Surface phases of GaAs and InAs (001) found in the metalorganic vapor-phase epitaxy environment

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We have characterized the (2×4) and (4×2) reconstructions of GaAs and InAs (001) that are present in a metalorganic vapor-phase epitaxy (MOVPE) reactor. Scanning tunneling micrographs show that these surfaces are terminated with arsenic and gallium (or indium) dimers. The (2×4) dimer row exhibits a mottled appearance, which is ascribed to the adsorption of alkyl groups on some of the sites. On the (4×2), <10% of the surface is covered with small (2×4) islands. These results show that, in the MOVPE environment, the GaAs and InAs surface structures are nearly the same as those found in ultrahigh vacuum molecular beam epitaxy. © *1998 American Institute of Physics.* [S0003-6951(98)02235-9]

The surface reconstructions of GaAs and InAs (001) have been studied extensively in ultrahigh vacuum after their preparation by molecular beam epitaxy (MBE).[1] By contrast, comparatively little is known of the surface structures generated in the chemically aggressive environment of a metalorganic vapor-phase epitaxy (MOVPE) reactor. This is because growth is carried out at 10–760 Torr, where photon-based techniques must be used. It has been found by reflectance difference spectroscopy (RDS)[2–4] and grazing incidence x-ray scattering (GIXS)[5–7] that the GaAs(001) surface exhibits $c(4\times4)$, (2×4), and (4×2) ''like'' structures in the MOVPE process gas. By $(m\times n)$ ''like,'' one means that the RDS spectra are similar, but not identical to that obtained on surfaces prepared by MBE, where the reconstructions are confirmed by reflection high-energy electron diffraction. In addition, the GIXS results recorded in the MOVPE environment always show a tetrahedral distortion in the diffraction pattern.[8] The origin of these discrepancies has not been resolved.

We have begun studying the surface reconstructions formed in the MOVPE process using *in situ* scanning tunneling microscopy. In a recent paper, we described the $c(4\times4)$ and (2×1) structures produced on GaAs(001) under arsenic-rich growth conditions.[9] Herein, results are presented for the (2×4) and (4×2) reconstructions of GaAs and InAs(001). Scanning tunneling micrographs taken of these structures immediately after MOVPE indicate that they consist of arsenic and gallium (or indium) dimers, and are analogous to the surfaces obtained in the MBE environment. However, x-ray photoelectron spectroscopy indicates that there is surface carbon associated with adsorbed alkyl groups. These groups produce characteristic features in the STM images of the (2×4), as described further below.

The GaAs(001) wafers used in these experiments were miscut 0.5° toward [011] and doped with 1×10^{18} Si atoms/cm^3 (AXT, Inc.). Gallium arsenide and indium arsenide films were deposited on these substrates using triisobutylgallium (TIBGa), triisopropylindium (TIPIn), tertiarybutylarsine

(TBAs), and hydrogen (H$_2$). The GaAs growth conditions were 570 °C, 20 Torr H$_2$, 4.5×10^{-4} Torr TIBGa, a V/III ratio of 50, and a space velocity of 30 cm/s over the wafer surface (relative to 0 °C and 760 Torr). The InAs growth conditions were the same, except that 5.0×10^{-6} Torr TIPIn was substituted for the TIBGa. The InAs was deposited on 0.5 μm of freshly grown GaAs, and the thickness was kept to less than 10 Å. After growth, the supply of organometallic precursors was terminated, and the temperature was either lowered to 550 °C for 20 min to produce the (2×4), or raised to 620 °C for 20 min to produce the (4×2). Then the sample was cooled to 40 °C at 1.3 °C/s, the hydrogen flow was stopped, the reactor was pumped down to 2×10^{-7} Torr, and the wafer was transferred to the ultrahigh system.

The long-range order on the surface was determined with a Princeton Instruments low-energy electron diffractometer (LEED). 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 (STM) 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.

Shown in Fig. 1 is an STM image of the (2×4) reconstruction immediately after removing the GaAs crystal from the reactor. One sees light gray rows extending along the [$\bar{1}$10] direction, which are characteristic of the (2×4) structure.[1] However, it is evident that the rows exhibit a mottled appearance, due to a random distribution of white spots within the gray rows. In the upper left-hand corner, a circle has been drawn to highlight a pair of bright spots. All these features disappear upon heating the sample above 300 °C in vacuum. Analysis of the surface by XPS reveals that the concentration of carbon on the surface drops from 5.0 at. % before heating to below 1.0 at. % afterwards. A similar decrease in the carbon concentration is observed upon annealing the $c(4\times4)$ surface produced in the MOVPE reactor.[9] In that study, it was shown by infrared spectroscopy that the carbon is due to adsorbed alkyl species.
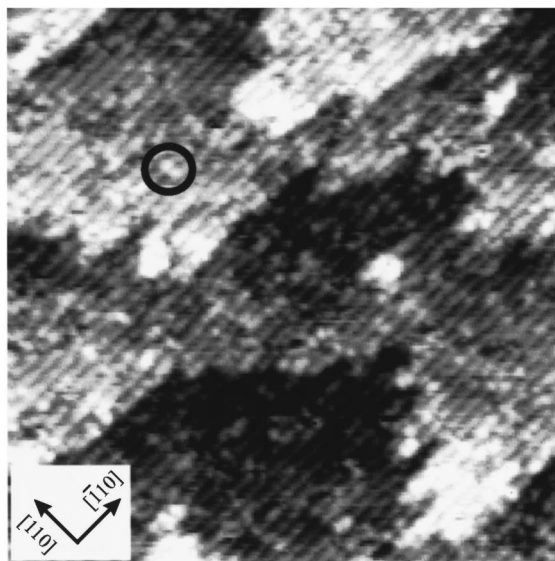
FIG. 1. Scanning tunneling micrograph of the GaAs(001) (2×4) reconstruction prepared in MOVPE reactor. Image size=600×600 Å². Sample bias =−2 V.

Therefore, we conclude that the bright spots in the STM image are produced by these adsorbates.

Presented in Fig. 2 is an image of the (2×4) GaAs(001) surface after annealing it in ultrahigh vacuum to 480 °C. The white spots are gone, and the As dimers comprising the (2×4) unit cell are clearly resolved.[10] This sample was then returned to the MOVPE reactor and heated to 550 °C for 20 min in 20 Torr of flowing hydrogen. After this treatment, XPS and STM analysis show that the (2×4) surface contains 5.0 at. % carbon as before, and its structure is identical to that presented in Fig. 1. Heating this sample above 300 °C in vacuum reduces the carbon concentration below 1.0 at. %, and regenerates the image given in Fig. 2. This procedure can be repeated over and over again without any degradation of the surface quality. Thus, the (2×4) structure is extremely stable in the hydrogen ambient of an MOVPE reactor.

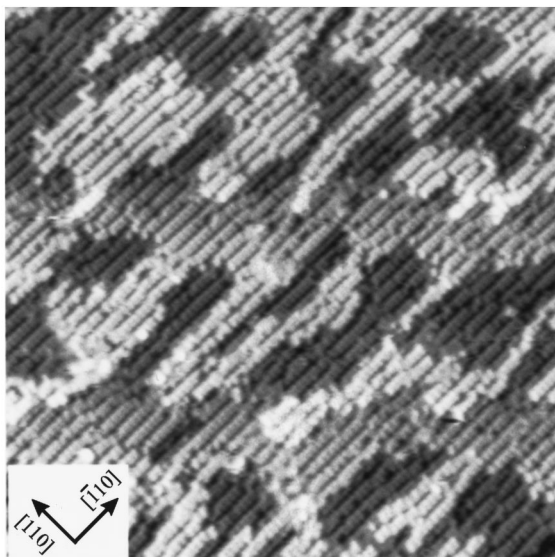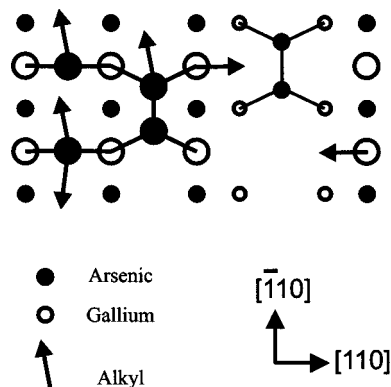The experiments described above for GaAs were re-

FIG. 3. Ball-and-stick model for the proposed alkyl terminated (2×4) structure.

peated for InAs films as well. We found that the (2×4) surface of InAs(001) behaves exactly the same way. The as-grown surface is contaminated with alkyl species that are readily desorbed by heating in vacuum. Also, the sample can be passed back and forth between vacuum and the MOVPE environment (20 Torr H_2 and 550 °C) with no loss of the structural integrity of the (2×4) reconstruction.

The results described above indicate that adsorbed alkyl groups are a common impurity on GaAs and InAs(001) surfaces prepared by MOVPE. Presented in Fig. 3 is a ball-and-stick model of these adsorbates on the (2×4) reconstruction. The alkyls can bond to several different sites, including As dimers and second-layer Ga atoms. It is likely that they are present as radicals in the MOVPE reactor,[11] and chemisorb onto the surface the same way as hydrogen atoms. The model presented in Fig. 3 is analogous to the model we have developed for hydrogen adsorption on (2×4) GaAs(001), and the reader is referred to this work for a more detailed discussion.[12] The reason why these species produce bright spots in the filled-state images is not clear at this time. It is possible that the alkyl groups are large enough to cause the tip to retract slightly as it scans over them. However, further experiments are underway to better understand these results.

In Table I, the XPS results are summarized for the two reconstructions of the GaAs and InAs(001) surfaces. For the GaAs samples, the Ga/As ratio increases from 1.09 to 1.35 as the surface is converted from (2×4) to (4×2). This is expected since the Ga coverage increases from 0.25 to 0.75 from the former to the latter reconstruction.[1] A similar trend is observed for the InAs surfaces. However, in this case, the Ga/As ratio is about ten times larger than the In/As ratio, indicating that gallium is the dominant element in the volume of the film analyzed by the spectrometer. It should be noted that the area ratios listed in Table I have not been corrected for the analyzer sensitivity factors. Although these will not change the results much, since the values reported

FIG. 2. Scanning tunneling micrograph of the GaAs(001) (2×4) reconstruction prepared in UHV. Image size=600×600 Å². Sample bias=−2 V.

TABLE I. The XPS Ga $2p_{3/2}$/As $2p_{3/2}$, and In $3d_{5/2}$/As $2p_{3/2}$ area ratios for the different GaAs and InAs(001) reconstructions.

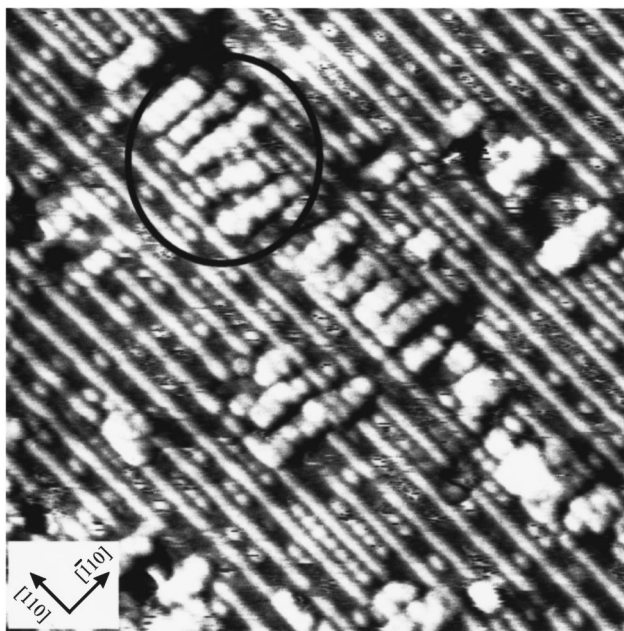|	Ga/As	In/As
GaAs (2×4)	1.09	0.000
InAs (2×4)	1.05	0.092
GaAs (4×2)	1.35	0.000
InAs (4×2)	1.45	0.104

FIG. 4. Scanning tunneling micrograph of the InAs(001) (4×2) reconstruction after annealing the GaAs crystal in MOVPE reactor at 620 °C. The image size=300×300 Å. Sample bias=−2.4 V.

by Physical Electronics are: $S_{Ga}=3.7$, $S_{In}=4.4$ and $S_{As}=2.4$.[13] One reason the Ga/As ratio is much larger than the In/As ratio is that the InAs layers are kept thin, ⩽10 Å, to avoid the formation of three-dimensional islands during growth. Gallium may also be present in the first and second layers of the InAs films, but further experiments are needed to verify this.

We next discuss the structures of the GaAs and InAs (4×2) surfaces prepared in the MOVPE environment. Scanning tunneling micrographs reveal that these surfaces are similar to the (4×2) reconstructions that are observed on films prepared by molecular beam epitaxy.[1,14] However, there are some notable differences. For example, small patches of arsenic-rich (2×4) domains are found mixed in with the (4×2) phase. This is due to the background arsenic pressure present in the MOVPE reactor at 20 Torr of H_2 and 620 °C. The population of the (2×4) varies from sample to sample, and can be as high as 20% of the surface area.

As an example of the (4×2) structure, we show in Fig. 4 an STM image of an InAs(001) film. This surface was obtained by depositing about 5 Å of InAs at 570 °C, heating the sample for 20 min at 620 °C in 20 Torr H_2, cooling it to 40 °C in 20 Torr H_2, and transferring it into vacuum. No vacuum annealing was performed. X-ray photoemission spectra of this sample also showed about 5.0 at. % carbon. Inspection of the STM image reveals that this structure consists of straight light gray rows, extending in the [110] and spaced 16 Å apart (4×). In between these rows are dark stripes that are partially filled with light gray spots. These spots repeat every 8 Å (×2). This structure is analogous to the InAs (4×2) prepared by MBE,[14] except that in the latter

case, the dark stripes are completely filled with the gray spots.

Arsenic-rich (2×4) domains are also evident in the STM images shown in Fig. 4. One of these domains is circled in the figure. These arsenic-rich unit cells aggregate together into small islands. The island contained within the circle extends about 32 Å in the [$\bar{1}$10] direction and about 90 Å in the [110] direction. Other islands seen in the image are generally smaller. These results are representative of the structures seen in many other images of (4×2) InAs.

The atomic structure of (4×2) InAs(001) has not been established. Several models have been proposed, including ones with indium dimers in the top layer and one in the third, and vice versa.[14,15] Clearly, there are other possibilities, especially if in the present case, gallium atoms are present in the top two layers.

Aspnes, Kisker and co-workers[2-8] reported that in 60 Torr of hydrogen and a few Torr of arsenic precursors, the GaAs surface exhibits several different structures, including (2×4) and (4×2) ''like'' phases. These results were obtained by RDS and GIXS, and showed some notable differences from the same structures prepared by molecular beam epitaxy. Based on the present study, the discrepancy between MOVPE- and MBE-grown materials may be due to (1) adsorbed alkyl groups, (2) the presence of mixed domains, and (3) defects within the unit cell. However, for the most part, the atomic structures of the compound semiconductor surfaces are the same in both process environments.

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