Aluminum nitride (AlN) is an attractive semiconductor material due to its wide bandgap of 6.1 eV and high thermal conductivity.\(^1\) Moreover, AlN is commonly used as a buffer layer for the heteroepitaxial growth of gallium nitride (GaN)\(^2\) because it has both a low lattice mismatch with and a similar thermal expansion coefficient to GaN. In AlN growth, metal-organic vapor phase epitaxy (MOVPE) is the most widely used technique because it is capable of large-area growth and because both the layer thickness and composition can be precisely controlled. However, the growth rate is generally limited by parasitic chemical reactions initiated by trimethyl-aluminum (TMA) and ammonia (NH\(_3\)) precursors.\(^3,4\) Creighton and Wang\(^6\) investigated the early stages of the reaction between TMA and NH\(_3\) using IR spectroscopy and density functional theory (DFT) calculations. They reported a parasitic reaction mechanism in which a TMA-NH\(_3\) adduct was first formed and subsequently decomposed into amide and methane, finally producing amide oligomers. Thus, the chemical pathway through the TMA-NH\(_3\) adduct is believed to cause the parasitic reactions that negatively impact AlN growth. However, the contribution of molecules derived from the parasitic reactions of AlN growth remains unclear, although several kinetic models that consider an AlN growth pathway through adduct-related molecules have been developed.\(^7,9\) Therefore, in the present study, we investigated the possibility of a chemical reaction pathway through the TMA-NH\(_3\) adduct using elementary reaction simulations and DFT calculations.

Elementary reaction simulations were carried out to determine the reactive species using a kinetic model for AlN growth reported by Mihopoulos et al.\(^9\) The basic concept of this growth mechanism is similar to that described by Creighton and Wang.\(^5\) The kinetic model has 10 gas-phase and 7 surface reactions. A perfectly stirred reactor (PSR) was selected for the simulation. In the calculations assuming a PSR, the gas conditions were computationally-optimized by adjusting parameters such as residence time, pressure, and temperature. Additionally, it is assumed that the gas is homogeneous at the moment of gas supply. The residence time of the gas was set to 1 s, the pressure was set to 100 Torr, and the V/III ratio was set to 115. These values were determined by referencing previous reports by Amano\(^10,11\) describing AlN growth with reduced parasitic reactions. The gas temperature was set at 600 °C lower than the surface temperature because the change in temperature at the thermal boundary layer is approximately 300 °C in the growth of nitride systems.\(^12\) The surface temperature was set to between 500 and 1500 °C.

For the gas-phase reactions, two main reaction routes were proposed. The first was the thermal decomposition of TMA into monomethyl-aluminum (MMA) (Route 1). The second involves a pathway through the TMA-NH\(_3\) adduct (Route 2).\(^13,15\) Route 2 includes the formation of a TMA-NH\(_3\) adduct with a negative activation energy, followed by the elimination of methane, thereby producing alkyl-aluminum amide DMA-NH\(_2\) or NH\(_3\):DMA:NH\(_2\). This pathway also leads to the formation of oligomers such as the dimer [DMA-NH\(_2\)]\(_2\) and trimer [DMA-NH\(_2\)]\(_3\), as pointed out by Creighton and Wang.\(^6\) These gas-phase reactions produce reactive species such as TMA, TMA-NH\(_3\), MMA, DMA-NH\(_2\), and [DMA-NH\(_2\)]\(_2\)\(^7\) that can be adsorbed on the AlN surface.

The contribution of each reactive species (S) was calculated based on the Arrhenius-type surface reaction rate. S was defined on the basis of the mole fraction and surface site concentration, which were obtained by elementary reaction simulations, expressed as:

\[
S = k [A]^a [B(s)]^b
\]  

where \(k\) is the Arrhenius rate coefficient, \([A]\) is the gas-phase concentration at the surface, \(a\) is the gas species stoichiometric coefficient, \([B(s)]\) is the surface site concentration, and \(b\) is the stoichiometric coefficient of the adsorbed species.

Figure 1 shows the mole fractions of the Al-containing species at the surface as a function of surface temperature. MMA was produced at 600 °C, and its mole fraction increased with increasing surface temperature. Oligomers were present in large numbers among the reactive species at all surface temperatures.

\(S\) was estimated using the mole fraction indicated in Fig. 1 and the surface site concentration. The obtained \(S\) values are shown in Fig. 2. For surface temperatures greater than 1000 °C, it was found that the AlN growth rate was controlled by the two main reactive species of MMA and DMA-NH\(_2\). Based on its mole fraction, MMA...
was produced at surface temperatures greater than 600 °C, and its contribution to AlN growth increased with increasing surface temperature. The contribution of DMA-NH$_2$ remained high, irrespective of the temperature, since DMA-NH$_2$ was produced in large quantities at all temperatures.

The above results indicate that MMA and DMA-NH$_2$ are important for AlN growth. In order to investigate the behavior of these molecules, we calculated the energies of the associated adsorption and elimination processes on the surface using a program based on the ab initio DFT plane-wave and pseudopotential method. The generalized gradient approximation potential exchange correlation functional was used. The wave function and the charge density cutoff energies were 25 and 225 Ry, respectively. Wurtzite AlN$_{16}$ with lattice parameters of $a = 3.110$ Å and $c = 4.980$ Å was used to construct a slab of 24 supercells. A periodic array of parallel slabs, each separated from its neighbors by 1.8 nm along the surface normal direction, was constructed. The bottom layer of the AlN was terminated by H atoms.

Initially, the AlN surface without any adsorbed molecules was optimized. Next, optimization of the bare AlN surface, which includes a distant adsorbate species, was performed. In the optimization of the bare AlN surface, the distance between the adsorbate and the surface was 1 nm. The energies of the adsorption processes were calculated by comparing the energies of the optimized structures of species-adsorbed and bare AlN surfaces. The calculations were performed for each Al- or N-terminated surface.

Figure 3 shows the growth pathways derived from MMA, as demonstrated in the energy calculations. The calculated energies are listed in Table I. First, TMA decomposes into MMA by thermal energy. The Al atom in MMA is then bound to a surface Al or N atom. The adsorbed energies on Al- and N-terminated surfaces are 1.14 and −6.42 eV, respectively. Therefore, Al atoms in the MMA are tightly bound to the N-terminated surface. Next, methyl radicals are eliminated from the adsorbed MMA. The energy of elimination is −3.04 eV, so the elimination of methyl radicals from adsorbed MMA molecules is a stable reaction. The remaining Al atoms on the surface are then incorporated into the AlN bulk.

The incorporation of MMA is a simple chemical reaction because MMA consists of one Al atom and one methyl group. On the other hand, the chemical pathway through DMA-NH$_2$ is more complicated because DMA-NH$_2$ consists of one Al atom, two methyl groups, and an amino group. In the kinetic model, oligomer formation originating from DMA-NH$_2$ is defined, but the decomposition of DMA-NH$_2$ has not yet been considered. Here, we investigated the DMA-NH$_2$ decomposition using energy calculations. It was assumed that the species generated from the decomposition of DMA-NH$_2$ were CH$_3$, NH$_2$, methyl H, and amino H, as shown in Fig. 4. The energy for DMA-NH$_2$ decomposition was obtained by calculating the difference in stable energy between bare and divided DMA-NH$_2$ molecules. The calculated decomposition energies for each species are summarized in Fig. 4. All of the decomposition energies were approximately 5 eV, too large for the chemical reactions to progress; therefore, the thermal decomposition of DMA-NH$_2$ does not occur in the gas phase.

Table I. Adsorption and elimination energies for MMA, according to DFT calculations.

|                      | Adsorption | Elimination from N$_{surface}$ |
|----------------------|------------|-------------------------------|
|                      | Al-Al$_{surface}$ | Al-N$_{surface}$ | Methyl radical |
| MMA                  | 1.14       | −6.42                         | −3.04          |

Figure 2. Surface reaction rate of Al-containing species calculated from the mole fraction and surface site concentration obtained from elementary reaction simulations. [DMA-NH$_2$]$_3$ is omitted.

Figure 3. Growth process, including gas-phase and surface reaction of AlN through MMA. The molecular structure of MMA and its adsorption and elimination energies at the surface are also shown.

Figure 4. Calculated energies of CH$_3$, NH$_2$, methyl H, and amino H separation from a DMA-NH$_2$ surface.
Table II. Adsorption and elimination energies for DMA-NH₂, according to DFT calculations.

| Adsorption          | Elimination from N_surface |
|---------------------|-----------------------------|
| DMAL-NH₂            |                             |
| Al-Al_surface       | 5.92                        | Methyl radical | −0.06                       |
| Al-N_surface        | −11.97                      | Mehtane        | −0.74                       |
| N-Al_surface        | −3.23                       |               |                             |
| N-N_surface         | 0.55                        |               |                             |

The chemical pathway of AlN growth through DMA-NH₂ is as follows. First, a TMA-NH₃ adduct is formed when a collision occurs between TMA and NH₃. Methane is eliminated from the TMA-NH₃ adduct, and DMA-NH₂ is produced by thermal energy. DMA-NH₂ formed near the substrate is adsorbed on the surface, after which methane elimination occurs, and the Al-N remains on the surface. Finally, the remaining Al-N is incorporated into the AlN bulk. As described above, although a monomolecular amide like DMA-NH₂ causes oligomerization, it also contributes to AlN growth.

In conclusion, the AlN growth pathway through the TMA-NH₃ adduct was investigated using elementary reaction simulations and DFT. The elementary reaction simulations indicated that DMA-NH₂ was one of the main reactive species. The stable-state energies of each reaction through DMAL-NH₂ were obtained, and the detailed growth pathways were determined using DFT calculations. In the pathway through DMA-NH₂, DMA-NH₂ is adsorbed on the surface, followed by the elimination of methane. Furthermore, DMA-NH₂ is not only the causal molecule for oligomerization, but is also one of the primary reactive species for AlN growth.

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