



Atomic structure of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}(001)$ (2×4) and (3×2) surfaces

L. Li^{a,*}, B.K. Han^a, R.F. Hicks^a, H. Yoon^b, M.S. Goorsky^b

^a *Chemical Engineering Department, University of California, Los Angeles, CA 90095, USA*

^b *Materials Science Departments, University of California, Los Angeles, CA 90095, USA*

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Abstract

We report the first atomic resolution scanning tunneling microscope images of the As-rich (2×4) and Ga-rich (3×2) reconstructions of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}(001)$ films ($0.001 < x < 0.012$) grown by metalorganic vapor-phase epitaxy. The (2×4) phase was obtained during annealing the sample at 480°C in an ultrahigh vacuum chamber. Annealing the (2×4) surface to 540°C produced the (3×2) phase which consists of single rows running parallel to the $[110]$ direction with a spacing of 12 \AA . The rows vary in length, being separated by defects which contain As dimers. A model is proposed for the (3×2) which consists of rows of Ga dimers alternating between the first and third layers. Since this structure exhibits a deficient of one electron, defects are required to expose As dimers in the second layer and neutralize the surface charge. © 1998 Published by Elsevier Science B.V. All rights reserved.

1. Introduction

Today nearly all compound semiconductor devices are produced by vapor-phase growth processes, i.e., either by molecular-beam epitaxy (MBE) [1], or by metalorganic vapor-phase epitaxy (MOVPE) [2,3]. The composition and structure of the films that are deposited in these processes depends to a large extent on reaction phenomena occurring on the film surface during growth. Therefore, it is important to understand the structure of compound semiconductor surfaces, and the relationship between surface structure and vapor-phase epitaxy.

The ideal (001) surface of III–V compound semiconductors with the zinc-blende structure is polar, so that it may be terminated entirely with cations or anions. Since the bulk atoms are sp^3 hybridized, two dangling bonds are associated with each cation and anion at the (001) surface. A reduction in the density of dangling bonds is achieved by dimerizing these atoms. Furthermore, the energy levels of the surface cation and anion are different. In the case of $\text{GaAs}(001)$, the energy levels of the Ga and As dangling bonds have been calculated [4]. The gallium dangling bonds lie above the bulk conduction band minimum and should be empty; while the arsenic dangling bonds lie below the bulk valence band maximum and should be filled. Therefore, stable reconstructions

*Corresponding author.

can be obtained for stoichiometries which allow the surface charge to remain neutral, with the Ga dangling bonds empty and the As dangling bonds filled. These results have been generalized as the electron counting model [5]. Most of the reconstructions observed on the III–V semiconductor surfaces obey this model [6–11].

Compared with binary compounds, the surface structures of the III–V ternary and quaternary alloys are much less studied. This is unfortunate because most compound semiconductor devices contain alloy films. On the surface of these materials, one must consider not only the V/III ratio, but also the distribution of the columns III and V elements. One of the important features of alloy films is bulk cation ordering [12–14]. This is thought to be induced by the surface reconstruction present during growth. Gomoyo et al. [13] reported spontaneous ordering on the sublattice of $\text{Al}_{0.48}\text{In}_{0.52}\text{As}$ films grown by molecular beam epitaxy (MBE). They found a direct link between the surface reconstruction and the crystal lattice. A triple period ordered phase was found in films that were grown on (2×3) reconstructed surfaces, while a CuPt type of ordering was observed when the surface was (2×1) reconstructed. Theoretical studies indicate that the dimerization of the atoms in the top-layer induces a strain field [15–17]. This provides certain sites which are favorable for smaller atoms and others which are favorable for larger atoms. Subsurface ordering is driven by the need to minimize the strain energy of the system by segregating the alloy elements among their most favorable sites. These considerations lead us to conclude that a thorough knowledge of the surface reconstructions of III–V alloys is essential for understanding the ordering phenomena.

In this paper, we report on a scanning tunneling microscope (STM) study of the surface structures of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}(001)$ films ($0.001 < x < 0.012$) grown by metalorganic vapor-phase epitaxy (MOVPE). A low indium content was chosen so that only a moderate amount of strain is induced by the lattice mismatch between the epilayer and the substrate. We observe a (2×4) reconstruction on the As-rich surface, and a new (3×2) reconstruction on the Ga-rich surface.

2. Experimental methods

The experiments were carried out in a UHV/MOVPE cluster tool [18]. One of the key features of this apparatus is the ability to quickly transfer the substrate back and forth between the MOVPE reactor and the STM instrument. This provides us with a means of monitoring the evolution of the film surfaces during growth.

The GaAs(001) wafers were miscut 0.5° toward the (110), and doped with 1×10^{18} Si atoms/cm³ (AXT, Inc.). The wafers were cleaved to 10×40 mm² pieces, and cleaned with acetone and methanol in a class 1000 cleanroom. Next, they were rinsed in de-ionized water, dipped in H_2SO_4 at 90°C , rinsed again, etched in $\text{H}_2\text{SO}_4:\text{H}_2\text{O}:\text{H}_2\text{O}_2 = 20:1:1$, and rinsed a third time. After this step, each sample was spin dried and placed on a molybdenum sample holder. Then the samples were placed in the loadlock and transferred to the MOVPE reactor.

Indium gallium arsenide films, about 0.5 mm thick, were grown using electronic grade triisopropylindium (TIPIIn), triisobutylgallium (TIBGa) (Morton), tertiarybutylarsine (TBAs) (Air Products) and hydrogen. The hydrogen carrier gas was purified by diffusion through a palladium membrane. The TIPIIn was prepared Dr. K.T. Higa (NAWCWPNS, Research and Technology Group, China Lake, California). The reaction conditions were $500\text{--}550^\circ\text{C}$, 20 Torr H_2 , 2.5 l/min total flow rate, 4.5×10^{-4} Torr of TIBGa, $0.5^{-2} \times 10^{-5}$ Torr of TIPIIn, and a V/III ratio of 34 to 100. After growth, the substrate was annealed at 600°C in 3.2×10^{-2} Torr TBAs and 20 Torr H_2 for 10 min, and then cooled to room temperature. The TBAs and H_2 flows were maintained until the wafer temperature reached 350° and 100°C , respectively. Immediately after stopping the H_2 flow, the vessel was pumped down to 5×10^{-7} Torr, and the wafer was transferred to the UHV system.

The STM experiments were performed in an UHV system containing low-energy electron diffraction (LEED) optics, X-ray photoelectron spectroscopy (XPS) and other surface analysis instruments. In the UHV chamber, the sample was slowly heated to 480°C to desorb the excess arsenic and other impurities from the surface.

A $(2 \times 4)/c(2 \times 8)$ LEED pattern was observed after this step. Further heating to 540°C produced a sharp (3×2) pattern. Scanning tunneling micrographs of these surfaces were obtained at 25°C with a sample bias between -2 and -4 V and a tunneling current of 0.1 – 0.5 nA. Double- and triple-axis x-ray diffraction (XRD) measurements were obtained by a Bede D³ diffractometer using a generator setting of 40 kV and 35 mA. The amount of indium in the film was determined by the separation of the XRD peak of the film from that of the substrate [19–21].

3. Results

Fig. 1 shows a high-resolution double-axis $\theta/2\theta$ X-ray diffraction scan for an epitaxial InGaAs film grown on GaAs(0 0 1) at 500°C and at a V/III ratio of 100. The substrate peak is located at 0 arcsec, while the epilayer produces a peak at -49 arcsec. Assuming that the film is fully strained, this peak splitting corresponds to an In mole fraction of 0.009 ± 0.001 [19]. The lack of diffuse scattering in the wings is a good indication that there is little strain relaxation in the film. The beat spacing in the fringe pattern is consistent with a film thickness of about $0.5 \mu\text{m}$. For the samples investigated, the indium content varies from 0.001 to 0.012 ± 0.001 .

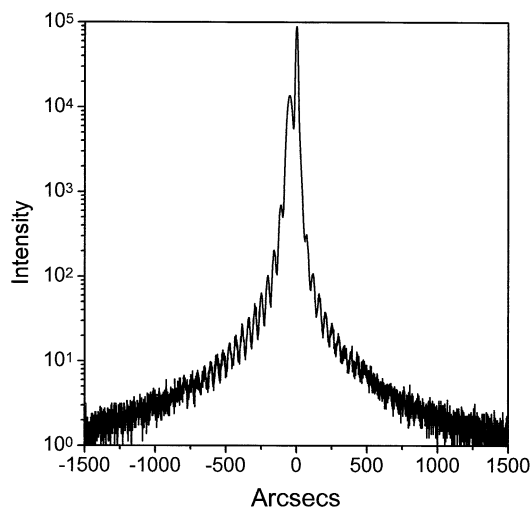
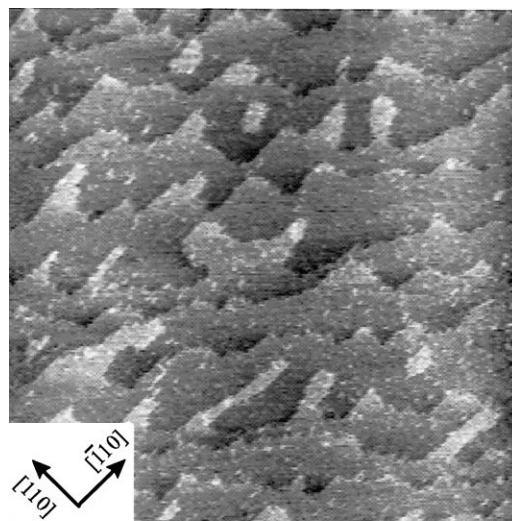
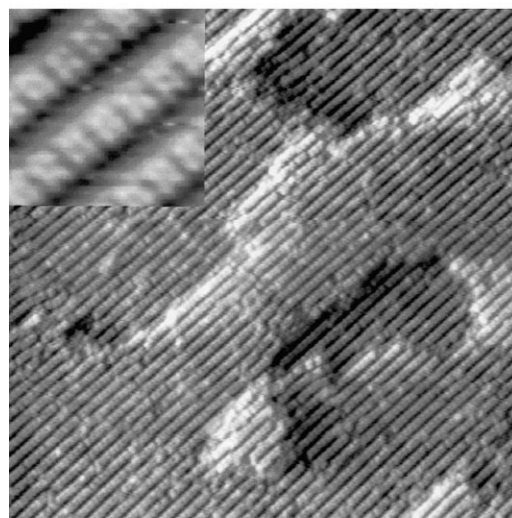


Fig. 1. Double axis $\theta/2\theta$ scan of an $\text{In}_x\text{Ga}_{1-x}\text{As}$ film ($x = 0.009$) grown on a GaAs (0 0 1) substrate.

Two STM images of an $\text{In}_{0.012}\text{Ga}_{0.988}\text{As}/\text{GaAs}(0 0 1)$ surface are shown in Fig. 2. A regular array of terraces are observed with an average terrace width of 300 \AA . The steps edges are primarily parallel to the $[0 1 0]$ direction. However,



(a)



(b)

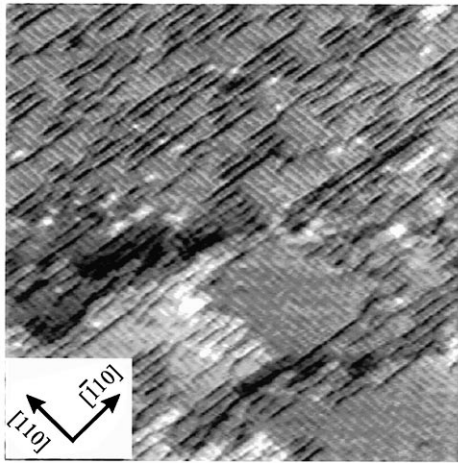
Fig. 2. Scanning tunneling microscope images of an $\text{In}_x\text{Ga}_{1-x}\text{As}$ (0 0 1) surface ($x = 0.012$) grown at 500°C and a V/III ratio of 100, and vacuum annealed at 480°C : (a) $3500 \text{ \AA} \times 3500 \text{ \AA}$, and (b) $650 \text{ \AA} \times 650 \text{ \AA}$. The inset in (b) shows a close-up view of the (2×4) structure on the terraces ($40 \text{ \AA} \times 40 \text{ \AA}$).

examination of the large-scale image reveals that the step morphology exhibits a saw-toothed pattern which greatly enhances the fraction of the total step length that runs parallel to the $[1\ 1\ 0]$ direction. This is consistent with the fact that A steps, i.e., steps with their edges parallel to the $[\bar{1}\ 1\ 0]$ axis, have a lower energy than B steps, i.e., steps with their edges parallel to the $[\bar{1}\ 1\ 0]$ axis [22].

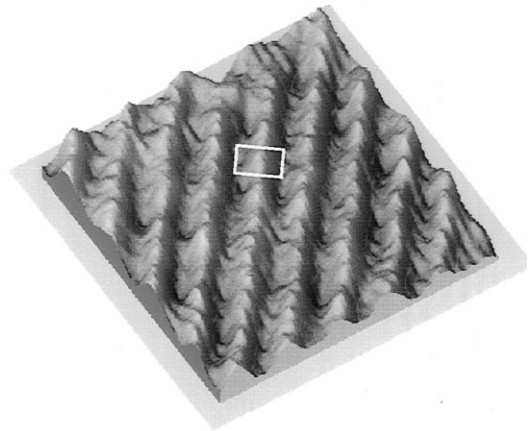
A close-up view of the structure on the terraces is shown in Fig. 2b. It reveals an As-rich (2×4) recon-

struction. The inset in the upper-left corner shows an atomic resolution image of the structure. The pairs of white dots which are compressed together in the $[\bar{1}\ 1\ 0]$ direction are due to the lone pair states on the individual As-dimer atoms. This reconstruction is essentially the same as the one observed on GaAs(0 0 1) and $\text{In}_{0.53}\text{Ga}_{0.47}\text{As}/\text{InP}(001)$ [6–8,18,23].

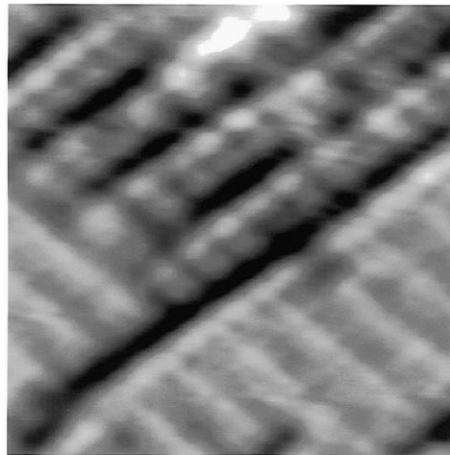
In Fig. 3a, an occupied state STM image of the (3×2) surface is shown. One sees that the (3×2)



(a)



(b)



(c)

Fig. 3. Scanning tunneling microscope images of an $\text{In}_x\text{Ga}_{1-x}\text{As}$ (0 0 1) surface ($x = 0.012$) grown at 500°C and a V/III ratio of 100, and vacuum annealed at 540°C : (a) $500\ \text{\AA} \times 500\ \text{\AA}$, (b) a 3-D presentation, $80\ \text{\AA} \times 80\ \text{\AA}$, with the unit cell outlined, and (c) a close-up view of the defect structure, $90\ \text{\AA} \times 90\ \text{\AA}$.

surface is composed of a series of gray rows aligned along the $[\bar{1} 1 0]$ crystal axis. These rows are sliced through by dark line defects. The spacing between the rows is 12 Å, which yields the $3 \times$ periodicity. A 3D close-up view of the structure is presented in Fig. 3b. Here one sees that the rows contain equally spaced bumps 8 Å apart, which gives rise to the $\times 2$ periodicity.

X-ray photoemission spectra indicate that the area ratio of the As 2p peak to the Ga 2p peak is 1.25 ± 0.10 for the (3×2) . This value is consistent with a Ga-rich surface [18,24]. The indium mole fraction determined by XPS is below 0.03, in agreement with the XRD results. Evidently, there is no significant enrichment of indium near the surface. In order to elucidate the details of the (3×2) structure, multiple-internal-reflection infrared spectroscopy was used to obtain the vibrational spectrum of adsorbed hydrogen on the surface [25]. Hydrogen atoms adsorb on Ga dimers yielding a characteristic broad adsorption band between 1700 and 1200 cm^{-1} . An intense band was observed for the Ga dimer sites on (3×2) , confirming that these species dominate the surface. Moreover, the polarization of the infrared band was consistent with the Ga dimer bond being oriented along the $[1 1 0]$ axis.

Shown in Fig. 3c is a detailed view of the defect structure present on the (3×2) . Two phases can be seen in the image: the lower right-hand side is (3×2) terminated, while the upper left-hand side is (2×4) terminated. Line-scans reveals that the depth of the line defect is 2.3 Å both in the (3×2) and (2×4) regions. Evidently, the line defects are the As-dimer vacancy rows of the (2×4) phase. The areal density of the line defects and the (2×4) domains varies from sample to sample, suggesting that they may be related to the amount of strain in the films.

4. Discussion

As can be seen in Fig. 2a, step-flow growth is achieved at 500°C under our experimental conditions. The morphology of the films show that the step edges are serrated, comprising peninsulas and bays that extend over a large portion of the under-

lying terraces. It is interesting to note that the step down direction is $[1 0 0]$, although the miscut quoted by the wafer supplier is towards the $[1 1 0]$. Step bunching and branching can cause a change in the step direction [26]. However, all the steps seen in the films are two layers high, and larger area scans ($2 \times 2 \mu\text{m}^2$) do not reveal any evidence of this phenomenon. The desorption of arsenic during the annealing procedure may cause the observed step morphology. Similar results were obtained in a previous study on GaAs(0 0 1) prepared by MBE [27].

Our results indicate that the (2×4) is a stable and well-ordered phase of InGaAs/GaAs(0 0 1) surfaces. Another study of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{InP}(0 0 1)$ films with $x \sim 50$ indium also observed the (2×4) reconstruction on the As-rich surface [23]. Thus, it may be concluded that this is probably the lowest-energy structure for As-rich InGaAs(0 0 1) surfaces.

We now discuss the structure of the (3×2) surface. The lattice of a tetrahedrally coordinated III–V semiconductor has twofold symmetry about the (0 0 1) axis, so that on a (0 0 1) surface, the $[1 1 0]$ and $[\bar{1} 1 0]$ directions are not equivalent. The group III dangling bonds always dimerize in the $[1 1 0]$ direction, whereas the group V dangling bonds always dimerize in the $[\bar{1} 1 0]$ direction. Since the (3×2) rows lie perpendicular to the vacancy rows of the (2×4) , i.e., along the $[1 1 0]$ axis, we can conclude that the (3×2) is terminated with Ga dimers. These Ga dimers are responsible for the $\times 2$ periodicity. This conclusion is also strongly supported by the infrared spectrum of adsorbed hydrogen as discussed above.

Taking into account the above considerations, we propose a model for the (3×2) as shown in Fig. 4. It consists of single rows of Ga dimers oriented along the $[1 1 0]$ direction and alternating between the first and third layers. The $3 \times$ periodicity is produced by one missing Ga row in the top layer, and the $\times 2$ periodicity is due to Ga dimerization along the $[1 1 0]$. Electron counting reveals that there is a one electron deficit per (3×2) unit cell. To compensate for this charge, domains that expose the underlying arsenic atoms are created. As can be seen in Fig. 3c, the structure of the As-rich domains are not unique and their size varies. However, they all contain the basic unit of the As rich (2×4) reconstruction. Thus, one As domain is also

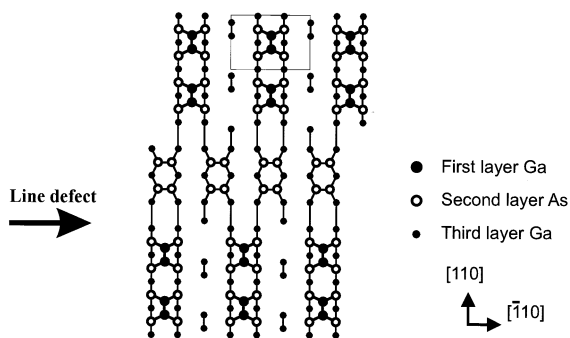


Fig. 4. Ball-and-stick model of the proposed structure for the (3×2) surface.

shown in Fig. 4, and it is terminated with As dimers that form a partial (2×4) pattern. These partial (2×4) structures are not charge neutral, and depending on the distribution of Ga(In) and As within the surface sites, they could provide the additional electrons needed to compensate for the missing electrons in the (3×2) phase.

In previous studies of phase transitions on GaAs(0 0 1), it has been reported that an intermediate phase exists during the conversion of the Ga-rich (2×6) to the Ga-rich (4×2) [27,28]. This phase is generally disordered, and one group of authors described it as “structureless” [27]. This disordered phase of GaAs(0 0 1) could be a close cousin of the InGaAs(001) (3×2) structure. During annealing, we also produce the (3×2) as an intermediate phase between the (2×6) and (4×2) . The addition of indium to the lattice may be necessary for this phase to become well ordered.

In a separate study, we produced the (3×2) reconstruction by decomposing carbon tetrachloride on the Ga-rich (4×2) surface [29]. The Cl ligands etch Ga off the surface as GaCl, and cause the less Ga-rich (3×2) structure to form. In addition, carbon deposited from the CCl_4 may donate electrons to the (3×2) , and balance the overall charge. This would explain why fewer line defects are observed on (3×2) structures produced from CCl_4 than those obtained by annealing InGaAs films [29]. Further experiments are underway to reveal the physics and chemistry of this interesting structure.

In conclusion, we have resolved the atomic structure of $\text{In}_x\text{Ga}_{1-x}\text{As}/\text{GaAs}(0\ 0\ 1)$ films ($0.001 < x <$

0.012) grown by MOVPE. Our results show a (2×4) reconstruction on the As-rich surface, and a (3×2) reconstruction on the Ga-rich surface. The (3×2) phase is terminated with single rows of dimers running along the $[1\ 1\ 0]$ direction with a spacing of $12\ \text{\AA}$. A model is proposed that assumes these are Ga dimer rows alternating between the first and third layers. Since this structure is electron deficient, line defects are required to expose second-layer As atoms and neutralize the surface charge.

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