The atomic arrangements of zinc blende structured GaN$_x$As$_{1-x}$ nanowires (NWs) surrounded by semiconductor templates are theoretically investigated using empirical interatomic potentials and Monte Carlo simulations. Our calculations demonstrate that the atomic arrangements of GaN$_x$As$_{1-x}$ NWs strongly depend on nitrogen composition $x$ and substrate lattice constant $a_{sub}$. For a certain nitrogen composition and substrate lattice constant, layered segregation is found in GaN$_x$As$_{1-x}$ NWs surrounded by templates. On the other hand, surface segregation appears on the side facets of freestanding NWs over the wide range of $x$ and $a_{sub}$. The surface segregation in freestanding NWs originates from the energy difference between Ga–N and Ga–As bonds, which leads to the preference of As atoms at the topmost layer of side facets. These calculated results thus suggest that various novel atomic arrangements in GaN$_x$As$_{1-x}$ NWs can be realized depending on $x$ and $a_{sub}$ which control degree of lattice constraint. [DOI: 10.1380/ejssnt.2014.45]

Keywords: Computer simulations; Atomic-solid reactions; Surface segregation; Superlattices; Semiconducting films

I. INTRODUCTION

Alloy semiconductor thin films have been attracted attentions in various research areas. This is because they often exhibit various novel atomic arrangements such as atomic ordering and surface segregation [1–9]. Especially, GaN$_x$As$_{1-x}$ has attracted considerable interests due to the potential application for optoelectronic devices [10]. Previous theoretical studies have revealed that the atomic arrangements of GaN$_x$As$_{1-x}$ thin films strongly depend on nitrogen composition $x$ and substrate lattice constant [11, 12]. In particular, there are correlations between atomic arrangements and surface segregation appearing in alloy semiconductor thin films with large lattice mismatch. On the other hand, the novel atomic arrangements such as layered segregation or ordered structures have been proposed in GaN$_x$As$_{1-x}$ thin films on V-grooved substrate at specific regions [11, 12]. However, it is still unclear for the correlation between atomic ordering and layered segregation appearing in alloy semiconductor thin films with large lattice mismatch.

Recently, core-shell metal-oxide NWs have been successfully fabricated by using coelectrodeposition of metal-oxide and polymer templates [13]. Since core parts of NWs are surrounded by templates, which control degree of lattice constraint, this experimental result inspires us to investigate the atomic arrangement of NWs surrounded by semiconductor templates. In this study, we extend our approach to investigate the atomic arrangements of GaN$_x$As$_{1-x}$ NWs surrounded by semiconductor templates using our empirical interatomic potentials [14] and Monte Carlo (MC) simulations. On the basis of equilibrium atomic arrangements obtained by the MC simulations, we clarify the relationship between lattice constraints and novel atomic arrangements such as layer segregation in terms of bond length distribution in GaN$_x$As$_{1-x}$ NWs surrounded by semiconductor templates.

II. COMPUTATIONAL METHODS

In order to investigate the system energy $E$ for zinc blende structured GaN$_x$As$_{1-x}$ NWs surrounded by sub-
for tetrahedrally bonded atom pairs. The potential parameters between neighbors, and energy differences among various crystal structures obtained by ab initio calculations and experiments. The MC simulations are performed to investigate equilibrium atomic arrangements of GaN\(_x\) NWs surrounded by semiconductor templates. Here, we consider GaN\(_x\) As\(_{1-x}\) NWs with various nitrogen composition surrounded by substrate with lattice parameter \(a_{\text{sub}}\) ranging from 4.5 to 5.5 Å. In the simulation for the GaN\(_x\) As\(_{1-x}\) NWs surrounded by templates, we employ model structures consisting of GaN\(_x\) As\(_{1-x}\) NW with triangular and hexagonal shapes, as shown in Fig. 1. In order to clarify the effects of surrounding templates, we also use the models for hexagonal freestanding NWs shown in Fig. 1(c). The periodic boundary condition along the [110] direction is imposed. In our calculations, the lattice parameters of substrate are fixed, whereas the atomic positions are varied to minimize the system energy. In the simulation procedure, randomly chosen atoms in the system are exchanged to equilibrate the system at a certain temperature \(T\) on the basis of Metropolis algorithm. Details of calculation procedure have been explained elsewhere [12]. In this study, equilibrium atomic arrangements at \(T = 1000\) K are obtained at 20,000 MC steps, where the system energy keeps constant within 0.27 meV/atom. Interdiffusion between NWs and substrate layer is neglected in this study.

### III. RESULTS AND DISCUSSION

Figure 2 shows the simulated equilibrium atomic arrangements for triangular GaN\(_x\) As\(_{1-x}\) NWs surrounded by templates. This figure reveals that the atomic arrangements depend on nitrogen composition \(x\) and substrate lattice constant \(a_{\text{sub}}\). For small or large nitrogen composition such as \(x = 0.1, 0.7,\) or 0.9, the NWs contain a lot of GaAs and GaN regions, each of which is composed of 10-20 atoms. These atomic arrangements indicate the phase separation of GaAs and GaN. Furthermore, the GaAs and GaN layers alternatively stacked along the [001] direction are found at \(a_{\text{sub}}\) ranging from 4.9 to 5.5 Å for \(x = 0.3\) and \(a_{\text{sub}} = 5.1\) and 5.5 Å for \(x = 0.5\). It should be noted that GaAs layers are formed at the interface between the NW and templates with the (001) orientation whenever layer segregation appears. Although the atomic arrangements with layer segregation have been seen in GaN\(_x\) As\(_{1-x}\) thin films on V-grooved substrate, the characteristics of atomic arrangements of GaN\(_x\) As\(_{1-x}\) NWs surrounded by templates are different from those of V-grooved substrate obtained by previous calculations [12]: only one monolayer (ML) of GaAs layer is formed at the interface of NWs surrounded by templates, while ~3 MLs of GaAs region are formed on the surface of GaN\(_x\) As\(_{1-x}\) thin films on V-grooved substrate. This difference can be interpreted in term of the bond length distribution. Figure 3 shows the bond length distribution of the GaN\(_{0.3}\) As\(_{0.7}\) and GaN\(_{0.5}\) As\(_{0.5}\) NWs with layered segregation, along with those of V-grooved substrate. For GaN\(_x\) As\(_{1-x}\) NWs, there are small and large peaks, each of which correspond to Ga-N and Ga-As bonds, respectively. In contrast, there are three peaks for GaN\(_x\) As\(_{1-x}\) thin films on V-grooved substrate. The large peak corresponds to Ga-N (Ga-As) bonds beneath the surface, whereas the small peak (allows in Fig. 3) to Ga-As bonds in the surface layers. Owing to the presence of surface which enables Ga-As bonds to relax to approach the equilibrium bond length, large number of Ga-As layers are formed in GaN\(_x\) As\(_{1-x}\) thin films on V-grooved substrate. Figure 4(a) shows the simulated equilibrium atomic arrangements for the GaN\(_x\) As\(_{1-x}\) NWs surrounded by templates with hexagonal shape. This figure reveals that the atomic arrangements also depend on \(x\) and \(a_{\text{sub}}\). For small or large nitrogen composition such as \(x = 0.1, 0.7,\) or 0.9, the NWs consist of a lot of GaAs and GaN regions, indicating the phase separation of GaAs and GaN. Furthermore, GaAs and GaN layers alternatively stacked along the [001] direction are found at \(a_{\text{sub}}\) ranging from 4.9 to 5.5 Å in GaN\(_{0.3}\) As\(_{0.7}\) and from 5.1 to 5.5 Å in GaN\(_{0.5}\) As\(_{0.5}\), where GaAs layers are formed at the interface between the NW and templates with the (001) ori-
FIG. 3: Calculated bond length distribution for Ga-As (red line) and Ga-N (blue line) in (a) GaN$_{0.5}$As$_{0.5}$ NWs surrounded by substrate at $a_{\text{sub}} = 5.3$ Å, (b) GaN$_{0.3}$As$_{0.7}$ NWs surrounded by substrate at $a_{\text{sub}} = 5.1$ Å, and (c) GaN$_{0.3}$As$_{0.7}$ NWs surrounded by substrate at $a_{\text{sub}} = 5.3$ Å. The bond length distributions of GaN$_x$As$_{1-x}$ thin films on V-grooved substrate in Ref. [12] are also shown by dashed lines. The bond length distributions corresponding to Ga–As around the surface region of GaN$_x$As$_{1-x}$ thin films on V-grooved substrate is indicated by arrows.

entation. The characteristics of atomic arrangements for the hexagonal GaN$_x$As$_{1-x}$ NWs are similar to those of the triangular GaN$_x$As$_{1-x}$ NWs. This implies that the atomic arrangements of GaN$_x$As$_{1-x}$ NWs surrounded by templates are independent of the NW shape.

Finally, we discuss the effects of lattice constraint on the atomic arrangements by comparing the results of hexagonal NWs surrounded by templates with those of freestanding NWs. Figure 4(b) depicts the simulated equilibrium atomic arrangements of freestanding GaN$_x$As$_{1-x}$ NWs. This figure shows that surface segregation on the NW facets appears over the wide range of $x$ and $a_{\text{sub}}$. This is because Ga–N bonds prefer to reside near the interface to relax the strain caused by the lattice mismatch [21]. Owing to lower bond energy of Ga–N (by 1.2 eV) compared with that of Ga–As bonds, surface segregation of As atoms occurs to reduce the number of Ga–N dangling bonds. This trend can be seen for freestanding GaN$_x$As$_{1-x}$ NWs excepting large $x$ and large $a_{\text{sub}}$, where lattice mismatch between GaN$_x$As$_{1-x}$ and the substrate is sufficiently small. These results thus indicate that lattice constraint from substrate is also crucial to determine the atomic arrangements of GaN$_x$As$_{1-x}$ NWs.

IV. CONCLUSION

We have theoretically investigated the atomic arrangements of GaN$_x$As$_{1-x}$ NWs surrounded by semiconductor templates on the basis of empirical interatomic potentials and MC simulations. We have revealed that for nitrogen composition $x = 0.3$ and 0.5 the layered segregation appears at the certain regions with lattice mismatch to the templates. This is because Ga–N bonds prefer to reside near the interface to relax the strain caused by semiconductor templates. We have also found that the atomic arrangements of GaN$_x$As$_{1-x}$ NWs surrounded by substrate at $a_{\text{sub}}$ is also crucial to determine the atomic arrangements of GaN$_x$As$_{1-x}$ NWs.

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arrangements of triangular NWs surrounded by semiconductor templates are similar to those of hexagonal NWs. In contrast, surface segregation appears in freestanding NWs due to the presence of dangling bonds on the side facets of NWs. Although we need further calculations using larger unit cell or incorporation of dislocations at the interfaces for quantitative discussion, our calculated results suggest that various novel atomic arrangements such as layered segregation in GaN$_x$As$_{1-x}$ NWs can be realized by choosing the substrate lattice constraint varied by $x$ and $a_{sub}$.

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