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A new theoretical approach to adsorption–desorption behavior of Ga on GaAs surfaces

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Abstract

We propose a new theoretical approach for studying adsorption–desorption behavior of atoms on semiconductor surfaces. The new theoretical approach based on the ab initio calculations incorporates the free energy of gas phase; therefore we can calculate how adsorption and desorption depends on growth temperature and beam equivalent pressure (BEP). The versatility of the new theoretical approach was confirmed by the calculation of Ga adsorption–desorption transition temperatures and transition BEPs on the GaAs(0 0 1)-$(4 \times 2)\beta 2$ Ga-rich surface. This new approach is feasible to predict how adsorption and desorption depend on the growth conditions.

Keywords: Adsorption kinetics; Semiconducting surfaces; Ab initio quantum chemical methods and calculations; Gallium arsenide

1. Introduction

Adsorption–desorption behavior on semiconductor surfaces is of fundamental importance in semiconductor science as well as semiconductor technologies. In particular, the behavior of component elements in III–V compound semiconductors must be known to understand surface and thin film growth-related phenomena such as change in surface reconstructions and growth as functions of temperature and III/V flux ratio. Daweritz and Hey [1] studied the relation of the reconstructed structures on GaAs(0 0 1) with growth conditions, i.e., growth temperature and III/V flux ratio, by the reflection high energy electron diffraction (RHEED) analysis, and clarified that the increase of Ga coverage due to the Ga adsorption induces the structural change from GaAs(0 0 1)-(2×4) to (4×2) via (1×1) and (3×1) structures. Suzuki et al. [2] and Fischer et al. [3] investigated the relation between growth rates and growth temperature (T) of GaAs under As-rich condition. They clarified that the growth rates is constant at $T < 910$ K, while the growth rate decreases with increasing the growth temperature at $T > 910$ K. This implies that the sticking

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coefficient of Ga is almost unity at $T < 910$ K because the growth rate is influenced only by the amount of desorbed Ga atoms during growth under As-rich conditions. These experimental results suggest that the adsorption–desorption behavior of Ga significantly influences on the structural change in surface reconstructions and growth mechanisms. Therefore, it is important for understanding the change in surface reconstructions and growth mechanisms to perform theoretical calculations for the adsorption–desorption behavior of Ga in atomic scale.

We have investigated the surface and growth-related phenomena such as structural and elemental growth processes on various GaAs surfaces using ab initio calculations [4,5] and electron counting Monte Carlo simulations [6]. These approaches, however, primarily address to structural stabilities of the ground state. Thus, they do not include effects from the growth temperature and beam equivalent pressure (BEP) on the structural stabilities during thin film growth. In the present paper, we propose a new theoretical approach based on the ab initio calculation that overcomes those shortcomings because it incorporates the free energy of the gas phase. To check the versatility of this new theoretical approach, we apply it to the Ga adsorption–desorption transition temperature and transition BEP on the GaAs $(0\,0\,1)$-$(4\times 2)\beta 2$ Ga-rich surface as follows.

2. Computational methods

Adsorption–desorption behavior can be described by comparing the free energy of ideal gas per one particle, which is called chemical potential (μ), with the adsorption energy (E_{ad}). That is, net adsorption of the atom proceeds when E_{ad} is less than μ, whereas net desorption occurs when μ is less than E_{ad}. The chemical potential and adsorption energy can be obtained by the following methods. The chemical potential μ for the ideal gas is given by

$$\mu = -k_B T \ln(g k_B T/p \times \zeta_{trans}\zeta_{rot}\zeta_{vibr}), \quad (1)$$

$$\zeta_{trans} = (2\pi m k_B T/h^2)^{3/2}, \quad (2)$$

$$\zeta_{rot} = (1/\pi\sigma)\{8\pi^3(I_A I_B \ldots)^{1/n} k_B T/h^2\}^{n/2}, \quad (3)$$

$$\zeta_{vibr} = \prod_i^{3N-3-n} \{1 - \exp(-h\nu_i/k_B T)\}^{-1}, \quad (4)$$

where ζ_{trans}, ζ_{rot} and ζ_{vibr} are the partition function for the translational motion, the rotational motion and the vibrational motion, respectively. Here, k_B is Boltzmann's constant, T the gas temperature, g the degree of degeneracy of the electron energy level, p the BEP of the particle, m the mass of one particle, h is Planck's constant, σ the symmetric factor, I_I the moment of inertia, n the degree of freedom for the rotation, N the number of atoms in the particle, i the degree of freedom for the vibration and ν the frequency. I_I and ν are written as

$$I_I = m_I r^2, \quad (5)$$

$$\nu = (f/m_I)^{1/2}/2\pi, \quad (6)$$

where m_I is the reduced mass, r the radius of gyration and f the spring constant. For the ideal gas of atomic Ga where $N = 1$ and $I = 0$, the chemical potential μ is

$$\mu = -k_B T \ln(k_B T/p \times g(2\pi m k_B T/h^2)^{3/2}). \quad (7)$$

Here, g and m for atomic Ga have values of 2 and 1.156117×10^{-25} kg, respectively. The values of g for other atoms are listed in Table 1. The adsorption energy of Ga from GaAs$(0\,0\,1)$-$(4\times 2)\beta 2$ surface is obtained by ab initio calculations. In the present work, we used the first-principles pseudopotential method based on the local-density functional formalism [7]. We adopt Kleinman–Bylanders separatable pseudopotentials and the

Table 1
Degeneracy of the electron energy level of the various elements

	Element	g
I	H, Li, Na, K, Rb, Cs, Cu, Ag, Au	2
II	Be, Mg, Ca, Sr, Ba, Zn, Cd, Hg	1
III	B, Al, Ga, In, Tl	2
IV	C, Si, Ge, Sn, Pb	3
V	N, P, As, Sb, Bi	4
VI	O, S, Se, Te, Po	3
VII	F, Cl, Br, I	2
0	He, Ne, Ar, Kr, Xe, Rn	1

cut-off value of local potential was carefully chosen so as to prevent ghost bands [8]. The conventional repeated slab geometry is employed to simulate the surface. The unit supercell consists of five atomic layers of GaAs, an atomic layer of fictitious H atoms and a vacuum region equivalent to about 15 atomic layers in thickness. The validity of the thickness in this repeated slab model was carefully checked.

3. Adsorption–desorption behavior of Ga on GaAs (0 0 1)-(4 × 2)β2

Fig. 1 illustrates the GaAs(0 0 1)-(4 × 2)β2 surface. The calculated results show that the Ga adatom is most stable at the "E" site on the surface where two Ga–Ga bonds (E-1 and E-2 bond) and a Ga–As bond (E-3 bond) are formed around the adatom. The adsorption energies E_{ad} can be calculated as the difference between the total energy when the Ga adatom is located at the most stable site ("E" site) and when the Ga atom is in the vacuum region. In the calculation, we gradually pulled the Ga apart from the E site to the vacuum region and confirmed the convergence of the total energy difference when the distance between the position of Ga atom and the E site is larger than ~4 Å. Consequently, the calculated adsorption energy E_{ad} for Ga at the E site on the Ga-rich surface is estimated to be ~−3.3 eV. This implies that the Ga droplets are formed when the chemical potential for Ga atom is larger than the calculated adsorption energy (≃−3.3 eV), since Ga droplets are easily formed on the GaAs (0 0 1)-(4 × 2) surface under the Ga-rich condition instead of structural change in surface reconstruction [9]. On the other hand, it is thought that the evaporation of Ga droplets occur when the chemical potential for Ga is less than the adsorption energy (≃−3.3 eV). The calculated adsorption energy (≃−3.3 eV) is consistent with the experimental one (= −2.8 eV [10]) which is the case of Ga adsorption on liquid Ga, and this suggests that the calculated value ($E_{ad} = -3.3$ eV) is valid to use in the following analysis. Fig. 2 shows the chemical potential for Ga atom as a function of gas temperature. Considering a typical BEP value ($p_{Ga} = 1.0 \times 10^{-5}$ Torr), the calculated line crosses the line of $\mu_{Ga} = -3.3$ eV at ~1000 K, therefore, the critical temperature for Ga adsorption is ~1000 K at this BEP value. By similar calculations to obtain crossing points at

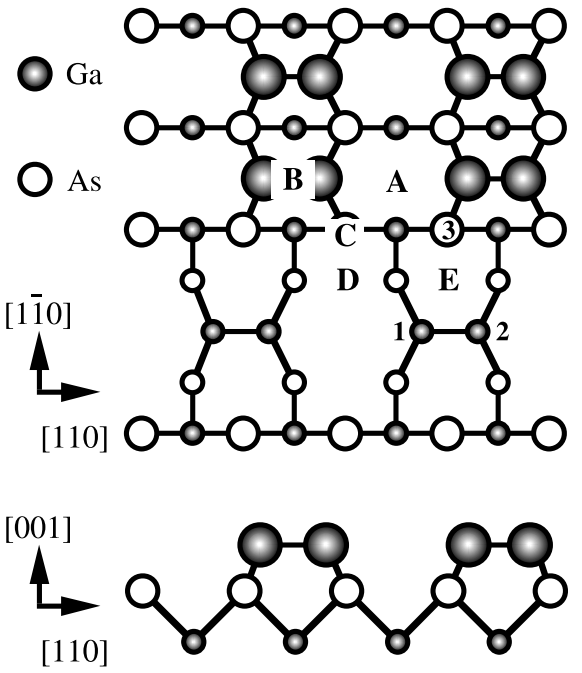

Fig. 1. Schematic of a GaAs(0 0 1)-(4 × 2)β2 surface. Adsorption sites are indicated by the letters A–E.

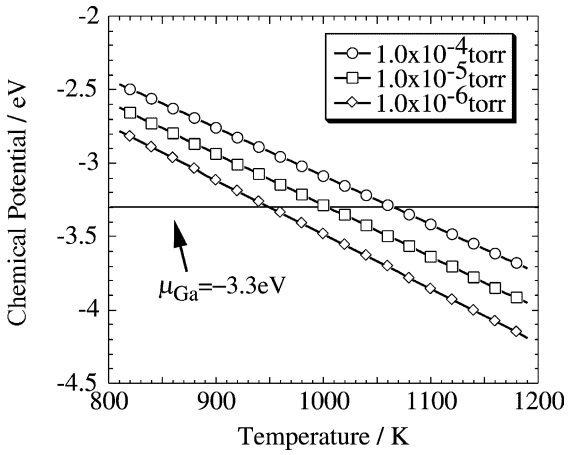

Fig. 2. Chemical potential as a function of substrate temperature.

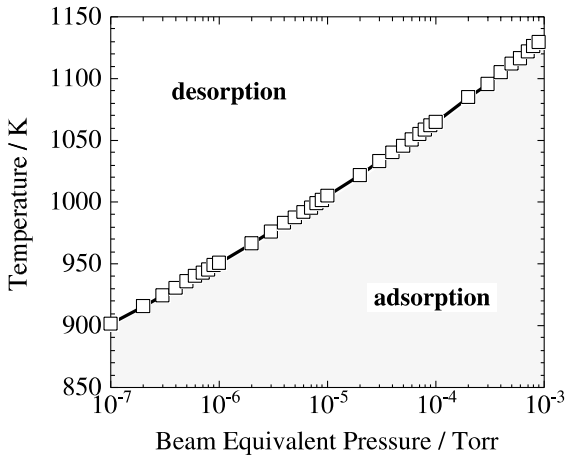

Fig. 3. p–T dependence of adsorption–desorption transition curve.

other BEPs, a p–T diagram for the adsorption–desorption transition was obtained as Fig. 3. This result agrees well with experiments, i.e., Ga droplets are observed at ~900 K during the conventional molecular beam epitaxy growth under the Ga-rich condition [11], whereas Ga desorption proceeds at ~970 K after turning off the Ga flux [12,13]. The results suggest that the new theoretical approach is feasible for predicting the dependence of adsorption–desorption behavior on temperature and BEP.

4. Summary

We propose a new theoretical approach applicable to prediction of the growth condition dependence of adsorption–desorption behavior by incorporating the free energy of the gas phase. Although the influence of lattice vibrations of the substrate and interactions between Ga atoms and As_2 molecules should be incorporated for accuracy, the new theoretical approach is valid for predicting the adsorption–desorption behavior. We are now applying the new theoretical approach to the structural changes in surface reconstructions and to the surface orientation dependence of Ga adsorption–desorption transition curves. Another problems of As adsorption and desorption will be reported in a later publication.

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