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Investigation of Growth Process of GaN Film on Sapphire by Computational Chemistry

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1. Introduction

Gallium nitride is one of the most attractive materials for optoelectronic devices because of its application in blue light-emitting diodes and lasers [1,2]. The heteroepitaxial growth of highly perfect GaN layers on sapphire (α-Al_2O_3) substrates by the metalorganic vapor phase epitaxy method has become possible due to the development of the GaN or AlN buffer layer deposition technique [3]. It is reported that the initial treatment of sapphire substrate, such as initial nitridation and low-temperature GaN buffer layer deposition, affects the surface morphology and crystallinity of grown GaN layers [4]. Grown GaN planes have a polar configuration, i.e., either Ga or N can occupy the first atomic layer. The polarity is a key parameter for the growth of high quality epitaxial GaN films on sapphire (0001) substrate [5]. However, as for the initial growth process of GaN films, the microstructure of GaN/sapphire interface and the growth mechanism are not well known yet. It is important to understand this mechanism, since the surface polarity can be controlled and this knowledge will achieve the high quality GaN materials as required for optoelectronic applications.

In this paper, we have investigated the microstructures and the electronic states of the GaN/sapphire (0001) heteroepitaxial interface by computational chemistry.

2. Computational Method

We studied the energetically stable sites of GaN on α-Al_2O_3 (0001) surface by quantum chemical calculations based on the periodic density functional theory (DFT). All DFT calculations were performed by solving Kohn-Sham equation self-consistently [6] as implemented in the DSolid program [7] provided by MSI. We employed the local density approximation (LDA) with the Vosko-Wilk-Nusair (VWN) functional [8] for geometry optimization. In order to calculate adsorption energies, we applied the Beck-Lee-Yang-Parr (BLYP) [9,10] nonlocal functional as a correction. Double numerical plus polarization functions (DNP) basis set was used.

Furthermore, we studied the effects of atomic interactions on GaN/α-Al_2O_3 interface for the initial growth process by molecular dynamics (MD) method. All MD calculations were carried out with the RYUDO program developed in our laboratory. The two-body central force interatomic potential, as shown in Equation (1), was used. In this equation, the first, second, and third terms refer to Coulomb, exchange repulsion, and Morse interactions, respectively.

$$u(r_{ij}) = Z_i Z_j e^2/r_{ij} + f_0 (b_i + b_j) \exp[(a_i + a_j - r_{ij})/(b_i + b_j)] + D_{ij} \{\exp[-2\beta_{ij} (r_{ij} - r^*_{ij})] - 2\exp[-\beta_{ij} (r_{ij} - r^*_{ij})]\} \quad (1)$$

where Z_i is the atomic charge, e is the elementary electric charge, r_{ij} is the interatomic distance, and f_0 is a constant. The parameters a and b represent the size and stiffness, while D_{ij}, r^*_{ij}, and β_{ij} represent bond energy, equilibrium bond distance, and stiffness.

The calculations were performed for 1,000,000 steps with a time step of 2.5 fs at 1200 K. The atomic behaviors of GaN have been analyzed on the α-Al_2O_3 (0001) surface.

3. Results and Discussion

Figure 1 shows the adsorption models of GaN molecules on α-Al_2O_3 (0001) substrate applied to the periodic DFT calculations. The Al atoms of the bottom layer were changed by the H atoms to compensate the charges of these models. Since the α-Al_2O_3 (0001) surface has two types of Al site with different heights (upper Al site and under Al site, see Fig. 1), we compared the adsorption energies for these sites. As a result, it is suggested that GaN tends to make the Al-N bond on the upper Al site strongly (Fig. 1(a)). This is supposed that the difference of coordination number of surface Al atoms affects the adsorption energies. Furthermore, we investigated the formation of the O-Ga bond and performed energy calculations for the O-Ga bond models (on top site, bridge site, 3-fold site) for this purpose. As a result, it is suggested that the Al-N bond is the most stable on the α-Al_2O_3 (0001) surface.

Figure 2 shows the snapshot of the initial heteroepitaxial growth process of GaN thin films on α-Al_2O_3 (0001) substrate at 1200 K obtained from the MD

calculations. The GaN molecules were deposited at regular time intervals and diffused over the α-Al_2O_3 surface. Since the N atoms of GaN interacted strongly with the Al atoms from α-Al_2O_3, the degree of surface diffusion of N atoms is not so large. Figure 3 illustrates the mean square displacement (MSD) of the Ga and N atoms on the α-Al_2O_3 surface. From this figure, it can be seen that the surface diffusion of the Ga atoms is larger than that of the N atoms. Furthermore, it has been observed that the Ga atoms diffused over the α-Al_2O_3 surface largely and tended to assemble around the step edge of that surface (Fig. 2).

Surface polarity of the GaN films was explained by the formation of more stable chemical bond when GaN attaches on sapphire substrate. Since the Al-N bond energy is stronger than the O-Ga bond energy and α-Al_2O_3 is tend to be terminated with the Al atoms in reductive atmosphere [11], Ga-N=Al-O sequence at the interface is expected to dominate, resulting in Ga termination on the GaN (0001) surface.

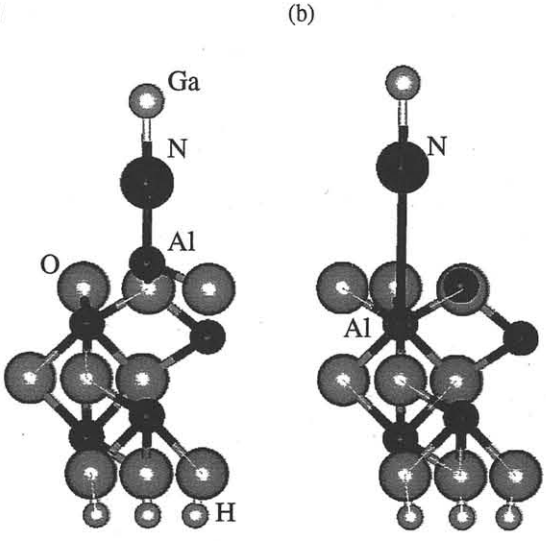

Fig. 1 GaN adsorption models on α-Al_2O_3 (0001) surface (a) upper Al site (b) under Al site.

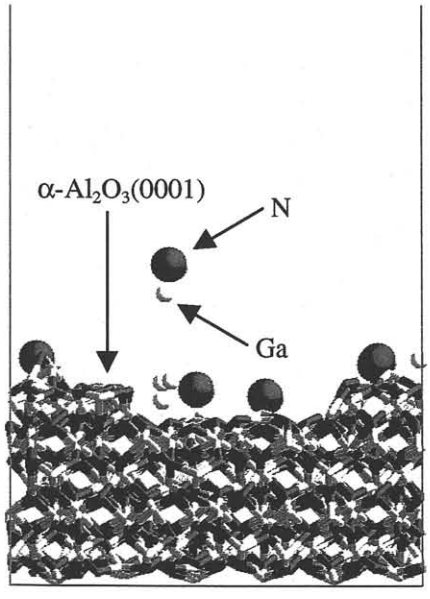

Fig. 2 The snapshot of the initial heteroepitaxial growth process of GaN thin films on the α-Al_2O_3 (0001) substrate at 1200 K.

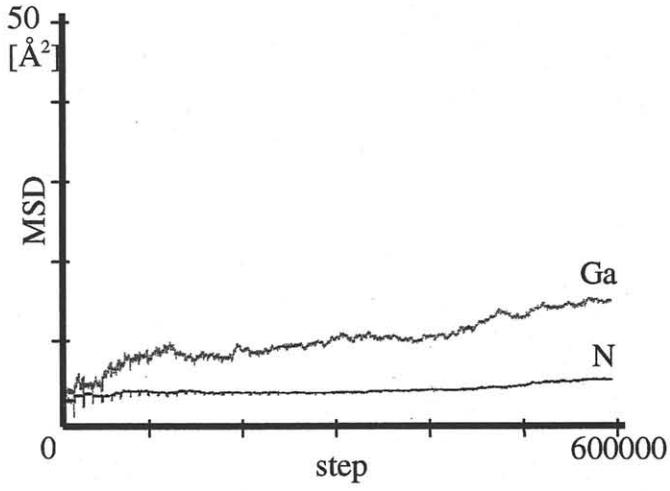

Fig. 3 MSD of the Ga and N atoms on the α-Al_2O_3 (0001) surface.

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