].

Substitution of In-In pairs.—Figure 2 shows the In-In pair interaction energy, J_{nn}. We see that:

(i) In the bulk, the in-plane ([110]) and out-of-plane ([001]) nn-pair interaction energies are both repulsive with $J_{\mathrm{nn}}^{[110]} = +34$ and $J_{\mathrm{nn}}^{[001]} = +27$ meV/pair. In contrast, elasticity theory predicts an attractive interaction for the [001] bulk nn-pair (Table I). The LDA values are consistently larger than those given by the elasticity theory due to the chemical effects. In the bulk, the In-In repulsion in the [001] direction is weaker than the [110] direction, because [001] is a softer crystal direction, and because the In-In separation along [001] is larger by a factor of $\sqrt{2}$.

(ii) At the surface, J_{nn} along [001] is slightly attractive for the $1a$-$3a$ pair and slightly repulsive for the $1b$-$3b$ pair. Thus, on average, the surface $J_{\mathrm{nn}}^{[001]}$ is negligible. The $1b$-$3b$ pair repulsion is a combined effect of the short-range chemical effect and surface reconstruction. Without this effect, the $1a$-$3a$ and $1b$-$3b$ pairs would be identical and attractive, as shown in Table I. Tersoff *et al.* [23] has predicted using continuum elasticity theory that two quantum dots would attract each other along the [001]. This is valid only if the spacing between the dots is large compared to the atomic spacing.

(iii) At the surface, the [110] interaction is repulsive and not a monotonic function of the distance h from the surface. In the bulk ($h \geq 5$), J_{nn} is positive, +34 meV/pair. Moving towards the surface, J_{nn} first increases and peaks

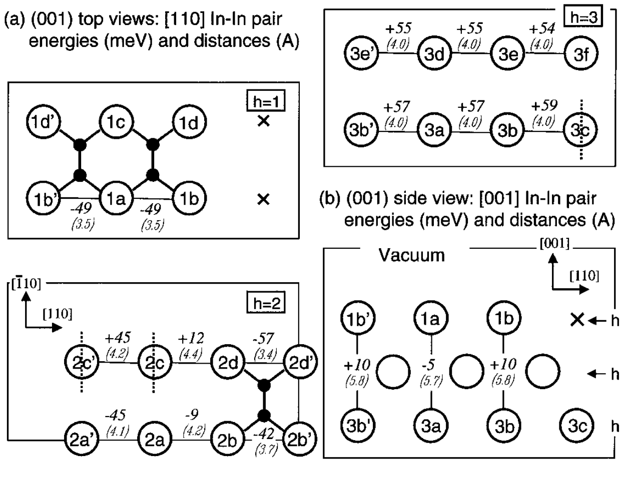


FIG. 2. (a) Three top ($h = 1$, 2, and 3) and (b) one side views of the (001) surface showing In-In nearest-neighbor pair $J_{\mathrm{nn}}(h\alpha, h'\beta)$ [Eq. (3)] and the corresponding pair distance (in parenthesis). Open circles are the Ga/In sites while the filled circles are the As sites. The crosses indicate missing atoms and the vertical dashed lines in (a) ($h = 2$ and 3) indicate the positions of the As-As dimers three layers above.

at +59 meV/pair at $h = 3$. For $h = 2$, however, only the nn pairs involving the strained sites directly under the As-As dimers (i.e., $2c$ and $2c'$) remain repulsive, while others become strongly attractive. Thus, elasticity theory misses the nonmonotonic behavior of J_{nn} while predicting correctly the reversal of the sign of J_{nn} at $h = 2$. For $h = 1$, $J_{\mathrm{nn}}^{[110]}$ is attractive. To test experimentally the attractive interaction on the $h = 1$ surface layer, one needs to perform an *in situ* STM study of the growth surface, not by post-growth ×-STM. So far, we are not aware of such a study.

Our results summarized in Table I provide a theoretical understanding of the In-In pair correlations in InGaAs alloys. Because most of the In atoms are segregated to a few monolayers near the surface, only near-surface layers ($h \leq 3$) determine the In distribution in the MBE growth. The observation of the repulsive [110] In-In interaction in Ref. [8] could be explained by the positive J_{nn} for the first buried layer ($h = 3$ and part of $h = 2$). The predicted absence of the [001] In-In correlation in the InGaAs alloys is consistent with the observation of Pfister *et al.* [7] for 12% In and by Chao *et al.* [8] for 5% In. In general, the predicted large anisotropy in the interaction energy J_{nn}'s could cause during growth a reorientation of the nn In-In pairs from the "hard" [110] direction to the soft [001] direction [24]. However, at the dilute limit, such an effect is negligible since only a few In atoms are nearest neighbors to each other (especially along the [110] direction, where due to the large repulsive J_{nn} the In atoms will keep away from each other via subsurface diffusion). The situation changes when the In concentration x_{In} exceeds the percolation threshold x_c (= 19.8% for the fcc sublattice [25]). Above this threshold, one cannot avoid creating a substantial number of In atoms that are mutual nearest neighbors. Thus, the preferred alignment of the nn In-In pairs along the soft [001] direction becomes increasingly important. This provides an explanation to the observation of (001) In-In orientation reported by Zheng *et al.* [6] where $x_{\mathrm{In}} = 20\% > x_c$.

In summary, we find that most of the In atoms segregate to the two topmost surface layers. In-In nn interaction near the surface shows large anisotropy, contrasting to the almost isotropic and repulsive interactions in the bulk. The [110] In-In nn pairs are mostly attractive for $h = 1$ and 2 but become large and repulsive for $h = 3$ and beyond, while the [001] In-In nn pairs have vanishing interactions and are thus expected to be random. These anisotropic interactions will lead to a redistribution of the In-In pairs at In concentrations exceeding the percolation threshold. From these results, we resolve the controversy in the previous ×-STM studies regarding In-In nearest-neighbor pair correlation functions.

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