Optimization of AlN films grown by atomic layer deposition

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Abstract. AlN thin films (~25 nm) have been grown with a Beneq TFS-200 ALD reactor on Si (111) substrates. TMA (trimethylaluminum) and NH3 were used as precursors. The substrate temperatures were 330°C, ALD cycles 550. In order to study the stoichiometry of AlN film the TMA and NH3 doses (pulses) were varied from 60 to 180 ms and from 60 to 90 ms, respectively. X-ray diffraction (XRD) data showed that the AlN films have amorphous structure. Chemical composition and bonding states were investigated by X-ray photoelectron spectroscopy (XPS). High resolution Al 2p and N 1s spectra confirmed the presence of AlN with peaks located at 73.6 and 396.8 eV, respectively for all layers. Furthermore, the atomic concentration of constituent elements has been calculated from the high-resolution XPS scan. The results revealed the Al/N ratio is close to the stoichiometric value (1:1) only for AlN film grown at TMA and NH3 doses/pulses of 180 and 90 ms, respectively. AFM analysis showed that RMS roughness value for AlN films grown at TMA: NH3 pulse ratio 2:1 is about 1 nm. The results are promising in view of further studies of AlN films for SAW device application.

1. Introduction
Aluminum nitride (AlN) which is III-V family compound offers a unique combination of material properties including wide and direct band gap of 6.2 eV, high thermal conductivity (320 W/mK at 300 K) and high sound velocity (up to 6000 m/s) [1-6] which makes it a suitable candidate for UV detectors, high power electronics and surface acoustic wave devices (SAW) for harsh environment [7-10].

Atomic layer deposition (ALD) is a special type of low temperature chemical vapor deposition where the substrate surface is exposed to sequential doses of two or more precursors separated by purging periods [11,12]. ALD stands out with eliminating the problems associated with the difference in thermal expansion coefficients between the film and the substrate [13,14]. As well ALD offers an excellent conformality and scale-up potential combined with precise thickness control regulated by the number of deposition cycles.
All these characteristics make ALD a proper choice for future device applications [13-16]. However, difficulties in achieving stoichiometry of the deposited III-nitrides films, are often reported [17].

In this work ALD is applied to study stoichiometry of AlN films while the TMA and NH₃ doses/pulses were varied from 60 to 180 ms and from 60 to 90 ms, respectively.

2. Experimental

Aluminium nitride films (~25 nm) were deposited in a Beneq TFS-200 ALD reactor. Pre-cleaned Si(111) substrates were used throughout the experiments. The substrate temperature was fixed at 330°C. The ALD cycles were set to 550 in order to obtain the desired thickness.

Trimethylaluminum (TMA) and NH₃ were used as Al and N sources, while N₂ (nitrogen) was the carrier/purging gas.

The deposition consisted of four stages: TMA pulse in the range of 60-180 s, 2 s N₂ gas purge, NH₃ pulse of 60-90 ms, followed by another 9s N₂ purge. The deposition conditions are summarised in table 1.

| Sample | TMA Pulse (ms) | TMA Purge (s) | NH₃ Pulse (ms) | NH₃ Purge (s) |
|--------|----------------|---------------|----------------|--------------|
| AlN-A  | 180            | 2             | 60             | 9            |
| AlN-B  | 120            | 2             | 60             | 9            |
| AlN-C  | 180            | 2             | 90             | 9            |
| AlN-D  | 60             | 2             | 60             | 9            |

Characterization measurements were carried out with the following techniques.

Film thickness estimation was performed using a J.A.Woollam spectroscopic ellipsometer. The ellipsometry data of angles (Ψ(55°, 65°, and 75°), Δ) in the spectral range of 193-1000 nm were used to calculate the thickness of the AlN films.

To study film structure, powder X-ray diffraction (XRD) measurements were performed using Bruker D8 Advance diffractometer (Germany) with Cu Kα radiation and LynxEye detector. Phase identification was performed with the Diffracplus EVA using ICDD-PDF2 Database.

The measurements of the surface roughness were accomplished by atomic force microscopy (AFM) using an Asylum Research, MFP-3D instrument in a non-contact AC mode using Si tips.

Surface elemental composition as well as the chemical bonding was determined by X-ray photoelectron spectroscopy (XPS). The X-ray photoelectron spectroscopy (XPS) studies were performed in a VG Escalab MKII electron spectrometer using AlKα radiation with energy of 1486.6 eV with total instrumental resolution 1 eV. The photoelectron lines of constituent element on the surface were recorded and corrected by subtracting a Shirley-type background and quantified using the peak area and Scofield’s photoionization cross-sections. The deconvolution of spectra if necessary was done with XPSPEAK41 software.

3. Results and discussion

The XRD scan of AlN-A sample (pulse ratio of TMA:NH₃ 3:1) displayed in figure 1 shows an amorphous hump in the range of 16-20 deg 2θ, which is probably due to the presence of AlN, Al₂O₃, Al₂OC and Al₃CON. Similar scans were obtained for the other films as well.

Figure 2 (a-b) shows the AFM surface morphologies of AlN films deposited at a pulse ratio of TMA:NH₃ 2:1 (sample AlN-C) and 1:1 (sample AlN-D).

The AFM analysis revealed that the use of 2:1 pulse ratio slightly improves surface roughness and decreases the highest peak in the z-axis direction (table 2). These results possibly suggest low acoustic loss in the AlN films and hence high performance of SAW devices can be expected [18].
Table 2. RMS roughness and the highest peak in the z-axis using AFM.

| Sample  | AlN-A  | AlN-B  | AlN-C  | AlN-D  |
|---------|--------|--------|--------|--------|
| RMS [nm]| 1.155  | 0.866  | 1.043  | 2.58   |
| z-axis max. [nm]| 21.5 | 8.80   | 11.69  | 16.86  |

Figure 1. 0-20 scan of the AlN-A film.

Figure 2. Surface morphology of ~25 nm thick AlN thin films deposited at different pulse ratios of TMA and NH$_3$ a) 2:1 and b) 1:1.

Figure 3 shows the results of the XPS survey scans for AlN-A sample. As evident, aluminium, nitrogen, carbon, silicon, and oxygen are present at the surface. In order to calculate the atomic concentration of the five elements, high-resolution scans were performed on the areas around the peaks Al 2p, N 1s, C 1s, O 1s and Si 2p (table 3).
Table 3. Surface concentration of the constituent elements.

| Sample  | Al, at.% | N, at.% | O, at.% | C, at.% | Si, at.% |
|---------|----------|---------|---------|---------|---------|
| AlN-A   | 28.78    | 12.79   | 28.01   | 24.05   | 6.37    |
| AlN-B   | 32.20    | 12.68   | 23.31   | 25.86   | 5.95    |
| AlN-C   | 11.09    | 6.87    | 25.42   | 28.61   | 28.00   |
| AlN-D   | 27.59    | 11.43   | 25.34   | 29.02   | 6.44    |

Table 3 shows that the atomic concentration of Al is about 2.5 times higher than that of N, which may be the result of the low dissociation efficiency of NH$_3$ on the growth surfaces due to the N-H bond strength (435 kJ/mol). Only for AlN-C film grown at a dose of TMA and NH$_3$ 180 and 90 ms, respectively, Al/N ratio is close to the stoichiometric value (1:1), which is important when applying AlN films to SAW devices [19].

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

Figure 3. Survey scan of AlN-A film.

For all samples the shape and the peak positions of Al2p (73.6 eV) [20] and N1s photoelectron spectra (396.6 eV) indicate formation of AlN, small amount of aluminium oxide (75.2 eV) as well as free nitrogen (399.5 eV) [21] (figure 4).

Figure 4. High-resolution XPS of a) Al 2p and b) N 1s photoelectron line in the AlN films.
XPS measurements reveal no hydrogen or carbon related impurities such as -NH\(_x\), N-C, and OH\(^-\) for all samples, which clearly indicate effectively saturated the surface reaction of TMA and NH\(_3\) during the deposition process [22,23].

4. Conclusions

AlN thin films (~25 nm) were deposited by ALD at substrate temperature 330°C. TMA and NH\(_3\) were used as Al and N sources, respectively with different pulse ratio (3:1, 2:1 and 1:1). The films were amorphous regardless of the pulse ratio selection. The AFM analysis reveals a very low surface roughness, about 1 nm as well low highest peak in the z-axis direction about 12 nm for AlN films grown at pulse ratio 2:1. XPS results reveal the presence of AlN with peak positions of Al 2p and N 1s photoelectron lines located at 73.6 and 396.6 eV, respectively for all layers. The atomic concentration of Al is about 2.5 times higher than that of N, only for AlN film grown at a dose of TMA and NH\(_3\) 180 and 90 ms, respectively, Al/N ratio is close to the stoichiometric value (1:1), which is important when applying AlN films to SAW devices.

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