Optical emission spectroscopy of Aluminum Nitride thin films deposited by Pulsed Laser Deposition

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Abstract. In this work we study the Aluminium Nitride plasma produced by Nd:YAG pulsed laser, (λ = 1064 nm, 500 mJ, τ = 9 ns) with repetition rate of 10 Hz. The laser interaction on Al target (99.99%) under nitrogen gas atmosphere generate a plasma which is produced at room temperature; with variation in the pressure work from 0.53 Pa to 0.66 Pa matching with a applied laser fluence of 7 J/cm². The films thickness measured by profilometer was 150 nm. The plasma generated was at different pressures was characterized by Optical Emission Spectroscopy (EOS). From emission spectra obtained ionic and atomic species were observed. The plume electronic temperature has been determined by assuming a local thermodynamic equilibrium of the emitting species. Finally the electronic temperature was calculated with Boltzmann plot from relative intensities of spectral lines.

1. Introduction

Pulsed laser deposition (PLD) using nanosecond pulses is considered to be one of the most promising techniques for the synthesis and deposition of thin films [1–4]. This method has advantages, such as high reproducibility, control of the film growth rate and stoichiometry, and low impurity concentration in the composition of deposited films. On the other hand aluminum nitride (AlN) exhibit attractive properties, such as thermal and chemical stability, high thermal conductivity, high dielectric permittivity, breakdown field, high-speed piezo-acoustic wave and the mechanical hardness [1]. AlN thin films with good morphological quality are essential for applications in surface acoustic wave (SAW) and UV optical devices. That’s why the scientific interest is focused on the preparation and study of high-quality films AlN. The aim of this work is to study the optical emission spectroscopy in of aluminum nitride thin films deposited by pulsed laser deposition on Si (100) substrate for use in optical applications.

2. Experimental

The experiments have made in usual PLD configuration consisting of a laser system Fig.1, a multiport stainless steel vacuum chamber equipped with a gas inlet, a rotating target and a heated substrate holder. The Nd:YAG laser that provides pulses at the wavelength of 1064 nm with 9 ns pulse duration and repetition rate 10 Hz was used. The laser beam was focused with an f = 23 cm glass lens on the target at the angle of 45°, with respect the normal. The target rotated to 2.2 rpm to avoid fast drilling. The distance between the target and the substrate was 6.5 cm. Before deposition the vacuum chamber was evacuated down to 1·10⁻⁵ mbar by using a turbo-molecular pump backed with a rotary pump.
Figure 1. AlN plume during the deposition process.

The films were deposited in nitrogen atmosphere as working gas, in an atmosphere of nitrogen reactive the nitrogen gas pressure varied between 0.39 Pa and 0.93 Pa and aluminum target (99.99%). The Films were deposited with a laser fluence of 7 J/cm$^2$ for 10 minutes on silicon (100) substrates.

The Plasma characterization was performed by optical emission spectroscopy (OES) by using a spectrometer model Jobin Yvon Triax 550 of 0.55 m, $f = 6.4$ equipped with two gratings of 1200 l/mm and 150 l/mm, coupled to a CCD camera model 3000 air-cooled multi-channel and 512 × 512 pixels Fig.2. For the morphological study used a scanning electron microscope Philips XL 30. It was determined the grain size and roughness by using Atomic Force Microscopy (AFM) measurements in atomic force microscopy Asylum Research MFP-3D-SA. The films thickness was measured with a Dektak 8000 profilometer.

Figure 2. Schematic diagram of the Nd:YAG laser deposition system [5].

Chemical composition analysis of the coatings was done with a Philips XL 30 FEG scanning electron microscopy, an X-ray detector and secondary electrons detector of Lithium Beryllium inside the chamber with the propose of amplify the signal in the EDS analysis.

3. Results and discussion

3.1 Plasma Diagnostics

The study of pulsed laser ablation plumes has increased the attention recently due to its importance in laser deposition. Plasma is a transient phenomenon in nature with characteristic parameters dependent on the component species and rapidly evolving. These parameters are highly dependent on the irradiation conditions, laser intensity, pulse duration, wavelength, composition and atmosphere [6]. Taking in account that the relationship between plasma and morphological quality in the films is very important, in this sense the AIN films are used as substrates for SAW sensors where the surface quality is a decisive factor in the sensors performance. This study focuses on the variation of nitrogen gas pressure between 0.53 Pa and 0.66 Pa in aluminum nitride deposition.
Identified a large number of emission lines attributed to emission bands of aluminum nitride, atomic spectral lines are also indicating the presence of Al and atomic N\(_2\) (Figs 3b and 3c). The oxygen presence it was observed in optical emission for the AlN with 0.53 Pa and 0.66 Pa, of which is a product of contamination in the vacuum chamber. All atomic emission lines were identified through the database of the National Institute of Standards and Technology-NIST. In Fig. 3 the most intense lines are emission aluminum species. Apparently, the main species emitted in the ablation of aluminum species, being once ionized aluminum (Al II). The strongest lines in the spectrum of XII in plasma are at 631.337 nm, for electron configuration 1s\(^3\)p - 1s\(^3\)d. Also it was observed emission lines of nitrogen species (neutral and multiply ionized) with most intense peaks at 618.909 nm (N I), 644.902 nm (N III), 740.359 nm (NIII). The emission peak of atomic Nitrogen was dominant compared to the emission peaks of atomic aluminum.

![Image](https://via.placeholder.com/150)

**Figure.** 3 Optical emission for the AlN plume with different values of nitrogen pressure: (a) emissivity for N\(_2\)\(^1\)\(^\text{st}\) positive system between 600nm and 800 nm, (b) Optical emission for the AlN with 0.53 Pa, and (c) optical emission for the AlN with 0.66 Pa.

The oxygen presence of is also attributed low flow of nitrogen gas during the degassing processes. The oxygen species are observed O II 762.882 nm 751.325 nm O III and OV in 676.585 nm and 743.153 nm. In 509.985 nm observed emission band of AlN (0.0) [7]. A second emission band, weaker, is analyzed in 523.060 nm for AlN (1.0) [8]. In this work the oxygen bands only are evidenced for a working pressure of 0.53 Pa. Moreover, in this work was found particle density in Debye sphere Nd = 2.46x10\(^{-1}\).

In this case is possible take in account that the plume is in local thermodynamic equilibrium [9], therefore, the emission line intensity (I) in a specific wavelength (\(\lambda\)m) may be expressed by:
where $\lambda_{mn}$ is the transition wavelength, $I_{mn}$ is the observed intensity transition line, $A_{mn}$ is the transition probability, $g_{mn}$ is the degeneracy of the upper level, $E_{mn}$ is the energy of the emitting level, $k$ is the Boltzmann constant and $T_e$ is the electronic temperature. A typical plot is reported in the Fig. 4 for the emission of the AlN plume. The higher temperature calculated in the presence under 0.53 Pa of N$_2$ can be associated to recombination phenomena occurring during plume expansion and the thin films deposition, in relation to local thermodynamic equilibrium (LTE) the electron density, such as is showed by the next equation:

$$n_e \geq 1.4 \times 10^{14} \frac{T_e^{12}}{\Delta E_{mn}}^{3} \text{cm}^{-3}$$

In this paper is reported a value of the 5.90x$10^{15}$ cm$^{-1}$ for the LTE approximation, which is agree with the literature [7,9].

3.2 Film characterization

EDS spectra from the AlN films surface showed the presence of (Al, N, O) element, which is characteristic of those materials. The presence of oxygen has been often found during the production of AlN is normally associated to residual oxygen in the chamber [7]. Therefore, is possible to observe dependence of work pressure on decreasing of Al content. The areas of the peaks were used to calculate the composition of both coatings; thus, the values from Fig. 5 indicated that our films were substoichiometrics. On the other hand, a careful correction has to be done in all stoichiometric analysis because EDS has low reliability for nitrogen concentration. Therefore, EDS elemental concentrations were obtained using the ZAF correction method; because certain factors related to the sample composition, called matrix effects associated with (atomic number (Z), absorption (A) and fluorescence (F)), can affect the X-ray spectrum produced during the analysis of electron microprobe and therefore, these effects should be corrected to ensure the development of an appropriate analysis.
The correction factors for a standard specimen of known compositions were determined initially by the ZAF routine. The relative intensity of the peak K was determined by dead time corrections and a referent correction for the X-ray measured. So, before each quantitative analysis of an EDS spectrum, a manual background correction and an automated ZAF correction was carried out [10]. Thus, Fig. 5 shows the energy-dispersive X-ray spectroscopy (EDS) values of AlN films deposited with different work pressures. All samples were observed via SEM and chemical analyses were done with an amplification of 20000x.

Figure 5 Correlation between work pressure in the Al-N plasma and aluminum, nitrogen and oxygen contents for deposited AlN thin films.

The observed dependence of the film surface morphology under nitrogen pressure during deposition is closely related with the film growth mechanism, associated to the surface diffusion length \( L \) which is given by:

\[
L \sim (D \tau)^{1/2}
\]  

(3)

where \( D \) is the diffusion coefficient and \( \tau \) is the residence time of adatoms. Larger values of diffusion length imply more time for the adatoms to find energetically favorable lattice positions, thus, reducing the density of surface defects and improving the crystal quality.

Figure 6 shows the surface morphology AlN films was studied by recording AFM images together SEM micrographs where is observed the random distribution of micro-particles or micro-droplets on these surfaces as function of deposition pressure (0.66 Pa and 0.53 Pa). Therefore, the deposition pressure affects clearly the increase of micro-drops; this can be possible due to low surface mobility when the pressure was varied from 0.39 Pa to 0.93 Pa. This surface mobility reduces the possibility that the micro-drops are anchored on the surface when arrives with high energy on AlN film. Other possible reason can be associated with the mean free path that produces surface diffusion of nano-drops or micro-drops which can decrease the overall number of particles.
4. Conclusion
In this work was found a dependency in relation to nitrogen concentration, roughness and grain size in the AlN films with the nitrogen work pressure, increasing in this sense the nitrogen concentration and the roughness on AlN films. The plasma pressure affects the stoichiometry and the morphological nature in the AlN films. The variation of nitrogen work pressure exhibit low effect on intensity of spectral lines emitted. The electron temperature value ($T_e = 8832.3$ K) presented in our aluminum nitride plasma is similar to previous works.

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Figure 6. Relationship among surface roughness, grain size and plasma pressure for AlN thin films within vacuum chamber for AlN thin film deposited with a pressure of 0.66 Pa and 0.53 Pa.