Understanding Reproducibility of Sputter-Deposited Metastable Ferroelectric Wurtzite $\text{Al}_{0.6}\text{Sc}_{0.4}\text{N}$ Films Using In Situ Optical Emission Spectrometry

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High-Sc $\text{Al}_{1-x}\text{Sc}_x\text{N}$ thin films are of tremendous interest because of their attractive piezoelectric and ferroelectric properties, but overall film quality and reproducibility are widely reported to suffer as $x$ increases. In this study, structural and electrical properties of metastable $\text{Al}_{0.6}\text{Sc}_{0.4}\text{N}$ films are connected with plasma changes during film growth, identified via glow discharge optical emission spectroscopy (GD-OES), and linked to the target mode changes. This in situ GD-OES technique uses changes in the N$_2$(I) intensity, correlated with DC bias hysteresis behavior of a $\text{Al}_{0.6}\text{Sc}_{0.4}$ target in metallic and poisoned modes, to identify films that subsequently exhibit unacceptable structural and electrical performance. Two representative samples deposited under identical conditions but possessing distinct properties related to phases present in the films are focused on. Films sputtered under a poisoned target mode produce pure wurtzite ferroelectric $\text{Al}_{0.6}\text{Sc}_{0.4}\text{N}$ with a reversible 80 $\mu$C cm$^{-2}$ polarization and 3.1 MV cm$^{-1}$ coercive field. When identical chamber settings are used but the process starts in metallic mode, a mixed wurtzite/rocksalt film is deposited which exhibits nanometer-scale changes to the film microstructure and a nonferroelectric response. These results illustrate the utility of optical emission spectroscopy for tracking target mode fluctuations when fabricating metastable materials such as high-Sc $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films.

1. Introduction

Interest in the growth of AlN-based group III metal nitride semiconductor alloys such as (Al,Ga)N and (Al,In,Ga)N continues to increase as the associated application space expands. First, the interest was driven by their tunable properties for light-emitting diodes (LEDs) and other optoelectronic applications [1] and by their wide bandgap (WBG) semiconductor properties for high electron mobility transistors (HEMTs) in radio frequency (RF) and power electronic applications [2]. Scandium additions to AlN were first reported to produce significant increases in piezoelectric response in 2002 [3] and were very quickly adopted for the piezoelectric thin film devices such as film bulk acoustic resonators (FBARs) in cell phones [4]. Recent reports on ferroelectricity in $\text{Al}_{1-x}\text{Sc}_x\text{N}$ for $x \geq 0.1$ have sparked additional scientific interest as the first wurtzite ferroelectric material [5,6] and significant technological interest as a candidate for hybrid logic-in-memory devices.

Large-scale commercial applications of piezoelectric $\text{Al}_{1-x}\text{Sc}_x\text{N}$ are still limited to relatively modest levels of Sc substitution ($x < 0.1$), though there are many literature reports of $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films having $x \geq 0.1$ with exceptional properties [1-12]. It has been widely reported that increasing Sc content, desired for increased piezoelectric response and lower field ferroelectric switching, increases the challenge of growing high-quality textured $\text{Al}_{1-x}\text{Sc}_x\text{N}$ films [13-15]. This challenge is driven in no small part by the thermodynamic driving force for phase separation in this highly metastable material system [16,17]. This degradation in film properties for large $x$ values has been correlated with wurtzite-(0002) texture reduction with the presence of misoriented grains [11] and the associated difficulties with reliably controlling the stress state in sputtered films [18]. However, in each case the conclusions are correlational and are drawn largely or entirely from ex situ measurements, so they are of limited value for deposition process control.

Many in situ monitoring techniques have been reported for tuning the deposition of AlN thin films: glow discharge optical emission spectrometry (GD-OES) [19,20], reflection high-energy electron diffraction (RHEED), [21,22] reflectance interferometry
2. Results

Figure 1a shows the X-ray diffraction (XRD) $\theta$–$2\theta$ patterns for two representative films grown using the same deposition conditions and pretreatments that have previously been optimized for this chamber (see Experimental Section). The patterns indicate that one film has a pure c-axis textured wurtzite structure (wz-AlScN) and the other is a mixed wurtzite/rocksalt structure (wz/rs-AlScN). The wz-(0002) peak appears at 36.3° and corresponds to a c-axis lattice parameter of 0.494 nm for each sample which closely matches previous reports for Al$_{0.6}$Sc$_{0.4}$N. The slight shoulder toward lower $2\theta$ for wz-AlScN is related to a transition from initially in-plane compressive strain to tensile strain as the film grows. In addition, there is a significant phase difference as indicated by the appearance of the (111) rocksalt peak at 35.7° as previously reported and in line with theoretical work on the thermodynamic relationship between wurtzite and rocksalt in Al$_{1-x}$Sc$_x$N. For samples grown using the same deposition conditions, it is interesting that there is a large discrepancy in phases. For both samples, the wz-(10-10) peak appears at 31.5° in Figure 1a. Figure 1b shows the wz-(0002) peak profile in $\chi$ space. This provides a similar film structure property as an $\omega$-rocking curve which measures the out-of-plane texture of a particular $2\theta$ position. 2D XRD patterns for each sample are provided in Figure S1, Supporting Information. In Figure 1b, we see similar out-of-plane texture between the two films, albeit a slightly lower full-width at half-maximum (FWHM) for wz-AlScN at 2.8° than the wz/rs-AlScN sample with 3.1°. Based on the broad $\chi$ FWHM (>10°), the (10-10) peak has poor out-of-plane texture.

Bright-field scanning transmission electron microscopy (BF-STEM) images in Figure 2 revealed a columnar structure in both films with thicknesses of 325 and 337 nm for wz-AlScN and wz/rs-AlScN, respectively. The wz-AlScN sample exhibits a uniform structure through the thickness of the film, whereas striations are apparent in the wz/rs-AlScN sample as indicated by the timestamps. Assuming an overall constant deposition rate, the features occur at minutes 44, 56, 59, and 74 of the 110 min deposition. The selected-area electron diffraction (SAED) pattern of the wz/rs-AlScN film bulk in Figure 2c reveals that the film grows along the wz-[0001] and rs-[111] directions.

From the high-resolution TEM (HR-TEM) images of the wz/rs-AlScN sample provided in Figure S2, Supporting Information, selected areas were processed with a fast Fourier transform (FFT) to calculate the out-of-plane lattice spacings. The resulting spacings measured from the FFT of the bottom (2.50 Å) and top (2.46 Å) areas of the film closely match the
calculated spacings from the XRD patterns for the rs-(111) (2.52 Å) and wz-(0002) (2.47 Å) peaks, respectively. STEM–energy-dispersive X-ray spectroscopy (EDS) maps and profiles show no indication of chemical segregation in either sample (Figure S3, Supporting Information).

Optical emission of the glow discharge near the substrate surface was collected for all growths. The line at 337 nm which corresponds to an excited molecular N$_2$(I) state was tracked during the deposition (Figure 3). A representative full emission spectrum is provided in Figure S4, Supporting Information. There are four peaks the N$_2$ line for the wz/rs-AlScN sample that occur at times 44, 55, 59, and 71 min in Figure 3b. These peaks align in time with microstructural features in Figure 2b. However, the nearly uniform nature of the emission lines for wz-AlScN points toward a stable deposition in Figure 3b which led to a single phase and pure (0002) textured film in Figure 3a. No corresponding fluctuations in the in situ residual gas analyzer (RGA) signal were observed (Figure S5, Supporting Information).

Polarization–electric field (P–E) hysteresis loops were measured on parallel plate capacitors fabricated from both thin film samples. In Figure 4a, the wz-AlScN P–E loop shows a saturated hysteresis loop indicative of the highly $c$-axis textured structure of the film. With a remanent polarization of 80 μC cm$^{-1}$ and a coercive field of 3.1 MV cm$^{-1}$, the properties of this sample are consistent with previous reports on $x=0.4$ chemistries in Al$_{1-x}$Sc$_x$N.[5,6] There is an ≈7% uncertainty associated with the polarization values due to uncertainty of the device area. In comparison, the mixed-phase layered wz/rs-AlScN sample did not exhibit ferroelectric switching up to 4.1 MV cm$^{-1}$; the maximum electric field sustained before catastrophic device failure. This result is consistent with the presence of a lower permittivity, nonferroelectric rocksalt phase in series with the ferroelectric wurtzite such that catastrophic macroscopic dielectric breakdown occurred before the portion of the field across the ferroelectric phase was sufficient to reverse polarization. The unsaturated P–E loops for wz/rs-AlScN in Figure 4a and apparent remanent polarization in Figure 4b are an effect of leakage currents during the voltage sweep and do not represent true ferroelectric behavior. Thus, the lack of ferroelectric properties in wz/rs-AlScN is due to series-connected rocksalt and wurtzite phases which are correlated with changes in target mode tracked by GD-OES during film growth.

3. Discussion

A variation in the intensity of the GD-OES lines in Figure 3 is linked to alterations of the target mode during sputtering which was determined by sweeping the ratio of $f=N_2/(N_2+Ar)$ gas...
flow during sputtering and monitoring both the DC bias and the intensity of N$_2$(I) (Figure S6, Supporting Information). The change from metallic to poisoned regime occurs close to $f = 0.2$. As the deposition conditions reported in this article are located at $f = 0.25$, the sputtering target is in a sensitive state, close to the boundary between metallic and poisoned regimes of the AlSc alloy target. Figure S6b, Supporting Information, shows hysteretic behavior in the DC bias for $0 < f < 0.25$ which we associate with shifts between metallic and poisoned target modes. In support of this, Figure S6a, Supporting Information, reveals that the N$_2$(I) line intensity is highly dependent on the N$_2$ fraction for $0 < f < 0.3$. The peak at $f = 0.4$ for the N$_2$(I) intensity is due to the relative electron cross-section for the gaseous species in which N$_2$ > Ar for an electron energy of 20 eV. Rather than sputtering in a pure N$_2$ atmosphere, a N$_2$/Ar gas mixture is used to increase the density of excited N$_2$(I) species and, therefore, the energy of the reactive deposition.

To track the active target mode during film deposition, the derivative of the N$_2$(I) line intensity with respect to time (dI/dt) is shown in Figure 3. By setting a threshold of $>$0.002, the shifts between different modes can be identified. For wz-AlScN (Figure 3a), it is apparent that the target sputters initially in a poisoned mode until minute 90 close to the end of a deposition where it transitions to a metallic mode. The wurtzite phase nucleates first and grows in the wz-[0001] direction, and the switch to the metallic mode has a low impact as the rocksalt phase is undetected by XRD in Figure 1a. For wz/rs-AlScN mixed phase films (Figure 3b), the target is operating initially in a metallic mode and rocksalt nucleates and grows in the rs-[111] as observed in XRD peaks in Figure 1a and the HR-TEM in Figure S2a,c, Supporting Information. Then, once the target switches to a poisoned state at minute 44 leading to wurtzite nucleation, and once the wurtzite grains are fully established at minute 74, continued wurtzite growth occurs with wz-(0002) texture.

To summarize observations for wz-AlScN in Figure 3a and for wz/rs-AlScN in Figure 3b, it appears that when the target state changes from poisoned to metallic modes, the wurtzite growth on wurtzite is energetically favorable compared with rocksalt nucleation on wurtzite. This is not surprising because AlN strongly prefers growth as a [0001]-textured wurtzite, though it is commonly observed that the first few nm of films are untextured before the favored growth of the [0001] grains begins to dominate. In contrast, ScN is stable in a rocksalt structure. So, if the target is initially in the metallic state, rocksalt nucleation is preferred, and rocksalt growth from rocksalt nuclei occurs. However, once the target switches to poisoned mode, wurtzite nucleation occurs and continues until completion of growth. The distinction between enhanced nucleation of wurtzite on rocksalt and suppressed nucleation of rocksalt on wurtzite is likely related to difference in relative mixing enthalpies of these two structures at $x = 0.40$ composition in a metastable Al$_{1-x}$Sc$_x$N alloy. A two-phase wurtzite–rocksalt mixture is the thermodynamic ground state for this heterostructural alloy, but the mixing enthalpy in WZ structure (350–400 meV $\mu$fu$^{-1}$) is smaller than in the RS structure (500–550 meV $\mu$fu$^{-1}$).

### 4. Conclusions

Metastable Al$_{0.6}$Sc$_{0.4}$N film deposition process changes observed by in situ time-resolved GD-OES influence the overall phase purity, microstructure, and properties of the samples, and can be linked to fluctuations in the target mode for an Al$_{0.6}$Sc$_{0.4}$N alloy target. Performing reactive RF sputtering close to the boundary between metallic and poisoned modes is important because it maximizes deposition rate, N$_2$ chemical potential, and helps quenching in chemical homogeneity despite severe thermodynamic metastability. However, such metastable material synthesis requires constant monitoring of the deposition process, by GD-OES and/or by monitoring the target DC bias. Particularly early in film growth, a metallic target mode can promote the growth of an undesired rocksalt phase, whereas a poisoned target mode promotes the growth of the wz-Al$_{0.6}$Sc$_{0.4}$N. These changes apparent in the XRD, SAED, and BF-STEM measurements directly connect phase segregation into rocksalt and wurtzite with changes in GD-OES signal which is linked to changes in the target mode. The in situ GD-OES technique also allows for monitoring subsequent film properties because the peaks in the N$_2$(I) emission lines relate to changes in the glow discharge that directly influence growth conditions. The results show that a poisoned target produces ferroelectric wz-Al$_{0.6}$Sc$_{0.4}$N with a reversible 80 $\mu$Ccm$^{-2}$ polarization and 3.1 MVcm$^{-1}$ coercive
field, whereas the mode fluctuations lead to no observable ferroelectric switching in the samples containing rocksalt phase. Monitoring the deposition by GD-OES or DC target bias will help to mitigate rocksalt phase formation and improve process reliability for emerging ferroelectric Al$_{1-x}$Sc$_x$N especially when pushing toward higher x.

5. Experimental Section

Thin-film Al$_{0.6}$Sc$_{0.4}$N samples were produced via reactive RF magnetron sputtering on (111) textured platinized silicon substrates (Pt/TiO$_2$/SiO$_2$/Si) with a rocking curve ($\omega$) FWHM < 1.3°. The growth chamber had a base pressure of $5 \times 10^{-7}$ Torr. During the deposition, the pressure was set to 2 mTorr with gas flow rates of 15/5 sccm for Ar/N$_2$. The substrate temperature was set to 400 °C while rotating at 20 rpm at a distance of 16.5 cm from the target. This relatively low substrate temperature was chosen to avoid spinodal decomposition.$^{[17]}$ A 3° Al$_{0.6}$Sc$_{0.4}$ alloy target (Stanford Advanced Materials, 99.9 at% pure) was used with a 6.6 W cm$^{-2}$ forward power density. The target was presputtered for 60 min under the same parameters as the deposition to reduce target surface oxidation.

In situ monitoring consisted of an OES and an RGA. The light emitted from the glow discharge was collected through a 3° collimator lens aimed at the substrate surface by an EPP2000-UVN-SR spectrometer (StellarNet Inc.) with a 0.5 nm resolution (Figure S7, Supporting Information). The fiber optic feedthrough was mounted by a ConFlat (CF) flange flange to the deposition chamber. The relative intensity of the N$_2$(I) line as a function of time $t$ shown in Figure 3a is a ratio of the I(t)/I$_0$, after subtracting the background signal which was collected prior to striking the glow discharge, where I$_0$ is the initial spectrum collected as a reference. For OES collection, ten spectra were subsequently collected for 5 s each and then averaged, which led to a 50 s time interval between each data point. For OES collection, ten spectra were subsequently collected for 5 s each and then averaged, which led to a 50 s time interval between each data point. This was performed to increase the signal to noise because the glow discharge density is much lower near the substrate surface than the target surface.

To investigate the crystal structure, XRD (Bruker D8 Discover) and SAED were used. A 2D detector XRD is used as a faster method for initial screening of sample quality than using a point detector for $\theta$–2$\theta$ and rocking curve scans. To produce 1D plots (intensity vs 2$\theta$) from the 2D detector on the Bruker XRD which simultaneously collects intensity in $\chi$ and 2$\theta$ space during a scan, the intensity is integrated across $\chi$ (60–120°). STEM images were acquired using an FEI Talos F200X at 200 kV with a camera length of 77 mm. Cross-sectional lamellae were prepared using an FEI Helios Nanolab 600i FIB/SEM. A cleaning pass was performed at 2 kV to remove Ga implantation and surface damage, which led to a 50 s time interval between each data point. This was performed to increase the signal to noise because the glow discharge density is much lower near the substrate surface than the target surface.

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The films were electrically characterized on parallel plate capacitors with Pt top electrodes deposited through a shadow mask by DC sputtering. Devices were driven from the bottom Pt electrode and sensed from the top Pt contact at an excitation frequency of 10 kHz. The maximum electric field was gradually reduced for each nested loop for determining the coercive field. P-E loops were generated with a Precision Multiferroic system from Radiant Technologies.

Supporting Information

Supporting Information is available from the Wiley Online Library or from the author.

Acknowledgements

This work was co-authored by Colorado School of Mines and the National Renewable Energy Laboratory, operated by the Alliance for Sustainable Energy, LLC, for the U.S. Department of Energy (DOE) under Contract No. DE-AC36-08GO28308. Funding was provided by the DARPA Tunable Ferroelectric Nitrides (TUFEN) program (DARPA-PA-19-04-03) as a part of Development and Exploration of FerroElectric Nitride Semiconductors (DEFENSE) project (diffraction, microscopy, and electrical characterization), and by Office of Science (SC), Office of Basic Energy Sciences (BES) as part of the Early Career Award “Kinetic Synthesis of Metastable Nitrides” (material synthesis and in-situ monitoring). The authors also express their appreciation to Dr. Wanlin Zhu and Prof. Susan Trollier-McKinstry of the Pennsylvania State University for providing Si samples were produced via reactive RF magnetron sputtering on (111) textured platinized silicon substrates (Pt/TiO$_2$/SiO$_2$/Si) with a rocking curve ($\omega$) FWHM < 1.3°. The growth chamber had a base pressure of $5 \times 10^{-7}$ Torr. During the deposition, the pressure was set to 2 mTorr with gas flow rates of 15/5 sccm for Ar/N$_2$. The substrate temperature was set to 400 °C while rotating at 20 rpm at a distance of 16.5 cm from the target. This relatively low substrate temperature was chosen to avoid spinodal decomposition.$^{[17]}$ A 3° Al$_{0.6}$Sc$_{0.4}$ alloy target (Stanford Advanced Materials, 99.9 at% pure) was used with a 6.6 W cm$^{-2}$ forward power density. The target was presputtered for 60 min under the same parameters as the deposition to reduce target surface oxidation.

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Supporting Information

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Conflict of Interest

The authors declare no conflict of interest.

Data Availability Statement

The data that support the findings of this study are available from the corresponding author upon reasonable request.

Keywords

aluminum scandum nitrides, ferroelectric films, metallic and poisoned targets, optical emissions, wurzite
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