Indium phosphide (001)-(2×1): Direct evidence for a hydrogen-stabilized surface reconstruction

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The surface structure of the indium phosphide (001)-(2×1) reconstruction has been clarified in this work. Infrared spectra collected during atomic deuterium titration of the InP (001)-(2×1) surface reveal a sharp P-H stretching mode at 2308 cm^{-1}. Based on theoretical cluster calculations using density-functional theory, this mode results from a single hydrogen atom bonded to one end of a buckled phosphorus dimer. These results confirm that the (2×1) structure is hydrogen stabilized as recently proposed in the literature.

Indium phosphide is an important semiconductor that finds many applications in optoelectronic devices. For this reason, the structure of the InP (001) surface is of scientific and technological interest.[1–14] Li and co-workers discovered a well-ordered (2×1) reconstruction that is produced following film growth by metalorganic chemical vapor deposition (MOCVD).[1,2] Scanning tunneling micrographs (STM) revealed that the (2×1) is terminated with a complete monolayer of buckled phosphorus dimers. Scanning tunneling spectroscopy indicated that this surface is semiconducting with a band gap of 1.2 eV. Many-body effects were invoked to explain the opening up of the gap.[1–3] A ball-and-stick model based on these findings is presented in Fig. 1(a). Each phosphorus dimer shares three valence electrons in its two dangling bonds.

Recently, Schmidt *et al.* have proposed that the (2×1) is a hydrogen-stabilized structure.[4] The ball-and-stick model for this reconstruction is presented in Fig. 1(b). First-principles calculations predict that this configuration is energetically favorable, and the simulated STM image exhibits a zig-zagging pattern that is in good agreement with the recorded pictures.[1,2,4] In addition, this surface is semiconducting with a predicted gap of 0.75 eV. However, the results presented by Schmidt *et al.* are mainly based on theoretical arguments. In this Rapid Communication, we provide direct experimental evidence that hydrogen is part of the (2×1) structure, thereby verifying the more recent model for this reconstruction.

Indium phosphide films, 0.3 μm thick, were grown in an EMCORE Discovery125 MOCVD system using tertiarybutylphosphine (TBP) and solution trimethylindium (TMIn) as precursors (Epichem Inc.). The InP (001) substrates were semi-insulating with a 0.3° miscut towards the [110] plane. The following conditions were used in epitaxy: substrate temperature at 585 °C, V/III ratio of 70, and a growth rate of 1.0 Å/s. After growth, the TBP flow was maintained until the substrate was cooled to 300 °C. Then the InP crystal was transferred to an ultrahigh vacuum (UHV) chamber without air exposure.

Once in the UHV system, the samples were annealed in 2.5×10^{-5} Torr of phosphine at 300 to 340 °C for 25 min to desorb any alkyl absorbates arising from the growth environment.[10] After cooling down to 25 °C, the surfaces were characterized by low-energy electron diffraction (LEED) and x-ray photoelectron spectroscopy. A sharp (2×1) diffraction pattern was observed with half-order streaks extending in the ×1 direction. Photoemission spectroscopy indicated that there was no carbon or other contaminants on the sample surface.

To investigate whether the InP (001)-(2×1) surface contains adsorbed hydrogen, deuterium atoms were dosed onto the surface while recording infrared spectra of the
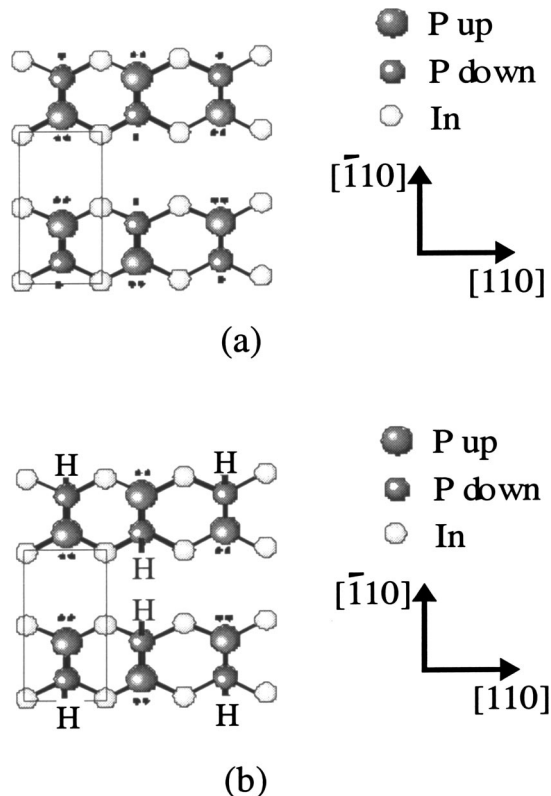

(a)

(b)

FIG. 1. Ball-and-stick models for the InP (001)-(2×1) reconstruction, assuming (a) clean surface (Ref. 1), or (b) hydrogen termination (Ref. 4).
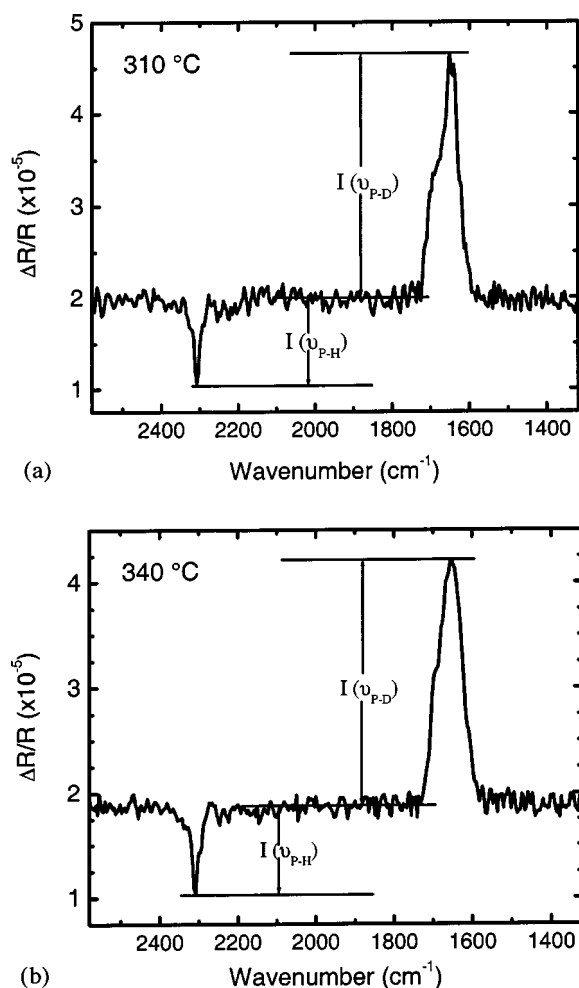
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FIG. 2. Infrared reflectance spectra of InP (001)-(2×1) following deuterium titration at 25 °C. The surfaces were annealed in PH$_3$ at 310 and 340 °C.
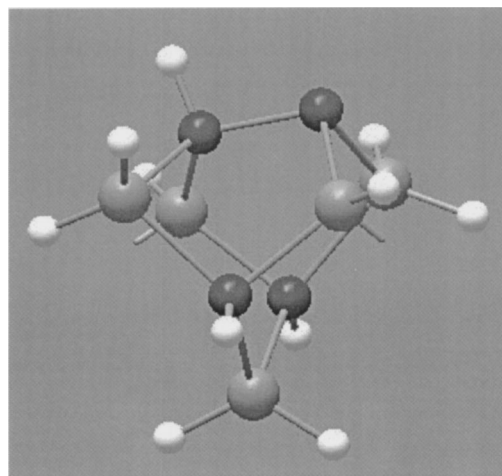

FIG. 3. An optimized molecular cluster of the (2×1) dimer structure. The P, In, H atoms are represented as black, gray, and white spheres, respectively.

sample. The D atoms will displace any adsorbed hydrogen, thereby producing a negative peak for each P-H vibrational mode initially present. The infrared spectra were recorded with a BIORAD FTS-40A spectrometer at a resolution of 8 cm^{-1} by multiple internal reflections through the indium phosphide. The crystals were cut into trapezoids that yielded 31 reflections off the front surface. Deuterium was introduced into the chamber at 3.0×10^{-5} Torr, and dissociated to atoms by a hot tungsten filament located 4 cm from the sample surface. Only 15 min was required to completely saturate the surface with D atoms. The vibrational spectra reported below were obtained by taking the ratio of single beam data collected during dosing to that recorded beforehand.

Presented in Fig. 2 are two infrared spectra of the InP (001)-(2×1) following deuterium titration at 25 °C. Samples (a) and (b) were annealed in PH$_3$ at 310 °C and 340 °C. No higher annealing temperatures were used because phosphorus desorption occurs above 350 °C and may produce mixed phases.[2] Note that the LEED pattern after dosing is a sharp (1×1). The positive bands observed between 1740 and 1580 cm^{-1} are due to absorbed deuterium atoms,

with the two most intense P-D stretching modes located at 1694 and 1655 cm^{-1}. The single negative peak, appearing at 2308 cm^{-1} on both samples, is assigned to a P-H vibrational mode. This negative peak was produced by deuterium displacement of the absorbed hydrogen initially present on the (2×1) reconstruction.

To compare the relative intensity of the P-H and P-D bands, a ratio is defined:

$$\eta = |I_{\nu(\text{P-H})}|/|I_{\nu(\text{P-D})}|,$$

where $I_{\nu(\text{P-H})}$ and $I_{\nu(\text{P-D})}$ are the peak height of the P-H and P-D vibrational modes, respectively. For sample (a), a ratio of 0.35 is obtained. The η factor remains essentially unchanged when the (2×1) is annealed at a higher temperature, and was equal to 0.37 for sample (b). The insensitivity of the intensity ratio to the annealing temperature implies that the absorbed hydrogen is an integral part of the (2×1) phase.

The structure of the (2×1) reconstruction has been further studied by *ab initio* molecular cluster calculations using the GAUSSIAN98 quantum chemistry suite.[3,11,15] To mimic the H:(2×1) reconstruction, a cluster was assembled that contains one hydrogen-bonded phosphorus dimer tethered to five "bulk" In atoms and two "bulk" P atoms. In the cluster, the truncated bulk atoms are terminated with hydrogen atoms, except that two of the bulk indium atoms are datively bonded to PH$_3$ groups. We have shown previously that such a cluster model provides a balanced description of the covalent and dative bonding effects in compound semiconductors, where charge neutrality is achieved while maintaining each atom in a fourfold coordination.[3,11] Since three valance electrons are shared between the two P dimer atoms, the maximum hydrogen coverage is one atom per dimer or 0.5 monolayers (without breaking the P-P dimer bond).

The calculations were performed using density-functional theory with Becke three-parameter exchange functional and the Lee-Yang-Parr correlation functional.[3,11,16,17] The $(18s/14p/9d)/[6s/5p/3d]$ contracted basis set and the

Dunning-Huzinaga $(11s/7p/1d)/[6s/4p/1d]$ contracted basis set (D95**) were chosen for indium and phosphorus, respectively. We used the D95** polarized double-ζ basis set for the single surface hydrogen atom, and the D95 double-ζ basis set for the bulk terminating hydrogen atoms. No geometric constrains were placed on the optimization process.

The optimized cluster structure is presented in Fig. 3.[18] The attachment of the single hydrogen atom leads to buckling of the surface phosphorus dimer. This configuration is consistent with the filled-states scanning tunneling micrograph of the (2×1).[1,2,4] In addition, the P-H vibrational mode is predicted to occur at 2302 cm^{-1} for the optimized cluster,[18] in good agreement with the negative P-H band shown in Fig. 2. The observation of several P-D bands indicates that the deuterium atoms break some of the phosphorus dimer bonds.

In summary, our results indicate that the model proposed by Schmidt et al.[4] is most likely the correct structure for the InP (001)-(2×1). Here the surface is covered with a complete layer of buckled phosphorus dimers with every other P atom terminated with hydrogen. Moreover, this structure obeys the electron counting model.[19,20]

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