Comparative spectroscopic study of aluminum nitride grown by MOCVD in H\textsubscript{2} and N\textsubscript{2} reaction environment

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Abstract

We report a comparative spectroscopic study on the thin films of epitaxial aluminum nitride (AlN) on basal plane sapphire (Al₂O₃) substrates grown in hydrogen (H₂) and nitrogen (N₂) gas reaction environments. AlN films of similar thicknesses (~3.0 µm) were grown by metal-organic chemical vapor deposition (MOCVD) for comparison. The impact of gas environment on the AlN epilayers was characterized using high-resolution x-ray diffraction (HR-XRD), x-ray photoelectron spectroscopy (XPS), Raman scattering (RS), secondary ion mass spectroscopy (SIMS), cathodoluminescence (CL), atomic force microscopy (AFM), and scanning electron microscopy (SEM). The study showed that AlN layers grown in a N₂ environment have 50% less stress (~0.5 GPa) and similar total dislocation densities (~10⁹/cm²) as compared to films grown in a H₂ environment. On the other hand, AlN films grown in a H₂ gas environment have about 33% lesser carbon and 41% lesser oxygen impurities than films grown in a N₂ growth environment and have close to the ideal Al:N stoichiometric ratio. This paper will discuss the possible mechanisms that influenced the structural quality and impurity incorporation for two different gas environments to grow AlN epilayers in the MOCVD system on sapphire substrates.

Introduction

Aluminum nitride (AlN) belongs to the family of III-Nitride materials with the largest bandgap (6.2 eV) for any semiconductor material that has the native substrate; in addition, it has high thermal, chemical, and mechanical stability [1, 2]. AlN has a very high Baliga figure-of-merit (BFOM) that spurred research for its use in high-power and high-temperature applications [3]. High-quality AlN films on sapphire substrate with low dislocation density were used as low-cost templates for III-nitride-based devices because high dislocations adversely affect their performance [4, 5, 6]. The most common method used to grow low-cost AlN templates is metal-organic chemical vapor deposition (MOCVD) with sapphire as a substrate [4]. AlN can be grown by MOCVD using different precursors, notably Trimethyl-Aluminum (TMA)/Triethyl-Aluminum (TEA) as aluminum source and Ammonia (NH₃) to be used as a nitrogen (N₂) source. The selection of TMA or TEA is made to control the carbon incorporation and growth rates [5]. The MOCVD system is usually complex and consists of several pressure/mass-flow controllers. The most common approach is to use hydrogen (H₂) as carrier/push gas to deliver precursors precisely on the substrate's surface in a reaction or growth chamber. Thus, the MOCVD process inside the growth chamber would occur in an H₂ environment. An alternative to that approach is to use N₂ as carrier/push gas since N₂ gas is cheaper and safer to use than H₂ gas. The use of N₂ as a carrier gas in AlN growth was first reported on SiC substrates in 2007 [6]. The first report of AlN growth on sapphire substrates with N₂ as a carrier gas was published in 2012, which reported low-quality samples [7]. Recently, we have reported that N₂ gas can be used as an alternative to H₂ carrier gas to grow high-quality AlN films [8, 9]. Thus, a comparative spectroscopic study is warranted to understand the AlN material growth accomplished in these two different gas environments.
This paper reports the spectroscopic comparison of 3 µm thick AlN samples on a sapphire substrate produced by the MOCVD process with N₂ and H₂ as carrier gases. The grown samples were characterized using spectroscopic techniques to understand the impurity incorporation, stress-strain, dislocations, and surface morphology.

**Experimental Methods**

The AlN samples used for this study were grown using the MOCVD process, and their details were presented in our recently published papers [8, 9]. We restricted the thickness of the AlN layers to 3 µm for comparison. In the case of the AlN sample grown with the H₂ carrier gas, an additional low-temperature interlayer was introduced to reduce the crack and achieve the 3 µm thickness. The grown AlN films were characterized for their surface morphology, dislocation densities, residual stress, and impurities. The surface morphology of grown AlN was observed with Digital Nanoscope 3100 atomic force microscopy (AFM). The Philips X’pert MRD triple-axis diffractometer with Cu-Kα1 x-ray source was used to calculate dislocation densities. A scanning electron microscope (SEM) Zeiss Supra 25 FE-SEM was used to study the AlN samples’ cross-section along the growth direction. Residual stress in the samples was measured by Raman spectroscopy using Horiba Raman Spectroscope with a 638 nm red excitation laser with 25% power with 2400 gr/mm grating and 100 µm diameter aperture and 50 µm slit size in backscattered mode with a spectral resolution of 0.5 cm⁻¹. X-ray photoelectron spectroscopy (XPS) was carried out using a Kratos AXIS Ultra DLD XPS (Kratos Analytical). The XPS system is equipped with a monochromatic Al Kα source operated at 15 keV and 150 W, a hemispherical analyzer, charge neutralizer, catalysis cell, and a load lock chamber for rapid introduction of samples without breaking vacuum. The X-rays were incident at an angle of 45°, with respect to the surface normal. XPS analysis was performed at a pressure of ~ 1 × 10⁻⁹ mbar, and high-resolution core-level spectra were measured with a pass energy of 40 eV. The XPS experiments were performed by using an electron beam directed on the sample for charge neutralization. The curve fitting procedure was carried out using the XPS Peak 41 software, and the peak approximation was carried out by a combination of Gaussian - Lorentzian functions, with subtraction of Shirley-type background [10, 11]. Secondary Ion Mass Spectroscopy SIMS measurements were performed at Georgia Tech Materials Characterization Facility using an IONTOF TOF-SIMS 5-300 instrument. As the primary ion source, Bi + ions were used, and Cs + ions were used in the sputter gun at 2KV. Room-temperature cathodoluminescence (CL) measurements were carried out using a monochromatic CL imaging system housed in a Jeol JSM 5900LV high-resolution Scanning Electron Microscope (SEM) using a 10KV accelerating potential.

**Results And Discussions**

The growth of AlN samples used for this study was initiated with the deposition of the AlN rough layer (thickness ~ 0.3 µm) at low temperatures (950°C), which acts as a buffer layer. On top of buffer layers, high temperature (1250°C) AlN was grown to produce a 3µm thick layer with an atomically smooth surface. The AFM images of 2µm×2µm dimensions for 3.0 µm AlN layers are shown in Fig. 1(a) and Fig.
1(b) using H\textsubscript{2} and N\textsubscript{2} as carrier gases, respectively. Both the samples have a similar root mean square (RMS) surface roughness. The carrier gasses, N\textsubscript{2} and H\textsubscript{2}, (growth environments) produce different morphologies of the buffer layers \[8, 9\]. The growth environments dependent morphologies stem from the differences in thermal conductivity of the substrates, the decomposition rates, and the diffusion coefficients of precursors due to differences in carrier gases \[12\]. We reported that the morphology of the buffer layer produced with the N\textsubscript{2} carrier gas has two distinct types of islands that help reduce strain in the thick, high temperature, fully coalesced layers without any interlayer \[13\]. The AlN buffer layer produced with the H\textsubscript{2} carrier gas, surface morphology is more like single-mode islands; thus, an early coalescence in subsequent high-temperature AlN layers happens, resulting in cracks around the thicknesses > 1.5 µm. A low-temperature interlayer was introduced to achieve a thickness of 3 µm for AlN layers grown with the H\textsubscript{2} carrier gas, a proven method to mitigate the cracking \[14\].

Fig. 2 shows the cross-section SEM images of 3 µm samples grown with a) H\textsubscript{2} carrier gas and b) with N\textsubscript{2} carrier gas. We observed that the void terminates close to the sapphire substrate for samples grown with the H\textsubscript{2} carrier gas due to early coalescence. Thus, we have to incorporate a low temperature 0.1 µm interlayer at the thickness of 1.5µm to achieve a 3 µm AlN thick layer. We have shown that the low-temperature buffer layer grown in the N\textsubscript{2} environment has two distinct islands that impede early coalescence; thus, Fig. 2 (b) shows the termination of voids at the larger thickness parallel to the growth directions, which helps to grow thick crack-free AlN samples without the low-temperature interlayer.

The 3 µm AlN samples were thoroughly analyzed with x-ray diffraction; the details of the method were reported in the reference \[8, 9\]. The full-width-at-half-maximum (FWHM) of the asymmetric (10\textsubscript{ī}2) scan of III-nitrides (AlN, GaN, and AlGaN) can indicate the total dislocation density of the material. The FWHM of (10\textsubscript{ī}2) (off-axis) \(\omega\) scan for 3 µm samples grown with H\textsubscript{2} carrier gas was \(~330\) arcsec whereas it was 307 arcsec for 3µm sample grown with N\textsubscript{2} carrier gas. The calculated screw dislocations were in the order of \(10^7\) cm\(^{-2}\), and total dislocation density was in the order of lower \(10^9\) cm\(^{-2}\) (using the Williamson and Hall method) \[9, 15, 16\]. The slightly lower off-axis value can be delayed coalescence or the absence of low-temperature interlayer in the AlN samples grown in N\textsubscript{2} gas environment. The uncoalesced layers can act as a secondary buffer layer to grow slightly reduced dislocation high-quality thick AlN; however, the differences in dislocation densities in both cases are within the margins of error in the calculations.

The XPS survey scans and high-resolution (HR) scans were performed at two locations – the surface and 5 nm depth from the surface of the samples. We will analyze the scan at a depth of 5 nm only because of ambiguities in the surface scan due to surface contamination associated with sample handling. The full spectra of two AlN thin films and all HR spectra were calibrated to the (carbon 1 s) C1s peak at 284.6 eV. Survey scan shows that XPS spectra are composed of aluminum, nitrogen, carbon, oxygen, and maybe hydrogen. There is a chance that both samples might contain some hydrogen, but hydrogen cannot be detected as it has only one electron and a small photoionization cross-section. Fig. 4 (a) and 4(b) show the deconvoluted C1s peak for the AlN samples grown with N\textsubscript{2} and H\textsubscript{2} carrier gases. The main peak of the spectra of C1s states measured at the surface of AlN is around 284.6 eV has high intensity, which
indicates C. We observed that the intensity of C1s drops significantly at 5 nm depth, leading to the actual amount of C in the sample. The C1s graph can be deconvoluted into four different chemical states such as C=C at 284.6 eV, C-C/C-N close to 286.6 eV, C-O close to 288.4 eV, and O-C=O bond close to 288.6 eV [10, 11]. The XPS high-resolution scan of (aluminum 2 p) Al2p chemical state at 5 nm depth is shown in Fig. 4(c) and 4 (d) for AlN samples grown in N2 and H2 with carrier gases, respectively. The atomic concentration of Al is higher in the case of Fig. 4 (d). Note that the deconvoluted peak positions are the same for both deconvoluted peaks confirming the same type of ionic bonding states in both samples [17, 18].

Table 1. Atomic concentration (AC) of AlN samples at the depth of 5 nm grown in N2 and H2 environments.

<table>
<thead>
<tr>
<th>AC of AlN</th>
<th>Grown in N2 environment (%)</th>
<th>Grown in H2 environment (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Al</td>
<td>24.8</td>
<td>29.4</td>
</tr>
<tr>
<td>C</td>
<td>12.3</td>
<td>12.9</td>
</tr>
<tr>
<td>N</td>
<td>43.6</td>
<td>42.3</td>
</tr>
<tr>
<td>O</td>
<td>19.3</td>
<td>15.4</td>
</tr>
</tbody>
</table>

Table 1 shows the XPS detected elements after 5 nm Ar ion etching where components are expressed in terms of atomic concentration (AC) in percentage. We observe that both samples exhibit the presence of C and O. In the case of sample grown in the H2 gas environment, the amount of oxygen is slightly less than the sample grown in the N2 gas environment. On the contrary, the amount of Al is much higher in the case of the sample grown in H2 gas environment, which can be expressed as the Al-N stoichiometric ratio that is closer to the ideal case. The source of the C and O containing impurities can be following - a) oxygen/carbon incorporation during the growth process from the a) growth precursors and carrier gases, b) impurities absorbed when sample exposed to air, c) Ar+ ion sputtering to check the elements at 5 nm depth, d) from the XPS chamber [19].

To further investigate the presence of impurities and at different depts from the sample surface in the AlN films, the secondary-ion mass spectrometry (SIMS) was utilized in time-of-flight (ToF) mode. The SIMS measurements were performed at the Georgia Tech. Material Characterization Facility. The ToF SIMS machine uses two ion guns: one for sputtering only and another one for analysis purposes. For sputtering, Cesium ions were used with an energy of 2 keV for creating a crater and bismuth ions with 25 keV for analyzing the sputtered area along the way. To measure these samples, they were mounted on a sample holder using Cu tape, and the sputtering created a crater area of 300 μm²; the area of analysis by the bismuth ions was 150 μm². Fig. 5 shows the average relative SIMS detected counts for Al2+, Al+, H+, N+, O+ (with respect to Al+ normalized to 1) for both AlN samples grown with N2 carrier and H2 carrier.
gases. No significant change was observed in the composition of various compounds up to 0.8 µm (and beyond data is not shown here). Compared to N$_2$ grown samples, H$_2$ grown samples have 33-39% less C, 33% less H, 41% less O; a similar trend was observed in XPS analysis of these samples.

To further understand the presence of impurities, the samples were studied by cathodoluminescence (CL). In III-nitride semiconductors near band edge emissions, such as free exciton or bound exciton recombination are characteristics of high-quality materials with lower impurity concentration and lower defect density [20, 21]. Fig. 6 shows CL spectra of the AlN sample grown with the N$_2$ carrier gas and H$_2$ carrier gas and the HVPE grown free-standing AlN. The peak close to 6.0 eV dominates in all the samples. Davis et al. simulated the CL spectra for aluminum gallium nitride, Al$_x$Ga$_{1-x}$N, samples, where x is the composition of the aluminum [22]. For x=1, in those calculations, the pure AlN near band edge emission is close to 6.0 eV, which matches our measurements. If we closely observe these peaks, we can see that there is hump-like peaks are present in all the samples close to 3.8 eV, which is well known for oxygen presence [20]. We have grown our samples on sapphire substrates, so to exclude the idea that this peak can come from sapphire substrate oxygen signal, we have measured the free-standing AlN grown by hydride vapor phase epitaxy (HVPE). We observed a peak close to the 3.8 eV for the free-standing AlN sample, confirming that the source of the oxygen-related peak is the AlN, not the sapphire substrate. In addition, the electron penetration depth is only a few nm in the AlN samples in the case of 10kV accelerating voltage. So, there is less probability of incident electrons reaching the sapphire substrate. Thus, we can conclude with certainty that the source of oxygen signal is from the oxygen impurities in the AlN samples. According to Youngman et al., the luminescence peak position from oxygen-related defects in AlN shifts from 4 eV to 3.3 eV as the oxygen increases from less than 0.1 to about 0.8% [23]. We have assigned the peak at 3.8 eV, which agrees with the previously reported data [20]. The near band edge emission (NBE) peak (~ 6.0 eV) peak arises from the free excitons or excitons bound to the shallow donor or acceptor impurities. The NBE peak of the samples grown with N$_2$ and H$_2$ carrier shows a blue shift with respect to HVPE grown free-standing AlN sample, which is related to stress in the MOCVD grown samples. In the next section, we evaluate the stress in these films by Raman spectroscopy measurement.

The impurities, point defects, and extended defects alter the stress values in the epitaxially grown films. Raman spectroscopy has been previously demonstrated as an effective tool to calculate stress in thin films [24]. In the case of AlN, high-resolution phonon linewidth can provide the crystalline quality of the thin films. It has been previously reported that for single-crystal bulk AlN, FWHM of E$_2$ (high) phonon mode is 3 cm$^{-1}$ [25]. For a 3 µm AlN sample grown with N$_2$ carrier gas, the E$_2$ (high) phonon linewidth was 3.8 cm$^{-1}$; on the other hand, a 3 µm AlN sample grown with of H$_2$ carrier, it was 5 cm$^{-1}$. We employed the biaxial stress coefficient to calculate stress based on the Raman shift. Biaxial stress coefficient () depends on the growth technique [24]. We considered 657.04 cm$^{-1}$, the bulk sample E$_2$(high) as the stress-free frequency, and calculated the stress based on ± 0.3 cm-1/GPa [24]. Figure 7 shows the normalized Raman spectra of E$_2$(high) phonon mode where the blue shift towards the right for the grown samples indicates compressive stress. The compressive stress in AlN film results from the lattice mismatch between sapphire substrate, thermal expansion coefficient mismatch, and stress generated
during the coalescence process and impurities [26]. We have previously demonstrated that, due to the delayed coalescence, the N\textsubscript{2} carrier grown samples show less compressive stress [8, 9].

**Conclusions**

We presented the spectroscopic comparison of 3 \textmu{}m thick AlN thin film on basal plane sapphire (Al\textsubscript{2}O\textsubscript{3}) substrates grown in H\textsubscript{2} and N\textsubscript{2} gas environments. Both samples have good crystalline quality as depicted by XRD measurement with FWHM of off-axis peak for (10\textit{i}2) planes of 307 and 330 arcsec in N\textsubscript{2} and H\textsubscript{2} respectively. XPS and SIMS measurements showed higher impurities of C, O in samples grown in the N\textsubscript{2} growth environment. Raman's study showed lower stress in AlN layers grown in the N\textsubscript{2} growth environment. The FWHM of AlN E\textsubscript{2}(high) phonon values were 3.8 cm\textsuperscript{-1} and 5 cm\textsuperscript{-1} for samples produced N\textsubscript{2} and H\textsubscript{2} environments, which could be related to buffer layers and higher impurities concentrations that may result in less stress. There are specific differences in the samples grown with H\textsubscript{2} and N\textsubscript{2} carrier gases that can affect the device performance; thus, selection of the gas should be made according to device design.

**Declarations**

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**Author contribution:**

S. H.: Conceptualization of this study, experimentation, Data curation, Methodology, Writing – original draft, M. J.: Revision, S. K.: XPS measurement and visualization, M.G.: SEM and CL measurement and visualization, I.A.: Conceptualization of this study, Visualization, Editing, Revision, PI of this study.

**Conflict of interest:**

The authors declare that they have no conflict of interest.

**Data availability**
The data generated during and/or analyzed during the current study are available from the corresponding authors on reasonable request.

References


4. V. Adivarahan, A. Khan, I. Ahmad et al., Semiconductor and template for growing semiconductors (Google Patents, 2018)


Figures
Figure 1

AFM images of 3 µm thick AlN layers grown by using a) H₂ as a carrier gas and b) a similar layer with N₂ as a carrier gas.

Figure 2

Cross-section SEM images show the voids’ formation for 3 µm thick AlN samples were grown with a) H₂ as a carrier gas and b) N₂ as a carrier gas [9].
Figure 3

Comparison of high-resolution XPS spectra of AlN showing the chemical states of C1 grown with a) N₂ carrier gas, b) H₂ carrier gas, and Al2p grown with c) N₂ carrier gas, d) H₂ carrier gas.
Figure 4

Depth profile for AlN SIMS spectra for different ions for AlN grown with a) N\textsubscript{2} carrier gas b) H\textsubscript{2} carrier gas sample.

Figure 5

Cathodoluminescence (CL) data for AlN samples grown with N\textsubscript{2} and H\textsubscript{2} carrier gases and HVPE grown free-standing AlN show the near band edge emissions.

Figure 6

Normalized Raman data of AlN samples grown in N\textsubscript{2}, H\textsubscript{2} carrier gases, and free-standing AlN grown by HVPE.