Ab initio-Based Approach to N--pair Formation on GaAs(001)-(2\times4) Surfaces*

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Nitrogen-pair formation processes on the GaAs(001)-(2\times4) surfaces found experimentally are systematically investigated using ab initio-based approach incorporating beam equivalent pressure \( p (p_{\text{N}} = 7.0 \times 10^{-6} \text{ Torr}) \) and temperature \( T = 830 \text{ K} \). The calculated surface phase diagrams elucidates that the (2\times4)\text{a}1 and (2\times4)\text{o}2 surfaces are stable at the growth conditions under As\text{2} and As\text{4}, respectively. The Monte Carlo simulations reveal that the N incorporation on the (2\times4)\text{a}1 and (2\times4)\text{o}2 surfaces proceeds with increase of energetically favorable Ga-N bonds in the third layer via series of events such as adsorption of N-As dimer, substitution of N for As located in the third layer, and As dimer desorption to form the N--pair in the third layer.

It is also found that the probability of the N--pair formation on the (2\times4)\text{a}1 surface is much larger than that on the (2\times4)\text{o}2 surface. This is because the strain around the N--pair on the (2\times4)\text{a}1 surface is smaller than that on the (2\times4)\text{o}2 surface where N-As surface dimer is formed to relax the larger strain. Furthermore, the N--pair formation probabilities \( P\) under As\text{2} and As\text{4} are estimated as a function of temperature including (2\times4)\text{a}1. N atoms incorporated on the GaAs(001) surface can form N--pair along [110] with \( P \sim 0.8 \) on the surface with two phase mixture of (2\times4)\text{a}1 and (2\times4)\text{o}2 at \( T = 830 \text{ K} \) under As\text{2} and As\text{4}.

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I. INTRODUCTION

Nitrogen (N) incorporated GaAs-based materials have been extensively investigated from experimental and theoretical viewpoints because of its potential applicability for low-wave laser diodes with high temperature stability [1], low-noise avalanche photodetectors [2], multi-band solar cells [3], and a new light source with a defined photon energy [4]. It is experimentally known that N atoms are substituted for matrix group V atoms to form N--pairs and act as isoelectronic traps resulting in sharp luminescence [5]. Kita et al. have developed a site-controlled N doping technique using molecular beam epitaxy (MBE) to study the fine structure of excitons bound to the N--pair centers oriented along [110] in GaAs [6-8]. From theoretical viewpoints, Jenichen et al. investigated stable subsurface lattice sites for N atoms on various GaAs(001) surfaces including (4\times4), (2\times4)\text{a}1, (2\times4)\text{o}2, (2\times4)\beta1, (2\times4)\beta2, and (4\times2)\gamma using density functional supercell calculations [9]. They claimed that N atoms hardly reside in their subsurface layer except GaN chain formation in [110] on the (4\times2)\gamma under Ga-rich condition and on the (2\times4)\beta1 under extreme Ga-rich condition. Although the calculated results suggest some possibilities for N--pair formation along [110] in GaAs, they cannot be directly compared with experimental results because of the lack of growth conditions such as temperature and beam equivalent pressure (BEP) in their calculations.

Our previous ab initio-based study incorporating the growth conditions has revealed that two N atoms on the (2\times4)\text{o}2 and (3\times3) surfaces can be substituted for As atoms located in the third layer at the conventional growth conditions [10]. Moreover, we also found that the stability of N atoms is dominated by the competition between energy profit due to the formation of Ga-N bonds and deficit resulting from strain accumulation around them in the third layer. In this study, N--pair formation processes on various GaAs(001)-(2\times4) surfaces are systematically investigated using the ab initio-based approach. The stable structures of the (2\times4) surface are determined by predicting surface phase diagrams as functions of temperature and BEPs of As\text{2} and As\text{4}. This approach is also applied to obtain phase boundaries for various N incorporated (2\times4) surfaces at growth conditions including BEP of N under As\text{2} and As\text{4}. On the basis of these results, the Metropolis Monte Carlo simulations are performed to clarify the N incorporation and N--pair formation processes on the stable (2\times4)\text{a}1 and (2\times4)\text{o}2 surfaces. The difference in the probabilities of N--pair formation are discussed in terms of interatomic bond species and strain around N--pair located in the subsurface layer. Furthermore, the ratio of N--pair formation along [110] at certain BEPs of N atom and As\text{2} or As\text{4} molecules are estimated as a function of temperature incorporating various stable surfaces such as (2\times4)\beta1 in addition to the (2\times4)\text{a}1 and the (2\times4)\text{o}2.

II. COMPUTATIONAL METHODS

The adsorption-desorption behavior of N atom on the GaAs(001)-(2\times4) surfaces can be determined by comparing the free energy of ideal gas per one particle (chemical potential) \( \mu_{\text{gas}} \) with the adsorption energy \( E_{\text{ad}} \) [11]. The chemical potential \( \mu_{\text{gas}} \) of ideal gas is given by the following equations:

\[
\mu_{\text{gas}} = -k_{\text{B}}T \left[ \frac{k_{\text{B}}T}{p} g_{\text{trans}} \text{cosh} K_{\text{vib}} \right].
\]
Here, $k_B$ is the Boltzmann’s constant, $T$ the gas temperature, $g$ the degree of degeneracy of electron energy level, $p$ the beam equivalent pressure of N atom or As molecules (As$_2$ and As$_4$), and $\zeta_{\text{trans}}, \zeta_{\text{rot}}$, and $\zeta_{\text{vib}}$ are the partition functions for translational, rotational, and vibrational motions, respectively. Here, $\zeta_{\text{gas}}$ and $\zeta_{\text{vib}}$ are used for As molecules. The adsorption energy $E_{\text{ad}}$ is obtained by

$$E_{\text{ad}} = E_{\text{total}} - E_{\text{substrate}} - E_{\text{atom}},$$

where $E_{\text{total}}$ is the total energy of the surface with adatoms, $E_{\text{substrate}}$ the total energy of the surface without adatoms, and $E_{\text{atom}}$ is the total energy of isolated atoms. Using the chemical potentials and adsorption energies, the adsorption and desorption behaviors on the surfaces under growth conditions are obtained as functions of temperature and BEP, i.e., the structure corresponding to adsorbed surface is favorable when $E_{\text{ad}}$ is less than $\mu_{\text{gas}}$, whereas desorbed surface is stabilized when $\mu_{\text{gas}}$ is less than $E_{\text{ad}}$. Based on these results, we obtain phase diagrams of GaAs(001)-(2×4) surfaces with/without N incorporation. In this study, the total-energy calculations are performed within the generalized gradient approximation (GGA) [12] and norm-conserving pseudopotentials for Ga and As atoms [13], and ultrasoft pseudopotential for N atom [14]. 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. We take the GaAs(001) models with a slab geometry 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 GaAs(001)-(2×4) unit cell.

Furthermore, the Metropolis Monte Carlo (MMC) simulations are performed to investigate the incorporation processes of N atoms on the GaAs(001)-(2×4) surfaces. We made the following assumptions in the MMC simulation. (i) Adsorption-desorption of As$^-$, N$^-$, and N–As dimers is randomly generated on the GaAs(001)-(2×4) surfaces under BEPs of As molecules ($p_{\text{As}} = p_{\text{As}} = 3.0 \times 10^{-6}$ Torr) and N atom ($p_{\text{N}} = 7.0 \times 10^{-6}$ Torr). (ii) During adsorption-desorption processes, an exchange between N and As atoms occurs within three layers below the surface layer. (iii) The system energies are obtained by Eqs. (1) and (2) for various configurations of N incorporated surfaces. (iv) The energy differences $\Delta E$ between old and new configurations are determined by $\Delta E = E_{\text{ad}} - \mu_{\text{gas}}$ for adsorption, $\Delta E = E_{\text{des}} + \mu_{\text{gas}}$ for desorption, and $\Delta E = E_{\text{new}} - E_{\text{old}}$ for exchange, where $E_{\text{des}}, E_{\text{new}}, E_{\text{old}}$ are desorption energy, system energies of new and old configurations for exchange, respectively. (v) If $\Delta E$ is negative, accept new configuration; otherwise, select a random number $R$ uniformly distributed over the interval (0,1); if $\exp(-\Delta E/k_BT) < R$, accept the old configuration; otherwise, use the new configuration and the new system energy as the current properties of the system. This procedure is repeated for suitable number of configurations (MC steps) in order to approach equilibrium configurations. The ratio of N–pair formation along [110] direction is obtained by 5000 samples at each temperature under the BEPs of As molecules and N atom.

III. RESULTS AND DISCUSSION

Figure 1 shows the calculated phase diagrams for GaAs(001)-(2×4) surfaces as functions of temperature and BEPs of (a) As$_2$ and (b) As$_4$. This figure also shows the top view of the surface structures such as (2×4)01, (2×4)02, and (2×4)31 considered in this study schematically. The phase diagrams imply that the (2×4) surface changes its structure from the (2×4)31 at low temperature region to the (2×4)02 at high temperature region via the (2×4)01 with increase of temperature promoting As desorption. Under As$_2$, the (2×4)31 is stable below ~540-770 K while As desorption realizes the (2×4)01 in the temperature range of ~540-770 K $\leq T \leq$~860-930 K. The (2×4)02 appears beyond ~860-930 K due to further desorption of As and Ga. On the other hand, the boundaries of the stable surfaces become low under As$_4$ such as $T \leq$~480-640 K for the (2×4)31, ~840-640 K $\leq T \leq$~750-800 K for the (2×4)01, and $T \geq$~750-800 K for the (2×4)02 because of small desorption energy of As under As$_4$. According to these results, it is found that the stable surface structures of GaAs(001) are the (2×4)01 under As$_2$ and the (2×4)02 under As$_4$ at growth conditions such as $T = 830$ K, $p_{\text{As}} = 3.0 \times 10^{-6}$ Torr. Therefore, we mainly employ these two surface structures as...
GaAs(001) surfaces to investigate N incorporation processes during MBE growth using the MMC simulations.

Since it has been experimentally known that 0.2 monolayer of N is successfully incorporated, we focus on the investigation of the (2×4) surface with two N atoms. Figure 2 depicts various N incorporation processes on (a) the (2×4)α1 and (b) the (2×4)α2 surfaces obtained by our MMC simulations assuming $p_N = 7.0 \times 10^{-6}$ Torr. These results suggest that N incorporation starts with N–As or N dimer adsorption and simultaneous As dimer formation on the surfaces. After N–As dimer adsorption, N–pair formation results from the successive fundamental events such as As dimer desorption, subsequent N–As adsorption, and N substitution for As located in the third layer to realize the N–pair along [110] direction. This is the main process for N–pair formation on the (2×4) surface. Once N dimer is rarely formed on the surface as shown in the lower part of Figs. 2(a) and 2(b), As dimer desorption and N substitution for As located in the third layer easily form the N–pair along [110] direction in the third layer. Moreover, it should be noted that another process at the beginning of these simulations such as As dimer adsorption (red arrow) on the (2×4)α1 and on the (2×4)α2 respectively produces the (2×4)α2 and the (2×4)β1 surfaces where the N incorporation processes newly start.

The stability of N–pair in the third layer can be interpreted in terms of energy difference between Ga–N and Ga–As interatomic bonds. Since the cohesive energy of Ga–N bond (5.37 eV/atom) is larger than that of Ga–As bond (3.36 eV/atom), Ga atoms favors forming interatomic bonds with N atoms rather than As atoms. The number of Ga–N bonds for N atoms located in the third layer $N_{Ga-N}$ = 4 is twice larger than that with N–As dimers in the topmost layer $N_{Ga-N}$ = 2. It is found that the N–pair formation processes shown in Fig. 2 proceed with increase of $N_{Ga-N}$ from the first N–As dimer adsorption with $N_{Ga-N}$ = 2 to final N–pair formation in the third layer with $N_{Ga-N}$ = 8 via one N atom substituted for As in the third layer with $N_{Ga-N}$ = 4 and subsequent N–As dimer adsorption with $N_{Ga-N}$ = 6. In addition, the lattice strain caused by Ga–N bonds is found to be crucial factor for the stability of N–pair formation in the third layer. It should be noted that N atom is favorably located near surface As dimers where the bond lengths of

FIG. 2: Prototypical N incorporation processes on GaAs(001)-(2×4) surfaces for (a) (2×4)α1 and (b) (2×4)α2 obtained by our MMC simulations at the growth conditions such as $T = 830$ K, $p_{As} = 3.0 \times 10^{-6}$ Torr, and $p_N = 7.0 \times 10^{-6}$ Torr.
Ga–N ~2.08 Å (6% larger than ideal Ga–N bond length) around the N atom located in the third layer are much shorter than those of ~2.17 Å (10% larger than ideal Ga–N bond length) for other atomic arrangements of the N atom located in the third layer away from As dimers. The large Ga–N bond lengths for the other atomic arrangements simply induce a large amount of strain accumulation around the N atoms away from surface As dimers to destabilize the system.

Figure 3 shows the calculated ratio of N–pair formation in the third layer as a function of temperature for (a) (2×4)α1 and (b) (2×4)α2 surfaces obtained by our MMC simulations. This elucidates that the N–pair arrangement located [110] is easily formed on the (2×4)α1, whereas the structure with N–As surface dimer and N atom isolated in the third layer appears in the third layer with large probability ~0.4 in addition to that with N–pair on the (2×4)α2. This reflects the difference between the strain around Ga–N interatomic bonds in the third layer on the (2×4)α1 and that on the (2×4)α2. On the (2×4)α1, the strain of Ga–N bonds around N–pair is estimated to be ~6% that is smaller than ~17% on the (2×4)α2. Considering the fact that N atom favors the lattice site in the third layer near As dimers, the (2×4)α1 with two As dimers is effectively lower the strain energy around Ga–N bonds while the strain relaxation is not sufficient around Ga–N bonds on the (2×4)α2 with one As dimer. Consequently, some of N atoms tend to reside in the topmost surface lattice sites on the (2×4)α2 to form N–As dimer and N atom isolated in the third layer in order to relax the large strain around N–pair in the third layer on the (2×4)α2.

As shown in Fig. 2, the (2×4)α1 and the (2×4)α2 surfaces respectively change their new structures to the (2×4)β1 and the (2×4)α2 with certain probability at growth conditions such as $T = 830$ K, $p_{\text{As}} = 3.0 \times 10^{-6}$ Torr, and $p_{\text{N}} = 7.0 \times 10^{-6}$ Torr. Therefore, N–N pair formation should be investigated for the N incorporation processes on these new surfaces simultaneously. Figure 4 shows the calculated appearance ratio of (2×4)α1{(2×4)α1–(2×4)α1} at low temperatures and (2×4)α1–(2×4)α2 at high temperatures. The shaded area denotes the region with two phase mixture of (2×4)β1–(2×4)α1 at low temperatures and (2×4)α1–(2×4)α2 at high temperatures. Atomic arrangements of N–pair on the surfaces are also shown in this figure.
cess shown in Fig. 2 occurs more easily than that under As$_2$. This also causes the small stable region of N–pair on the (2×4)α1 under As$_4$ resulting from the difficulty of As dimer adsorption. Consequently, ~80% of N atoms incorporated on the GaAs(001) surface can form N–pair along [110] on the surface with two phase mixture of (2×4)α1 and (2×4)α2 at the growth conditions of $T = 830$ K, $p_{As} = 3.0 \times 10^{-6}$ Torr, and $p_N = 7.0 \times 10^{-6}$ Torr under As$_2$ and As$_4$.

IV. CONCLUSIONS

We have systematically investigated N–pair formation on the GaAs(001)-(2×4) surfaces using ab initio-based approach at the growth conditions such as BEPs of $p_{As} = 3.0 \times 10^{-6}$ Torr, and $p_N = 7.0 \times 10^{-6}$ Torr and temperature $T = 830$ K. The calculated surface phase diagrams elucidate that (2×4)α1 and (2×4)α2 surfaces are stable at the growth conditions under As$_2$ and As$_4$, respectively. The MMC simulations reveal that the N incorporation on the (2×4)α1 and (2×4)α2 surfaces proceeds with increase of energetically favorable Ga–N bonds in the third layer via series of events such as adsorption of N–As dimer, substitution of topmost N for As located in the third layer, and As dimer desorption to form N–pair along [110] in the third layer. It is also found that the probability of the N–pair formation on the (2×4)α1 surface is much larger than that on the (2×4)α2 surface. This is because the strain around the N–pair on the (2×4)α1 surface is much smaller than that on the (2×4)α2 surface where N–As surface dimer is formed to relax the large strain. Further MMC simulations simultaneously taking various (2×4) surfaces into account clarify that the N–pair is effectively formed on the (2×4)α1 in the temperature range of 650-750 K under As$_2$ and 550-750 K under As$_4$. Moreover, ~80% of N atoms incorporated on the GaAs(001) surface can form the N–pair along [110] on the surface with two phase mixture of (2×4)α1 and (2×4)α2 at the growth conditions of $T = 830$ K under As$_2$ and As$_4$.

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