An ab initio based approach to adsorption-desorption behavior of Si adatoms on GaAs(111)*A*-(2×2) surfaces

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The adsorption-desorption behavior of Si adatoms on GaAs(111)*A*-(2×2) surfaces is investigated using our *ab initio*-based approach, in which adsorption and desorption behavior of Si adatoms is described by comparing the calculated desorption energy obtained by total-energy electronic-structure calculations with the chemichal potential estimated by quantum statistical mechanics. We find that the Si adsorption at the Ga-vacancy site on the (2×2) surfaces with As adatoms occurs less than 1140-1590 K while the adsorption without As adatom does less than 630-900 K. The change in adsorption temperature of Si adatoms by As adatoms is due to self-surfactant effects of As adatoms: The promotion of the Si adsorption triggered by As adatoms is found to be interpreted in terms of the band-energy stabilization. Furthermore, the stable temperature range for Si adsorbed surfaces with As adatoms agrees with the experimental results. The obtained results provide a firm theoretical framework to clarify *n*-type doping processes during GaAs epitaxial growth.

Key words: GaAs(111)*A*; Si doping; As adatom; Self surfactant effect; Electron counting; Surface phase diagram

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1. Introduction

Silicon is one of the most important and interesting dopants in GaAs. Regarding its incorporation processes, several experimental studies have been carried out. [1-4] In particular, Si-doped GaAs layers grown on GaAs(111)*A* surfaces by molecular beam epitaxy (MBE) exhibit a very interesting property. The grown layer becomes *p*-type when it is grown under conventional MBE growth condition whereas the layer becomes *n*-type under extremely high As overpressure [5,6]. This phenomenon implies that the adsorption sites of Si adatoms on GaAs surfaces depend on the growth condition. Thus, investigations for Si incorporation on GaAs(111)*A* surfaces considering the growth condition is necessary to clarify the amphoteric nature of GaAs layers.

From theoretical viewpoints, Shiraishi et al. have investigated the adsorption behavior of Si adatoms on GaAs(001)-(2×4) surfaces, which are crucial to interpret resultant novel characteristics appearing in GaAs thin film growth. They revealed the coverage dependence of Si adsorption sites based on its adsorption energy. [7,8] As for the stable structure of Si adatoms on the GaAs(111)*A* surface, Taguchi *et al.* clarified the most stable adsorption site for a single Si adatom on a GaAs(111)*A* surface is a Ga lattice site [Ga-vacancy site] of the GaAs lattice.[7] Despite these findings, there have been very few theoretical studies on the Si incorporation process during thin film growth on GaAs(111)*A* surfaces taking account of the growth condition such as beam equivalent pressure (BEP) and temperature.

In our previous study, we have successfully clarified the adsorption-desorption behavior of adatom during GaAs epitaxial growth on GaAs(001) and GaAs(111)*B* surfaces using our *ab initio* based approach in which surface phase diagrams depending on temperature and pressure are described by comparing the calculated adsorption energy with chemical potential estimated by quantum statistical mechanics. [9-14] In this work, the adsorption-desorption behavior of Si adatoms on the Ga lattice site under the MBE condition is investigated on the basis of our *ab initio* approach. Since we here focus on the formation of *n*-type GaAs layer, we calculate surface phase diagrams of a Si adatom located at the Ga-lattice site on the GaAs(111)*A*-(2×2) surface. Effects of preadsorbed As atoms are also examined using the calculated surface phase diagrams.

2. Calculation method

Figure 1 shows the (2×2) surface models considered in this study. The stable reconstruction on GaAs(111)*A* surface is the (2×2) surface with Ga vacancy shown in Fig. 1(a) . To realize *n*-type GaAs layers, the Si adatom should be adsorbed at the Ga-vacancy site shown in Fig. 1(b). [15] Thus, the surface phase diagram for the adsorption of Si adatoms at the Ga-vacancy is calculated using Figs. 1(a) and 1(b). In the MBE conditions with extremely high As overpressure , excess As atoms can exist on the surface. Taking account of such As-rich condition, effects of As adatoms on the Si adsorption are examined by taking the (2×2) surfaces with As adatoms shown in Figs. 1(c) and 1(d). Their counterparts without Si adatom (not shown here) are also taken in order to obtain the surface phase diagrams.

Using these surfaces, the adsorption-desorption behavior of Si adatom can be described by comparing the chemical potential of Si atom μ_{Si} with that of Si molecular species in vapor phase μ_{gas}. [13, 14] Here, μ_{Si} is obtained using the adsorption energy of a Si adatom E_{de} (μ_{Si} = -E_{de}), which is calculated by the energy difference between the stable structures with and without Si adatom defined as

$$E_{de} = E_{Si}^{2\times2} - E^{2\times2} - E_{gas}\,, \tag{1}$$

where $E_{\mathrm{Si}}^{2\times2}$, $E^{2\times2}$, and E_{gas} are the total energies of the (2×2) surface with Si adatom, the (2×2) surface without Si adatoms, and Si molecular species per Si atom. These values can be obtained by the total-energy calculations within density functional theory. μ_{gas} is calculated by the following procedure: The chemical potential of Si atom in vapor phase μ_{gas} is given by the equation [16],

$$\mu_{gas} = \left[\frac{k_B T}{P} \times g\left(2\pi k_B T \big/ h^2\right)^{3/2}\right] \tag{2}$$

,

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 Si atom. Using μ_{gas} and μ_{Si}, the adsorption and desorption behavior of Si adatoms on the GaAs(111)*A*-(2×2) surfaces under Si flux is obtained as functions of temperature and Si pressure, i.e., the adsorption of Si adatom occurs when μ_{Si} is lower than μ_{gas}, whereas desorption occurs when μ_{gas} is lower than μ_{Si} under Si flux. Surface phase diagrams of GaAs(111)*A*-(2×2) surfaces are then obtained based on these comparisons.

The total-energy calculations are performed within the generalized gradient approximation (GGA) and norm-conserving pseudopotentials. [17, 18] For Ga atoms, *3d* electrons are treated by using partial core correction. [19] The conjugate-gradient minimization technique is used for both the electronic-structure calculation and the geometry optimization. [20] 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 [21] 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.

3. Results and discussion

Figure 2 shows the calculated phase diagram of the (2×2) surfaces as functions of temperature and Si pressure for the surface without taking account of excess As atoms. The phase boundary between the (2×2) surface with Ga vacancy [Fig. 1(a)] and that with Si adatom at the Ga-vacancy site [Fig. 1(b)] indicates the (2×2) surface with Si adatom is stable at temperature less than ~630 K, whereas that without Si adatom is stabilized beyond ~630 K. [22] This transition temperature for Si adsorption is, however, lower than the growth temperature (770 K~) [23] of *n*-type layer over a wide range of Si partial pressure, indicating that Si adatoms cannot be incorporated at the Ga-vacancy site on the GaAs(111)*A*-(2×2) surface.

Owing to the excess As atoms which correspond to high As overpressure of *n*-type growth conditions, the transition temperature drastically is changed. Figures 3(a) and 3(b) show the phase diagrams of the (2×2) surfaces with one and two As adatoms, respectively. The (2×2) surfaces with Si are stabilized below 1140 (1340) K when one (two) excess As atoms are adsorbed. This indicates that Si adatoms can be incorporated at the Ga-vacancy site for temperature below 1140 K. The change in the transition temperature is due to the lower adsorption energy of Si adatom for As adsorbed surfaces. The calculated adsorption energies for As adsorbed surfaces (-4.40 and -5.23 eV for Fig.1(c) and (d), respectively) are lower than that without As atoms (-2.37 eV), suggesting that the Si adsorption is promoted by As adatom called “self-surfactant effect”. Furthermore, the temperature range for the stabilization of Si-incorporated surfaces considering excess As atoms agrees with the growth temperature during the

MBE (770-870 K).

In order to clarify the physical mechanism for the self-surfactant effect of As adatoms, we now discuss the band energy stabilization using the electron counting (ECM) model. Basically, the stable Si/GaAs surfaces satisfy the electron counting model in which Si and Ga dangling bonds are empty and As dangling bonds are fully occupied. [24] This kind of charge transfer is caused by the difference in the energy level of sp^3 hybridized orbitals shown in Fig. 4. The energy level of As is located below the valence band, whereas that of Si (Ga) is located below (above) the conduction band. Since the band-energy stabilization is originates from charge transfer from Si and 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.

Table 1 shows Z_{dev} and the change in Z_{dev} before and after the Si adsorption, $\Delta Z_{dev,}$ for the (2×2) surfaces without As adatoms, with one As adatom, and two As adatoms, along with their adsorption energy E_{ad} for the Si incorporation. It is found that ΔZ_{dev} becomes small with increasing the number of As adatoms. This indicates that the stabilization caused by Si adsorption becomes predominant as the number of As adatom increases. Indeed, the change in ΔZ_{dev} reflects the calculated adsorption energy. In particular, the Si adsorbed (2×2) surface with two As adatoms satisfies the ECM. Therefore, the Si adsorbed (2×2) surface with two As adatoms is thought to be the most stable structure among possible surface structure during Si incorporation processes.

The calculated band structure shown in Fig. 5 supports the discussion based on Z_{dev} mentioned above. As shown in Figs. 5 (a) and 5 (b), the band structure of the Si adsorbed (2×2) surfaces without As adtoms and with one As adatom exhibits metallic character, where Si dangling bond states are partially occupied. The electronic structure of these surfaces is consistent with the values of Z_{dev}. In contrast, the band structure of the Si adsorbed (2×2) surface with two As adatoms is consistent with Z_{dev}=0, which exhibits semiconducting. We actually find that the electronic states due to Si dangling bonds, which are located near the conduction band, are empty.

4. Conclusion

We have investigated the adsorption-desorption behavior of Si adatoms on GaAs(111)*A*-(2×2) surfaces using our *ab initio*-based approach. The calculated surface

phase diagrams have revealed that the Si adsorption at the Ga-vacancy site on the (2×2) surfaces with As adatom occurs less than 1140-1590 K while the adsorption without As adatom does less than 630-900 K. The change in transition temperature for Si adsorption by As adatoms is due to self-surfactant effects of As adatoms: The promotion of the Si adsorption triggered by As adatoms is found to be interpreted in terms of the band-energy stabilization. The stable temperature range for Si adsorbed surfaces with As adatoms agrees with the experimental results, implying that our approach is feasible to investigate elemental processes during dopant incorporation on semiconductor surfaces.

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15) Our calculations for stable adsorption site clarify that the Si adatom located at the Ga-vacancy site is the most stable, although the energy of other adsorption site such the As site and hollow site is almost comparable to that of the Ga-vacancy site.
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22) Since the adsorption energies of Si adatom at the holllow and As sites are almost the same as that at the stable Ga-vacancy site, it is expected that the transition temperatures for these sites are almost the same as that at the Ga-vacancy site. Although the Si adsorption for various sites including As sites could occur at low temperatures, our calculations imply that the Si adsorption without self-surfactant effect cannot be realized under growth condition in the MBE.

23) The MBE growth on GaAs(111)*A* surfaces is performed at temperature less than ~890 K. See, D. A. Woolf, D.I. Westwood, R.H. Williams, Appl. Phys. Lett. 62 (1993) 1370.

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Table I: Deviation from the electron counting model Z and adsoption energy E_{ad} for the (2×2) surface without As adatoms shown in Fig. 1 (a), with one As adatom shown in Fig. 1 (c), and with two As adatoms shown in Fig. 1 (d).

	(2×2) surface without As adtoms	(2×2) surface with one As adatom	(2×2) surface with two As adatoms
Z_{dev} without Si atom	0	-1	+4
Z_{dev} with Si atom	+4	+1	0
ΔZ_{dev}	+4	0	-4
E_{ad} (eV)	-2.37	-4.40	-5.29

Figure Captions

Fig. 1: Top and side views of GaAs(111)*A*-(2×2) surfaces (a) without Si adatoms, (b) with a Si atom, (c) with a Si atom and one As adatom, (d) with a Si atom and two As adatoms.

Fig. 2: Calculated surface phase diagrams of GaAs(111)*A*-(2×2) surfaces as functions of temperature and Si pressure. The area below the phase boundary denotes the stable region of Si adatoms. Light blue area donotes the temperature range of n-type Si doped GaAs(111)*A*-(2×2) surface (Ref. 6). Atomic configurations represented by purple (Ga), gray (As), orange (Si).

Fig. 3: Calculated surface phase diagrams of GaAs(111)*A*-(2×2) surfaces with (a) one As adatom (b) two As adatoms as functions of temperature and Si pressure. The area below the phase boundary denotes the stable region of Si adatom. Light blue area donotes the temperature range of *n*-type Si doped GaAs(111)*A*-(2×2) surface (Refs. 6). Atomic configurations represented by purple (Ga), gray (As), orange (Si).

Fig. 4: Schematic energy diagram of Si adsorbed GaAs surface. Si (Ga) dangling bonds are located just below (above) the conduction band. As dangling bonds are located just below the valence band.

Fig. 5: Khon-Sham band structure of (2×2) sufaces, with a Si adatom (a) witout As adatoms and (b) with one As adatom (c) with two As adatoms in Figs. 1 (b), (c), (d), respectively. The origin of energy is set to the Fermi energy.

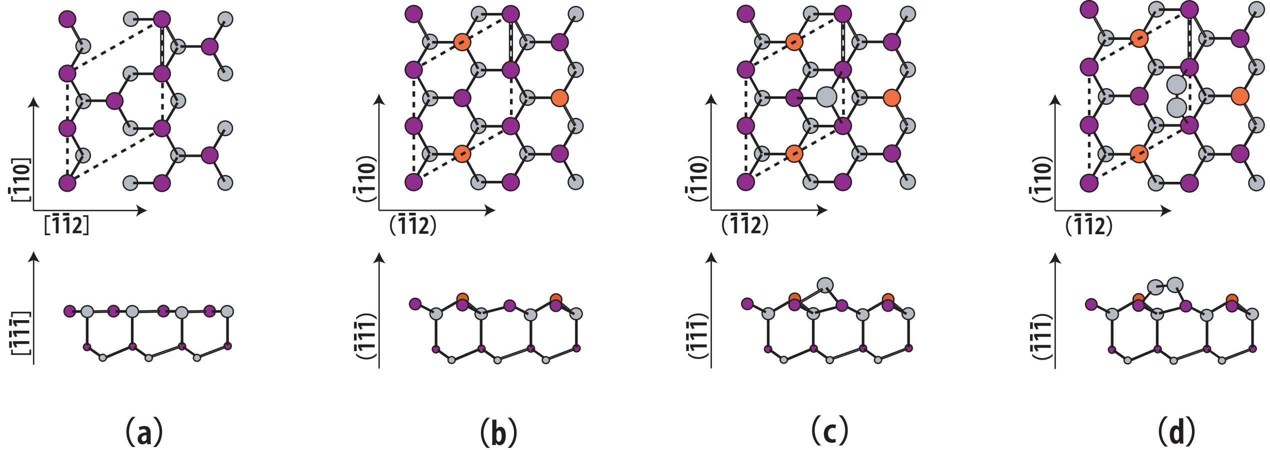


Figure 1

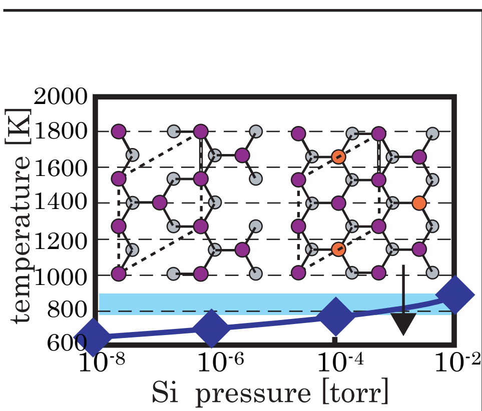
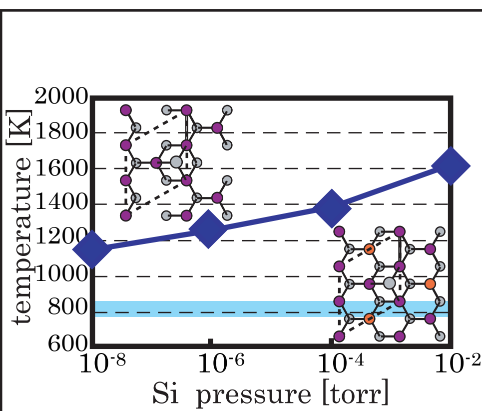
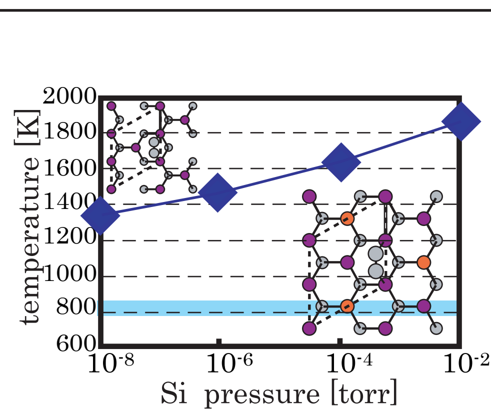


Figure 2



(a)



(b)

Figure 3

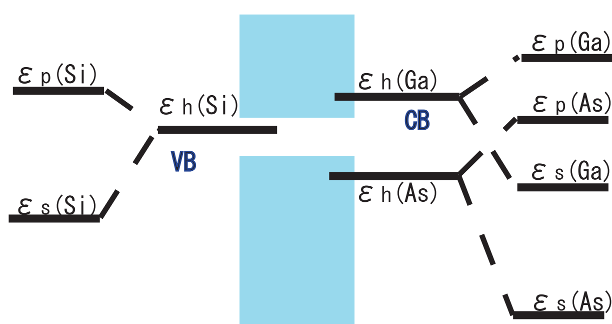
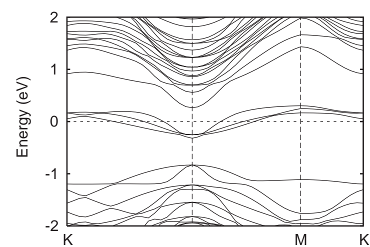
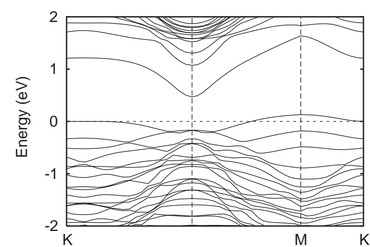


Figure 4



(a)



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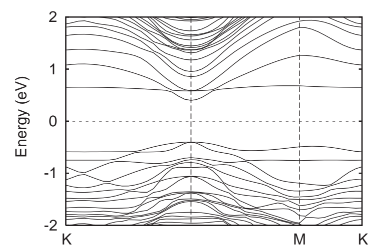

(c)

Figure 5