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Theoretical investigations on the formation of wurtzite segments in group III–V semiconductor nanowires

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Abstract

Structural trends in group III–V semiconductor nanowires (NWs) are systematically investigated based on Monte-Carlo simulations using our empirical potential calculations. The calculated NW stacking sequences for the selective area growth demonstrate that the averaged periodicity between wurtzite segments, which is independent of the NW size, decreases with increasing ionicity of semiconductors f_i. It is also found that the periodicity is affected by the nucleus size of NWs: The calculated periodicity in InP (InAs) NWs with the nucleus size consisting of $\sim$ 10 atoms are 0.76 (0.86) nm, reasonably consistent with the experimentally reported one. On the other hand, the nucleus size to reproduce the experimentally reported periodicity in GaAs NWs is estimated to be more than 70 atoms. These results thus imply that the nucleus size as well as f_i is of importance in determining the averaged periodicity between wurtzite segments.

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Keywords: Nanowires; Monte-Carlo simulation; Rotational twins; Nucleus size; Ionicity

1. Introduction

One-dimensional nanostructures such as semiconductor nanowires (NWs) are expected to play a key role in future nanotechnology due to their potential application as building blocks in electronics and optoelectronics. In particular, NWs of group III–V materials have attracted much attention because of their specific optical properties and are expected to be applied to light-emitting diodes [1–3], photodetectors [4,5] and lasers [6–8]. Hence, considerable efforts have been devoted to fabricate these NWs by employing various methods such as metal-organic vapor-phase epitaxy and molecular beam epitaxy. It is experimentally known that there are some structural characteristics different from bulk crystals. Observation by high resolution transmission electron microscopy (HRTEM) has revealed that group III–V NWs fabricated by the selective area metal-organic vapor-phase epitaxy (SA-MOVPE) often include wurtzite (W) segments in the zinc blende (ZB) structure. This results in the formation of rotational twins in GaAs NWs at 750 °C [9], 4H-like structure in InAs NWs at 540 °C [10] and W structure in InP NWs at 600 °C [11]. Despite these experimental findings, the systemization for the propensity to incorporate W segments in NWs grown by the SA-MOVPE has been rarely carried out at present.

In our previous study, the relative stability between ZB and W structures in group III–V NWs has been successfully investigated based on an empirical interatomic potential calculations [12]. The relative stability can be explained in terms of the ionicity of semiconductors f_i. We have also investigated the formation of rotational twins in InP NWs grown along the [1 1 1] direction by the vapor–solid–liquid (VLS) reaction and by the SA-MOVPE based on a Monte-Carlo (MC) simulations using our empirical potential [13]. The results imply that the nucleus formation at the top of growing NW crucially affects the W segments formation. In this study, we extend our approach to group III–V NWs fabricated by the SA-MOVPE to clarify the chemical trends for the incorporation of W segment formation systematically. We discuss the span between W segments in terms of the nucleus size and f_i.

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2. Computational methods

Since the stacking sequences corresponding to the W stacking sequence (ABAB$\cdots$) can be incorporated in the ZB stacking sequence (ABCABC$\cdots$) along the [1 1 1] direction, there are many types of stacking sequence available along this direction. In order to determine the stacking sequence of double layer under the crystal growth, we perform MC simulations by employing our empirical potential calculations. In the calculation procedure, we first calculate the NW cohesive energy of double layer for various stacking sequences using a six double-layer unit cell. The NW cohesive energy is obtained by using our empirical interatomic potential which is given by

$$E = E_0 + \Delta E_{\mathrm{W-ZB}} \tag{1}$$

$$E_0 = \frac{1}{2}\sum_{i,j} V_{ij} \tag{2}$$

where E_0 is the NW cohesive energy calculated by Kohr–Das Sarma type empirical interatomic potential V_{ij} within the second nearest neighbors [14–16]. $\Delta E_{\mathrm{W-ZB}}$ is the energy difference between W and ZB structures in the bulk form, which is caused by the electrostatic interaction [17]. Here, we use the energy difference between W and ZB structures in the bulk form obtained from *ab initio* calculations [18]. The values of f_{i} and $\Delta E_{\mathrm{W-ZB}}$ used in this study are listed in Table 1. Using Eq. (1), the relationship between stacking sequence and cohesive energy is obtained.

Next, we consider a NW model with hexagonal shape which can minimize the surface dangling bonds in the ZB structure [13]. Although the fabrication of NWs with anisotropic side facets is reported [10], we consider NWs consisting of 500 double layers with isotropic flat (1 1 0)-like facets as a representative of the NW models. We then calculate their cohesive energies by summing the cohesive energy of each double layer obtained by using Eq. (1). Considering that the nuclei formation is one of the key processes to determine the crystal strucure in epitaxial growth, we here take account of the influence of the critical nuclei formation on the stacking sequence preference by evaluating the energy difference in the MC step. The energy difference ΔE_{nc} is calculated by the energy of nucleus, which is given by

$$\Delta E_{\mathrm{nc}} = N_{\mathrm{nc}}(E_{\mathrm{f}} - E_{\mathrm{i}}) \tag{3}$$

Table 1
The ionicity f_{i} used in this study and energy difference $\Delta E_{\mathrm{W-ZB}}$ (meV/atom) between wurtzite and zinc blende structures for group III–V compound semiconductors in the bulk form obtained by *ab initio* calculations [18]

	GaSb	AlSb	InSb	GaAs	AlAs	InAs
f_i	0.15	0.16	0.19	0.218	0.221	0.29
$\Delta E_{\mathrm{W-ZB}}$	9.9	9.5	8.2	8.3	8.2	5.3

	GaP	AlP	InP	AlN	GaN	InN
f_i	0.295	0.298	0.35	0.69	0.74	0.83
$\Delta E_{\mathrm{W-ZB}}$	5.8	5.7	3.4	−13	−12.7	−15.5

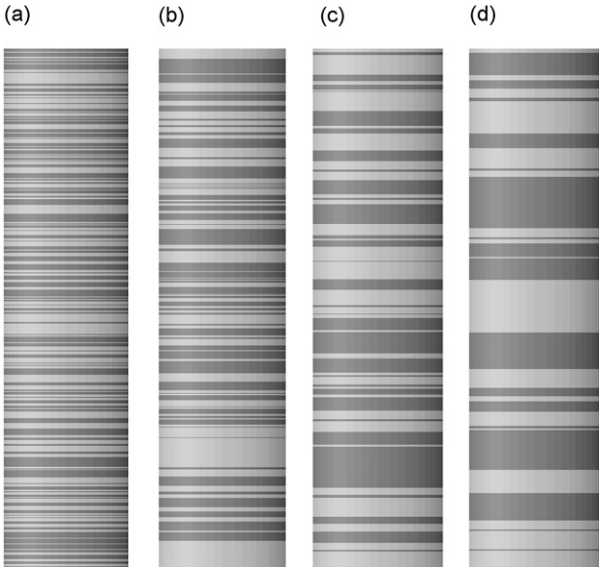

Fig. 1. Calculated stacking sequences of InAs NWs with diameter of 50 nm obtained by the MC simulations at 540 °C for (a) N_{nc}=10, (b) N_{nc}=30, (c) N_{nc}=50, and (d) N_{nc}=70. Light and dark regions correspond to the stacking sequences of ZB structure along the [1 1 1] direction. Boundaries between light and dark regions represent the W-type stacking sequence corresponding to rotational twins. The calculated periodicity between W segments is obtained from the distance between these boundaries.

where N_{nc} is the number of atoms consisting the nuclei. E_{f} and E_{i} are the cohesive energies before and after the replacement in the MC step, respectively. We assign the two dimensional nucleation at the top layer of growing NW, which could be applied to the crystal nucleation in the SA-MOVPE [13]. In the present study, we consider different size for N_{nc} (=10, 30, 50, and 70) to clarify effects of nucleus size on the W segment formation.[1]

The MC simulations are performed for NWs ranging from 1.4 to 80 nm to confirm the size dependence of W segment formation in the SA-MOVPE. In the MC scheme, a randomly chosen double layer is replaced by another randomly chosen double layer which can be stacked in the host layers using Eq. (3). The stacking sequence preference during NW growth is assigned to the equilibration by the MC step.

3. Results and discussion

Fig. 1 displays the calculated stacking sequence of InAs NWs for the SA-MOVPE by the MC simulations. Here, we find that the averaged periodicity P between W segments in group III–V NWs with diameters ranging from 10 to 80 nm is independent of the NW size. As shown in the light and dark contrasts shown in Fig. 1, P increases as the nucleus size becomes large. This is because the energy difference in Eq. (3) becomes large for N_{nc} with large number of atoms. The large energy difference results in taking the ZB stacking sequence

[1] Effects of the polarity along the growth direction might be included in the size of critical nuclei.