Correlation between optical, morphological and compositional properties of Aluminum Nitride thin films by Pulsed Laser Deposition

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Abstract. AlN thin films were grown in a N₂ atmosphere onto a Si/Si₃N₄ substrate by pulsed laser ablation. We have varied the substrate temperature for the thin film growth, using X-ray Reflectometry (XRR) analysis, we have characterized the thickness and density of the thin layer and the interface roughness from the X-ray reflectivity profiles. Experimental data showed that the root-mean-square roughness was in the range of 0.3 nm. X-ray photoelectron spectroscopy (XPS) was employed to characterize the chemical composition of the films. These measurements detected carbon and oxygen contamination at the surface. In the high-resolution X-ray photoelectron spectroscopy Al₂p data, binding energies for Al-N and Al-O species were identified but no Al-Al species were present. In the N¹s data, N-O species were not detected, but chemically bonded O was present in the films as Al-O species. Furthermore the value of optical energy gap, E_g was about 5.3 (± 0.1) eV. The composition varied with process conditions, and the nitrogen content decreased in AlN films processed above 500°C.

Index Terms—Acoustic materials, Coatings, Laser sintering, Plasma materials processing, SAW filters, Wide band gap semiconductors

I. INTRODUCTION

Recent experiments indicate that aluminum nitride (AlN) can be used as an insulator of integrated circuits [1,2].

AlN has a large direct band gap of 6.2 eV, high thermal conductivity (up to 320 W m⁻¹ K⁻¹) high decomposition temperature (2700 K). Because of these excellent physical properties, AlN thin films have a great potential for microelectronic devices [3]. Thus, using AlN as an insulator could be essentially reduced the influence of the self-heating effect of traditional devices. In Addition, AlN thin films have a low thermal expansion coefficient, high breakdown dielectric strength, high chemical and thermal stability, and the highest reported acoustic wave velocity surface among piezoelectric materials [4, 5]. All these properties make AlN a promising material for application in microelectronic and optoelectronic devices such as high power and high temperature devices, short wavelength emitters, surface acoustic wave devices (SAW), and electronic packaging [6].

A variety of methods have been used to deposit AlN thin films, including reactive magnetron sputtering [7], molecular beam epitaxy (MBE) [8, 9], pulsed laser deposition (PLD) [10, 11], etc. In most of the previous work sapphire, Silicon or SiC was used as the substrate, but it is believed that Si/Si₃N₄ substrate provides further flexibility in the development of Si-based technological applications [12]. PLD in particular lends itself to low temperature processing because the average energy of particles in the laser-evaporated plume is considerably higher (10 eV) than the thermal evaporation energy (0.1 eV). Surface analysis techniques are widely used in the characterization of semiconductor thin films, as well as in in-situ monitoring device production processes. With the continuing minimization of thin film devices, characterization techniques with high reliability and precision are required.

X-ray reflectivity (XRR) is believed to be able to offer accurate thickness values for both thin films and multilayer with the same precision, as well as densities, surface and interface roughness [13]. In the present investigation, we prepared AlN thin films on Si/Si₃N₄ substrates using PLD technique. The AlN coatings were prepared at different substrate temperatures and nitrogen gas pressure was kept fixed at 0.9 Pa. The coatings were characterized using X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS) techniques.
II. EXPERIMENTAL METHODS

AlN thin films were deposited by PLD system which can be evacuated to the background pressure of 4·10^{-6} Pa. A commercial Aluminium (5N purity) target was ablated using a Nd:YAG laser of 1064 nm wavelength and 9 ns pulse duration (Spectra Physic). An energy density of 10 J/cm² and a laser frequency of 10 Hz were used, respectively. A more detailed description of this deposition technique can be found elsewhere [14, 15]. The ablated species were deposited onto Si/Si₃N₄ substrate, which was placed at a distance of 50 mm from the target. AlN thin films were grown at different substrate temperatures ranging from room temperature to 600 °C. During the deposition of AlN, N₂ gas (99.999% purity) was introduced into the growth chamber, The N₂ pressure was fixed at 0.9 Pa. Under these growth conditions, up to 250 nm-thick AlN with a deposition time around 10 min. The X-ray diffraction with low angle or X-ray reflectivity (XRR) measurements have been performed on a Bruker D8 Discover diffractometer, the incident beam (Cu Kα radiation, λ= 1.5418 Å). Measurements were taken in a θ−2θ geometry from 0.1° to 3.0° at 40 kV/20 mA tube power to maintain linearity in the detector response. X-ray photoelectron spectroscopy (XPS) measurement was carried out to characterize the bonding structure and compositional properties of the deposited thin films. XPS measurements were carried out using a PHOIBOS HSA3500 spectrometer with monochromatic Mg Kα 1253.6 eV X-ray source with a power of 200 W. The optical characterization was performed with spectroscopy (Shimadzu, UV-3600 UV-Vis-NIR spectrophotometer).

III. RESULTS AND DISCUSSION

A. SEM analysis

In previous works, we have shown the influence of the surface quality of the AlN nanostructures as substrates for Surface Acoustic Wave sensor (SAW) [16], its composition and surface roughness have a critical impact on the quality of the device. As the surface acoustic wave is only propagated on the surface, all the energy is concentrated almost within a wavelength from the surface to the inside. When the surface roughness are more than a wavelength, apparently the surface acoustic wave is not able to pass through. Generally, the surface roughness of the film are required to be less than 30 nm. Figure 1.

Micrographs obtained from SEM sample and analysis of the surface quality obtained by AFM; show the reduction of the roughness with increasing deposition temperature going from 3.6 nm to a substrate temperature of 200°C - Fig.1a-, then to a surface roughness of 1.5nm to 500°C - Fig.1b-, and finally stabilize at a roughness of 1.2 nm for a growth temperature of 600°C- Fig.1c-, which conforms to the requirements of SAW devices for the surface roughness of AlN films.

In Figure 2. Roughness and surface defects due to the high bombardment caused by high power during deposition of the samples are observed. In this case is a disadvantage as it may cause a drastic decrease in the speed of the surface waves and even cause short circuits in the configurations of the fingers.

Usually, the thin films are deposited with a substrate temperature that allows increasing the surface mobility of the atoms in the substrate and surface uniformity provide preventing these droplets. In previous work has been studied more thoroughly a description of the influence of substrate temperature and morphological quality frequency response of the SAW sensors. [15]
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B. XRD analysis

In order to identify the crystalline nature of the films, XRD measurements were performed for as-deposited samples. These measurements were carried out for the samples prepared on Si/Si$_3$N$_4$ substrates in the range from 10° to 68° for 2θ. The effect of temperature substrate on the structure of AlN films is systematically investigated.

These thin films exhibit no XRD peaks, did not show any characteristic AlN diffraction pattern, suggesting that the films were amorphous. The results reveal no influence of substrate. The lack of crystalline in these films appears to be related to the low growth temperature. In general, it has been observed that regardless of the growth technique employed, the growth of AlN thin films on various substrates at temperature higher than 600°C has resulted in preferentially oriented films, while depositions at temperatures below 600°C have produced amorphous films. These trends strongly suggest that to achieve crystallinity in thin films, a high temperature and high energy are essential requirements for deposition of AlN films on Si/Si$_3$N$_4$ substrates.

C. X-ray Reflectivity Measurement

X-ray diffraction with low angle or X-Ray Reflectivity (XRR) has been widely recognized as a fundamental method for independently obtaining the thickness, density, and roughness at thin films, without the need standards.

The unknown parameters were determined through a fitting process using the commercial software Panalytical X’pert reflectivity. A one-layer on the substrate was enough to describe the experimental data for all films [17]. Figure 3 shows the XRR pattern of the as-deposited samples at very low angles (all of the incident X-rays are reflected) and the simulated curves for 0.9 Pa pressure AlN films grown at 200°C, 500°C and 600 °C. The thickness of the films is derived from the oscillation amplitude of the XRR measurements. By the procedure called Generic Algorithm an iterative criterion is used to compare experimental data with the initial parameters of the simulation set up to obtain a curve fit close to the real curve of reflective spectra. One can see that the simulated curves fit the experimental data quite well. The estimated interfacial layer thickness is less than 1 nm for all of the substrates.

With the thickness values of the thin films, we calculated the average deposition rate, which is approximately 10.5nm/min. It is well known that the slope of oscillation determines the surface roughness of the samples, when comparing figures 3a, 3b and 3c, the slopes are slightly equal, indicating that the samples have approximately the same surface roughness. However, for sample prepared in 200 °C the oscillation amplitude persist even at higher incidence angle, which is indicative for smooth films.

The values of thickness, roughness and density of the AlN thin films were given by the simulation process of the software and it can be seen in Table I.
TABLE I
VALUES GIVEN BY THE SIMULATION PROCESS OF X’PERT REFLECTIVITY SOFTWARE

<table>
<thead>
<tr>
<th>Growth Temperature</th>
<th>Density (g/cm²)</th>
<th>Thickness (nm)</th>
<th>Roughness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>1.25</td>
<td>100.60</td>
<td>0.21</td>
</tr>
<tr>
<td>500</td>
<td>1.45</td>
<td>100.90</td>
<td>0.31</td>
</tr>
<tr>
<td>600</td>
<td>1.25</td>
<td>81.37</td>
<td>0.30</td>
</tr>
</tbody>
</table>

Units: Temperature (°C) Celsius. Density (g·cm⁻²) g = gram, cm = centimeter, Thickness (nm) Roughness (nm) = nanometers.

D. XPS spectroscopy

XPS measurement was performed to investigate chemical states of AlN thin films. In Figure 4, XPS spectra are shows typical XPS spectrum of AlN films prepared at nitrogen gas pressure of 0.9 Pa with respect to the different substrate temperatures. In addition to aluminum, carbon, and nitrogen, these spectra show also the presence of silicon and oxygen. It is important to note that this technique is highly sensitive and extremely superficial, relating information from a few tens of nanometers. XPS spectra correspond to temperatures of 200 °C, 500 °C and 600 °C and these elements to the expected continuous and homogeneous samples of Al-N observed. Similarly, a thin layer of O1s related to phase formed of typical oxynitrides for AlN layers bonded to surface oxygen is observed. Finally, C1s surface indicates the formation of carbon dioxide associated with the existing carbon and surface contamination but after the first etching for XPS measurements in high resolution is not observed.

Likewise, variations in the conductivity of the surface can cause significant fluctuation in the speed of the surface acoustic wave, which eventually leads to a change in the measurement frequency. The possible formation of CO molecules on the surface of the thin film and electric dipoles interact, as modifying the work function is very low. Mainly due to low carbon content - less than 4% - that is only on the surface before the measures of ultra-high vacuum XPS.

In addition to the survey scan, high-resolution scans were obtained for the Al2p, N1s and O1s. Figure 5 shows the XPS core level spectra of Al2p (a), N1s (b) and O1s (c) regions obtained from the surface of AlN films deposited at different substrate temperature. The peak positions were calibrated using the C1s peak at 284.8 eV as the reference. Both the XPS Al (2p) and N (1s) peaks are lightly asymmetric indicating the presence of different bonding types and configurations associated to nitrogen within the films. Since the monochromator Mg Ka radiation was used as X-ray source, the resolution of these spectra should be good enough to analyze. The Al2p core-level spectra recorded from the as-deposited films at different substrate temperature presented in Fig. 5a and centered at 74.3 eV. Al2p peak of the AlN film should be decomposed into two components, i.e., Al-O, AlN, the major contribution at 600°C, is centered at 74.1 eV, which can be associated with the presence of Al-N bonds [18], whereas the small peak at a higher binding energy is assigned to Al in oxide-like bonding (75.0 eV). It can be seen that the binding energy of Al2p shifts slightly with the increasing temperature from 200 °C to 600 °C. The shift of binding energy (BE) maybe attribute to the formed unstoichiometric AlNx compounds. However, there were no systematic trends in the data that would indicate that there was a correlation between the peak position and substrate temperature.

All aluminum Al2p peaks were fitted as one or more pairs of spin-orbit split sub-peaks with a separation of 0.4 eV between the Al2p3/2 and Al2p1/2 components. The ratio of the area of the 2p3/2 component to the area of the 2p1/2 component was fixed at 2:1. All Al 2p sub-peaks were fitted as 95% Gaussian. For this study, the binding energy of a fitted Al2p spin-orbit sub peak pair is reported as the centroid of the pair. The centroid of the spin-orbit pair in eV was calculated as shown in Equation 1:

$$Al\text{2p Centroid}(eV) = \frac{A_{Al2p3/2} \cdot E_{Al2p3/2} + A_{Al2p1/2} \cdot E_{Al2p1/2}}{A_{Al2p3/2} + A_{Al2p1/2}}$$

Where $A$ is the adjusted sub peak integrated area and $E$ is the adjusted sub peak binding energy in eV. The N1s data were fitted with four sub peaks, with all sub peaks fitted as 90% Gaussian. The O1s data were fitted with three sub peaks, also fitted as 90% Gaussian [19].

The N1s spectrum in Fig. 5(b) showed a peak centered at a BE of 397.0 eV, corresponds to N in Al-N, which agrees well with the previously reported spectra for AlN films [19, 20]. Decomposition of the N1s spectrum was curve fitted with two peaks, one at 396.7 eV, the value of this peak matches very well with that of N1s in Al–N bonds [21], and the other at 398.38 eV, corresponds to the BE of free nitrogen.

Figure 4. XPS survey scan of AlN on Si/Si1−xNx deposited at 0.9 Pa and different substrate temperature using a Nd:YAG laser (pulsed = 9 ns and 7 J/cm²). The carbon and oxygen species were associated with adventitious hydrocarbon and an oxidized AlN surface that resulted from exposure to air after the film was grown.
The peak area ratio in the spectra shows the relative amount of N atoms bounded with Al atoms change, although there is no clear tendency. The areas obtained from the curves are shown in Table II. The profile of N 1s spectrum has a similar trend to that shown by Al 2p, suggesting the formation of aluminum nitride in the layer.

The results of XPS indicate that the Al–N is the main bonds in the films, with some surplus aluminum in them, which may be due to the higher evaporation rate of aluminum under PLD technique, and will probably, influence the insulating characteristics of the AlN thin films. N 2 gas added during deposition could greatly enhance the N:Al ratio. The peak of O 1s - in Fig. 4(c) - could also be found in the XPS spectra, which probably comes from aluminum oxides on target surface and a little oxide within AlN films.

### Table I

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>(%) N 1s N unbounded</th>
<th>(%) Al 2p</th>
<th>Al-N</th>
<th>Al-O</th>
</tr>
</thead>
<tbody>
<tr>
<td>200</td>
<td>71.5</td>
<td>28.5</td>
<td>83.6</td>
<td>16.4</td>
</tr>
<tr>
<td>500</td>
<td>89.6</td>
<td>10.4</td>
<td>81.3</td>
<td>18.7</td>
</tr>
<tr>
<td>600</td>
<td>73.7</td>
<td>26.3</td>
<td>90.7</td>
<td>9.3</td>
</tr>
</tbody>
</table>

Units: Temperature (°C).

The reflectance of the aluminum and the eye sensibility are shown for comparison. The spectra of the samples show high reflectance’s for long wavelengths, near to 62% for the AlN films deposited with room temperature and close to 28% for AlN films deposited with 600°C. These results agree with our previous results [26] in which the incorporation of nitrogen response varies in reflectance of the samples and the last location in the color map [26]. These new results Transmittance - UV-Vis show the direct relationship between the incorporation of nitrogen and the gap of AlN.

Transmittance measurements in UV-Vis NIR were performed in order to determine the effect of the incorporation of nitrogen and substrate temperature on the optical properties of AlN films. The optical gap of the films was calculated using the Tauc model [27] can be described by the equation:

$$ \alpha hv = A (hv-E_g)^m $$  \hspace{1cm} (2)

In this expression A is a constant of proportionality, $hv$ is the photon energy, $E_g$ is the optical band gap; $m=2$ which is a characteristic value for semiconductors transitions from the valence band to the conduction band $\alpha hv$ vs $hv$ value being the energy gap $E_g$ the intersection of the linear part of the graph obtained with the axis of the energies the incident photon. The optical energy gap, $E_g$, determined from Tauc model (Figure 6), was about 5.3 ($\pm$ 0.1) eV for AlN films with amorphous structure. These results agree with the literature for thin films of AlN.

On the other hand the low value of 5.3 ($\pm$ 0.1) eV was attributed is attributed to localized electronic states due to vacancies in the links Al-N as no transitions hybridization were observed around the Al2p orbital at different deposition temperatures.

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films of AlN and are consistent with those reported in the literature for thin energy of 5.3 (± 0.1) eV for AlN thin films. These values AlN thin films.

will probably, influence the insulating characteristics of the may be due to the higher evaporation rate of aluminum, and in the films, with some surplus aluminum in them, which The results of XPS indicate that the Al main bonds in the films, with some surplus aluminum in them, which different substrate temperature. XRD and XPS investigations reveal that the AlN film quality strongly

IV. CONCLUSION

We have successfully AlN thin films on Si/Si112 substrates using Nd:YAG ablation of Al target at low gas pressure and different substrate temperature. XRD and XPS investigations reveal that the AlN film quality strongly depends on the growth temperature. The surface roughness value of the films was as low as [0.3nm] 3.5 nm.

The results of XPS indicate that the Al–N is the main bonds in the films, with some surplus aluminum in them, which may be due to the higher evaporation rate of aluminum, and will probably, influence the insulating characteristics of the AlN thin films. UV visible results show a low band gap energy of 5.3 (± 0.1) eV for AlN thin films. These values are consistent with those reported in the literature for thin films of AlN and III-V nitrides.

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