

# Nucleation and growth behavior of aluminum nitride film using thermal atomic layer deposition



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## ABSTRACT

Aluminum nitride (AlN) film possesses wide band gap energy (~6.2 eV) and a high dielectric constant (~9.2), and is resilient to thermal and chemical stimuli. It also exhibits several functionalities, such as piezoelectricity and pyroelectricity. Therefore, AlN film has been used for electronic and optoelectronic devices and micro-electromechanical systems (MEMSs). Among the various methods of AlN thin film growth, atomic layer deposition (ALD) can control film thickness at the nanoscale. Uniform and conformal film growth is possible at temperatures lower than that of chemical vapor deposition or molecular beam epitaxy. Because the ALD process relies on surface chemical reactions, it shows substrate dependency. To control film uniformity from the beginning, an understanding of nucleation and growth behavior on the substrate is necessary. Therefore, the nature of nucleation and growth behaviors on different substrates is investigated. In this study, AlN films are grown on bare Si and TiN substrates at 295–342 °C by thermal ALD using trimethyl aluminum (TMA) and ammonia. Facile nucleation and linear growth on the TiN substrate, and substrate-inhibited nucleation on the Si substrate, are observed. NH<sub>3</sub> pretreatment may enhance the growth rate at the nucleation stage. Therefore, the dissociation of NH<sub>3</sub> on the substrate is crucial to making uniform nuclei for the subsequent growth of AlN film.

## 1. Introduction

Aluminum nitride (AlN) has a variety of characteristics, such as a wide and direct bandgap (~6.2 eV), high dielectric constant (~9.2), high thermal conductivity (285 W/m·K for single crystal), and good thermal and chemical stability [1–4]. On account of its usefulness, AlN thin film has been studied for use in various applications, for instance, ultra violet light emitting diodes, gate dielectrics for field effect transistors and high-electron mobility transistors, actuators, resonators for micro-electromechanical systems (MEMSs), and a resistive switching layer for resistive random-access memory (ReRAM) [2,5–12]. Conventionally, AlN film can be grown through sputtering, metal-organic chemical vapor deposition (MOCVD), and molecular beam epitaxy (MBE). These methods generally require a high processing temperature to the high film quality and throughput requirements [6,8,13–16]. However, in the field of nanoelectronics, it is important to control the thickness of very thin AlN films on three-dimensional structures at relatively low temperatures (< 600 °C), making high-temperature deposition processes unsuitable for this type of purpose [7,17,18].

Atomic layer deposition (ALD), in contrast, can control monolayer-level thickness, uniformity, and step coverage at relatively low temperatures. During the ALD process, thin films are deposited based on chemical surface reactions due to sequential precursor dosing. When a precursor is dosed in the vapor phase, the precursor molecule is chemisorbed on the surface through a self-limiting reaction where only the monolayer reacts, meaning that the surface of a structure with a high aspect ratio can be deposited by thin film. As such, film thickness can be precisely controlled by the number of the reaction cycle [3,19–22].

Recently, various studies have been conducted on depositing AlN thin films using thermal and plasma-enhanced ALD [3,19,23,24]. Moreover, AlN/GaN combinations are in the spotlight for applications of GaN-based power electronics. In many papers, the mechanism of nucleation and growth of ALD-grown AlN layers as a function of surface treatment and their structural and electrical properties have been studied in AlN/GaN system [25–27]. However, the nucleation and growth kinetics of AlN thin films for different substrates are still unknown. It is important to understand the nucleation and growth mechanisms in the early stage of thin film deposition because extremely thin and uniform

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films are necessary in various electronic applications [28,29]. In general, chemical reactions are affected by the chemical and physical nature of the substrate surface. The ideal ALD involves layer-by-layer growth based on a self-limiting reactions that allow for conformality and thickness control [21,30]. However, in reality, ALD processes in the nucleation stage have non-idealities that prevent layer-by-layer growth, which results in nucleation delays and island growth and can lead to a rougher surface morphology. Island growth is more prevalent in thermal ALD than in plasma-enhanced ALD because of the lack of nuclei formation [31,32]. Therefore, to control nonuniformity in the nucleation stage, understanding nucleation and growth behavior on a substrate is necessary.

In this study, we investigated the nucleation and growth behaviors of AlN films on TiN and Si substrates. The metallic TiN substrate is a crucial material because it is widely used in the semiconductor industry as an electrode material. In addition, it has been reported that AlN films on TiN could be useful in the various fields. For example, surface acoustic wave sensors based on AlN thin film were reported with improved performance using TiN nucleation buffer layer as plate electrode. [33] K. Makisev et al. reported TiN/AlN/TiN Josephson junctions on MgO substrates for superconducting qubit applications. [34] More recently, the semiconductor-like AlN/TiN nanolaminated film was combined with graphene to fabricate a vertical heterojunction device. [35] AlN/TiN can form the thermodynamically stable interface, therefore, its combination has been studied as the nitride-based memristors as well. [7,9]. In the thermal ALD process of AlN using trimethylaluminum (TMA) and  $\text{NH}_3$ , the effects of deposition temperature and pretreatment of the surface on the nucleation of AlN film were systematically studied. The dissociative adsorption of  $\text{NH}_3$  by pretreatment on both TiN and Si was effective in enhancing the formation of nuclei and thus suppressing nucleation delay.

## 2. Materials and methods

The AlN films were deposited by thermal ALD using TMA and  $\text{NH}_3$  as a precursor and reaction gas, respectively. The experiments were carried out with Si and TiN substrates in the temperature range of 295–342 °C. A narrow temperature range was utilized because thermal ALD of AlN using TMA and  $\text{NH}_3$  is sensitive to deposition temperature according to previous studies.

Fig. 1 shows the schematics of the ALD cycle and pulse sequence in this experiment. When TMA is injected into the chamber, TMA

molecules are absorbed on the substrates and form a monolayer. Then,  $\text{N}_2$  removes the remaining TMA and reaction byproducts. Next,  $\text{NH}_3$  is injected into the chamber, and it reacts with the absorbed TMA. The byproducts produced by the TMA and  $\text{NH}_3$  reaction are then removed. The precursor pulse condition for the AlN ALD was as follows: TMA pulse (0.5 s),  $\text{N}_2$  purge (5 s),  $\text{NH}_3$  pulse (5 s), and then  $\text{N}_2$  purge (60 s). This ALD cycle was repeated, and the AlN films were grown on each substrate.

To confirm the effects of pretreatment on the initial nucleation stage,  $\text{H}_2\text{O}$  and  $\text{NH}_3$  pretreatments were performed. After 10 cycles of  $\text{H}_2\text{O}$  (1 s) feeding followed by  $\text{N}_2$  (30 s) purging as one cycle, the AlN ALD process was executed.  $\text{NH}_3$  pretreatment also proceeded 10 cycles with  $\text{NH}_3$  feeding (5 s) and an  $\text{N}_2$  (60 s) purging pulse. The thickness of the films was measured by an *ex situ* ellipsometer (FS-1, Film-Sense, USA). To observe the interface between the AlN film and the substrate, cross-sections were prepared using a focused ion beam (FIB; Nova 200, FRI, Netherlands), and imaging was performed using a high-resolution transmission electron microscopy (HRTEM; JEM-2100F, JEOL, Japan).

## 3. Results and discussion

The thickness of AlN film on the Si and TiN substrates was monitored at different growth temperatures. Fig. 2(a) and (b) illustrate the thickness of AlN film on each substrate as a function of the number of the ALD cycle. The growth rate of the AlN film can be acquired using the slope of linear fit in the figure. The growth rate increased as the temperature increased for both substrates. This is because the dissociation of the TMA occurs rapidly with an increasing temperature, while the change in the growth rate was not proportional to that in the temperature; a stronger temperature dependence on the growth rate was observed from 295 °C to 308 °C [17,19]. There is a retarded growth region in the initial cycle for the Si substrate, whereas fluent growth is observed in the beginning for the TiN substrate, which results in thicker film growth on TiN. Table 1 summarizes the growth rates of AlN by temperature and substrate. Here, initial and saturated growth rates are separated to differentiate the transition.

To more closely compare the change in the growth rate and the ALD cycle, growth-per-cycle (GPC) is defined as the derivative of the thickness to the number of cycles. Fig. 3(a) and (b) compare the GPC to the number of cycles of Si and TiN at different temperatures. As shown in Fig. 3 (a), the GPC for Si is lower in the beginning, but it increases with an increase in the number of cycles, which is defined as substrate-

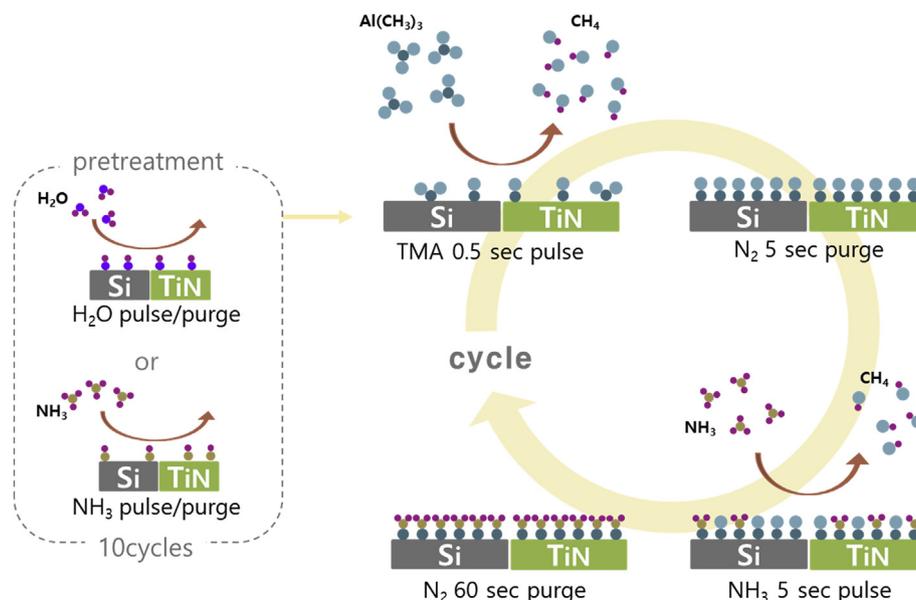


Fig. 1. Schematic of ALD cycle and pulse sequence.

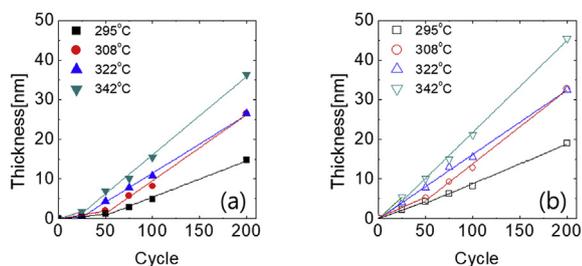


Fig. 2. Growth per cycle of AlN (a) on the Si substrate and (b) on the TiN substrate.

Table 1  
Growth rate of AlN films deposited at 295–342 °C.

Temperature (°C)	Growth rate (Å/cycle)			
	Si		TiN	
	Initial	Saturated	Initial	Saturated
295	0.26	0.92	0.8	0.99
308	0.39	1.66	1.03	1.86
322	0.28	1.52	1.61	1.62
342	0.72	1.97	2.2	2.32

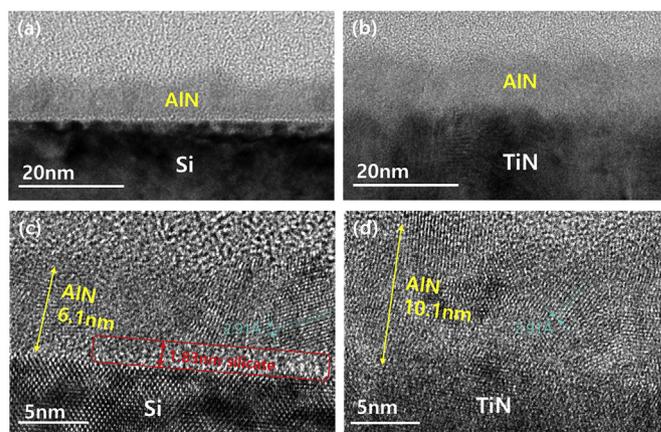


Fig. 4. TEM image of AlN film on the (a) Si and (b) TiN substrates.

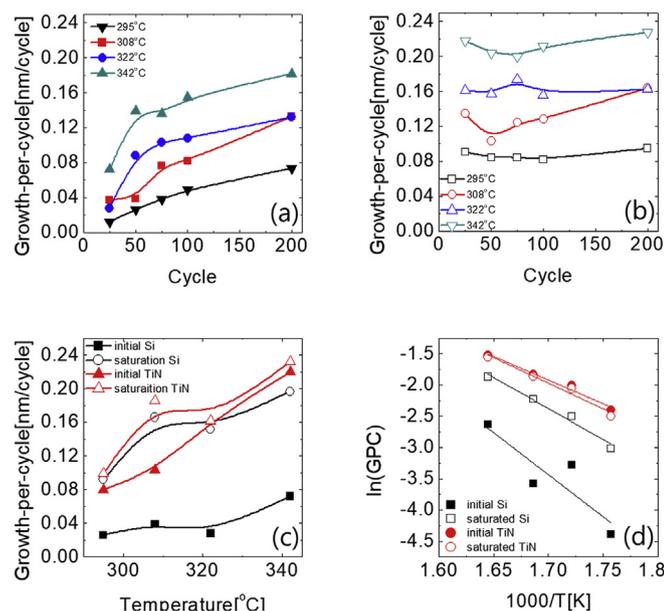


Fig. 3. The dependency of GPC on the number of cycles for (a) the Si substrate and (b) the TiN substrate. (c) The growth rate in a temperature range of 295–342 °C. and (d) an Arrhenius plot.

inhibited growth [36]. This phenomenon occurs because the substrate surface has fewer reaction sites, meaning that many incubation cycles are needed to form the nuclei. Once the surface is covered by the growing film, a saturated GPC may then appear. And then, the recovery of the GPC quickens at elevated temperatures. Nucleation delay is considered to occur because of the low reactivity of precursor molecules combined with fewer reactive sites on the substrate surface; however, the reaction for nucleation can be activated through sufficient thermal energy provided by heating the substrate [37,38].

In contrast, the GPC of the AlN films grown on the TiN substrate is almost constant and without a nucleation delay, as shown in Fig. 3(b). This linear growth behavior generally occurs when the number of reactive sites on the surface is unchanged regardless of an increase in the number of cycles or a change on the surface. In other word, the ratio of

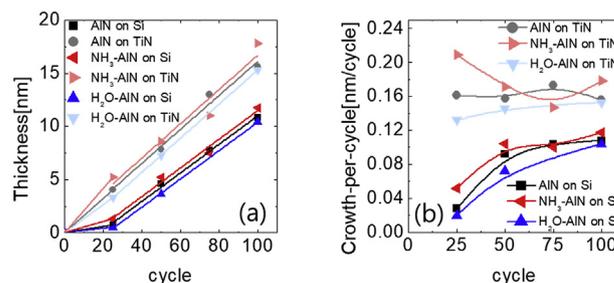


Fig. 5. (a) GPC of the pretreated AlN ( $T_{dep} = 322$  °C). (b) Dependency of the GPC on the number of cycles.

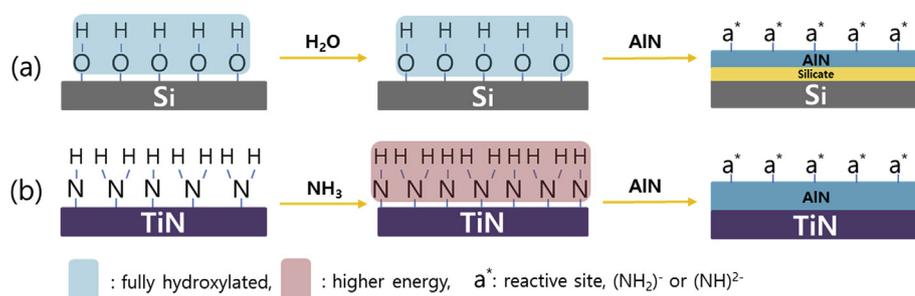
Table 2  
Growth rates of AlN films deposited after H<sub>2</sub>O and NH<sub>3</sub> pretreatment at 322 °C.

Pretreatment	Growth rate (Å/cycle)			
	Si		TiN	
	Initial	Saturated	Initial	Saturated
No treatment	0.28	1.33	1.61	1.59
H <sub>2</sub> O	0.2	1.33	1.32	1.60
NH <sub>3</sub>	0.52	1.34	2.09	1.61

the number of ligands to central species (CH<sub>3</sub>/Al or H/N in this case) of the adsorbed species is kept constant, and the adsorbed species are fully reacted with them [36–38].

In Fig. 3 (c), the GPC of the initial and saturated number of ALD cycles for both substrates are compared as a function of substrate temperature. The GPC of the initial Si is much lower compared to the saturated GPC on subsequent Si or GPCs on TiN. The Arrhenius plots of initial and saturated GPCs are shown in Fig. 3 (d). Based on the slope of Arrhenius plot, the activation energy for the ALD reaction can be calculated. There was a higher activation energy on the initial Si (111.91 J/mol) than that on the saturated Si (82.66 J/mol) or TiN substrate (68.02 J/mol). Therefore, it is concluded that a greater amount of thermal energy is required for the ALD reaction of AlN film on the initial Si substrate [31,32,36–39].

To confirm the microstructure of AlN film and the interface between the film and substrate, cross-sectional TEM images are compared in Fig. 4 (a)–(d). Fifty cycles of AlN films were grown on Si and TiN at 342 °C simultaneously. A rough surface of the AlN film can be observed in Fig. 4 (a) on the cleaned Si which has a smooth surface, whereas the AlN film grew along with the rough surface of TiN in Fig. 4 (b). A high-resolution TEM, as shown in Fig. 4 (c), depicts the crystalline and amorphous mixed phases observed in the AlN deposited on the Si, while



**Fig. 6.** Schematics of nucleation after (a)  $\text{H}_2\text{O}$  and (b)  $\text{NH}_3$  pretreatment. The blue region, the red region and  $\text{a}^*$  represent the fully hydroxylated state, a higher energy state, and a reactive site such as dissociated  $\text{NH}_3$ , respectively. (For interpretation of the references to colour in this figure legend, the reader is referred to the Web version of this article.)

the  $\text{AlN}$  deposited on TiN is observed to be mostly crystalline phase, as shown in Fig. 4 (d). In addition, no interfacial layer was present at the  $\text{AlN}/\text{TiN}$  interface, whereas a thin ( $< 2$  nm) interfacial layer made of amorphous silicate ( $\text{SiAlON}$ ) was observed at the  $\text{AlN}/\text{Si}$ , where the elemental mapping was confirmed by energy dispersive spectroscopy (EDS) in combination with a scanning TEM (data not shown). Previous studies have shown that amorphous  $\text{SiN}_x$  is formed at the  $\text{AlN}/\text{Si}$  interface through interdiffusion between Si and N [14–16,40]. This result may provide the explanation for the nucleation delay on the Si substrate.

Si substrates initially had fewer reactive sites (i.e., surface functional  $\text{OH}^-$  group) than did the TiN substrates. Since  $\text{NH}_3$  has a limited dissociation into  $(\text{NH}_2)^-$  or  $(\text{NH})^{2-}$  on Si at low temperatures ( $< 400$  °C), the TMA can react with these surface functional groups [41–44]. Therefore,  $\text{AlN}$  film initially grows by forming an interfacial silicate layer on Si. Regarding the TiN substrate, the number of reactive sites appears to be nearly the same as that of the growing  $\text{AlN}$  surface, indicating that the GPC on the TiN remains nearly constant.

To confirm the previous explanation for the discrepancy in nucleation, *in-situ* pretreatments of  $\text{H}_2\text{O}$  and  $\text{NH}_3$  reactant gas were performed on both the Si and TiN substrates before the ALD process. Both pretreatments and subsequent  $\text{AlN}$  depositions were proceeded at 322°C. Fig. 5 (a) and (b) show the growth rate and GPC trends after the water and ammonia pretreatments. In general, the hydroxyl group on the surface affected nucleation in the ALD process of oxide films [45–48], but the growth rate of  $\text{AlN}$  appears to be nearly the same irrespective of water pretreatment. Pyeon et al. reported that there is no difference between water pretreatment and no pretreatment in the Pt ALD process because the surface is already hydroxylated before water exposure [46]. Therefore, water pretreatment does not contribute to the increase in the number of reactive sites on Si for the  $\text{AlN}$  nucleation. In contrast, the growth rate of  $\text{AlN}$  on Si and TiN increased after the  $\text{NH}_3$  pretreatment. This is because the ammonia pretreatment effectively raises the surface energy and makes the reaction occur more easily due to the dissociation of  $\text{NH}_3$ . It was reported that dissociated ammonia after pretreatment reduced the nucleation delay of Pt and Cu ALD [46,49,50]. As shown in Fig. 5 (b), both substrates initially showed a higher GPC after  $\text{NH}_3$  pretreatment. Substrate-enhanced growth mode was observed in particular on TiN, which means that the number of reactive sites on TiN after pretreatment was even higher than that of the growing  $\text{AlN}$  film [28,36,46,51] (see Table 2).

The plausible mechanisms of the nucleation of  $\text{AlN}$  on Si and TiN after pretreatment are suggested. As shown in Fig. 6 (a), water pretreatment does not affect the nucleation of  $\text{AlN}$  because the surface is already hydroxylated; therefore, there is no change in site species after the water pretreatment. Fig. 6 (b) shows that ammonia pretreatment promotes nucleation because ammonia increases the number of reaction sites on the substrate, making it easier to grow  $\text{AlN}$  nuclei. It was reported that the ammonia pretreatment could form dissociation of  $\text{NH}_3$  into  $(\text{NH}_2)^-$  or  $(\text{NH})^{2-}$ , which in turn, surface reaction could be further progressed with those  $\text{NH}$ -molecule and subsequent TMA molecule by forming  $\text{Al-NH}_2\text{-Al}$  linkages over the entire surface. [52] Therefore, more reactive sites are formed on the surface by  $\text{NH}_3$  pretreatment,

which increases the energy of reactive sites to makes the subsequent ALD reaction easily to occur.

#### 4. Conclusion

The nucleation and growth behavior of  $\text{AlN}$  films grown using thermal ALD were substrate-dependent. For both the Si and TiN substrates, the growth rate tended to increase as the substrate temperature increased. The nucleation of the  $\text{AlN}$  film was delayed on the Si substrate when compared to the initial and saturated GPC. In contrast, the  $\text{AlN}$  film was grown on the TiN without any nucleation delay. Substrate-inhibited growth on the Si surface was attributed to the fewer reactive sites. Water pretreatment did not enhance the nucleation delay, while an ammonia pretreatment effectively promoted nucleation on both substrates. Therefore, ammonia pretreatment can be applied to grow uniform  $\text{AlN}$  thin film for the thermal ALD process.

#### Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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