Initial conditions for preparation of thin AlN films by atomic layer deposition

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Abstract. Thin AlN films were grown on Si substrates in a Beneq TFS-200 ALD reactor. The atomic layer deposition (ALD) process consisted of two half cycles – aluminum adsorption and nitridization separated by a purging step. TMA (trimethylaluminum) and NH3 were used as precursors, and nitrogen (N2), as a carrier gas. The pulse duration, purging time, deposition temperature and other deposition conditions were varied to obtain AlN films with desired properties. The X-ray diffraction (XRD) data showed that the AlN films had an amorphous character. The films’ chemical composition and bonding states were investigated by X-ray photoelectron spectroscopy. The high resolution Al 2p and N 1s spectra confirmed the presence of AlN with peaks located at 74.1 eV and 397.7 eV, respectively, for all layers.

1. Introduction

Aluminum nitride (AlN) is a large band gap (~6.2 eV) III-V compound with high thermal conductivity (320 W/mK at 300 K), high chemical stability (2500 K), good dielectric properties and low expansion at high temperature [1-6]. When prepared in the form of thin films, AlN finds applications as an insulator for thin-film transistors [7], surface acoustic wave devices (SAW) [8-9], active layers [10] for extreme UV light-emitting diodes and photodetectors, gas sensors [11] and surface passivation layers for surface-channel field-effect transistors [12]. AlN has been grown by several methods, including sublimation [13-14], metalorganic chemical vapor deposition (MOCVD) [15], magnetron sputter deposition [16] and pulsed laser deposition.

Although MOCVD offers capabilities of depositing high-quality materials at a significant growth rates, deposition of AlN requires high temperatures (>1000 °C) [17]. Atomic layer deposition (ALD) is
a special type of low-temperature chemical vapor deposition whereby the substrate surface is exposed to sequential pulses of two or more precursors separated by purging periods by an inert carrier gas [18, 19]. Under precisely adjusted experimental conditions, i.e. deposition temperature, reactant dose, length of the precursor and purge pulses, each pulse leads to surface reactions that terminate after the adsorption of one monolayer. The ALD stands out with its self-limiting growth mechanism, which enables one to prepare thin films of high uniformity and conformality, while controlling their thickness on a sub-nanometer scale by the number of deposition cycles [20-22].

The aim of this study was to establish the conditions for deposition of thin AlN films of small thickness. The effects were studied of the deposition temperature, the reactant dose length of the precursors and the number of deposition cycles on the growth rate, crystalline structure, surface morphology and chemical composition of the films.

2. Experimental details
The thin AlN films were deposited on pre-cleaned substrates at temperatures ranging from 300-340 °C in a Beneq TFS-200 ALD apparatus. A schematic diagram of the equipment is shown in figure 1.

![Figure 1. Schematics of the ALD and the pulsing technique.](image-url)

TMA (trimethylaluminum) and NH₃ (ammonia) were used as precursors, and N₂ (nitrogen), as a carrier gas. Prior to deposition, Si(100), Si(111) and Si/SiO₂ substrates were cleaned by sequential boiling in acetone and ethanol and rinsing in deionized water, dried by a N₂ flow, and then loaded in the growth chamber. The deposition conditions are summarized in table 1.

Ellipsometric spectra of the films were recorded in the wavelength range of 193–1000 nm at three angles of incidence (55°, 65°, and 75°) by a Woollam M2000D rotating compensator spectroscopic ellipsometer. The data acquisition and analysis software used was CompleteEASE 5.10 J.A.Woollam Co., Inc.

| Sample | Substrate | Temp. °C | TMA Pulse (ms) | NH₃ Purge (s) | NH₃ Pulse (ms) | NH₃ Purge (s) | AlN films thickness (nm) |
|--------|-----------|----------|---------------|---------------|---------------|---------------|--------------------------|
| AlN-1  | p-Si(100) | 340      | 180           | 1             | 30            | 9             | 500                      | 16                       |
| AlN-2  | p-Si(100) | 340      | 180           | 2             | 30            | 9             | 1500                     | 83                       |
| AlN-3  | Si/SiO₂   | 340      | 180           | 2             | 30            | 9             | 500                      | 9                        |
| AlN-4  | p-Si(111) | 330      | 180           | 2             | 60            | 9             | 550                      | 26                       |
| AlN-5  | Si/SiO₂   | 330      | 180           | 2             | 60            | 9             | 550                      | 26                       |
The optical constants of the AlN layers were assumed to be isotropic. The values used for the optical constants of the silicon substrate, the silicon native oxide and the silicon thermal oxide were taken from the CompleteEASE software database.

The thin AlN film thicknesses were represented by the Cauchy dispersion function [23].

Powder X-ray diffraction (XRD) patterns were collected within the range 20° to 60° 2θ with a constant step of 0.03° 2θ and counting time 52.5 sec./step on a Bruker D8 Advance diffractometer (Germany) with Cu Kα radiation and a LynxEye detector. Phase identification was performed by the Diffracplus EVA using the ICDD-PDF2 Database. The surface morphology of the samples was studied by an MFP-3D Asylum Research (Oxford Instruments) atomic force microscope operating in a non-contact AC mode using Si tips. The chemical composition and bonding states of the AlN films were determined by X-ray photoelectron spectroscopy (XPS) using a Kratos AXIS Supra spectrometer with a non-monochromatic Mg X-ray source. Each analysis started with a survey scan from 0 – 1200 eV, pass energy of 160 eV at steps of 0.5 eV with 1 sweep. For the high-resolution analysis, the number of sweeps was increased and the pass energy was lowered to 20 eV at steps of 100 meV. The C1s photoelectron line at 285 eV was used for calibrating the recorded spectra.

3. Results and discussion

To determine the thicknesses of the AlN layers, the spectroscopic ellipsometry data Ψ and Δ were analyzed by a multiple-layer model different for each type of substrates used. For AlN layers deposited on Si substrates with a 2.5-nm thick native oxide, a two-layer model was applied consisting of a Si substrate, silicon native oxide as a first layer and an AlN layer as a second layer to model the experimental data Ψ and Δ in the transparent wavelength range from 500-1000 nm.

To determine the thickness of the AlN layers deposited on silicon with 720-nm thermal SiO₂ on top, a three-layer model was used consisting of a Si substrate, a 1-nm thick intermix layer as a first layer, silicon thermal oxide as a second layer and an AlN layer as a third layer. The experimental data Ψ and Δ were modeled in the transparent wavelength range from 500-1000 nm.

The AlN thickness increased with the number of cycles, suggesting that the film thickness can be digitally controlled (table 1).

The thin AlN film (sample AlN-2) deposited at 340 °C was amorphous as determined by XRD. Figure 2 shows a θ-2θ scan of a ~86-nm thick AlN film on a Si (100) substrate, where an amorphous hump in the range 36-50 deg 2θ is observed, which is probably due to the combination of Al and AlN phases (see table 3). A similar θ-2θ scan was obtained for the films deposited on Si(111) and Si/SiO₂.

Figure 3 shows the surface morphology of a ~9-nm thick AlN film (sample AlN-3) deposited on a Si/SiO₂ substrate.

![Figure 2](image1.png)  **Figure 2.** θ-2θ scan of a ~86-nm AlN film deposited on p-Si(100).

![Figure 3](image2.png)  **Figure 3.** 5×5 µm² AFM scan taken from sample AlN-3.

Table 2 lists the root-mean-square (RMS) roughness and the highest peak in the z-direction. In the case of the Si/SiO₂ substrate (samples AlN-3 and AlN-5), the RMS and the highest peak in the z-axis
direction are comparatively small, which conforms to the requirements to the surface roughness of AlN films in SAW devices.

| Sample  | AlN-1 | AlN-2 | AlN-3 | AlN-4 | AlN-5 |
|---------|-------|-------|-------|-------|-------|
| RMS [nm]| 2.49  | 1.35  | 0.34  | 1.45  | 0.33  |
| z-axis max. [nm]| 14.44 | 27.54 | 3.59  | 47.96 | 9.66  |

The composition of the ~9-nm thick AlN film (sample AlN-3) was characterized by using XPS. Detailed spectra are shown in figure 4.

![Figure 4](image)

**Figure 4.** High-resolution XPS of a) Al 2p and b) N 1s photoelectron line in the AlN film after deconvolution.

The Al2p photoelectron spectra for this thin film were deconvoluted using two peaks, one at 74.1 eV, a position typical for AlN [24], and a second one at around 75.2 eV associated with the formation of aluminum oxide (figure 4 a). The N1s photoelectron peak is asymmetric, which point to the existence of different bonding types and configurations associated with nitrogen within the films (figure 4 b). The peaks are located respectively at 397.7 eV and 399.5 eV. These binding energies coincide well with those reported previously for AlN, where the first one is an A-N bond, and the second one is characteristic of free nitrogen [25].

The surface concentrations of the constituent element were calculated and the results are presented in the table 3. As seen, the N concentration is about twice as low as that of Al, which may be the result of the low dissociation efficiency on the growth surface due to the N-H bond strength (435 kJ/mol).

The other elements present are related to the typical contaminants of AlN.

| sample  | C, at.% | Al, at.% | N, at% | O, at% | Si, at.% |
|---------|--------|---------|-------|-------|--------|
| AlN-3   | 36.11  | 17.65   | 7.22  | 38.13 | 0.89   |

4. Conclusions

AlN thin films (thickness of 9 to 83 nm) were deposited by ALD from TMA and NH$_3$. The films were amorphous regardless of the substrate selection, as determined by XRD, which is most probably due to the relatively low growth temperature (340 °C) being not sufficient to make the species moving faster and forming polycrystalline grains. Consequently, the XRD scan did not exhibit the peak characteristic of a polycrystalline material. We thus concluded that a precise tuning of the deposition conditions is needed to achieve a better AlN quality. It was found that the deposition temperature, pulse durations and purging time are very important factors for the surface reactions between TMA and NH$_3$. Judging from the results obtained in parallel experiments on another ALD equipment, we anticipate that the
growth temperature has to be increased to the range of 400-450 °C, the other conditions kept unchanged. The RMS surface roughness of the AlN layers grown on Si/SiO₂ substrates was about 0.33 nm, which satisfies the requirements for SAW devices.

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