Atomic layer deposition of AlN using trimethylaluminium and ammonia

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Abstract. Thin AlN films were grown in a Picosun R-200 atomic layer deposition (ALD) reactor on Si substrates. Trimethylaluminium (TMA) and NH3 were used as precursors; the substrates were cleaned in-situ by H2 and N2 plasma. The surface morphology of the films grown was studied in the temperature range 350 – 450°C. The films’ crystalline structure was investigated by grazing incidence X-ray diffraction. The AlN films were polycrystalline with a hexagonal wurtzite structure regardless of the substrate temperature.

The results of scanning electron microscopy (SEM) revealed nanometer-sized crystallites, with the size increasing from 10 nm to 30 nm as the deposition temperature was increased. The results are promising in view of further studies of the properties of thin AlN films.

1. Introduction
Aluminium nitride (AlN), which belongs to the class of III-nitride semiconductors, possesses many outstanding properties, such as a wide direct bandgap (~6.2 eV at 300°C), a high thermal conductivity (320 W/mK at 300 K), a high chemical stability (2500 K), a low dielectric constant (ε0 = 8), and a high sound velocity (~105 cm/s) [1-6]. AlN is a promising material for diverse applications, for example, it has been shown that AlN can be used in surface acoustic wave (SAW) devices [7-8], as a buffer layer for GaN growth [9] in gas sensors [11] and as a surface passivation layer in surface-channel field-effect transistors [11]. AlN has been grown by several methods, including sublimation [12-13], metalorganic chemical vapor deposition (MOCVD) [14], magnetron sputter deposition [15] and molecular beam epitaxy (MBE). Although MOCVD offers the ability to deposit high-quality materials at significant growth rates, deposition of AlN requires high temperatures (>1000 °C) [16]. Hence, the process temperature in this method is over 400 °C, which may be too high for many applications.

Atomic layer deposition (ALD) is a chemical thin-film deposition technique based on sequential surface-limited reactions. Gaseous precursors are alternately supplied to the substrate. Between reactant pulses, the process chamber is purged with inert carrier gas. Unless decomposition of the precursor occurs, each pulse leads to surface reactions that terminate after the adsorption of a single monolayer. In an ideal case, the surface reactions are self-controlled and the film thickness can be accurately regulated by the number of deposition cycles [17-19].

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In this paper, we report studies on the growth temperature effect on the surface morphology and crystalline structure of AlN prepared by ALD.

2. Experimental details

AlN thin films were grown in a Picosun R-200 reactor without a load-lock chamber at a total pressure of 6 hPa. TMA (trimethylaluminium) and NH3 (ammonia) were used as precursors; N2 and H2 plasma was used to pre-treat the substrate prior to growing the AlN films. One cycle of AlN deposition consisted of a TMA pulse (carried by 100 sccm N2, 0.5 s), a purge with N2 for 10 s, exposure to NH3/Ar (300/100 sccm, 40 s), followed by a 10-s purge; the AlN cycle was then repeated until the desired thickness (~100 nm) was obtained. The schematic of the ALD cycle for AlN deposition is shown in figure 1.

![Figure 1. Schematic of the ALD cycle for AlN deposition.](image)

The substrates used were Si(100) wafers. They were sequentially boiled in acetone, 2-propanol and deionized water and dried in an N2 flow. The thickness of the deposited films was measured by a PanAnalytical X’Pert Pro apparatus in an X-ray reflectometry mode. X-ray diffraction (XRD) analysis was performed to determine the crystallinity of the AlN films by using an Empyrean PanAnalytical X’Pert system with a Philips Bragg-Brentano diffractometer equipped with a parallel beam detector. The Cu Kα radiation source (λ = 0.154 nm) was operated at 40 kV and 40 mA. A grazing-incidence X-ray diffraction (GIXRD) mode was used to minimize the intensity from the substrate peaks, because of the films’ small thickness. The surface morphology of the samples was studied using a high-resolution Leo 1550 Gemini field-emission scanning electron microscope (SEM).

3. Results and discussion

The AlN ALD process has a temperature range of ~400 – 425 °C that we defined as the working temperature window (figure 2a), where growth saturation may be observed. The temperature of 400 °C was used to study the growth-rate variation with the TMA pulse time, which was varied in the range 0.1 – 0.7 s in order to obtain the exposure time required for the reaction to reach saturation. The average saturated growth-rate values for TMA pulse times of 0.1 – 0.7 s were measured to be within the range 2.6 – 2.67 Å/cycle (figure 2b).

The thin AlN films deposited at 400 °C were polycrystalline, as detected by GIXRD. The polycrystalline wurtzite structure of AlN is clearly visible in the recorded GIXRD spectrum (figure 3), where (100), (002), (101), (304), (112) and (104), and (112) reflections of the hexagonal phase are observed. The broad peak near 55° can be attributed to the oxygen content in the film.

The lattice parameters a and c were calculated using the 26 positions of the (002) and (101) reflections. The interplanar spacings (d_{hkl}) of the (002) and (101) planes were calculated from Bragg’s law and were inserted in equation (1) to obtain the a-axis and c-axis lattice parameters, which were thus calculated to be 3.12 Å and 5.02 Å. They are in good agreement with earlier results [20].

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\frac{1}{d^2} = \frac{4}{3} \left( \frac{h^2 + hk + k^2}{a^2} + \frac{l^2}{c^2} \right)
\]
Figure 2. Growth per cycle for AlN/Si(100) processes in the 350 - 450 °C temperature range (a) and for different TMA pulse times (b).

Figure 3. GIXRD pattern of a ~100-nm thick AlN film deposited on Si(100). The film is polycrystalline with a hexagonal wurtzite structure.

Figure 4. Top-view SEM images of AlN films deposited at 350, 400, 450 °C.

Figure 4 shows top-view SEM images of AlN films grown at different deposition temperature (350 – 450 °C). The AlN films consist of uniform crystallites of nanometer size, which increases from 10 nm to 30 nm as the deposition temperature is increased. This can be explained by the lower concentration of initially-formed nuclei and their lateral expansion due to the higher surface diffusion of adatoms at higher deposition temperature.

4. Conclusions
In this study, we deposited thin crystalline AlN films on Si(100) by ALD from TMA and NH$_3$ within the 350 – 450 °C temperature range after N$_2$ and H$_2$ plasma substrate pre-treatment. The thin AlN films were polycrystalline with a hexagonal wurtzite structure regardless of the substrate temperature. The SEM analysis revealed crystallites of size of about 30 nm for the AlN film grown at 450 °C due to the lateral growth being favored at higher deposition temperatures. These results are a good prerequisite in establishing the growth conditions suitable for synthesis of thin AlN layers by self-limiting ALD.

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