Systematic theoretical investigations for contribution of lattice constraint to novel atomic arrangements in alloy semiconductor thin films

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Abstract

The atomic arrangements in zinc blende structured GaN_xAs_{1-x} thin films coherently grown on V-grooved substrates are theoretically investigated using empirical interatomic potentials and Monte Carlo simulation. The resultant atomic arrangements in GaN_xAs_{1-x} strongly depend on concentration x and substrate lattice parameter a_{sub}. Surface segregation of As or N is mainly found in GaN_xAs_{1-x} with large lattice mismatch to the substrate. On the other hand, the novel atomic arrangements such as layered segregation or ordered structure are found in GaN_xAs_{1-x} at the specific region such as (x, a_{sub}) = (0.5, 5.3), (0.3, 5.3), and (0.3, 5.1). This specific region corresponds to that with negative excess energy and with sufficient N and As atoms remaining in thin film layers even after surface segregation of them. The formation of the novel atomic arrangements is discussed in terms of bond lengths in the surface layers. These results suggest that various novel atomic arrangements in alloy semiconductor thin films appear depending on x and a_{sub} which control degree of lattice constraint.

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Keywords: GaN_xAs_{1-x} thin films; V-grooved substrate; Lattice constraint; Layered segregation; Surface segregation; Empirical interatomic potential

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1. Introduction

Alloy semiconductor thin films including $Si_{1-x}Ge_x$, $In_{1-x}Ga_xP$, and $In_{1-x}Ga_xN$ often exhibit various novel atomic arrangements such as atomic ordering and surface segregation [1-9]. Previous theoretical studies reveal that these novel atomic arrangements in thin films are closely related to the lattice constraint from the substrate. Zunger et al. systematically demonstrated epitaxial effects for stabilization of a bulk-ordered compound, solid solubility, order-disorder transition temperature, and composition pinning ("lattice latching") of alloy semiconductors [10,11]. However, the contribution of lattice constraint to the atomic arrangements has not been directly clarified by showing resultant atomic arrangements in alloy semiconductor thin films but has been mainly investigated by considering excess energy for them. In particular, there have been very few studies for the correlation between atomic ordering and surface segregation appearing in alloy semiconductor thin films with large lattice mismatch. We have directly investigated atomic arrangements in $In_{1-x}Ga_xN$ thin films on GaN(0001) using our empirical interatomic potentials and Monte Carlo (MC) simulation, where it is shown that the large lattice constraint enhances In surface segregation [12]. In this study, we extend our approach to hypothetical zinc blende structured GaN_xAs_{1-x} thin films on the V-grooved substrate to vary wide range of strain due to the lattice constraint from the substrate. On the basis of equilibrium atomic arrangements obtained in the MC simulation, we clarify how the lattice constraint contributes to the formation of the novel atomic arrangements such as layered segregation and surface segregation in terms of excess energy and bond length distribution in GaN_xAs_{1-x} thin films on the V-grooved substrate.

2. Computational methods

In order to investigate the system energy E for zinc blende structured GaN_xAs_{1-x} thin films on the V-grooved substrate, we employ our simple energy formula and the empirical interatomic potential V_{ij} [13-18]. This is given by the following equations:

$$E = \frac{1}{2}\left[\sum_{ij} V_{ij} + \sum_{ij} V_{es}\right]. \tag{1}$$

$$V_{ij} = A\exp[-\beta(r_{ij} - R_i)^{\gamma}] \times [\exp(-\theta r_{ij}) - \frac{B_0}{Z_i^{\alpha}}\exp(-\lambda r_{ij})G(\eta)], \tag{2}$$

$$V_{es} = K\left[\frac{3}{2}(1 - f_i)\frac{Z_{bond}^2}{r_{bb}} - f_i\frac{Z_{ion}^2}{r_{ii}}\right]. \tag{3}$$

Here r_{ij} is the distance between the atoms; Z_i the effective coordination number of 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. In eq. (3), V_{es} is the electrostatic interaction between bond charges Z_{bond} (=-2) and that between ionic charges Z_{ion} (=4 for group IV, 3 for III-V and 2 for II-VI semiconductors) beyond the second nearest neighbors depending on ionicity f_i, which corresponds to the first-neighbor interlayer interaction J_1 [19,20]. The coefficient K is 8.7 meV•Å determined by reproducing the energy difference of 25.3 meV/atom between 3C and 2H for C with f_i=0 obtained by ab initio calculations [20]. Using eq. (1), the system energies are calculated for GaN_xAs_{1-x} thin films on the (001)-oriented V-grooved substrate.

The MC simulation is performed to investigate equilibrium atomic arrangements in the GaN_xAs_{1-x} thin films on the V-grooved substrate with (001) orientation. Here we consider the GaN_xAs_{1-x} thin films with concentration x=0.1, 0.3, 0.5, 0.7, and 0.9 and the V-grooved substrate with lattice parameter a_{sub}=4.5 Å, 4.7 Å, 4.9 Å, 5.1 Å, 5.3 Å, and 5.5 Å. In the simulation for the GaN_xAs_{1-x} thin films coherently grown on the V-grooved substrate, we employ the model structure consisting of the GaN_xAs_{1-x} thin films with V-shaped unit cell with $58 \times 4 \times 58$. The periodic boundary condition along the y-direction is imposed. Figure 1 shows the model structure for the GaN_xAs_{1-x} thin films on the (001)-oriented V-grooved substrate. The N and As atoms are randomly distributed in the GaN_xAs_{1-x} thin films. The lattice parameter of the V-grooved substrate a_{sub} is fixed, whereas the atomic positions are varied to minimize the system energy. We assume ideal (1×1) surface as a representative surface for the GaN_xAs_{1-x}.

In the simulation procedure, randomly chosen atoms in the system are exchanged to equilibrate the system at certain temperature T according to the following rules on the basis of Metropolis algorithm. (i) Select atoms at random; (ii) select random exchanges of atoms; (iii) calculate the change in system energy ΔU after exchanging the chosen atoms; (iv) if ΔU is negative, accept the new configuration; (v) otherwise, select a random number h uniformly distributed over the interval (0,1); (vi) if $\exp(\Delta U/kT)<h$, where k is the Boltzmann constant, accept the old configuration; (vii) otherwise, use the new configuration and the new system energy as the current properties of the system. This procedure is repeated for suitable number of configurations (MC steps) in order to approach equilibrium configurations. In this study, equilibrium atomic arrangements at T=1000 K are obtained at 13,000 MC steps where the system energy keeps constant. Interdiffusion between thin film and substrate layers is neglected in this study.

In order to discuss thermodynamic stability of the GaN_xAs_{1-x} thin films on the V-grooved substrate, we also calculate the excess energies $\Delta E(x)$ for the GaN_xAs_{1-x} thin films using the following equation:

$$\Delta E(x, a_{sub}) = E(x, a_{sub}) - \left[xE_{\mathrm{GaN}}(a_{sub}) + (1-x)E_{\mathrm{GaAs}}(a_{sub}) \right], \quad (4)$$

where $E(x, a_{\mathrm{sub}})$, $E_{\mathrm{GaN}}(a_{\mathrm{sub}})$, and $E_{\mathrm{GaAs}}(a_{\mathrm{sub}})$ are the system energies for GaN_xAs_{1-x}, GaN, and GaAs constrained by the V-grooved substrate lattice with lattice parameter a_{sub}, respectively.

3. Results and discussion

Figure 2 shows the simulated equilibrium atomic arrangements for the various GaN_xAs_{1-x} thin films on the (001)-oriented V-grooved substrate. Here red-colored, blue-colored, and green-colored regions correspond to GaAs, GaN, and GaN_xAs_{1-x} solid solution regions, respectively. This figure reveals that the surface segregation appears over the entire range of (x, a_{sub}). This is because the GaAs or GaN pair with larger lattice mismatch to the substrate tends to be excluded from the substrate region to the surface region to relax the strain caused by the lattice mismatch [12]. In particular, the surface segregation of GaAs appears in the wide range of x and a_{sub}, whereas the GaN surface layers are found only at certain (x, a_{sub}) such as (0.5, 5.5), (0.7, 5.3), (0.7, 5.5), (0.9, 5.1), (0.9, 5.3), and (0.9, 5.5). Figure 3 shows the bond length distribution in the $GaN_{0.5}As_{0.5}$ at a_{sub}=5.5 Å (GaN surface segregation) and in the $GaN_{0.5}As_{0.5}$ at a_{sub}=5.1 Å and 4.7 Å (GaAs surface segregation). It is clear that the bond lengths in the $GaN_{0.5}As_{0.5}$ exhibit bimodal distribution for Ga-As (red line) and Ga-N (blue line) interatomic bonds. Moreover, this figure implies that the bond length distribution of Ga-As interatomic bonds is narrower than that of Ga-N interatomic bonds. This suggests that the Ga-As interatomic bonds with smaller elastic stiffness are easily deformed to more effectively lower the system energy than those between Ga and N with larger elastic stiffness. As a result, the GaN_xAs_{1-x} thin films mainly make GaAs layers segregate near their surfaces to stabilize themselves.

Furthermore, the GaAs and the GaN layers alternatively stacked along the [001] direction are found at (x, a_{sub}) = (0.5, 5.3), (0.3, 5.3), and (0.3, 5.1) highlighted by light blue in Fig. 2. Figure 4 shows the bond length distribution for the $GaN_{0.5}As_{0.5}$ at a_{sub}=5.3 Å, the $GaN_{0.3}As_{0.7}$ at a_{sub}=5.3 Å, and the $GaN_{0.3}As_{0.7}$ at a_{sub}=5.1 Å with layered segregation. This figure implies that the bond length distribution of Ga-As interatomic bonds (red line) has two peaks, where one is that in the GaN_xAs_{1-x} beneath the surface layers and the other corresponds to that in the surface layers (denoted by arrows at ~2.4 Å). The peak value of ~2.4 Å for the Ga-As interatomic bond length is consistent with equilibrium bond length for GaAs d=2.45 Å. Therefore, the Ga-As interatomic bonds in the surface layers are easily deformed to approach their equilibrium bond length and form the stable GaAs layers near the surfaces. Moreover, it should be noted that this peak only appears in these three GaN_xAs_{1-x} thin films with layered segregation (compare

with Fig. 3).

Figure 5 shows the calculated excess energy contour map for GaN_xAs_{1-x} thin films constrained by the V-grooved substrate lattice as a function of x and a_{sub}. The coordinates of (x, a_{sub}) with layered segregation are also shown in this figure. The excess energies have negative values in the region within the green line, where the constituent pair such as GaAs favors different constituent pair GaN as a neighbor pair. The coordinates with layered segregation are located in this region, e.g., meaning when GaAs layer is formed, GaN layer is favored beneath the GaAs layer. According to these results obtained in this study, we conjecture the formation of the layered segregation in the GaN_xAs_{1-x} thin films at (x, a_{sub}) = (0.5, 5.3), (0.3, 5.3), and (0.3, 5.1) on the V-grooved substrate as follows. First of all, GaAs layers are favorably located near the (001) surface, since the strain in the surface GaAs layers is fairly relaxed by easily deforming their bond length almost equal to the equilibrium bond length. Once the GaAs surface layres are formed, the GaN layers are favored beneath the GaAs surface layers, since the excess energy has negative value at (x, a_{sub}) = (0.5, 5.3), (0.3, 5.3), and (0.3, 5.1) on the V-grooved substrate. Therefore, alternative stacking of GaAs and GaN subsequently occurs to form the layered structure along the [001] direction. However, the layered structure is suppressed as decrease of the film thickness as shown in Figs. 2 and 5. This is because the lattice constraint from the V-grooved substrate is enhanced at the small film thickness to exclude GaN from the substrate region and form GaN_xAs_{1-x} solid solution (green area). Consequently, the novel atomic arrangements such as layered segregation in the GaN_xAs_{1-x} are formed by choosing the suitable x and a_{sub} that produce negative excess energy and the bond length in the GaAs surface segregation layers almost equal to the equilibrium bond length of the GaAs.

4. Conclusion

We have theoretically investigated the novel atomic arrangements such as layered segregation and surface segregation in terms of excess energy and bond length distribution in GaN_xAs_{1-x} thin films on the V-grooved substrate. The calculated results revealed that the surface segregation appears over the entire range of (x, a_{sub}). This is because the GaAs or GaN pair with larger lattice mismatch to the substrate tends to be excluded from the substrate region to the surface region to relax the strain caused by the lattice constraint. Furthermore, the GaAs and the GaN layers alternatively stacked along the [001] direction were found at (x, a_{sub}) = (0.5, 5.3), (0.3, 5.3), and (0.3, 5.1). This phenomenon is closely related to the GaAs surface segregation with the bond lengths almost equal to the equilibrium bond length of GaAs. The Ga-As interatomic bonds in

the surface layers are easily deformed to approach their equilibrium bond length and form the stable GaAs layers near the surface. Subsequent excess energy calculations implied that the GaN_xAs_{1-x} thin films with layered segregation have negative excess energy due to the lattice constraint from the substrate, e.g., meaning GaN layer favors alternative stacking with GaAs beneath the GaAs surface layers along the [001] direction. Although we need further calculations using larger unit cell or incorporating dislocation formation at the interface for quantitative discussions, these results qualitatively suggest that the novel atomic arrangements in alloy semiconductors such as layered segregation on the V-grooved substrate can be formed by choosing the suitable lattice constraint varied by x and a_{sub} that produce negative excess energy and approach the bond length to the equilibrium value of semiconductor material segregated in the surface layers.

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References

[1] K. Nakagawa, M. Miyao, J. Appl. Phys. 69 (1991) 3058.

[2] S. Fukatsu, K. Fujita, H. Yaguchi, Y. Shiraki, R. Ito,Appl. Phys. Lett. 59 (1991) 2103.

[3] N. Ohtani, S. M. Mokler, B. A. Joyce, Surf. Sci. 295 (1993) 325.

[4] D. E. Jesson, S. J. Pennycook, J. –M. Baribeau, D. C. Houghton, This Solid Films 222 (1992) 98.

[5] T. S. Kuan, T. F. Kuech, W. I. Wang, E. L. Wilkie, Phys. Rev. Lett. 54 (1985) 208.

[6] A. Gomyo, T. Suzuki, K. Kobayashi, S. Kawata, I. Hino, T. Yuasa, Appl. Phys. Lett. 50 (1987) 16.

[7] O. Ueda, M. Takikawa, J. Komeno, I. Umebu, Jpn. J. Appl. Phys. 26 (1987) L1824.

[8] N. Grandjean, J. Massies, S. Dalmasso, P. Vennegues, L. Siozade, L. Hirsch, Appl. Phys. Lett. 74 (1999) 3616.

[9] N. Duxbury, U. Bangert, P. Dawson, E. J. Thrush, W. Van der Stricht, K. Jacobs, I. Moerman, Appl. Phys. Lett. 76 (2000) 1600.

[10] D. M. Wood, A. Zunger, Phys. Rev. B 38 (1988) 12756.

[11] A. Zunger, D. M. Wood, J. Crystal Growth 98 (1989) 1.

[12] T. Ito, S. Inahama, T. Akiyama, K. Nakamura, J. Crystal Growth 298 (2007) 186.

[13] K. E. Khor, S. Das Sarma, Phys. Rev. B 38 (1988) 3318.

[14] T. Ito, K. E. Khor, S. Das Sarma, Phys. Rev. B 41 (1990) 3893.

[15] T. Ito, J. Appl. Phys. 77 (1995) 4845.

[16] T. Ito, Jpn. J. Appl. Phys. 37 (1998) L574.

[17] T. Suda, Y. Kangawa, K. Nakamura, T. Ito, J. Crystal Growth 258 (2003) 277.

[18] T. Ito, T. Suda, T. Akiyama, K. Nakamura, Appl. Surf. Sci. 244 (2005) 170.

[19] C. Cheng, R. J. Needs, V. Heine, J. Phys. C 21 (1988) 1049.

[20] T. Ito, Jpn. J. Appl. Phys. 37 (1998) L1217.

Figure captions

Fig. 1: Schematic of the model structure consisting of the GaN_xAs_{1-x} thin films on the (001) substrate with V-shaped unit cell with 58×4×58 used in this study.

Fig. 2: Simulated results for the atomic arrangements in the GaN_xAs_{1-x} thin films on the V-shaped substrates with lattice parameter a_{sub}. The red-colored, blue-colored, and green-colored regions correspond to GaAs, GaN, and GaN_xAs_{1-x} solid solution regions, respectively. The GaN_xAs_{1-x} thin films with layered segregation are highlighted by light blue.

Fig. 3: Calculated bond length distribution for Ga-As (red line) and Ga-N (blue line) in (a) the $GaN_{0.5}As_{0.5}$ at a_{sub}=5.5 Å (GaN surface segregation), (b) the $GaN_{0.5}As_{0.5}$ at a_{sub}=5.1 Å, and (c) the $GaN_{0.5}As_{0.5}$ at 4.7 Å (GaAs surface segregation).

Fig. 4: Calculated bond length distribution for Ga-As (red line) and Ga-N (blue line) in the $GaN_{0.5}As_{0.5}$ at a_{sub}=5.3 Å, the $GaN_{0.3}As_{0.7}$ at a_{sub}=5.3 Å, and the $GaN_{0.3}As_{0.7}$ at a_{sub}=5.1 Å with layered segregation.

Fig. 5: Calculated excess energy contour map (in meV/atom) for GaN_xAs_{1-x} thin films constrained by the V-grooved substrate lattice as a function of x and a_{sub}.

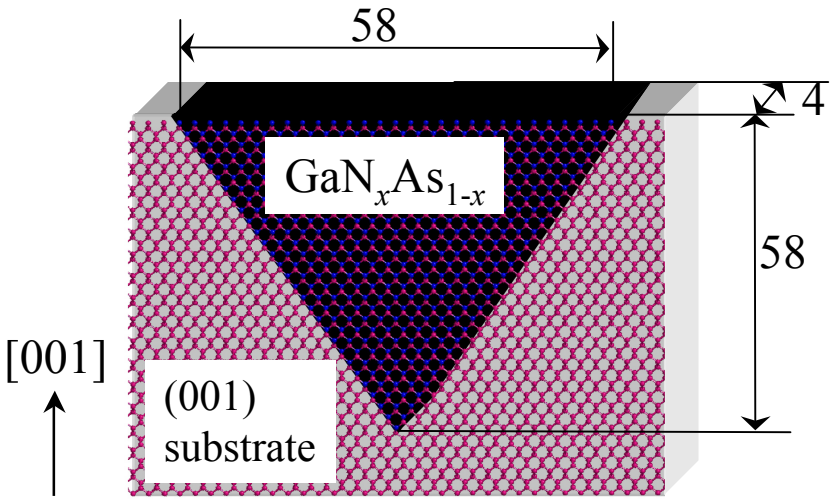

Fig. 1
T. Ito

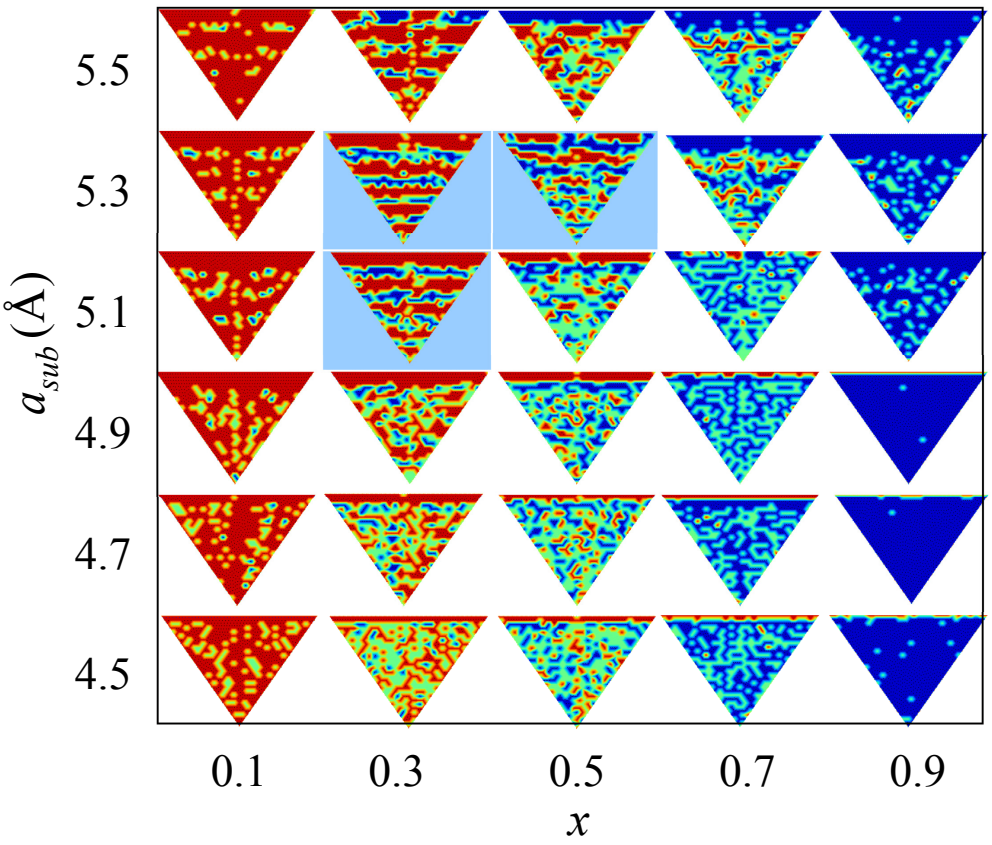

Fig. 2
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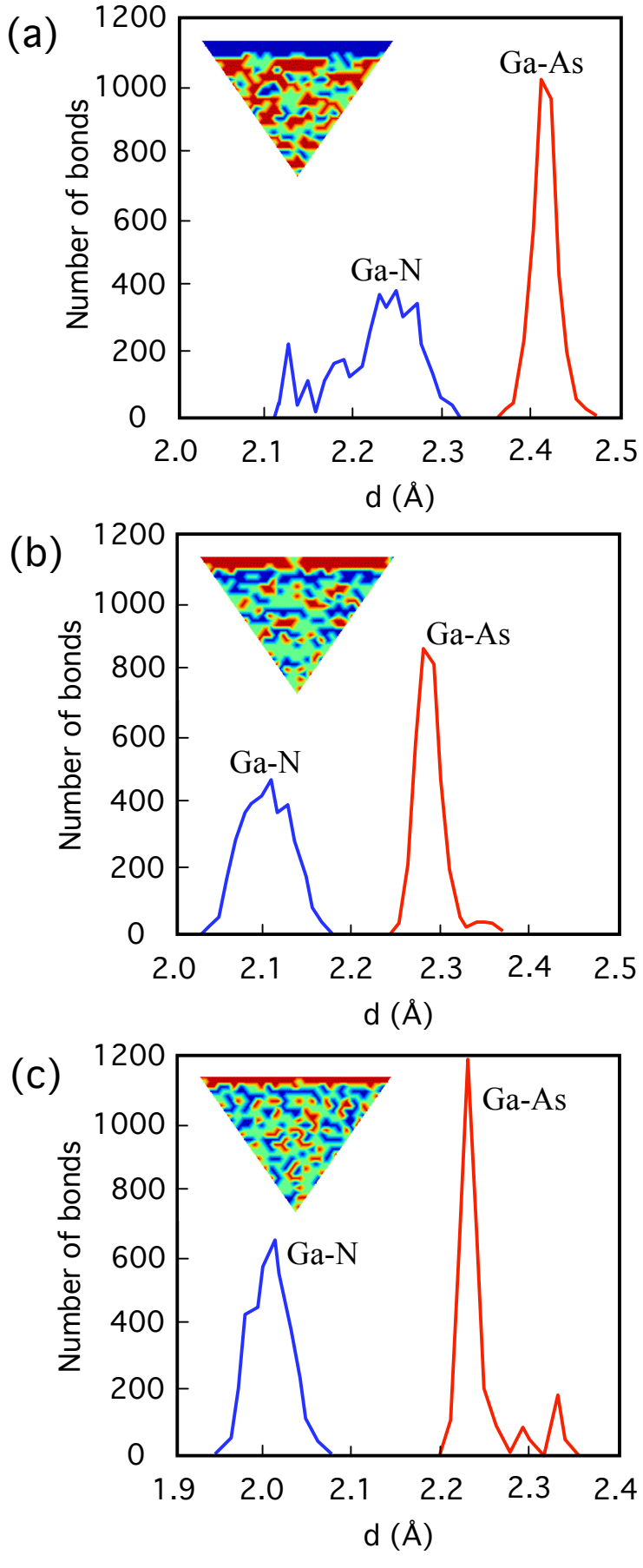
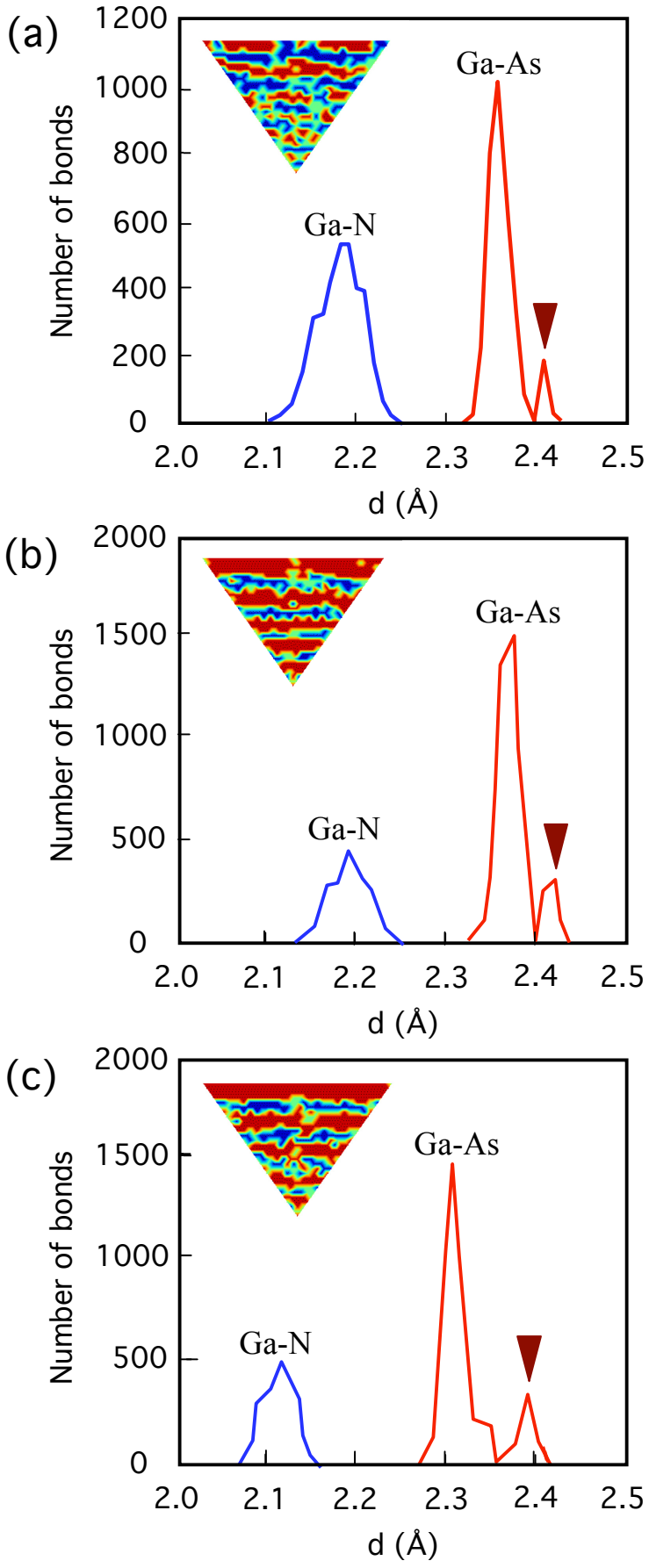

(a)
Number of bonds
1200
1000
800
600
400
200
0
Ga-As
Ga-N
2.0
2.1
2.2
2.3
2.4
2.5
d (Å)
(b)
Number of bonds
1200
1000
800
600
400
200
0
Ga-As
Ga-N
2.0
2.1
2.2
2.3
2.4
2.5
d (Å)
(c)
Number of bonds
1200
1000
800
600
400
200
0
Ga-As
Ga-N
1.9
2.0
2.1
2.2
2.3
2.4
d (Å)

Fig. 3
T. Ito


(a)
Number of bonds
1200
1000
800
600
400
200
0
Ga-As
Ga-N
2.0
2.1
2.2
2.3
2.4
2.5
d (Å)
(b)
Number of bonds
2000
1500
1000
500
0
Ga-As
Ga-N
2.0
2.1
2.2
2.3
2.4
2.5
d (Å)
(c)
Number of bonds
2000
1500
1000
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Ga-As
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d (Å)

Fig. 4
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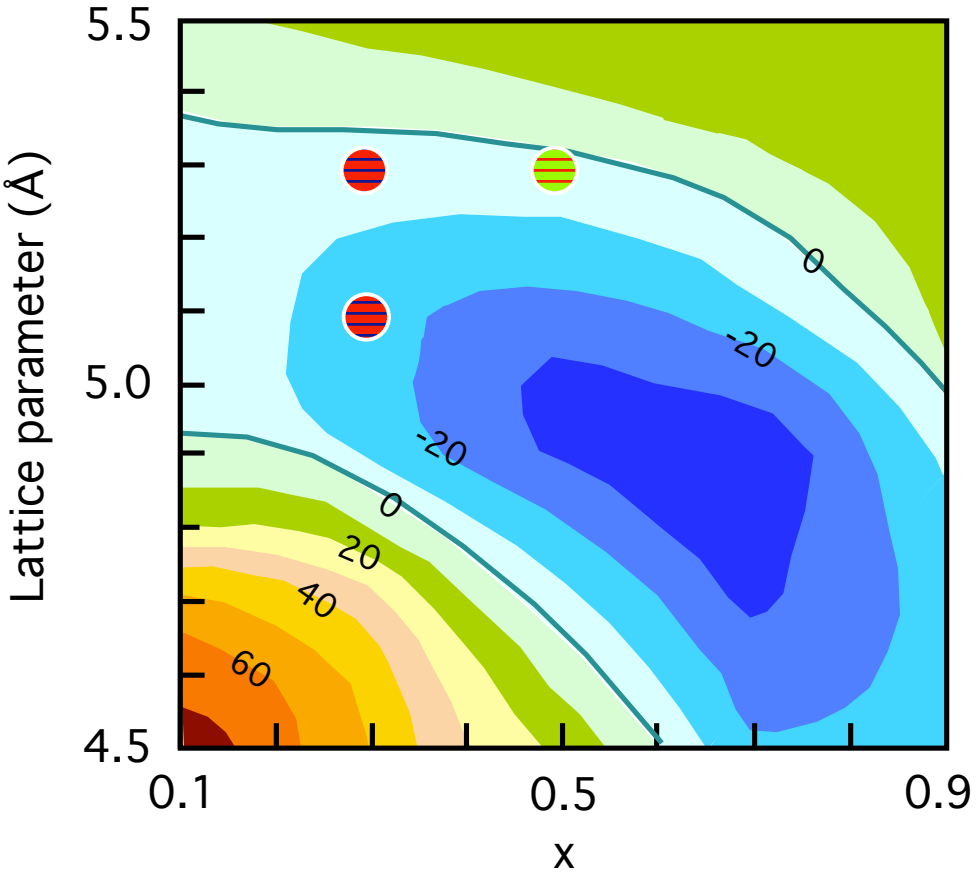

Fig. 5
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