CHARACTERIZATION OF AlN THIN FILMS FABRICATED BY REACTIVE DC SPUTTERING: EXPERIMENTAL MEASUREMENTS AND HÜCKEL CALCULATIONS

MANUEL GARCÍA-MÉNDEZ
Laboratorio de Nanociencias y Nanotecnología,
Facultad de Ciencias Físico-Matemáticas de la UANL,
División de Posgrado. Manuel L. Barragán S/N, Edif. de Posgrado,
CIDIT-UANL, Km. 10, nueva carretera al aeropuerto, 66600, Apodaca, N.L. México
mgarcia@fcfm.uanl.mx

SANTOS MORALES-RODRÍGUEZ
Programa de Posgrado en Ing. Física Industrial,
Facultad de Ciencias Físico-Matemáticas de la UANL,
División de Posgrado. Manuel L. Barragán S/N, Edif. de Posgrado,
Ciudad Universitaria, San Nicolás de los Garza, N.L., C.P. 66450, México
smorfi@hotmail.com

DONALD H. GALVÁN and ROBERTO MACHORRO
Centro de Ciencias de la Materia Condensada,
Universidad Nacional Autónoma de México Km. 107,
Carretera Tijuana-Ensenada, Ensenada, B.C., C.P. 22800, México
roberto@cnyn.unam.mx
donald@cnyn.unam.mx

Received 19 June 2008

A set of AlN thin films was prepared by reactive magnetron sputtering at room temperature. The effect of oxygen impurities on the structural and optical properties of AlN films is discussed. The structural and optical properties were characterized using X-ray diffraction (XRD) and spectroscopic ellipsometry, respectively. Depending on the deposition conditions, films can grow hexagonal (würzite, P6₃m3) or cubic (zinc-blende, Fm3m) in microstructure. From the optical measurements, the ellipsometric parameters \((\psi, \Delta)\) and the real refractive index as a function of energy were obtained. From the ellipsometric measurements, a model of Lorentz single-oscillator was employed to estimate the optical band gap, \(E_g\). In the theoretical part, a calculation of density of states (DOS) and band structure was performed to be compared with the experimental results.

Keywords: DOS; ellipsometry; AlN thin films; reactive sputtering.

*Corresponding author.
Aluminium Nitride (AlN) is a material with a broad range of applications in electronic and optoelectronic devices due to its many physical and chemical properties. AlN has a high thermal conductivity ($260 \text{ Wm}^{-1}\text{K}^{-1}$), a direct band gap ($E_g = 5.9 - 6.2 \text{ eV}$), high hardness ($2 \times 10^3 \text{ kgf mm}^{-2}$), high fusion temperature ($2400^\circ\text{C}$) and a high acoustic velocity.\textsuperscript{1-6} Polycrystalline AlN thin films oriented along the c-axis can be implemented as a part of integrated (Ultra Large Scale Integrated) devices, optical sensors in the UV range or in acoustic-optic devices.\textsuperscript{1-7} The optimal performance of developing devices depends directly on the crystallographic and electronic properties of the AlN layer.\textsuperscript{3,4,8-10} In addition, oxidized AlN (AlNO) is a material with good thermal and chemical stability. AlNO can be used as a protective coating and dielectric film in electronic circuits. With AlNO, it is possible to manufacture Metal Insulator Structures (MIS). For example, an AlNO film can replace the conventional passivating films of Si$_3$N$_4$ or SiO$_2$ on p-silicon solar cells.\textsuperscript{1-5} AlNO has also been investigated as dosimetric material for ionizing radiation and UV radiation. Besides, AlNO possesses a spectral sensitivity similar to that of human skin, which makes the AlNO a candidate material to be used in medical applications for UV dosimetry.\textsuperscript{11}

AlN films (pure and oxidized) can be prepared with several techniques: chemical vapor deposition (CVD),\textsuperscript{12-14} molecular beam epitaxy (MBE),\textsuperscript{15,16} ion beam assisted deposition\textsuperscript{17,18} or direct current (DC) reactive magnetron sputtering. Application of magnetron technique facilitates the growth of polycrystalline AlN films on large substrates at a low temperature (as low as 200$^\circ\text{C}$ or even at room temperature) with the same properties like those films obtained through CVD and MBE.\textsuperscript{19-22}

In a reactive-magnetron process, molecules of a reactive gas combine with the sputtered atoms from a metal target to form a compound thin film on a substrate. Thereby, the optical, electronic and structural properties of the resulting films can be modified by the experimental deposition conditions. Due to the affinity of AlN with oxygen,\textsuperscript{23} AlN films create a surface oxide layer, which can modify their electronic structure and promote shifts in luminescence peaks.\textsuperscript{24,25} The luminescence properties of AlN are determined mainly by the presence of oxygen impurities in the host lattice.\textsuperscript{11} In the design of optoelectronic devices, the correlation between the physical dimensions and the optical parameters is required, thus a good characterization is needed.

In this work, a set of samples were grown by reactive magnetron-sputtering with varying deposition time, magnetron power, gas pressure and gas mixture. It is well-accepted that the properties of the films depend on the deposition conditions such as substrate temperature, working pressure, gas flow rate and the incidence angle for sputtered particles. In general, the procedure for deposition consists of varying one deposition parameter at a time while keeping all others fixed, in an attempt to maximize a given thin film property. The purpose of this work was to study the
effect of oxygen impurities on the structural and optical properties of AlN films. Electronic structure calculations are performed to determine the density of states (DOS) and to relate it to the observed optical properties.

2. Experimental Procedure

2.1. Films deposition

Depositions were carried out in a high-vacuum pirex chamber connected to a mechanical and turbomolecular pump (100 lt/sec of pumping speed). Depositions started when the chamber reaches a base pressure of $1.33 \times 10^{-6}$ mbar. The chamber was equipped with a magnetron on which the target was placed. The substrate holder is located at 5 cm in front of the target. The substrate holder was equipped with a heater and a thermocouple. The magnetron was connected to a direct current (DC) energy power-supply. The power-supply allowed to control the voltage (Volts) and to measure the current (Amperes) and power (Watts) on target. The input of high purity gases (Ar, N$_2$, O$_2$: purity of 99.999 wt.%) into the chamber was controlled by individual rotometers. The gas pressure was measured using a Pirani (from 1 bar to $6.6 \times 10^{-3}$ mbar) and cold cathode (from $6.6 \times 10^{-3}$ mbar to $1.33 \times 10^{-6}$ mbar) gauges.

A disc of aluminum (2.54 cm diameter, 0.317 cm thick, 99.99% purity) was used as a target and glass microscope slides as substrates. Substrates were rinsed in acetone as solvent and ultrasonically cleaned before being placed into the chamber. The aluminum target was sputter-cleaned with argon during 20 min. There was a shutter placed between magnetron/substrate during cleaning. After cleaning, the argon gas was replaced by a gas mixture previously prepared with a specific composition. Then the shutter was opened and deposition of the films in the gas mixture took place. For the growth of AlN films, the sputtering process was carried out with a preset mixture of Ar + N$_2$. For the growth of AlNO films, the sputtering process was carried out with the mixture of Ar + N$_2$ + O$_2$. No heating was applied during the growth of the samples. The deposition process was carried out at a steady temperature of about 323 K. This temperature increases a few degrees because of the heat generated by the sputtering process on the target. Temperature was similar for each sample included here. In this paper, a set of four samples was selected for presentation.

For Sample 4, the electronic properties at the surface level were characterized with X-ray Photoelectron Spectroscopy (XPS). Analyzing the surface reaction which takes place between Al with N$_2$ and O$_2$ can provide information about the nitride/oxide formation during the growth on the films at the substrate.

The experimental conditions utilized for the growth of thin films are summarized in Table 1. For Sample 1, Sample 2 and Sample 4, the sputtering process started with the gas mixture of Ar + N$_2$. For Sample 3, the sputtering process started with the gas mixture of Ar + N$_2$ + O$_2$. 
2.2. Films characterization

2.2.1. Structural characterization

Structural characterization of the films was performed by X-ray diffraction (XRD) methods using a Philips X’ Pert equipment (copper anode, K\textsubscript{α} radiation, wavelength, \(\lambda = 1.54 \text{ Å}\), step size 0.005\(^{\circ}\)). Measurements were taken in theta/2theta scans of Bragg–Brentano geometry.

For indexation, the reflection peaks of the experimental diffractogram were compared with the standards of the JCPDS database.\(^{26}\) Thereafter, the PowderCell Software\(^{\circledR}\) was employed to determine the preferred orientation of films. The fitting of lattice parameters was obtained using a multiple correlation analysis with a least squares optimization. The planes and angles were the variables. The lattice parameters “a” and “c” were the fitting constants.

2.2.2. Optical characterization

The dielectric function, \(\varepsilon\), film thickness, \(d\), and the chemical composition of AlN films were determined by ellipsometry. When an incident linearly-polarized light impinges on the sample, the ellipsometer measures the polarization state, expressed with \((\psi, \Delta)\) the orientation and eccentricity of the ellipse generated by the perpendicular component, “s”, relative to the component, “p”, of a monochromatic polarized reflected light at the surface. The measurable parameters \((\psi, \Delta)\) are related to the film and substrate using the complex reflectance ratio,

\[
\rho \equiv r_p/r_s = \tan \psi \exp(i\Delta),
\]

where “\(r_p\)” and “\(r_s\)” are the Fresnel reflection coefficients for light polarized parallel and perpendicular to the plane of incidence, respectively.

Experimental ellipsometric measurements were obtained using a Woollam spectro-ellipsometer. Thickness and band gap of deposited samples are estimated by fitting a parameterized model to the measured data.\(^{27}\)

2.2.3. Electronic characterization

The electronic properties were characterized with an AES-XPS PHI 548 system (Al and Mg anode). The system was mounted on an Ar ion-gun operated at 4 KeV.

### Table 1. Experimental conditions utilized for the growth of films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Deposition time (min.)</th>
<th>Voltage (V)</th>
<th>Current (A)</th>
<th>Power (W)</th>
<th>(P_{\text{Ar}})</th>
<th>(P_{\text{Ar}+\text{N}_2})</th>
<th>(P_{\text{Ar}+\text{N}_2+\text{O}_2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>10</td>
<td>300</td>
<td>0.5</td>
<td>150</td>
<td>9.3</td>
<td>12.5</td>
<td>*</td>
</tr>
<tr>
<td>2</td>
<td>15</td>
<td>300</td>
<td>0.4</td>
<td>120</td>
<td>9.5</td>
<td>12.2</td>
<td>*</td>
</tr>
<tr>
<td>3</td>
<td>15</td>
<td>300</td>
<td>0.2</td>
<td>60</td>
<td>9.4</td>
<td>10.3</td>
<td>11.9</td>
</tr>
<tr>
<td>4</td>
<td>10</td>
<td>370</td>
<td>0.5</td>
<td>200</td>
<td>26.6</td>
<td>28.9</td>
<td>*</td>
</tr>
</tbody>
</table>
Characterization of AlN Thin Films

2.3. Computational procedure

The calculations reported in this work have been carried out using the tight-binding method\textsuperscript{30} within the extended Hückel framework\textsuperscript{31} using YAehHMOP computer package.\textsuperscript{32} The extended Hückel method is a semiempirical approach to solve the Schrödinger equation for a system of electrons based on the variational theorem. In this approach, explicit correlation is not considered except for the intrinsic contributions included in the parameter set. This method has been already described elsewhere.\textsuperscript{33}

The structure of hexagonal AlN is illustrated in Fig. 1. Hexagonal AlN belongs to the space group 6 mm (würzite), with lattice parameters $a = 3.11$ Å and $c = 4.97$ Å.\textsuperscript{26} Hexagonal AlN can be visualized as a matrix of distorted tetrahedrons. In a tetrahedron, each aluminum atom is surrounded by four nitrogen atoms. The four bonds can be categorized in two kinds. The first kind is formed by three equivalent Al–N$_x$, ($x = 1, 2, 3$) bonds, on which the N atoms are located in the same plane normal to the [0001] direction. The second kind is the Al–N$_0$ bond, on which the Al and N$_0$ atoms are aligned parallel to the [0001] direction (see Fig. 1). This last bond is the most ionic and has a lower binding energy than the other three.\textsuperscript{1,4,9}

When an AlN film is oxidized, it has been reported that the oxygen atom can substitute the nitrogen atom in the weakest Al–N$_0$ bond. In the mean time, the

![Fig. 1. Tetrahedral structure of AlN. The Al atom is surrounded by four N atoms. Al is located in the tetrahedral site at (2/3a, 1/3a, 1/2c), where “a” and “c” are the lattice parameters. The Al–N$_0$ bond is aligned along the c-axis direction.](image)
displaced nitrogen atom can occupy an interstitial site in the lattice.\textsuperscript{1} For würzite AlN, there are four atoms per hexagonal unit cell where the positions of the atoms for Al and N are: Al (0, 0, 0), (2/3, 1/3, 1/2); N (0, 0, u), (2/3, 1/3, u + 1/2), where “u” is a dimensionless internal parameter that represents the distance between the Al-plane and its nearest neighbor N-plane, in the unit of “c”, according to the JCPDS database.\textsuperscript{26} In search for the best matching of our theoretical results with the available experimental information, experimental lattice parameters were used instead of optimized values. Our calculations considered a total of 16 valence electrons corresponding to four atoms within the unit cell for AlN.

Band structures were calculated using 51 \( k \)-points sampling the first Brillouin zone (FBZ). Reciprocal space integration was performed by \( k \)-point sampling.

Calculations are carried out considering first: (1) a würzite-like AlN structure. Thereafter, calculations for the same structure are performed with the oxygen atom in different sites: (2) placing the oxygen atom in substitution of the N atom in the weakest Al–N\(_0\) bond (substitution); (3) placing the oxygen atom inside the interstitial site of the tetrahedral arrangement (intercalated); (4) placing the oxygen atom on top of the AlN surface (at the surface).

3. Results and Discussion

3.1. Structural properties

The X-ray diffraction patterns of samples are shown in Fig. 2 (intensity in linear scale versus 2\( \theta \)). In these diffractograms, contribution to signal from the substrate was subtracted.

The XRD pattern of Sample 1 did not show well-defined crystalline features. However, some traces of possible reflections assigned to a hexagonal structure can be observed. In this case, the diffractogram shows that this sample can contain different phases of AlN and aluminium oxide of low crystalline order.

For Sample 2, peaks at 2\( \theta \) = 33.1°, 35.9°, 37.8° and 49.8° were assigned to the (100), (002) (101) and (102) reflections respectively, of a würzite hexagonal-phase (group 186, file 00-025-1133), with lattice parameters \( a = 3.11 \) Å, \( c = 4.97 \) Å.\textsuperscript{26} The peak of highest intensity at 2\( \theta \) = 35.9° indicates that this sample is mainly formed by crystallites oriented at the [001] \( c \)-axis direction.

For Sample 3, peaks at 2\( \theta \) = 33.1°, 35.9° and 37.8° were assigned to the (100), (002) and (101) reflections respectively. Similar to the Sample 2, reflections belong to a würzite hexagonal-phase (group 186, file 00-025-1133).\textsuperscript{26} The peak of highest intensity at 2\( \theta \) = 33.1° indicated that this sample is mainly formed by crystallites oriented at the\textsuperscript{2} \( a \)-axis direction.

For Sample 4, peaks at 2\( \theta \) = 38.5° and 44.7° were assigned to the (111) and (200) reflections respectively, of a zinc blende cubic-phase (group 225, file 00-46-1200), with lattice parameter \( a = 4.04 \) Å.\textsuperscript{26} The peak of highest intensity at 2\( \theta \) = 38.5° indicates that this sample is formed mainly by crystallites oriented at the [111]
direction. For all samples, the varying deposition conditions produced films with different crystallographic features.

In this token, it has been reported that the morphological properties of sputtered AlN films depend on the kinetics of arriving species and the surface migration of the atoms at/on the substrate$^{3,4}$: at low pressure, sputtering species possess enough energy to form AlN layers of hexagonal structure. Authors of Ref. 3, deposited AlN films by RF sputtering. They found a change in the orientation of films from (002) to (001) directly related with the deposition pressure ($\sim 10^{-3}$ mbar). In this case, the morphological differences were attributed to the changing pressure inside the chamber, which altered the direction, mobility and mean free path of atoms. For our samples, the utilized pressure to grow the Sample 2 and Sample 3 was very similar (see Table 2). However, for Sample 3 there was a competition between the $\text{N}_2$ and the $\text{O}_2$ to react with Al. Also, it has been reported that the oxygen can induce defects on the growth of AlN layers, producing a degree of amorphization.$^{1,4,22,34}$

For Sample 4, the chamber was more Ar-saturated than the other samples during deposition process (see Table 1). This higher pressure into the chamber reduced
the mean free path and the deposition rate of sputtering species. Consequently, the kinetic energy was not high enough to form a würzite-like structure.

3.2. Optical properties

The ellipsometric measurements \((\psi, \Delta)\) are presented in Fig. 3 for the three samples. The solid line represents the model response, while the broken line represents the experimental measurement. The experimental and modeled curves were compared

![Ellipsometric spectra for selected samples. Theoretical simulated-curves utilizing a three-layer model, Glass/AlN + voids/AlN + Al_2O_3 + voids, are included. Obtained parameters from fitting are presented in Table 2.](image)
using a least square process by minimizing
\[ \chi^2 = \sum [(\psi_m - \psi_e)^2 + (\Delta_m - \Delta_e)^2], \] (2)
where the indices “\(m\)” and “\(e\)” correspond to the modeled and experimental values, respectively. The equivalent refractive index of the composite layer was calculated using the effective-medium-approximation theory.

During film growth, there were differences in the obtained optical properties because of the changes in the preparation conditions.

As a first approach, the model compared the experimental optical data starting from a single homogeneous AlN layer.

Taking into account our deposition conditions (low pressure/temperature), the films were at the lower end of the Movchan and Demchishin zone-model.\textsuperscript{35,36} In addition to the expected columnar growth, experimental conditions produce voids in the AlN films.\textsuperscript{35} Then, when voids were considered in the model, an improvement in the fitting was obtained. Considering the reactivity of the aluminium, a very thin layer of AlN at the top of the oxide layer is added. Thus, a mixture of layers, Al\(_2\)O\(_3\) + AlN + voids, was considered, producing a meaningful improvement in the fittings. Under our experimental conditions, the growth of the films is diffusion limited and hence void formation is likely.

The glass substrate (SiO\(_2\)) was characterized and the optical data for Al\(_2\)O\(_3\) was taken from Ref. 37. The volume fraction and thickness of the layers varied from sample to sample.

The refractive index model used in our simulation was expressed through the Lorentz dispersion equation:
\[ \varepsilon(E) = \varepsilon_\infty + \frac{A}{(E_0^2 - E^2) - iBE} , \] (3)
where the parameter “\(A\)” is the oscillator amplitude, “\(B\)” is the broadening, “\(E_0\)” is the resonance frequency expressed in energy units of the material, and epsilon-infinity is the function value at very high frequencies.

The method of the Lorentz oscillators describes the interaction between the electromagnetic field and an atom. However, this model is widely used to simulate the optical response of the material. The resonance energy location “\(E_0\)” is not formally related with the optical band gap, \(E_g\), but it provides a good idea of its position, arguing that at “\(E_0\)” the material has its resonance frequency. At this frequency, the material absorbs the light energy more efficiently. In the following lines, we will consider this assumption as valid.

The resulting parameters obtained from ellipsometric measurements are included in Table 2. The variation of the real refractive index \((n)\) versus energy (eV) for the three selected samples is presented in Fig. 4.

Sample 1 and Sample 2 were deposited with a similar gas mixture (see Table 1). The difference between them was the deposition time, which accounted also for the differences in the estimated thickness (see Table 2). For Sample 3, oxygen was
Table 2. Resulting parameters obtained from fitting. Ellipsometric spectra for each sample are included in Fig. 2.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Layer 1</th>
<th>Layer 2</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Thickness (Å)</td>
<td>$E_g$ (eV)</td>
</tr>
<tr>
<td>1</td>
<td>444.37</td>
<td>2.5171</td>
</tr>
<tr>
<td>2</td>
<td>79.237</td>
<td>0.78916</td>
</tr>
<tr>
<td>3</td>
<td>170.79</td>
<td>0.98289</td>
</tr>
</tbody>
</table>

Fig. 4. Variation of refractive index versus photon energy (eV). At 2.3 eV, refractive index is $n = 2.10$, $n = 2.11$ and $n = 2.0$ for Sample 1, Sample 2 and Sample 3, respectively.

added in the gas mixture during the sputtering process. The thickness of this sample was slightly lower than the value obtained for Sample 2, for the similar deposition time. For Sample 3, the difference in thickness could be explained in the basis of its lowest power (60 W, compared with 120 W of Sample 2). This loss of power could be attributed to a nitruration/oxidation of the target during the sputtering process. In the process, a layer of oxide/nitride was formed at the surface of the target. This layer acted as an electrostatic barrier for the impinging Ar$^+$ ions, which could promote a reduction in the deposition rate of sputtered species.

Also from Table 2, differences in the estimated values of the band gap can be observed. The band gap of $E_g = 9.9$ eV of Sample 1 did not fall within the reported value for AlN. This sample is thinner than the Sample 2; therefore, surface roughness is a factor which can induce a deviation in the measurement during the Lorentz-oscillator modeling. Also, the different crystalline phases contained in Sample 1 are the other factor which produced this value of 9.9 eV during the modeling.

For Sample 2, the calculated band gap of $E_g = 6.6$ eV falls within the reported values for polycrystalline AlN thin films. For Sample 3, the calculated band gap of $E_g = 7.95$ eV was higher than the value reported for AlN. In this case, oxygen was introduced in the gas mixture during deposition. The oxygen content
inside the resulting film could be the factor which modified the band-gap value. This issue is discussed in Sec. 3.5.

From the graph in Fig. 4, the refractive index of Sample 1, Sample 2 and Sample 3 (at 533 nm, 2.3 eV) have a value of \( n = 2.10 \), \( n = 2.11 \) and \( n = 2.02 \), respectively. The refractive index for AlN films has been reported in a wide range of values, among them: being \( n = 1.9 \) for polycrystalline AlN films deposited by DC reactive sputtering,\(^{41}\) and \( n = 2.1 \) for a bulk-like AlN\(^{41}\); \( n = 1.9 \) to 2.1 for polycrystalline AlN films deposited by DC reactive sputtering\(^{19}\); \( n = 1.9 \) for highly textured [0001] oriented AlN films deposited by RF sputtering\(^{39}\); \( n = 1.7 \) for [10-10] and [11-20] oriented polycrystalline AlN films deposited by DC reactive sputtering.\(^{39}\) Authors of Ref. 41 report that an increase in the flow of N during deposition tends to change the value of the refractive index. This change in value is attributed to a density variation of the films. The reported values of refractive index for polycrystalline AlN films\(^{19,39,41}\) cover our results obtained by ellipsometry for Samples 1, 2 and 3. The crystalline features of these samples are supported by the XRD measurements too.

### 3.3. Electronic properties

Figure 5 displays the high-resolution XPS spectra of Sample 4, which was taken after 15 minutes of erosion with the Ar ion-gun. The deconvoluted curve for the Al\(_{2p}\), N\(_{1s}\) and O\(_{1s}\) transition-peaks are included. The peaks were composed of several contributions corresponding to Al, N, C and O in different chemical states. The Al\(_{2p}\) transition was the sum of three individual components: Al–N (73.9 eV),\(^{42,43}\) Al–O (75.6 eV)\(^{42,44}\) and Al–C–O complex (78.1 eV).\(^{45}\) The N\(_{1s}\) transition contained the only component N–Al (397.8 eV).\(^{42,45}\) The O\(_{1s}\) transition was the sum of two components: O–Al (532 eV)\(^{42,43}\) and O–C (534.1 eV).\(^{42,43}\) This sample was not intentionally oxidized, but XPS detected traces of oxygen and carbon. In this case, O\(_2\) remained in the chamber as a residual gas and C remained as an impurity. During the deposition process, this residual oxygen can react with aluminum forming Al\(_x\)O\(_y\)

![Fig. 5. XPS spectra high-resolution windows for Al\(_{2p}\), N\(_{1s}\) and O\(_{1s}\) transitions corresponding to Sample 4. Calculations of relative atomic concentrations are included in Table 3.](image-url)
compounds at the near surface of the AlN film. The oxygen and carbon impurities can be originated from the “dark zone” of the magnetron.

The results of calculated atomic concentration are summarized in Table 3. The column labeled “Al + N + O” was the calculated elemental-concentration taking into account the Al 2p, N 1s and O 1s transitions. The column labeled “Al+N” was the calculated elemental-concentration taking into account the Al 2p and N 1s transitions. In this last case, the O 1s transition was not considered in the calculation. The last column C(Al)/C(N), was the ratio of aluminium to nitrogen concentration; this ratio was of \( \approx 3.9 \). With the area below the curve of deconvoluted components “Al–N” (from “Al 2p” transition) and “N–Al” (from “N 1s” transition), the relative concentration obtained for Al and N was of \( \approx 62.6\% \) and \( \approx 37.3\% \), respectively. Table 4 presents the contribution in percentage (%) of each component for the Al 2p transition. Taking into account the Al–N and Al–O components (not considering the Al–C–O component), it can be observed that the Al tends to react with N 2 and/or O 2 in the same proportion.

Based on the results provided by the XPS data, it can be observed that it is difficult to get rid of the oxygen by the current deposition method. Besides, the oxygen and carbon content detected on Sample 4 can also be attributed to the sputtering process (the Ar + treatment before XPS measurements). During a sputtering process, it is well-known that oxygen and carbon can be trapped inside the ion gun. These elements can then be adsorbed at the surface of the sample. For this reason, their corresponding signals can appear in the XPS spectra. As the BEs of the adsorbed C and O are very characteristic, we can discard them at the time to perform concentration measurements. From Fig. 5, the Al–C–O (Al 2p window) and O–C (O 1s window) components can be attributed to an adsorbed C and O at the surface. For the Al–O (Al 2p window) and O–Al (O 1s window) is rather difficult
Table 5. Energy gaps (direct/indirect) for (1) AlN hexagonal, (2) AlN\((1-x)O_x\) with substitution of N by O and (3) AlN\((1-x)O_{(x)}\) with O at an interstitial site. In calculations, localization of the Fermi energy is included too. Values are given in eV.

<table>
<thead>
<tr>
<th>Energy Gap (eV)</th>
<th>(1) AlN Hexagonal</th>
<th>(2) Substitution of N by O</th>
<th>(3) Interstitial O</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Direct</td>
<td>Indirect</td>
<td>Direct</td>
</tr>
<tr>
<td></td>
<td>(\Gamma \rightarrow M)</td>
<td>(M \rightarrow \Gamma)</td>
<td>(H \rightarrow \Gamma)</td>
</tr>
<tr>
<td>(E_g)-direct</td>
<td>7.2</td>
<td>0.82</td>
<td>1.3</td>
</tr>
<tr>
<td>(E_g)-indirect</td>
<td>8.2</td>
<td>1.19</td>
<td></td>
</tr>
<tr>
<td>(E_F)</td>
<td>-13.32</td>
<td>-7.18</td>
<td>-9.51</td>
</tr>
</tbody>
</table>
Fig. 6. Band structure for 2H–AlN hexagonal, sampling the first Brillouin zone (FBZ). The Fermi level ($E_F = 0$) is indicated by a horizontal dotted line.

Fig. 7. Total and projected Density of States (DOS) for Al–p and N–p. The dotted (N) and hatched (Al) lines emphasize the contribution to the total DOS from each atom.

values, it could be noticed that $r_O$ was almost 10 times higher than $r_N$. This fact would imply that when the oxygen atom takes the place of the nitrogen atom (by substitution or intercalation of O), the crystalline lattice expands because of the higher size of oxygen. Any change in the distance among atoms, together with the extra valence electron of the oxygen, might alter the electronic interaction, thereby, the value of the band gap.
3.5. **Comparison between experimental results and theoretical calculations**

The theoretical results predicted a change in the band gap (and also a change in the electronic properties of the material) when oxygen was placed in the AlN lattice, whether by intercalation ($E_g = 1.3$ eV) or substitution ($E_g = 0.82$ eV). These calculations were in opposition to the results obtained by the ellipsometric measurements. The band gap of Sample 2 ($E_g = 6.61$ eV) was different from the one of Sample 3 ($E_g = 7.95$ eV). In other words, the experimental comparison shows that the $E_g$ increases with O$_2$ incorporated, while the theoretical calculation indicates the opposite tendency.

In order to obtain a clearer interpretation/comparison of the experimental versus theoretical results, an additional calculation was performed. Instead of placing the oxygen inside the AlN crystalline structure, oxygen was located at the surface, while the original atoms of Al and N remained in their original wurtzite-like atomic positions. Figure 8 displays the calculations of band structure for 2H-AlN hexagonal with an oxygen atom at the surface level. For this system, an indirect band gap of $E_g = 6.31$ eV ($\Gamma - M$) was obtained. It was a change in the band gap, but this value is closer to the original AlN wurtzite-like system ($E_g = 7.2$ eV) than the other two cases ($E_g = 1.3$ eV and 0.82 eV for intercalation and substitution, respectively).

In this case, theoretical results say to us that when the oxygen is not inside the Bravais lattice, this band-gap value will be closer to the one of the pure wurtzite, just $\cong 1.0$ eV away. This difference is lower when compared with the values of $\cong 5.9$ and $\cong 7.0$ away for intercalation and substitution, respectively.

In the experimental side, the term “at the surface” means that the oxygen is not found inside the AlN wurtzite-structure. In this case, the N$_2$ and the O$_2$ compete

![Fig. 8. Band structure for 2H-AlN hexagonal with an oxygen atom at surface level, sampling the first Brillouin zone (FBZ). The Fermi level ($E_F = 0$) is indicated by a horizontal dotted line.](image-url)
between them to get attached to the Al, thereby forming separated phases of AlN and Al\textsubscript{x}O\textsubscript{y}. This issue is open to discussion, but with the information about the ionic size of the oxygen, it seems that in terms of energy and stability, is more favorable for the system to form separated phases of AlN and Al\textsubscript{x}O\textsubscript{y} in the film.

During the growth of AlN films, the Al\textsubscript{x}O\textsubscript{y} phase had been reported at large depths\textsuperscript{22,42}. Based on microstructural observations, Hwang \textit{et al.}\textsuperscript{22} proposed a growth mechanism for AlN thin films. In this model, the oxygen could react favorably with aluminum, forming a phase of amorphous Al\textsubscript{2}O\textsubscript{3} (even an Al\textsubscript{2}O\textsubscript{3} layer). The \textit{c} content of the oxide phase then induces stacking faults on the growing AlN layers. In thermodynamical terms, Al\textsubscript{2}O\textsubscript{3} is more possibly formed by gaseous phase reaction of Al + (3/2)O\textsubscript{2} than AlN of Al + (1/2)N, since \( \Delta G(\text{Al}_2\text{O}_3) = -1480 \text{ KJ/mol} \) and \( \Delta G(\text{AlN}) = -253 \text{ KJ/mol} \).

In Sample 3, the oxide phase Al\textsubscript{x}O\textsubscript{y} can induce stacking faults in the film. However, this sample still presents preferential growth of the nitride AlN phase along the “\textit{a}-axis” direction. The measured band gap of 7.9 eV seems to indicate the coexistence of the nitride and oxide phases in the layer. Sample 3 is the equivalent, in the theoretical analysis, to the case on which the oxygen is attached to the AlN at the surface and a notorious change of band gap, compared with the one of pure wurtzite AlN, is not expected.

On the other hand, the XPS results performed on Sample 4 corroborates the similar possibility of the Al to attach to the N\textsubscript{2} and/or the O\textsubscript{2}. In that context, Fig. 9 displays the total and projected density of states (PDOS) for hexagonal AlN with an oxygen atom at surface. Like Fig. 7, information about the hybridization in this compound is given. It is possible to see that the Fermi level is shifted up due to the extra O atom located on the surface. The contribution from each atom to the total DOS is as follows: Al\textsubscript{p} – contributed with \(~1\%\), N\textsubscript{p} – with \(~60\%), and O\textsubscript{p} – states contributed with \(~60\%).

![Fig. 9. Total and projected Density of States (DOS) for Al–p, N–p and O–p. The oxygen atom is located at the surface.](image-url)
Theoretical calculations for w"urzite AlN band-gap had been performed with several approaches: Ferreira da Silva et al.\textsuperscript{48} performed a local density approximation (LDA) within the density functional theory (DFT) with a correction $\Delta_g$, using a quasi-particle method proposed by Bechstedt and Del Sole. With this method, the LDA + $\Delta_g$ band gap reported was 6.05 eV, for direct transition energy. On the other hand, Rezaei et al.,\textsuperscript{49} utilized the more empirical pseudopotential method (EPM). In this case, an analytical function using a fitting procedure for both symmetric and antisymmetric parts, a potential is constructed. The band gap obtained with EPM was 6.2 eV. In the mean time, Persson et al.,\textsuperscript{50} calculated the band gap of AlN w"urzite using the full potential linear muffin-tin orbital method (FPLMTO). The band gap found with this method was 4.24 eV. In the same work, authors utilized FPLMTO with a corrected band gap $\Delta_g$.\textsuperscript{49,50} With this correction, the band gap gave a value of 6.15 eV.

When we compared our theoretical calculations with other related works, differences in the band gap were noticed. In our results, the band gap calculated for AlN was 7.2 eV: slightly different from the reported experimental-value of $\approx$6.2 eV, and to the theoretically calculated-value of $\approx$6.0 eV. About this issue, an important factor to stress is that in our calculations, spin-orbit effects were not considered throughout the analysis. Henceforth, some differences arise, especially when an energy-band analysis is performed. Some bands could be shifted up or down in energy due to these contributions. However, our method was simpler, computationally efficient and the electronic structures obtained could be optimized to closely match the experimental and/or \textit{ab initio} results

4. Conclusion

A set of AlN thin films was prepared by DC reactive magnetron sputtering. The films were analyzed by X-ray diffraction (XRD) and spectroscopic ellipsometry. The reaction of N$_2$ and O$_2$ with Al was analyzed with XPS. The effect of oxygen incorporation into AlN and the change of energy band gap was discussed in detail with theoretical analyses. The next conclusions are obtained:

Depending on the deposition conditions, AlN thin films can grow in hexagonal or cubic microstructure. X-ray measurements indicated a polycrystalline mode of growth on films.

The refractive index measured for deposited samples corresponds to polycrystalline AlN thin films. The calculated band gap of 9.9 eV for Sample 1 does not correspond to AlN. In this case, the surface roughness and the coexistence of AlN and Al$_x$O$_y$ phases in the layer accounts for this calculated value of $E_g$. The band gap of 6.6 eV for Sample 2 agrees with the reported values of AlN polycrystalline thin films. For Sample 3, a band gap of 7.9 eV is obtained.

Theoretical calculations shows that depending on the site that the oxygen occupies in the w"urzite structure, different values of $E_g$ are expected. XRD measurements and theoretical calculations suggest that Sample 3 can be conformed
of coexisting phases of AlN and Al$_x$O$_y$. The aluminium oxide content can induce stacking faults in the growing film, affecting the crystalinity and preferential orientation of the resulting layer.

Acknowledgments
This work was sponsored by CONACyT-México (project CO2-43707), PAICYT-UANL (CA1256-06) and PAPIIT-DGAPA (IN110607-2). M. García Méndez would like to thank Dr. Miguel Ávalos Borja, from CCMC-UNAM, Ensenada, for the facilities granted for the use of XRD equipment and to Eloisa Aparicio Ceja for the technical support. The authors also thank Azahel Bueno for his ellipsometric measurements.

References