DFT Study for Growth of \(m\)-Plane GaN/ZnO Interfaces

Yasuhiro Oda* and Akira Ishii

Department of Applied Mathematics and Physics,
Tottori University, Koyama, Tottori-City, Tottori 680-8552, Japan

Katsutoshi Fujiwara
NiCeRa Advanced Technology R&D Center, Nippon Ceramic Co., Ltd., 204-8 Hirooka, Tottori 689-1116, Japan

(Received 8 February 2012; Accepted 14 May 2012; Published 9 June 2012)

We have performed density-functional theory calculations to investigate the alignment of gallium (Ga) and nitrogen (N) atoms at \(m\)-plane wurtzite GaN/ZnO hetero-interfaces. The potential energy surface (PES) for Ga adatom and N adatom on the clean \(m\)-plane ZnO(10 \(\bar{1}\)0) and \(m\)-plane ZnO(10 \(\bar{1}\)0) with co-adsorbed Ga and N adatoms are calculated. The most stable alignments in each calculation for PES show us that the hetero-interface structure between GaN and ZnO changes depending on the growth condition. Under the Ga-rich condition, the stable site of N adatom changes because of the self-surfactant effect of the Ga atoms. Under the stoichiometric condition, the stripe structure will be obtained along [0001] direction and the self-surfactant effect of Ga atoms dose not work. Under the N-rich condition, the N adatom forms N
\[2\] molecule with the N on the surface and desorb from the surface. We found the condition for growing up an ideal crystal in this hetero-interface.

[DOI: 10.1380/ejssnt.2012.221]

Keywords: Density functional calculations; Gallium nitride; Zinc oxide

I. INTRODUCTION

Non-polar GaN has attracted much attention as a material for short-wavelength optical devices such as ultraviolet and green light-emitting devices because undesired spontaneous and piezoelectric polarizations perpendicular to the interfaces of the quantum wells are eliminated [1–3]. ZnO has been regarded as one of the most promising substrate for GaN growth because ZnO and GaN perfectly share the same crystalline symmetries and the lattice mismatches between them are as small as 1.9 % and 0.4 % for the \(a\)-axis and \(c\)-axis, respectively. However, the interfacial structure of non-polar GaN on non-polar ZnO has not yet been well investigated theoretically. Moreover, the growth mechanism of the interface poorly understood, because the growth mechanism depends strongly on the temporal quasi-stable structures of the supplied adatoms on the growth surface.

In this study, we simulate the adsorption of Ga and N adatoms on \(m\)-plane wurtzite ZnO as the early stage of the growth of the interface of non-polar GaN on non-polar ZnO during the growth using the first-principles calculations, because the first-principle calculation has been proven to be a powerful tool for the investigation of the growth mechanisms of different semiconductors [4, 5].

II. CALCULATION METHOD

Our first-principles density functional total-energy calculations are based on the density-functional theory (DFT) [6, 7] using the Vienna ab initio simulation package (VASP) [8]. We used the local density approximation (LDA) [9, 10] for the exchange correlation and projector augmented wave (PAW) [11, 12] method. The Zn and Ga 3d electrons are treated as part of the valence band. The cutoff energy for the plane-wave basis is set to be 500 eV. We employed supercells containing eight atomic layers of ZnO and a vacuum region of 15 Å. The bottom layer of the slab is passivated with hydrogen atoms. The Zn and O atoms of the two layers on this side of the slab are kept fixed and all other atoms are allowed to relax in order to simulate the constrains coming from the underlying semi-infinite bulk. The \(4\times4\times1\) k-point sets were used in the calculations of optimization of structure.

The structure of the \(m\)-plane wurtzite ZnO is shown in Fig. 1. For calculating the potential energy surface(PES) for Ga and N adatom, we kept the surface coordinates of the adatom. In other words, the surface adatoms such as Zn and O and co-adsorbed Ga and N atoms were allowed to relax.

III. RESULTS

The calculated potential energy surface for Ga and N on the \(m\)-plane ZnO(1010) surface are shown in Fig. 2. According to our calculation, as we can find in the figure that the tendency of the migration of Ga adatom is one-dimensional-like. The migration easy direction is the [11\(\bar{2}\)0] direction. In contrast to the case of Ga, N adatom
FIG. 2: The calculated potential energy surface for Ga and N adatom on m-plane ZnO(10¯10). (a) is for Ga and (b) is for N. The gray circles and the red circles indicate the Zn atoms and the O atoms of the substrate, respectively. The green and blue circle in the figures indicate the original position of the next site of Ga and N as the wurtzite structure of GaN on ZnO.

The calculated PES for Ga adatom on m-plane ZnO(10¯10) surface is not mobile and the migration of N is not one-dimensional-like. The stable position of Ga adatom is very close to the original position of the next site of Ga as the wurtzite structure of GaN on ZnO. On the other hand, for N adatom, the calculated stable position is shifted by a/2 to the [11¯20] direction from the next lattice position of the N atom as the wurtzite structure. The next lattice position for N on the m-plane ZnO(10¯10) surface is very unstable for the N adatom.

The calculated PES for Ga adatom on m-plane ZnO(10¯10) with co-adsorbed N adatom and the calculated PES for N adatom on m-plane ZnO(10¯10) with co-adsorbed Ga adatom are shown in Figs. 3 (a) and (b). These figures show that the most stable positions of the Ga and N are shifted by a/2 to the [11¯20] direction from the next lattice positions of Ga and N on the surface, respectively. In this case, the most stable alignment of the co-adsorbed Ga and N adatoms is the GaN dimer structure shifted by a/2 to the [1120] direction in Fig. 4.

Figure 5 (a) is PES for Ga adatom with the GaN dimer on m-plane ZnO. This figure shows us that the stable position of the Ga adatom in Fig. 2 is no more stable in the case of the existence of another GaN dimer. The most stable position of the Ga adatom is on the GaN dimer (see Figs. 5 (b) and (c)). Moreover, we found that the new added GaN dimer is positioned on the previous GaN dimer with the alignment shifted at a/2 to the [1120] direction in Fig. 4.

IV. DISCUSSION

As for the process of the crystalline growth in the interface, the following cases are thought from the above-mentioned result.

1. As the Ga-rich condition;
FIG. 4: Top view (a) and side view (b) of the most stable alignment of the co-adsorbed Ga and N atom on m-plane ZnO. The grey and red circles indicate Zn and O atoms of substrate. The filled green and blue circles indicate Ga and N adatom. The open green and blue circles indicate the original positions of the next lattice site of Ga and N as the wurtzite structure of GaN on ZnO. These figures show that the most stable positions of the Ga and N are shifted by $a/2$ to the [11 $\bar{2}$0] direction from the next lattice positions.

FIG. 5: (a) is the calculated PES for Ga adatom on structure of Fig. 4. The gray circles and the red circles indicate the Zn atoms and the O atoms of the substrate, respectively. The green and blue circles indicate the default position of co-adsorbed N and Ga adatom, respectively. (b) and (c) are side view and top view when the Ga atom adsorbs the stable position.

(a) The Ga and N atoms adsorb the surface, and the GaN dimer is made at the position that shifted by $a/2$ to the [11 $\bar{2}$0] direction from the next original lattice positions of Ga and N on the surface (Fig. 4).

(b) The stable site of N adatom changes because of the self-surfactant effect of the Ga atoms. In a ward, GaN dimer is returned to the original lattice position (Fig. 7).

(c) The GaN dimer which returned to the original lattice position fills an interface (Figs. 9 (a) and (b)).

(d) Afterwards, it grows up as well as homoepitaxial growth.

2. As the stoichiometric condition (self-surfactant effect of Ga atoms works);

(a) The Ga and N atoms adsorb the surface, and the GaN dimer is made at the position that shifted by $a/2$ to the [11 $\bar{2}$0] direction from the next original lattice positions of Ga and N on the surface (Fig. 4).

(b) Because the Ga atom that diffuses easily moves or the N adatom forms N$_2$ molecule with the N on the surface and desorb from the surface, the condition of the crystalline growth partially becomes Ga-rich.

(c) It happens similar to since 1b and 1c of the Ga-rich condition.

(d) Afterwards, it grows up as well as homoepitaxial growth.

3. As the stoichiometric condition (self-surfactant effect of Ga atoms does not work);

(a) The Ga and N atoms adsorb the surface, and the GaN dimer is made at the position that shifted by $a/2$ to the [11 $\bar{2}$0] direction from the
FIG. 8: Side view (a) and top view (b) of the most stable alignment of N adatom on structure of Fig. 5. These figures show that the new added GaN dimer is positioned on the previous GaN dimer with the alignment that shifted at a/2 to the [1120] direction maintained under the stoichiometric condition.

FIG. 9: (a) and (b) are side view of the interface which grow up to be an original lattice position as the wurtzite structure of GaN on ZnO. (c) and (d) are side view of the structure of an interface when self-surfactant effect of Ga atoms does not work.

(a) Side View
(b) Top View
(c) Next original lattice positions of Ga and N on the surface.
(d) Afterwards, it grows up as well as homoepitaxial growth.

At the Ga-rich condition, the structure that shifted at a/2 to the [1120] direction is canceled by self-surfactant effect of the Ga atoms (1b). In a word, an ideal crystal growth is possible. As the stoichiometric condition, the same phenomenon as Ga-rich happens locally, the structure that shifted at a/2 to the [1120] direction is canceled, and it becomes an ideal structure (2b, 2c). However, in other portions, the structure of Figs. 9 (c) and (d) is formed (3c). So the structure of two interfaces is intermingled. Since the structure of these interfaces may cause a defect of a crystal, We think that crystal growth in the hetero-interface should be performed in Ga-rich condition.

The GaN dimers of Fig. 7 and Fig. 8 are parallel to the c axis of ZnO and the polarity of the cation and anion of the GaN dimers is the same as that of ZnO substrate. These results of our calculations well explain the recent experimental result [13].

V. CONCLUSION

The tendency of the migration of Ga adatom on m-plane ZnO is one-dimensional like and the migration easy direction is the [1120] direction. N adatom on m-plane ZnO surface is not mobile and the migration of N adatom is not one-dimensional-like. The most stable alignment of the co-adsorbed Ga and N adatoms is the GaN dimer structure shifted by a/2 to the [1120] direction. Under the Ga-rich condition, the stable site of N adatom changes because of the self-surfactant effect of the Ga atoms. Even under the stoichiometric condition, the surface can be considered as slight Ga-rich because of the two reasons: Ga adatoms are far mobile than nitrogen and nitrogen adatom can desorb spontaneously as N$_2$ molecule. The GaN dimer is return to the original lattice position as the wurtzite structure because of the self-surfactant effect of Ga atoms. In other parts of the surface, the stripe structure that shifted at a/2 to the [1120] direction from the next lattice position of the Ga and N atoms as the wurtzite structure is formed along [0001] direction. After the formation of the stripe structure, the half-period-shifted structure is kept even in the growth with the Ga-rich condition. The structure of two interfaces is intermingled in the stoichiometric condition. The crystal growth in the hetero-interface should be performed in Ga-rich condition.

Acknowledgments

Figure 1, Fig. 4, Figs. 5 (b) and (c), Fig. 7, Fig. 8 and Fig. 9 were drawn by VESTA [14].