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P-terminated InP(100) surface studied using a first-principles energy-minimization approach

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Using a first-principles energy-minimization approach, we have found a half-monolayer P-terminated InP(100) surface structure, which is characterized by Y-shaped tetramers and may account for recent scanning tunneling microscopy observations by MacPherson *et al.* [Phys. Rev. Lett. **77**, 691 (1996)]. For the monolayer P-terminated surface, we find that the 2×1 dimer structure is most favorable, which may be related to recent reflection high-energy electron-diffraction observations of Yang *et al.* [Jpn. J. Appl. Phys. **35**, 1267 (1996)] of a (2×1)-reconstructed surface. [S0163-1829(98)10535-0]

Due to technological importance, InP has been the subject of recent intensive experimental investigations.[1–24] Since the electronic properties of bulk InP are similar to those of GaAs, the surface structures of InP were once thought to be similar to those of GaAs. However, recent scanning tunneling microscopy (STM) and reflection high-energy electron-diffraction (RHEED) observations have found that the structural properties of InP(100) are quite different from those of GaAs(100). Most recently, MacPherson *et al.* found a dimer-free 2×4 P-terminated InP(001) surface structure, which has a half-monolayer coverage of P surface atoms, i.e., $\theta=0.5$, with P surface atoms forming Y-shaped tetramers rather than pairs of dimers.[23] For a high-coverage P-terminated surface, Yang *et al.*[24] observed a 2×1 RHEED pattern. Since the electron-counting rule (ECR) predicted that a monolayer 2×1 dimer structure was unstable, Yang *et al.*[24] concluded that the P-rich InP(100) sample had excess P atoms. However, they were unable to clarify the microstructure of this structure. If the coverage of excess P atoms was not large, the 2×1 RHEED pattern could still be due to a monolayer 2×1 surface with a reduced effective area, and the ECR might not be valid in this case. Both experimental observations were very important because dimers have been thought to be the building blocks of the zinc-blende (100) surfaces of semiconductors, and the ECR has been widely used by many researchers to choose structural models for theoretical studies and explanations of experimental data. Thus further theoretical studies are important for clarifying and better understanding the surface properties of InP(100).

In this paper, we report our study of the P-terminated InP(001) surface using the density-functional local-orbital molecular-dynamics method[25–27] in the energy-minimization application. This method is based on the norm-conserving pseudopotential method[28,29] with the s, p_x, p_y, and p_z local-orbital basis set, and has been shown to work well for usual semiconductor surface systems.[30–33] The present study concerns surface structures with unusual chemical bonds and rehybridizations. To our knowledge, this is the first application of our method to this kind of surface structure. Since within our method it is not trivial to increase the number of basis wave functions, we cannot do the convergent test used in plane-wave-based calculational methods. Thus the reliability of our method in this study will rely on a comparison with data. As stated below, our calculational results seem to support the STM observations of MacPherson *et al.* The theoretical lattice constant 5.969 Å, which is determined by bulk InP calculations, and a repeated six-layer-slab (i.e., supercell) model with a vacuum region 7.4 Å wide, are used for our structural models. For the $\theta=0.5$ P-terminated surface, we have considered three 2×4 structural models. One contains P dimer pairs to be denoted as the $2d$ model. The second is the one proposed by MacPherson *et al.*[23] to be denoted the Y_1 model. The third model, denoted the Y_2 model, has Y-shaped P tetramer like those of the Y_1 model except that the exposed second-layer atoms are arranged differently, as described below. For the $\theta=1$ P-terminated surface, we considered three structural models by analogy with GaAs(100);[32] they are (1) the 2×1 dimer model, (2) the 2×4 three-dimer–shifted-dimer model, and (3) the 2×4 dimer-pair–shifted-dimer-pair model. For all models, we have chosen the same 2×4 unit cell in order to compare total energies on the same footing. We sample the $\bar{\Gamma}$ point in the energy-minimization process. The bottom-layer atoms are assigned an arbitrarily large mass, so that they are essentially motionless, to simulate bulk atoms. We started the energy-minimization calculations with corresponding geometries with distances between nearest-neighbor surface atoms roughly equal to twice the covalent radius of the P or In atom.[34] Our method calculates the charge density self-consistently using Johnson's mixing scheme,[35] with a tolerance of $0.002e$ (where e is the magnitude of the electronic charge) for each atom. The Newtonian equation of motion used for energy minimization is solved numerically for a time step of 0.62 fs using the fifth-order Gear algorithm.[36] We use a quenching scheme[26,37] rather than the simulated annealing to let atoms settle to their stable or metastable positions, with the criterion that the force acting on each atom is less than about 0.1 eV/Å. After the stable or metastable atomic positions are found, we sample four special $\vec{k}$ points in the irreducible Brillouin zone for a two-dimensional rectangular lattice[38] to calculate the total energies. We tested with 16 special-$\vec{k}$ points; the results are essentially the same.

The relaxed geometries of models $2d$ and Y_2 are shown in Figs. 1(a) and 1(b), respectively. The $2d$ model has pairs of P dimers and pairs of missing dimers. The bond lengths of the two dimers in the dimer pair are 2.468 and 2.304 Å; the

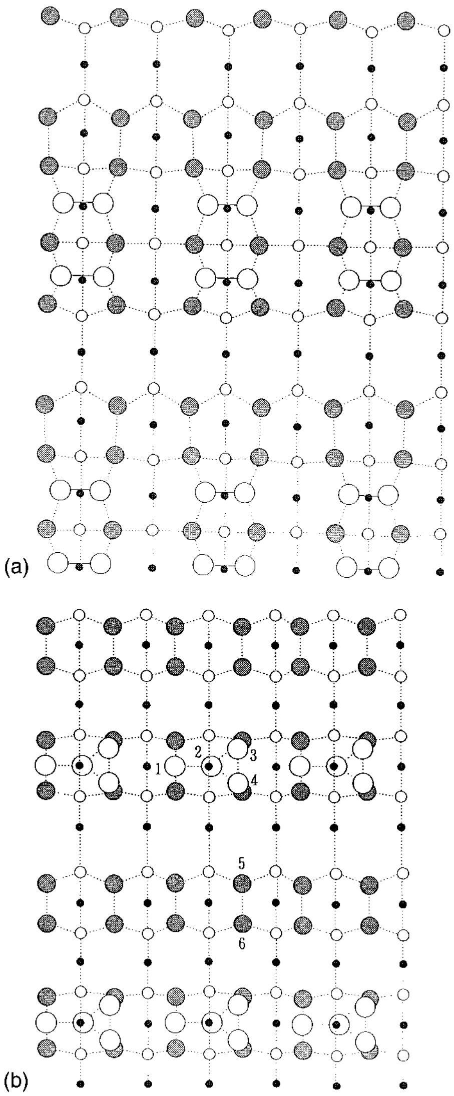

FIG. 1. Top view of the (a) dimer-pair model $2d$, and (b) the alternative tetramer model Y_2. Large and small open circles are the surface- and third-layer P atoms, respectively. The small filled circles are second-layer In atoms.

corresponding heights relative to the second layer are 1.727 and 1.214 Å. The related Y_1 model is similar to that proposed by MacPherson *et al.*[23] [Fig. 2(d)], with some distortion in the second In layer, in which the exposed second-layer In atoms are rebonded to the In atoms at the edges. The Y-shaped P tetramers in the Y_2 model also closely resemble those of MacPherson *et al.* The difference between the Y_2 and Y_1 models is that the exposed second-layer In atoms, represented by atoms 5 and 6 in Fig. 1(b), form a dimer row rather than being rebonded to the edge atoms. The four P atoms in the Y-shaped tetramer are denoted as atoms 1, 2, 3, and 4, as shown in Fig. 1(b). The bond lengths between atoms 1 and 2, atoms 2 and 3, atoms 2 and 4, and atoms 3 and 4 are 2.050, 2.388, 2.390, and 2.446 Å, respectively. They are close to the P-P bond length of 2.21 Å.[39] Relative to atoms 3 and 4, which are about 2.50 Å above the second-layer In atoms, atoms 1 and 2 sink down by 0.66 and 1.21 Å, respectively. Atom 1 is bonded to two second-layer In atoms and one P surface atom like the atom in a dimer. Atom 2 is bonded to three P surface atoms. Each of atoms 3 and 4 is bonded to one second-layer In atom and two P surface atoms. In comparison with dimer-pair model $2d$, the P surface atoms have more P-P bonds than P-In bonds. Inferred from the diatomic P-P and P-In bond strengths of 5.07 and 2.05 eV, respectively,[39] the Y-shaped P tetramer is expected to be more favorable than the dimer pair if the P ions have a suitable size, so that the formation of extra P-P bonds will not give rise to large strain. In addition, the P tetramer leaves more exposed second-layer In atoms, so that In dimer rows can be formed, as shown in Fig. 1(b). We find that models Y_1 and Y_2 have total energies of -0.121 and -2.095 eV/(1×1) cell, respectively, relative to model $2d$. Model Y_2 is much more favorable than models Y_1 and $2d$. Thus our total-energy results are consistent with these energetics arguments. Though model Y_2 is different from that proposed by MacPherson *et al.*, i.e., model Y_1, it still accounts for the STM observations because its surface layer has the same Y-shaped tetramers, and the difference in the second layer between Y_1 and Y_2 cannot be resolved by STM measurements.

The fully relaxed atomic arrangements for the top three layers for models (1), (2), and (3) of the $\theta=1$ P-terminated surface as shown in Figs. 2(a), 2(b), and 2(c). For model (1), the average dimer bond length is 2.352 Å. The average dimer bond lengths for model (2) are 2.365 and 2.377 Å for the three-dimer unit and shifted dimer, respectively. For model (3), the two dimer pairs have average bond lengths of 2.356 and 2.372 Å. With respect to the ideally truncated surface, the second-layer In and third-layer P atoms relax inwards by about 0.133 and 0.089 Å; respectively, for model (1). For model (2), the corresponding inward relaxations are 0.124 and 0.097 Å. For model (3), they are 0.107 and 0.091 Å. For models (1), (2), and (3), all dimers are essentially symmetric dimers within 0.04 Å, with a distance of about 1.24 Å from the second layer. Our total-energy results show that the 2×1 dimer structure is the most favorable among the three models considered. Models (2) and (3) have total energies of 0.178 and 0.068 eV/(1×1) cell, respectively, higher than that of the 2×1 structure. These results are different from that of GaAs(100),[32] for which model (2) is the most favorable. The different structural properties of anion-terminated InP(100) may be due to the P-P covalent bonding, which is stronger than the As-As covalent bonding, which give rise to stronger attractive dimer-dimer couplings, so that the dimers ''prefer'' to form long dimer rows. This argument is supported by the diatomic P-P bond strength of 5.07 eV, which is larger than that of As-As (3.96 eV).[39] Recently, Yang *et al.* found that the RHEED patterns for P-terminated InP(100) showed a 2×1 reconstruction. They could not clarify the microstructure of this 2×1 surface because the ECR led them to think that the (2×1)-reconstructed surface of InP fully covered by one layer of P dimers is unstable. In fact, the ECR is based on the assumptions that the bond charge can be rigidly counted as one-quarter of the number of valence electrons, and that the surface electronic structures are bulklike, so that dangling bond states of anions and cations lie close to valence-band maximum and conduction-band minimum, respectively.

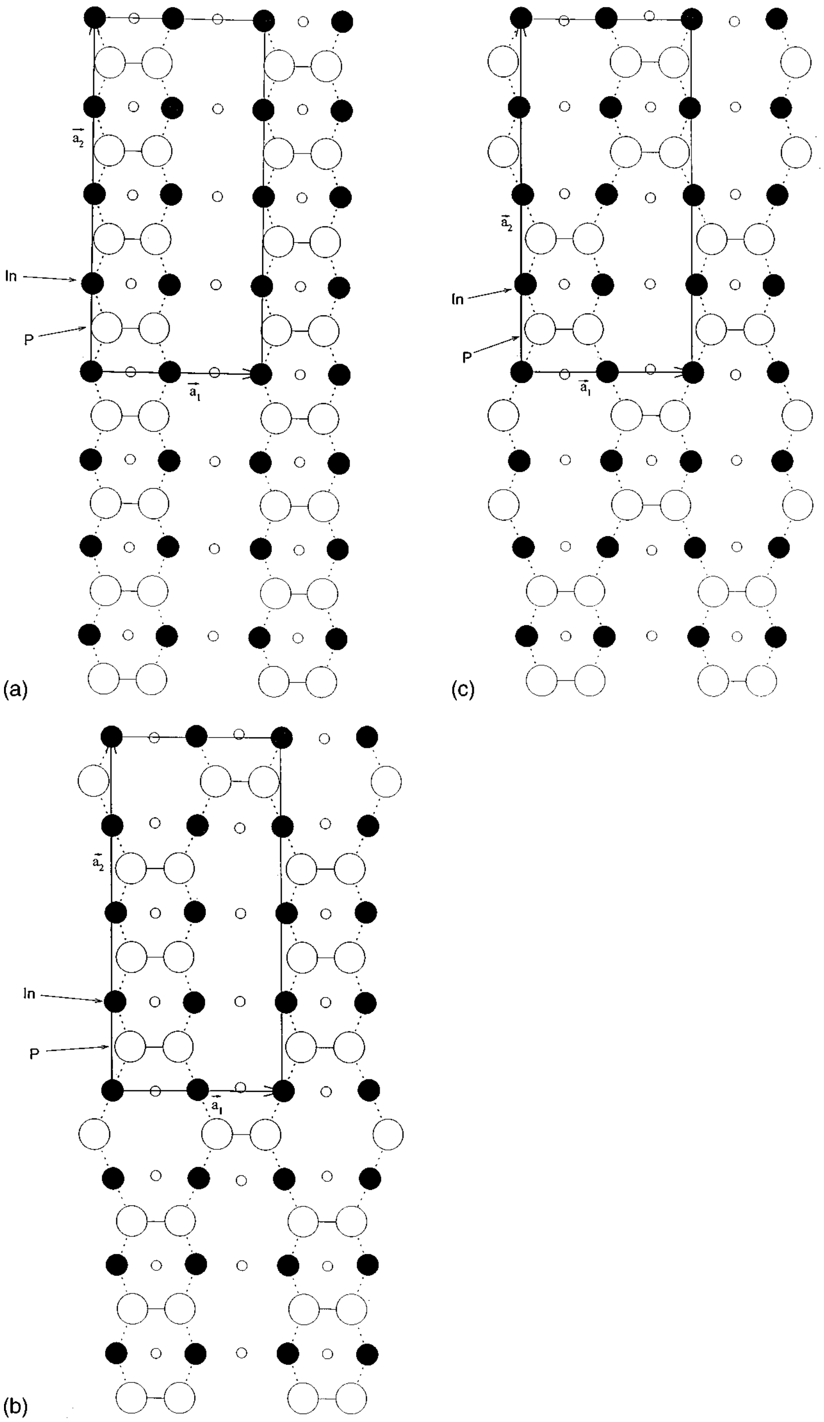

FIG. 2. Top view of the (a) 2×1 dimer model, (b) three-dimer–one-shifted-dimer model, and (c) dimer-pair–shifted-dimer-pair model of the P-terminated InP(100) surface. Large and small open circles are the surface- and third-layer P atoms, respectively. The small filled circles are second-layer In atoms.

These assumptions may not be valid for all compound semiconductors with so wide a variety of chemical and electronic properties. Our results show that InP(100) may be an exception of this rule.

In summary, the results of our energy-minimization calculations for $\theta = 0.5$ P-terminated InP(100) surfaces may account for the Y-shaped P tetramers observed in STM measurements by MacPherson *et al.* For the $\theta = 1$ P-terminated surface, we find that the 2×1 dimer structure is the most favorable among the models considered. This structure may be related to the microstructure that yielded the 2×1 RHEED pattern observed by Yang *et al.*[24]

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