Contents lists available at ScienceDirect

Journal of Alloys and Compounds

journal homepage: http://www.elsevier.com/locate/jalcom

Growth of Al-rich AlGaN thin films by purely thermal atomic layer deposition

Seok Choi^a, Abu Saad Ansari^b, Hee Ju Yun^a, Hogyoung Kim^c, Bonggeun Shong^{b, **}, Byung Joon Choi^{a, *}

^a Department of Materials Science and Engineering, Seoul National University of Science and Technology (Seoultech), Seoul, 01811, South Korea

^b Department of Chemical Engineering, Hongik University, Seoul, 04066, South Korea

^c Department of Visual Optics, Seoul National University of Science and Technology (Seoultech), Seoul, 01811, South Korea

ARTICLE INFO

Article history: Received 21 July 2020 Received in revised form 11 September 2020 Accepted 12 September 2020 Available online 15 September 2020

Keywords: Atomic layer deposition Aluminum gallium nitride III-Nitride semiconductor Surface reaction mechanism Dielectric constant

ABSTRACT

AlGaN films with high Al content (Al/Ga ~5.5) were successfully grown via thermal atomic layer deposition at low temperature (342 °C) using trimethylaluminum and triethylgallium as Al and Ga precursors, respectively, and ammonia as reactant gas. Incorporation of GaN into AlN is evidenced by the dependence of the growth rate on the pulse ratio of AlN and GaN subcycles. Chemical analysis reveals the composition of the AlGaN film and the existence of GaN chemical bonding state irrespective of the pulse ratio. Although the chemical composition of AlGaN film was little affected by the pulse ratio between AlN and GaN cycles, the electrical properties of the films could be modulated. Layer-by-layer growth with close to theoretical dielectric constant could be achieved by the introduction of sufficient number of AlN subcycles. Density functional theory calculations were utilized to assess the surface reaction mechanism of the Al and Ga precursors and ammonia reactant during deposition, which show smaller reactivity of the Ga precursor compared to that of Al would affect the doping ratio of the ALD AlGaN films.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

The group III-nitride semiconductors, including AlN, GaN, InN, and their alloys, are key materials in light-emitting diodes and Vis-UV lasers and are being increasingly used in power electronics and high-electron-mobility transistors (HEMTs) [1]. This is mainly because III-nitride semiconductors have a direct and tunable band gap, high saturation drift velocity, and high breakdown field. Among them, AlGaN – a pseudobinary alloy of AlN with a band gap of 6.2 eV and GaN with a band gap of 3.4 eV – has been extensively studied, especially in terms of controlling the ratio of AlN and GaN, and, in doing so, the properties such as wavelengths, band gaps, and lattice constants can be adjusted within a range [2–5]. This controllability has resulted in a variety of applications; short wavelength light is used for full color displays, laser printers, high density information storage, and communication under water [6]. Recently, transistors with Al-rich AlGaN (Al content exceeding 70%)

** Corresponding author.

channel have been attracting more interest owing to the high temperature stability (up to 500 °C), which may be, in the future, useful in automobile engines, advanced power distribution systems, all-electric vehicles, and avionics [6,7].

High-quality III-nitride growth often rely on high temperature chemical processes (>900 °C); molecular-beam epitaxy (MBE) and metalorganic chemical vapor deposition (MOCVD) have been used [8–10]. These processes are difficult to expand to glass and/or flexible substrates as well as Silicon-based CMOS process. To reduce the deposition temperature, plasma enhanced ALD (PEALD) has been used. III-nitrides deposition processes for pure AlN, GaN, and InN, their alloys, and nanolaminates have been reported [11–13]. There are disadvantages related with plasma usage; ions and radiation inside the plasma may limit film conformality when deposited on a high-aspect-ratio structure and damage the substrate or the growing film [14,15]. Therefore, great efforts have been recently focused on reducing the plasma damage and enhancing the homogeneity of the film by using remote plasma source or changing the more reactive precursors [13,16–19].

On the contrary, the growth of AlGaN films using thermal ALD has been rarely reported so far. The necessity of thermal ALDgrown high-quality AlGaN films is that pure thermal process can





^{*} Corresponding author.

E-mail addresses: bshong@hongik.ac.kr (B. Shong), bjchoi@seoultech.ac.kr (B.J. Choi).

enrich the usefulness of III-nitride electronics to realize the various type of lateral transistor structures and novel electronic devices including nanoscale three-dimensional features. For example, different compositions of AlGaN film can be used as barrier, channel, and gate dielectric materials in HEMTs and metal-semiconductor FETs (MESFETs) [7]. We recently reported that thermal ALD-grown AlGaN film on n-type GaN could successfully reduce the gate leakage current by annihilating the oxygen-related defects in the interface of AlGaN/GaN [20,21]. In addition, since nitride compound semiconductors can also serve as memristive switching materials — which is also called as the resistive random access memory — the integration of nitride memristors onto HEMTs is favorable by using the combination of their ALD processes [11].

The current critical issue hindering thermal ALD of AlGaN is the difficulty in choice of the appropriate Al and Ga precursors working in the same temperature range [22]. There have been previous studies regarding thermal ALD of AlN film using trimethyl aluminum (TMA), aluminum chloride, or tris(dimethylamido) aluminum as Al precursors with NH₃ reactant gas [23-26]. However, the process temperature for thermal ALD of AlN was limited to below 370 °C because of thermal decomposition of the Al precursors. On the other hand, Banerjee et al. recently reported that pure thermal ALD of GaN film using trimethyl gallium (TMG) and NH₃ demands higher temperature range of 375-425 °C [27]. It was asserted that the conversion of surface adducts into Ga-NH2-Ga linkages under high pressure (>1 mbar) was essential for the successful deposition of GaN film: otherwise, even higher temperature (>500 °C) would be required. On the other hand, in a recent related theoretical study on ALD of group-III oxides using their trimethyl precursors, we have confirmed that the difference in the reactivity originates from the chemical properties of Al and Ga [28].

In this study, we grew Al-rich AlGaN (Al/Ga ~5.5) thin film on Si and TiN substrates through purely thermal ALD at 342 °C without the aid of plasma. Considering the difficulty of direct growing GaN with NH₃ below 400 °C, a supercycle of GaN and AlN subcycles – a combination of digital pulsing of GaN and AlN film was used [29]. The presence of GaN was investigated by chemical analysis and electrical properties of thin films as a function of the supercycle used. Density functional theory (DFT) calculations elucidated possible surface reactions of precursors and the reactant, revealing the difference in the chemical reactivity between Al and Ga precursors adsorbed on the surface.

2. Experimental

AlGaN thin film was deposited using thermal ALD system (Atomic Classic, CN-1, Korea) at a wafer temperature of 342 °C. TMA (UP Chemical, Korea) and triethyl gallium (TEG; Lake Materials, Korea) were used as metal precursors for Al and Ga, respectively. NH3 and N2 were used as reactant and purge gas, respectively. As established in our previous study, AlN subcycle was composed of TMA feeding (0.5 s) - N₂ purge (5 s) - NH₃ feeding (5 s) - N₂ purge (60 s) [26]. Similarly, GaN subcycle was composed of TEG feeding $(0.3 s) - N_2$ purge $(5 s) - NH_3$ feeding $(5 s) - N_2$ purge (60 s). TMA and TEG were introduced by vapor draw due to their high vapor pressure at room temperature. N₂ purge gas and NH₃ reactant gas were introduced at a flow rate of 200 and 60 SCCM (standard cubic centimeters per minute), respectively. AlGaN thin film was grown either on p-type Si (100) precleaned with acetone and isopropyl alcohol or on TiN sputter-grown on a thermally grown SiO₂/Si wafer. The thickness of a TiN layer was 100 nm.

An ellipsometer (FS-1, Film-Sense, USA) was used to determine the growth rate by measuring the film thickness. X-ray photoelectron spectroscopy (XPS; PHI 5000 Versa Probe, ULVAC-PHI, Japan) with a monochrome Al K α (1488.6 keV) source and auger electron spectroscopy (AES; PHI 700, ULVAC-PHI, Japan) were used for the analysis of chemical composition and bonding state. In the case of XPS, the analysis was performed after surface etching by sputtering for 0.1 min with 2 kV Ar + ions. The microstructure of the film was analyzed by high resolution transmission electron microscopy (HR-TEM; JEM-2100F, JEOL, Japan). Energy dispersive X-ray spectroscopy (EDS; JEM-2100F, JEOL, Japan) was used for the chemical analysis.

DFT calculations were performed using Gaussian 16 program suite [30]. The geometries were optimized using M06L exchangecorrelation functional [31] which is known to have a good performance toward organometallic thermochemistry [32], with def2-TZVP basis set for H, C, N, Al, and Ga atoms and def2-SVP basis set for Si. The substrate surface is modeled as a NH₂-terminated Si(100)-like cluster (Si₁₅H₁₈(NH₂)₂), all of whose atoms were allowed to relax during optimization. The transition state geometries were guessed from relaxed surface scans and confirmed after optimization to have a single imaginary vibrational frequency along the reaction coordinate. The reported energy values are without zero-point energy correction. The bond dissociation energy (BDE) values are obtained for homolytic cleavage of the respective bonds in MX₃ molecules (M = Al or Ga; X = CH₂CH₃ or NHCH₃).

To verify the electrical properties, devices were fabricated using Pt (100 nm) as a top electrode and TiN (100 nm) as a bottom electrode on SiO2/Si substrate. Pt top electrode was deposited via radio frequency sputtering using a shadow mask (diameter: $200 \,\mu$ m). The sputter-grown TiN blanket layer on SiO2 was used as a bottom electrode. A semiconductor parameter analyzer (SPA; HP-4155A, Agilent, USA) was used for measurements of DC current (*I*) – voltage (*V*) curves at room temperature. In addition, LCR meter (HP-4284A, Agilent, USA) was used for capacitance (*C*) – voltage (*V*) measurements at room temperature using the frequency of 500 kHz.

3. Results and discussion

The deposition process was performed using a supercycle consisting of AlN and GaN ALD subcycles as shown in Fig. 1(a). During the deposition, the chamber pressure was approximately 920 mTorr and a substrate temperature was maintained at 342 °C. Fig. 1(b) shows a schematic diagram of various subcycle sequences in a supercycle. The main three kinds of supercycles used had the combination of AlN and GaN subcycles in the ratios of 2:1 (A2G1), 1:1 (A1G1), and 1:2 (A1G2). These supercycles were repeated through the whole deposition process. Maximum temperature of the instrument was selected for the facile ALD reaction but lower than thermal decomposition temperature of precursors.

Thickness of AlGaN films deposited on Si and TiN substrates as a function of the number of total cycles is shown in Fig. 2(a) and (b). Here, total number of cycles is the sum of numbers of AIN and GaN subcycles used during deposition process. The data for AlN [26] and GaN thin films grown on Si and TiN substrates is shown for comparison. Films with the 1:4 ratio (A1G4) and reversed supercycle sequence (G1A1) were also deposited to measure dependence on the pulse ratio and effect of supercycle sequence. Growth rate of a film was acquired as the slope of the linear fitting. AlN thin film showed the highest growth rate, whereas no GaN film was grown on both Si and TiN substrates. Between these two extreme cases, the growth rate decreased in the following order: A2G1, A1G1, A1G2, and A1G4. Therefore, it was concluded that the increase in thickness is mainly affected by the number of AlN subcycles. Regarding G1A1 supercycle deposition, increase in the GPC on both Si and TiN substrates was observed.

To verify the effect of the number of subcycle ratio, the growth per cycle (GPC) - the growth rate obtained from the linear growth



Fig. 1. (a) Schematic of ALD supercycle with AlN and GaN subcycles; (b) three different ALD supercycles for growing AlGaN on Si substrate.

divided by the total number of cycles – is presented as a function of the pulse ratio of AlN subcycle (a/(a+b)) in Fig. 2(c). As stated above, higher GPC could be achieved by increasing the pulse ratio of AlN subcycle. It is also noted that the higher pulse ratio of AlN corresponds to a larger difference between GPC on Si and TiN substrates. It was confirmed that incubation cycle of AlN film was observed on Si substrate, while fluent growth of AlN film was possible on TiN [33]. However, from the results above, it was not confirmed whether GaN was indeed incorporated into the AlN to form AlGaN film.

The growth rate of the supercycle-grown AlGaN per the number of AlN subcycles is shown in Fig. 2(d) to assess whether the GaN subcycle influences the growth of AlN and AlGaN film. It was assumed that only AlN subcycles are reflected in the change of thickness through the GPC value. If there was no difference in the GPC with subcycle ratio, neither GaN was grown nor surface was changed through reconstruction of the surface. However, the data showed that lower GPC values were observed when a subcycle of GaN was added compared to GPC when AlN cycles were only used. In other words, the surface changes by a GaN subcycle affected the subsequent growth during an AlN subcycle. Increasing the number of GaN subcycles led to the lower observed GPC. Therefore, it is considered that the GPC of AlGaN and AlN itself is hindered by a GaN subcycle.

To confirm the incorporation of GaN into AlN, the chemical composition and bonding state were analyzed by XPS. For this purpose, both A1G1 (4.8 nm) on Si and A1G1 (6.9 nm) on TiN were analyzed and compared. The surface analysis was performed after Ar ion sputtering. Ga 2p 3/2, Al 2p, and N 1s spectra for A1G1 on Si are shown in Fig. 3(a)-(c), respectively, and the same spectra for A1G1 on TiN are shown in Fig. 3(d)-(f). First of all, Ga 2p 3/2 spectra shown in Fig. 3(a) and (d) demonstrate the existence of Ga in the



Fig. 2. Thickness of AlGaN thin films as a function of total number of cycles when deposited on (a) Si and (b) TiN substrates. Growth per cycle (GPC) as a function of pulse ratio of AlN subcycle, where the number of cycles is defined as (c) the total number of subcycles (AlN + GaN) and (d) the number of AlN subcycles only.

films. The peak energies for Ga 2p 3/2 spectra were 1118.3 eV for both films on Si and TiN. Using the peak deconvolution, binding energies (BEs) of Ga–N and Ga–O are found to be 1117.9 eV and 1119 eV for Si (1117.8 eV and 1118.9 eV for TiN), while the reported BEs of Ga–N and Ga–O are 1117.6–1118.2 eV and 1120 eV, respectively [34,35]. Thus, although Ga–N is a major bonding state in AlGaN, a considerable amount of Ga–O bonding was also found.

In Fig. 3(b) and (e), XPS spectra of Al 2p show the peak energies of 74.7 and 74.8 eV for A1G1 films on Si and TiN substrates, respectively. The reported BEs for Al-N and Al-O are 73.5-74.7 eV and 74.5–75.6 eV, respectively [36]. From our measurements, by peak deconvolution, the BEs for Al-N are 74.6 eV for both substrates and those for Al-O are 75.4 eV for Si and 75.2 eV for TiN. In Fig. 3(c) and (f), XPS spectra of N 1s show the peak energies of 397.4 eV for the film on Si and 397.2 eV for the film on TiN substrate. The reported BEs of possible bonding states N–Ga, N–Al, and N–O are 396.5-397.4 eV, 396.8-397.9 eV, and 398.4-399 eV, respectively [35–38]. By the peak deconvolution, the BEs of N–Ga are 398.1 eV (Si) and 398.2 eV (TiN), those of N-Al are 397.1 eV (Si) and 397.1 eV (TiN), and those of N-O are 399.5 eV (Si) and 399.5 eV (TiN). In addition, Ga Auger subpeaks were observed in the N 1s spectra. Therefore, there were no significant differences between the BEs for AlGaN films on Si and TiN substrates.

Although the Ga–N bonding state and the formation of AlGaN film was confirmed by XPS analysis, chemical composition of the

films did not depend significantly on the ALD supercycle used. Four samples were analyzed by AES: A2G1 (13.8 nm), A1G1 (12.1 nm), and A1G2 (12 nm) grown on Si and A1G1 (16 nm) deposited on TiN. Fig. 4 (a)-(d) show the depth profile for each element and average atomic concentrations are sum marized in Table 1. The Al/Ga ratio was 7.2 (Al/Ga ~36/5 or 88/12) for A2G1, while it was slightly decreased to 5.5–5.7 (Al/Ga ~85/15) with increasing the number of GaN subcycles. Thus, the Al-rich AlGaN composition was obtained for all supercycles used in this study. The A1G1 film grown on TiN had similar Al/Ga content but less oxygen impurities.

Possible origin of oxygen and carbon impurity is considered. Water and oxygen molecules adsorbed at the surface may react with TMA during the deposition process. Ex-situ surface oxidation after the process could be additional oxygen source. It is probable that oxygen, moisture, and hydrocarbon could be diffused into the film through the grain boundary of columnar structure in the polycrystalline film [39]. In case of TiN substrate, higher crystallinity may lead to the less surface oxidation compared to the film with less crystallinity or amorphous phase. 5–7% of non-negligible C impurity was observed in the depth profiles of all the AlGaN films. It was considered that incomplete ligand removal could be related to C impurity in the film during the deposition process.

To explain the dependence of the GPC of AlGaN on the ALD subcycle ratio, DFT calculations were performed. Fig. 5(a) depicts the reaction coordinate diagrams for the ALD half reactions of TMA



Fig. 3. XPS spectra corresponding to (a,d) Ga 2p3/2, (b,e) Al 2p, and (c,f) N1s measured on A1G1 supercycle-grown AlGaN films on (a-c) Si and (d-f) TiN substrate, respectively.

and TEG on NH2-terminated surface. During a precursor pulse, the precursors are assumed to react with two NH₂ surface sites, converting them to Si(NH)₂-M-R* (M-R = Al–CH₃ for TMA, -Ga-C₂H₅ for TEG; * denoting surface species), according to the following sequential steps.

$$Si(NH_2)_2^* + MR_{3(g)} \rightarrow Si(NH_2)(NH - MR_2)^* + RH_{(g)}\uparrow$$
 (1)

$$Si(NH_2)(NH - MR_2)^* \rightarrow Si(NH)_2(MR)^* + RH_{(g)}\uparrow$$
 (2)

According to the DFT-calculated energies, the adsorption of both TMA and TEG can be expected to be facile upon thermal activation, since both reactions are highly exothermic and involve moderate activation energies (*Ea*; 128 kJ/mol for TMA, 147 kJ/mol for TEG). The observed *Ea* values for precursor adsorption are comparable to those for ALD reactions known to proceed at low temperatures calculated using similar models [40,41].

On the contrary, Fig. 5(b) depicts the reaction coordinate diagram for NH₃ with the Al-CH₃* (Ga-C₂H₅*) surface sites, representing the half reactions during a NH₃ reactant pulse. Noticeably, the reaction of NH₃ on the Ga-C₂H₅* surface shows higher Ea of 189 kJ/mol compared to that of the Al–CH₃* surface (155 kJ/mol). The high barrier on the Ga-C₂H₅* surface would hinder removal of the ethyl group from the Ga-terminated surface. Therefore, while adsorption of Ga on the NH-terminated surface at the first GaN ALD cycle could be allowed, continuous deposition of GaN during its repeated ALD cycles is thermally limited by decreased reactivity of the surface Ga species toward the NH₃ half reaction. Current results explain that the previously reported ALD growth of GaN being achievable at higher temperatures than those for AlN. Furthermore, incorporation of more GaN subcycles in the supercycle deposition of AlGaN would only generate Ga-C₂H₅* moieties on the surface. As a result, even with larger fraction of GaN subcycles, the overall GPC would have decreased from that of AIN ALD, and incorporation of Ga in the film is limited. The chemical origin of the difference in the reactivity for Al and Ga, regardless of adaptation of chemically

similar ligands in the precursors (CH₃ and C₂H₅), could be associated with the differences between Al and Ga in the energies of the bonds that are formed (metal-nitrogen) or cleaved (metal-carbon). The BDEs of [Al–N, Ga–N, Al–C, and Ga–C] bonds are calculated as [409.1, 333.4, 325.5, and 299.4 kJ/mol], respectively. In other words, while Al–C bond is stronger than Ga–C bond for only 26.1 kJ/mol, the strength of Al–N bond is 75.7 kJ/mol greater than that of Ga–N. As a result, substitution of Al–C bond into Al–N bond during the deposition reactions provides greater exothermicity compared to that of Ga–C.

Meanwhile, it seems that PEALD does not suffer from such a Ga deficiency. Ozgit et al. and Nepal et al., independently reported that the growth of AlGaN films with different Ga content was enabled by digital alloying, that is, ALD supercycle [42,43]. By repeating GaN subcycles, Al/Ga ratio could be reached up to $68/32 \sim 2.1$ for 3 GaN subcycles at 200 °C, and even 75% Ga-rich AlGaN film could be achieved for 8 GaN subcycles at 400 °C. In the case of PEALD, NH₃ or N₂/H₂ reactant gas dissociates into NH_x and H radicals with the help of plasma. These radicals recombine with adsorbed Ga clusters on the substrate. Therefore, to achieve higher Ga incorporation by pure thermal ALD process, film growth at higher temperature (≥ 400 °C) or more reactive precursor and reactant gas at the lower temperature should be considered [44,45].

Cross-sectional TEM combined with EDS analysis revealed the formation of AlGaN film and its structural and chemical properties in agreement with the results obtained by XPS and AES analyses. Fig. 6(a) and (d) shows a cross-sectional high resolution TEM image of an AlGaN film grown on Si and TiN substrates using 220 A1G1 supercycles. It can be seen that uniform and smooth film is formed. The film thickness is consistent with the growth rate measured by ellipsometer. Partially crystalline phase is observed, which is similar to that of AlN films grown by thermal ALD [26]. Amorphous ~2 nm-thick layer can be seen, which corresponds to a silicate interfacial layer formed by the reaction of native oxide and adsorbed OH- groups with TMA molecules on the surface of Si substrate. On the other hand, AlGaN film on TiN has denser interface and



Fig. 4. AES depth profiles of elements in AlGaN thin films grown by supercycle (a) A2G1, (b) A1G1, (c) A1G2 on Si, and (d) A1G1 on TiN.

J

 Table 1

 Element composition of AlGaN films grown using different supercycles obtained by AES depth profile.

Supercycle (Substrate)	Al (%)	Ga (%)	N (%)	0 (%)
A2G1 (Si)	36	5	52	7
A1G1 (Si)	33	6	46	15
A1G2 (Si)	34	6	44	16
A1G1 (TiN)	33	7	51	9

larger crystalline phase as shown in Fig. 6(d). That is, no obvious interfacial layer and higher crystallinity are observed. Fig. 6(b) and (c) show a scanning TEM image of the film and the corresponding elemental line profile. The elemental composition of Al, Ga, N, and O in the film were 30, 7, 46, and 17% on Si substrate, respectively. These values agreed well with those obtained from AES analysis. Fig. 6(e) and (f) are those from AlGaN on TiN substrate, where smaller oxygen is detected in the AlGaN/TiN interface.

Although the chemical composition of AlGaN film was marginally affected by the supercycle used, the electrical properties were strongly affected by the deposition process. The I-V characteristics of the Pt/AlGaN/TiN devices were measured to probe the electrical properties. AlGaN films were fabricated using A2G1 (12.1 nm), A1G1 (11.3 nm), and A1G2 (11.1 nm) supercycles. To compensate for the different film thicknesses and device areas, current density (J) – electric field (*E*) curves are presented in Fig. 7(a). As can be seen, current densities of all curves show a similar level, with that of A1G1 slightly lower than those of A2G1 and A1G2 devices. To further differentiate the electrical properties, *J*-*E* curves were fitted using the Pool-Frenkel emission model, as shown in Fig. 7(b). It follows Eq. (3) given below;

$$I = E \exp\left(\frac{-q\left(\Theta_r - \sqrt{qE/(\pi\varepsilon_0\varepsilon_r)}\right)}{k_B T}\right),\tag{3}$$

where *J* is the current density, *E* is the applied electric field, *q* is the elementary charge, \emptyset_r is the trap barrier height (in zero applied electric field) that an electron must cross to move from one atom to another in the site, ε_0 is the vacuum permittivity, ε_r is the dielectric constant, k_B is Boltzmann's constant and *T* is the absolute temperature. By fitting using the model, dielectric constant of the film was obtained from the slopes and Eq. (3).

Furthermore, dielectric constant of AlGaN film could be directly obtained by measuring *C*–*V* characteristics. Fig. 7(c) shows *C*–*V* curves of the A2G1, A1G1 and A1G2 devices. Capacitance formula $C = \varepsilon_0 \varepsilon_r A/d$ was used to find the dielectric constant, where, *A* is the area between parallel electrodes and *d* is the distance between electrodes, that is, the film thickness. Dielectric constants acquired from the Poole-Frenkel plots and *C*–*V* measurements are



Fig. 5. Reaction coordinate diagrams for (a) TMA (black) and TEG (red) on the NH₂ terminated Si (100) surface, and (b) NH₃ on a Al–CH₃* (black) and Ga–C₂H₅* (red) surface site, respectively. Asterisks denote surface species; white, gray, blue, light pink, dark pink, and green balls denote H, C, N, Al, Ga, and Si atoms, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the Web version of this article.)

summarized in Table 2. The results obtained by the two measurements were similar.

In addition to measuring the values, theoretical values for the dielectric constants were calculated for the comparison. Effective medium approximation (EMA) model based on Maxwell-Garnett equation gives the effective dielectric constant in terms of the dielectric constants and the volume fraction of the inclusions in a surrounding medium [46]:

$$\left(\frac{\varepsilon_{eff} - \varepsilon_m}{\varepsilon_{eff} + 2\varepsilon_m}\right) = \delta_i \left(\frac{\varepsilon_i - \varepsilon_m}{\varepsilon_i + 2\varepsilon_m}\right),\tag{4}$$

where ε_{eff} , ε_m and ε_i are the effective dielectric constant of the medium, and the dielectric constants of the matrix and inclusions. δ_i is the volume fraction of the inclusions. Here, it is assumed that the matrix is AlN and the inclusion is GaN. To obtain the effective

dielectric constant, the Maxwell-Garnett equation is solved using the following equation [47,48]:

$$\varepsilon_{\text{eff}} = \varepsilon_m \frac{2\delta_i(\varepsilon_i - \varepsilon_m) + \varepsilon_i + 2\varepsilon_m}{2\varepsilon_m + \varepsilon_i - \delta_i(\varepsilon_i - \varepsilon_m)},\tag{4-1}$$

The volume fraction was estimated using the atomic percentages of Al and Ga from the AES analysis. The dielectric constants used for AlN and GaN were 9.14 and 8.9, respectively [49–51].

The results of theoretical calculations and measurements are summarized in Table 2. According to the theoretical calculations, dielectric constants have similar values of approximately 9.1. However, the experimental values are dependent on the supercycles used to deposit films. The dielectric constant of the A2G1 film is close to the theoretical value, whereas, that of A1G1 shows the largest difference from the EMA model. Therefore, it is considered that A2G1 supercycle deposits the film in the layer-by-



Fig. 6. (a), (c) Cross-sectional high resolution TEM image of an A1G1 supercycle-grown AlGaN film on Si and TiN (inset: electron diffraction pattern); (b), (e) Scanning TEM image and (c), (f) corresponding elemental line profiles by EDS analysis.



Fig. 7. Electrical properties of Pt/AlGaN/TiN devices, where AlGaN films were deposited using A2G1, A1G1, and A1G2 supercycles, respectively. (a) *J*-*E* curves and (b) their fitting results by Poole-Frenkel emission model; (c) *C*-*V* curves.

layer growth mode. Considering the DFT calculations, sufficient (2x) TMA adsorption creates the uniform TMA-NH₃ reaction sites, which result in the uniform TEG adsorption. On the other hand, the

insufficient TMA adsorption by A1G1 and A1G2 supercycles and the incorporation of oxygen-related defects may cause the lower dielectric constant of AlGaN films.

Table 2

Comparison of dielectric constants of AlGaN films acquired by theoretical model (MGA) and experimental methods.

Supercycle	Dielectric constant (ϵ_r)	Dielectric constant (ϵ_r)			
	Theoretical	Measured	Measured		
	Maxwell-Garnett	I–V	C–V		
A2G1	9.106	9.350	9.401		
A1G1	9.097	7.347	7.218		
A1G2	9.098	8.289	8.275		

4. Conclusion

The Al-rich AlGaN films were deposited using thermal ALD with TMA and TEG as Al and Ga metal precursors and NH3 as the reactant gas at 342 °C. Supercycles composed of AlN and GaN subcycles were used to incorporate GaN into AlN thin films. Chemical bonding state of GaN was confirmed through XPS analysis. However, the percentage of Ga atoms in the deposited films was limited to 5-7%. DFT calculations confirmed smaller reactivity of the surface Ga species as the reason for reduced reactivity caused by incorporation of GaN subcycles. TEM analysis revealed the formation of uniform and smooth AlGaN film containing small crystallites within an amorphous matrix. Electrical properties of AlGaN films were affected by the different subcycle ratios of supercycles used for fabricating the films. Electrical measurements demonstrated that the film grown using A2G1 supercycle had the effective dielectric constant that is close to the value predicted by EMA modeling. This implies that A2G1 supercycle is capable of producing AlGaN film in layer-by-layer growth mode by providing enough TMA-NH₃ sites on the surface. Although the amount of incorporated Ga was limited in this work, Al-rich AlGaN film was successfully grown at the relatively low temperature and the growth mechanism was elucidated. This study paves the way for the deposition of Al-rich AlGaN films using a purely thermal ALD process.

CRediT authorship contribution statement

Seok Choi: Conceptualization, Methodology, Investigation, Visualization, Writing - original draft. **Abu Saad Ansari:** Methodology, Software, Investigation, Visualization, Writing - original draft. **Hee Ju Yun:** Investigation, Visualization, Writing - review & editing. **Hogyoung Kim:** Investigation, Writing - review & editing. **Bonggeun Shong:** Conceptualization, Methodology, Software, Writing - review & editing, Supervision. **Byung Joon Choi:** Conceptualization, Methodology, Writing - review & editing, Supervision.

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.

Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF), funded by the Ministry of Education (2017R1D1A1A09000809) and Nano-Material Technology Development Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Science, ICT and Future Planning (2009-0082580). This work was also supported by the National Research Foundation of Korea (NRF) grant funded by the Korea government (MSIT) (NRF-2019R1F1A1058615), and by the National Supercomputing Center with supercomputing resources including technical support (KSC-2018-CHA-0037).

References

- D. Wickramaratne, J.X. Shen, C.E. Dreyer, A. Alkauskas, C.G. Van De Walle, Electrical and optical properties of iron in GaN, AlN, and InN, Phys. Rev. B 99 (2019) 205202.
- [2] F. Yun, M.A. Reshchikov, L. He, T. King, H. Morkoç, S.W. Novak, L. Wei, Energy band bowing parameter in Al_xGa_{1-x}N alloys, J. Appl. Phys. 92 (2002) 4837–4839.
- [3] H. Angerer, D. Brunner, F. Freudenberg, O. Ambacher, M. Stutzmann, R. Höpler, T. Metzger, E. Born, G. Dollinger, A. Bergmaier, S. Karsch, H.J. Körner, Determination of the Al mole fraction and the band gap bowing of epitaxial Al_xGa_{1-x}N films, Appl. Phys. Lett. 71 (1997) 1504–1506.
- [4] Y.C. Tsai, C. Bayram, Structural and electronic properties of hexagonal and cubic phase AlGaInN alloys investigated using first principles calculations, Sci. Rep. 9 (2019) 6583.
- [5] S. Zhao, S.Y. Woo, S.M. Sadaf, Y. Wu, A. Pofelski, D.A. Laleyan, R.T. Rashid, Y. Wang, G.A. Botton, Z. Mi, Molecular beam epitaxy growth of Al-rich AlGaN nanowires for deep ultraviolet optoelectronics, Apl. Mater. 4 (2016), 086115.
- [6] S.C. Jain, M. Willander, J. Narayan, R. Van Overstraeten, III-nitrides, Growth, characterization, and properties, J. Appl. Phys. 87 (2000) 965–1006.
- [7] A.G. Baca, A.M. Armstrong, B.A. Klein, A.A. Allerman, E.A. Douglas, R.J. Kaplar, Al-rich AlGaN based transistors, J. Vac. Sci. Technol. 38 (2020), 020803.
- [8] F. Nakamura, S. Hashimoto, M. Hara, S. Imanaga, M. Ikeda, H. Kawai, AlN and AlGaN growth using low-pressure metalorganic chemical vapor deposition, J. Cryst. Growth 195 (1998) 280–285.
- [9] P. Ruterana, G. De Saint Jores, M. Laügt, F. Omnes, E. Bellet-Amalric, Evidence for multiple chemical ordering in AlGaN grown by metalorganic chemical vapor deposition, Appl. Phys. Lett. 78 (2001) 344–346.
- [10] S. Tamariz, D. Martin, N. Grandjean, AlN grown on Si(111) by ammoniamolecular beam epitaxy in the 900–1200 °C temperature range, J. Cryst. Growth 476 (2017) 58–63.
- [11] B.J. Choi, A.C. Torrezan, J.P. Strachan, P.G. Kotula, A.J. Lohn, M.J. Marinella, Z. Li, R.S. Williams, J.J. Yang, High-speed and low-energy nitride memristors, Adv. Funct. Mater. 26 (2016) 5290–5296.
- [12] C. Ozgit, I. Donmez, M. Alevli, N. Biyikli, Atomic layer deposition of GaN at low temperatures, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 30 (2012), 01A124.
- [13] P. Deminskyi, P. Rouf, I.G. Ivanov, H. Pedersen, Atomic layer deposition of InN using trimethylindium and ammonia plasma, J. Vac. Sci. Technol. 37 (2019), 020926.
- [14] H.B. Profijt, S.E. Potts, M.C.M. van de Sanden, W.M.M. Kessels, Plasma-Assisted atomic layer deposition: basics, opportunities, and challenges, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 29 (2011), 050801.
- [15] A.Y. Kovalgin, M. Yang, S. Banerjee, R.O. Apaydin, A.A.I. Aarnink, S. Kinge, R.A.M. Wolters, Hot-wire assisted ALD: a study powered by in situ spectroscopic ellipsometry, Adv. Mater. Interfaces 4 (2017) 1700058.
- [16] P. Rouf, N.J. O'Brien, S.C. Buttera, I. Martinovic, B. Bakhit, E. Martinsson, J. Palisaitis, C.-W. Hsu, H. Pedersen, Epitaxial GaN using Ga(NMe₂)₃ and NH₃ plasma by atomic layer deposition, J. Mater. Chem. C. (2020) 8457–8465.
 [17] A. Mohammad, D. Shukla, S. Ilhom, B. Willis, B. Johs, A.K. Okyay, N. Biyikli,
- [17] A. Mohammad, D. Shukla, S. Ilhom, B. Willis, B. Johs, A.K. Okyay, N. Biyikli, Real-time in situ ellipsometric monitoring of aluminum nitride film growth via hollow-cathode plasma-assisted atomic layer deposition, J. Vac. Sci. Technol. 37 (2019), 020927.
- [18] P. Ma, J. Sun, G. Zhang, G. Liang, Q. Xin, Y. Li, A. Song, Low-temperature fabrication of HfAlO alloy dielectric using atomic-layer deposition and its application in a low-power device, J. Alloys Compd. 792 (2019) 543–549.
- [19] H.C.M. Knoops, T. Faraz, K. Arts, W.M.M. (Erwin, Kessels, Status and prospects of plasma-assisted atomic layer deposition, J. Vac. Sci. Technol. 37 (2019), 030902.
- [20] H. Kim, S. Choi, B.J. Choi, Influence of AlN and GaN pulse ratios in thermal atomic layer deposited AlGaN on the electrical properties of AlGaN/GaN Schottky diodes, Coatings 10 (2020) 489.
- [21] H. Kim, S. Choi, B.J. Choi, Forward current transport properties of AlGaN/GaN Schottky diodes prepared by atomic layer deposition, Coatings 10 (2020) 194.
- [22] M. Leskelä, M. Mattinen, M. Ritala, Review Article: atomic layer deposition of optoelectronic materials, J. Vac. Sci. Technol. B 37 (2019), 030801.
- [23] H. Van Bui, M.D. Nguyen, F.B. Wiggers, A.A.I. Aarnink, M.P. de Jong, A.Y. Kovalgin, Self-limiting growth and thickness- and temperature- dependence of optical constants of ALD AlN thin films, ECS J. Solid State Sci. Technol. 3 (2014) 101–106.
- [24] Z. Chen, Z. Zhu, K. Härkönen, E. Salmi, Batch processing of aluminum nitride by atomic layer deposition from AlCl 3 and NH 3, J. Vac. Sci. Technol. 37 (2019), 020925.
- [25] G. Liu, E. Deguns, L. Lecordier, G. Sundaram, J. Becker, Atomic layer deposition of AlN with tris(Dimethylamido)Aluminum and NH, ECS Trans 41 (2011) 219–225.
- [26] Y. Kim, M.S. Kim, H.J. Yun, S.Y. Ryu, B.J. Choi, Effect of growth temperature on AlN thin films fabricated by atomic layer deposition, Ceram. Int. 44 (2018)

S. Choi, A.S. Ansari, H.J. Yun et al.

17447-17452.

- [27] S. Banerjee, A.A.I. Aarnink, D.J. Gravesteijn, A.Y. Kovalgin, Thermal atomic layer deposition of polycrystalline gallium nitride, J. Phys. Chem. C 123 (2019) 23214–23225.
- [28] A.S. Ansari, S.S. Raya, B. Shong, Mechanistic investigation on thermal atomic layer deposition of group 13 oxides, J. Phys. Chem. C 124 (2020) 17121–17134.
- [29] J. Sheng, E.J. Park, B. Shong, J.S. Park, Atomic layer deposition of an indium gallium oxide thin film for thin-film transistor applications, ACS Appl. Mater. Interfaces 9 (2017) 23934–23940.
- [30] M.J. Frisch, G.W. Trucks, H.B. Schlegel, G.E. Scuseria, M.A. Robb, J.R. Cheeseman, G. Scalmani, V. Barone, G.A. Petersson, H. Nakatsuji, X. Li, M. Caricato, A.V. Marenich, J. Bloino, B.G. Janesko, R. Gomperts, B. Mennucci, H.P. Hratchian, J.V. Ortiz, A.F. Izmaylov, J.L. Sonnenberg, D. Williams-Young, F. Ding, F. Lipparini, F. Egidi, J. Goings, B. Peng, A. Petrone, T. Henderson, D. Ranasinghe, V.G. Zakrzewski, J. Gao, N. Rega, G. Zheng, W. Liang, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, K. Throssell, J.A. Montgomery Jr., J.E. Peralta, F. Ogliaro, M.J. Bearpark, J.J. Heyd, E.N. Brothers, K.N. Kudin, V.N. Staroverov, T.A. Keith, R. Kobayashi, J. Normand, K. Raghavachari, A.P. Rendell, J.C. Burant, S.S. Iyengar, J. Tomasi, M. Cossi, J.M. Millam, M. Klene, C. Adamo, R. Cammi, J.W. Ochterski, R.L. Martin, K. Morokuma, O. Farkas, J.B. Foresman, D.J. Fox, Gaussian 16, Gaussian Inc., Wallingford CT, 2016.
- [31] Y. Zhao, D.G. Truhlar, A new local density functional for main-group thermochemistry, transition metal bonding, thermochemical kinetics, and noncovalent interactions, J. Chem. Phys. 125 (2006) 194101.
- [32] D.G. Gusev, Assessing the accuracy of M06-L organometallic thermochemistry, Organometallics 32 (2013) 4239–4243.
- [33] H.J. Yun, H. Kim, B.J. Choi, Nucleation and growth behavior of aluminum nitride film using thermal atomic layer deposition, Ceram. Int. 46 (2020) 13372–13376.
- [34] S. Banerjee, A.Y. Kovalgin, A comparative study of low-temperature III-V nitrides ALD in thermal and radical-enhanced modes, ECS Trans 86 (2018) 21–29.
- [35] R. Stoklas, D. Gregušová, M. Blaho, K. Fröhlich, J. Novák, M. Matys, Z. Yatabe, P. Kordoš, T. Hashizume, Influence of oxygen-plasma treatment on AlGaN/ GaN metal-oxide-semiconductor heterostructure field-effect transistors with HfO₂ by atomic layer deposition: leakage current and density of states reduction, Semicond. Sci. Technol. 32 (2017), 045018.
- [36] P. Motamedi, K. Cadien, XPS analysis of AlN thin films deposited by plasma enhanced atomic layer deposition, Appl. Surf. Sci. 315 (2014) 104–109.
- [37] M. Alevli, A. Haider, S. Kizir, S.A. Leghari, N. Biyikli, Comparison of trimethylgallium and triethylgallium as "Ga" source materials for the growth of ultrathin GaN films on Si (100) substrates via hollow-cathode plasma-assisted

Journal of Alloys and Compounds 854 (2021) 157186

atomic layer deposition, J. Vac. Sci. Technol. A Vacuum, Surfaces, Film. 34 (2016), 01A137.

- [38] Q. Wang, X. Cheng, L. Zheng, L. Shen, J. Li, D. Zhang, R. Qian, Y. Yu, Interface engineering of an AINO/AlGaN/GaN MIS diode induced by PEALD alternate insertion of AIN in Al₂O₃, RSC Adv. 7 (2017) 11745–11751.
- [39] K.S.A. Butcher, H. Timmers, Afifuddin, P.P.T. Chen, T.D.M. Weijers, E.M. Goldys, T.L. Tansley, R.G. Elliman, J.A. Freitas, Crystal size and oxygen segregation for polycrystalline GaN, J. Appl. Phys. 92 (2002) 3397–3403.
- [40] T.T. Ngoc Van, A.S. Ansari, B. Shong, Surface chemical reactions during atomic layer deposition of ZnO, ZnS, and Zn(O,S), J. Vac. Sci. Technol. 37 (2019), 020909.
- [41] S. Seo, T. Nam, H.B.R. Lee, H. Kim, B. Shong, Molecular oxidation of surface $-CH_3$ during atomic layer deposition of Al_2O_3 with H_2O , H_2O_2 , and O_3 : a theoretical study, Appl. Surf. Sci. 457 (2018) 376–380.
- [42] N. Nepal, V.R. Anderson, J.K. Hite, C.R. Eddy, Growth and characterization of III-N ternary thin films by plasma assisted atomic layer epitaxy at low temperatures, Thin Solid Films 589 (2015) 47–51.
- [43] C. Ozgit-Akgun, E. Goldenberg, A.K. Okyay, N. Biyikli, Hollow cathode plasmaassisted atomic layer deposition of crystalline AlN, GaN and Al_xGa_{1-x}N thin films at low temperatures, J. Mater. Chem. C. 2 (2014) 2123–2136.
- [44] P. Rouf, N.J. O'Brien, S.C. Buttera, I. Martinovic, B. Bakhit, E. Martinsson, J. Palisaitis, C.W. Hsu, H. Pedersen, Epitaxial GaN using Ga(NMe₂)₃ and NH₃ plasma by atomic layer deposition, J. Mater. Chem. C. 8 (2020) 8457–8465.
- [45] Y.C. Jung, S.M. Hwang, D.N. Le, A.L.N. Kondusamy, J. Mohan, S.W. Kim, J.H. Kim, A.T. Lucero, A. Ravichandran, H.S. Kim, S.J. Kim, R. Choi, J. Ahn, D. Alvarez, J. Spiegelman, J. Kim, Low temperature thermal atomic layer deposition of aluminum nitride using hydrazine as the nitrogen source, Materials 13 (2020) 3387.
- [46] T.C. Choy, Effective Medium Theory, Clarendon Press, Oxford, 1999.
- [47] O. Levy, D. Stroud, Maxwell Garnett theory for mixtures of anisotropic inclusions: application to conducting polymers, Phys. Rev. B Condens. Matter 56 (1997) 8035–8046.
- [48] T. Liu, Y. Pang, M. Zhu, S. Kobayashi, Microporous Co@CoO nanoparticles with superior microwave absorption properties, Nanoscale 6 (2014) 2447–2454.
- [49] A. Konar, T. Fang, D. Jena, Effect of high-κ gate dielectrics on charge transport in graphene-based field effect transistors, Phys. Rev. B Condens. Matter 82 (2010) 115452.
- [50] Q. Qian, B. Li, M. Hua, Z. Zhang, F. Lan, Y. Xu, R. Yan, K.J. Chen, Improved gate dielectric deposition and enhanced electrical stability for single-layer MoS₂ MOSFET with an AIN interfacial layer, Sci. Rep. 6 (2016) 27676.
- [51] Y. Wang, D. Zheng, L. Li, Y. Zhang, Enhanced efficiency of flexible GaN/ perovskite solar cells based on the piezo-phototronic effect, ACS Appl. Energy Mater. 1 (2018) 3063–3069.