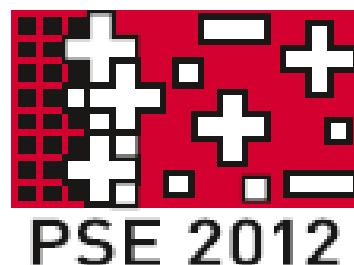


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Optical emission spectroscopy study of a DC magnetron discharge in Ar/(O₂-N₂)Joel Borges¹, Nicolas Martin², Filipe Vaz¹, Luis Marques¹¹Centre/Department of Physics, U. Minho, Braga, Portugal ²FEMTO-ST, Département MN2S, Besançon, France

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Metallic (Me) oxynitrides (MeN_xO_y) are attracting the attention of many researchers for the last two decades due to a unique set of versatile properties, resulting from the combination of those from the pure metals and those of the correspondent binary nitrides and oxides. Among the group of already studied oxynitrides, and due to the combination of aluminium and aluminium nitride and oxide, aluminium oxynitride (AlN_xO_y) has some interesting potential applications in different technological fields, but the available knowledge of this system is very reduced and mostly related with its *spinel* structure. Recent results showed that AlN_xO_y thin films deposited by PVD present a particular changing morphology, consisting of Al nanoparticles embedded in a AlN_xO_y matrix and, depending on the amount of oxygen and nitrogen in the matrix, very different electrical and optical responses. This work presents a study of the evolution of several discharge parameters (target voltage, reactive gases partial pressures) and plasma emission spectrum responses during thin film deposition, for different N₂ and/or O₂ gas flows, in order to understand the effect of processing conditions on the chemical composition and bonding characteristics, and its effect on the morphological and structural features, which, all together, explain the wide range of property variations that can be obtained in the AlN_xO_y film system. The partial pressure of each reactive gas was monitored using a mass spectrometer and the Al, Ar, N₂ and O₂ emission lines were recorded using an optical emission spectrometer at two different discharge spots, one close to the target and the other close to the substrate. For the Ar-N₂ based reactive gas mixtures, a smooth evolution of the different discharge parameters was observed as a function of reactive gas flow. On the other hand, for Ar-O₂ mixtures, there was an abrupt transition in the different parameters for certain critical O₂ flows. For the pure Ar discharge, the plasma density and temperature could be obtained, using a simple collisional radiative model, based on the Ar emission lines.

KeywordsAlN_xO_y

OES

magnetron discharge in Ar/(O₂-N₂)

OPTICAL EMISSION SPECTROSCOPY STUDY of a DC MAGNETRON DISCHARGE In Ar/(O₂-N₂)



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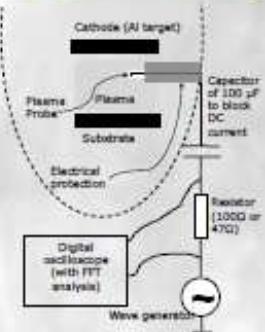
Metallic (Me) oxynitrides (Me_xN_yO_z) are attracting the attention of many researchers for the last two decades due to a unique set of versatile properties, resulting from the combination of those from the pure metals and those of the correspondent binary nitrides and oxides. Among the group of already studied oxynitrides, and due to the combination of aluminum and aluminum nitride and oxide, aluminum oxynitride (Al_xN_yO_z) has some interesting potential applications in different technological fields, but the available knowledge of this system is very reduced [1-2]. This work presents a study of the evolution of several discharge and plasma parameters as well as the plasma-emission spectrum responses during thin film deposition, for different N₂+O₂ partial pressures, in order to better understand and control the deposition conditions of the Al_xN_yO_z films system.

EXPERIMENTAL DETAILS

DC magnetron sputtering
Target: Aluminum, 99.5 % purity
Substrate: Glass, Silicon <100>
Substrate temperature (before discharge): 373 K
Partial pressure of Argon: 0.3 Pa
Reactive gas: N₂+O₂ (17:3)
Bias: GND
Target current density: 75 A.m⁻²
Discharge parameters monitored by a Data Acquisition Switch unit Agilent 34970A
Plasma parameters: Floating probe (harmonic method)
Plasma compositions: Optical emission spectroscopy



Floating probe electrical circuit



Plasma parameters calculations (harmonics technique):

Applying a sinusoidal wave (or triangular) with frequency f and amplitude V_0 , it is possible to observe currents of multiple harmonics, due to the non-linearity of the probe sheath. The electron temperature (T_e) can be estimated using the ratio of the first two harmonics (I_2 and I_1) since $I_2/I_1 = I_1/I_0$ (I_1 and I_0 are solutions of the modified Bessel function of the first kind). Since I_2/I_1 is a function of $q_e V_0 / T_e$, assuming a Maxwell-Boltzmann distribution for the electrons, the electron temperature can be calculated according to ($V_{1/2}$ corresponds to I_1/I_0) [3]:

$$T_e = \frac{q_e V_0}{V_{1/2}} \quad \text{Eq. 1}$$

The ion flux (Γ^+) can be calculated using the electron temperature (eq. 1), the intensity of the first harmonic (I_1), the probe area (A_p) and the $V_{1/2}$ value of the function I_0/I_1 versus $q_e V_0 / T_e$ for the electron temperature determined by eq. 1 (I_0 and I_1 are solutions of the modified Bessel function of the first kind), according to [3]:

$$\Gamma^+ = \frac{i_{1f}}{2q_e A_p} V_{1/2} \quad \text{Eq. 2}$$

CONCLUSIONS

When the N₂+O₂ reactive gas mixture is added to the argon atmosphere not only reacts with the sputtered aluminum to form compounds in the substrate, but also interacts with the surface of the cathode leading to chemisorption, ion implantation and, consequently, compound formation. These processes increase the ion induced secondary electron emission coefficient of the target, manifested in the decrease of the target potential and the raise of the electron temperature; and, on the other hand, diminish the sputtering yield, manifested in the decrease of Al line intensity and in the values of the deposition rate.

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RESULTS AND DISCUSSION: Plasma parameters (near the cathode)

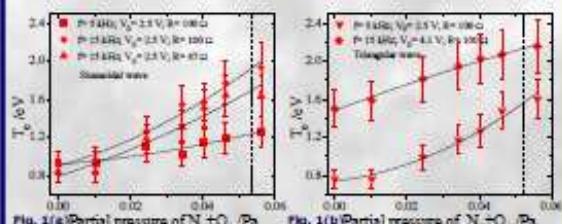


Fig. 1 Electron temperature estimated using the harmonic method by applying (a) sinusoidal waves and (b) triangular waves.

The electron temperature (near the cathode) gradually increases as a function of the reactive gas partial pressure mainly due to the raise of the ion induced secondary electron emission coefficient of the target, which increases the population of fast electrons accelerated in the cathode sheath.

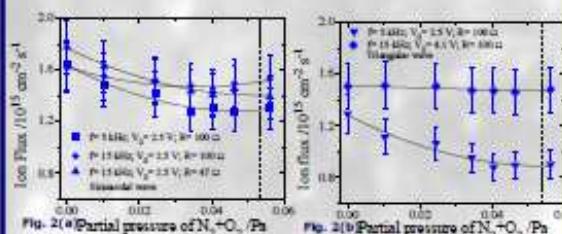


Fig. 2 Ion flux estimated using the harmonic method by applying (a) sinusoidal waves and (b) triangular waves.

The ion flux, measured in a region of the plasma near the cathode, is approximately constant as the partial pressure of reactive gas increases. This is due to the fact that the current was kept constant during the depositions ($J = 75 \text{ A.m}^{-2}$).

Optical Emission Spectroscopy

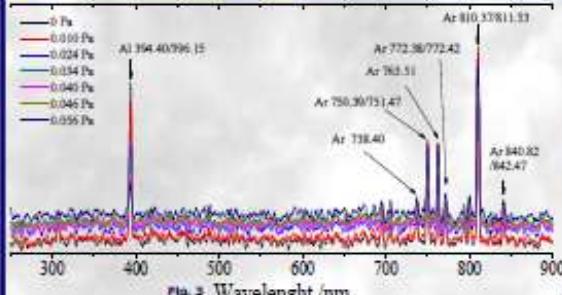


Fig. 3 Optical emission spectroscopy spectra for different partial pressures of N₂+O₂ reactive mixture.

In the plasma emission spectrum one can observe the excited aluminum emission line decreases as the partial pressure of reactive gas increases, due to a decrease of the target sputtering yield as it is becoming poisoned with nitrides and/or oxides.

No significant variations can be seen in the intensity of the Ar emission lines.

Target Potential and Deposition Rate

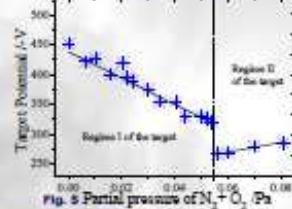


Fig. 5 Target potential.

The target potential [1,2] is clearly influenced by the gas mixture partial pressure. It gradually decreases in regime I as it is becoming poisoned (mainly with nitrides) due to the increase of the ion induced secondary electron emission coefficient (this coefficient is higher for AlN than for Al). In regime II the target is completely poisoned (possibly with aluminum oxide) and the cathode voltage is low since the secondary electron emission coefficient of Al₂O₃ is higher than that of Al.

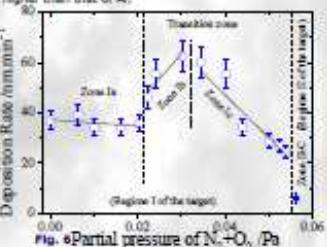


Fig. 6 Deposition rate of the AlN_xO_y coatings.

The deposition rate of the films deposited in the regime I of the target have distinct variations, (I because the sputtering yield is decreasing, as can be confirmed by the decrease of Al line intensity (Fig. 4)); (II) the morphology [1,2] of the films changes from columnar-like (in zone Ia) towards cauliflower-type (in the transition zone); in zone II-C the target is totally poisoned with a very low sputtering yield, thus explaining the low deposition rates.

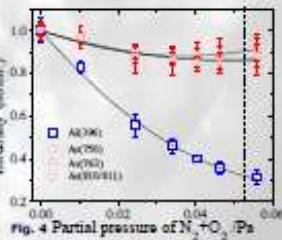


Fig. 4 Peak intensity (normalized to the respective line intensity observed for the discharge without reactive gas)

The intensity of the excited aluminum emission line decreases as the partial pressure of reactive gas increases, due to a decrease of the target sputtering yield as it is becoming poisoned with nitrides and/or oxides.

No significant variations can be seen in the intensity of the Ar emission lines.