Example of a Compound Semiconductor Surface that Mimics Silicon: The InP(001)-(2 × 1) Reconstruction

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An InP(001)-(2 × 1) reconstruction was prepared by metal-organic vapor-phase epitaxy. Scanning tunneling micrographs and infrared spectra of adsorbed hydrogen revealed that the (2 × 1) is terminated with a complete layer of buckled phosphorous dimers, giving rise to $p(2 \times 2)$ and $c(4 \times 2)$ domains. A surface band gap of 1.2 ± 0.2 eV was measured by scanning tunneling spectroscopy. The buckling can be explained by electron correlation among the dangling bonds of pairs of phosphorous dimers. This allows the surface to achieve a lower energy, semiconducting state. This reconstruction mimics the Si(100)-(2 × 1), which is terminated with buckled silicon dimers.   [S0031-9007(99)08534-8]

Semiconductor surfaces, particularly those of silicon (001) and gallium arsenide (001), have been studied for over twenty years ([1,2], and references therein). Based on this work, a number of principles have been developed to explain the reconstructions observed on these surfaces. First, the atoms in the top layer form dimers to minimize the number of dangling bonds. Then, to achieve a semiconducting surface of lower energy, electron transfer occurs between the dangling bonds. On Si(001), a complete layer of dimers terminates the surface, forming a (2 × 1) reconstruction. This leaves one electron in each dangling bond. However, the energy is lowered by pairing the electrons within each dimer, such that one dangling bond is filled and pushed up, while one dangling bond is empty and pulled down [3]. This phenomenon gives rise to buckled dimers that in the scanning tunneling microscope exhibit $p(2 \times 2)$ and $c(4 \times 2)$ unit cells [4].

On GaAs(001), the surface is terminated with rows of arsenic or gallium dimers and dimer vacancies. Then, to achieve a semiconducting state, electron transfer occurs from the gallium to the arsenic dangling bonds, such that the former are empty and the latter are filled [5,6]. In addition, the As and Ga dimers are arranged within the unit cell to yield the lowest possible electrostatic energy [7]. These rules have been successful in explaining the reconstructions observed on GaAs(001), and on several other compound semiconductor surfaces [1,2].

In this Letter, we report on a new reconstruction of indium phosphide (001), the (2 × 1). This structure does not follow the dimer-missing scheme found on gallium arsenide (001), but instead is analogous to the (2 × 1) reconstruction observed on the silicon (001) surface. Our results show that the InP(001)-(2 × 1) is terminated with a complete layer of buckled phosphorous dimers, exhibiting $p(2 \times 2)$ and $c(4 \times 2)$ domains. The surface is semiconducting, indicating that electron correlation occurs among the dangling bonds. Below, we present our experimental findings and give a possible explanation for why this structure is formed.

The indium phosphide films were grown in a metal-organic vapor-phase epitaxy (MOVPE) reactor that is directly interfaced to an ultrahigh vacuum surface-analysis system [8,9]. The InP(001) wafers were miscut $\sim 0.1°$ towards the [100] direction and doped with 1×10^{18} S atoms/cm^3. The films were deposited at 550 °C, 9.4×10^{-4} Torr triisopropylindium (TIPIn), 0.12 Torr tertiarybutylphosphine (TBP), 20 Torr hydrogen, and a space velocity of 30 cm/s over the wafer surface (relative to 0 °C and 760 Torr). After growth, the crystals were cooled to 300 °C in TBP and H$_2$, and to 40 °C in H$_2$ only. After stopping the flow, the vessel was pumped down to 2×10^{-7} Torr, and the sample transferred to the UHV system.

The long-range order on the InP(001) surface was assessed with a Princeton Instruments low-energy electron diffractometer (LEED) at 50 eV. Scanning tunneling micrographs (STM) were obtained with a Park Scientific AutoProbe VP at 30 °C. Infrared spectra of adsorbed hydrogen were collected with a BIO-RAD spectrometer at 8 cm^{-1} resolution by multiple internal reflections through the crystal. The crystals were cut into trapezoids that yielded 31 reflections off the front face. Hydrogen was leaked into the chamber at 5×10^{-7} Torr and ionized over a white-hot tungsten filament located 4 cm above the crystal. The reflectance spectra shown herein are the ratio of a spectrum taken after a saturation dosage of hydrogen to that taken beforehand.

Immediately after removing the InP(001) crystal from the MOVPE reactor, a sharp single-domain (2 × 1) LEED pattern is observed with the 2× periodicity along the [$\bar{1}$10] direction. This pattern is shown in Fig. 1(a). X-ray photoemission spectroscopy indicates that the surface is covered with about 20 at. % carbon. This carbon is due to adsorbed alkyl groups, which are generated by the decomposition of the organometallic precursors [8–10]. These adsorbates have been identified by recording infrared spectra during deuterium titration of the sample surface [10]. The deuterium displaces the adsorbates from
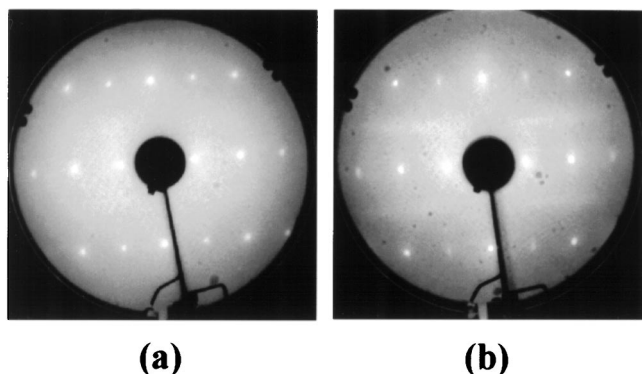
(a)   **(b)**

FIG. 1. The (2×1) LEED pattern of the InP(001) surface recorded (a) after removing the sample from the MOVPE reactor, and (b) after annealing in 1.0×10^{-5} Torr of PH_3 for 5 min at 300 °C.

FIG. 2. Scanning tunneling micrograph of the InP(001)-(2×1) reconstruction (image area $= 190 \times 190$ Å^2 and sample bias $= -3.8$ V).

the surface, yielding negative vibrational bands that are characteristic of the C-H stretching and bending modes of the alkyl species.

The alkyl adsorbates desorb from the surface upon heating the InP(001) crystal to 300 °C for 5 min in ultrahigh vacuum. To ensure that there was no change in the phosphorous coverage, this step was carried out in the presence of 1.0×10^{-5} Torr of phosphine. Electron diffraction patterns obtained after this step are still single domain (2×1), except that weak, half-order streaking is observed in the $\times 1$ direction, as shown in Fig. 1(b). This streaking is consistent with the surface containing a mixture of in-phase and out-of-phase $p(2 \times 2)$ and $c(4 \times 2)$ domains. An analogous LEED pattern has been reported for the $c(4 \times 2)$ reconstruction on Si and Ge(001) [11,12].

Presented in Fig. 2 is a scanning tunneling micrograph of the clean InP(001)-(2×1) reconstruction. Inspection of the image reveals that the surface is terminated with rows of buckled dimers. If the dimers in adjacent rows are out of phase, a $c(4 \times 2)$ honeycomb structure is produced (this unit cell is highlighted with a white diamond). Conversely, if the dimers in adjacent rows are in phase, a $p(2 \times 2)$ structure results (this unit cell is highlighted by a white square). The $c(4 \times 2)$ is the ground-state structure of the reconstructed Si(001) surface [13,14] and can be imaged with a tunneling microscope at low temperature [4].

The image shown in Fig. 2 also contains white and black patches interspersed over the gray dimer rows. The white features are due to small islands of (2×1) termination that are two layers up from the main terrace, while the black patches are vacancies that expose the crystal two layers below. In larger scale images, one sees more islands, varying in size from just a few dimers to more than one hundred. On the larger islands, the (2×1) dimer reconstruction is more easily resolved with the STM. It also should be noted that the islands are elongated in the $[\bar{1}10]$ direction, with the anisotropy being on average about six to one.

In order to resolve the composition of the surface, the dangling bonds have been titrated with hydrogen atoms
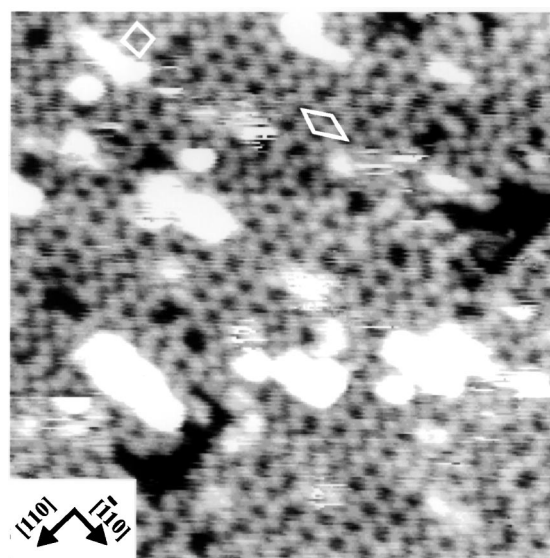
and infrared spectra recorded of the hydride stretching vibrations. We have previously used this technique to identify the adsorption sites on GaAs(001) reconstructions [15,16]. Presented in Fig. 3 are polarized infrared reflectance spectra of hydrogen adsorbed at the saturation coverage on the InP(001)-(2×1) surface. At this coverage, the LEED pattern is (1×1). In the figure, a group of overlapping bands are observed at 2339, 2321, 2300, 2262, 2225, and 2213 cm^{-1}, all of which are due to phosphorus hydride stretching vibrations. The bands at or above 2300 cm^{-1} are assigned to dihydrides, while those below 2300 cm^{-1} are assigned to monohydrides. These assignments are consistent with the vibrational properties of gas-phase organophosphine molecules [17,18], with prior
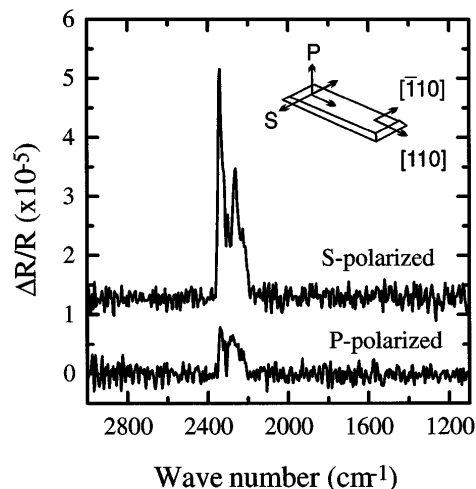

FIG. 3. Polarized infrared reflectance spectra of adsorbed hydrogen on the (2×1) surface after dosing with 1800L H$_2$ at 30 °C.

studies of phosphine adsorption on Si(001), and with hydrogen adsorption on InP(110) [19,20]. Further inspection of Fig. 3 reveals that the P-H vibrational bands are polarized in the $[\bar{1}10]$ direction, suggesting that the P-H dipole moment has a strong component along the dimer bond axis. Perusal of the spectrum between 1700 and 1200 cm^{-1} reveals no additional bands due to indium hydride stretching vibrations [10]. Thus, it may be concluded that the InP(001)-(2 × 1) surface is terminated with a complete layer of phosphorous dimers.

Insight into the electronic properties of the (2 × 1) has been obtained by scanning tunneling spectroscopy. Shown in Fig. 4 are the current-voltage characteristics of this structure. The I-V curve measures a single point on the surface under conditions where the tunneling gap is held at a sample bias of −3.6 V and a tunneling current of 1.0 nA. A surface band gap of 1.2 ± 0.2 eV is recorded, indicating that the surface is semiconducting. The log(I)-V plot in the figure inset accentuates the current variations in order to reveal the gap more clearly.

The (2 × 1) reconstruction of InP(001) exhibits many similarities to the (2 × 1) reconstruction of Si(001). Both of these surfaces are covered with dimers, there are no dimer vacancy rows, and the dimers are buckled. In addition, both of these surfaces are semiconducting. Such a result is surprising for a III/V compound semiconductor surface, because terminating it with a complete layer of group III or group V dimers should result in partially filled dangling bonds, and hence, should be metallic. However, the observation of a semiconducting surface indicates that electron correlation occurs among the dangling bonds to create filled and empty orbitals. This is where the analogy to the Si(001)-(2 × 1) surface ends. The electronic structure of the buckled Si dimer arises from the weak pi interaction between the dimer dangling bonds. This semiconducting state is adequately described by a one-electron theory of the band structure [3]. In the case of
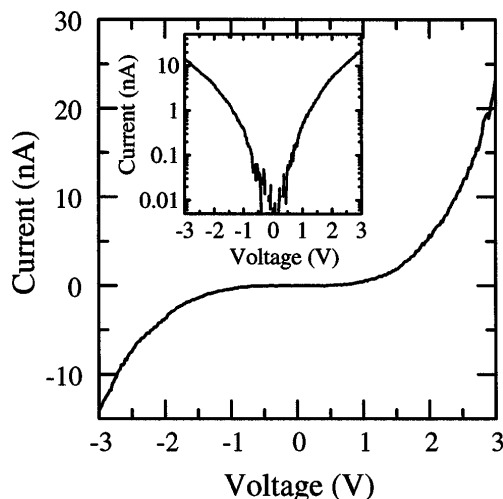
InP(001), it appears that electrons correlate in neighboring dangling bonds, which requires one to account for spin interactions, as in the Mott-Hubbard theory [21]. Electron correlation effects have been recently proposed to explain the electronic structure of the SiC(0001)-($\sqrt{3} \times \sqrt{3}$) reconstruction [22,23].

A model of the semiconducting InP(001)-(2 × 1) surface is presented in Fig. 5. Two variations are shown: (a) out-of-phase correlating dangling bonds yielding a $c(4 \times 2)$ unit cell; and (b) in-phase correlating dangling bonds yielding a $p(2 \times 2)$ unit cell. Electron correlation is depicted by pairing electrons from neighboring orbitals across the rows (circle around two dots). Pairing could also take place along the rows and still yield the same structures. The $c(4 \times 2)$ and $p(2 \times 2)$ cells are both seen in the STM image shown in Fig. 2. We expect that resonance may occur between the interacting orbitals, such that the dangling bonds on both dimers appear lower in the image. This would explain why all the dimers are buckled.

Another reconstruction reported for InP(001) is the (2 × 4) [24]. In filled-states STM images of this surface, three bright spots, in the shape of an equilateral triangle, appear in each unit cell. These triangles stack together forming rows along the $[\bar{1}10]$ direction. MacPherson $et\ al.$ [24] proposed that each group of three spots is due to a phosphorous trimer-adatom structure. On the other hand, Schmidt $et\ al.$ [25] performed total energy calculations on several different models of the (2 × 4) and concluded that the lowest energy phase is a single In-P dimer sitting on top of an indium-terminated layer. The two In-In
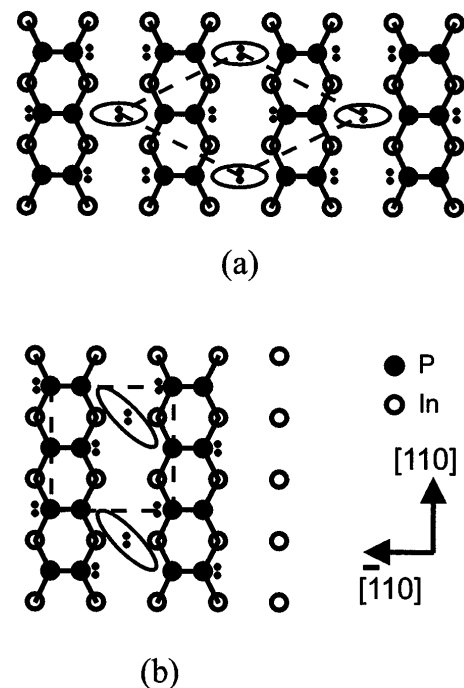

(a)

● P
○ In

[110]

[$\bar{1}$10]

(b)

FIG. 5. Ball-and-stick models of the InP(001) surface structures: (a) $c(4 \times 2)$ and (b) $p(2 \times 2)$. Electron pairs are represented by two small dots.

FIG. 4. Current-voltage characteristics of the (2 × 1) surface. The log(I)-V plot is shown in the inset.

back bonds and the phosphorous lone pair are presumed to be responsible for the three spots seen in the STM micrographs. Nevertheless, further work is needed to fully characterize this phase.

The InP(001)-(2 × 1) is unlike any reconstruction observed for GaAs(001). In the latter case, a combination of arsenic or gallium dimers and dimer vacancies provides the conditions necessary to achieve a semiconducting state [1,2]. The difference between these two materials may be related to the relative strengths of the dimer bonds compared to the anion-cation back bonds. The ratio of the As-As/Ga-As diatomic bond energies is 1.82, whereas the ratio of the P-P/In-P diatomic bond energies is 2.47 [26]. Thus, under group V rich conditions, there is a substantially greater thermodynamic driving force on InP compared to GaAs for completely covering the surface with group V dimers. Another factor to consider is the ability of the back bonds to "stretch" under the strain induced by dimerization of the top layer. The electric polarizabilities of gallium and indium are $(8.12$ and $9.65) \times 10^{-24}$ cm^3, respectively [26,27], indicating that the orbitals of the latter atom can more readily stretch to accommodate bonding with a layer of buckled group V dimers.

In summary, a new reconstruction of indium phosphide (001) has been discovered in which the surface is terminated by buckled phosphorous dimers, giving rise to $p(2 \times 2)$ and $c(4 \times 2)$ domains. Scanning tunneling spectroscopy indicates that the surface is semiconducting, which can be explained by electron correlation between dangling bonds on neighboring dimers. Nevertheless, further studies need to be undertaken to firmly establish the structural model proposed in Fig. 5. This includes photoemission measurements to determine the surface band structure and total energy calculations that include many electron effects. It would also be interesting to study temperature-dependent phase transitions by scanning tunneling microscopy and ultraviolet photoemission spectroscopy.

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[1] C. B. Duke, Appl. Surf. Sci. **65**, 543 (1993).
[2] Q.-K. Xue, T. Hashizume, and T. Sakurai, Prog. Surf. Sci. **56**, 1 (1997).
[3] D. J. Chadi, Phys. Rev. Lett. **43**, 43 (1979); P. Krüger and J. Pollmann, Phys. Rev. Lett. **74**, 1155 (1995).
[4] R. A. Wolkow, Phys. Rev. Lett. **68**, 2636 (1992).
[5] W. A. Harrison, J. Vac. Sci. Technol. **16**, 1492 (1979).
[6] M. D. Pashley, Phys. Rev. B **40**, 10 481 (1989).
[7] J. E. Northrup and S. Froyen, Phys. Rev. B **50**, 2015 (1994).
[8] L. Li, B.-K. Han, and R. F. Hicks, Appl. Phys. Lett. **73**, 1239 (1998).
[9] B.-K. Han, L. Li, Q. Fu, and R. F. Hicks, Appl. Phys. Lett. **72**, 3347 (1998).
[10] L. Li, B.-K. Han, Q. Fu, C. Li, D. Law, and R. F. Hicks (to be published).
[11] D. Haneman, Rep. Prog. Phys. **50**, 1045 (1987).
[12] S. D. Kevan, Phys. Rev. B **32**, 2344 (1985).
[13] J. E. Northrup, Phys. Rev. B **47**, 10 032 (1993).
[14] J. Dabrowski, E. Pehlke, and M. Scheffler, J. Vac. Technol. B **12**, 2675 (1994).
[15] H. Qi, P. E. Gee, and R. F. Hicks, Phys. Rev. Lett. **72**, 250 (1994).
[16] R. F. Hicks, H. Qi, Q. Fu, B.-K. Han, and L. Li (to be published).
[17] H. C. Beachell and B. Katlafsky, J. Chem. Phys. **27**, 182 (1957).
[18] E. R. Nixon, J. Phys. Chem. **60**, 1054 (1955).
[19] J. Shan, Y. Wang, and R. J. Hamers, J. Phys. Chem. **100**, 4961 (1996).
[20] H. Nienhaus, S. P. Grabowski, and W. Mönch, Surf. Sci. **368**, 196 (1996).
[21] J. Hubbard, Proc. R. Soc. London A **281**, 401 (1964).
[22] J. E. Northrup and J. Neugebauer, Phys. Rev. B **57**, R4230 (1998).
[23] J. Furthmüller, F. Bechstedt, H. Hüsken, B. Schröter, and W. Richter, Phys. Rev. B **58**, 13 712 (1998).
[24] C. D. MacPherson, R. A. Wolkow, C. E. J. Mitchell, and A. B. McLean, Phys. Rev. Lett. **77**, 691 (1996).
[25] W. G. Schmidt and F. Bechstedt, Phys. Rev. B **57**, 14 596 (1998).
[26] *CRC Handbook of Chemistry and Physics,* edited by David R. Lide (CRC, Boca Raton, FL, 1998), 79th ed.
[27] *Chemistry of Aluminum, Gallium, Indium and Thallium,* edited by A. J. Downs (Chapman and Hall, London, 1993).