Doping Effects on Polytypism in Semiconductor Nanowires: A First-Principles Study*  

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(Received 6 December 2013; Accepted 15 January 2014; Published 31 January 2014)  

The effects of dopants on the crystal structure of InP and GaAs NWs are theoretically investigated by means of density functional calculations. The calculated energy differences among various crystal structures with substitutional Zn (C) atoms in InP (GaAs) are found to be similar to those of bulk phase. This indicates that the contribution of dopants to the energy difference among different crystal structures in NWs is negligible. Furthermore, we reveal that the difference in the step-edge formation energy between zinc blende and wurtzite structures with dopants is similar to that without dopant within 0.01 eV/Å. These results thus imply that the role of dopants for the supersaturation of nanowire formation is crucial to determine the crystal structure of NWs.  

[DOI: 10.1380/ejssnt.2014.18]  

Keywords: Density functional calculations; Growth; Gallium arsenide; Indium phosphide; Nano-wires, quantum wires, and nanotubes  

I. INTRODUCTION  

Semiconductor nanowires (NWs) have proven a versatile building block for the realization of novel structures which allow for new device concepts. The optimization of crystal quality and crystal phase control lead to successful demonstration of nanowire-based devices such as photovoltaic cells [1, 2], photo detectors [3], laser diodes [4], and transistors [5, 6]. In fact, periodic arrangements of nanowires can be used in the function of solar cells [1, 2], photo detectors [3], laser diodes [4], and transistors [5, 6]. Recently, periodic arrangements of nanowires have been reported for a variety of group III-V semiconductor NW systems such as InAs [7–10], InP [11–14], and GaAs NWs [15]. The crystal structure of InP NWs has now been controlled by Zn doping during the vapor-liquid-solid (VLS) growth: the addition of small amounts of Zn to vapor phase results in the growth of NWs with ZB structure [13–18]. The growth of InP NWs on InP(111)B substrate has also been successfully controlled by supplying Zn dopants during the selective area growth [19]. Furthermore, the morphology and structure of gold assisted GaAs NWs have been found to be strongly modified by the presence of C dopants during the growth of metalorganic vapor phase epitaxy: the GaAs NWs grown with C dopants have shown zinc blende (ZB) structure without stacking fault, while the NWs grown without doping exhibit a high density of stacking faults [20].  

To understand the effects of doping on the crystal structure of NWs during the VLS growth, Algra et al. have discussed the role of Zn dopants on the basis of two-dimensional nucleation, where the growth of InP NWs proceeds by repeated formation of two-dimensional nuclei on the top faces [13]. The boundary between ZB and wurtzite (WZ) structures in a kinetic phase diagram is calculated by  

\[ \frac{f(\theta_{\text{ZB}})}{f(\theta_{\text{WZ}})} \left\{ \frac{1}{1 - \Delta \gamma/\gamma_{\text{sl,ZB}}} \right\} = \left\{ 1 - \frac{\Delta E_{\text{WZ-ZB}}}{\Delta \mu_{\text{ZB}}} \right\}^{-1}, \]  

where \( f(\theta) = (\theta - 0.5 \sin 2\theta)/\pi \) with contact angle \( \theta \) given by \( \cos \theta = (\gamma_{\text{lv}} - \gamma_{\text{sv}})/\gamma_{\text{lv}} \) comes from the equilibrium shape of a circular two-dimensional nucleus in contact with a straight nanowire edge shown in Fig. 1(a), \( \gamma_{\text{lv}} \) and \( \gamma_{\text{sv}} \) are the free energies of the nucleus at the nanowire edge and at the mother phase at the nanowire edge, respectively, \( \Delta \gamma = \gamma_{\text{sl,ZB}} - \gamma_{\text{sl,WZ}} \) is the difference in the free energy of the boundaries between the nucleus and the mother phase between ZB and WZ structures, \( \Delta E_{\text{WZ-ZB}} \) is the energy difference between ZB and WZ structures, and \( \Delta \mu_{\text{ZB}} \) is the difference in chemical potential of the solute in the droplet and in the solid phase with ZB structure. Figure 1(b) shows a possible phase diagram as functions of normalized free energy difference between WZ and ZB structures \( \Delta\gamma/\gamma_{\text{sl,ZB}} \) and chemical potential difference for supersaturation \( \Delta \mu_{\text{ZB}} \) obtained by Eq. (1). Red (solid) line denotes the boundary between WZ and ZB structures using \( \Delta E_{\text{WZ-ZB}} \) for bulk InP (5.1 meV/atom in this study) and green (dashed) line the boundary using \( \Delta E_{\text{WZ-ZB}} \) = 10 meV/atom. Atomic configurations of ZB and WZ structures are also shown.  

*This paper was presented at the 12th International Conference on Atomically Controlled Surfaces, Interfaces and Nanostructures (ACSN-12) in conjunction with 21st International Colloquium on Scanning Probe Microscopy (ICSPM21), Tsukuba International Congress Center, Tsukuba, Japan, November 4-8, 2013.  
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NWs by Zn doping is due to a reduction of $\Delta \gamma$ upon Zn addition [13]. However, there still remains unclear how the addition of Zn affects $\gamma_{i,ZB}$ and $\gamma_{i,WZ}$. Moreover, the difference in chemical potential between ZB and WZ structures, $\Delta E_{\text{ZB-WZ}}$, with Zn dopants in InP NWs has not clarified at present.

In this study, effects of dopants on the crystal structure of NWs are theoretically investigated by means of total-energy calculations within the density-functional theory (DFT). In particular, we focus on the dependence of $\Delta E_{\text{ZB-WZ}}$ and $\Delta \gamma$ on the addition of Zn (C) dopants in InP (GaAs) NWs. The relative stability among various polytype and the stability between WZ and ZB structures at the step edge including substitutional atoms in InP and GaAs are discussed by considering ionic and covalent interactions using our simple analytical approach [21].

II. CALCULATION PROCEDURE

The total-energy calculations are performed within the generalized gradient approximation (GGA) [22] in the DFT. To describe the electron-ion interaction, we adopt norm-conserving (for In, P, Ga, and As) and ultrasoft (for C) pseudopotentials generated using the Troullier-Martin scheme [23]. 3$d$ (4$d$) electrons in Ga (In) atoms are treated by using partial core correction [24]. The conjugate-gradient minimization technique is used for both the electronic structure calculation and the geometry optimization [25, 26]. In the optimized geometries the remaining forces acting on the atoms are less than $3 \times 10^{-3}$ Ry/Å. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 16 Ry, which gives enough convergence of total energy to discuss the relative stability.

The effects of dopants on $\Delta E_{\text{ZB-WZ}}$ are discussed on the basis of the relative stability among various polytype in the bulk region of NWs with substitutional atoms. We employ $\sqrt{3} \times \sqrt{3}$ with six-double-layer unit cells for ZB, 6H and WZ structured InP and GaAs, while the four-double-layer unit cell for 4H and WZ structures is used to normalize the relative energy differences among ZB, 6H, and 4H structures. To maximize the accuracy in the Brillouin zone integration, we use 18- and 27- point grids perpendicular to the layers within 3 meV/atom. The calculated results thus reveal that the most stable structure with substitutional atoms (ZB structure) is the same as that without substitutional atom. Furthermore, the $\Delta E$ with substitutional atoms is similar to that without substitutional atom within 3 meV/atom. The calculated results thus reveal that the most stable structure with substitutional atoms (ZB structure) is the same as that without substitutional atom.

III. RESULTS AND DISCUSSION

A. Effects of dopants in bulk region of NWs

Figure 2 shows the calculated energy differences $\Delta E$ among ZB (3C), 6H, 4H, and WZ (2H) structured InP and GaAs with substitutional Zn and C atoms at In and As sites, respectively, where the total energy of ZB structure is employed as an energy origin. This figure also includes the energy difference without substitutional atom. For both InP and GaAs, the energy of ZB structure takes the lowest value. Furthermore, the $\Delta E$ with substitutional atoms is similar to that without substitutional atom. Therefore, the incorporation of dopants at substitutional sites does not affect the relative stability among various polytype in bulk region of InP and GaAs NWs.

The relative stability among various polytype with substitutional atoms can be qualitatively understood by considering the interaction between bond and ionic charges. We have previously reported that the energy difference between nH (n=2, 4, and 6) and ZB (3C) structures depending on ionicity $f_i$ is expressed as [21]

$$\Delta E_{nH-ZB} = \frac{n}{2} K \left\{ h(1-f_i) \frac{Z_i^2}{r_{bb}} - f_i \frac{Z_i^2}{r_{ii}} \right\}, \tag{2}$$

where $r_{ii}$ is the distance between ionic charges $Z_i$ (=3 for III-V semiconductors) located at the third nearest neighbor lattice sites, $r_{bb}$ is the distance between bond charges $Z_b$ (=2) located at the center of interatomic bonds, and $h=3/2$ (1) for n=2 (4 and 6). The coefficient $K$ is 8.7 meV·A that is determined by reproducing the energy difference of 25.3 meV/atom between ZB and WZ structures for C with $f_i=0$ obtained by DFT calculations. Figure 3 shows the calculated decrease in the bond charges around Zn and C in InP and GaAs, respectively. The decrease of bond charges is found to be predominant around Zn and C atoms, indicating that bond charges for Zn-P and Ga-C bonds are smaller that those of bulk In-P and Ga-As bonds. By employing the value of bond charges $Z_b$ and ionic charges $Z_i$, such as $Z_b=1.75$ (1.75) and $Z_i=2$ (4) for substitutional Zn (C) impurity, the energy differences among different polytype are estimated using Eq. (2). Here, we use the value of $f_i=0.30$ (0.07) for InP (GaAs) fitted to the energy difference between ZB and WZ structures obtained by DFT calculations. The calculated values of $\Delta E$ between ZB and WZ structures are 4.7 (25) meV/atom in InP (GaAs) with substitutional atoms, qualitatively consistent with those obtained by DFT calculations. Therefore, InP and GaAs with substitutional atoms favor ZB structure even though substitutional atoms induce large deficit of bond charges.
FIG. 2: Calculated energy differences $\Delta E$ among zinc blende (3C), 6H, 4H, and wurtzite (2H) structures of (a) InP with substitutional Zn at the In site and (b) GaAs with substitutional C at the As site, as a function of hexagonality. Dashed lines denote $\Delta E$ without substitutional atom.

B. Effects of dopants during nucleation at step edges

Figure 4 shows the geometries of substitutional Zn and C atoms at the step edge on InP and GaAs(111)B substrates, respectively. The energy of a Zn (C) atom located in the second (first) layer of the step edge of InP (GaAs) is found to be $\sim-0.68 \ (0.41)$ eV lower than that of the other structure. This indicates that Zn and C atoms in InP and GaAs are stably located in the second and first layer of the step edge, respectively. Table I shows the energy differences in the step-edge formation energy between ZB and WZ structures with substitutional atoms $\Delta \gamma_{\text{WZ-ZB}}$ and those without substitutional atom $\gamma_{\text{WZ-ZB}}$, along with the formation energies $\gamma_{\text{step,ZB}}$ and $\gamma_{\text{step,WZ}}$ in WZ and ZB structures, respectively [31]. Although the substitution of atoms located at the step edge by an impurity atom heightens (lowers) the energy of WZ structure in InP (GaAs), its change is not significant. The normalized energy differences with substitutional atoms $\Delta \gamma_{\text{WZ-ZB}}/\gamma_{\text{WZ-ZB}}$ in InP (GaAs) is lower (higher) than those without substitutional atom $\Delta \gamma_{\text{WZ-ZB}}/\gamma_{\text{WZ-ZB}}$ only by $\sim0.02$, which is much smaller.

FIG. 3: Isosurfaces of charge density difference for (a) InP and (b) GaAs with a substitutional atom in ZB structure. The difference is obtained by subtracting the charge density of InP (GaAs) without substitutional atom from that of InP (GaAs) with substitutional Zn (C) atoms at the In (As) site. Isosurfaces for InP and GaAs are $-0.003$ and $-0.008$ electron/Å$^3$, respectively. Cyan (gray) circles represent Zn (C) atoms. The periodic unit cell used in this study is enclosed by rectangles.

FIG. 4: Geometries and isosurfaces of charge density difference of (a) Zn in InP and (b) C in GaAs at the step edge of (111)B surfaces in ZB structure. Blue and yellow isosurfaces are $+0.004$ and $-0.004$ electron/Å$^3$, respectively. Cyan and gray circles represent Zn and C atoms, respectively. White circles represent pseudohydrogen atoms.
TABLE I: Calculated step-edge formation energies (in meV/Å) in WZ and ZB structures without substitutional atom, $\gamma_{\text{step,ZB}}$ and $\gamma_{\text{step,WZ}}$, respectively, the energy differences in the step-edge formation energy between WZ and ZB structures without substitutional atom $\Delta\gamma_{\text{WZ-\,ZB}} = \gamma_{\text{step,ZB}} - \gamma_{\text{step,WZ}}$ and that with an substitutional atom $\Delta\tilde{\gamma}_{\text{WZ-\,ZB}} = \tilde{\gamma}_{\text{step,ZB}} - \tilde{\gamma}_{\text{step,WZ}}$ on InP(111)B and GaAs(111)B surfaces.

|                | $\gamma_{\text{step,ZB}}$ | $\gamma_{\text{step,WZ}}$ | $\Delta\gamma_{\text{WZ-\,ZB}}$ | $\Delta\tilde{\gamma}_{\text{WZ-\,ZB}}$ |
|----------------|-----------------------------|-----------------------------|----------------------------------|----------------------------------------|
| InP(111)B      | 239                         | 230                         | 8.4                              | 2.3                                    |
| GaAs(111)B     | 195                         | 189                         | 6.0                              | 10.1                                   |

than the range of normalized energy difference shown in Fig. 1(b). It is thus concluded that the incorporation of dopants at substitutional sites at the step edge does not affect the relative stability between ZB and WZ structures during the nucleation processes of InP and GaAs NWs. It is likely that the chemical potential difference for supersaturation $\Delta\mu_{\text{s}}$ in Eq. (1) is drastically affected by dopant incorporation during nucleation processes. By applying the surface phase diagrams, which have been successfully applied to clarify epitaxial growth processes of semiconductors [32, 33], we are currently investigating effects of the addition of dopants on the supersaturation of nanowire formation taking account of the growth conditions.

The effect of dopant atoms on the relative stability at the step edge can also be qualitatively interpreted by considering the interaction between bond and ionic charges. Figure 4 displays the calculated decrease in the bond charges around Zn and C at the step edge of InP and GaAs, respectively. It is found that the accumulation of electrons around Zn-P and Ga-C bonds and the depletion on the dangling bond at the topmost layer of step edge are predominant. This indicates that excess electrons of dangling bonds compensate for deficit electrons in Zn-P and Ga-C bonds. Since dangling bonds at the topmost layer of the step edge hardly contribute the energy difference between ZB and WZ structures in Eq. (2), the electrostatic interaction among ionic charges causes the energy difference between $\Delta\gamma_{\text{WZ-\,ZB}}$ and $\Delta\tilde{\gamma}_{\text{WZ-\,ZB}}$. Indeed, the estimated values of $\Delta\tilde{\gamma}_{\text{WZ-\,ZB}}$ using Eq. (2) in InP and GaAs are $-1.5$ and $1.0$ meV/A, respectively, qualitatively consistent with those obtained by DFT calculations.

IV. CONCLUSION

We have investigated the effects of dopants on polytypism of InP and GaAs NWs on the basis of DFT calculations. The calculated energy differences among different polytype with substitutional atoms are similar to those of bulk phase. This indicates that the contribution of dopants to the chemical potential difference among different crystal structures in NWs is negligible. We have also revealed that the difference in the step-edge formation energy with dopants is similar to that without dopant within 10 meV/A. Although larger number of atom unit cells should be employed in the calculations for quantitative discussions, these results imply that the role of dopants for the supersaturation of nanowire formation is crucial to determine its crystal structure.

Acknowledgments

This work was supported in part by a Grant-in-Aid for Scientific Research (No. 24560025) from the Japan Society for the Promotion of Science. Computations were performed at RCCS (National Institutes of Natural Sciences).

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