Determination of 2D Pair Correlations and Pair Interaction Energies of In Atoms in Molecular Beam Epitaxially Grown InGaAs Alloys

Kuo-Jen Chao and Chih-Kang Shih*

Department of Physics, University of Texas, Austin, Texas 78712

D. W. Gotthold and B. G. Streetman

Department of Electrical and Computer Engineering, University of Texas, Austin, Texas 78712
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Intra- and interlayer atom-atom correlations in molecular beam epitaxially grown dilute InGaAs alloys were studied using cross-sectional scanning tunneling microscopy. By imaging individual chemical constituents we construct a large ensemble of "atom maps" from which two-dimensional In-In pair correlation functions were deduced. We found a total absence of interlayer pair correlation along [001] and a strong negative correlation for the nearest neighbor (nn) pair along [110], corresponding to a repulsive interaction energy of 0.1 eV for the nn In pairs along [110]. In addition, a weak long-range oscillation in the correlation function along [110] is observed. [S0031-9007(97)04728-5]

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Since the first observation of ordered structure in AlGaAs alloys [1] the subject of order vs disorder in substitutional semiconductor alloys has attracted intensive research activities. This interest arises not only for the intriguing influence of ordering on the electronic structure but also for the conceptual challenges in understanding the atomic processes that lead to the formation of ordered alloys. Experimentally, observations of the ordered structures in substitutional alloys have been reported in many other III-V compounds [2]. Recent work has made further progress in kinetic manipulations of the spontaneous ordering and the compositional modulations, aiming for a novel band structure engineering technique [3]. Theoretically, much effort has focused on using first principle calculation of atomic scale energetics from which thermodynamic parameters can be deduced and the order-disorder phase diagram can be predicted [4,5]. However, despite such intensive investigations, atomistic understanding of order-disorder alloy formation mechanism remains unclear. Obviously the experimental determination of real-space atom correlations and atomic interaction energies will be critically important to shed new light onto this problem.

In this Letter, we report real-space investigations of In-In correlations in dilute $In_xGa_{1-x}As$ alloys grown using molecular beam epitaxy (MBE). Cross-sectional view scanning tunneling microscopy (XSTM) was used to study both *intra-* and *inter*layer In-In pair correlations during the epitaxial process. From these correlations we quantitatively deduce the effective pair interaction energy. Such quantitative information serves to test the predictability of first principle calculations of atomic scale energetics. In addition, it provides important input parameters for theoretical calculations of order-disorder phase diagrams. This usage of an experimentally measured pair correlation function to find the pair interaction energy was developed using field-ion microscopy (FIM)

to deduce the pair interaction energies of adatoms on metal surfaces [6], and more recently with an STM to determine the Coulomb interaction between charged surface defects [7]. However, these previous studies have assumed an isotropic medium, while in the case discussed here, the inherent anisotropy of inter- vs intralayer correlations invalidates such an isotropic medium approach.

The samples studied are MBE-grown $In_xGa_{1-x}As$ alloys on GaAs (001) substrates. While samples with a composition ranging from $x = 0.02$ to $x = 0.20$ were studied, only the $x = 0.05$ samples were investigated in detail to provide statistically significant information of pair correlations. The $In_{0.05}Ga_{0.95}As$ layers were grown at a thickness of 200 Å (below the critical thickness) on GaAs substrate at a temperature of 525 °C. The samples were cleaved *in situ* in STM chamber (base pressure $< 4 \times 10^{-11}$ torr) to create "cross-sectional surfaces" that expose the *buried* epitaxial structure. The atomic configurations of the epitaxial structure along the time line of the growth history are studied layer by layer, noting that only the projection to one cross-sectional surface is revealed.

Shown in Figs. 1(a) and 1(b) are empty-state and filled-state STM images of $In_{0.02}Ga_{0.98}As$. As shown by Zheng *et al.* [8] and Pfister *et al.* [9], the bright spots in the empty-state image are due to an increase in the density of empty states concentrated around a cation atom and represent the location of the surface In atoms. Weaker bright spots are also observed in the filled state image where the electron density concentrates around the As atoms. Following Pfister *et al.* [9], this effect is due to a geometric size effect: The In-As bond length is longer than the Ga-As bond length, thus As atoms bonded to the second layer In atoms are raised slightly. Thus the empty- and filled-state images together can be used to identify the location of first and second layer In atoms on the cross-sectional surface. Because of their larger signature, only the surface In atoms are used to study
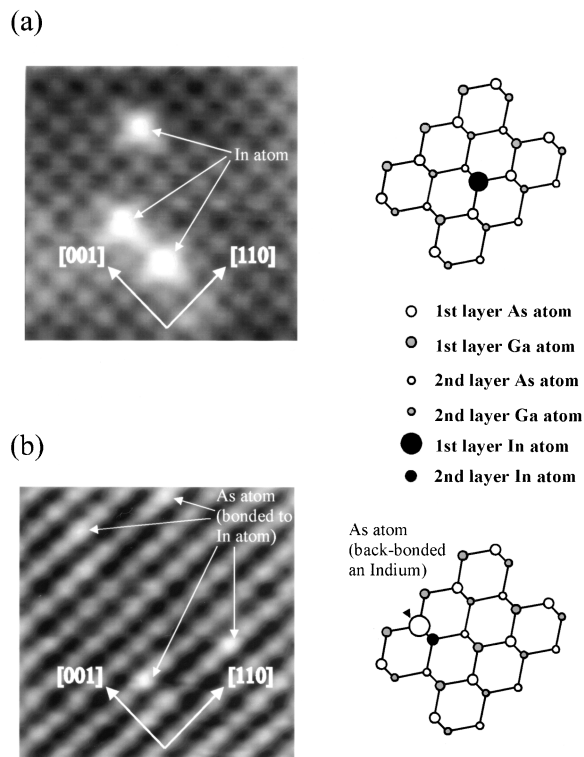
(a)

(b)

FIG. 1. (a) A 50 Å × 50 Å empty-state image of $In_{0.02}Ga_{0.98}As$ acquired at a sample bias of 2.0 V and a tunneling current set to below 0.1 nA (left). A schematic diagram on the right shows the relative position of an Indium atom on the top surface (right). (b) A 50 Å × 50 Å filled-state image of $In_{0.02}Ga_{0.98}As$ acquired at a sample bias of −20 V and a tunneling current of 0.1 nA.

the In-In correlations in the alloys. In addition, among the two inequivalent cleaved surfaces, (110) and ($\bar{1}$10), we only concentrated on the ($\bar{1}$10) surface to maintain the consistency of our determination of 2D correlations [10].

Shown in Fig. 2(a) is a 175 Å by 175 Å empty-state image of $In_{0.05}Ga_{0.95}As$ acquired at a sample bias of +1.9 V. The local bright spots represent the positions of the surface In atom position. One notes from this image that at 5% In concentration, the long-range influence of local electronic structure due to In substitution starts to overlap. This long-range influence on the topography can be removed in the "curvature image" shown in Fig. 2(b) which allows for a better identification of individual In atoms. On this image, which has 31 sites along [001] and 43 sites along [110], we have identified 67 surface In atoms, corresponding precisely to an InAs concentration of 5%. Images like this provide an "In-atom map" in the GaAs matrix. One can also view this as a "dilute lattice gas" problem for In atoms in the GaAs matrix. To obtain a statistically significant basis for the construction of two-dimensional (2D) In-In correlation functions, hundreds of such "atom maps" were used.

The 2D pair correlation function $C(\mathbf{r}_1, \mathbf{r}_2)$ is defined as follows: $C(\mathbf{r}_1, \mathbf{r}_2) = P(\mathbf{r}_1, \mathbf{r}_2)/R^*(\mathbf{r}_1, \mathbf{r}_2)$. Here $P(\mathbf{r}_1, \mathbf{r}_2)$ is the probability of finding two atoms at $\mathbf{r}_1$ and $\mathbf{r}_2$, respectively, and $R^*(\mathbf{r}_1, \mathbf{r}_2)$ is the same probability for
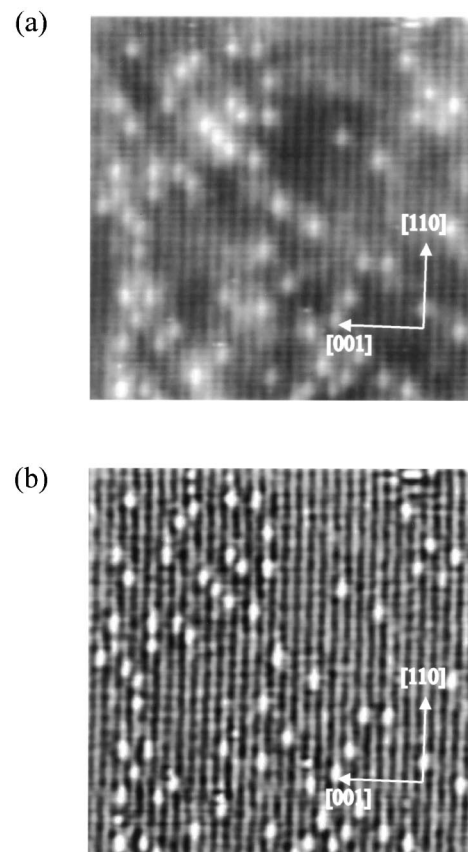
(a)

(b)

FIG. 2. (a) A 175 Å × 175 Å empty-state image of $In_{0.05}Ga_{0.95}As$ acquired at a sample bias of 2.6 V and a tunneling current set to below 0.1 nA. Brighter round dots indicate locations of In atoms on the surface. (b) This image is the curvature-enhanced image of (a). The location of each In atom on the surface is clearly identified.

a theoretically random distribution. On each image like Fig. 2(a) we choose a region of 30 × 30 sites which has an average of 45 In atoms, corresponding to an ensemble of 990 In-In pairs. As the typical width of InGaAs layers is 35 unit cells, the choice of 30 × 30 sites avoids the nonideal InGaAs/GaAs interface. The theoretically random pair distribution is obtained using a computer generated random distribution of the same number of In atoms on 30 × 30 grids, and by averaging more than 10 000 ensembles of these random pairs, corresponding to a statistical base of $10 × 10^6$ pairs.

Shown in Fig. 3(a) is the 2D In-In pair correlations using a statistical base of more than 140 "atom maps." The vertical scale is $-\ln[C(\mathbf{r}_1, \mathbf{r}_2)]$ where the positive number represents a negative correlation (or anticorrelation). Statistically, the most significant term is the negative correlation of the neighboring site along the [110] direction [11]. On the other hand, the correlation or anticorrelation along the growth direction of [001] is completely absent. Shown in Fig. 3(b) are the 1D projections along these two major axes. A large number of ensembles are necessary to obtain statistically meaningful pair correlations. An important question arises as to how large is enough, namely, "how much of the observed deviation from the ideal
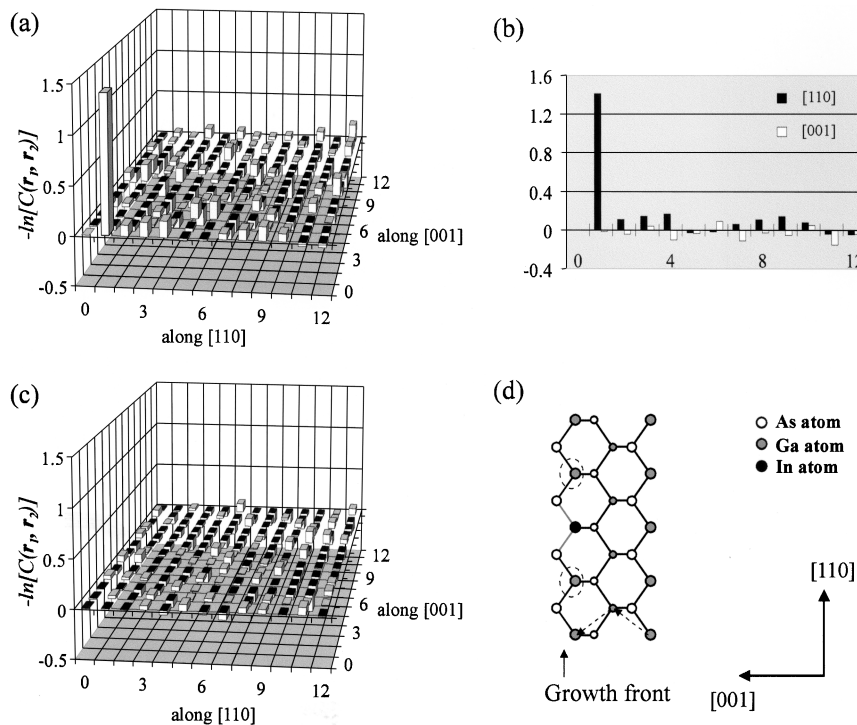
FIG. 3. (a) Two-dimensional In-In pair correlation functions with the x-y axes along the [110] and [001] directions, respectively. The vertical scale is presented in negative log values. (b) The pair correlation function along [001] and [110] directions are plotted separately. Note the strong correlation/anticorrelation along the [110] and the lack of correlation along [001]. (c) The simulation result of random fluctuation of two-dimensional pair correlation due to finite ensembles. (d) A schematic diagram of showing the strain effect due to the presence of In atom in the GaAs lattices. Since the In-As bond length is longer, the bond to the As atom is strained and distorts from the perfect lattice site. Bonding to a second In atom (marked by the dashed circles) in a neighboring site will cause much more strain at this As site. The dashed arrows indicate that the position vector of the neighboring cation-cation along [001] consists of the combination of position vectors along $\frac{1}{2}[101]$ and along $\frac{1}{2}[\bar{1}01]$.

random distribution can originate from the random fluctuation due to finite sampling?" This fluctuation is estimated by using a finite ensemble of randomly generated pair distributions, $R_n(\mathbf{r}_1, \mathbf{r}_2)$, in the same area and comparing the result to the theoretical distribution, $R^*(\mathbf{r}_1, \mathbf{r}_2)$. Shown in Fig. 3(c) is the plot of $-\ln[R_n(\mathbf{r}_1, \mathbf{r}_2)/R^*(\mathbf{r}_1, \mathbf{r}_2)]$ where $R_n(\mathbf{r}_1, \mathbf{r}_2)$ is obtained from 128 ensembles of randomly generated pair distributions. As is apparent in the plot, an average of 128 ensembles with 990 In-In pairs in each ensemble gives rise to a statistical fluctuation of no more than 5%–10% (5% fluctuation corresponds to ±0.05 in the log plot). This statistical fluctuation increases at larger pair distances (not shown here), presumably due to the finite size of the sampling area.

Note that these samples were grown using MBE where the surface processes dominate. The lack of correlation along the [001] direction implies that the atomic processes of In atoms in each layer are independent of the In atoms in the other layers. However, a significant negative correlation (or anticorrelation) is observed along the direction parallel to the surface, not surprising for a growth method where surface processes dominate. The anticorrelation indicates nearest neighbor repulsive interactions of In-In pairs along the [110] direction. This anticorrelation can be explained by considering the strain effect as visualized in the schematic shown in Fig. 3(d). On the growth front when an In atom is incorporated in the lattice, the local bond length of In-As is longer than that of the Ga-As bond, producing a compressive strain effect on the neighboring cation sites. This strain effect significantly increases the difficulty for another In atom to be incorporated in these sites which are already under compressive strain.

Because the surface diffusivity of In atoms is very high, short-range local equilibrium is established on a very fast time scale. Furthermore, in the limit of a dilute lattice gas, the pair correlations are dominated by the two-body pair interactions. The combination of local thermal equilibrium and dilute limit allows us to quantitatively determine an effective repulsive pair interaction energy of 0.1 ± 0.01 eV for the nearest neighbor In-In pairs along [110] by using the relation

$$E_I(\mathbf{r}_1, \mathbf{r}_2) = -kT \ln[C(\mathbf{r}_1, \mathbf{r}_2)].$$

However, the lack of correlation for In atoms at different layers does not necessarily imply negligible pair interaction energy along [001]. In this case, the interlayer correlation can be kinetically limited by the deposition rate and the interlayer diffusion. Note that on a cross-sectional surface of (110) or (1̄10), only atoms on every other layer along the [001] direction are present on the surface. The interlayer (or more properly, inter-double-layer) neighboring correlation along [001] has to be established through a combination of two interlayer neighboring correlations along $\frac{1}{2}[101]$ and along $\frac{1}{2}[\bar{1}01]$ [shown as two dashed arrows in Fig. 3(d)].

We do note that our result of the absence of interlayer correlation is in contrast to the result of the strong tendency of In clustering along [001] reported by Zheng et al. [8] for the MBE-grown InGaAs alloys at 20% In concentration. We note that Pfister et al. [9] also reported the lack of In clustering beyond the statistical fluctuation in $In_{0.12}Ga_{0.88}As$ alloys. One possibility is the lack of statistical sampling in Zheng et al. [8]. Another scenario is that in the dilute alloys, only pair interactions are important while in more concentrated alloys, higher

order In-In pair interactions (such as the one through the combination of pair interactions along $\frac{1}{2}[101]$ and along $\frac{1}{2}[\bar{1}01]$) can become more important. Furthermore, the compositional dependent strain field will also influence the outcome of the atomic correlations. This is an open issue only further studies can address.

As the atomic interaction energies ultimately determine the order versus disorder structures of semiconductor alloys, quantitative determinations of such a quantity is important and should have strong bearing on the predictability of the theoretical calculations. We noted that based on a *bulk* calculation, Wei *et al.* [12] have predicted anticlustering of In-In in InGaAs. Although such bulk calculations would not lead to any anisotropy in anticlustering, later work by Bernard *et al.* [13] which included the surface effect did show that the atomic configurations of alloys on the surface is independent of the configurations in the layers beneath the surface. Furthermore, Chen and Sher [14] have reported reduced excess energy of -0.06 eV for a 5-atom cluster with 2 In and 2 Ga atoms surrounding an As atom. While these theoretical calculations do not deal specifically with In-In interactions in the GaAs matrix in MBE or MOCVD (metalorganic chemical-vapor deposition) growth, they do show qualitative consistency with the experimental finding.

In Fig. 3(b) one can also observe a weak oscillation with a periodicity of about six lattice sites in the pair correlations along the $[110]$ direction. The amplitude of this weak oscillation is a factor of 3 larger than the statistical fluctuation estimated in Fig. 3(c). The observation of this oscillation in the pair correlations is rather interesting. In the earlier work of Re adatoms on W(110) surface by Tsong [6], an oscillation of pair correlations was also reported. However, in that case, it was the manifestation of sharp Fermi function in the metallic system which results in the oscillatory behavior of atom-atom interactions similar to the Friedel oscillation [15]. On the other hand, here we are dealing with a semiconductor medium, and therefore the oscillatory behavior of the pair correlation cannot be due to the same reason. Since the $[110]$ direction is also the As-dimer row direction and the typical MBE growth is operated under (2×4)-$c(2 \times 8)$ condition [10], it is likely that the $6\times$ periodicity in the weak oscillation of pair correlations along the $[110]$ is a consequence of the mixture of $4\times$ and $8\times$ periodicities along the As-dimer row. Again, this would also be a manifestation of the surface strain effect.

In summary, we have used cross-sectional STM to study the inter- and intralayer In-In pair correlations in dilute InGaAs alloys. With significant statistical ensembles, we conclude that the In atoms are uncorrelated along the growth direction and strongly anticorrelated for the nearest neighbors along the $[110]$ direction parallel to the growth surface. Within the dilute limit and local thermal equilibrium approximation, we determine, for the first time, an effective repulsive interaction energy of 0.1 eV between nearest In-In pairs along the $[110]$ direction. This repulsive nature can be understood in terms of the strain effect. In addition, a weak long-range oscillation of the pair correlation function along the $[110]$ direction with periodicity of six lattice units is observed.

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*Author to whom all correspondence should be addressed.

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