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The influence of nitrogen and oxygen additions on the thermal characteristics of aluminium-based thin films

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HIGHLIGHTS

- AlN_x, AlO_y and AlN_xO_y films were deposited by magnetron sputtering.
- Discharge characteristics were compared between systems.
- Different x and y coefficients were obtained.
- Composition, structure and morphology were correlated with physical properties.
- Thermal behaviour was studied using modulated IR radiometry.

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ABSTRACT

The ternary aluminium oxynitride (AlN_xO_y) system offers the possibility to obtain a wide range of properties by tailoring the ratio between pure Al, AlN_x and AlO_y and therefore opening a significant number of possible applications. In this work the thermal behaviour of AlN_xO_y thin films was analysed by modulated infrared radiometry (MIRR), taking as reference the binary AlO_y and AlN_x systems. MIRR is a non-contact and non-destructive thermal wave measurement technique based on the excitation, propagation and detection of temperature oscillations of very small amplitudes. The intended change of the partial pressure of the reactive gas (N_2 and/or O_2) influenced the target condition and hence the deposition characteristics which, altogether, affected the composition and microstructure of the films. Based on the MIRR measurements and their qualitative and quantitative interpretation, some correlations between the thermal transport properties of the films and their chemical/physical properties have been found. Furthermore, the potential of such technique applied in this oxynitride system, which present a wide range of different physical responses, is also discussed. The experimental results obtained are consistent with those reported in previous works and show a high potential to fulfil the demands needed for the possible applications of the systems studied. They are clearly indicative of an adequate thermal response if this particular thin film system is aimed to be applied in small sensor devices or in electrodes for biosignal acquisition, such as those for electroencephalography or electromyography as it is the case of the main research area that is being developed in the group.

1. Introduction

Thin films based on metal nitrides and oxides are established materials with great interest to the academic communities due to

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their numerous industrial applications and still with a promising future [1,2]. The industrial importance of these materials keeps growing rapidly, not only in the well-established applications based on the strength and refractory nature of these materials such as cutting tools and abrasives, but also in new and promising fields such as electronics, optoelectronics and medical device applications [3–9]. More recently and using the idea of tailoring the film's properties between those of metal nitrides, MeN_x, and those of the correspondent insulating oxides, MeO_y, a new class of materials gained more importance in several technological applications: the metal oxynitrides MeN_xO_y, where Me can be Al [10–13], Cr [14], Ta [15], Nb [16], Zr [17] [18], Mo [19], Ti [20,21], among others. These ternary materials allow, in principle, merging the benefits of the basic characteristics of both metal nitrides and oxides. Their relevance arises from the fact that the addition of oxygen and nitrogen to metallic elements allows a vast number of stoichiometries, opening the possibility of tuning the band gap, the electrical conductivity, and the crystallographic order between nitride and oxide and hence the electronic and (micro)structural properties of the materials, and thus the overall set of properties [2].

An example of such systems is the ternary aluminium oxynitride (AlN_xO_y), which might combine the advantages of metallic aluminium with those of the correspondent binary systems, AlN_x and AlO_y. The wide difference between the properties of these three base materials opens the possibility to combine some of their advantages by simply changing the C_{N+O}/C_{Al} atomic ratio of the film. In previous works the authors carried out a systematic study of the AlN_xO_y system, taking as reference the corresponding AlN_x and AlO_y base binary systems. It was showed that by using different pressures of reactive gas (N_2 and/or O_2), in the magnetron sputtering deposition process [12], it was possible to tune the films composition with different structural and morphological characteristics. These features induced a wide range of electrical [22], optical [11] and electrochemical [23] properties, making this films potentially useful for biomedical sensors or solar applications [23]. Nevertheless, in order to scan the possibility of using this type of films in or near heat sources, such as solar power systems [24], a detailed knowledge about the thermal transport properties and their correlation with the deposition conditions and resulting microstructural features is fundamental for the successful development of such materials.

In order to study the thermal transport properties of the films, modulated IR radiometry (MIRR), also called modulated photothermal radiometry, is ordinarily applied, since it's a non-destructive and contactless thermal wave method appropriate for the characterization of the thickness and the thermal properties of thin films [25,26]. In terms of thermal behaviour, this technique can be useful to determine the thermal diffusivity and the thermal effusivity of the materials. The thermal diffusivity reflects the capacity of the materials to spread out the thermal energy and thus it is a very important parameter since a very low value can lead to a high localized heating, eventually damaging the sample. Thermal effusivity can be seen as a measure of thermal inertia and it is crucial in controlling heat propagation between different media. In particular, the thermal effusivity ratio between the film and the substrate is a fundamental parameter to understand the way heat propagates in layered materials. Furthermore, if the effusivity of the substrate is known, the effusivity of the film material can be calculated.

In this work, the thermal parameters, such as the thermal effusivity ratio between film and substrate, the thermal diffusion time and the thermal diffusivity of AlO_y, AlN_x and AlN_xO_y films were calculated based on MIRR measurements. Since the thermal properties of these materials rely on their composition and microstructure, which depend on the deposition conditions, a detailed analysis of these interdependencies is also a major concern. In section 2 experimental details related to the film's production and characterization are given, whereas the basic description of the experimental setup for thermal properties, the description of the two-layer model and interpretation of signals amplitude and phase of the MIRR can be found in section 3. In section 4 the target potential evolution and the growth rate of the three systems of films are compared each other and some correlations with (and between) the composition and microstructure are also analysed with detail. The results of the thermal behaviour of the films are presented in section 5, along with some correlations with other basic characteristics and physical properties (electrical and optical) of the films.

2. Details of thin films deposition and characterization

The thin films were produced by reactive DC magnetron sputtering, in a laboratory-sized deposition system [22], using silicon wafers with <100 > orientation (used for structural, morphological and composition analysis) and glass lamellae (ISO 8037) (used for thermal characterization). The substrates were placed in a grounded holder at 70 mm from the target, in a rotation mode-type (9 r.p.m.), and kept at a constant temperature of 100 °C before discharge ignition by using a Joule effect resistor. Before the depositions, the substrates were subjected to an *in-situ* etching process, using pure argon with a partial pressure of 0.3 Pa (70 sccm), and a pulsed current of 0.6 A (T_{on} = 1536 ns and f = 200 kHz) for 900 s. A DC current density of 75 A m^{-2} was used on the aluminium target (99.6% purity) with dimensions 200 × 100 × 6 mm^3, being sputtered using a gas atmosphere composed of argon (working gas) and a reactive gas (different for each system). The argon flow used was the same for all depositions (70 sccm), corresponding to a partial pressure 0.3 Pa (measured before discharge ignition). The maximum flows/partial pressures of reactive gases used were i) 9 sccm/0.07 Pa of O_2 in the AlO_y system; ii) 45 sccm/0.32 Pa of N_2 to produce the AlN_x films; and iii) 27.5 sccm/0.22 Pa of a mixture composed of nitrogen and oxygen with a constant N_2:O_2 ratio of 17:3 (85% of N_2/15% of O_2), in order to prepare the oxynitride films, AlN_xO_y. In the particular case of the reactive mixture, the two gases used (N_2 and O_2) are mixed in the same bottle. Furthermore, different N_2:O_2 ratios were tested, including 19:1 and 9:1 ratios, however the ratio 17:3 was selected since it allows the incorporation of a wider range of nitrogen and oxygen in the films, simultaneously. In fact, one of the main objectives to use such a gas mixture was to avoid an early formation of oxide-like films, trying to extend as much as possible the deposition of thin films with a mixed composition between those of the metallic-like films (Al), semi-conductor (AlN) and oxide ones (Al_2O_3). Since oxygen is much more reactive than nitrogen, the latter is not incorporated in the film above a certain partial pressure of N_2+O_2 mixture. The partial pressure of the reactive gas was measured before discharge ignition, without argon, being directly proportional to the flow rate. The argon and the reactive gas are controlled by two flow metres and they are injected into the chamber using a circular tube (with small holes) positioned close to the internal wall of the chamber.

Before each deposition, a target cleaning process was carried out in pure argon until the target voltage reached a steady state. Further details about the experimental setup and deposition conditions can be found elsewhere [11].

The chemical composition of the films was determined by Rutherford Backscattering Spectrometry (RBS) technique and the spectra analysed with the code NDF [27,28]. The structure and the phase distribution of the coatings were assessed by X-Ray diffraction (XRD), using a PANalytical X'Pert PRO– MPD. The XRD patterns were deconvoluted assuming to be Pearson VII functions using