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Theoretical investigations of adatom behavior on non-planar surfaces with GaAs(*n* 1 1)A

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Abstract

The behavior of Ga and As adatoms on non-planar surfaces consisting of GaAs(0 0 1)-(2 × 4)β2 top and GaAs(*n* 1 1)A (*n* = 2, 3 and 4) facet surfaces are investigated by empirical interatomic potentials with the aid of ab initio calculations. The calculated results imply that Ga adsorption energies strongly depend on the surface orientation, whereas As adsorption energies keep almost constant. The difference in adsorption energies can be interpreted by considering strain energy. In particular, Ga adatom is stabilized on the (3 1 1)A surface by the smallest strain energy forming interatomic bonds with three As atoms located at the regular fcc sublattice. Furthermore, we roughly simulate resultant surface profile of GaAs thin films on non-planar surface consisting of the (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces based on the rate equation. The simulated results reveal that the non-planar surface consisting of the (0 0 1)-(2 × 4)β2 top and (3 1 1)A facet surfaces forms unique surface profile because of preferential Ga adsorption on the (3 1 1)A and Ga migration from the (0 0 1)-(2 × 4)β2 toward (3 1 1)A. Consequently, growth on the (3 1 1)A facet surface exhibits a unique cross sectional surface profile compared with that on the non-planar surfaces consisting of (2 1 1)A and (4 1 1)A facet surfaces.

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Keywords: GaAs; Computer simulation; Adsorption; Migration; Growth; Molecular beam epitaxy

1. Introduction

Recently, semiconductor quantum well (QW) devices, e.g., a surface emitting diodes, lasers and QW tunneling devices, have been significantly improved by better-defined epitaxial layers grown by molecular beam epitaxy (MBE). These QW devices can be fabricated using the high index GaAs(*n* 1 1)A (*n* = 1, 2, 3 and 4) substrates because of their possibility of high luminescence emission efficiency. In order to realize the high efficiency, there have been many experimental studies for fabricating thin films with smooth surface.

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Asai and co-workers extensively investigated surface profile of MBE grown GaAs/AlGaAs thin films on non-planar surfaces using atomic force microscopy and found that the substrate surface orientation affects the surface profile [1–3]. Zhou et al. examined the influence of substrate surface orientation on InAlAs/AlGaAs quantum dots (QDs) grown on (0 0 1) and (n 1 1)A (n = 3 and 5) GaAs substrate by MBE [4]. In particular, Nötzel et al. found that the GaAs(3 1 1)A surface had a unique growth mechanism [3], and fabricated the GaAs sidewall QWs, QDs and coupled wire-dot arrays by functional self-organized epitaxy on patterned GaAs(3 1 1)A [5]. Despite these successful applications, the mechanism of the dependence of surface profile on orientation is still unclear.

In the present paper, we theoretically investigate the behavior of Ga and As adatoms on non-planar surfaces consisting of GaAs(0 0 1)-(2 × 4)β2 top and GaAs(n 1 1)A (n = 2, 3 and 4) facet surfaces using empirical interatomic potentials [6,7] with the aid of ab initio calculations. The calculated results for migration and adsorption energies are discussed in terms of the number of electrons in Ga dangling bonds and strain energy contributions. Moreover, we roughly simulate resultant surface profile of GaAs thin films on non-planar surfaces consisting of the (0 0 1)-(2 × 4)β2 top and (n 1 1)A facet surfaces using rate equation [8]. In the calculation procedure, the migration potentials and adsorption energies on these surfaces are used.

2. Computational methods

We construct non-planar surface systems consisting of GaAs(0 0 1)-(2 × 4)β2 top and (n 1 1)A (n = 2, 3 and 4) facet surfaces to calculate the system energy difference between the case of Ga and As attached to the (0 0 1)-(2 × 4)β2 top and that to the (n 1 1)A facet surfaces. The calculated system energy difference corresponds to the value of adsorption energy difference between the surfaces. The system energy E is represented by the following equations [9–12]:

$$E = E_{\text{bond}} + \Delta E_{\text{bond}}, \tag{1}$$

$$E_{\text{bond}} = \frac{1}{2}\sum V_{ij}, \tag{2}$$

$$\Delta E_{\text{bond}} = C|\Delta Z|, \tag{3}$$

where E_{bond} is the cohesive energy estimated by empirical interatomic potential V_{ij} [6] which incorporates the contribution of strain energy, and ΔE_{bond} the correction term due to the charge redistribution between dangling bonds on the surface. ΔZ is the number of electrons remaining in Ga dangling bonds and the coefficient C has a value of 0.40 eV/electron. This simple energy formula have been successfully applied to the migration and adsorption energy calculations on the non-planar surfaces in addition to those on flat surfaces [10–13].

The empirical interatomic potential V_{ij} [6,7] in Eq. (2) is written by:

$$V_{ij} = A\exp\{-\beta(r_{ij} - R_i)^{\gamma}\} \times \left[\exp(-\theta r_{ij}) - \frac{B_0}{Z_i^{\alpha}}\exp(-\lambda r_{ij})\right], \tag{4}$$

where 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, θ, λ, α, β, γ and η were determined using the cohesive energy, bulk modulus and relative stability among various structures obtained by ab initio calculations and experiments.

In order to obtain surface profile of GaAs thin films, we employ the rate equation [8]. This equation is given by

$$\begin{aligned}\Delta n_i \propto & -n_i(N - n_{i-1})\exp\left\{\frac{(-E_{i-1} + E_i)}{kT}\right\} \\ & - n_i(N - n_{i+1})\exp\left\{\frac{(-E_{i+1} + E_i)}{kT}\right\} \\ & \times (N - n_i)n_{i+1}\exp\left\{\frac{(-E_i + E_{i+1})}{kT}\right\} \\ & + (N - n_i)n_{i-1}\exp\left\{\frac{(-E_i + E_{i-1})}{kT}\right\},\end{aligned} \tag{5}$$

where N is the number of atoms, E_{i-1}, E_i and E_{i+1} are the cohesive energy at each lattice site (i−1, i and i + 1), k is Boltzmann's constant and T the temperature. In this equation, the first and second terms indicate migration of adatoms from the lattice site i. The third and fourth terms indicate migration of adatoms from the lattice site i− 1 and i + 1.

Results and discussion

Fig. 1 shows the calculated adsorption energy differences between the case of Ga and As attached to the preferable lattice sites on (0 0 1)-(2 × 4)β2 top and that on the (*n* 1 1)A facet surfaces. The computational systems are employed for each non-planar surface consisting of the (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surface shown in Fig. 2. Here, we let the system energy when the Ga and As attached to the (0 0 1)-(2 × 4)β2 top surface such be the energy origin. The calculated results imply that Ga adsorption energies strongly depend on the surface orientation, whereas As adsorption energies keep almost constant. In particular, it should be noted that the Ga adsorption energy when it adsorbs on (3 1 1)A [14] is the largest amongst all the other surfaces. This suggests that the Ga adatom on (3 1 1)A surface is the most stable compared with that on the other surfaces. In order to check the feasibility of our approach, we also performed ab initio pseudopotential calculations for Ga adsorption energies of Ga adatom on the (0 0 1)-(2 × 4)β2, (2 1 1)A and (4 1 1)A [15] surfaces. The calculated results imply that adsorption energy differences for non-planar surfaces including (2 1 1)A and (4 1 1)A have a value of 1.4 and 0.0 eV, respectively. These values can be favorably compared with the values of 0.9 and 0.0 eV for non-planar surfaces including (2 1 1)A and (4 1 1)A obtained by our interatomic potential calculations, respectively. This implies that our interatomic potential calculations are feasible to estimate the adsorption energy difference for non-planar surfaces considered in this study.

The preferable lattice sites for Ga adatom and As adatom on each surface are illustrated in Figs. 3 and 4. It is found that the Ga adatom on the (3 1 1)A and (2 1 1)A surfaces stably resides in the lattice site forming interatomic bonds with surface atoms without any strain, since these surface atoms are located at the regular fcc sublattices. On the other hand, Ga adatom on the (0 0 1)-(2 × 4)β2 and (4 1 1)A surfaces is strongly stretched by As-dimers. This increases E_{bond} and destabilizes the Ga adatom on the (0 0 1)-(2×4)β2 and (4 1 1)A surfaces compared with that on the (2 1 1)A and (3 1 1)A surfaces. Similar qualitative trend in relative stability is also found in As adatom as shown in Fig. 4, although the stable lattice sites for As adatom on the (0 0 1)-(2 × 4)β2 and (4 1 1)A surfaces are different from those for Ga adatom. It should be noted that energy difference among the surfaces is smaller than that for Ga adatom. This is because As adatom mainly forms weak As–As interatomic bonds with surface atoms, which do not significantly increase strain energy due to As-dimers.

Based on these findings, we roughly simulate resultant surface profile of GaAs thin films on non-planar

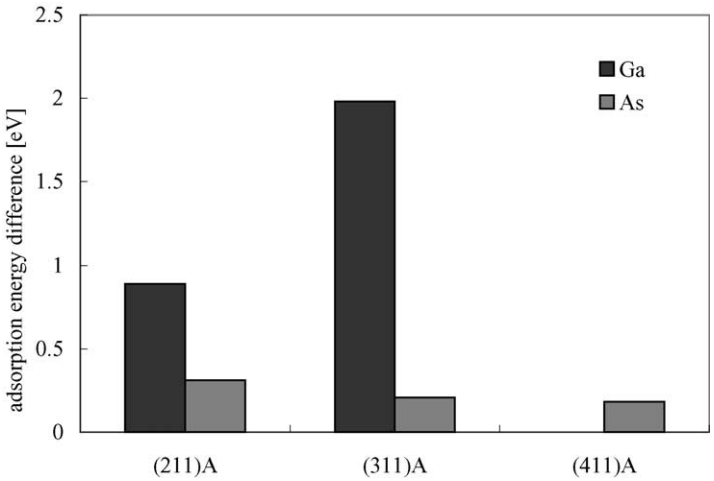

Fig. 1. Ga and As adsorption energy difference in the case of that on GaAs(0 0 1)-(2 × 4)β2 top and on (*n* 1 1)A facet surfaces, where the adsorption energy on (0 0 1)-(2 × 4)β2 is energy origin. The results were obtained by interatomic potential calculations.

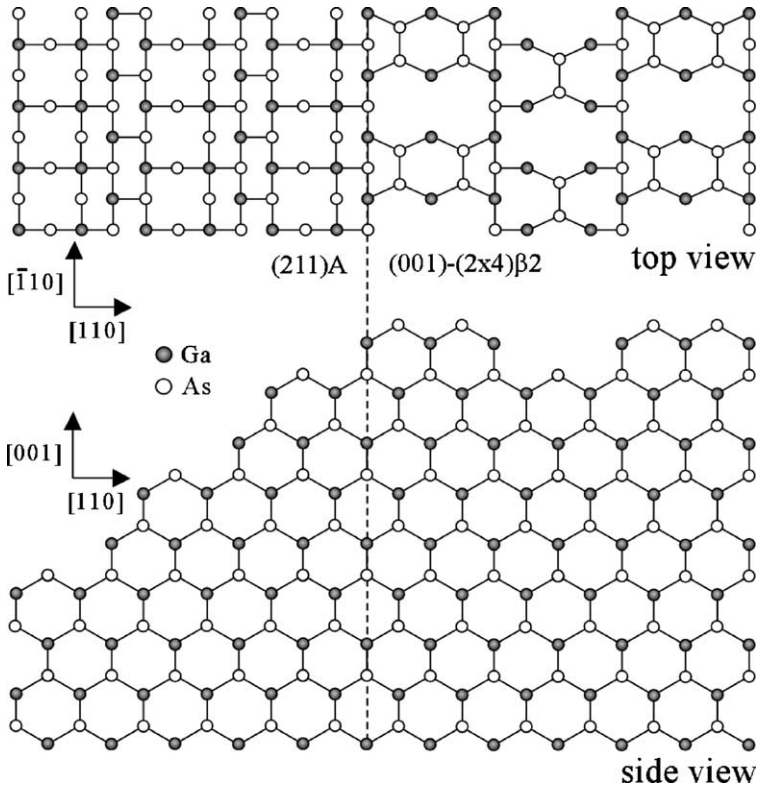

Fig. 2. Computational model of the non-planar surface consisting of GaAs(0 0 1)-(2 × 4)β2 top and (2 1 1)A facet surfaces used in the interatomic potential calculations, where periodic boundary conditions are imposed in the *x*–*y* plane. Similar systems are employed for the other non-planar surface with (*n* 1 1)A.

surfaces consisting of the (0 0 1)-(2×4)β2 top and (*n* 1 1)A facet surfaces based on the Eq. (5). And we simulate in assumption that As adatom naturally adsorbs when Ga adatom stuck to non-planar surfaces consisting of the (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces because of the behavior of Ga adatom was dominant. Here, we listed the values of Ga migration potentials near the boundary between (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces and adsorption energies on these surfaces used in this study in Table 1. The value of Ga migration potentials was obtained by averaging the energies along [0 $\bar{1}$ 1] direction at each cross sectional lattice points on each surface. This implies that Ga adatom preferably adsorbs on the (3 1 1)A and also easily migrates from (0 0 1)-(2 × 4)β2 to the (3 1 1)A in contrast with Ga adatom on non-planar surface consisting of the (0 0 1)-(2 × 4)β2 top and (4 1 1)A facet surfaces.

Fig. 5 shows the calculated surface profile of GaAs thin films on non-planar surfaces consisting of the (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces at 893 K.

Here, thick solid line is unit cell of non-planar surface, where step-like periodic boundary condition is imposed in the *x*–*z* plane. The form of the (*n* 1 1)A facet surfaces was arranged 45° because of the surface profile does not depend on substrate form but it greatly depends on the parameter of *E* and the deposited number of atoms *N* on each site from Eq. (5). The simulated results reveal that the GaAs growth on non-planar surface consisting of the (0 0 1)-(2 × 4)β2 top and (3 1 1)A facet exhibits unique surface profile, where the growth predominantly proceeds to fill up the (3 1 1)A facet surface. This is because Ga adatoms predominantly adsorb on the (3 1 1)A and Ga adatoms impinging on the (0 0 1)-(2 × 4)β2 surface preferen-

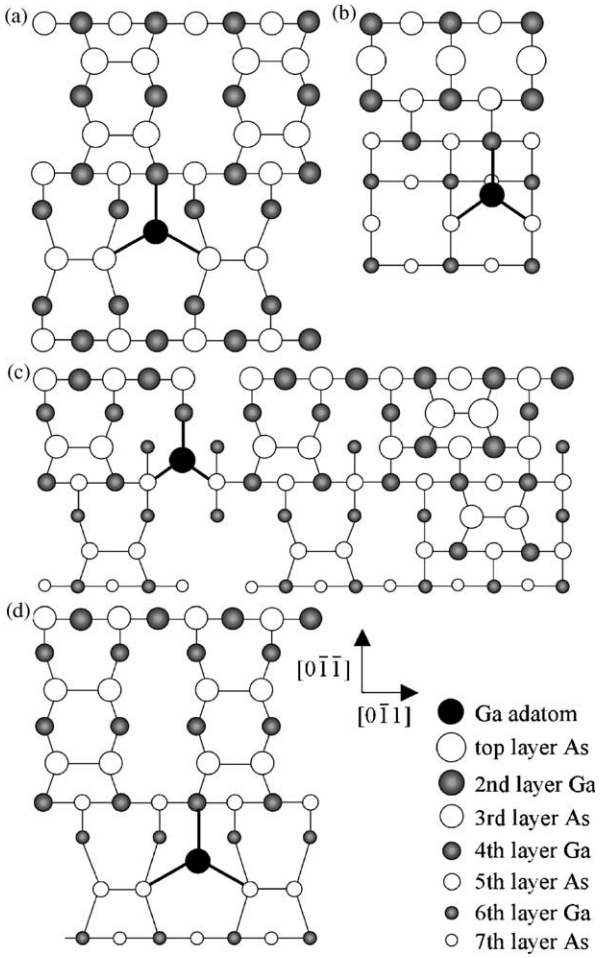

Fig. 3. Schematic of top view of GaAs (a) (0 0 1)-(2 × 4)β2 surface. And schematic top view of GaAs facet surfaces such as (b) (2 1 1)A, (c) (3 1 1)A, (d) (4 1 1)A. Bold lines show the bonds around the Ga adatom.

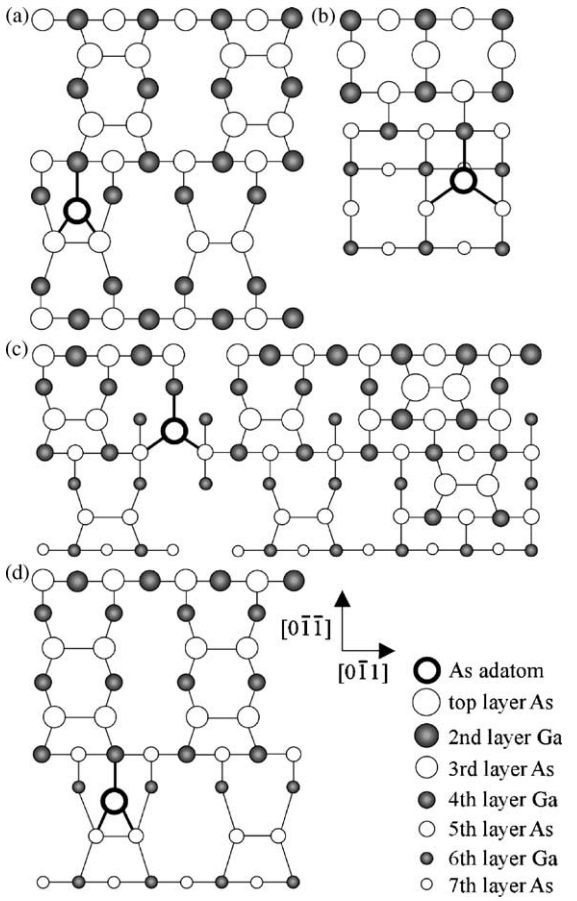

Fig. 4. Schematic of top view of GaAs (a) (0 0 1)-(2 × 4)β2 surface. And schematic top view of GaAs facet surfaces such as (b) (2 1 1)A, (c) (3 1 1)A, (d) (4 1 1)A. Bold lines show the bonds around the As adatom.

tially migrate toward (3 1 1)A due to the adsorption and migration energy differences as shown in Table 1. On the other hand, the growth on the non-planar surface consisting of (0 0 1)-(2 × 4)β2 top and (2 1 1)A facet surfaces forms GaAs thin films with homogeneous film thickness. This results from the competition between preferential adsorption on the (2 1 1)A and migration toward (0 0 1)-(2 × 4)β2. Similar results are

Table 1
Ga adsorption energy difference on the (n 1 1)A surfaces relative to that on the (0 0 1)-(2 × 4)β2 top surface, and Ga migration energy difference at boundary between (0 0 1)-(2 × 4)β2 top and (n 1 1)A facet surfaces

Surface	Adsorption energy difference [eV]	Migration energy difference at boundary [eV]
(2 1 1)A	0.89	−0.35
(3 1 1)A	1.98	1.56
(4 1 1)A	0.00	0.80

A negative value of the migration energy difference at boundary indicates the difficulty of Ga migration from (0 0 1)-(2 × 4)β2 toward (n 1 1)A. While a positive value indicates the ease of Ga migration from (0 0 1)-(2 × 4)β2 toward (n 1 1)A.

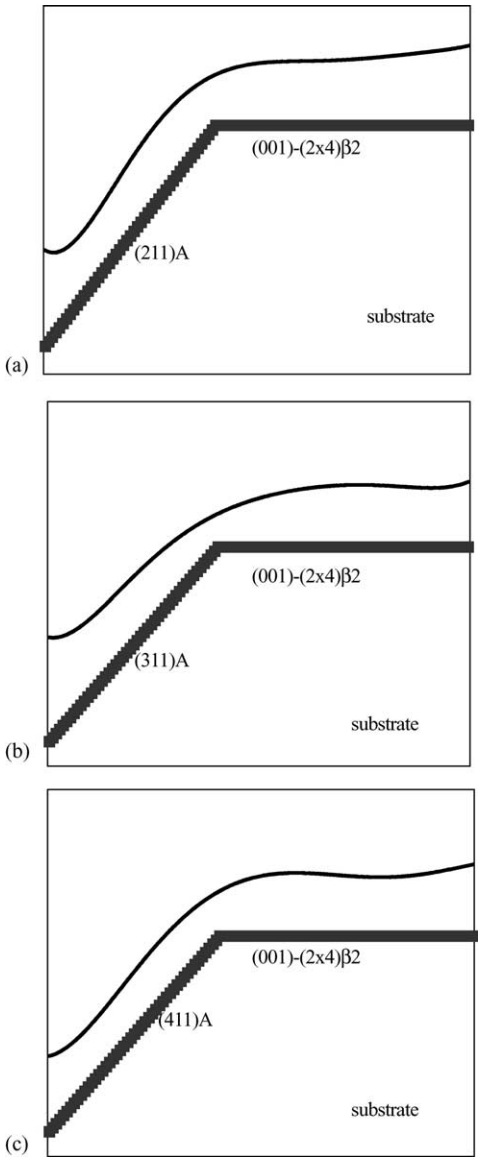

Fig. 5. Calculated surface profile of GaAs thin films on the non-planar surfaces consisting of (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces using the rate equation. The surface profile of GaAs thin films such as (a) (2 1 1)A, (b) (3 1 1)A, (c) (4 1 1)A. Thick solid lines are the substrate with (*n* 1 1)A, and solid line is the calculated surface profile.

found in the surface profile on non-planar surface consisting of the (0 0 1)-(2 × 4)β2 top and (4 1 1)A facet surfaces. These results are consistent with experimental results [2,3], where the non-planar surface with (3 1 1)A facet surface forms smoother convex curved shape than the other non-planar surface with (*n* 1 1)A (*n* = 2, 4 and 5). Thus, according to these results, Ga adatom behavior plays an important for the growth mechanism on non-planar surfaces consisting of the (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces.

Conclusion

We have theoretically investigated the behavior of Ga and As adatoms on the non-planar surfaces consisting of GaAs(0 0 1)-(2 × 4)β2 top and GaAs(*n* 1 1)A (*n* = 2, 3 and 4) facet surfaces using empirical interatomic potentials with the aid of ab initio calculations. The calculated results imply that Ga adsorption energies strongly depend on the surface orientation, whereas As adsorption energies keep almost constant. In particular, Ga adatom on (3 1 1)A is the most stable amongst all the other (*n* 1 1)A and (0 0 1)-(2 × 4)β2 surfaces because the strain around the Ga adatom is the smallest in the systems. Furthermore, we roughly simulate resultant surface profile of GaAs thin films on non-planar surfaces consisting of the (0 0 1)-(2 × 4)β2 top and (*n* 1 1)A facet surfaces based on the rate equation. The simulated results reveal that the non-planar surface consisting of (0 0 1)-(2 × 4)β2 top and (3 1 1)A facet surfaces forms the unique surface profile because of preferential Ga adsorption on the (3 1 1)A and Ga migration from the (0 0 1)-(2 × 4)β2 toward (3 1 1)A. Consequently, Ga adatoms play an important role for the unique surface formation of GaAs thin films on the non-planar surface consisting of GaAs(0 0 1)-(2 × 4)β2 top and (3 1 1)A facet surfaces. These theoretical predictions are consistent with previously reported experimental results. Although these results should be checked from various viewpoints including ab initio calculations in detail, the hybrid approach using the simple energy formula and rate equation is feasible for predicting resultant surface profile for the nanostructure formation.

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