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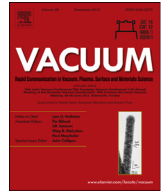

Properties of tantalum oxynitride thin films produced by magnetron sputtering: The influence of processing parameters

D. Cristea [a,b], D. Constantin [a,b], A. Crisan [b], C.S. Abreu [c,d], J.R. Gomes [d], N.P. Barradas [e], E. Alves [e], C. Moura [a], F. Vaz [a], L. Cunha [a,*]

[a] Centro de Física, Universidade do Minho, Campus de Gualtar, 4710-057 Braga, Portugal
[b] Department of Materials Science, Transylvania University, 500036 Brasov, Romania
[c] Physics Dep., School of Engineering (ISEP), Polytechnic of Porto, Portugal
[d] Centre for Mechanical and Materials Technologies (CT2M), University of Minho, Campus de Azurém, 4800-058 Guimarães, Portugal
[e] Instituto Superior Técnico, Universidade Técnica de Lisboa, Estrada Nacional 10, 2686-953 Sacavém, Portugal

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ABSTRACT

The main purpose of this work is to present and to interpret the change of structure and physical properties of tantalum oxynitride (TaN_xO_y) thin films, produced by dc reactive magnetron sputtering, by varying the processing parameters. A set of TaN_xO_y films was prepared by varying the reactive gases flow rate, using a N_2/O_2 gas mixture with a concentration ratio of 17:3. The different films, obtained by this process, exhibited significant differences. The obtained composition and the interpretation of X-ray diffraction results, shows that, depending on the partial pressure of the reactive gases, the films are: essentially dark grey metallic, when the atomic ratio $(N + O)/Ta < 0.1$, evidencing a tetragonal β-Ta structure; grey-brownish, when $0.1 < (N + O)/Ta < 1$, exhibiting a face-centred cubic (fcc) TaN-like structure; and transparent oxide-type, when $(N + O)/Ta > 1$, evidencing the existence of Ta_2O_5, but with an amorphous structure. These transparent films exhibit refractive indexes, in the visible region, always higher than 2.0.

The wear resistance of the films is relatively good. The best behaviour was obtained for the films with $(N + O)/Ta \approx 0.5$ and $(N + O)/Ta \approx 1.3$.

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1. Introduction

Transitional metal oxynitrides are a new class of materials with properties that could be implemented in industrial applications. The main advantage of such coatings is the possibility to tune their chemical, mechanical, electrical and optical properties to suit the desired application. By varying the ratio between the nitrogen and oxygen, one could obtain properties ranging from nitride-like hard, metallic and chemically inert coatings to oxide-like electrically insulating coatings, suited for dielectric, optical or decorative applications [1–8]. Tantalum oxynitride can benefit from the properties exhibited by tantalum nitride, which is known to be used as a hard and refractory material for tribological and mechanical purposes [9], for electrical applications as either a conductive or insulating material [10–12] and also from optical, dielectric and decorative properties of the tantalum oxide [13–15], as well as for its biomedical potential applications [16,17]. Thus, tuning the nitrogen/oxygen ratio may lead to potentially attractive properties. This paper presents the findings related to the chemical and structural evolution as a function of the reactive DC sputtering deposition parameters and the influence of such parameters on the composition, structure and on the optical and tribological behaviour of tantalum oxynitride thin solid films.

2. Experimental details

For the present work, TaO_xN_y thin films were deposited onto glass, silicon (100), high-speed steel (AISI M2) and stainless steel (AISI 316) substrates, by DC reactive magnetron sputtering, using a laboratory-size deposition chamber. The configuration of the deposition system is two unbalanced type II magnetrons with a rectangular shape, facing each other. For this study only one of the magnetrons was used, in a closed field configuration. A dc current density of 50 A/m^2 was used during all depositions. The tantalum

* Corresponding author. Tel.: +351 253604066; fax: +351 253604079.
E-mail address: lcunha@fisica.uminho.pt (L. Cunha).

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target dimensions are (200 × 100 × 6) mm and its purity is 99.6%. The films were obtained in a rotation mode, to improve their homogeneity, and the substrate holder was positioned at a distance of 70 mm, in front of the target, during all runs. All the samples were produced with grounded substrates. Before each deposition, the substrates were plasma-etched during 500 s, using a pulsed current of approximately 0.6 A in a pure argon atmosphere with a partial pressure around 0.3 Pa. During depositions the atmosphere inside the chamber was composed of a mixture of $Ar + N_2 + O_2$. An argon flow of 60 sccm was kept constant during all depositions, while the 85% N_2 + 15% O_2 gas mixture (17/3 concentration ratio) was varied between 2.5 and 30 sccm. For comparison purposes one of the samples was deposited without the presence of reactive gases. The working pressure varied between 0.4 Pa and 0.65 Pa, depending on the flow rate of the reactive gas mixture. The substrate holder was maintained at a temperature of 100 °C.

The atomic composition was measured by Rutherford Backscattering Spectrometry (RBS) using protons with energy of 2.25 MeV, at an angle of incidence of 0° and with three detectors in the chamber: standard at 140°, and two pin-diode detectors located symmetrically to each other, at 165°. The resulting profiles were generated using the IBA DataFurnace NDF software program [18]. X-ray diffraction investigations were performed on Si substrates samples using a Philips PW diffractometer (Cu-Kα radiation) in a Bragg-Brentano geometry configuration. The resulting patterns were processed with a Pearson VII function in order to obtain the peak characteristics: position, intensity and full width at half maximum (FWHM).

The reflectance and transmittance were measured on a UV–Vis–NIR spectrophotometer (Shimadzu UV–Vis–NIR 2505) in the spectral range of 250–800 nm.

Film colour was determined from the reflectance spectra obtained in the wavelength range 400–700 nm, using a Minolta (Cm-2600d) portable spectrophotometer. The colour was represented by the parameters L*, a*, b*, according the CIELAB 1976 colour space. In this three coordinate system, L* represents the lightness which varies from 0 (black) to 100 (diffuse white), taking into account that specular white is evidence of higher values. The chromaticity coordinates are a* and b*: a* varies from green (negative values) to red/magenta (positive values); and b*varies from blue (negative values) to yellow (positive values). In the case of chromaticity coordinates, the farther from (0,0), the higher the colour saturation.

The thickness of the films was obtained by ball-cratering, while residual stress values were calculated with Stoney's equation [19], using the curvature radii of the stainless steel samples before and after the film depositions. The tribological characterization of the high speed steel coated samples was carried out on a reciprocating tribometer, under ambient conditions, using silicon nitride balls with 5 mm diameter as a counterpart material, and a constant normal applied load of 0.5 N. In all tests, the track length and the frequency of the oscillating motion of the plate were kept constant at values of 6 mm and 1 Hz, respectively.

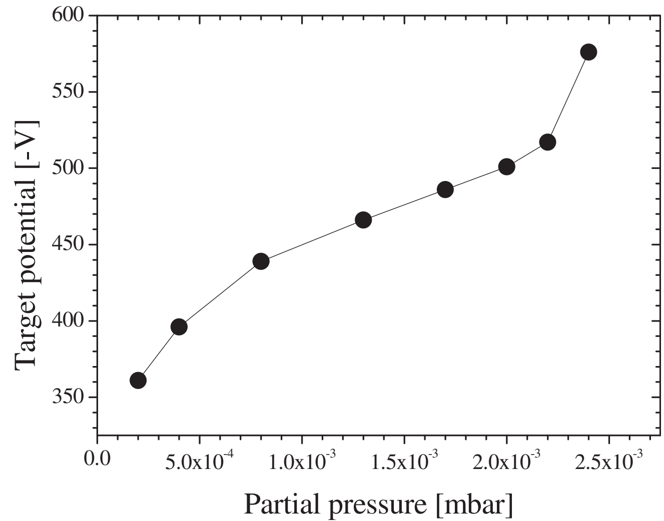

Fig. 1. Target potential as a function of the partial pressure of the reactive gases.

3. Results and discussion

3.1. Deposition rate and film composition

In Table 1 are registered the different deposition conditions and some characteristics of the deposited tantalum oxynitride films.

The registered partial pressure of the reactive gases was measured before the discharge ignition. The films revealed low values of residual stress, less than 1 GPa and compressive in nature. Only in the case of the sample $TaN_{0.55}O_{0.45}$, a small tensile stress (~270 MPa) was detected.

Fig. 1 shows the evolution of the target potential as a function of the partial pressure of the reactive gas mixture. As is readily seen, an increase of the partial pressure results in an increase of the target potential. This may be due to the increase in the overall reactive gas flow, which enhances the target poisoning effect.

The influence of the partial pressure of the reactive gases on the deposition rate can be observed in Fig. 2. The deposition rate does not vary significantly with the increase of the partial pressure (between ~18 nm/min and ~22 nm/min). Nevertheless a pattern seems to emerge. There can be seen a gradual increase in the deposition rate up to a partial pressure of the of reactive gas mixture of 1.7×10^{-3} mbar, followed by a gradual decrease. This decrease may be explained by the target poisoning effect and by the structural evolution of the samples. As will be shown in the structural evolution discussion, between 1.7×10^{-3} mbar and 2.0×10^{-3} mbar, a change from the possibly nitride-like structure to a more oxide-oriented structure occurs. The higher reactivity of the oxygen might lead to an increase above the maximum gettering capacity of the reactive gas, which translates in a higher quantity of

Table 1
Characteristics and different deposition conditions of the produced TaN_xO_y films: Φ ($N_2 + O_2$) – reactive gases flow; P ($N_2 + O_2$) – reactive gases partial pressure; t_f, films' thickness; σ – residual stress.

Samples	Atomic ratio (N + O)/Ta	Φ ($N_2 + O_2$) [sccm]	P ($N_2 + O_2$) [mbar]	t_f [μm]	σ [GPa]
Ta N_0O_0	0	0.0	0	1.42 ± 0.07	–
$TaN_{0.07}O_{0.03}$	0.10	2.5	2.0×10^{-4}	1.15 ± 0.10	−0.30 ± 0.05
$TaN_{0.27}O_{0.20}$	0.47	5.0	4.0×10^{-4}	1.26 ± 0.07	−0.75 ± 0.10
$TaN_{0.55}O_{0.45}$	1.00	10.0	8.0×10^{-4}	1.30 ± 0.08	+0.27 ± 0.11
$TaN_{0.54}O_{0.49}$	1.03	15.0	1.3×10^{-3}	1.34 ± 0.09	−0.64 ± 0.08
$TaN_{0.47}O_{0.67}$	1.14	20.0	1.7×10^{-3}	1.37 ± 0.08	−0.91 ± 0.11
$TaN_{0.41}O_{0.91}$	1.32	22.5	2.0×10^{-3}	1.31 ± 0.10	−0.11 ± 0.09
$TaN_{0.39}O_{0.91}$	1.30	25.0	2.2×10^{-3}	1.21 ± 0.04	−0.05 ± 0.03
$TaN_{0.32}O_{1.24}$	1.56	30.0	2.4×10^{-3}	1.13 ± 0.08	−0.26 ± 0.12

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