An ab initio-based approach to phase diagram calculations for GaAs(001) surfaces

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Surface phase diagram of GaAs(001) is systematically investigated by using our ab initio-based approach. The phase diagrams of the c(4×4) and (2×4) surfaces are clarified as functions of temperature and As pressure. The calculated results reveal that c(4×4)β and (2×4)γ surfaces are strongly affected by As-molecular species such as As₂ and As₄. The c(4×4)β surface consisting of As dimers disappears under As₄ because of small desorption energy of As dimers. The (2×4)γ surface appears only at high As pressure and low temperatures buried in the stable region of c(4×4)β under As₄. These results are compared with experimental results to check the versatility of our approach to the surface phase diagram calculations. [DOI: 10.1380/ejssnt.2005.488]

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I. INTRODUCTION

GaAs(001) surfaces have attracted much attention in general technological fields as well as in the field of surface science because these surfaces are the most popular for epitaxial growth. Many studies, both experimental and theoretical, have been conducted to investigate the structural and physical properties of GaAs(001) surfaces. It is also well known that these surfaces reveal a large variety of surface superstructures depending on the substrate temperature and As pressure. In particular, GaAs(001)-c(4×4) and - (2×4) surfaces have been intensively studied because of their technological importance for thin film fabrications and scientific interest in surface phase transition between c(4×4) and (2×4) when the substrate temperature and As pressure are changed. Recently, Ohtake et al. proposed the new structure model of the c(4×4)α surface with three Ga-As dimers per c(4×4) unit cell in addition to the conventional c(4×4)β surface with three As dimers [1, 2]. Furthermore, They also clarified that the c(4×4)β surface is limited under As₄ [3]. These findings inspire us to revisit the stability of GaAs(001) surfaces from theoretical viewpoints.

In our previous studies, we systematically investigated the surface structures of c(4×4) under As₂ and phase transition from c(4×4) to (2×4)/β using our ab initio-based approach [4, 5]. Although our investigations reveal the stability of the c(4×4) under As₂ and the phase transition between c(4×4) and (2×4)/β surfaces, phase stability among various (2×4) surfaces such as α, β, and γ is still unclear as functions of As pressure and temperature. Furthermore, clarifying the dependence of phase stability on As₄ pressure is also crucial for extending our approach to realistic predictions of surface phase diagrams. In this study, our ab initio-based approach is applied to investigate the stability of the GaAs(001)-c(4×4) and - (2×4) surfaces depending on As species such as As₂ and As₄. The phase boundaries among various c(4×4) and (2×4) surfaces are determined by clarifying adsorption-desorption behavior of surface dimers and atoms under As₂ and As₄. The calculated results are compared with experimental results to check the versatility of our approach to the surface phase diagram calculations.

II. COMPUTATIONAL

Figure 1 shows various GaAs(001) surface structures including c(4×4)α, c(4×4)β, (2×4)α, (2×4)α-II, (2×4)β-II, (2×4)β-II and (2×4)γ considered in this study. Two kinds of (2×4)α and three kinds of (2×4)β are classified by the number of surface dimer constituents such as As-As and Ga-As. The change in stable structure of the c(4×4) and (2×4) surfaces is clarified by considering adsorption or desorption of surface dimers or surface atoms as functions of As pressure and temperature. For example, Ga adsorption on the (2×4)/β surface changes its structure from the (2×4)/β to the (2×4)α, while Ga desorption from the (2×4)α surface produces the (2×4)/β.

The adsorption-desorption behavior can be described by comparing the free energy of ideal gas per one particle (chemical potential) μ with the adsorption energy E_{ad}. The chemical potential μ_Ga of the ideal gas such as Ga atom is given by the following equations [6, 7].

$$\mu_{Ga} = -k_B T \ln \left( \frac{k_B T}{p_Ga} \times g \times \zeta_{trans} \right).$$

Here, k_B is Boltzmann’s constant, T the gas temperature, g the degree of degeneracy of electron energy level, p the beam equivalent pressure (BEP) of the particle, m

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the mass of one particle, \( h \) Planck’s constant, \( \zeta_{\text{trans}} \) is the partition function for the translational motion. The chemical potential of As\(_2\) in the vapor phase \( \mu_{\text{As}_2} \) is given by:

\[
\mu_{\text{As}_2} = -k_B T \ln \left[ \frac{k_B T}{\rho_{\text{As}_2}} \times g \times \zeta_{\text{trans}} \times \zeta_{\text{rot}} \times \zeta_{\text{vibr}} \right],
\]

where \( \zeta_{\text{rot}} \) and \( \zeta_{\text{vibr}} \) are the partition functions for the rotational motion and the vibrational motion, respectively [8]. Similar equation with different expressions of the partition functions \( \zeta_{\text{rot}} \) and \( \zeta_{\text{vibr}} \) from those for As\(_2\) is used for the chemical potential \( \mu_{\text{As}_4} \) of As\(_4\) in the vapor phase. Moreover, \( \mu_{\text{Ga-As}} \) for Ga-As dimer is approximately estimated by the summation of \( \mu_{\text{Ga}} \) and \( \mu_{\text{As}_2/2} \) under As\(_2\) or \( \mu_{\text{As}_4/4} \) under As\(_4\).

The adsorption energy \( E_{\text{ad}} \) is obtained by total energy for the solid phase and chemical potential in the vapor phase. In the total energy calculations for various GaAs(001) surfaces shown in Fig. 1, we used the first-principles pseudopotential method based on the local-density functional formalism [9] and Kleinman-Bylander’s separable pseudopotentials [10]. The wave functions are expanded by the plane-wave basis set corresponding to the kinetic energy cut-off of 7.29 Ry. We use 5-k points sampling in the Brillouin zone integration. The conventional repeated slab geometry is employed to simulate the surface. The unit super cell consists of six atomic layers of GaAs, an atomic layer of fictitious H atoms and a vacuum region equivalent to about 15 atomic layers in thickness. Details of ab initio calculations have been set in previous studies [4–8, 11].

Using these chemical potentials \( \mu \) and adsorption energies \( E_{\text{ad}} \), the adsorption-desorption behavior of the surface dimers and atoms on the GaAs(001) surfaces is clarified as functions of temperature and As pressure. Relative stability between \( c(4 \times 4) \) surfaces and between \( (2 \times 4) \) surfaces is determined by comparing \( \mu \) with \( E_{\text{ad}} \) for various dimers or atoms. That is, net adsorption proceeds when \( E_{\text{ad}} \) is less than \( \mu \), whereas net desorption occurs when \( \mu \) is less than \( E_{\text{ad}} \). Based on these results, we obtain surface phase diagrams of the \( c(4 \times 4) \) and \( (2 \times 4) \) surfaces. Furthermore, Metropolis Monte Carlo method is applied to determine the stability of Ga-As dimer arrangements on the \( c(4 \times 4) \) and \( (2 \times 4) \) surfaces using the energy difference, obtained by our ab initio calculations, between ordered arrangements as shown in Fig. 1 and disordered arrangements consisting of two Ga-As dimers and one As-Ga (Ga and As are substituted by each other). We found that the ratio of disordered dimer arrangements is only \( \sim 10\% \) even at 700 K. This is because the energy of disordered dimer arrangements is higher than ordered dimer arrangements by 0.1-0.3 eV per \( c(4 \times 4) \) or \( (2 \times 4) \) surface unit cell. These results are consistent with experimental results obtained by Ohtake, et al., where STM observations for the \( c(4 \times 4) \) surfaces reveal that the disordered dimer arrangements appear only up to \( \sim 18\% \) at \( \sim 750 \) K [3]. Therefore, we employ the surface structures without disordered dimer arrangements as stable \( c(4 \times 4) \) or \( (2 \times 4) \) surfaces considered in this study.

III. RESULTS AND DISCUSSION

Figure 2 displays the calculated phase diagram of the GaAs(001)-\( c(4 \times 4) \) surfaces with different dimer constituents as functions of temperature and As pressure (As\(_2\) in Fig. 2(a) and As\(_4\) in Fig. 2(b)). Figure 2(b) implies that the \( c(4 \times 4) \) surface with As dimers is stable at low temperatures less than \( \sim 400 \) K whereas the \( c(4 \times 4) \) surface with Ga-As dimers is stabilized at high temperatures in the range of \( \sim 400-700 \) K under As\(_4\). This reflects the desorption energy of As dimer (1.78 eV) is smaller than that of Ga-As dimer (4.31 eV). In Fig. 2(b), on the other hand, the \( c(4 \times 4) \) surface does not appear at low temperatures under As\(_4\). This is because the desorption energy of As dimer becomes almost zero (0.12 eV) in contrast with still large value of Ga-As dimer (3.48 eV) under As\(_4\). These results are qualitatively consistent with experimental results under both As\(_2\) and As\(_4\) fluxes, where the \( c(4 \times 4) \) is limited under As\(_4\) [3]. In Figs. 2(a) and 2(b), it should be noted that shaded area beyond the phase boundary of the \( c(4 \times 4) \) surface denotes the stable region of the \( (2 \times 4) \) surfaces. Our previous study suggests that the \( c(4 \times 4) \) changes its structure to the \( (2 \times 4) \) consisting of Ga-As dimers such as \( (2 \times 4) \beta 2-II \) beyond the phase boundary [5].

Figure 3 shows the calculated phase diagram of
GaAs(001)-(2 × 4) surfaces with different dimer constituents as functions of temperature and As pressure (As$_2$ in Fig. 3(a) and As$_4$ in Fig. 3(b)). The stable region of the c(4 × 4) surface is also shown as shaded area in these figures. The calculated phase diagram shown in Fig. 3(a) reveal that GaAs (001) surface changes its structure from (2 × 4)$_\gamma$ to (2 × 4)$_\alpha$ via (2 × 4)$_\beta$-II, (2 × 4)$_\beta$ and (2 × 4)$_\alpha$-II as temperature increases at As$_2$ pressure of $10^{-7}$ Torr. Moreover, the surface changes from (2 × 4)$_\beta$-II to (2 × 4)$_\gamma$ via (2 × 4)$_\beta$ as As pressure decreases at temperature of 750 K. This tendency is reasonable, since increasing temperature and decreasing As pressure destabilize As dimers on the GaAs(001) surfaces including the c(4 × 4) as shown in Fig. 2. Similar results are found at As$_4$ pressure of $10^{-7}$ Torr in Fig. 3(b). Furthermore, the phase boundary between (2 × 4)$_\alpha$ and (2 × 4)$_\beta$ agree well with experimental results under As$_4$ fluxes [12]. Here the phase boundary of (2 × 4)$_\alpha$ is independent of As pressure, since the boundary is determined by adsorption-desorption behavior of Ga atoms independent of As pressure in our formalism as described in Eq. (1).

Although some aspects of the GaAs(001) surface structure are successfully reproduced by our phase diagram calculations, our results does not sufficiently predict the stable region of the (2 × 4)$_\gamma$ in the As pressure range of $10^{-7}$-$10^{-6}$ Torr. The (2 × 4)$_\gamma$ surface appears only at higher As$_2$ pressure beyond $10^{-5}$ Torr and is buried in the c(4 × 4) stable region under As$_4$ as shown in Figs. 3 (a) and 3(b), respectively. Shrinkage of the (2 × 4)$_\gamma$ stable region under As$_4$ is similar to that in the results for...
the \(c(4 \times 4)\), where excess As dimers adsorbing on the GaAs(001) surfaces tend to be destabilized because of the stability of tetrahedral \(As_4\) molecule in the vapor phase. The discrepancy between experimental and theoretical results for the \((2 \times 4)\) surface should be carefully investigated by considering the stable structure of the \((2 \times 4)\) surface. We are currently in the process of clarifying the stability of the \((2 \times 4)\) surface including the mixed phase of the \(c(4 \times 4)\) and \((2 \times 4)\) surfaces observed by STM [13].

IV. CONCLUSIONS

The stability of various GaAs(001)-c\((4 \times 4)\) and -(2\( \times 4)\) surfaces has been systematically investigated by using our ab initio-based approach. The phase diagrams of the \(c(4 \times 4)\) and \((2 \times 4)\) surfaces have been successfully obtained as functions of temperature and As pressure. The calculated results reveal that \(c(4 \times 4)\beta\) and \((2 \times 4)\gamma\) surfaces with excess As atoms are strongly affected by As molecular species such as \(As_2\) and \(As_4\). The \(c(4 \times 4)\beta\) surface consisting of As dimers disappears under \(As_4\) because of small desorption energy of As dimers. This is qualitatively consistent with experimental results. Furthermore, the phase boundary between \((2 \times 4)\alpha\) and \((2 \times 4)\beta\) surfaces also agree well with experimental results. The \((2 \times 4)\gamma\) surface, however, appears only at high As pressure and low temperatures buried in the stable region of \((c(4 \times 4)\) under \(As_4\). This contradicts the experimental results. Although further studies particularly for the \((2 \times 4)\gamma\) surface is necessary, this approach using chemical potential with ab initio calculations are feasible for realistic surface diagram calculations for compound semiconductors as functions of temperature and BEPs.

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