Ab initio-based approach to initial growth processes on GaAs(111)*B*-(2×2) surfaces: Self-surfactant effect of Ga adatoms revisited

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The initial growth processes on GaAs(111)*B*-(2×2) surfaces are investigated using our *ab initio*-based approach, in which desorption behavior of As atoms is described by comparing the calculated desorption energy obtained by total-energy electronic-structure calculations with the chemical potential estimated by quantum statistical mechanics. We find that the As-trimer desorption on the (2×2) surfaces with Ga adatoms occurs beyond 400–700 K while the desorption without Ga adatom does beyond 800–1000 K. The promotion of the As-trimer desorption triggered by Ga adatoms called "self-surfactant effect" is also found to be interpreted in terms of the band-energy stabilization.

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GaAs(111)*B* surfaces have attracted much attention in general technological fields as well as in the field of surface science because these surfaces are one of the most popular for epitaxial growth. Furthermore, these surfaces are recently receiving considerable attention due to their advantages in fabricating nanostructures such as nanodots and nanowires: The growth of these nanostructures on GaAs(111)*B* is predominant.[1–5] As for the structural and physical properties of GaAs(111)*B* surface, many experimental and theoretical studies[6–16] have been devoted and found that GaAs(111)*B* surfaces take various surface reconstructions such as (2×2) and $(\sqrt{19}\times\sqrt{19})R23.4°$ depending on temperature and As pressure. The scanning tunneling microscopy (STM) observations have shown that the change from the $(\sqrt{19}\times\sqrt{19})R23.4°$ to the (2×2) reconstruction occurs below 560 °C in molecular beam epitaxy (MBE).[15] From theoretical viewpoints, surface energy calculations for various surface structures have revealed that the stable surface reconstruction depends on the chemical potential of As and the (2×2) surface with As trimer is stable over a wide range of As chemical potential.[8,11] Therefore, these results indicate that the (2×2) surface with As trimer appears in the growth condition of the MBE (~500 °C).[12,15] Despite these findings, atom-scale understanding of adsorption-desorption behavior of Ga and As atoms on this surface is far less examined.

In our previous study, we have successfully clarified that preadsorbed Ga atoms act as "self-surfactant atoms" and induce rearrangement of As atoms during GaAs epitaxial growth on GaAs(001) surfaces.[17] Furthermore, the influence of As_2 pressure on the growth mechanism of GaAs on GaAs(001)-$c(4\times4)$ surface has been successfully clarified by comparing the calculated adsorption energy and the chemical potential of Ga atom estimated by quantum statistical mechanics.[18,19] From these results, one can infer that Ga adatoms also act as self-surfactant atoms on GaAs(111)*B* surfaces and the growth processes can be described by means of temperature and beam equivalent pressure (BEP) of As molecular species. In this Brief Report, we apply our *ab initio*-based approach to investigate the growth processes on GaAs(111)*B*-(2×2) surfaces, such as adsorption-desorption behavior of Ga and As atoms. As shown in Table I, many experimental results imply that the (2×2) surface with As trimer appears in a certain temperature range (720–830 K),[8–10,12–15] although the MBE growth with low As_4/Ga flux ratio has shown that the (2×2) surface appears in a very narrow temperature range (770–820 K).[16] We here consider GaAs(111)*B*-(2×2) surfaces as a representative of surface reconstructions, since the growth temperature in the MBE corresponds to the temperature range of the (2×2) reconstruction. Surface phase diagrams both for As_2 and As_4 molecules as As molecular species are calculated by comparing the calculated desorption energy with the estimated chemical potential. The As-trimer desorption, which is necessary to maintain the layer-by-layer growth, is discussed based on the calculated surface diagrams. Self-surfactant effect of Ga adatoms is also examined based on the As-trimer desorption energy, which is interpreted in terms of the band-energy stabilization.

Figure 1(a) shows the (2×2) surface with As trimer considered in this Brief Report. Using this surface, the desorption behavior of As trimer can be described by comparing the chemical potential of As trimer μ_{trimer} with that of As molecular species in vapor phase μ_{gas}.[18,19] μ_{trimer} is obtained using the desorption energy of As trimer E_{de} ($\mu_{\text{trimer}}=-E_{\text{de}}$),

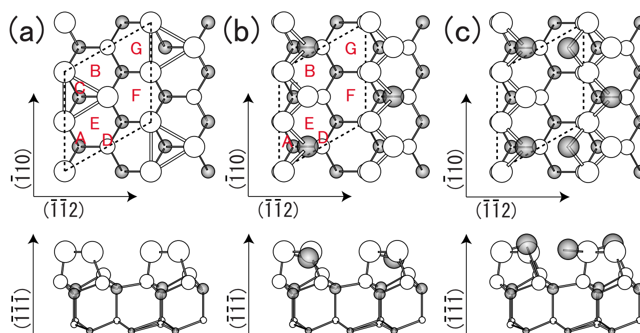

FIG. 1. (Color online) Top and side views of GaAs(111)*B*-(2×2) surfaces (a) without Ga adatom, (b) with one Ga adatom, and (c) with two Ga adatoms. Filled and empty circles denote Ga and As atoms, respectively. Adsorption sites considered in this Brief Report are indicated by A, B, C, D, E, F, and G. A (2×2) unit cell is represented by a rhombus with dashed lines. Ga adatoms and As atoms constituting As trimer are represented by large circles.

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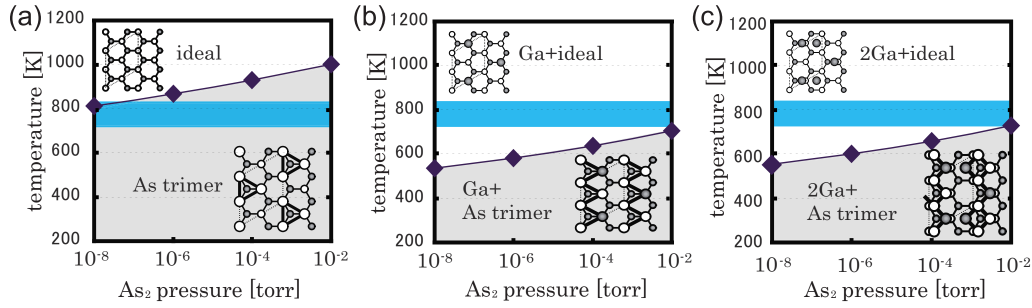

FIG. 2. (Color online) Calculated surface phase diagrams of GaAs(111)B-(2×2) surfaces (a) without Ga adatom, (b) with one Ga adatom, and (c) with two Ga adatom as functions of temperature and As_2 pressure. Gray (shaded) area denotes the stable region of As trimer. Cyanic (darkly shaded) area denotes the temperature range of GaAs(111)B-(2×2) surface (Refs. 8, 9, 12, and 15). Atomic configurations represented by filled (Ga) and empty (As) circles are also shown.

which is calculated by the energy difference between the stable structures with and without As trimer defined as

$$E_{\mathrm{de}} = E^{2\times 2}_{\mathrm{As}_3} - E^{2\times 2} - 3E_{\mathrm{gas}}, \quad (1)$$

where $E^{2\times 2}_{\mathrm{As}_3}$, $E^{2\times 2}$, and E_{gas} are the total energies of the (2×2) surface with As trimer, the (2×2) surface without As trimer, and As molecular species (per As atom) such as As_2 and As_4, respectively. These values can be obtained by the total-energy calculations within density-functional theory. μ_{gas} is calculated by the following procedure: For instance, the chemical potential of As_2 molecule in vapor phase μ_{As_2} is given by the equation,[20]

$$\mu_{\mathrm{As}_2} = -k_B T \ln\left(\frac{k_B T}{p} \times g \times \zeta_{\mathrm{trans}} \times \zeta_{\mathrm{rot}} \times \zeta_{\mathrm{vib}}\right), \quad (2)$$

where k_B is the Boltzmann constant, T is the gas temperature, g is the degree of degeneracy of electron energy level, and p is the BEP of the particle. ζ_{trans}, ζ_{rot}, and ζ_{vib} are the partition functions for translational, rotational, and vibrational motions, respectively. Similar equation with different expressions of the partition functions ζ_{rot} and ζ_{vib} from those for As_2 are used for the chemical potential of As_4 molecule μ_{As4}. Using μ_{trimer} and μ_{As2} (μ_{As4}), the adsorption and desorption behavior of As trimer on the GaAs(111)B-(2×2) surfaces under As_2 (As_4) are obtained as functions of temperature and As pressure, i.e., adsorption of As trimer occurs when μ_{trimer} is lower than $\frac{3}{2}\mu_{\mathrm{As}_2}$ ($\frac{3}{4}\mu_{\mathrm{As}_4}$), whereas desorption occurs when $\frac{3}{2}\mu_{\mathrm{As}_2}$ ($\frac{3}{4}\mu_{\mathrm{As}_4}$) is lower than μ_{trimer} under As_2 (As_4) flux. Surface phase diagrams of GaAs(111)B-(2×2) surfaces are then obtained based on these comparisons.[21]

The total-energy calculations are performed within the generalized gradient approximation (GGA) (Ref. 22) and norm-conserving pseudopotentials.[23] For Ga atoms, 3d electrons are treated by using partial core correction.[24] The conjugate-gradient minimization technique is used for both the electronic-structure calculation and the geometry optimization.[25] The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 12.25 Ry. We take the (2×2) model with a slab geometry of eight atomic layers with artificial H atoms[26] and a vacuum region equivalent to nine atomic layer thickness. 9-k points are employed to sample the irreducible Brillouin zone for the (2×2) unit cell. In order to investigate effects of Ga adatoms on the As-trimer desorption, we consider three types of desorptions: the As-trimer desorptions without Ga adatom, with one Ga adatom, and with two Ga adatoms. We put one and two Ga adatoms on various adsorption sites of the GaAs(111)B-(2×2) surface shown in Fig. 1(a) and we determine the stable adsorption sites for the (2×2) surfaces with one and two Ga adatoms, respectively.

Figure 1(b) depicts the stable structure of the (2×2) surface with one Ga adatom. This structure is obtained when the Ga adatom is located at A site in Fig. 1(a). Due to the relaxation, the Ga adatom moves toward D site and two Ga-As bonds are formed between the Ga adatom and top As atoms, each of which constitutes each As trimer. In addition, another Ga-As bond is formed between the Ga adatom and the substrate As atom located at D site. Since the energy of this structure is more than 0.11 eV lower than those of the other symmetrically inequivalent adsorption sites, the formation of three Ga-As bonds stabilizes the Ga adatoms. Figure 1(c) shows the stable structure of the (2×2) surface with two Ga adatoms. Similar to the surface with one Ga adatom, one of the adsorbed positions is located between A and D sites in Fig. 1(b). The other adsorbed position is located at G site shown in Fig. 1(b). In this case, there is no substrate As atom, which can form a Ga-As bond with the additional Ga adatom. The additional Ga adatom forms two Ga-As bonds between top As atoms constituting the neighboring As trimer. Since the Ga-As bond is basically the most energetically favorable configuration among Ga-Ga, Ga-As, and As-As bonds, the stable positions of Ga adatoms can be understood by stable Ga-As bond formation.

Using these stable structures, the phase diagrams of the (2×2) surfaces under As_2 flux are calculated as shown in Fig. 2. Figure 2(a) indicates that the (2×2) surface with As trimer is stable at temperature less than ~800 K, whereas that without As trimer is stabilized beyond ~800 K. In contrast, the (2×2) surface without As trimer is stable beyond ~560 K for Ga adsorbed surfaces [Figs. 2(b) and 2(c)]. The low transition temperatures from the (2×2) surfaces with As trimer to those without As trimer in the Ga adsorbed cases suggest that the As-trimer desorption is promoted by Ga adatoms. This is because the desorption energy of As trimer with Ga adatoms (3.6–3.8 eV) is much lower than that without Ga adatom (5.4 eV). The decrease in the desorption energy

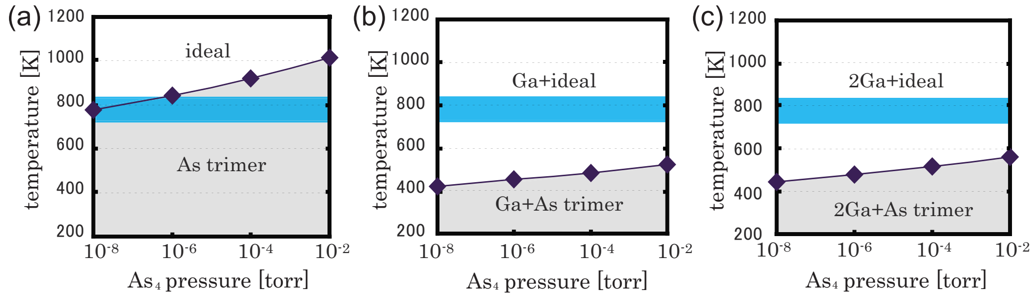

FIG. 3. (Color online) Calculated surface phase diagrams of GaAs(111)*B*-(2×2) surfaces (a) without Ga adatom, (b) with one Ga adatom, and (c) with two Ga adatom as functions of temperature and As_4 pressure. The same notation as in Fig. 2.

clearly manifests self-surfactant effect where Ga adatoms induce As rearrangement during GaAs epitaxial growth, as clarified in GaAs(001) (Ref. 14) and GaAs(111)*A* surfaces.[27] Moreover, it should be noted that the difference in the transition temperature for the As-trimer desorption between the (2×2) surfaces with one and two Ga adatoms is less than 20 K. This reflects the small energy difference in E_{de} (within 0.2 eV), implying that the growth can be promoted even if one Ga atom is adsorbed on the (2×2) surface unit.

Figure 3 displays the calculated phase diagrams for the (2×2) surfaces under As_4. As shown in Figs. 3(b) and 3(c), the desorption temperatures for As trimer drastically decrease due to Ga adsorption even if we consider As_4 molecule as As molecular species. We note that the transition temperatures for the As-trimer desorption in the (2×2) surfaces with Ga adatoms under As_4 flux are shifted toward low temperature by ~100 K compared to those under As_2 flux, while the temperatures without Ga adatom under As_4 are similar to those under As_2. These features reflect that the gas-phase chemical potential is mainly dominated by translational motion at high temperature. However at low temperature the contribution of rotational and vibrational motions is prominent. The differences in ζ_{rot} and ζ_{vib} between As_2 and As_4 lead to low μ_{As_4} compared to μ_{As_2} at low temperature, while the same value in ζ_{trans} results in similar values in μ_{As_2} and μ_{As_4} at high temperature.

The stable region of As trimer shown in Figs. 2(a) and 3(a) is less than 850 K at $p=2.0\times10^{-6}$ Torr, consistent with the experimentally reported temperature range exhibiting the (2×2) surface (720–830 K) shown in Table I.[8–10,12–15] However, the figures also indicate that the As-trimer desorption, which is necessary to maintain the layer-by-layer growth, does not occur around the growth temperature in the MBE (~750 K).[12–15] In contrast, the As-trimer desorption becomes prominent at temperature higher than ~600 (~500) K under As_2 (As_4) flux at $p=2.0\times10^{-6}$ Torr in Figs. 2(b) and 2(c) [Figs. 3(b) and 3(c)], reasonably consistent with the growth temperature in the MBE. The findings obtained from the surface phase diagrams thus imply that in both As_2 and As_4 cases the As-trimer desorption is promoted only when Ga atoms are adsorbed on GaAs(111)*B*-2×2 surfaces, and the layer-by-layer growth is dominated by the adsorption of Ga atoms.

In order to clarify the physical mechanism for the self-surfactant effect of Ga adatoms, we now focus on the band-energy stabilization. Basically, the stable GaAs surfaces satisfy the electron counting model in which Ga and As dangling bonds are empty and fully occupied, respectively.[28] Since the band-energy stabilization originates from charge transfer from Ga dangling bonds to As dangling bonds, the deviation of the electron number given by the electron counting model Z_{dev} is one of the criteria for the band-energy stabilization.

Figure 4 shows E_{de} per As atom in Eq. (1) as a function of the change in Z_{dev} before and after the As-trimer desorption, ΔZ_{dev}, for GaAs(111)*B*-(2×2) and GaAs(001)-*c*(4×4) (Ref. 17) surfaces. In the case of the (2×2) surface without Ga adatom, Z_{dev} is zero and three before and after the As-trimer desorption, respectively. The ΔZ_{dev} without Ga adatom is thus +3.0, indicating that large band-energy destabilization occurs on the ideal GaAs(111) surface. In contrast, ΔZ_{dev} becomes small for Ga adsorbed surfaces [$\Delta Z_{dev}=-1.0$ and -3.0 in the (2×2) surfaces with one Ga adatom and two Ga adatoms, respectively[29]]. Therefore, the band-energy stabilization is expected to be remarkably induced in Ga adsorbed surfaces. Furthermore, the figure implies that the desorption energy increases as ΔZ_{dev} increases and the energy dependence on Z_{dev} in GaAs(111)*B*-(2×2) surfaces agrees well with that in GaAs(001)-*c*(4×4) surfaces. The characteristics in E_{de} thus support that the self-surfactant effect of Ga adatoms can be universally interpreted by the

TABLE I. Experimental data for surface reconstructions, temperature range, and available As/Ga flux ratio on GaAs(111)*B* surfaces. References are also shown. Only the ratios, which we were able to find out, are shown.

Reconstruction	Temperature (K)	As/Ga flux ratio	Ref.
(2×2)	~770		8
(2×2)	~830		9
(2×2)	830	8	10
(2×2)	770		12
(2×2)	830	15	13
(2×2)	750		14
(2×2)	720	~50	15
(1×1)	~790	0.8	16
($\sqrt{19}\times\sqrt{19}$)	770~		8
($\sqrt{19}\times\sqrt{19}$)	830~		9
($\sqrt{19}\times\sqrt{19}$)	830~	0.8	16

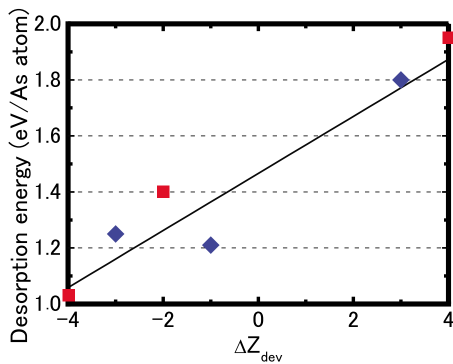

FIG. 4. (Color online) Calculated desorption energy per As atom as a function of the change in the deviation of the electron numbers given by the electron counting model before and after As desorption ΔZ_{dev}. Squares and diamonds represent the calculated desorption energies in GaAs(001)-$c(4\times4)$ (Ref. 17) and GaAs(111)B-(2×2) surfaces, respectively. The energy of an As_2 molecule is used to calculate E_{de} in Eq. (1).

band-energy stabilization, suggesting that the crystal growth on GaAs(111)B-(2×2) surfaces proceeds in accordance with the electron counting model.

In summary, we found that preadsorbed Ga atoms act as self-surfactant atoms and control the excess As atoms on GaAs(111)B-(2×2) surfaces. The calculated surface phase diagrams clarified that the As-trimer desorption occurs under a growth condition of the MBE when Ga atoms are adsorbed on the (2×2) unit. These results imply that Ga adsorption crucially affects the initial growth of GaAs on GaAs(111)B-(2×2) surface, offering one of universal characteristics in semiconductor epitaxial growth processes.

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