Interface Segregation and Clustering in Strained-Layer InGaAs/GaAs Heterostructures Studied by Cross-Sectional Scanning Tunneling Microscopy

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Interface roughness due to segregation and clustering has been studied in atomic detail for the first time, using a cross-sectional scanning tunneling microscope and its spectroscopic ability to distinguish In and Ga atoms in GaAs/$In_{0.2}Ga_{0.8}As$/GaAs strained layers. In the $In_{0.2}Ga_{0.8}As$ layers, InAs is found to cluster preferentially along the growth direction with each cluster containing 2–3 indium atoms. Indium segregation induced an asymmetrical interface broadening. The interface of GaAs as grown on $In_{0.2}Ga_{0.8}As$ is found to be broadened to about 5–10 atomic layers, while that of InGaAs on GaAs is about 2–4 layers broad.

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Interface segregation and clustering in alloy materials is one of the fundamental problems in materials science. These phenomena are key in determining the atomic scale structure and roughness of III-V heterostructure interfaces, a subject of intensive studies in the last 20 years [1]. By using a recently developed approach, where scanning tunneling microscopy (STM) is applied in cross section [2], we have studied for the first time the atomic scale details of segregation and clustering of indium in substitutional semiconductor alloys of $In_{0.2}Ga_{0.8}As$ in $In_{0.2}Ga_{0.8}As$/GaAs multiple layers grown by molecular beam epitaxy (MBE). We have distinguished the segregating species by using the spectroscopic capability of STM to determine the local electronic structure [3–5]. This kind of detailed information cannot be obtained by conventional methods including Auger spectroscopy, photoelectron spectroscopy, transmission electron microscopy (TEM) [6], etc., that average over many surface layers parallel or perpendicular to the interface.

Until now, clustering in III/V heterostructures has been studied only by indirect methods such as Raman spectroscopy [7,8]. Segregation has been studied using surface sensitive techniques such as photoelectron spectroscopy *in situ* during epitaxy growth [9] and analyzed by secondary ion mass spectroscopy [10] after growth. STM studies of chemical fluctuations in III-V semiconductor heterostructures have been previously reported by Salemink and co-workers [11].

In this Letter, we report the first direct observation of the spatial distribution of individual indium atoms in GaAs/$In_{0.2}Ga_{0.8}As$/GaAs strained layers. InAs is found to cluster along the growth direction within the $In_{0.2}Ga_{0.8}As$. Indium segregation at the two GaAs/$In_{0.2}Ga_{0.8}As$/GaAs interfaces and the resulting asymmetrical broadening is also studied on an atomic scale. We find that clustering and segregation of indium are the main reasons for the roughness of GaAs/$In_{0.2}Ga_{0.8}As$/GaAs interfaces.

The studies were conducted using STM in cross section in an ultrahigh-vacuum (UHV) environment (8×10^{-11} Torr). The sample is a multiple quantum well structure with three undoped 80 Å thick $In_{0.2}Ga_{0.8}As$ layers as quantum wells, separated by two undoped 100 Å thick GaAs layers as barriers. The 80 Å $In_{0.2}Ga_{0.8}As$ layer thickness is below the critical value so that no dislocations are present and the structure is strained [12]. The sample was grown by MBE at 540 °C on [001] oriented n^+ GaAs substrate. It is exposed for STM studies by cleavage in UHV along the (110) plane, perpendicular to the [001] growth direction. Our home-built STM similar in design to that of Frohn *et al.* [13] allows a precise location of the tip to the multiple layers at the crystal edge of the cleavage (110) plane. The STM tips are electrochemically etched Pt-Rh wires (0.25 mm in diameter), and all images were taken in a constant current mode.

Figure 1 is a 2000 Å×2000 Å STM image of the cleaved (110) surface. The three 80 Å thick $In_{0.2}Ga_{0.8}As$ wells are imaged as the brighter bands running from the bottom left to top right and are separated by two darker GaAs layers. The black and white bands from bottom right to the top left are single atomic steps created by the cleavage. In the constant current mode, the $In_{0.2}Ga_{0.8}As$ region is imaged 0.5 Å higher than the GaAs one at the condition of Fig. 1. This height difference is due to electronic effects and is superimposed on the topography of the stepped surface. Figure 2 shows two 150 Å×120 Å atomic resolution STM images obtained in the smaller regions enclosed by the boxes in Fig. 1. It shows the atomic details of GaAs on InGaAs and InGaAs on GaAs interfaces. The image is taken at positive sample bias, corresponding to electrons tunneling from the tip to the empty states of the sample surface. Since empty states are located preferentially at the group III (cation) sites, the atoms imaged in the GaAs region are gallium and those in the $In_{0.2}Ga_{0.8}As$ region are gallium or indium. A very remarkable feature of this image is the presence of bright

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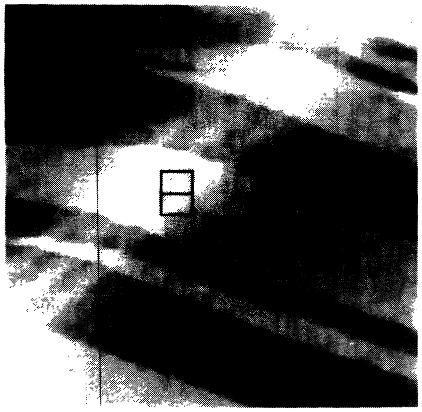

FIG. 1. 2000 Å×2000 Å STM image of GaAs cleaved along the (110) surface. The image is acquired with a tunneling current of 0.5 nA at sample bias of −2.0 V. Three $In_{0.2}Ga_{0.8}As$ multiple quantum wells appear as bright bands running from bottom left to top right, superimposed on the monatomic steps created by the cleavage.

spots in the $In_{0.2}Ga_{0.8}As$ region which are stable for many days after cleavage. These spots are ascribed to indium atoms at the group III lattice sites as discussed below.

Figure 3(a) is an expanded empty state STM image of an area inside $In_{0.2}Ga_{0.8}As$ layer. In this image, the bright spots in Fig. 2 can be better observed as individual brighter atoms that have higher corrugation [~0.3 Å higher as seen in Fig. 3(b)]. We assign these brighter spots to indium atoms based on the following arguments. First of all, the fraction of bright spots is constant in all STM images and accounts for (20 ± 5)% of all the group III sublattice sites in the images, which agrees well with the nominal concentration of 20% In. Second, since indium is associated with empty states with lower energy than gallium, the tunneling probability is larger when the tip is located at the indium site rather than at the gallium site [Fig. 3(c)]. The difference between the atomic radii of indium and gallium is too small to account for the observed corrugation difference, indicating that this must be the result of an electronic effect. In Fig. 3(a), an individual indium atom, a pair of two indium atoms along the growth direction, and four indium atoms in two close pairs are seen.

Close inspection of many images reveals that the ternary $In_{0.2}Ga_{0.8}As$ alloy region tends to have InAs clusters containing 2–3 indium atoms each. A few of these are indicated by arrows in Fig. 2. Statistically, 90% of the clusters contain 2–3 indium atoms [see Fig. 4(a)]. We find that the indium atoms are aligned preferentially along the [001] growth direction as seen by the chains of bright spots in Fig. 2. Since indium atoms are bound to arsenic atoms, each chain is in fact a cluster of InAs. We disregard the possibility of platelike clustering on the $(1\bar{1}0)$ planes (perpendicular to the surface) that are imaged edge on. This platelike clustering should also be

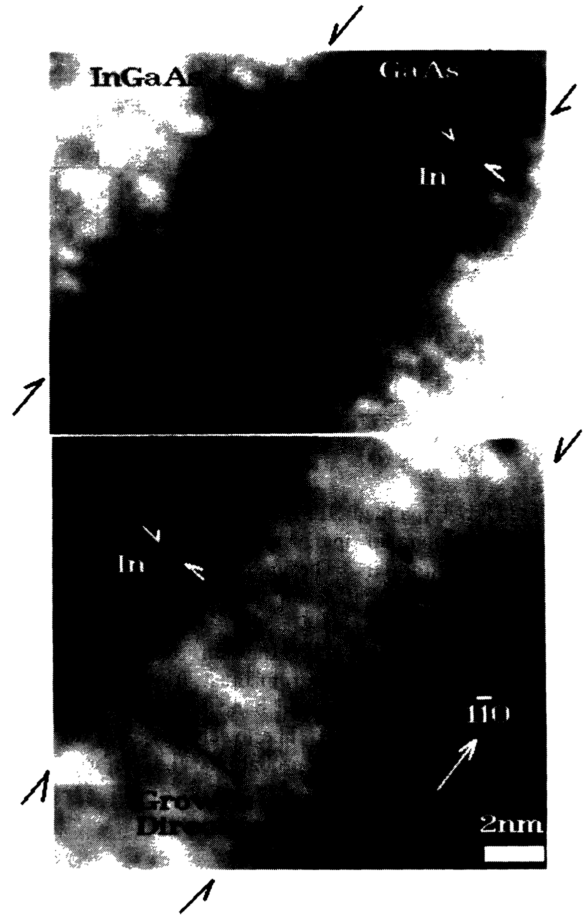

FIG. 2. 2000 Å×2000 Å STM image of GaAs cleaved along the (110) surface. The image is acquired with a tunneling current of 0.5 nA at sample bias of −2.0 V. Three $In_{0.2}Ga_{0.8}As$ multiple quantum wells appear as bright bands running from bottom left to top right, superimposed on the monatomic steps created by the cleavage.

seen on the (110) cleavage plane because it is identical to $(1\bar{1}0)$ by symmetry. Thus the clustering is concluded to be chainlike along the [001] growth direction. In the GaAs region near the $In_{0.2}Ga_{0.8}As$ layer, the relatively darker background provides sufficient contrast that some slightly brighter features are seen (see Fig. 2). These features occupy two rows of atoms along the [001] direction. This is readily understood if we attribute these slightly bright features to the presence of a cluster of InAs in the second layer below the cleavage surface. Geometrically, the second layer group III site is located in between the top layer group III sites. These InAs molecules enhance the local tunneling and highlight the two neighboring surface gallium atoms. From the chainlike arrangement of these slightly brighter surface gallium atoms, it can be inferred that the second layer InAs is clustered in the same way as the top layer InAs. This indicates that the clustering of In on the top (110) cleavage

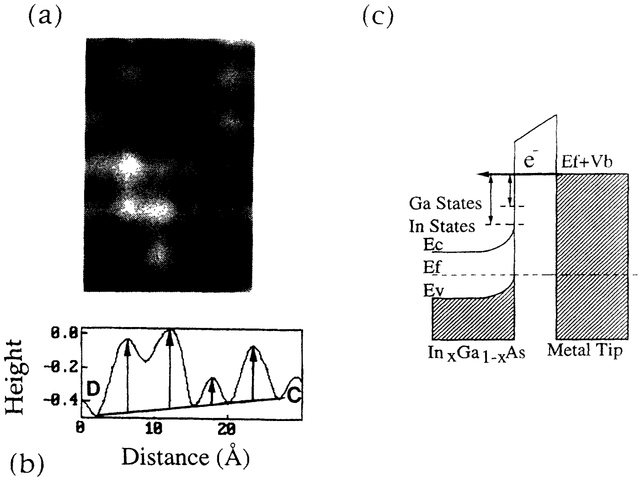

FIG. 3. (a) Expanded STM image of the empty states in the $In_{0.2}Ga_{0.8}As$ region showing bright spots that are attributed to individual indium atoms. The image is acquired with a tunneling current of 0.5 nA at a sample bias of +2.0 V. (b) Line profile along the arrows at C and D showing the variation in corrugation from the brighter (indium) to dimmer (gallium) atoms. (c) Energy band diagram illustrating the electron tunneling process. The tip induced band bending at the semiconductor surface is considered. The lower energy of the In states explains the higher tunneling probability and the bright appearance of indium atoms.

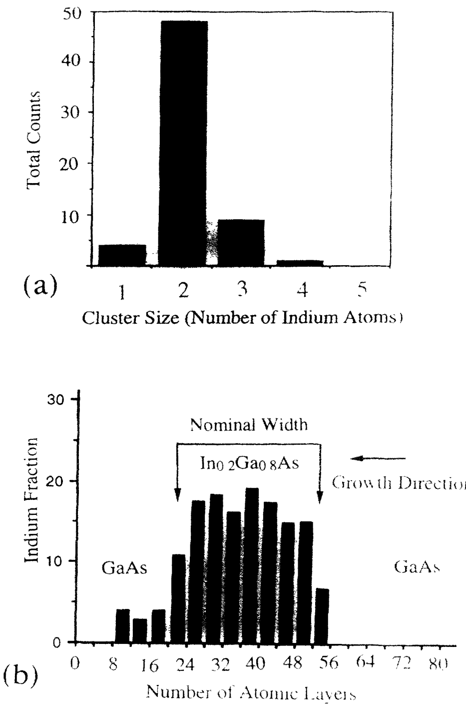

FIG. 4. Histograms showing (a) the distribution of cluster sizes and (b) the distribution of indium atoms across the $GaAs/In_{0.2}Ga_{0.8}As/GaAs$ heterostructure. The vertical bars are obtained by counting the number of indium atoms in rows of group III atoms along the $(1\bar{1}0)$ direction. The total number of atoms for each bar is about 100. The position of the zero (0) layer is arbitrary.

plane is not due to a surface or cleavage induced effect.

While the presence of clusters is an experimental observation, the mechanism of its formation is not clear yet. We propose that this is the result of local strain rather than random clustering or chemical effects. In substitutional ternary III/V alloys with two group III elements, the clustering probability as a result of random arrangement is high when the percentage of the substitutional group III element is large enough. However, random clustering should lead to a wide distribution of cluster sizes [14]. In our results, random clustering is very unlikely since 90% of the clusters contain 2–3 indium atoms [see Fig. 4(a)]. Chemical effects may enhance the possibility of clustering, especially since the larger bonding energy of indium to indium relative to that of indium to gallium would tend to produce indium adatom aggregation on a growing surface [15]. If such aggregates are the reason for clustering, we would expect to observe clustering both in the growth direction and in the transverse direction. The fact that only preferential clustering along the growth direction is observed indicates that other nonchemical effects are operative.

We propose the following explanation based on a local strain model. During the MBE growth of $In_{0.2}Ga_{0.8}As$ on GaAs, incorporation of indium into the group III lattice causes strain because its size is larger than that of gallium. Indium atoms tend to segregate on the growing surface and lead to a high concentration of surface indium adatoms [15]. Near equilibrium, indium atoms can be incorporated into the lattice by kinetic freezing [16]. Once an indium atom is at a group III site on the top growing layer, strain is built up locally. The strain is mostly in the horizontal (001) growth plane [8] because the vertical strain is relaxed at the free surface. This strain tends to expand the lattice locally, and thus might favor the incorporation of a second indium atom at the site on the top of the first one in the growing layer since the lattice is already expanded locally. However, this process is not likely to incorporate more than a few indium atoms because the increasing local strain along the growth direction will limit the cluster size to a few indium atoms, making it more favorable for indium atoms to be incorporated at a new site.

In addition to observing InAs clustering, the ability to differentiate indium from gallium allows the study of its segregation at the $GaAs/In_{0.2}Ga_{0.8}As/GaAs$ interfaces. The histogram in Fig. 4(b) shows the indium distribution in detail. It is obtained by counting the indium atoms within groups of two rows of cations along the $[1\bar{1}0]$ direction. The interface of $In_{0.2}Ga_{0.8}As$ grown on GaAs is about 2–4 layers wide. The interface of the GaAs grown on $In_{0.2}Ga_{0.8}As$, on the other hand, is more diffuse, spanning 5–10 layers, with quite a few indium atoms incorporated deep in the GaAs layer. This clearly shows that the interfaces are asymmetrically broadened.

We can understand this result by considering the conditions in the MBE growth of $In_{0.2}Ga_{0.8}As$. It is known that indium tends to segregate on the growing surface and is present in excess concentration [15]. In the growth of the first few atomic layers of $In_{0.2}Ga_{0.8}As$, when indium has not reached the saturation value, there is insufficient incorporation of indium. After several layers, when sufficient segregated indium exists on the growing surface, the $In_{0.2}Ga_{0.8}As$ will grow with more uniform indium incorporation. At the GaAs on $In_{0.2}Ga_{0.8}As$ interface, on the other hand, even after the indium flux has been stopped, the existing excess indium on the surface will result in its incorporation into the growing GaAs. It is interesting to notice that these indium atoms in the GaAs region also form InAs clusters containing ~2 indiums oriented along the growth direction, similar to these inside the $In_{0.2}Ga_{0.8}As$, even far above the GaAs/$In_{0.2}Ga_{0.8}As$ interface.

The lumpy nature of the clusters gives the interface a wavy nature with a length scale of the distance between clusters. Indium segregation broadens the interfaces asymmetrically. The results allow us to conclude that clustering and segregation are the main reasons for interface roughness in the GaAs/$In_{0.2}Ga_{0.8}As$ system.

The asymmetrical interface broadening observed here is consistent with previous studies by photoelectron spectroscopy [9] and by TEM chemical lattice image studies of InGaAs/AlGaAs heterostructures [17]. The interface roughness has a length scale of about ~20 Å, as directly seen here in the images (Fig. 2). The interface observed by TEM is generally averaged over ~30 layers. While photoluminescence (PL) indicates apparent smooth interfaces of GaAs/$In_{0.2}Ga_{0.8}As$/GaAs heterostructures [18], PL does not probe fluctuations smaller than the confined exciton diameter (~100 Å) [19].

In summary, by using cross-sectional STM in combination with its spectroscopic capability to distinguish Ga and In, we have demonstrated a new exciting capability of STM for the study of segregation and clustering at the atomic scale across interfaces. We have applied this methodology to the study of strained layer $In_{0.2}Ga_{0.8}As$/GaAs heterostructures. We find that InAs clusters in $In_{0.2}Ga_{0.8}As$ preferentially along the growth direction in the form of chains containing 2–3 indium atoms. We have observed the segregation induced asymmetrical broadening of the two interfaces of GaAs/$In_{0.2}Ga_{0.8}As$/GaAs. The interface of $In_{0.2}Ga_{0.8}As$/GaAs has a width of 2–4 atomic layers and that of GaAs/$In_{0.2}Ga_{0.8}As$ is about 5–10 atomic layers.

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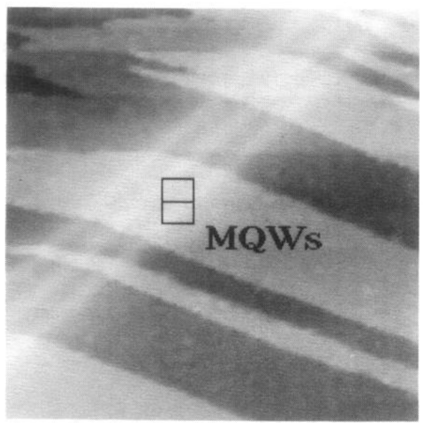


FIG. 1. 2000 Å×2000 Å STM image of GaAs cleaved along the (110) surface. The image is acquired with a tunneling current of 0.5 nA at sample bias of −2.0 V. Three $In_{0.2}Ga_{0.8}As$ multiple quantum wells appear as bright bands running from bottom left to top right, superimposed on the monatomic steps created by the cleavage.

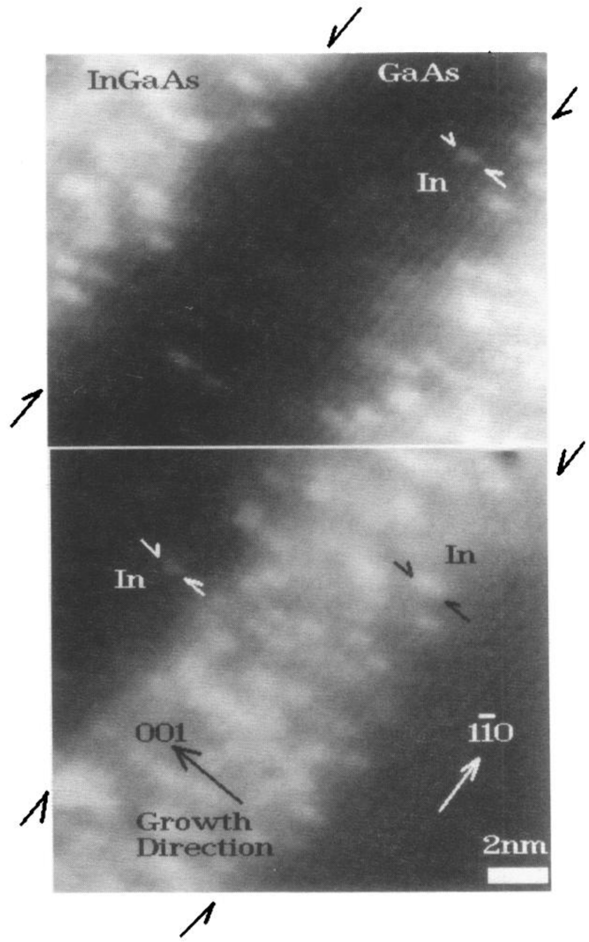
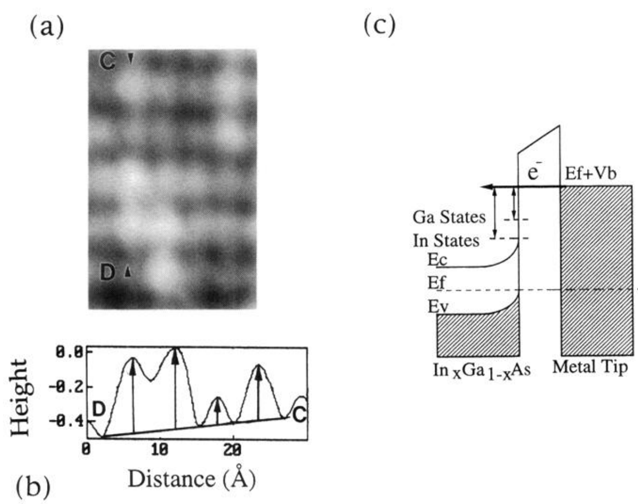


FIG. 2 2000 Å × 2000 Å STM image of GaAs cleaved along the (110) surface. The image is acquired with a tunneling current of 0.5 nA at sample bias of −2.0 V. Three $In_{0.2}Ga_{0.8}As$ multiple quantum wells appear as bright bands running from bottom left to top right, superimposed on the monatomic steps created by the cleavage.



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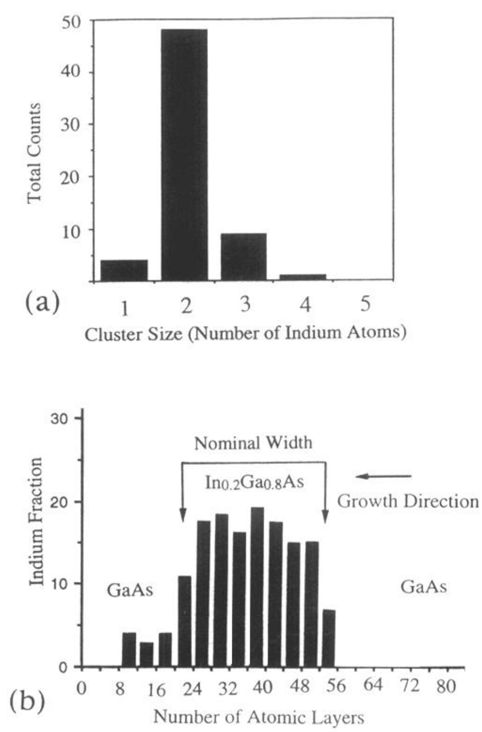

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