

A phosphorous-rich structure of InP (001) produced by metalorganic vapor-phase epitaxy

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A phosphorous-rich structure is generated on the InP (001) surface during metalorganic vapor-phase epitaxy. It consists of phosphorous dimers, alkyl groups, and hydrogen atoms adsorbed onto a layer of phosphorous atoms. The adsorbed dimers produce $c(2\times 2)$ and $p(2\times 2)$ domains, with total phosphorous coverages of 2.0 and 1.5 ML. The alkyl groups and hydrogen atoms adsorb onto half of the exposed phosphorous atoms in the first layer. These atoms dimerize producing a (2×1) structure. It is proposed that the first layer of phosphorous atoms is the active site for the deposition reaction, and that the organometallic precursors compete with phosphorous dimers, alkyl radicals, and hydrogen for these sites during growth. © 1999 American Institute of Physics.

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Compound semiconductors, containing elements of groups III and V of the Periodic Table, find applications in a variety of devices, including light-emitting diodes, quantum-well lasers, space solar cells, and high-speed transistors.¹ Metalorganic vapor-phase epitaxy (MOVPE) is an essential technology for manufacturing compound semiconductor devices, particularly those containing phosphide-based materials. One of the goals of scientists working in this field is to develop detailed numerical models that capture the coupled transport phenomena and reaction kinetics of this process.²⁻⁵ These models could then be used to optimize the reactors for the growth of devices. Studies of indium phosphide MOVPE have found that at 500–700 °C, the deposition rate is determined by the mass transfer rate of the group III precursor to the crystal surface.² However, the decomposition rate of the group V precursor, phosphine, or tertiarybutylphosphine, is determined by the heterogeneous reaction kinetics. This kinetic effect is clearly evident in the nonlinear dependence of the composition of MA_sP_{1-x} alloys ($M=Al, Ga, \text{ or } In$) on the relative concentrations of the group V sources in the gas.³ In order to characterize this phenomenon, one must thoroughly understand the surface upon which these reactions take place.

The surface structure of indium phosphide (001) has been examined by several researchers.⁶⁻¹⁰ Films have been grown by metalorganic vapor-phase epitaxy or molecular beam epitaxy, then the samples transferred into an ultrahigh vacuum system and annealed at different temperatures to reveal the reconstructions. These studies have found that there are two main phases of InP (001), the phosphorous-rich (2×1) and the indium-rich (2×4) . On the other hand, Ozanyan *et al.*¹¹ monitored the InP (001) surface during molecular beam epitaxy using reflection high-energy electron diffraction. They found that as the phosphorous pressure decreased and the substrate temperature increased, the reconstructions changed from $c(4\times 4)$ to (2×2) to (2×1) and lastly to (2×4) . The $c(4\times 4)$ and (2×2) have not been reported in

the other studies, presumably because the excess phosphorous desorbed during the vacuum annealing step.

In this letter, we report on the structure and composition of a phosphorous-rich InP (001) surface generated by metalorganic vapor-phase epitaxy. It is composed of a mixture of phosphorous dimers, alkyl radicals, and hydrogen atoms adsorbed on top of a complete layer of phosphorous atoms. We propose that surfaces with these same basic features are present under MOVPE growth conditions. A detailed analysis of the phosphorous-rich phase is presented below.

Indium phosphide films, 0.5 μm thick, were deposited on InP (001) substrates under the following conditions: 600 °C, 20 Torr of hydrogen, 6.5×10^{-4} Torr of triisopropylindium (TIPIn), $3.2\text{--}13.0\times 10^{-2}$ Torr of tertiarybutylphosphine (TBP) (V/III ratios of 50–200), and a total flow rate of 2.5 l/min normal temperature and pressure (NTP). After the supply of TIPIn was stopped, the samples were cooled with the TBP and H_2 flows maintained until the wafer reached 300 and 40 °C, respectively. The cooling rate in both cases was 1.3 °C/s. When 40 °C was attained, the reactor was immediately pumped down to 2×10^{-7} Torr, and the wafer was transferred to an ultrahigh vacuum system.

Once inside the vacuum system, the surface was characterized by scanning tunneling microscopy (STM), x-ray photoemission spectroscopy (XPS), and infrared spectroscopy. The STM images were taken of the filled states at a sample bias of -2.8 V and a tunneling current of 1.0 nA. The XPS spectra were acquired with a multichannel detector and hemispherical analyzer at a takeoff angle of 35° and a pass energy of 23.5 eV. The infrared spectra were recorded by internal reflection through a trapezoidal crystal ($40.0\times 10.0\times 0.64$ mm³) with 31 reflections off the front face, and at a resolution of 8 cm⁻¹. Bulk film composition, including the carbon doping level, was determined by secondary ion mass spectroscopy (SIMS) at Charles Evans Associates.

Scanning tunneling micrographs of the film surface, taken directly after removing the indium phosphide crystal from the reactor, show an array of terraces, which is indicative of step-flow growth. All steps are on average parallel to

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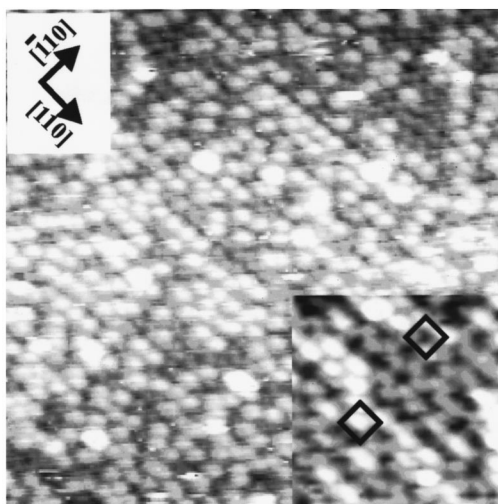


FIG. 1. Scanning tunneling micrograph of the InP (001), showing the $c(2 \times 2)$, $p(2 \times 2)$, and (2×1) reconstructions (large image = $250 \times 250 \text{ \AA}^2$, and inset = $62 \times 62 \text{ \AA}^2$).

the [010] crystal axis and are approximately 500 \AA wide. In addition, the steps are 2.8 \AA in height, i.e., equal to two atomic layers. Two close-up views of this surface are presented in Fig. 1. Rows can be seen extending along the [110] direction. Dispersed on top of these rows are elongated white spots that occupy approximately 65% of the total surface area. The remainder of the surface is covered with a zigzag pattern of gray spots extending in the same direction.

The two main features on the surface can be clearly seen in the inset image in the lower right corner of Fig. 1. The elongated white spots are spaced 8.2 \AA apart along the rows ($\times 2$), and 4.1 \AA apart across the rows ($\times 1$). Note that the spots in neighboring rows are out of phase with each other, yielding half of a $c(2 \times 2)$ unit cell (highlighted square in the lower left quadrant). In addition, white spots are sometimes isolated from one another, or in phase with spots in neighboring rows 8.2 \AA distant (highlighted square in upper right quadrant). This geometry corresponds to a $p(2 \times 2)$ unit cell. The zigzag pattern of gray spots in the next lower layer produces a (2×1) structure. This pattern is sometimes out of phase with the adjoining rows, and yields a local $c(4 \times 2)$ pattern (the honeycomb arrangement in the center of the inset image). Conversely, the zigzag pattern can be in phase with the neighboring row, which gives a local $p(2 \times 2)$ pattern. The (2×1) structure has been reported previously by us and corresponds to a complete layer of buckled phosphorous dimers.¹⁰ The oblong white spots sitting on top of the (2×1) are evidently adsorbed phosphorous dimers.

Analysis of the InP (001) surface by x-ray photoemission reveals that the concentration of carbon on the surface ranges from 12 to 18 at.%. This carbon most likely arises from the adsorption and decomposition of tertiarybutyl groups from the TBP source. In order to learn more about the adsorbates on the surface, a deuterium titration experiment has been performed. The procedure used is as follows: a freshly grown InP (001) film is transferred from the MOVPE reactor into the vacuum chamber. Then deuterium is dosed into the chamber at 5×10^{-7} Torr, while a hot tungsten filament, located 4 cm from the crystal, ionizes the D_2 gas. The deuterium atoms adsorb onto the surface, displacing any spe-

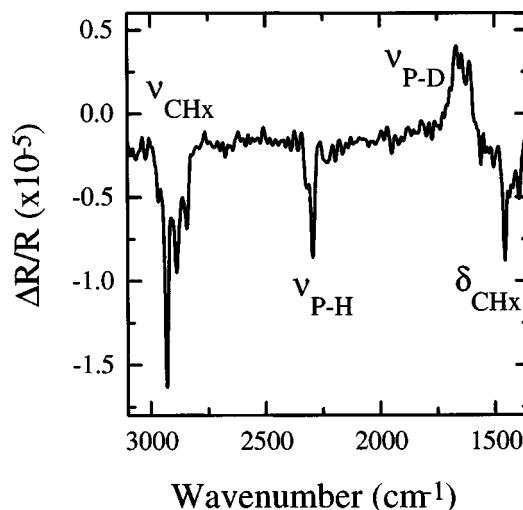


FIG. 2. Infrared spectrum of the freshly grown InP (001) surface following deuterium titration at $30 \text{ }^\circ\text{C}$.

cies that had accumulated there while in the MOVPE reactor. Infrared spectra are collected on the InP surface before and after dosing the D atoms, and the desorbed species appear as negative peaks in the spectrum.

Shown in Fig. 2 is the infrared spectrum of the indium phosphide surface following deuterium titration at $30 \text{ }^\circ\text{C}$. Negative bands from 3000 to 2800 cm^{-1} are due to adsorbed hydrocarbon species. The peaks observed at 2964 and 2887 cm^{-1} are assigned to the asymmetric and symmetric C–H stretching vibrations of methyl groups, while the peaks at 2931 and 2840 cm^{-1} are due to the asymmetric and symmetric C–H stretching vibrations of methylene groups.¹² Another negative peak at 1458 cm^{-1} is due to a C–H bending mode. The negative peaks seen at 2301 and 2292 cm^{-1} are assigned to P–H vibrational modes.¹³ Finally, positive phosphorous deuteride stretching vibrations are seen at 1666 , 1645 , and 1609 cm^{-1} . These results demonstrate that upon removal from the MOVPE environment, a significant fraction of the indium phosphide surface is terminated with alkyl radicals and hydrogen atoms. This is similar to what we have observed previously for MOVPE-grown gallium arsenide (001) films.^{14,15}

The observation of a relatively high coverage of alkyl radicals suggests that there might be significant carbon contamination in the InP films. For example, Oh *et al.*¹⁶ showed that a carbon doping level of $1 \times 10^{19} \text{ cm}^{-3}$ was obtained in material grown by chemical beam epitaxy with tertiarybutylphosphine. To check if there was intrinsic doping from the TBP source during MOVPE, we analyzed several films by SIMS. It was found that for our growth conditions, the carbon concentration in the bulk averages $2.2 \pm 0.1 \times 10^{16} \text{ cm}^{-3}$. Therefore, it may be assumed that the adsorbed alkyls desorb cleanly during growth and do not significantly contaminate the epitaxial layer.

Ball-and-stick models of the structures present in the MOVPE environment are shown in Fig. 3. These models conserve the number of valence electrons involved in bonding.¹⁷ A mixture of $c(2 \times 2)$ and $p(2 \times 2)$ unit cells is created by adsorbing phosphorous dimers on top of a phosphorous terminated layer, as illustrated in part (a). Although the model shows an ordered array of unit cells, the STM

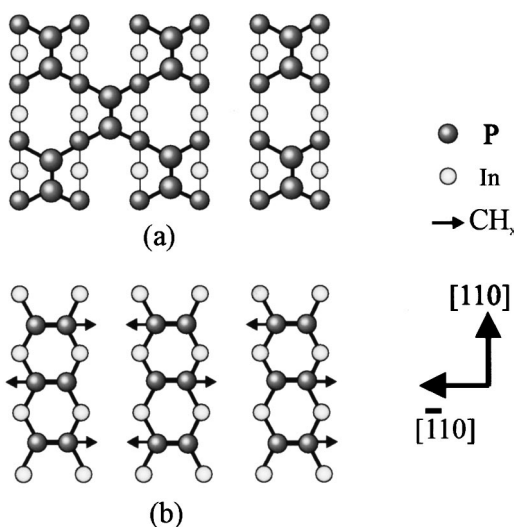


FIG. 3. Ball-and-stick model of (a) the $p(2 \times 2)$ and $c(2 \times 2)$ structures, and (b) the alkyl- and hydrogen-terminated (2×1) structure.

images indicate that the real surface is composed of a random array of complete and partial (2×2) unit cells. The underlying phosphorous-terminated layer reconstructs into a (2×1) structure as shown in part (b). Since each phosphorous dimer initially has three electrons in its two dangling bonds, the maximum coverage of alkyl groups and H atoms is one per dimer, or 0.5 ML. These adsorbates are indicated by the small arrows in the model. During MOVPE growth, the InP (001) surface comprises a mixture of phosphorous dimers, alkyl radicals, and hydrogen atoms adsorbed onto a full layer of phosphorous atoms. The exact coverage of each of the adsorbates depends on many factors, such as the temperature, the partial pressures of the group V and group III sources, the total pressure, and the type of sources used, e.g., PH_3 vs TBP.

Based on the results present above, a picture of the InP (001) surface during MOVPE growth emerges. It seems reasonable that, at temperatures of 500–700 °C and V/III ratios in excess of ten, the active sites for adsorption and decomposition of the organometallic precursors are the phosphorous dimers of the (2×1) structure. In order for reaction to proceed, the group III source must effectively compete with gas-phase phosphorous dimers, hydrocarbon radicals, and hydrogen atoms for these sites.

A similar situation holds for gallium arsenide MOVPE. We have shown that at 500–700 °C and under arsenic-rich growth conditions, the GaAs (001) surface is terminated with a mixture of As dimers and alkyl groups (and a small amount of H atoms) sitting on top of a layer of arsenic atoms.¹⁴ Nevertheless, there is a significant difference in the relative stability of the adsorbates on the InP and GaAs (001) surfaces. For example, when a freshly grown GaAs (001) film is

heated in vacuum to 350 °C, the alkyl groups desorb, leaving behind a well-ordered $c(4 \times 4)$ phase with the top layer of arsenic dimers intact.¹⁴ By contrast, when a freshly grown InP (001) film is heated in vacuum to 350 °C, all the adsorbed species detach from the surface, thereby producing the phosphorous-terminated (2×1) reconstruction.¹⁰ The lower binding energy of the phosphorous-rich phase compared to the arsenic-rich phase has important implications for the MOVPE process. For example, it is well known that growing a heterojunction with arsenide material first and phosphide material second results in a more diffuse junction than if one deposits the layers in the reverse order.¹⁸ This may be explained by a higher surface coverage of arsenic ($\theta_{\text{As}} = 1.5\text{--}1.7$ ML) relative to phosphorous ($\theta_{\text{P}} = 1.0$ ML), which allows for the As to be redistributed into subsequent layers. As we learn more about the dynamics of arsenic and phosphorous adsorption on compound semiconductor surfaces, we should be able to better understand the evolution of heteroepitaxial thin films during metalorganic vapor-phase epitaxy.

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¹M. Meyer, *Compd. Semicond.* **3**, 30 (1997).

²G. B. Stringfellow, *Organometallic Vapor-Phase Epitaxy: Theory and Practice* (Academic, San Diego, 1989), p. 9.

³M. L. Hitchman and K. F. Jensen, *Chemical Vapor Deposition: Principles and Applications* (Academic, London, 1993), p. 265.

⁴N. K. Ingel, C. Theodoropoulos, T. J. Mountziaris, R. M. Wexler, and H. Moffat, *J. Cryst. Growth* **167**, 543 (1996).

⁵S. D. Adamson, B.-K. Han, and R. F. Hicks, *Appl. Phys. Lett.* **69**, 3236 (1996).

⁶B. X. Yang, Y. Ishikawa, T. Ozeki, and H. Hasegawa, *Jpn. J. Appl. Phys., Part 1* **35**, 1267 (1996).

⁷M. Zorn, T. Trepk, J.-T. Zettler, B. Junno, C. Meyne, K. Knorr, T. Wethkamp, M. Klein, M. Miller, W. Richter, and L. Samuelson, *Appl. Phys. A: Mater. Sci. Process.* **65**, 333 (1997).

⁸C. Goletti, N. Esser, U. Resch-Esser, V. Wagner, J. Foeller, M. Pristovsek, and W. Richter, *J. Appl. Phys.* **81**, 3611 (1997).

⁹T. K. Johal, S. D. Barrett, M. Hopkinson, P. Weightman, and J. R. Power, *J. Appl. Phys.* **83**, 480 (1998).

¹⁰L. Li, B.-K. Han, Q. Fu, and R. F. Hicks, *Phys. Rev. Lett.* **82**, 1879 (1999).

¹¹K. B. Ozanyan, P. J. Parbrook, M. Hopkinson, C. R. Whitehouse, Z. Sobiesierski, and D. I. Westwood, *J. Appl. Phys.* **82**, 474 (1997).

¹²L. H. Little, *Infrared Spectra of Adsorbed Species* (Academic, New York, 1966), p. 120.

¹³V. M. McConaghie and H. H. Nielsen, *J. Chem. Phys.* **21**, 1836 (1953).

¹⁴B.-K. Han, L. Li, Q. Fu, and R. F. Hicks, *Appl. Phys. Lett.* **72**, 3347 (1998).

¹⁵L. Li, B.-K. Han, and R. F. Hicks, *Appl. Phys. Lett.* **73**, 1239 (1998).

¹⁶J.-H. Oh, J. Shirakashi, F. Fukuchi, and M. Konagai, *Appl. Phys. Lett.* **66**, 2891 (1995).

¹⁷M. D. Pashley, *Phys. Rev. B* **40**, 10481 (1989).

¹⁸A. Y. Lew, C. H. Yan, R. B. Welstand, J. T. Zhu, C. W. Tu, P. K. L. Yu, and E. T. Yu, *J. Electron. Mater.* **26**, 64 (1997).