Systematic Theoretical Investigations for Miscibility of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ Thin Films*Takahiro Makihara,[†] Toru Akiyama, Kohji Nakamura, and Tomonori Ito

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The atomic arrangements of zinc blende structured $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films coherently grown on $\text{GaAs}(001)$ substrates are theoretically investigated using empirical interatomic potentials and Monte Carlo simulations. The resultant atomic arrangements of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ strongly depend on N composition x and substrate lattice parameter a_{sub} . It is found that the incorporation of N atoms in GaAsBi results in the formation of layered structures consisting of GaN, GaAs, and GaBi regions. This is because Ga–N interatomic bonds tend to be located around Ga–As interatomic bonds to approach its equilibrium bond length. Furthermore, either GaBi or GaN surface segregation appears to reduce the strain caused by lattice constraint. These results suggest that the miscibility of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films can be controlled by choosing suitable lattice constraint varied by x and a_{sub} that approach the bond length of the equilibrium values for semiconductor material. [DOI: 10.1380/ejsnt.2014.171]

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I. INTRODUCTION

Bismuth containing III-V alloys have been proposed as promising semiconductor materials for laser diodes (LDs) to optical fiber communication with temperature-insensitive band gaps [1, 2]. For instance, the temperature-insensitivity of band gap in $\text{GaAs}_{0.946}\text{Bi}_{0.054}$ /GaAs multiquantum well is almost 40% of that in GaAs [3]. However, GaAsBi is not suitable for the fabrication of LDs because lattice mismatch between GaAsBi and GaAs substrates is quite large. GaAsBi alloys with a band gap suitable for optical fiber communication have not been obtained yet. In contrast, nitrogen incorporated GaAsBi (GaNAsBi) has attracted much attentions because its band gap suitable for the optical fiber communication waveband has been recently achieved [4, 5]. Furthermore, by taking account of the lattice constants of GaBi (6.46 Å [6]) and GaN (4.53 Å [7]) in zinc blende structure, GaNAsBi pseudo ternary alloy is expected to be lattice-matched to the GaAs substrate. Therefore, controlling N and Bi compositions is necessary for the realization of temperature-insensitive devices using GaNAsBi. It has been experimentally reported that $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ with Bi composition y less than 0.05 have been successfully grown on the $\text{GaAs}(001)$ substrate by molecular beam epitaxy (MBE) [8–10]. Moreover, coherently grown $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ epilayers have been successfully formed by adjusting N composition in the MBE [4, 5]. Despite these experimental findings, little is known about the miscibility of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films from theoretical viewpoints.

In our previous studies, the miscibility of GaNAs and InGaN in bulk phase and those in thin films over the entire composition range has been systematically investigated using empirical interatomic potentials [11–15]. Our previous studies have elucidated that the miscibility of GaNAs and InGaN is improved by lattice constraint of

substrate. In this study, we extend our approach to investigate the miscibility of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films by means of empirical interatomic potentials using Monte Carlo (MC) method. Effects of nitrogen incorporation and lattice constraint of substrate are discussed in terms of bond length distribution in $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films on the $\text{GaAs}(001)$ substrate.

II. COMPUTATIONAL METHODS

In order to calculate the system energy E in zinc blende structured $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films, we employ the empirical interatomic potential V_{ij} [16–21]. This is given by the following equations:

$$E = \frac{1}{2} \sum_{i,j} V_{ij}, \quad (1)$$

$$V_{ij} = A \exp \{ -\beta(r_{ij} - R_i)^\gamma \} \times \{ \exp(-\theta r_{ij}) - B_0 \exp(-\lambda r_{ij}) G(\eta) / Z_i^\alpha \}. \quad (2)$$

Here, r_{ij} is the interatomic distance, Z_i the effective coordination number for atom i , R_i the minimum distance between neighbors, and $G(\eta)$ the bond bending term for tetrahedrally bonded atom pairs. The potential parameters A , B_0 , α , β , γ , θ , λ , and η are determined using the cohesive energy, elastic moduli, and relative energy differences among various crystal structures obtained by *ab initio* calculations and experiments. We use the parameters corresponding to Ga–As, Ga–N, Ga–Ga, As–As, and N–N bonds obtained by previous calculations [19–21]. Furthermore, the parameters for GaNAsBi systems such as Ga–Bi, Bi–Bi, Bi–As, Bi–N, and As–N bonds are determined in this study, as shown in Table I. In the system energy calculations of epitaxial layers, we assume coherent growth conditions: the lattice parameter a of basal plane is fixed to be that of substrate lattice parameter a_{sub} , and the lattice parameter c along the [001] direction and positions of atoms are relaxed to minimize the system energy.

The MC simulations are performed to investigate the equilibrium atomic arrangements of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films on the substrate with the (001) orientation. Here, we consider $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films with nitrogen composition $x = 0, 0.05, 0.1, 0.15$, and 0.2 and

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TABLE I: Potential parameters for Ga–Bi, Bi–Bi, Bi–As, Bi–N, and As–N bonds determined in this study.

	A (eV)	B_0	θ ($\text{\AA}^{-1}$)	λ ($\text{\AA}^{-1}$)	α	β	γ	η
Ga–Bi	1057.2434	0.297868	2.15809	1.36135	0.404692	12.61216	3.33019	0.672908
Bi–Bi	6461.3441	0.013398	2.88639	0.92446	0.563055	8.95399	3.13772	0.000000
Bi–As	5593.9018	0.016593	3.05706	1.00522	0.556012	13.51960	3.38463	0.000000
Bi–N	2541.1714	0.506926	2.37205	1.90292	0.178585	21.80313	3.40732	0.000000
As–N	1302.5868	0.180118	2.93857	1.58457	0.429437	32.44373	3.36574	0.000000

FIG. 1: Contour plots of atomic arrangements for $\text{GaN}_x\text{As}_{0.5-x}\text{Bi}_{0.5}$ thin films on the (001) substrate with substrate lattice parameter a_{sub} . Green, red, and blue regions correspond to GaBi, GaAs, and GaN solid solution regions, respectively.

the substrate with lattice parameter a_{sub} varying from 5.25 to 6.05 Å. In this study, Bi composition is fixed at $y = 0.5$. We employ the unit cell consisting of 524 atoms. The thickness of unit cell is 32 layers [22]. We assume $c(4 \times 4)\alpha$ surface consisting of three III-V dimers in the surface unit cell as a representative of reconstructed surface of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films. This reconstruction has been found to be favorable on the GaAs(001) surface under typical MBE growth conditions less than 700 K [23].

In the MC simulation procedure, randomly chosen group-V element atoms in $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films are exchanged to equilibrate the system at a certain temperature T according to the Metropolis algorithm [15]. Details of calculation procedure are explained elsewhere [15]. This procedure is repeated for suitable number of configurations (MC steps) in order to approach the equilibrium configurations. In this study, the equilibrium atomic arrangements at $T = 673$ K are obtained at 25000 MC steps, where the system energy keeps constant within 1×10^{-2} eV/atom.

III. RESULTS AND DISCUSSION

Figure 1 shows the contour plots of simulated equilibrium atomic arrangements for various $\text{GaN}_x\text{As}_{0.5-x}\text{Bi}_{0.5}$

FIG. 2: Calculated bond length distribution for Ga–Bi (green), Ga–As (red), and Ga–N (blue) bonds in (a) $\text{GaN}_{0.1}\text{As}_{0.4}\text{Bi}_{0.5}$ and (b) $\text{GaN}_{0.2}\text{As}_{0.3}\text{Bi}_{0.5}$ at $a_{\text{sub}} = 5.65$ Å in the equilibrium state. Dashed line denotes bond length distribution in the solid solution. Contour plots of atomic arrangements are also shown.

thin films on the (001) substrate. This figure reveals that the atomic arrangements of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films strongly depend on x and a_{sub} . The surface segregation appears over the entire range of x and a_{sub} . Bi atoms tend to be excluded from the substrate to the surface region when the lattice constant of substrate is less than 5.85 Å, whereas N atoms in N incorporated thin films tend to be excluded for lattice constants larger than 5.85 Å. Furthermore, GaN, GaAs, and GaBi layers are alternatively stacked along the [001] direction for N incorporated thin films. In particular, GaN and GaBi layers are sandwiched by GaAs layers and this trend becomes marked for thin films with large nitrogen composition. The thickness of GaN, GaAs, and GaBi layers are 4, 4, and 6 layers, respectively.

Our analysis of the interatomic bond distribution clarifies that the layered segregation of GaN sandwiched by GaAs layers originates from the stability of Ga–N

FIG. 3: Calculated bond length distribution for Ga-Bi (green), Ga-As (red), and Ga-N (blue) in $\text{GaN}_{0.1}\text{As}_{0.4}\text{Bi}_{0.5}$ at (a) $a_{\text{sub}} = 5.25 \text{ \AA}$ and (b) $a_{\text{sub}} = 6.05 \text{ \AA}$ in the equilibrium state. Contour plots of atomic arrangements are also shown.

bonds. Figure 2 shows the interatomic bond distribution of $\text{GaN}_{0.1}\text{As}_{0.4}\text{Bi}_{0.5}$ and $\text{GaN}_{0.2}\text{As}_{0.3}\text{Bi}_{0.5}$ at $a_{\text{sub}} = 5.65 \text{ \AA}$ in the equilibrium state, along with those in the solid solution. There are three large peaks (around 2.29, 2.45, and 2.62 $\text{\AA}$), each of which corresponds to Ga-N, Ga-As, and Ga-Bi bonds, respectively. Furthermore, several small peaks corresponding to Bi-related bonds (ranging from 2.64 to 2.98 $\text{\AA}$) near the surface are found in the equilibrium state. It should be noted that the peak corresponding to Ga-N bonds in the equilibrium state are much shorter than those in the solid solution and close to the equilibrium Ga-N bond length. The reduction of Ga-N bond length in the equilibrium state compared with that in the solid solution implies that Ga-N bonds are deformed to approach to their equilibrium bond length and form the stable GaN layers surrounded by GaAs layers. Indeed, the averaged interatomic potential for Ga-N bonds in the equilibrium state is lower than that in the solid solution by $\sim 0.235 \text{ eV/atom}$, suggesting that the stabilization of Ga-N bonds is crucial for the atomic arrangements in term of the lattice constraint of substrate.

The contribution of lattice constraint to the atomic arrangements is exemplified by comparing the result of $\text{GaN}_{0.1}\text{As}_{0.4}\text{Bi}_{0.5}$ at $a_{\text{sub}} = 5.25 \text{ \AA}$ with that at $a_{\text{sub}} = 6.05 \text{ \AA}$, where surface segregation of GaBi and GaN occurs at $a_{\text{sub}} = 5.25$ and $6.05 \text{ \AA}$, respectively. Figure 3 shows the interatomic bond distribution of $\text{GaN}_{0.1}\text{As}_{0.4}\text{Bi}_{0.5}$ at $a_{\text{sub}} = 5.25$ and $6.05 \text{ \AA}$ in the equilibrium state. For $a_{\text{sub}} = 5.25 \text{ \AA}$, as shown in Fig. 3(a), there are three large peaks (around 2.22, 2.40, and 2.58 $\text{\AA}$), each of which

FIG. 4: Averaged interatomic potentials for Ga-Bi, Ga-As, and Ga-N bonds in the equilibrium state as a function of substrate lattice parameters a_{sub} in $\text{GaN}_{0.1}\text{As}_{0.4}\text{Bi}_{0.5}$ thin films. Squares, triangles, and circles represent values of Ga-Bi, Ga-As, and Ga-N bonds, respectively.

corresponds to Ga-N, Ga-As, and Ga-Bi bonds, respectively, along with several small peaks corresponding to Bi-related bonds (ranging from 2.69 to 2.97 $\text{\AA}$) near the surface. In contrast, the distribution of $a_{\text{sub}} = 6.05 \text{ \AA}$ shown in Fig. 3(b) exhibits two large peaks corresponding to Ga-As and Ga-Bi bonds (around 2.55 and 2.70 $\text{\AA}$, respectively) with several small peaks corresponding to N-related bonds (ranging from 2.17 to 2.40 $\text{\AA}$). These differences in the bond length distribution imply that the lattice constraint of substrate crucially affects the stability of interatomic bonds.

The stability of interatomic bonds depending on a_{sub} is quantified by the averaged values of interatomic potentials for constituent atomic bonds. Figure 4 shows the calculated interatomic potentials corresponding to Ga-N, Ga-As, and Ga-Bi bonds as a function of a_{sub} . This figure reveals that the averaged interatomic potential corresponding to Ga-Bi bonds for small a_{sub} takes the largest value (-1.15 eV at $a_{\text{sub}} = 5.25 \text{ \AA}$), resulting in the surface segregation of GaBi to release the strain accumulated in the substrate region. In contrast, the averaged interatomic potential corresponding to Ga-N bonds for large a_{sub} takes the largest value (-1.45 eV at $a_{\text{sub}} = 6.25 \text{ \AA}$), so that the surface segregation of GaN occurs to reduce the strain accumulated in the substrate region. The averaged interatomic potential corresponding to Ga-Bi bonds (squares in Fig. 4) decreases and that to Ga-N bonds (circles in Fig. 4) increases with substrate lattice constant. Consequently, there is a crossover in the averaged value of interatomic potential between Ga-N and Ga-Bi bonds at $6.05 \text{ \AA}$. In addition, this crossover is strongly related to the boundary between surface segregation of GaBi and that of GaN. It is thus suggested that the surface segregation of either GaN or GaBi in GaNAsBi thin films occurs to reduce the number of interatomic bonds with large potential value due to the lattice constraint.

IV. CONCLUSIONS

We have theoretically investigated the atomic arrangements of zinc blende structured $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin

films coherently grown on GaAs(001) substrates using empirical interatomic potentials with the MC method. We have revealed that the atomic arrangements of $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films strongly depend on both N composition x and substrate lattice parameter a_{sub} . The layered segregation consisting of GaN layers sandwiched by GaAs layers appears in the substrate region over the wide range of a_{sub} and x . Furthermore, we have found that either GaBi or GaN surface segregation occurs to reduce the strain caused by lattice constraint. These results indicate that the incorporation of N atoms in GaAsBi is crucial for the miscibility, resulting in the layered segregation in $\text{GaN}_x\text{As}_{1-x-y}\text{Bi}_y$ thin films: The novel atomic arrangements in alloy semiconductor thin films such as

the layered segregation on the substrate can be formed by choosing suitable lattice constraint varied by x and a_{sub} that approach the bond length of the equilibrium values for semiconductor material.

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