Scanning Tunneling Microscopy Study of InP(100)-(2 × 4): An Exception to the Dimer Model

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We report the first atomic resolution scanning tunneling microscopy images of the InP(100)-(2 × 4) surface. High resolution images were obtained for both occupied and unoccupied states. The ×4 periodicity is due to missing rows, and the ×2 periodicity to the repetition of what appear to be trimer units. It is demonstrated that the images are inconsistent with dimer-based models proposed for related semiconductor surfaces such as GaAs. [S0031-9007(96)00675-8]

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There has been great success in explaining the surface structure of nonpolar (110) cleaved faces of III-V compound semiconductors such as GaAs and InP. The surface structures have been found to be identical for all of the different compounds when scaled to the bulk lattice parameter [1]. The reconstruction of the technologically important (100) surface is more complex, and has been a subject of continuing interest over the past 20 years [2]. The ideal (100) surface is polar, being terminated either entirely by group III (e.g., Ga or In) or group V (e.g., As or P) atoms. However, the ideal termination is not observed. Depending on the surface stoichiometry, many different reconstructions have been reported, with the most common being $2 \times 4/c(2 \times 8)$ and $4 \times 2/c(8 \times 2)$ [3]. A large number of experimental and theoretical studies, performed primarily on GaAs, have led to the formulation of some general principles concerning these surfaces [2,3]. The cation (e.g., Ga) dangling bonds are significantly higher in energy than the anion (e.g., As) dangling bonds. Stable reconstructions can be obtained for stoichiometries which allow the surface to remain uncharged, with the cation dangling bonds empty and the anion dangling bonds filled (this condition is sometimes referred to as the electron counting rule) [4–6]. Energy reduction also occurs through the dimerization of the surface atoms, leading to a reduction in the density of dangling bonds at the surface [3]. Other details of the reconstruction involve a minimization of the total energy, including the surface strain energy and the energy of the surface state bands [1]. Application of these principles has led to a class of models for the (100)-(2 × 4) and -(4 × 2) reconstructions, all of which involve a combination of dimers and missing dimers. For example, a three As dimer–one missing dimer model and a two As dimer–two missing dimer model have been proposed for the GaAs(100)-$(2 \times 4)/c(2 \times 8)$ surface to explain diffraction, electronic structure, and scanning tunneling microscopy (STM) results [7–11]. While most of the work that has been conducted on (100) surfaces involves GaAs, it is generally believed that the results of these studies apply, with minor modifications, to the (100) surfaces of other III-V semiconductors [3,12]. In this Letter, we present the first atomic resolution STM images of the InP(100)-(2 × 4) reconstruction. A trimerlike structure is observed which does not resemble any previously reported structure for the (100) surface of III-V semiconductors. Dimer models proposed for the (100) surfaces of other III-V compound semiconductors are found to be unsatisfactory in describing the observed features. These results therefore call into question the universality of dimer-based models for the (100) III-V surfaces.

It has been claimed that ion bombardment and annealing (IBA) preparation of InP(100) results in a surface with an In-rich $4 \times 2/c(8 \times 2)$ reconstruction [13,14], analogous to that obtained on GaAs(100) [15]. However, Mitchell *et al.* have shown that this treatment results in a 2 × 4 reconstruction, in agreement with the results of Sung *et al.* [16,17]. We have found that this reconstruction is also obtained by simple heating of the oxidized surface to above 550 °C in UHV. Few STM studies have been performed on the InP(100) surface. The existing images are of low resolution, and have been obtained on surfaces prepared by heating in an As flux, where an unknown amount of As is incorporated in the surface layers [18]. On the basis of the row structure observed in these previously reported images, a two In dimer–two missing dimer reconstruction was suggested. To the best of our knowledge, the results reported here are the first STM images of any III-V compound semiconductor surface prepared by the thermal desorption of the oxide layer in the absence of a group V (i.e., P or As) atmosphere. We find that the ×4 periodicity is indeed due to missing rows, but that the ×2 periodicity is due to the repetition of what appear to be trimer units.

The STM experiments were performed in an UHV chamber (base pressure of 4×10^{-11} Torr) containing low energy electron diffraction (LEED) optics and a hemispherical analyzer for performing Auger electron

spectroscopy. All STM images were obtained at room temperature. Both n type (Sn-doped, carrier concentration 1.2×10^{18} cm^{-3}) and p type (Zn-doped carrier concentration 12.6×10^{18} cm^{-3}) InP(100) samples (Crystacomm) were used. The samples were polished on one side only, and the [011] direction was indicated on the wafer by the manufacturer. The epiready samples were inserted into the vacuum untreated, and resistively heated to above 550 °C. After this treatment, a sharp 2×4 LEED pattern was observed with streaking of the $\frac{1}{2}$ order spots along the $\times 4$ direction [19]. Monitoring the LEED pattern during sample heating revealed only a diffuse 1×1 pattern before the appearance of the 2×4 pattern. Auger analysis revealed no carbon or oxygen contamination. After the heat treatment, the surface was visibly cloudy. Optical and atomic force microscopy analysis revealed the presence of droplets ranging in size up to several microns. Such features have previously been attributed to In droplets [20]. Between the droplets, STM imaging revealed large terraces of clean InP(100)-(2×4) [21]. STM images were obtained reproducibly for both n and p type samples, from several different tips, and from several different areas on the sample. The observed structures were not altered with repeated imaging.

In Fig. 1(a), an occupied state STM image of InP(100)-(2×4) is shown. Parallel to the $[0\bar{1}1]$ direction, rows which give rise to the $\times 4$ periodicity are clearly visible [22]. The more lightly shaded rows in Fig. 1(a) indicate another terrace. All steps were observed to be double steps, with a height of 3.1 Å. If the same reconstruction is to exist on all the terraces, the alternation of In and P layers in the bulk does not allow single steps. An enlarged view of the area enclosed in the rectangle of Fig. 1(a) is shown in Fig. 1(b). Trimerlike structures are clearly resolved within the rows. The trimer "heads" (single feature, labeled h) are more prominent (~ 0.5 Å higher) than the "ears" (double feature, labeled e) and the spacing within the trimerlike units is 4 Å between the ears, and 3 Å between the ears and the head along the $[0\bar{1}1]$ direction. The features are referred to as trimerlike because they appear to be cohesive units and not just chance juxtapositions of heads and ears. The trimerlike unit is repeated every 8 Å, giving rise to the $\times 2$ periodicity in the $[0\bar{1}1]$ direction. The head-ear-head pattern within a row can be interrupted, such that heads or ears face each other. The trimer units are often out of phase in adjacent rows, leading to a streaking of the $\times 2$ LEED spots along the [011] direction [this is sometimes referred to as a disordered $c(2 \times 8)$ structure] [23]. Occasionally, the trimer units are replaced by a row of prominent headlike features [circled region of Fig. 1(b)], which have $\times 2$ periodicity in the $[0\bar{1}1]$ direction [24]. Bordering the trimers on each side, a row of features (labeled z) can be observed, which are separated by 4 Å along the $[0\bar{1}1]$ direction and 10 Å across the trimer row along the [011] direction. These "zipperlike" rows are 1.3 Å below the trimer ears suggesting a vertical separation of one atomic layer. There is a small modulation in the corrugation of a zipper row such that zipper features next to a head appear slightly higher (~ 0.2 Å) than those next to ears.

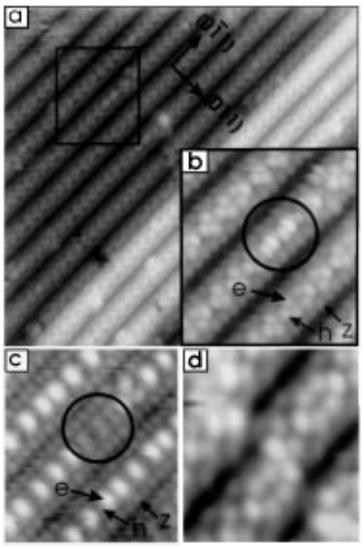

FIG. 1. Constant current (0.04 nA) STM images of InP(100)-(2×4) after annealing at 560 °C for several seconds. (a) A 218 Å $\times$ 204 Å area recorded at -1.5 V. An enlarged view of the area enclosed in the rectangle (51 Å $\times$ 52 Å) of (a) is shown in (b). An unoccupied state image ($+1.5$ V) that is in registry with (b) is shown in (c). The head, ear, and zipper features are labeled "h," "e," and "z," respectively. An occupied state image (-2.2 V) showing a section of a phase break (34 Å $\times$ 34 Å) in which staggered trimers with heads separated by 4 Å in the [011] direction is shown in (d).

In general, it has been found very difficult to obtain unoccupied state images on the (100) surfaces of III-V semiconductors [12,25]. Figures 1(b) and 1(c) show registered occupied and unoccupied state images, respectively. Ear features in the occupied state images (labeled e) appear as one merged feature in unoccupied states. The feature in occupied state images that we refer to as the head (labeled h) is much less prominent in unoccupied states. The height difference between the ears and head is ~ 0.5 Å in the unoccupied state images, the reverse of that observed in occupied state images. The row of headlike features found in the occupied state image [circled region of Fig. 1(b)] is greatly diminished in unoccupied states [circled region of Fig. 1(c)]. The zipper maxima are separated by 12 ± 0.5 Å across the trimer row in the [011] direction in the unoccupied state image, compared to 10 ± 0.5 Å in the corresponding occupied state image. Unoccupied state images show a modulation in the corrugation of the zipper row (~ 0.2 Å) similar to that observed in occupied state images.

The $2 \times 4/c(2 \times 8)$ reconstructions of the (100) surfaces of III-V semiconductors have been interpreted in

terms of simple dimer models [2]. It is thus natural to begin by considering our images in terms of such a model. In attempting to construct a dimer–missing dimer model for the structure depicted in Fig. 1, the orientation of any In or P dangling bonds relative to the $\times 2$ and $\times 4$ directions needs to be established. The lattice of a tetrahedrally coordinated III-V semiconductor has only twofold symmetry about the [100] axis, and thus on the (100) surface, the [011] and $[0\bar{1}1]$ directions are not equivalent. Cation (e.g., In) dangling bonds will always lie along [011], and anion (e.g., P) dangling bonds along the $[0\bar{1}1]$ direction [14,26]. Since the reconstruction that we have obtained is oriented such that the $\times 2$ direction lies along $[0\bar{1}1]$ and the $\times 4$ direction along [011], any P dangling bonds will lie along the $\times 2$ direction, and any In dangling bonds along the $\times 4$ direction. This immediately rules out a reconstruction in which the $\times 2$ periodicity is due to the dimerization of surface In atoms. We therefore must consider dimer models in which the surface is P terminated. It is known that when InP(100) is heated to above 350 °C, P is preferentially lost, and In starts to accumulate in droplets on the surface [27]. The presence of In droplets on thermally treated surfaces makes the determination of surface coverage difficult, and direct verification that the surface is P terminated has not been possible.

A P-terminated two dimer–two missing dimer model, equivalent to the alpha 1-(2×4) structure reported for the As-rich GaAs(100) surface [28], is shown in Fig. 2(a). This model is attractive for several reasons. It is known to be a stable structure, at least for GaAs(100) [7], and satisfies electron counting [6]. Indium atoms bordering the missing row region are in a position consistent with the observed zipper features. In addition, line profiles along the $[0\bar{1}1]$ direction, within the missing row(s), reveal a $\times 2$ periodicity in our occupied state images, consistent with the presence of P dimers in the missing rows, as required by the two dimer–missing dimer model. These features are weak, and positioned as they are, within the trough of the missing row, it is not possible to rule out a multiple tip interaction as their origin. The dimer model of Fig. 2(a) breaks down, however, on several important points. The trimerlike features exhibit an asymmetry along the $[0\bar{1}1]$ direction which is not explained by a sequence of symmetric dimers. Variations such as buckled dimers are not helpful, since they would not be expected to introduce the central head feature. One might imaging a twisting of the dimers in the surface plane, as suggested by the arrows in Fig. 2(a). Such a distortion might arise from replacement of a second layer In atom by P, but this structure is not without problems [29]. Further difficulties with dimer-based structures emerge when examining the juxtapositions of dimerlike structures found at phase boundaries as shown in Fig. 1(d). There, staggered trimerlike units are observed, in which heads aligned along the [011] direction are separated by 4 Å. Figure 2(b) models this phase break for the two dimer–two missing dimer model case making it evident that atom *A* is required to dimerize with both atoms *B* and *C*, which is not possible. We have also considered a three P dimer–one missing dimer model as shown in Fig. 2(c). While it is tempting to assign the head and ear features to the "up" ends of alternately buckled dimers, this structures would result in separation of ear features along the [011] direction of ~ 8 Å, not 4 Å as observed. In any case, all dimer–missing dimer models suffer from the same similar shortcomings as that discussed above for the case of two dimer–two missing dimer model. Our observations place stringent requirements on any model for the InP(100)-(2×4). It is apparent that the surface structure cannot be interpreted solely in terms of dimers and missing dimers.

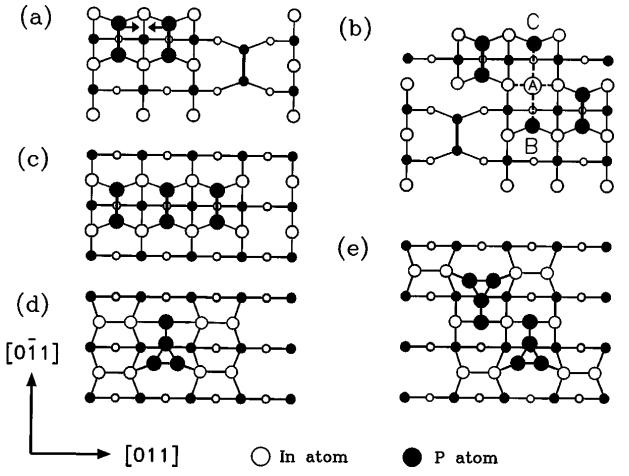

FIG. 2. (a) A two P dimer–two missing dimer model. Twisting of one end of the P dimers in the surface plane is indicated by the arrows. (b) An attempt to model the phase break shown in Fig. 1(d) by a two dimer–two missing dimer model. Note that the atom labeled *A* would be required to dimerize with both atoms *B* and *C*, which is not possible. (c) A three P dimer–one missing dimer model. (d) A proposed P trimer adatom model of the InP(100)-(2×4) reconstruction. (e) The phase break of Fig. 1(d) modeled using the P adatom trimer structure shown in (d). Topmost atoms are indicated by the largest circles. One 2×4 unit cell is shown in (a), (c), and (d).

One of the most striking aspects of the observed surface structure is the incorporation of a nearly threefold symmetric trimerlike structural unit onto a surface lattice that lacks threefold symmetry. The reconstruction that we observe is more reminiscent of structures found on threefold symmetric surface lattices, such as the (111) surfaces of the III-V semiconductors and of Si [30,31]. Both the occupied and unoccupied states images of our trimers show strong similarities to images of Sb trimers on the Si(111)-$(\sqrt{3} \times \sqrt{3})$-Sb surface [30]. A *tentative* model in which the trimer unit is due to threefold-coordinated P adatoms is shown in Fig. 2(d). This model satisfies electron counting. In filled state images, one can attribute the trimer features to the occupied orbitals of the

P trimer atoms, and the zipper features to valence band states associated with the In dimers. For the unoccupied state images, the head and ear features can be associated with the P trimers and the zipper features with the dangling bonds on the In dimers. We note that this model can account for differences seen for "heads" and "ears"—since the head shares only P-P bonds, it will have somewhat different character than the ears which have two P-P bonds and one P-In bond. It follows that the head features have minimal density in unoccupied states. We speculate that In-P antibonding states continue to account for the unoccupied state character of the ears. Furthermore, in Fig. 2(e) it is demonstrated that the P trimer structure can produce juxtaposition headlike features along the [011] direction which are separated by 4 Å, as observed at the phase break shown in Fig. 1(d). Any proposed model for the reconstruction must be able to account for the row of headlike features (which retain $\times 2$ periodicity along the $[0\bar{1}1]$ direction) that are occasionally observed [circled region of Fig. 1(b)]. The P adatom trimer model [Fig. 2(d)] can account for such a feature by replacement of the four atom P unit with a P dimer. Based on ion scattering and LEED studies of InP(100)-(2×4), Sung *et al.* proposed a model involving the trimerization of In atoms in the [011] direction [16]. Although their particular model is inconsistent with our images, it is noteworthy that their results were also inconsistent with conventional dimer models. While our model is attractive for the reasons outlined above, total energy calculations are needed to establish if the structure is stable. In addition, this model assumes one missing row; however, we cannot rule out models based on two missing rows.

In conclusion, we have reported the first atomic resolution STM images of the InP(100)-(2×4) surface for both occupied and unoccupied states. The images reveal a structure unlike any that has been reported previously on the (100) surface of a III-V semiconductor. We have demonstrated that the images are inconsistent with conventional dimer–missing dimer models.

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