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Ab initio-based approach to incorporation of N atoms on GaAs(001) surfaces

Tatsuhiko Sugitani*, Toru Akiyama, Kohji Nakamura, Tomonori Ito

Department of Physics Engineering, Mie University, Tsu 514-8507, Japan

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ABSTRACT

The incorporation of N atoms on GaAs(001)-(2 × 4)α2 and -(3 × 3) surfaces under the growth conditions is theoretically investigated on the basis of surface phase diagrams which are obtained by comparing the adsorption energy given by *ab initio* calculations with the gas-phase chemical potentials. The calculated surface phase diagrams demonstrate that a single N–As dimer is formed on GaAs(001)-(2 × 4) and -(3 × 3) surfaces. Furthermore, two N atoms of surface are found to be substituted for As atoms located at the third layer of the surface. The analysis of stable structures reveals that the stability originates from the competition between energy profit in Ga–N bond formation and energy deficit in strain accumulation due to N located at the third layer. These results suggest that the bond energy as well as lattice strain are crucial for N incorporation processes on GaAs(001) substrate.

1. Introduction

N-containing GaAs has been attracting considerable interest from both a fundamental perspective and their potential device applications such as long-wavelength laser diodes, low-noise avalanche photodetectors, and multi-band solar cells. Such N-containing GaAs can be achieved by N-doping technique using molecular beam epitaxy (MBE). Kita et al. have developed a site-controlled N δ-doping technique using MBE, and have studied the fine structure splitting of excitons bound to the N-pair centers in GaAs [1]. It has been experimentally known that nitridation on GaAs(001)-(2 × 4) surface results in the formation of the (3 × 3) reconstructed structure [2]. On the basis of scanning tunneling microscopy (STM) observation, Gwo et al. proposed a (3 × 3)-reconstruction model with two N dimers [3]. On the other hand, Imayoshi et al. found (3 × 3)-reconstruction consisting of As surface dimers and 0.2 monolayer (ML) of N located in the subsurface layer [4]. Furthermore, Ohtake recently proposed several (3 × 3) structure models, such as (3 × 3)D1 with N dimer and (3 × 3)D2 with two As dimers, on the basis of STM observation [5]. From theoretical viewpoints, Jenichen et al. investigated nitrogen substitutions in various GaAs(001) surfaces such as (2 × 4), c(4 × 4), and (4 × 2) using density functional supercell calculations [6]. They claimed that nitrogen atoms hardly reside in their subsurface layer even at 0 K. Despite the importance of nitrogen incorporated GaAs(001) surfaces, there have been very few theoretical studies for the stability of nitrogen on GaAs(001)-(3 × 3) surfaces.

In our previous study, we have successfully investigated adsorption behavior on GaAs(001) and GaAs(111) surfaces using our *ab initio*-based approach in which surface phase diagrams depending on temperature and BEP are obtained by comparing calculated adsorption energy with gas-phase chemical potentials [7–11]. In this study, we extend our approach for the incorporation of nitrogen on the GaAs(001)-(2 × 4) and -(3 × 3) surfaces. On the basis of surface diagrams, we systematically determine stable nitrogen incorporated surfaces which are feasible for nitridation of GaAs(001) surfaces.

2. Computational methods

The total-energy calculations are performed within the density functional theory in the generalized gradient approximation (GGA) [12]. Norm-conserving pseudopotentials [13] are used for Ga and As atoms, and ultrasoft pseudopotential [14] is used for N atoms. The conjugate gradient minimization technique is used for both the electronic-structure calculation and the geometry optimization [15]. The valence wave functions are expanded by the plane-wave basis set with a cutoff energy of 25 Ry. GaAs(001) surface is simulated by slab geometry consisting of eight atomic layers with artificial H atoms [16] and a vacuum region equivalent to 10 Å thickness. Two *k* points are employed to sample the irreducible Brillouin zone for the (2 × 4) and (3 × 3) unit cells.

The adsorption behavior is determined by comparing the chemical potential (μ_{gas}) in the gas phase with the adsorption energy E_{ad}. The adsorption energy E_{ad} is obtained by the following equation:

$$E_{\mathrm{ad}} = E_{\mathrm{total}} - E_{\mathrm{substrate}} - E_{\mathrm{atom}}, \quad (1)$$

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* Corresponding author.
E-mail address: 411M608@m.mie-u.ac.jp (T. Sugitani).

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where E_{total} is the total energy of the surface with adatom, $E_{\text{substrate}}$ is the total energy of the surface without adatom, and E_{atom} is the total energy of isolated atom. The chemical potential [17] is given by the following equations:

$$\mu_{\text{gas}} = -k_B T \ln\left[\frac{k_B T}{p} g \zeta_{\text{trans}} \zeta_{\text{rot}} \zeta_{\text{vib}}\right], \tag{2}$$

where k_B is the Boltzmann constant, T is the gas temperature, g is the degree of degeneracy of electron energy level, p is the beam equivalent pressure (BEP) of atom, and ζ_{trans}, ζ_{rot}, and ζ_{vib} are the partition functions for translational, rotational, and vibrational motions, respectively. Using the chemical potentials and adsorption energy, the adsorption and desorption behaviors on the surfaces under growth condition are obtained as functions of temperature and BEP, *i.e.*, the structure corresponding to the adsorbed surface is stabilized or favored when E_{ad} is less than μ_{gas}, while the desorbed surface is stabilized when μ_{gas} is less than E_{ad}.

3. Results and discussion

It has been well known that there are several reconstructions such as (2 × 4)α,(2 × 4)β2, and (2 × 4)γ on GaAs(001) surface depending on growth conditions [18]. By comparing the calculated surface phase diagram [9] and experimental conditions for nitridation [1], it is expected that the (2 × 4)α surface could appear during the nitridation. To clarify detailed surface structure during the nitridation, we focus here on the (2 × 4)α and (2 × 4)α2 surfaces. Fig. 1 shows the calculated surface phase diagram of the GaAs(001)-(2 × 4) surface as functions of temperature and As_4 BEP. The phase boundary between (2 × 4)α and (2 × 4)α2 surfaces on GaAs(001) in the range 750–800 K depending on As_4 BEP. This reveals that the (2 × 4)α2 reconstruction is stabilized under growth conditions (temperature: 830 K, As_4 BEP: 3.0×10^{-6} Torr). Therefore, we employ the (2 × 4)α2 reconstruction as the GaAs(001)-(2 × 4) surface. Since it has been experimentally known that 0.2 monolayer (ML) of N is successfully incorporated, we here investigate the structures with two N atoms on (2 × 4)α2 surface. On the (2 × 4)α2 surface, it is found that an N–N dimer does not stably reside in the surface lattice sites because of its positive adsorption energy (E_{ad}=1.29 eV). This result implies that the adsorption of N–N dimer on the (2 × 4)α2 surface is a sort of physisorption and hardly contributes to the incorporation of N atoms into the third layer of GaAs surface: N incorporation cannot be interpreted by only adsorption of N–N dimers.

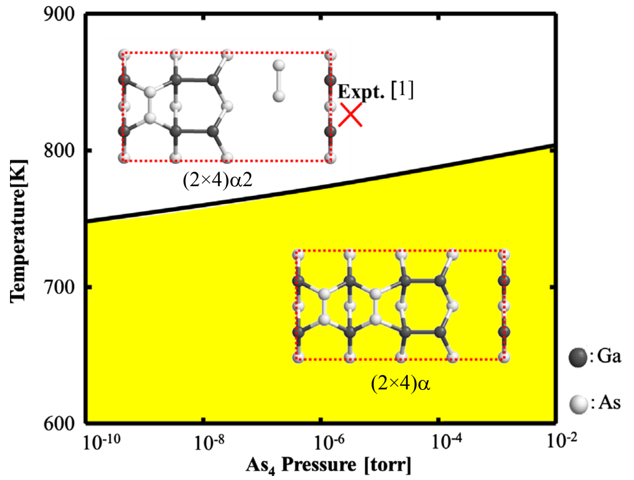

Fig. 1. Surface phase diagram of (2 × 4)α2 and (2 × 4)α structures on GaAs(001), as functions of temperature and As_4 BEP. Experimental condition in Ref. [1] is represented by the cross mark.

To clarify the stability of N atoms, we next consider N substitution for As atoms. Our examinations for adsorption and desorption of N–As and As–As dimers on GaAs(001)-(2 × 4)α2 surface reveal that the As–As dimer on the (2 × 4)α2 desorbs and two N–As dimers stably reside on the surface under nitridation conditions, as shown in Fig. 2. This implies that two N atoms are incorporated on the (2 × 4)α2 surface, resulting in the formation of the (2 × 4)β2 like structure shown in Fig. 3(a). In order to determine the most stable configuration for substitutional N atoms on this surface structure, we consider all possible configurations with N atoms at the third layer shown in Fig. 3(a). Fig. 3(b) shows the calculated energy difference among these configurations. This figure shows that the surface with N atoms located at sites H and I in Fig. 3(a) [(2 × 4)-I] is the most stable. The stability of this configuration can be interpreted in terms of energy difference between Ga–N and Ga–As bonds. Since the energy of a Ga–N bond (5.37 eV) is larger than that of a Ga–As bond (3.36 eV), Ga atoms tend to bind with N atoms rather than As atoms. The number of Ga–N bonds for the surface with N atoms located in the third layer (sites H and I, for instance) is twice larger than that with N–As dimers (sites A and D, for instance). In addition, the lattice strain caused by Ga–N bonds is found to be crucial for the stability of (2 × 4)-I. The bond lengths of Ga–N around the N atom located in the third layer for (2 × 4)-I (10% larger than ideal Ga–N bond length) are much shorter than those for other structures (for instance H and J sites). The large Ga–N bond lengths (~2.17 Å) for the other structures imply a large amount of strain accumulation around the N atoms.

On the basis of these stable configurations, the stable (2 × 4) surface with N atoms can be determined. Fig. 4 shows the calculated surface phase diagram of N incorporated (2 × 4) surfaces as functions of temperature and N BEP at As_4 pressure of 3.0×10^{-6} Torr. The (2 × 4)-I is stabilized at low temperatures regardless of N pressure. However, one of two As–As dimers on the (2 × 4)-I desorbs from the surface beyond 625 K. This results in the formation of the surface with single N–As dimer and substitutional N atom at the third layer ((2 × 4)-II). It is thus concluded that (2 × 4)-II is favorable under experimental nitridation conditions [1]. It should be noted that (2 × 4)-II is not stable under high temperature and low N pressure conditions. The surface with single substitutional N atom at the third layer is stabilized beyond 1300 K at N pressure of 1×10^{-10} Torr.

Similar results are obtained for N incorporation on the (3 × 3) surface. On the basis of the STM observation where the (3 × 3) surface consists of two anion dimers, we take account of various nitrogen-containing configurations with N–N, As–As, and N–As dimers. For the surface with two N atoms, we consider all possible configurations with N atoms shown in Fig. 5(a). Fig. 5(b) shows the calculated energy difference among these configurations. This figure shows that the surface with N atoms located at sites A and H in Fig. 5(b) ((3 × 3)-I) is the most stable. In contrast to (2 × 4)-I, one N–As dimer resides on the surface and a substitutional N atom is located at the third layer. This is because the lattice strain accumulated in (3 × 3)-I is less than that on the surface with N atoms located at the third layer (sites E and H): the deviations of Ga–N–Ga bond angle from the ideal value (109.4°) in (3 × 3)-I (~118.2°) is much smaller than that in the surface with N atoms located at the third layer (~122.6°). In the case of the (3 × 3) surface, the stability is thus interpreted in terms of the strain accumulation in addition to the formation of Ga–N bonds.

Fig. 6 shows the calculated surface phase diagram of N incorporated (3 × 3) surface as functions of temperature and N BEP at As_4 pressure of 3.0×10^{-6} Torr. The (3 × 3)-I is stabilized below 1500 K, while the surface with an N atom at the third layer [(3 × 3)-II] is favored beyond 1500 K. Therefore, (3 × 3)-I emerges under experimental nitridation conditions [1]. Since the surface