Phase transitions of III–V compound semiconductor surfaces in the MOVPE environment

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Abstract

The structure of gallium arsenide and indium phosphide (0 0 1) surfaces in the metalorganic vapor-phase epitaxy (MOVPE) environment has been investigated. During growth at V/III ratios in excess of 10, both materials are terminated with group V ad-dimers (As or P), alkyl groups and hydrogen atoms. These species sit on top of a complete layer of the group V atoms. As the V/III ratio decreases, the top layer of arsenic or phosphorous desorbs from the surface. However, the resulting structures are different on GaAs and InP (0 0 1). In the former case, the phase transition occurs with gallium out-diffusion and nucleation of elongated islands. These islands have a $\beta 2(2 \times 4)$ structure that contains only 0.75 monolayer of arsenic dimers. The resulting surface is rough, exposing on average six atomic layers. Conversely, on InP (0 0 1), no indium out-diffusion occurs following desorption of the phosphorous ad-dimers. Instead, the underlying P atoms dimerize, forming a (2×1) structure with a phosphorous coverage of 1.0 monolayer. © 2001 Elsevier Science B.V. All rights reserved.

1. Introduction

The surface reconstructions of gallium arsenic and indium phosphide (0 0 1) have been subject to many ultrahigh vacuum studies as they play an important role during the epitaxial growth of thin film devices [1–4]. While our knowledge of these materials has advanced significantly in the last two decades, it is still unclear whether the structures seen in the vacuum apply directly to those present during processing. For example, many compound semiconductor devices are made by metalorganic vapor-phase epitaxy (MOVPE) at pressures between 20 and 100 Torr. This process is usually operated at V/III feed ratios above 10, in order to passivate the surface with less reactive arsenic or phosphorous atoms [5]. On the other hand, a low V/III ratio is sometimes used to incorporate carbon as a p-type dopant into the GaAs film. This is done during the fabrication of InGaP/ GaAs heterojunction bipolar transistors (HBTs), where a p + base is highly desired for reducing the base resistance to improve the high frequency performance. In addition, the interface may be graded in these materials to suppress the conduction band spike that can act as a barrier to electron

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injection [6]. Thus, the surface coverage and interface smoothness are properties that the crystal grower must control during epitaxy. To achieve this goal, one must have a detailed understanding of the surface structures in the process environment.

In this paper, we have studied the surface structures of GaAs and InP (0 0 1) present in the MOVPE environment by varying the V/III ratio. It is found that at V/III ratio above 10, both materials exhibit smooth surface. At lower V/III ratios, a surface roughening is observed on GaAs (0 0 1), while the smooth surface is preserved on InP (0 0 1). The surface morphology difference between these two materials can be attributed to their different surface reconstructions.

2. Experimental methods

Gallium arsenide and indium phosphide films, 0.5 μm thick, were grown on nominally flat GaAs and InP (0 0 1) substrates. A horizontal flow, metalorganic vapor-phase epitaxy reactor was used for this purpose. Gallium arsenide and indium phosphide films were deposited on these substrates using triisobutylgallium (TIBGa), tertiarybutylarsine (TBAs), triisopropylindium (TIPIn), and tertiarybutylphosphine (TBP), in an H_2 carrier gas. The GaAs growth conditions were 550°C, 20 Torr total pressure, and a V/III ratio of 5–15. For InP, the growth conditions were 600°C, 20 Torr total pressure, and a V/III ratio of 5–10. The surface structures of both materials during MOVPE are found to be independent of the growth rate. The samples were transferred to the UHV cluster tool via a vacuum interface chamber. Details of this system have been described elsewhere [7].

Real-space images of the surface reconstructions were obtained using a Park Autoprobe/VP scanning tunneling microscope. Tunneling was out of filled states with a sample bias of −3.0 to −4.0 V and with a tunneling current of 1 nA. The chemical identities of adsorbates were studied by internal-reflection infrared spectroscopy, and by X-ray photoelectron spectroscopy.

## 3. Results and discussion

3.1. The phase transition of GaAs (0 0 1)

At a V/III ratio of 15, the gallium arsenide (0 0 1) surface exhibits a (1×2) structure after being pulled out of the reactor [5]. By using infrared spectroscopy, we have identified that the (1×2) is formed by adsorbing alkyl groups on top of the arsenic-rich $c(4 \times 4)$ surface. These groups exhibit characteristic C–H stretching vibrations at 2957, 2869 and 2926 cm^{-1} [5]. Annealing the sample at 300°C in vacuum produces an ordered $c(4 \times 4)$ reconstruction as shown in Fig. 1(a). It contains two different structural mosaics, as indicated by the white circles labeled 1 and 2. In circle 1, the light gray blocks are square, indicating that they are composed of two arsenic dimers. Whereas in circle 2, the light gray blocks are rectangular, indicating that they are formed by a group of three arsenic dimers. Perusal of large-area STM images reveals that these two structures are equally distributed across the surface.

Shown in Fig. 1(b) is an STM image taken on a sample grown at a V/III ratio of 5. With a reduced arsenic supply, β2(2×4) unit cells appear on the topmost layer of the surface. Note that the distance traversed from white to black in the STM image is approximately 5.4 Å (a single GaAs lattice constant). The β2(2×4) unit cells appear as white or gray rectangles, with their long axis in the [1 1 0] direction. Multiple β2(2×4) unit cells are aligned along the [1 1 0] direction, and are delineated by the dark dimer vacancies separating each row. Some of the β2(2×4) unit cells are highlighted in a rectangular box. Obviously, a phase transition occurs at low V/III ratios that exposes three atomic bilayers of the crystal. These bilayers correspond to the white, gray, and black terraces in the STM image.

A striking observation is that the β2(2×4) unit cells are visible in the topmost layer. By contrast, a predominantly $c(4 \times 4)$ reconstruction is in the next-lower layer, as can be seen by the highlighted white circle in Fig. 1(b). The appearance of β2(2×4) domains on top of $c(4 \times 4)$ domains indicates that a phase transition occurs involving the exchange of arsenic and gallium atoms and
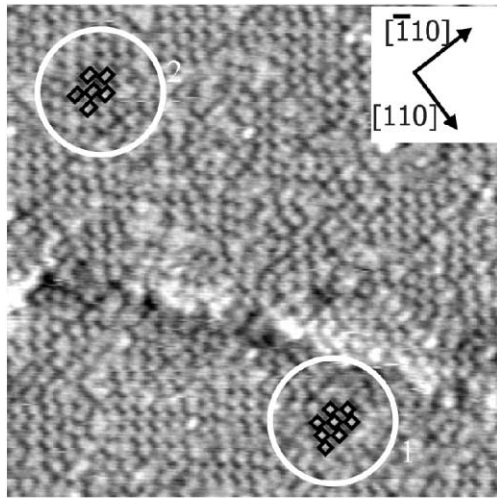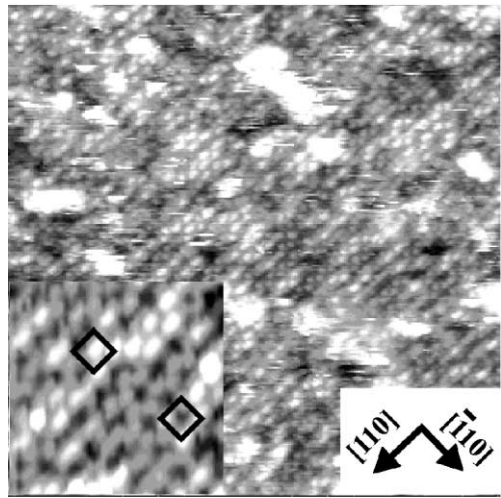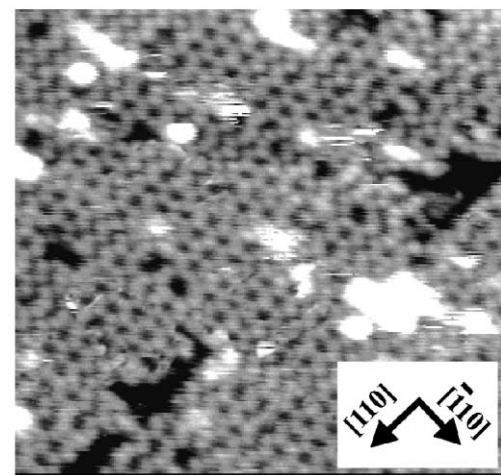
(a)
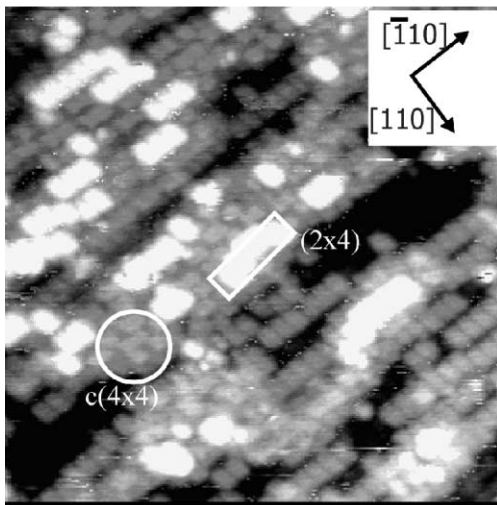
(b)

Fig. 1. Scanning tunneling micrographs of the GaAs (0 0 1) surface prepared in the MOVPE reactor at (a) a V/III ratio of 15; and (b) a V/III ratio of 5. The image areas are 350×350 and 250×250 Å^2, respectively.

(a)

(b)

Fig. 2. Scanning tunneling micrographs of the InP (0 0 1) surface prepared in the MOVPE reactor at (a) a V/III ratio of 10; and (b) a V/III ratio of 5. The image areas are 350×350 and 190×190 Å^2, respectively.

migration of gallium atoms onto the surface [8]. The liberated Ga atoms migrate across the $c(4 \times 4)$, react with adsorbed As atoms, and nucleate the β2(2×4) islands. Gallium migration on the $c(4 \times 4)$ has been observed by Kanisawa et al. during the molecular beam epitaxy of GaAs (0 0 1) [9]. The theoretical studies suggest that gallium adatoms diffuse occurs readily across the As-rich $c(4 \times 4)$ reconstructions [10,11].

3.2. Phase transition of InP (0 0 1)

Shown in Fig. 2(a) and (b) are filled-states STM images of an InP (0 0 1) film grown at V/III ratios of 10 and 5, respectively. In Fig. 2(a), the surface is composed of rows extending along the [1 1 0] direction. On top of these rows are elongated white spots that cover about 65% of the surface. These white spots form $c(2 \times 2)$ and $p(2 \times 2)$ unit

cells (highlighted squares in the inset picture). Between the white spots, a zigzag pattern of gray spots is seen extending along the [1 1 0] direction. The white spots are identified as phosphorous ad-dimers sitting on a complete layer of phosphorous, whereas the gray spots are buckled phosphorous dimers bound to a layer of indium. In addition, adsorbed alkyl groups and hydrogen are also detected on the surface by infrared spectroscopy with deuterium titration [3].

With a decreasing phosphorous supply at a lower V/III ratio, the phosphorous ad-dimers desorb from the surface, yielding the STM image shown in Fig. 2(b). This picture was taken after heating the sample to 200°C in vacuum to desorb any hydrocarbon species. Measurement of the P $2p^{3/2}$ XPS peak confirms that no phosphorous desorption occurs during this treatment. Inspection of the image in Fig. 2(b) reveals that the surface is terminated with rows of buckled dimers. The adjacent dimers correlate to each other to form in-phase and out-of-phase structures. Infrared spectroscopy has shown that those dimers are formed by 1.0 ML (1 ML: 1 monolayer = one phosphorous atom per (1×1) unit cell) of phosphorous atoms [2]. Comparing to gallium arsenide, the indium phosphide film exhibits a smoother surface morphology. No indium out-diffusion and P/In exchange reactions are observed. The GaAs (0 0 1) surface is composed of $\beta2(2 \times 4)$ unit cell with 0.75 ML of arsenic, whereas the InP (0 0 1) surface is composed of (2×1) unit cell with 1.0 ML of phosphorous.

The surface reconstructions control the evolution of the surface morphology in the MOVPE environment. For GaAs, the $c(4 \times 4)$ is stable at an arsenic coverage of 1.5–1.75 ML. As shown in Fig. 3(a), 0.75 ML of arsenic ad-dimers sit on top of a complete layer of arsenic atoms. The $\beta2(2 \times 4)$ reconstruction, shown in Fig. 3(b), is stable at arsenic coverage of 0.75 ML. Within each $\beta2(2 \times 4)$ unit cell, a bilayer trench separates every two As dimers. Inside the trench, a single row of gallium atoms has been removed, leading to dimerization of As atoms in the third layer. Thus, to convert the $c(4 \times 4)$ to the $\beta2(2 \times 4)$, one quarter of gallium
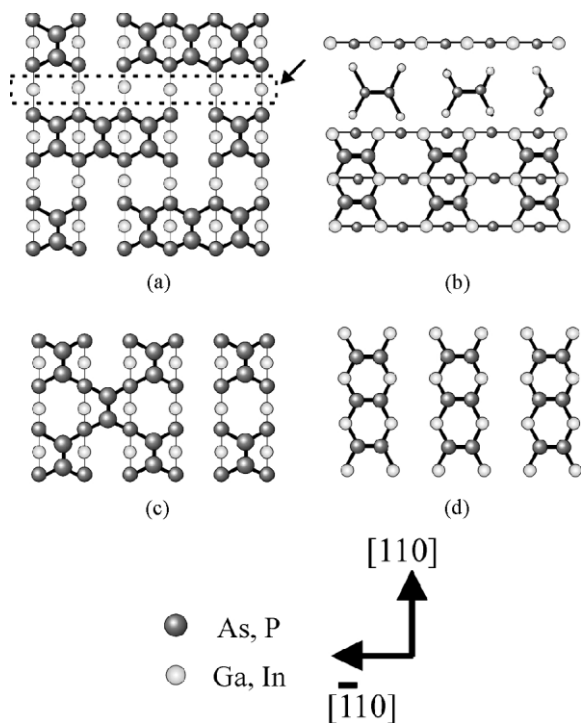

Fig. 3. Ball-and-stick models of compound semiconductor reconstructions: (a) GaAs (0 0 1)-$c(4 \times 4)$, (b) GaAs (0 0 1)-$\beta2(2 \times 4)$, (c) InP (0 0 1)-$c(2 \times 2)/p(2 \times 2)$, and (d) InP (0 0 1)-$(2 \times 1)$.

atoms must diffuse out on top of the surface (highlighted row in Fig. 3(a)). These migrating gallium atoms must nucleate and grow $\beta2(2 \times 4)$ islands.

Conversely, on InP (0 0 1)-(2×1), the surface is covered with a complete layer of phosphorous dimer as shown in Fig. 3(d). The phase transition from $p(2 \times 2)/c(2 \times 2)$ (Fig. 3(c)) simply involves the desorption of the phosphorous ad-dimers and dimerization of the P atoms underneath.

The gallium arsenide surface roughening that occurs at low V/III ratios could affect the properties of InGaP/GaAs heterojunctions. For example, in a heterojunction bipolar transistor, a diffuse interface between the base and the emitter could suppress the conduction band spike, and improve the efficiency of electron injection. Nevertheless, further research is needed to test this idea.

4. Conclusion

In summary, we have studied the phase transition of GaAs and InP (0 0 1) during MOVPE. It is found that for gallium arsenide, the transition from $c(4 \times 4)$ to $\beta2(2 \times 4)$ involves As desorption, As/Ga exchange, and Ga out-diffusion, leading to a roughened surface. For InP (0 0 1), the phase transition from $p(2 \times 2)/c(2 \times 2)$ to (2×1) only involves phosphorous desorption, and maintains a microscopically smooth surface. This work represents our first attempt to explore the dynamics of growing semiconductor heterojunctions. Much more work must be done to fully understand how these structures evolve during metalorganic vapor-phase epitaxy.

Acknowledgements

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