

Effects of Zn Doping on the Surface Structure and Initial Growth Processes of InP Thin Film Layers on InP(111)B Substrate*

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The effects of Zn atoms as a dopant on the surface structure and initial growth processes on InP(111)B substrate are theoretically investigated on the basis of surface phase diagrams which are obtained by comparing the adsorption energy given by *ab initio* calculations with the gas-phase chemical potentials. The calculated surface phase diagrams demonstrate that the Zn-incorporated surface is stabilized under the growth conditions with high Zn supply ratio. Furthermore, In atoms tend to easily adsorb on the Zn-incorporated surface as an In-P dimer due to the formation of Zn-P and P-P bonds, implying that the adsorption of In atoms and resultant growth processes are promoted on the Zn-incorporated InP(111)B surface which is stabilized under Zn-rich conditions. These results suggest that effects of Zn doping on the surface structure and initial growth processes are crucial for understanding the bidirectional growth mechanisms of InP nanowires on InP(111)B substrate. [DOI: 10.1380/ejsnt.2015.147]

Keywords: Computer simulations; Indium phosphide; Zinc; Surface structure

I. INTRODUCTION

Semiconductor nanowires (NWs) have attracted much attention because of their unique electrical and optical properties applicable for various nanoscale devices [1-3]. In particular, InP-based NWs are promising for high-speed electrons, optoelectronic, and photovoltaic devices because of their superior material property and possibility to develop various kinds of heterostructures. One of important issues for fabricating such applications is to control nanowire shapes and crystal structure. Indeed, many types of NWs such as hexagonal pillar, tapered pillar, and irregular wire structures have been synthesized depending on the growth conditions. There have been intensive experimental studies to control nanowire shapes and structures in InP NWs, where growth temperature and V/III supply ratio are crucial factors [4-6].

Recently, various types of morphology of InP NWs have been observed in the selective-area metalorganic vapor phase epitaxy (SA-MOVPE) on the InP(111)B substrate [7, 8]. InP NWs tend to form a tripod structure that consists of three NWs pointing toward three-fold symmetric [111]A direction. However, the structure of InP NWs is dramatically changed by introducing Zn atoms which are used as *p*-type dopant. Under high Zn supply (high II/III ratio) conditions, hexagonal pillar structures with vertical sidewall grown along the [111]B direction have been fabricated while tripod structures are obtained under low Zn supply (low II/III ratio) conditions. These results indicate that the growth directions of InP NWs during the SA-MOVPE on InP(111)B substrate switch from the [111]A direction to the [111]B direction by changing Zn supply ratio, exhibiting bidirectional behavior. Despite these experimental findings, little is known about the mechanisms of this bidirectional behavior.

In order to obtain qualitative insights for the bidirectional growth of InP NWs on InP(111)B substrate, we here investigate the growth of InP thin film layers on

InP(111)B substrate. We assume that the topmost layer of nanowire growth is similar to that of InP(111)B surface. Effects of Zn atoms on the initial surface structure and growth processes are discussed on the basis of *ab initio* calculations.

II. COMPUTATIONAL METHODS

The total-energy calculations are performed within the generalized gradient approximation [9] in the density-functional theory. We use norm-conserving pseudopotentials [10] with partial core correction [11]. The conjugate-gradient minimization technique is used for both electronic-structure calculation and geometry optimization [12,13]. In the optimized geometries the remaining forces acting on the atoms are less than 5×10^{-3} Ry/Å. The valence wave functions are expanded by the plane-wave basis set with a cut-off energy of 20.25 Ry, which gives enough convergence of total energy to discuss the relative stability. We take (2×2) slab models consisting of seven atomic layers with pseudohydrogen atoms [14] and a 10 Å vacuum region [15]. The atoms belonging to bottom bilayer are fixed at their ideal positions. 10-*k* points sampling in the surface Brillouin zone is used throughout this study.

Surface phase diagrams are obtained by considering the adsorption-desorption behavior, which can be described by comparing the free energy of ideal gas per particle (chemical potential) μ_{gas} to the adsorption energy per atom E_{ad} . The chemical potential of a molecule is expressed as [16, 17]

$$\mu_{\text{gas}} = -k_{\text{B}}T \ln \left(\frac{k_{\text{B}}T}{p} \times g \times \xi_{\text{trans}} \times \xi_{\text{rot}} \times \xi_{\text{vib}} \right), \quad (1)$$

where k_{B} is Boltzmann's constant, T is the gas temperature, g is the degree of degeneracy of the electron energy level, and p is the pressure. ξ_{trans} , ξ_{rot} and ξ_{vib} are the partition functions for translational, rotational and vibrational motions, respectively. Details of these partition functions are expressed elsewhere [16, 17]. In the chemical potential calculations, we assume the form of In and Zn (P) in gas phase as In and Zn atoms (P_2 molecule), respectively. The relative stability between two structures

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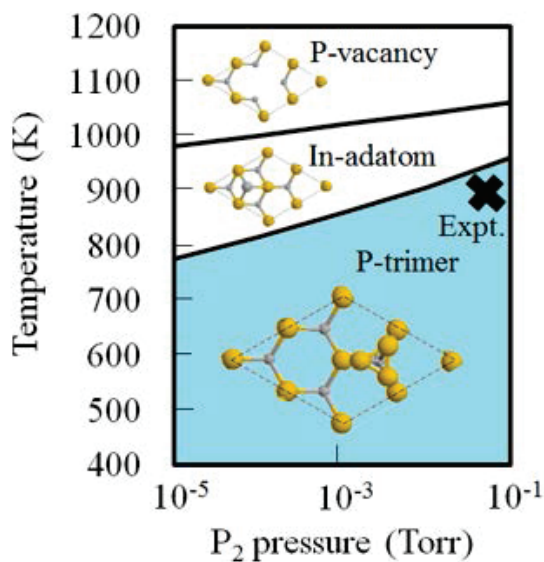


FIG. 1. Calculated surface phase diagram of InP(111)B surface as functions of temperature and P_2 pressure. Solid lines show boundaries between stable surface structures. The experimental growth condition in Ref. 8 is also shown by cross mark. In and P atoms are represented by gray and yellow circles, respectively.

is determined by comparing μ_{gas} to E_{ad} , *i.e.*, the structure corresponding to the adsorbed surface is favorable when E_{ad} is less than μ_{gas} , whereas the desorbed surface is stabilized when μ_{gas} is less than E_{ad} .

As a typical example of surface phase diagram on InP(111)B surface, Figure 1 shows the calculated phase diagram of the InP(111)B surface as functions of temperature and P_2 pressure. This figure reveals that there are several reconstructions depending on temperature and P_2 pressure. The surface with P-trimer (P-trimer, hereafter) is stabilized over the wide range of temperatures and P_2 pressure. This trend is consistent with previous calculations in which the P-trimer is favorable over the wide range of phosphorus chemical potential [18]. The stability of this surface structure can be explained in terms of the electron counting rule [19, 20]. Considering the experimental condition for the growth of InP NWs in the SA-MOVPE (cross mark in Fig. 1), the P-trimer emerges under the growth conditions of the SA-MOVPE [7,8].

III. RESULTS AND DISCUSSION

Figure 2 shows the calculated surface phase diagrams of Zn-incorporated surfaces as functions of temperature and P_2 pressure under low and high Zn pressure conditions (Figs. 2(a) and 2(b), respectively). As shown in Fig. 2(a), under low Zn pressure conditions the surface with Zn-P pair (Zn-P pair, hereafter) is stabilized below 850 ~ 910 K, whereas the P-trimer is favorable beyond 850 ~ 910 K. It is thus likely that the P-trimer is stable in the SA-MOVPE with low II/III ratio [8]. In contrast, the stable temperature and pressure area for the stabilization of Zn-P pair under high Zn pressures is larger than that

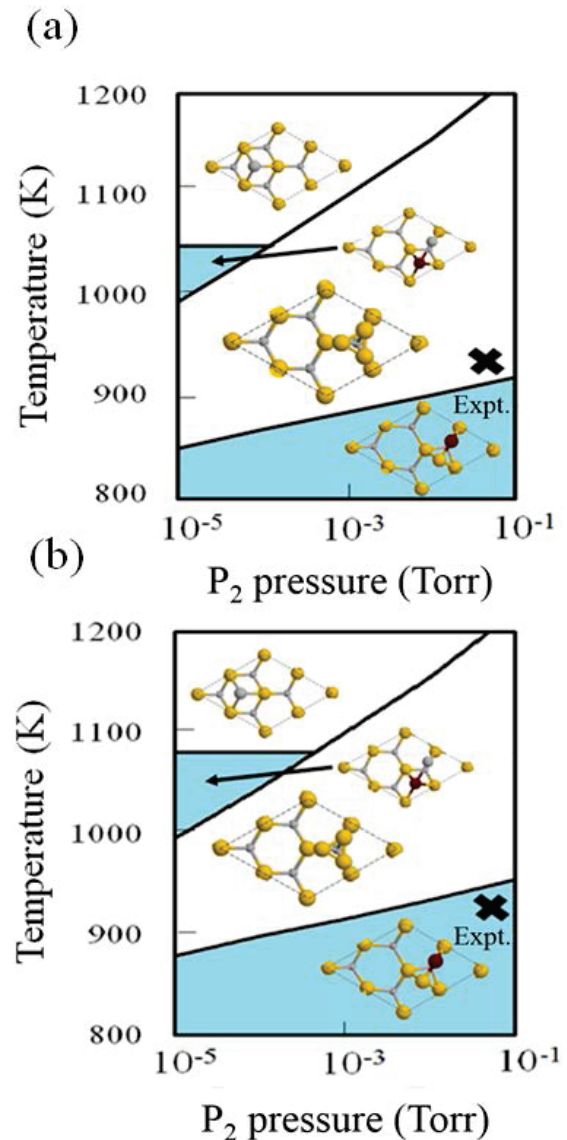


FIG. 2. Calculated surface phase diagrams of Zn-incorporated InP(111)B surfaces as functions of temperature and P_2 pressure under (a) low (6.0×10^{-4} Torr) and (b) high (4.6×10^{-3} Torr) Zn pressures. Note that low and high Zn pressures are obtained by the experimental partial pressure of Zn in Ref. 8. The experimental growth condition in Ref. 8 is also shown by cross mark. In, P, and Zn atoms are represented by gray, yellow, and brown circles, respectively. The Zn-incorporated surfaces are stabilized in the regions emphasized by shaded area.

under low Zn pressures. As shown in Fig. 2(b), the Zn-P pair is stabilized beyond 880 ~ 970 K. Therefore, the Zn-P pair is expected to be favorable in the SA-MOVPE with high II/III ratio [8]. The stabilization of Zn-P pair can be interpreted in terms of the number of P dangling bonds N_{DB} on the surface. The number of P dangling bonds in Zn-P ($N_{\text{DB}} = 2$) is smaller than that of P trimer ($N_{\text{DB}} = 4$), so that the number surface states originating from P dangling bonds, which are located above the valence band maximum [18], becomes small in the Zn-P pair. Therefore, the electronic contribution is decisive for the relative stability between Zn-P pair and P-trimer.

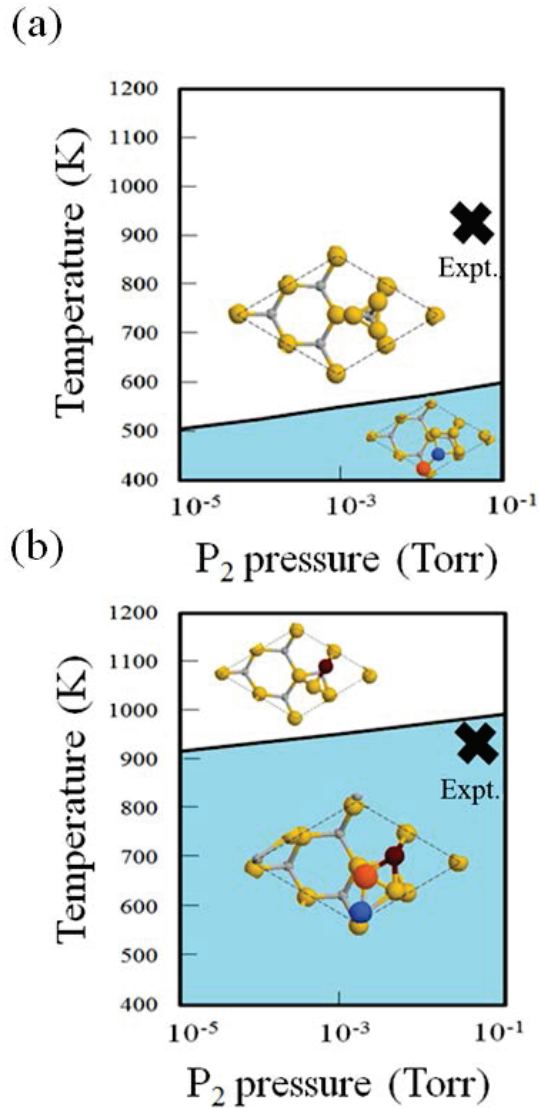


FIG. 3. Calculated surface phase diagrams for the adsorption of In-P dimer on InP(111)B surface as functions of temperature and P_2 pressure under (a) low (6.0×10^{-4} Torr) and (b) high (4.6×10^{-3} Torr) Zn pressures. Shaded area denotes stable temperature and pressure range for the surface with In-P dimer. The experimental growth condition in Ref. 8 is also shown by cross mark. In, P, and Zn atoms are represented by gray, yellow, and brown circles, respectively. Blue and orange circles denote In and P atoms of In-P dimer, respectively.

On the basis of the calculated surface structures, we furthermore investigate the initial growth processes on the InP(111)B surfaces. This is accomplished by considering the adsorption behavior of In and P atoms. Table I shows the calculated adsorption energies of In and P atoms, along with In-P dimer on the P-trimer and Zn-P pair, which are favorable under low and high Zn pressures, respectively. It is found that the adsorption energies of In and P atoms on the Zn-P pair (-2.48 and -1.30 eV, respectively) are lower than those on the P-trimer by 0.42 and 1.74 eV, respectively. However, these values are too large to adsorb on the surface under the growth condition around 930 K. In the case of adsorption as In-P dimer, the adsorption energy on the Zn-P pair is much

TABLE I. Calculated adsorption energies E_{ad} (in eV) of In and P atoms, and of In-P dimer on the InP(111)B surfaces with P trimer and Zn-P pair.

Surface	In	P	In-P
P-trimer	-2.06	0.44	-2.29
Zn-P pair	-2.48	-1.30	-4.37

lower than that on the P-trimer, and this In-P dimer can adsorb on the surface even under the growth condition. Figure 3 shows the calculated surface phase diagrams for the adsorption of In-P dimer on the InP(111)B surface as functions of temperature and P_2 pressure under low and high Zn pressure conditions (Figs. 3(a) and 3(b), respectively). As shown in Fig. 3(a), the stable region for In-P dimer is ranging below $500 - 580$ K. This indicates that In-P dimer on the P-trimer desorbs from the surface in the SA-MOVPE with low II/III ratio [8]. On the other hand, as shown in Fig. 3(b), In-P on the Zn-P pair is stabilized below $910 \sim 960$ K, implying that In-P dimers can adsorb on the surface in the SA-MOVPE with high II/III ratio [8]. The low adsorption energy of In-P dimer on the Zn-P pair originates from the formation of covalent bonds. On the Zn-P pair the formation of Zn-P and P-P bonds occurs in addition to the formation of three In-P bonds, which are also generated in the adsorption of In-P dimer on the P-trimer.

The calculated results on the surface structures and adsorption-desorption behavior on the InP(111)B surfaces mentioned above offer a possible explanation for the bidirectional growth of InP NWs [8]. Under low II/III ratio conditions in the SA-MOVPE, the P-trimer is the most stable surface structure and In atoms hardly adsorb on the surface. In this case, the growth along the $[111]A$ direction, in which the adsorption of In and P atoms easily occurs on the InP(111)A surface [21], preferentially proceeds by forming tripods tilted to the InP(111)B substrate. In contrast, under high II/III ratio, the Zn-P pair is the most stable and In atoms adsorb on the surface as In-P dimers. The formation of Zn-P pair enables the vertical growth of InP layers on the InP(111)B surface. Although details of growth processes on these surfaces should be carefully examined, our scenario obtained by the calculated results is consistent with the experimental results.

IV. CONCLUSIONS

We have theoretically investigated the effects of Zn atoms on the surface structure and initial growth processes on InP(111)B substrate by performing first-principles total-energy calculations. We have revealed that the surface reconstruction strongly depends on the growth conditions such as Zn pressure. The surface with Zn-P pair is found to be stabilized under high Zn pressure. The formation of Zn-incorporated surface leads to the adsorption of In-P dimer due to the formation of Zn-P and P-P bonds, suggesting that InP layers on the InP(111)B substrate under high Zn pressures can be formed more

easily than the surface under low Zn pressures. We have proposed that role of Zn doping on the surface structure and initial growth processes are crucial for understanding the bidirectional growth mechanisms of InP nanowires on InP(111)B substrate.

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- [1] H. M. Hang, S. Mao, H. Feick, H. Yan, Y. Wu, H. Kind, E. Weber, R. Russo, and P. Yang, *Science* **292**, 1897 (2001).
 - [2] T. H. Ng, J. Han, T. Yamada, P. Nguyen, and Y. P. Chen, *Nano Lett.* **4**, 1247 (2004).
 - [3] J. Xiang, W. Lu, Y. Hu, Y. Wu, H. Yan, and M. C. Lieber, *Nature* **441**, 489 (2006).
 - [4] P. Mohan, J. Motohisa, and T. Fukui, *Nanotechnology* **16**, 2903 (2005).
 - [5] K. Ikejiri, Y. Kitauchi, K. Tomioka, J. Motohisa, and T. Fukui, *Nano Lett.* **11**, 4314 (2011).
 - [6] Y. Kitauchi, Y. Kobayashi, K. Tomioka, S. Hara, K. Hiruma, T. Fukui, and J. Motohisa, *Nano Lett.* **10**, 1699 (2010).
 - [7] M. Inari, J. Takeda, J. Motohisa, and T. Fukui, *Physical E.* **21**, 620 (2004).
 - [8] K. Ikejiri, I. Fumiya, T. Katsuhiko, and T. Fukui, *Nano Lett.* **12**, 1744, (2012).
 - [9] J. P. Perdew, K. Burke, and M. Ernzerhof, *Phys. Rev. Lett.* **77**, 3865 (1996).
 - [10] N. Troullier and J. L. Martins, *Phys. Rev. B* **43**, 1993 (1991).
 - [11] S. G. Louie, S. Froyen, and M. L. Cohen, *Phys. Rev. B* **26**, 1738 (1982).
 - [12] J. Yamauci, M. Tsukada, S. Watanabe, and O. Sugino, *Phys. Rev. B* **54**, 5586 (1996).
 - [13] H. Kageshima and K. Shiraishi, *Phys. Rev. B* **56**, 14985 (1997).
 - [14] K. Shiraishi, *J. Phys. Soc. Jpn.* **59**, 3455 (1990).
 - [15] In this study, we use the (2×2) surface to determine local atomic structures of the surfaces with Zn atom. The effect of unit cell size have been checked by using the $(2\sqrt{3} \times 2\sqrt{3})$ supercell, and found that the adsorption energy difference depending on the size of supercell is ~ 0.2 eV. This value corresponds to 50 K in the surface phase diagrams shown in Figs. 2 and 3. Therefore, the effect of pressure in the unit cell is negligible and the main contribution of pressure comes from the gas-phase chemical potentials in Eq. (1).
 - [16] Y. Kangawa, T. Ito, A. Taguchi, K. Shiraishi, and T. Ohachi, *Surf. Sci.* **190**, 517 (2002).
 - [17] Y. Kangawa, T. Ito, Y. S. Hiraoka, A. Taguchi, K. Shiraishi, and T. Ohachi, *Surf. Sci.* **285**, 507 (2002).
 - [18] S. Haibo, C. Xiaoshuang, Z. Xiaohao, D. Zongling, and L. Wei, *J. Phys. Chem. C* **114**, 10195 (2010).
 - [19] D. M. Pashley, *Phys. Rev. B* **40**, 10481 (1989).
 - [20] X. L. Zhang, G. E. Wang, K. Q. Xue, B. S. Zhang, and Y. Z. Zhang, *Phys. Rev. Lett.* **97**, 126103 (2006).
 - [21] T. Yamashita, T. Akiyama, K. Nakamura, and T. Ito, *Surf. Sci.* **610**, 16 (2013).