

## Structure and composition of the $c(4 \times 4)$ reconstruction formed during gallium arsenide metalorganic vapor-phase epitaxy

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Surfaces of GaAs (001) were prepared by metalorganic vapor-phase epitaxy and characterized by scanning tunneling microscopy, x-ray photoelectron spectroscopy, infrared spectroscopy, and low-energy electron diffraction. Upon removal from the reactor, the gallium arsenide surface exhibits a  $(1 \times 2)$  reconstruction, which is a disordered variant of the  $c(4 \times 4)$ . The disorder arises from the presence of adsorbed alkyl groups. Heating the sample to 350 °C desorbs the hydrocarbons and produces a well-ordered  $c(4 \times 4)$  structure. A model is proposed for the alkyl-terminated  $(1 \times 2)$  reconstruction. © 1998 American Institute of Physics. [S0003-6951(98)04125-4]

The structure of gallium arsenide surfaces present during metalorganic vapor-phase epitaxy (MOVPE) have been probed by optical spectroscopy, such as reflectance difference spectroscopy,<sup>1-3</sup> and by grazing incidence x-ray scattering (GIXS).<sup>4-8</sup> Although these techniques have provided interesting insights into the surface phases and the growth process, they have been unable to provide unequivocal information on the structure and composition of GaAs (001). In this regard, scanning tunneling microscopy (STM) is unsurpassed in its ability to provide real-space images of epitaxially grown semiconductor surfaces.<sup>9-13</sup> Prior STM studies of material grown by MOVPE have used an arsenic-capping procedure to protect the surface during transfer from the reactor to ultrahigh vacuum (UHV). Then the samples were annealed in vacuum above 200 °C to desorb the excess arsenic and reveal the GaAs surface.<sup>14,15</sup> Unfortunately, the structures revealed by this method were more representative of the vacuum annealing process than of the MOVPE environment.

In this study, a MOVPE reactor was directly interfaced to an UHV system that housed a scanning tunneling microscope and other instruments for surface analysis.<sup>12,13</sup> This apparatus has allowed us to simply stop the growth process, take the sample out of the reactor, and immediately characterize the structure and composition of the film surface. We have found that a  $(1 \times 2)$  reconstruction is present immediately after growth under arsenic-rich conditions. This structure has been characterized in detail and the results are presented below.

The GaAs (001) wafers used in these experiments were miscut 0.5° toward [011] and doped with  $1 \times 10^{18}$  Si atoms/cm<sup>3</sup> (AXT, Inc.). Gallium arsenide films were deposited on these substrates using triisobutylgallium (TIBGa), tertiarybutylarsine (TBAs), and hydrogen (H<sub>2</sub>). The growth conditions were 570 °C, 20 Torr H<sub>2</sub>,  $4.5 \times 10^{-4}$  Torr TIBGa, a V/III ratio 50, and a space velocity of 30 cm/s over the wafer surface (relative to 0 °C and 760 Torr). After growth, the sample was cooled to 40 °C at 1.3 °C/s. The TBAs and H<sub>2</sub> flows were maintained until the wafer reached 300 and

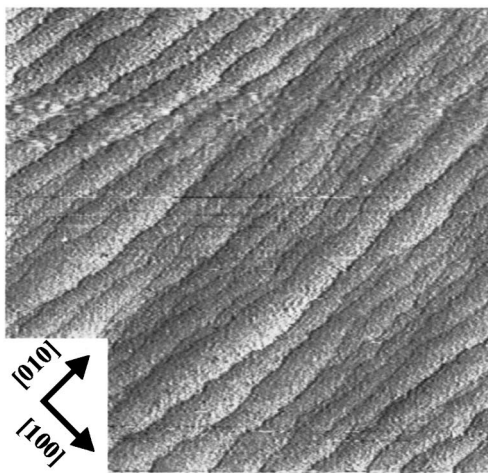
40 °C, respectively. Immediately after stopping the H<sub>2</sub> flow, the vessel was pumped down to  $2 \times 10^{-7}$  Torr, and the wafer was transferred to the UHV system.

The long-range order on the surface was determined with a Princeton Instruments low-energy electron diffractometer (LEED). Whereas the chemical composition of the surface was measured with a Physical Electronics x-ray photoelectron spectrometer (XPS), equipped with a multichannel detector and a hemispherical analyzer. These data were acquired at a take-off angle of 35° and a pass energy of 23.5 eV. The scanning tunneling micrographs were obtained with a Park Scientific AutoProbe VP at 30 °C with a sample bias of -2 to -4 V and a tunneling current of 0.1-0.5 nA. Infrared spectra of adsorbates present on the surface after growth were acquired with a BIO-RAD FTS-40 A infrared spectrometer. These measurements were made by internal reflection through the GaAs crystal with 31 reflections off the front face.

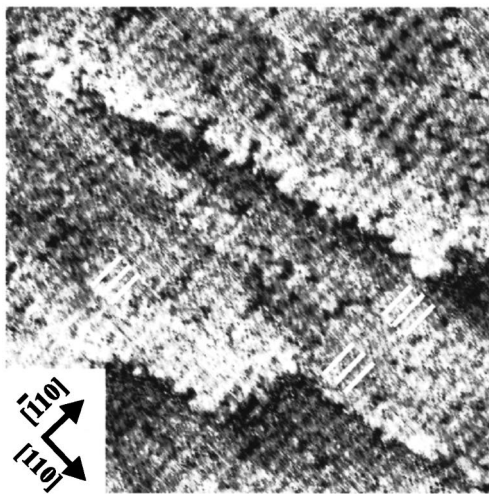
Shown in Fig. 1 are two STM images of the gallium arsenide (001) surface immediately after MOVPE. In the large-scale picture, one sees a regular array of terraces, indicative of step-flow growth. The step edges are on average parallel to the [010] crystal axis and are approximately 300 Å wide. The close-up view of this surface [Fig. 1(b)] reveals that it is terminated with light gray rows, extending along the  $[\bar{1}10]$  direction. White lines are inserted in the picture to emphasize the row structure. The rows are 8 Å apart, which corresponds to two unit cells of GaAs (001); and since one cannot discern any periodicity along the rows, the surface reconstruction by STM is  $(1 \times 2)$ . However, note that the LEED pattern of this surface is a weak  $c(4 \times 4)$  pattern superimposed on intense  $(1 \times 1)$  spots.

Next, the sample was annealed in vacuum at 350 °C for 10 min. This produced a sharp  $c(4 \times 4)$  LEED pattern. A STM image of this surface is shown in Fig. 2. It contains two different structural domains, as indicated by the circles labeled A and B. In circle A, the light gray blocks are square, indicating that they consist of a chain of two arsenic dimers. In circle B, the light gray blocks are rectangles, whose long axis is parallel to the  $[\bar{1}10]$  direction. These blocks consist of a chain of three arsenic dimers. Inspection of over 20 micrographs reveals that the two domains cover equal areas. The

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(a)



(b)

FIG. 1. Scanning tunneling micrographs of the GaAs (001) surface immediately after transfer from the MOVPE: (a)  $5500 \times 5500 \text{ \AA}^2$ ; and (b)  $260 \times 260 \text{ \AA}^2$ .

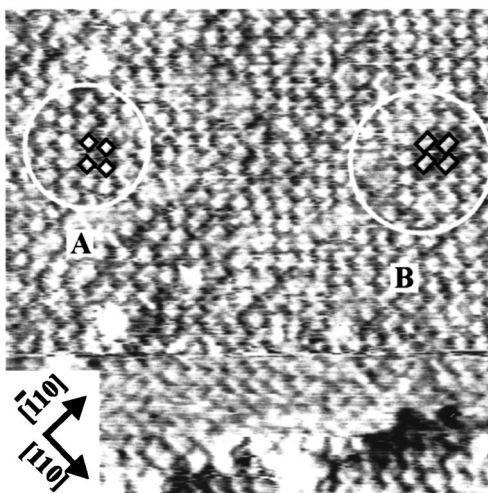


FIG. 2. Scanning tunneling micrograph of the  $c(4 \times 4)$  reconstruction after annealing the GaAs crystal in vacuum at  $350 \text{ }^\circ\text{C}$ . The image area is  $260 \times 260 \text{ \AA}^2$ .

TABLE I. Dependence of the XPS As  $2p_{3/2}$ /Ga  $2p_{3/2}$  and C  $1s$ /Ga  $2p_{3/2}$  area ratios on the sample annealing temperature in vacuum.

| Temperature ( $^\circ\text{C}$ ) | As/Ga | C/Ga    | Reconstruction  |
|----------------------------------|-------|---------|-----------------|
| 30                               | 1.38  | 0.0194  | $(1 \times 2)$  |
| 100                              | 1.39  | 0.0151  | $(1 \times 2)$  |
| 200                              | 1.40  | 0.0104  | $(1 \times 2)$  |
| 300                              | 1.36  | 0.00839 | $(1 \times 2)$  |
| 350                              | 1.34  | 0.00518 | $c(4 \times 4)$ |

mixed domain structure seen in the STM images is consistent with the previous work of Kisker and co-workers.<sup>7,8</sup> They obtained grazing incidence x-ray scattering spectra of the GaAs (001) surface in the MOVPE environment. Based on an intensity analysis of the crystal truncation rods, it was concluded that the surface consists of a mixture of As-dimer chains two and three dimers in length.

X-ray photoemission analysis of the GaAs surfaces indicates that only three elements are present after MOVPE growth: gallium, arsenic, and carbon. Presented in Table I are the area ratios of the As  $2p_{3/2}$  and C  $1s$  peaks relative to the Ga  $2p_{3/2}$  peak. The arsenic to gallium ratio remained constant as the crystal was annealed to  $350 \text{ }^\circ\text{C}$ . This indicates that for annealing at temperatures below  $300 \text{ }^\circ\text{C}$ , no arsenic desorbs from the surface. Conversely, the carbon to gallium ratio decreases from 0.0194 to 0.00518, indicating that the carbon is removed from the surface.<sup>16</sup>

In an attempt to identify the adsorbates present on the surface, infrared reflectance spectra were collected before and after annealing the sample for 10 min at temperatures between 100 and  $400 \text{ }^\circ\text{C}$ . In Fig. 3, reflectance spectra are presented of the C–H stretching region of the infrared spectrum, from  $3040$  to  $2780 \text{ cm}^{-1}$ . These spectra are ratios of the reflectance spectrum collected after heating to that collected beforehand. Negative peaks are observed because the adsorbates are removed from the surface. The peaks observed at  $2957$  and  $2869 \text{ cm}^{-1}$  are most likely due to the asymmetric and symmetric stretching vibrations of adsorbed

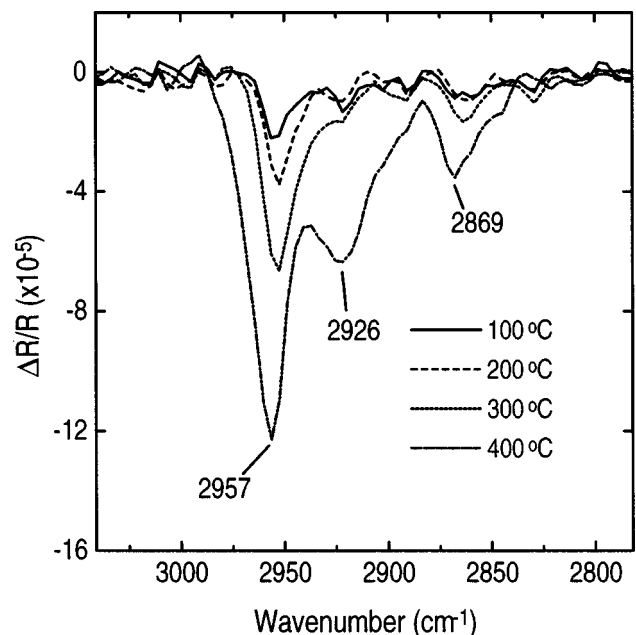


FIG. 3. Infrared reflectance spectra of the C–H stretching region after heating the sample in vacuum to temperatures between 100 and  $400 \text{ }^\circ\text{C}$ .

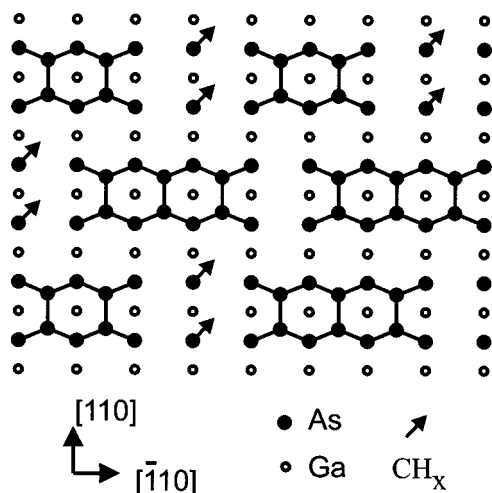


FIG. 4. Ball-and-stick model for the proposed  $(1 \times 2)$  structure.

methyl groups,<sup>17,18</sup> while the peak at  $2926 \text{ cm}^{-1}$  is characteristic of a  $\text{CH}_2$  stretching vibration.<sup>19</sup> No peaks are found at  $1930\text{--}1800 \text{ cm}^{-1}$  and  $2200\text{--}1930 \text{ cm}^{-1}$ , indicating that the surface is not terminated with hydrogen.<sup>19</sup> These results indicate that the carbon detected by XPS is due to adsorbed alkyl groups.

The results present above show that the  $(1 \times 2)$  and the  $c(4 \times 4)$  have the same arsenic coverage, but that hydrocarbon compounds are present on the  $(1 \times 2)$  surface. The STM images indicate that the  $(1 \times 2)$  evolves into the  $c(4 \times 4)$  upon annealing at  $350 \text{ }^\circ\text{C}$ . In Fig. 4, a proposed model for the  $(1 \times 2)$  reconstruction is shown. This model contains a mixture of As-dimer chains that are two and three dimers in length. In the gap between the chains with two As dimers, alkyl groups are bonded to exposed As atoms (arrows in Fig. 4). These exposed As atoms have up to two dangling bonds, and should exhibit a high propensity for reaction with the gas-phase alkyl radicals present in the MOVPE reactor. A random distribution of three-dimer chains, two-dimer chains, and adsorbed alkyls along the  $[\bar{1}10]$  direction will produce the  $(1 \times 2)$  periodicity as observed in the STM image presented in Fig. 1(b).

Kamiya *et al.*<sup>1-3</sup> reported that under flow of hydrogen

and arsenic precursors the GaAs surfaces exhibited a disordered  $c(4 \times 4)$  structure. Similar results were found in GIXS studies by Kisker *et al.*<sup>4-6,8</sup> The conditions used to produce these surfaces were analogous to those employed by us in this study. Therefore, we conclude that the disorder  $c(4 \times 4)$  seen previously is the adsorbate-covered  $(1 \times 2)$  structure identified herein.

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