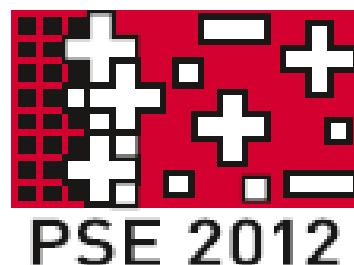


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Effects of annealing on the electrical and optical properties of AlN_xO_y thin films

Joel Borges¹, Roxana Arvinte¹, Nuno Barradas², Eduardo Alves², Sophie Camelio³, Thierry Girardeau³, Fabien Paumier³, Filipe Vaz¹, Luis Marques¹

¹Centre/Department of Physics, U. Minho, Braga, Portugal ²ITN, Sacavém, Portugal ³Institute PRIME, Université de Poitiers, Futuroscope Chasseneuil, France

joelborges@fisica.uminho.pt

Aluminium oxynitride is known to be a ceramic material with high strength and hardness, resulting from a stabilization of alumina (Al_2O_3) with nitrogen, in a cubic *spinel* structure, at thermodynamic conditions very different from those found in low plasma temperature deposition processes. Beyond this stable phase of AlN_xO_y , the available knowledge on this system is still very reduced and the interest on studying this material arises from the fact that it may combine some of the advantages of the three base systems, Al, AlN and Al_2O_3 , by changing the concentration of aluminium, oxygen and nitrogen in the films. In fact, recent studies showed that AlN_xO_y thin films deposited by physical vapour deposition presents unusual changes in the growing morphology and structure that may be quite different from those of *spinel*, consisting of Al nanoparticles embedded in an amorphous AlN_xO_y matrix. Depending on the amount of oxygen and nitrogen in the matrix, a wide variation in the electrical properties, as well as peculiar optical responses, such as an unusual large broadband absorption for some films, can be found in the samples.

In this work, the thermal stability of representative AlN_xO_y coatings was tested in vacuum, using annealing temperatures ranging from 200 to 800°C. No significant changes in the Al-type structure were observed for annealing temperatures of up to 600 °C, below the aluminium melting point. On the contrary, for higher temperatures, new crystalline phases were found, which resulted in significant changes in the optical properties, and gradual changes in the values of electrical resistivity.

Keywords

AlN_xO_y

Annealing

Electrical and optical properties

EFFECT OF ANNEALING ON THE ELECTRICAL AND OPTICAL PROPERTIES OF AlN_xO_y FILMS

J. Borges¹, R. Arvinte¹, N. P. Barradas², E. Alves², S. Camelo³, T. Giradeau³, F. Paumier³, F. Vaz⁴, L. Marques¹

¹Centre of Physics and Department of Physics, Campus de Guimarães, 4710-057 Braga, Portugal

²Instituto Superior Técnico/ITI, Universidade Técnica de Lisboa, E.N. 10, 2686-953 Sacavém, Portugal

³Institut PRUME - UPR 3346 CNRS-Université de Poitiers-BNSMA

Département de Physique et Mécanique des Matériaux B8E, SP2MI - Téléport 2, BP 30179 RN6962 Futuroscope Chasseneuil Cedex - France



GFCT (Computational and Theoretical Physics Group) - www.gfct.fisica.uminho.pt and GRF (Functional Coatings Group) - <https://online.uminho.pt/journal/pfct/>

Recent studies [1, 2] showed that AlN_xO_y thin films deposited by reactive DC magnetron sputtering presents unusual changes in the growing morphology and structure that may be quite different from those of AlN spinel structure, consisting of Al nanoparticles embedded in an amorphous AlN_xO_y matrix. Depending on the amount of oxygen and nitrogen in the matrix, a wide variation in the electrical properties, as well as peculiar optical responses, such as an unusual large broadband absorption for some films, can be found. In this work, the thermal stability of representative AlN_xO_y coatings was tested in vacuum, using temperatures ranging from 200 to 800°C, in order to study the structure variations, electrical and optical properties as a function of annealing temperature.

EXPERIMENTAL DETAILS

DC magnetron sputtering:

Target: Aluminum, 99.8 % purity
Substrates: Glass, Silicon <100>
Substrate temperature: 373 K.
Partial pressure of Argon: 0.3 Pa
Reactive gas: N_2+O_2 (17.3)
Rotating substrates: 9 r.p.m.
Bias: GND
Target current density: 75 A.m⁻²
Discharge parameters monitored by a Data Acquisition Switch unit Agilent 34970A



Annealing conditions:

The annealing of the samples was done in vacuum (10^{-4} Pa), being subjected to a heating process during t minutes: $T_{\text{min}} = 120 + 0.2T_{\text{m}} + 180$ (with T_{m} the annealing temperature)

Characterization techniques:

Scanning electron microscopy (Leica Cambridge 5525) for thickness and morphology (cross-sections)
Rutherford Backscattering Spectrometry (IN - Labor) for chemical composition
X-Ray diffraction (Philips PW 1710) for structure
Four point probe method (linear geometry and Van der Pauw) for electrical resistivity and TCR measurements (low resistivity coatings)
I-V curve method (bulk) for electrical resistivity (high resistivity coatings)
UV-3101 PC UV-VIS-NIR with 60 mm integrating sphere for reflectance and transmittance measurements
Minolta CM-2500d portable spectrophotometer for reflectivity of annealed samples

DEPOSITION CHARACTERISTICS

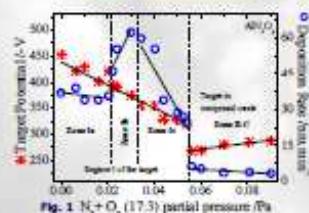


Fig. 1 Target potential and deposition rate of the as-deposited samples.
The target potential is clearly influenced by the gas mixture partial pressure. It gradually decreases in regime I as is becoming polarized, and in regime II the target is completely polarized.
The deposition rate (thickness/deposition time) has also distinct variations.

CONCLUSIONS

The composition and structure of the films are strongly dependent of the target condition and deposition characteristics [1]. The properties of the AlN_xO_y system can be explained assuming that the films consist in a percolation network of aluminum nanoparticles embedded in an oxide/nitride matrix [2]. No significant changes in the Al-type structure were observed. For high annealing temperatures (above the Al melting point) some changes in the electrical properties were found, increasing for the samples with positive TCR and decreasing for the sample with negative TCR. The low reflectance observed for some of as-deposited samples (zone IIc) is maintained in visible range, even with annealing.

[1] J. Borges, F. Vaz, L. Marques, *Applied Surface Science* 257/5 (2010) 1478

[2] J. Borges, N. Martin, N.P. Barradas, E. Alves, D. Bylki, M.F. Beaumont, J.P. Rivière, F. Vaz, L. Marques, *Thin Solid Films* 520/21 6709

RESULTS AND DISCUSSION (as-deposited samples)

Atomic ratio:

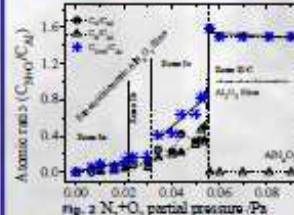


Fig. 2 Atomic ratio of the as-deposited samples. Four different tendencies can be found for the atomic ratios of the AlN_xO_y films.

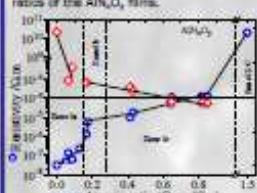


Fig. 4 Electrical resistivity and temperature coefficient of resistance (TCR) of the as-deposited samples.



Fig. 3(a) XRD of some representative samples and (b) SEM cross section of the as-deposited samples subjected to annealing.

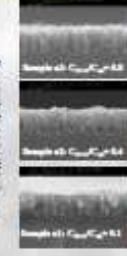


Fig. 3 (a) XRD of some representative samples and (b) SEM cross section of the as-deposited samples subjected to annealing.

The Al-type structure is maintained in the sub-stoichiometric films (zones IIa and IIb), becoming amorphous in zone IIc, ending up completely amorphous in zone II-C (close stoichiometric AlN_xO_y films).

The type of growth gradually changes from columnar-type (zone IIa) to cauliflower (zones IIb and IIc) ending up as dense and featureless (zone II-C).

Fig. 3(b)

RESULTS AND DISCUSSION (annealed samples)

Sample a1 ($C_{\text{AlN}}/C_{\text{AlO}}=0.1$):

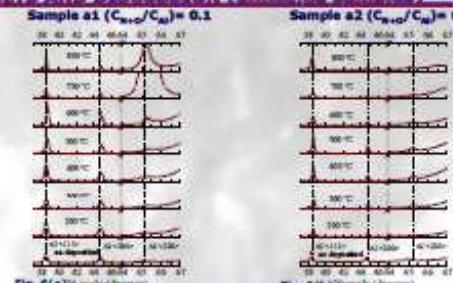


Fig. 6(a) XRD patterns of sample a1.

Sample a2 ($C_{\text{AlN}}/C_{\text{AlO}}=0.4$):



Fig. 6(b) XRD patterns of sample a2.

Sample a3 ($C_{\text{AlN}}/C_{\text{AlO}}=0.8$):



Fig. 6(c) XRD patterns of sample a3.

Fig. 6 XRD patterns of the (a) sample a1, $C_{\text{AlN}}/C_{\text{AlO}}=0.1$; (b) sample a2, $C_{\text{AlN}}/C_{\text{AlO}}=0.4$ and (c) sample a3, $C_{\text{AlN}}/C_{\text{AlO}}=0.8$. The samples with atomic ratios of 0.1 and 0.4 maintain the Al-type structure as the annealing temperature increases and a new orientation of the Al-type grains can clearly be found in the sample with higher content of aluminum. The quasi-amorphous as-deposited sample (atomic ratio of 0.8) crystallizes in an Al-type structure for high annealing temperatures.

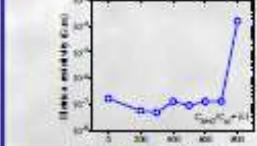


Fig. 7 Electrical resistivity of the (a) sample a1; (b) sample a2 and (c) sample a3.

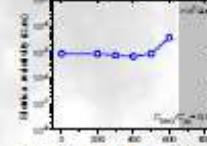


Fig. 7(b) Electrical resistivity of sample a2.

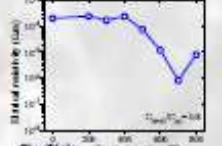


Fig. 7(c) Electrical resistivity of sample a3.

Fig. 7 Electrical resistivity of the (a) sample a1; (b) sample a2 and (c) sample a3. The as-deposited samples with positive TCR and subjected to annealing reveal approximately constant resistivities for temperatures up to 800°C and an increase for higher temperatures (above the Al melting point). An opposite behaviour is found for the sample with atomic ratio of 0.8 (with negative TCR,) where the resistivity tends to decrease for temperatures higher than 400 °C.

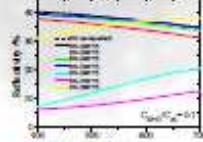


Fig. 8 Reflectivity of the (a) sample a1; (b) sample a2 and (c) sample a3.

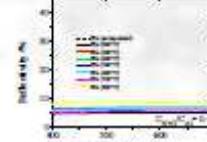


Fig. 8(b) Reflectivity of sample a2.

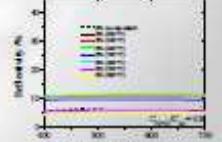


Fig. 8(c) Reflectivity of sample a3.

Fig. 8 Reflectivity of the (a) sample a1; (b) sample a2 and (c) sample a3. The as-deposited samples with atomic ratios of 0.4 and 0.8 maintain the low reflectivity in visible region when subjected to annealing.

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