Step Structures on III-V Phosphide (001) Surfaces: How Do Steps and Sb affect CuPt Ordering of $GaInP_2$?

Iskander G. Batyrev, W. E. McMahon, S. B. Zhang, J. M. Olson, and Su-Huai Wei
National Renewable Energy Laboratory, Golden, Colorado 80401, USA

(Received 14 May 2004; published 9 March 2005)

The observation of III-V phosphide (001)-(2×2) surfaces makes it possible to solve a long standing mystery of step structures. First-principles calculations show that a bulklike type-*B* step on a hydrogenated 2×2 surface is more stable than a rebonded one by 1.1 eV/unit step. In contrast, this energy difference for a H-free $\beta(2 \times 4)$ surface is only 0.5 eV/unit step. The large difference explains why the CuPt ordering of GaInP is stronger in metal-organic chemical vapor deposition than in molecular beam epitaxy. However, a minute amount of Sb will preferentially attach to the 2×2 surface steps and induce additional step structures that cause ordering disruption.

DOI: 10.1103/PhysRevLett.94.096101 PACS numbers: 68.43.Bc, 61.30.Hn, 68.35.−p, 81.15.Gh

Atomic ordering in epitaxially grown semiconductor alloys is a widely observed physical phenomenon that has broad applications, particularly for band-gap engineering. What drives the ordering is, however, a complex matter that often does not have a good explanation. Taking the CuPt ordering in $Ga_{0.5}In_{0.5}P$ (hereafter GaInP) as an example, intensive studies have been carried out over the last 15 years [1]. This ordering is unstable in the bulk [2], and only forms when stabilized by the surface during growth. In the leading dimerization-induced ordering model [3] for III-V alloys [4], the (001) surface dimers insert a modulating subsurface atomic strain that provides two-dimensional (2D), in-plane site selectivity for the Ga and In atoms. However, surface steps are needed in order to obtain the observed three-dimensional (3D) CuPt pattern, and, moreover, surface miscut can significantly affect the degree of order [5]. Model studies suggest that a uniform step structure in the growth front is required to place 2D ordered layers in the correct 3D registry [6]. In a more phenomenological growth model, the ordering is a result of two adjacent inequivalent surface sites near the step edge during step-flow growth [7]. However, such a model has not been supported by first-principles calculations.

The difficulty of proving or disproving the step effect on the ordering resides in the inability to atomically determine the energetics among the various step models, because the III-V (001) surfaces, with trenched 2×4 reconstructions [8], are inherently complex. With perhaps only one exception [9,10], first-principles calculations for III-V (001) steps have not been attempted, even though such steps are often important for step-flow growth [11] and for the fabrication of nanowires [12]. This lack of structural information often makes such studies difficult, and is in sharp contrast to the well understood step structures for elemental semiconductors such as Si. Recently, however, it was found that phosphide surfaces grown by metal-organic chemical vapor deposition (MOCVD) do not actually have the 2×4 reconstruction. Instead, 2×2 and $c(4 \times 2)$ surfaces have been observed for GaP [13], InP [14], and GaInP (Fig. 1). A recent calculation [15] showed that 2×2 and $c(4 \times 2)$ surface reconstructions are much simpler than 2×4 surfaces, as they only involve rows of P dimers, very much like the dimerization of a Si(001) surface. The only significant difference from Si(001) is that surface hydrogen atoms take alternating sites to passivate the P dimers, as required by the electron counting (EC) model. As will be shown below, these studies pave the way for realistic calculations of III-V phosphide surface step structures and for the determination of the role of steps on CuPt ordering. In addition, it is known that antimony disrupts the CuPt ordering of GaInP [16]. While a model for the disruption, based on dimerization-induced ordering on flat terraces, has been proposed, our experimental studies [17] indicate that just a minute amount of Sb, far from being enough to cover the entire surface, can cause the observed effect.

In this Letter we carry out a comprehensive study of the atomic structures of type-*B* steps on the 2×2 surface of GaP and InP (001), the CuPt ordering in GaInP, and the

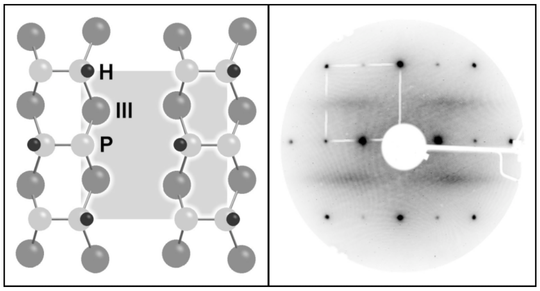

FIG. 1. (Left) Schematic top view for an MOCVD-prepared GaP or InP (001) surface. Each P-P dimer is passivated by a single H atom. A 2×2 reconstruction (shaded gray) forms when the H attachment sites alternate in phase, as shown. If the H attachment on adjacent rows is out of phase, the reconstruction becomes $c(4 \times 2)$. (Right) A LEED pattern for MOCVD-prepared GaInP, showing a mixture of 2×2 and $c(4 \times 2)$. A white square has been drawn with 1×1 diffraction spots at its corners.

effect of antimony on the ordering. We construct, in analogy to the double-layer silicon (001) steps [18], bulklike and rebonded steps which satisfy the EC model with the help of surface hydrogen. We find that bulklike steps are consistently more stable than rebonded steps by 1.1 eV per unit step (where one unit step contains one P step-edge site). Such a large energy difference establishes a uniform step structure across the surface, which is important for the observation of strong 3D CuPt ordering. As will be discussed later, a mixture of step structures can disrupt long-range ordering.

These results for 2×2 surface steps also shed light on other (001) surfaces. For example, the same step energy difference for a H-free $\beta(2 \times 4)$ surface is only 0.5 eV/unit step. Hence, hydrogenation plays a crucial role in the degree of ordering, which is stronger in MOCVD samples than in H-free molecular beam epitaxy (MBE) samples. We also find that, at low coverage, Sb adatoms on a vicinal 2×2 surface have a strong tendency to occupy step edges instead of staying on the terraces. The calculated energetics suggest that Sb adsorption leads to an incoherent mixture of different step structures, which in turn disrupts the ordering. These results point to a new mechanism for the observed CuPt ordering disruption by Sb, particularly suited for when the Sb coverage is low.

Our calculations were performed using the density-functional theory within the local density approximation and Vanderbilt ultrasoft pseudopotentials, as implemented in the Vienna *ab initio* simulation package (VASP) code [19]. The cutoff energy in the plane wave expansion is 150 eV. We used a skewed unit cell with the back surface passivated by pseudohydrogen atoms [9]. The slab in the flat area contains five monolayers. A vacuum layer of six-monolayer thickness is used to separate two adjacent slabs. All atoms, except for the bottom-layer P and pseudo H, are fully relaxed until the forces are less than 0.05 eV/Å. For the largest, 308-atom unit cell we used a $2 \times 2 \times 1$ mesh for the Brillouin zone integration, or 2 irreducible k points.

Figure 1 (left) shows, in a top view, the model for the MOCVD-grown 2×2 surface. The surface satisfies the EC model, in which a P atom donates 5/4 electrons to each of its four bonds whereas a Ga (In) atom donates 3/4 electrons. When 2 P atoms form a dimer without the hydrogen, there is an excess of $2 \times 5/4 - 2 = 1/2$ electrons in the dimer bond that must be transferred to the remaining P dangling bonds. Thus, each P dangling bond has $5/4 + (1/2)/2 = 6/4$ electrons. The P dangling bond lies near the top of the valence band and is hence an acceptor for $2 - 6/4 = 1/2$ electrons. In other words, each bare P-P surface dimer is a net one-electron acceptor. Surface hydrogen, as a result of the MOCVD growth, provides this required electron.

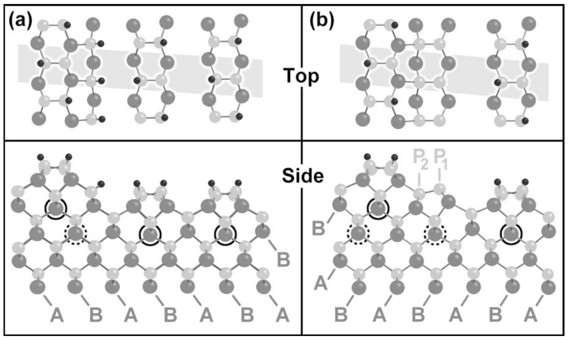

FIG. 2. (a) Bulklike and (b) rebonded type-*B* steps on GaP and InP (001). A 1x step unit for each step has been shaded gray. For simplicity, steps shown here do not satisfy the EC model. To satisfy the model, one H per four step units was removed from the step edge in (a), and added to step site P_1 in (b) in our calculations. When applied to GaInP ordering, Ga and In will preferentially occupy the *A* and *B* planes, respectively, as established by surface dimer-induced compression of the circled sites.

Since the 2×2 surface satisfies the EC model, it is natural to first consider the step models that also satisfy the EC model. For example, for the bulklike type-*B* step in Fig. 2(a), the P edge atom is threefold coordinated with a dangling bond filled with 5/4 electrons. Thus, it is a $2 - 5/4 = 3/4$ electron acceptor. Three hydrogen atoms are required to passivate every four P edge atoms. For the rebonded step in Fig. 2(b), however, a threefold P edge atom (P_1) is bonded to a neighboring fourfold P (P_2). Only 3/4 electrons are used for the rebonding, so the remaining dangling bond on P_1 has $(5/4 - 3/4) + 5/4 = 7/4$ electrons. Thus, in this case, the P edge atom is a $2 - 7/4 = 1/4$ electron acceptor. In other words, only one H is required for every four P edge atoms. Our calculations show that, with a H chemical potential equal to that of an H_2 molecule in vacuum ($\mu_H = 0$), a bulklike step has a lower energy than a rebonded one by 1.11 and 1.13 eV per unit step for GaP and InP, respectively. If instead one uses the chemical potential of $PH_3(\mu_H = -0.07$ eV per H), these results change by less than 0.1 eV. Thus, under most growth conditions with hydrogen, bulklike steps should dominate over rebonded steps.

TABLE I. Energy of rebonded steps with respect to bulklike steps (in eV per unit step). The full cell is four unit steps wide and satisfies the EC model. The reduced cells are two unit steps wide and hence do not satisfy the EC model. Numbers in the parentheses are with respect to the full cell.

Materials	Full cell (EC satisfied)	Reduced cell (0.25 hole/unit step)	Reduced cell (0.25 electron/unit step)
GaP	1.11	0.97[−0.14]	1.20[0.09]
InP	1.13	1.00[−0.13]	1.23[0.10]

Next, we consider step energy differences using reduced supercells where the EC model is only approximately satisfied. The reason for such an exercise is to test how robust the bulklike step is with respect to the rebonded one, because during growth the exact EC rule may not be valid. Table I shows that, to within 0.1 eV, the energy differences are practically the same as long as the two steps have the same excess of electrons or holes.

So far, our discussion concerns only binary systems. Here, we show that all of the binary results readily apply to ternary systems for the following reasons: First, the hydrogen-induced $(2 \times 2)/c(4 \times 2)$ reconstruction is also observed for GaInP as shown in Fig. 1 (right). Second, upon placing cation atoms at their size-preferred sites, the calculated step energy difference between the bulklike and rebonded GaInP steps of 1.16 eV is only 0.04 eV off from $(1.11 + 1.13)/2 = 1.12$ eV, the average between GaP and InP. Since such a difference (0.04 eV) is completely negligible when compared with the calculated step energy difference (1.12 eV), in the forgoing discussion for Sb we will calculate only GaP and InP, and interpolate from them the results for GaInP.

To illustrate how the direction of the ordering planes is determined by the step structure, we show in Fig. 2 how ordered GaInP will consist of *A* planes preferentially occupied by Ga, and *B* planes preferentially occupied by In. The group-III sites in the second cation layer directly underneath the P-P dimers are compressed and are hence preferred by the smaller cation atoms, i.e., Ga. We have marked these sites by solid circles. To determine which group-III sites further into the bulk should be Ga sites, we consider the step-flow growth process, but backwards in time. In both cases [2(a) and 2(b),] the step edges would retract to the left, leaving behind only flat (lower) terraces in Fig. 2. To be consistent with the already existing surface dimers, the Ga sites on the newly exposed lower terraces have to be those marked by dashed circles. If this exercise were to be continued using bulklike steps in (a) and rebonded steps in (b), the circled sites (both solid and dashed) would develop into the *A* planes shown. Note that the directions of the *A* planes in Figs. 2(a) and 2(b) are opposite. Only the one in Fig. 2(a) (termed "normal" hereafter) has been observed experimentally, whereas the one in Fig. 2(b) (termed "reversed") has never been observed [6]. Thus, the calculated large energy difference here establishes for the first time the microscopic origin for the exceptional stability of the normal ordering in MOCVD.

On bare Si (001) surfaces, the rebonded step is known to be more stable than the bulklike one [18], in contrast to what was found here. To understand this qualitative difference, we have calculated the energy without hydrogen on the step edges but otherwise maintaining those on the dimers of the flat terraces. We found that the energy difference is reduced by about 0.8 eV, to 0.3 eV per P atom. This hydrogen effect is in fact universal. For example, the energy difference between the two steps on a H-free $\beta(2 \times 4)$ surface is only 0.5 eV/P. This explains why CuPt ordering is stronger in MOCVD samples than in H-free MBE samples.

Turning to antimony, because Sb has a much larger atomic radius than P (1.4 Å vs 1.06 Å), one may expect that the degree of ordering could be reduced when Sb is used as a surfactant. This is because, according to the dimer-induced-strain model, replacing the shorter P-P dimer bonds by the longer Sb-Sb dimer bonds would significantly reduce subsurface strain, thus reducing the driving force for in-plane ordering. Indeed, CuPt ordering disruption by Sb has been observed experimentally [16], and is often cited in support of the Sb-Sb dimer model.

To study the Sb effects here, we first consider Sb adatoms on the flat (001) surfaces of GaP and InP. An Sb atom can either reside above the 2×2 surface as part of an Sb-Sb ad-dimer, or substitute for a surface P atom, which in turn goes to its bulk reservoir of (black) phosphorous. In either case, the surface hydrogen density does not change. We find that Sb substituting for P is favored, but only modestly, by 0.05 and 0.2 eV/Sb for GaP and InP, respectively. However, neither the Sb ad-dimer nor the substitutional Sb on the terraces is stable. Instead, they all prefer to occupy step-edge sites. This finding jeopardizes any ordering disruption model based on the Sb-Sb dimers.

We therefore studied a variety of Sb-induced step structures and found the three low-energy ones in Fig. 3 to be of particular interest: (a) Sb trimers, (b) zigzagged Sb chains, and (c) bulklike steps with Sb substituting for P at the step edge [a variation of Fig. 2(a)]. In essence, type-*B* step edges are $(\bar{1}\,\bar{1}\,\bar{1})$ minifacets. Trimers and chains are com-

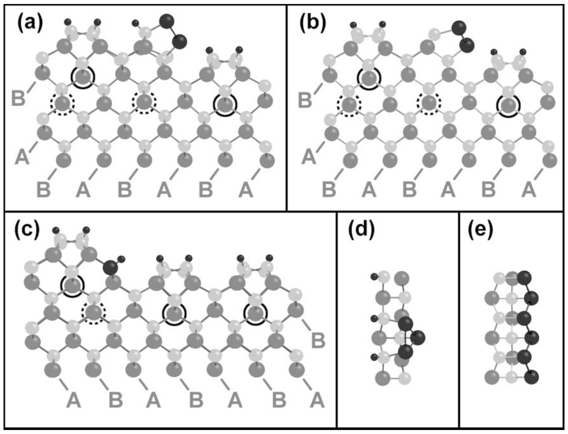

FIG. 3. Sb-terminated type-*B* steps on GaP and InP (001): (a) with an Sb trimer, (b) with an Sb chain, and (c) bulklike with substituted Sb. (d) and (e) are top views for the Sb trimer and Sb chain structures, respectively. The *A* and *B* planes have the same meaning as in Fig. 2. In (a) and (b), the direction of the ordering planes is reversed with respect to the normal direction induced by a bulklike step. Similar to Fig. 2, the steps as shown here do not satisfy the EC model.

mon features on the Sb-covered $(\bar{1}\,\bar{1}\,\bar{1})$ surfaces of GaAs [20], InSb [21], Si [22], and Ge [23]. Note that in (a) and (b), the edges of the steps have shifted by one bulk unit, similar to the rebonded steps. Had the trimers and chains formed on bulklike steps without the shift, their energies would be significantly higher. To calculate the energy lowering by forming these structures with respect to substitutional Sb on flat terraces, we used as an Sb reservoir the bulk chemical potential to conserve the number of Sb atoms. The energy lowering for GaP (InP) is 0.42 (0.34), 0.55 (0.58), and 0.47(0.56) eV/Sb for cases (a), (b), and (c), respectively. These energies are significant and indicate that Sb prefers the step sites instead of the terrace sites. However, in contrast to Sb-free steps, the Sb-decorated steps are energetically similar, e.g., the difference between (b) and (c) is only 0.08(0.02) eV/Sb for GaP (InP).

In addition, our calculations show that P trimers and chains at the step edges have significantly higher energies than P dimers on the flat terraces. Therefore, Sb will never have to compete with P for either trimer or chain sites, as it must for substitutional sites. This makes trimer- and chain-covered step edges particularly attractive to Sb during growth in which the gas-phase P/Sb ratio is greater than 10^4 [16].

Hence, the surface will be a mixture of different step structures: P-terminated bulklike, Sb-terminated bulklike, Sb trimer, and Sb chain. In the cases of Sb trimers and chains, the ordering direction will be reversed, similar to the rebonded steps. A random mixture of all three different step structures would change the ordering direction randomly on a length scale of nanometers, disrupting the ordering even at very low Sb coverages. Other Sb-attachment related mechanisms are likely to further disrupt the ordering. For example, Sb adatoms may hinder the interchange of Ga and In atoms at step edges as they incorporate into the bulk. Antimony may also block the movement of kinks at step edges, which in turn would alter the step propagation and surface morphology. Because Bi forms trimers on the $(\bar{1}\,\bar{1}\,\bar{1})$ surfaces of GaAs [24] and Si [25], and chains on the (110) surface of InAs [26], Bi may also disrupt ordering [27] via the same mechanisms as Sb.

In summary, type-*B* step structures on III-V phosphide (001) surfaces are studied by first-principles calculations. The role of steps in the three-dimensional CuPt ordering of GaInP is established. Hydrogen is found to play an important role in stabilizing the bulklike steps over the rebonded steps. This explains why CuPt ordering is stronger in MOCVD samples than in H-free MBE samples. We also find that, at low coverage, Sb adatoms have a strong tendency to occupy 2×2 surface step-edge sites, resulting in a random mixture of bulklike and nonbulklike steps. Their coexistence on the GaInP surface may disrupt the CuPt ordering in a variety of different ways, including the formation of a dense, irregular network of antiphase boundaries.

We would like to acknowledge T. Hannappel and A. G. Norman for helpful discussions. This work was supported by BES and OER, U. S. Department of Energy, under Contract No. DE-AC36-99GO10337, and by NERSC for MPP time.

[1] *Spontaneous Ordering in Semiconductor Alloys*, edited by A. Mascarenhas (Kluwer Academic, New York, 2002).

[2] P. Gavrilovic *et al.*, J. Cryst. Growth **93**, 426 (1988).

[3] F. K. LeGoues *et al.*, Phys. Rev. Lett. **64**, 2038 (1990).

[4] J. E. Bernard in *Reactive Phase Formation at Interfaces and Diffusion Processes*, edited by Y. Limoge and J. L. Bocquet, Materials Science Forum 155–56, (Trans Tech Publications Inc., Zurich, Switzerland, 1994), p. 131.

[5] A. Gomyo *et al.*, Jpn. J. Appl. Phys. **28**, L1728 (1989); M. Suzuki, Y. Nishikawa, M. Ishikawa, and Y. Kokubun, J. Cryst. Growth **113**, 127 (1991); S. R. Kurtz *et al.*, J. Appl. Phys. **75**, 5110 (1994).

[6] T. Suzuki and A. Gomyo, J. Cryst. Growth **111**, 353 (1991).

[7] M. Ishimaru, S. Matsumura, N. Kuwano, and K. Oki, Phys. Rev. B **51**, 9707 (1995).

[8] Q.-K. Xue, T. Hashizume and T. Sakurai, Prog. Surf. Sci. **56**, 1 (1997); and references therein.

[9] S. B. Zhang and A. Zunger, Phys. Rev. B **53**, 1343 (1996).

[10] S. B. Zhang and A. Zunger, J. Cryst. Growth **163**, 113 (1996).

[11] H.-C. Jeong and E. D. Williams, Surf. Sci. Rep. **34**, 171 (1999).

[12] M. Shibata, I. Sumita, and M. Nakajima, Phys. Rev. B **57**, 1626 (1998); P. Segovia, D. Purdie, M. Hensberger, and Y. Baer, Nature (London) **402**, 504 (1999); I. K. Robinson, P. A. Bennett, and F. J. Himpsel, Phys. Rev. Lett. **88**, 096104 (2002).

[13] L. Töben *et al.*, Surf. Sci. Lett. **494**, L755 (2001).

[14] L. Li, B.-K. Han, Q. Fu, and R. F. Hicks, Phys. Rev. Lett. **82**, 1879 (1999); P. Vogt *et al.*, Phys. Rev. B **60**, R5117 (1999); G. Chen *et al.*, Phys. Rev. B **68**, R121303 (2003).

[15] W. G. Schmidt *et al.*, Phys. Rev. Lett. **90**, 126101 (2003).

[16] J. K. Shurtleff, R. T. Lee, C. M. Fetzer, and G. B. Stringfellow, Appl. Phys. Lett. **75**, 1914 (1999).

[17] J. M. Olson (unpublished).

[18] D. J. Chadi, Phys. Rev. Lett. **59**, 1691 (1987).

[19] G. Kresse and J. Hafner, Phys. Rev. B **47**, 558 (1993).

[20] P. Moriarty, P. H. Beton, M. Henini, and D. A. Woolf, Surf. Sci. Lett. **365**, L663 (1996); R. H. Miwa and G. P. Srivastava, Phys. Rev. B **63**, 125341 (2001).

[21] T. Nakada and T. Osaka, Phys. Rev. Lett. **67**, 2834 (1991).

[22] P. Mårtensson, G. Meyer, N. M. Amer, E. Kaxiras, and K. C. Pandey, Phys. Rev. B **42**, 7230 (1990).

[23] R. G. van Silfhout *et al.*, Surf. Sci. **271**, 32 (1992).

[24] R. H. Miwa and G. P. Srivastava, Phys. Rev. B **64**, 195328 (2001).

[25] T. Takahashi, K. Izumi, T. Ishikawa, and S. Kikuta, Surf. Sci. **183**, L302 (1987).

[26] M. G. Betti *et al.*, Phys. Rev. B **59**, 15 760 (1999).

[27] S. W. Jun *et al.*, Appl. Phys. Lett. **76**, 2716 (2000).