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REACTIVE SPUTTERED ALUMINUM NITRIDE (ALN) FILMS WITH PREFFERED 002 PLANE OF C-AXIS ORIENTATION

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Abstract. In this work, we develop the fabrication process for AlN film with preferred 002 planes strongly oriented in the c-axis, which is a key membrane of the piezoelectric transducers. Reactive sputtering was used to deposit AlN on a substrate Si+SiO_2. Aluminum was used as a target material. The mean free path and the number of collisions affecting the growth of the preferred 002 c-axis-orientated crystal are investigated. Different modifications were done to the in-house sputtering machine to control the flow of reactive gas(N_2) in the chamber and study the variation in the 002 peaks. An ellipsometry model for AlN on Si+SiO_2 substrate was created to measure the deposited film thickness and understand the deposition rate. A scanning Electron Microscope was used to examine the morphology of the crystal grain. Energy Dispersive Spectroscopy (EDS) was used to confirm the chemical composition of Al and N in the film. The oxygen content which affects the mechanical and thermal behavior of the device is also noted. X-ray diffraction was used to record the XRD peak spectrum. The position of different planes and crystal orientation for AlN film were investigated by comparing the experimental data with standard JCPDS data. The result of AlN shows a strong preferred orientation of the 002 planes using the diffractometer. The lowest FWHM value obtained from Sample 16 is ~0.18°, which shows that the optimized process can deposit high-quality AlN film 002 planes strongly oriented in the c-axis.

Key words: Aluminum nitride, Reactive Sputtering, Piezoelectric transduced, Mean free path.

1 INTRODUCTION

Aluminum Nitride (AlN) has emerged as a promising material for a wide range of electronic and optoelectronic applications due to its excellent thermal, mechanical, and electrical properties. AlN films with a preferred orientation along the 002 c-axis plane have attracted significant interest for their high thermal conductivity, piezoelectricity, and optical

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transparency [1-3]. However, the deposition of high-quality AlN films with such preferred orientation remains a challenge due to the inherent difficulties in controlling crystal growth during deposition. Among various deposition techniques, reactive sputtering has shown great promise in producing high-quality AlN films with excellent crystalline structure and orientation control. Reactive sputtering is a widely used technique for depositing thin films with precise control over composition, structure, and thickness. In this process, a target material is bombarded with high-energy ions existing in the formation of plasma in a low-pressure gas environment, leading to the ejection of target atoms. Reactive sputtering involves introducing a reactive gas, such as nitrogen, into the plasma to react with the target material, resulting in the deposition of a compound film. The use of reactive sputtering allows for precise control over the film composition and properties, making it an attractive technique for producing AlN films with desired properties. In recent years, considerable research efforts have been focused on optimizing the reactive sputtering process for the deposition of high-quality AlN films with the desired preferred orientation along the 002 c-axis plane [4-6]. Various factors such as deposition parameters, target material, substrate temperature, and gas flow rates have been investigated to achieve optimal film properties. Despite the significant progress made in this area, there is still a need for further research to understand the fundamental mechanisms of crystal growth during deposition and to optimize the deposition parameters for improved film quality.

In this study, we investigate the reactive sputtering process for the deposition of AlN films with preferred orientation along the 002 c-axis plane. We systematically vary the deposition parameters to modify the mean free path of the atoms, including target material, substrate temperature, gas flow rates, and deposition time, to investigate their effects on film properties such as crystalline structure, orientation, and morphology. Through a detailed characterization of the deposited films using various analytical techniques, we aim to gain insights into the mechanisms of crystal growth and to optimize the deposition parameters for improved film quality. By providing a detailed understanding of the reactive sputtering process for the deposition of AlN films, this study has the potential to contribute to the development of high-performance AlN-based electronic and optoelectronic devices.

2 SPUTTERING EXPERIMENTAL SETUPS

The sputtering of AlN film was carried out using an "ATC 20x20x30 Manufacturer: AJA International Inc" sputtering system. A 99.999% pure aluminum target was used during the deposition process. Nitrogen (N_2) was used as a reactive gas, while argon (Ar) was used as a process carrier gas. Si+SiO_2 wafer of 3 inch was used as a substrate. The Al target was placed to sputter upward. The rotor inside the chamber rotates the substrate during the sputtering process, giving rise to a more homogeneous film deposition. The total gas flow was monitored using the flow meter and kept at 58 sccm in most cases and 9 sccm for Sample 16. The work pressure and the chamber's base pressure were measured by the system's gauges and well controlled according to our process designs. Pre-sputtering was carried out by keeping the shutter open and closed for the designated pre-sputter time of 20-25 minutes, which helps to clean the chamber from any contamination and reduce the oxygen level inside the chamber. The RF power supply was fed to the chamber, and plasma was tuned during the process to achieve the lowest reflected power. The substrate to target distance (TSD) is a crucial parameter for determining the number of collisions of sputtered atoms on the way to the substrate. The sputtering system in house has a minimum TSD of 15 cm. In the normal operation, a suggested TSD by the manufacturer is 20 cm. However, the specific mean free path of sputtered atoms in the working pressure suggests that the shorter the TSD, the smaller number of collisions, and the higher kinetic energy of the sputtered atoms that arrive at the substrate. The film quality will largely depend on the kinetic energy of arrived atoms on the substrate. Therefore, a substrate was placed on the shutter, which eventually minimized the TSD to ~3.5 cm. Therefore, the only options available for TSD are 20 cm to 15 cm and 3.5 cm. We are not able to modify the TSD changing from 3.5 cm to 15 cm, thus, the sputtering processes are designed accordingly. The sensor inside the sputtering system that displays the film thickness was optimized only for TSD of 20 cm, resulting in inaccurate results for other TSD values.

3 FILM GROWTH AND CHARACTERIZATION

To achieve better film quality and stoichiometry, the sputter is configurated to ensure the proper diffusion of gases for the film growth.

The first configuration is the normal setup, where the reactive gas passed through a gas tube close to the top of the shutter gun, and the process carrier gas passed through the back of the sputter gun, seen in figure 1. This setup was used for samples 1 to 5.

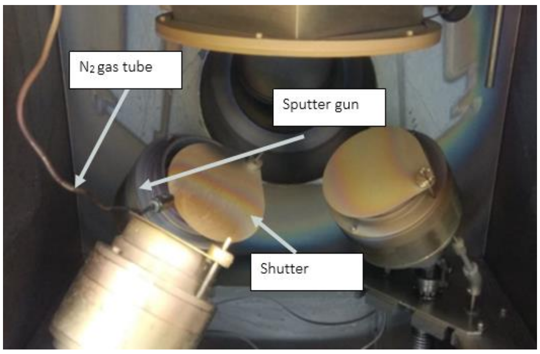

Figure 1. Normal configuration

The figure 2 presents the second configuration that is the first modified setup, where a long gas tube was connected to the existing reactive gas tube and allowed to pass through the back of the sputter gun, resulting in constant diffusivity between the gases. This setup was used to deposit the film for samples 6 to 14. The third configuration is the second modified setup, where both the process carrier gas and reactive gas were connected using a T-shaped tube and passed together to the sputter gun to ensure proper diffusion of gases, seen figure 3. This modified setup was used for samples 15-16.

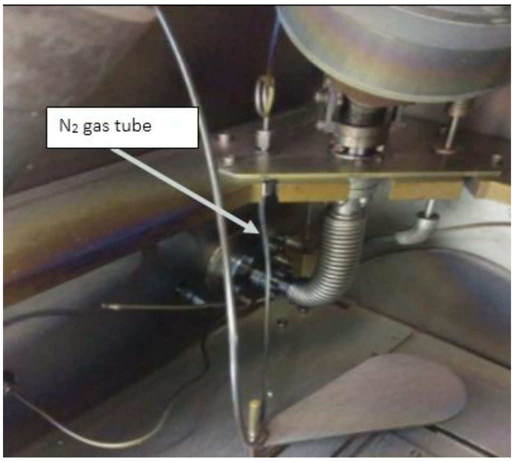

Figure 2. Seconde configuration

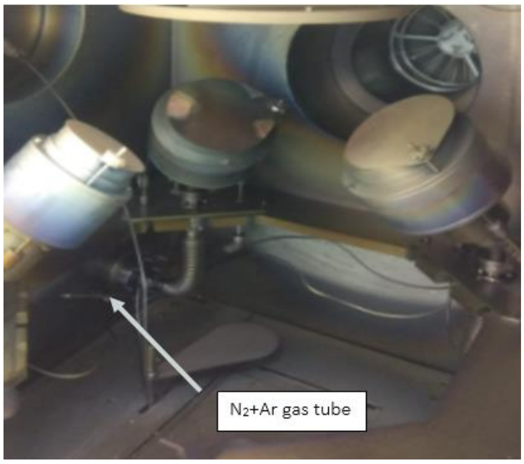

Figure 3. Third configuration

In the above three configurations, we used TSD equal to 3.5 cm, 15 cm and 20 cm respectively. Samples 1, 2, and 16 were deposited at TSD equal to 20 cm, while Sample 4-5 were deposited at TSD equal to 15 cm. All other samples were deposited at TSD of 3.5 cm.

The sputtering parameters were designed for the first 5 experiments listed in Table 1. After successful deposition of Sample 1 at 550W, it was observed that the Al target has a defect of pore-like structure developed on its surface. This led to the reduction of power to 500W for later experiments. After deposition, the analysis of trial samples and target conditions helped us to formulate the deposition parameters for strong 002 c-axis oriented AlN film.

Table 1: The first 5 sets of sputtering deposition parameters

Sample No.	Power (W)	Work Pressure (mT)	Base Pressure (μT)	Total gas sccm	Gas flow (Ar: N_2)	Substrate Temp. (°C)	TSD (cm)	Config. No.	Deposit. Time (hr)	Note
S1	**550**	34	1.2	58	3:7	350	20	1	3.5	
S2	500	34	0.43	58	3:7	350	20	1	3.5	
S3	500	34	0.73	58	3:7	25	3.5	1	4	No uniform
S4	500	34	0.1	58	0:1	25	15	1	3.5	
S5	500	34	0.1	58	3:7	400	15	1	3.5	

When TSD equals 3.5 cm, we must scarify the rotating substrate due to the mechanic structure limitations, and the deposition could only be carried out at room temperature, which results in non-uniform film growth, see optical picture for sample 3 in figure 4. The sample 3 was examined using XRD for the quality of AlN film regarding to 002 c-axis orientation. The XRD diffraction pattern is also shown in figure 4 and we see a predominant 002 reflection with higher interatomic spacing at 35.62°. The intensity of other peaks like (101), (100), (010) were negligible. The FWHM value obtained from MATCH 3! Software for 002 AlN reflection is 1.037°, indicating a preferred 002 orientation of AIN crystal. These results indicate a good quality AIN regarding 002 c-axis oriented film except for the uniformity issues. It was subsequently decided to repeat the same parameters and verify the results obtained for Sample 3.

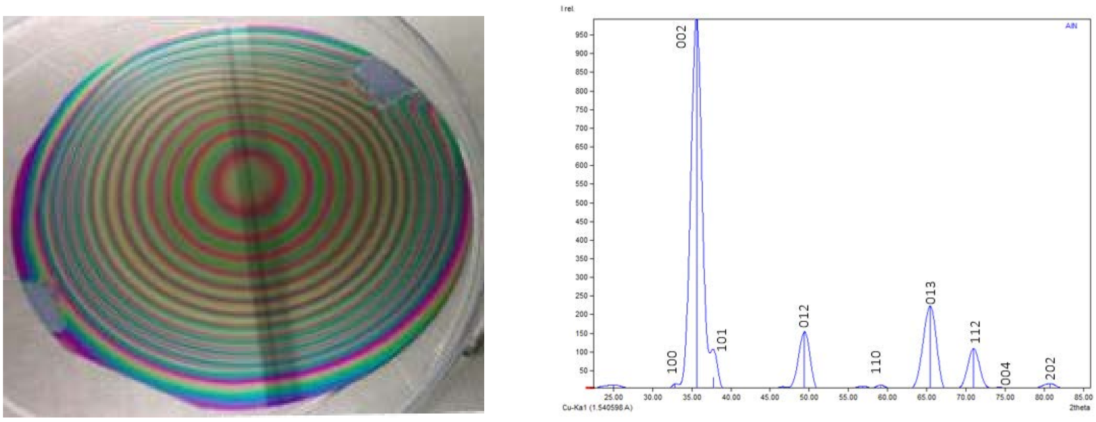

Figure 4. Sample 3 no uniform growth at TSD = 3.5 cm. optical image at lift side; XRD spectrum at right side.

3.1 MEAN FREE PATH OF SPUTTERED ATOMS

Crystalline formation during the sputtering process will impact the kinetic energy of the sputtered atoms that arrive at the substrate. The kinetic energy of the sputtered atoms is related to their length of mean free path compared to the TSD. For Sample 1-5, according to their depositing parameters, the mean free paths of Al and N ions can be evaluated using the equation (1) [7]. The number of collisions of the sputtered atom can be calculated using equation (2),

$$\lambda = 2.33x10^{-20} \frac{T}{P\, d^2} \qquad [1]$$

$$N = \frac{Target\ to\ Substrate\ Distance(TSD)}{mean\ free\ path(\lambda)} \qquad [2]$$

where T is the substrate temperature measured in Kelvin, P is the working pressure in Torr and d is the molecular diameter in cm, N represents the number of collisions of sputtered atoms on the way to the substrate.

The ionic radius of Al^{+3} is 0.53 Å, and that of the N^{-3} is 1.55 Å [8]. The size ratio of Aluminum cation and nitrogen anion is thus given as 0.3419. Aluminum has a radius of 1.18 Å. Nitrogen gets absorbed by the aluminum ions to form an AlN compound with radius varying from 0.53 to 0.9 Å. The mean free path of sputtered atoms calculated for Sample 1-5 was ~7.3 cm at d = 0.53 Å. and it is obverse that samples placed at 20 cm and 15 cm underwent a higher number of collisions than sample 3 placed at ~3.5 cm. This suggests that sputtered atoms have a high probability of agglomeration before reaching the substrate in case of large TSD. Therefore, Sample 3 has a low probability of agglomeration and we expect that the sputtered atoms arriving at substrate with high kinetic energy. Therefore, sample 3 will have high quality crystalline structure, which we have seen from its XRD spectrum shown in figure 4.

It was subsequently decided to repeat the same parameters as for deposit sample 3 with consideration of improving the uniformity of the film. The optimization processes are given in Table 2. The S16 was designed to achieve a long mean free path for sputtered atom comparable with that in depositing sample 3 by reducing work pressure at TSD of 20 cm.

Table 2: The optimization sets of sputtering deposition parameters

Sample No.	Power (W)	Work Pressure (mT)	Base Pressure (µT)	Total gas sccm	Gas flow (Ar: N_2)	Substrate Temp. (°C)	TSD (cm)	Config. No.	Deposit. Time (hr)	Note
S6	500	34	0.73	58	3:7	25	3.5	2	4	
S7	500	34	0.69	58	3:7	25	3.5	2	4	
S8	500	34	1.5	58	3:7	25	3.5	2	1.10	
S9	500	34	3.7	58	3:7	25	3.5	2	1	
S10	500	34	1.6	58	3:7	25	3.5	2	1	
S11	500	26.6	0.73	44	3.5:6.5	25	3.5	2	2	
S12	500	34	0.73	58	3:7	25	3.5	2	2.45	
S13	500	34	1.6	58	3:7	25	3.5	2	4	
S14	500	4.8	0.73	8	3.3:6.7	25	3.5	2	4	
S15	500	34	0.73	58	3:7	25	3.5	3	4	
S16	500	5.9	2.1	9	3:7	25	20	3	4	Best

3.2 THICKNESS AND UNIFORMITY OF THE FILM

Spectroscopic ellipsometry was used to measure the thickness of deposited AlN films. The measurement was carried out using an Ellipsometer (Alpha S), which allowed LED illumination at different incidence angles of 75°, 70°, and 65°. The analysis of the film thickness was performed in three steps. The first step involved confirming the thickness of the Si+SiO_2 substrate using the ellipsometer. The value obtained in this step was used while formulating the model for measuring the thickness of deposited AlN films. The existing transparent SiO_2 was defined using the CompleteEase software by J.A Woollam. In the second step, the existing model of B-Spline predefined for the metal layer was used to define the layer of aluminum nitride. This step gives the basic model of AlN on top of SiO_2. In the third step, a different angle of incidence was used to measure the SE spectra (Ψ and Δ), and the obtained spectra were fitted against the basic model. The optical and dielectric constants of the B-Spline model with a substrate layer of SiO_2 were varied until they fit the experimental data. The number of oscillations coming from the sample surface of the thin film was used to vary the existing model of AlN. The higher the number of oscillations, the thicker the films (Table 3). To achieve a precise fit, the acceptable mean squared error (MSE) must be below 10. Upon verification at all incidence angles, the MSE was consistently low, with a value as small as approximately 1.71. The newly defined model for AlN with SiO_2 substrate was later used to measure the thickness of Samples 1-16 at various regions, and the average thickness was calculated. Sample

3 and Sample 12-15 deposited using TSD = 3.5 cm show a huge variation in the thickness across the wafers.

Table 3: Average thickness of deposited films measured using ellipsometry

S/N (Sample *)	Average thickness (nm)
1	20.4
2	35.3
3	400-3456
4	34
5	24.7
10	285-730
11	393-1230
12	402-1821
13	392-3512
15	367-3346
16	267

Samples 2, 4, and 5 had a thickness of less than ~32 nm, implying a significantly low deposition rate. On the other hand, sample 3 had a mean free path twice that of TSD, resulting in a high deposition rate. Sample 16, sputtered at a low work pressure of 5.9 mTorr with TSD equal to 20 cm, had an average thickness of approximately 267 nm, indicating a low deposition rate. This was due to the usage of a small amount of process carrier gas (Ar) at 2.7 sccm to sustain the low working pressure.

3.3 XRD SPECTRUM ANALYSIS

The crystallinity of thin-film AlN was analyzed for four distinct samples, namely samples 3, 12, 15, and 16, using Cu-Kα1 (1.5405Å) radiation and glancing incidence angle XRD. To obtain XRD diffraction patterns of AlN films, peaks interfering from the substrates to the thin film were suppressed. These patterns were analyzed using MATCH 3! and FullProf software, which matched them with the standard data (JCPDS Card No. 96-900-8861) for AlN crystal structure. The AlN crystal's lattice parameters were calculated to be a=3.11Å and c=4.9780 Å, and it was identified to belong to the hexagonal space group P63mc [9].

As previously discussed, sample 3 had an FWHM value of 1.037° for the 002 AlN reflection, while sample 12, which was deposited using the second configuration, showed similar results in figure 5, but with increased intensity of 002 reflections at a diffraction angle of 35.79°. The FWHM value for sample 12 was found to be 0.25°, indicating a significant improvement in preferred crystal orientation. In figure 6, the XRD diffraction pattern for sample 15, which was deposited using the third configuration, is presented. We observed a shift in the diffraction angle for 002 peaks towards a higher value compared to sample 3, at 36.14°. The 002 peak was predominantly oriented, but a very noticeable 013 reflection was also observed. The FWHM value obtained for sample 15 was 0.3397°.

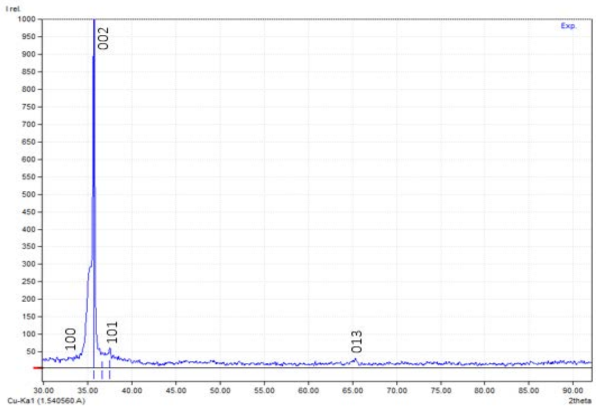

Figure 5: XRD spectrum for sample 12 showing preferred 002 AlN reflection.

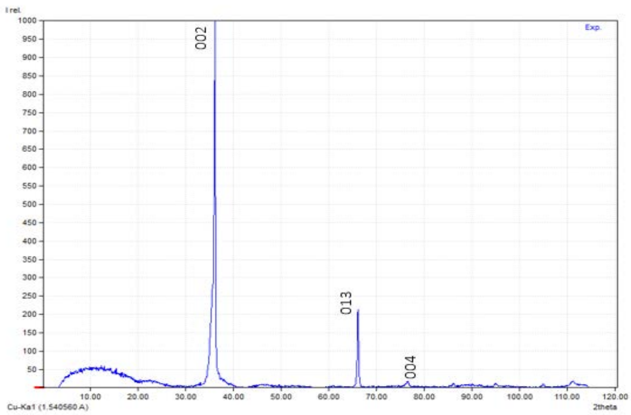

Figure 6. XRD spectrum for sample 15 showing preferred 002 AlN reflection.

Sample 16 was deposited using the second configuration with a different approach, where the deposition parameters were formulated by keeping the number of collisions between the sputtered atoms the same as that for sample 3 and calculating the pressure for TSD equal to 20 cm. The relationship between mean free path, processing pressure, and TSD is presented by equation (1) and equation (3).

$$\lambda \propto \frac{1}{p} \tag{3}$$

Based on the calculation, the deposition for sample 16 was carried out under work pressure p equal to 5.9 mTorr and with TSD of 20 cm. The XRD pattern of sample 16, shown in figure 7, displays a similar spectrum to the other samples, with a preferred 002 plane c-axis orientation. The FWHM value for sample 16 is 0.183°, which is the best among all the discussed samples. The diffraction angle for the 002 planes is 36.11°, and noticeable 101 and 012 peaks are also observed. It is worth noting that the XRD peaks for all the samples were shifted from the standard data used as a reference, which may be attributed to the changes in lattice strain. The shift towards the higher 2θ suggests that the films were under compressive stress.

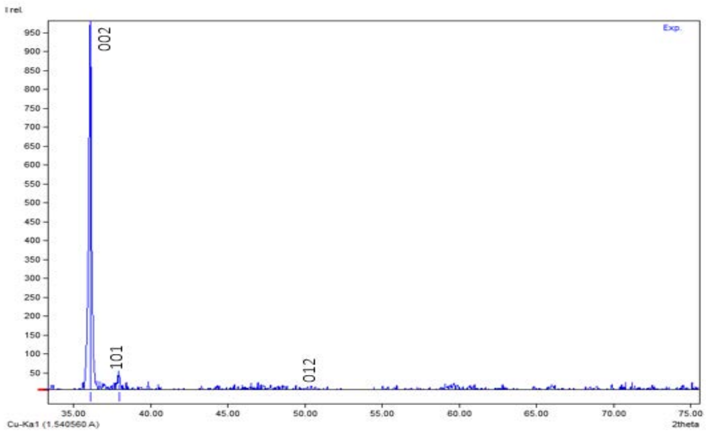

Figure 7: XRD spectra for Sample 16 showing preferred 002 AlN reflection

3.4 MORPHOLOGY of THE CRYSTAL GRAIN

Scanning Electron microscope (SEM) were applied to study the morphology of the deposited AlN film by using SU3500 operating at 15kV. Image of both Scanning Electron (SE) mode for microstructure contrast and backscattered electron (BSE) for element contrast are achieved to visualize the grain distribution in the AlN film. Figure 8 shows the SEM images of sample 3.

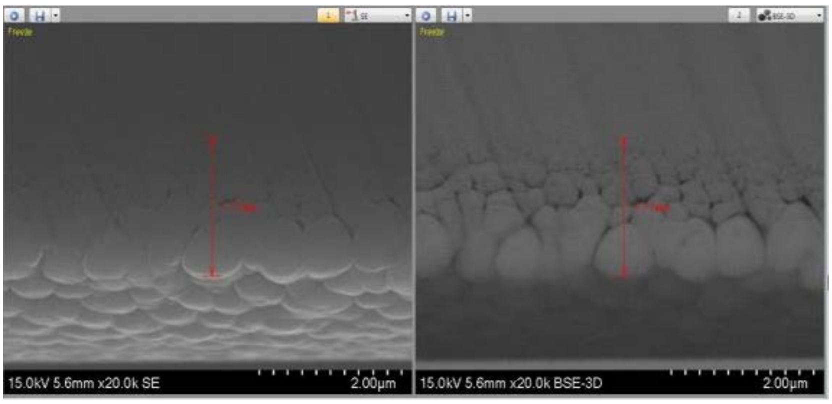

Figure 8. Sample 3, SE image at left side and BSE image at right side

Figure 8 reveals that the AlN film is composed of polycrystalline structures, as observed in both BSE and SE images. The crystal grains exhibit a columnar morphology. To determine the thickness of the film, a cross-sectional SEM image was utilized. The measurements acquired from ellipsometry, and SEM images were in agreement within a 5% margin, validating the precision of the ellipsometry measurement.

3.5 CHEMICAL COMPOSITION of Al AND N

The elemental composition of the AlN film sample 3 and 6 was analyzed using EDS. The outcomes are outlined in Tables 4 and 5, respectively. In the case of sample 3, which displayed non-uniform thickness across the wafer, a rectangular area was chosen for analysis at different acceleration voltages. The data indicated that the AlN film had a nearly 1:1 distribution of Al and N elements, with oxygen contamination within the range of 5-6 atomic percent.

Table 4: Elemental composition in Sample 3 at different acceleration voltage

Acceleration Voltage (keV)	Al (Atom. C%)	N (Atom. C%)	O (Atom. C%)
7	44.87	45.43	5.20
10	50.33	41.25	5.86
12	51.70	39.81	5.17

For Sample 16, 1:1 stoichiometry composition is also achieved. However, the oxygen content was as high as 16%, indicating a higher affinity of aluminum with oxygen. The lower base pressure used for depositing Sample 16 may have resulted in a higher partial pressure of oxygen during deposition, which has resulted in an increased reaction rate between the deposited AlN and the residual oxygen in the deposition chamber. Therefore, we see high oxygen contamination in the film. This high oxygen content affects the mechanical and thermal properties of the AlN film which can have a negative impact on application of the film.

Table 5: Elemental composition in Sample 16 at different acceleration voltage

Acceleration Voltage (keV)	Al (Atom. C%)	N (Atom. C%)	O (Atom. C%)
4	39.73	44.95	15.31
5	40.13	41.32	16.39
10	26.05	20.21	30.62

4 CONCLUSIONS

The study has provided insights into the growth of AlN films using RF magnetron sputtering. The ratio of mean free path to TSD has been identified as a crucial design parameter for sputter process development. Film quality, deposition rate, and target material degradation are affected by work pressure, reactive gas flow rate, and base pressure. To deposit AlN films at low base pressure, it is necessary to minimize oxygen contamination. XRD analysis reveals that when the mean free path of sputtered atoms is comparable to TSD, strongly c-axis oriented AlN films with plane 002 exhibiting maximum scattering intensity (FWHM value 0.183°) are obtained. The study also highlights challenges such as the development of compressive stress on the film when deposited at shorter TSD.

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