

論文の内容の要旨

論文題目 **Growth mechanisms of InN on zirconia surfaces**
(ジルコニア表面上での InN の成長メカニズム)

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1. Introduction

InN has been considered to be a promising material for the fabrication of high-speed electronic devices because of its high electron mobility and high saturation drift velocity. A growth technique for obtaining high-quality InN films for use in the fabrication of InN-based devices is highly sought after because device performance is often restricted by a high density of threading dislocations caused by large lattice mismatches between the InN films and certain substrates such as sapphire or GaN. Therefore, the use of substrates that result in a small lattice mismatch is critically important. Yttria-stabilized zirconia (YSZ) (111) substrate is an ideal substrate for the growth of *c*-plane InN films because it shares threefold rotational symmetry with the InN (0001) surface and has a lattice mismatch of as small as 2.7%. In fact, InN films have been grown epitaxially on YSZ (111) substrates. However, phenomena that occur during the initial stage of InN growth on YSZ have not yet been well understood on the atomic scale. To understand the growth mechanisms of this material system, it is important to develop a theoretical approach because the experimental techniques that are applicable for this highly resistive substrate are limited. In this work, the initial stages of InN growth on cubic zirconia (111) substrates are discussed on the basis of first-principle calculations.

2. Computational Method

The energy calculations with geometry optimizations were performed within the framework of the density-functional theory (DFT) using the generalized gradient approximation (GGA). Wavefunctions were expanded in a plane-wave basis set with a cutoff energy of 60 Ry. Ultrasoft pseudopotentials were used and the electronic configurations of pseudopotentials for In, N, Y, Zr, and O are $4d^{10}5s^25p^1$, $2s^22p^3$, $4s^24p^64d^15s^2$, $4s^24p^64d^25s^2$, and $2s^22p^4$, respectively. The cubic zirconia (111) slab used in the calculations contained 12 layers that consisted of four sets of O-Zr-O trilayers. Vacuum layers with the thickness of 15 Å were inserted to eliminate interactions between the adjacent slabs. The supercell consisted of a 2×2 array of zirconia (111) surface unit cells and contained 48 atoms. The Brillouin-zone integration was calculated with a $2 \times 2 \times 1$ *k*-point grid which was generated by the Monkhorst-Pack method. Pseudohydrogens were introduced to terminate the dangling bonds on the bottom surface of the slab. Positions of atoms in the slab were optimized with a lattice constant obtained from calculations for a bulk crystal. In this optimization process, the layers in the bottom O-Zr-O trilayer were fixed at the bulk positions, while the top nine layers were fully relaxed. Cubic zirconia (111) surface was employed as Y-segregation-free substrate. In contrast, we replaced the top two Zr layers with Y

layers in cubic zirconia (111) surface and treated it as the Y-segregated substrate after structural optimization.

3. Results and discussion

3.1 Epitaxial relationships of InN on YSZ

Adsorption energies of In and N on the surface were investigated to elucidate the growth mechanism of InN on YSZ (111) substrates at the initial stage. Seven highly-symmetric adsorption sites on the Y-segregation-free YSZ surfaces were selected. These adsorption sites consist of three on-top sites, three bridge sites, and one hollow site. The three on-top sites are labeled as Top O_u , Top Zr, and Top O_d , where O_u (up) is an O atom in the first layer and O_d (down) is an O atom in the third layer. The three bridge sites are labeled as Bridge O_u -Zr, Bridge Zr- O_d , and Bridge O_u - O_d . The hollow site sitting on the center of an O_u atom, a Zr atom, and an O_d atom is labeled as Hollow. On the other hand, five highly-symmetric adsorption sites on the Y-segregated YSZ surfaces were selected. The three on-top sites are labeled as Top O, Top V_o and Top Y. The bridge site is labeled as Bridge Y-O. The hollow site sitting on the center of O, Y, and V_o are labeled as Hollow, where V_o is an oxygen vacancy. Adsorption energies of In and N atoms on Y-segregation-free YSZ surfaces and Y-segregated YSZ surfaces were calculated. It was found that the differences in the adsorption energies of the In atoms at various sites were less than those in the adsorption energies of the N atoms at various sites. This result indicates that the migration of the indium atoms on YSZ (111) surfaces occurs readily. On the other hand, the larger differences in the adsorption energies of the N atoms at various sites suggests that nitrogen atoms tend to stay at the sites with the largest adsorption energy, which are the Bridge O_u -Zr sites and the Top Y sites.

This assumption suggests that the first layer of InN (0001) should be the N layer. The most stable interfacial structures could be deduced from these calculations. It can be readily confirmed that this alignment of atoms leads to the in-plane epitaxial relationship of InN (0001) // YSZ (111) and InN $[11\bar{2}0]$ // YSZ $[1\bar{1}0]$, which is the same as the previously-obtained experimental result.

Furthermore, a detail analysis of the local density of states (DOS) for a nitrogen atom at the surface reveals that the hybridization effect between the $N2p$ and $O2p$ orbitals plays a crucial role in determining the interface structure for the growth of InN on YSZ (111) surfaces. There exists a clear hybridization between $N2p$ and $Zr4d$ on the Y-segregation-free surface. On the other hand, no hybridization between $N2p$ and $Y4d$ is observed on the Y-segregated surface probably due to the difference of the number of valence electrons for Zr and Y atoms. As a result, the adsorption of the nitrogen atom on the Y-segregation-free surface is stable.

3.2 Mechanism of polarity determination for InN/YSZ

It is well known that polarity control of InN (0001) films on YSZ substrates, which have no polarity, is crucial issue because mixture of N-polar and In-polar InN growth affects device performance. Although the polarity control of InN (0001) films on YSZ (111) substrates has been reported, phenomena have not yet been well understood on the atomic scale. Therefore, to understand the mechanism of polarity determination, adsorption energies of an In atom on the nitrogen layer covering Y-segregation-free and Y-segregated YSZ surfaces were calculated. It was found that the growth of In-polar InN on the Y-segregated YSZ surfaces is more stable than that of N-polar InN. On the contrary, the energy difference between In-polar and N-polar InN on the

Y-segregation-free YSZ surfaces is quite small. These results are consistent with previously-reported experimental data.

A detailed analysis of the local DOS was performed. There is clear hybridization between In5s and O2p on the Y-segregated surface. On the other hand, no hybridization between In5s and O2p is observed on the Y-segregation-free surface. These results are attributed to the distance between an In atom and an O atom, and the hybridization between N2p and *d*-orbitals metal cations.

3.3 InN on manganese stabilized zirconia (MnSZ)

Further improvement in crystalline quality of InN films is highly sought after. Therefore, the development of lattice-matched substrates is a crucial issue. Mn-stabilized zirconia (MnSZ) is a promising candidate for a lattice-matched substrate due to a smaller ion radius of Mn³⁺ in comparison with Y³⁺. A substitution of two Mn³⁺ ions for two Zr⁴⁺ ions in substrates generates one oxygen vacancy to maintain electron neutrality.

Adsorption of In and N atoms on the MnSZ (111) surface are investigated to elucidate the growth mechanism at the initial stage of InN growth. Nitrogen atoms are more strongly adsorbed to the surface than indium atoms, suggesting that the first layer of InN (0001) should be a nitrogen layer. These results also lead to the in-plane epitaxial relationships of InN [1120] // MnSZ [110] same as those on YSZ (111) substrates with/without the Y-segregation. Moreover, it was shown that the adsorption of an indium atom preferentially occurs at the center of the three nitrogen atoms stacked on the MnSZ substrate, which leads to the formation of In-polarity InN. All of these results indicate that MnSZ (111) substrates work as lattice-matched substrates to obtain high quality InN films.

4. Summary

Growth mechanisms of InN on cubic zirconia (111) surfaces were investigated by first principles calculation. Calculated adsorption energies reveals that nitrogen atoms are more strongly adsorbed on the zirconia (111) surfaces than indium atoms, suggesting that the first layer of InN (0001) should be a nitrogen layer. These arrangements lead to the experimentally-confirmed epitaxial relationship of InN [1120] // zirconia [110]. These phenomena can be explained by the hybridization between N2p and O2p and that between N2p and *d*-orbitals of metal cations.

Mechanism of polarity determination of InN on Y-segregation-free and Y-segregated surfaces was also investigated. The energy difference between In-polar and N-polar InN on the Y-segregation-free YSZ surface was quite small. On the other hand, In-polar InN on Y-segregated surfaces was more stable than N-polar InN. These results are consistent with the experimental data. The hybridization effect between N2p and *d*-orbital of metal cations plays a crucial role in determining the polarity of InN films on YSZ (111) surfaces. Control of the hybridization between N2p and *d*-orbital of metal cations would be a promising technique to realize the growth of high quality InN films. Theoretical study enables us to investigate the InN growth on the MnSZ substrate when the experiment is limited. The results indicate that the use of MnSZ substrates for growth of InN films is quite promising.