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Composition and structure variation for magnetron sputtered tantalum oxynitride thin films, as function of deposition parameters

D. Cristea [a], M. Pătru [a], A. Crisan [a], D. Munteanu [a], D. Crăciun [b], N.P. Barradas [c], E. Alves [d], M. Apreutesei [e,f], C. Moura [g], L. Cunha [g,*]

[a] Department of Materials Science, Transilvania University, 500036 Brasov, Romania
[b] Laser Department, National Institute for Laser, Plasma, and Radiation Physics, Magurele, Romania
[c] Centro de Ciências e Tecnologias Nucleares, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 ao km 139,7, 2695-066 Bobadela LRS, Portugal
[d] Instituto de Plasmas e Fusão Nuclear, Instituto Superior Técnico, Universidade de Lisboa, E.N. 10 ao km 139,7, 2695-066 Bobadela LRS, Portugal
[e] Université de Lyon, Institut des Nanotechnologies de Lyon INL-UMR 5270, CNRS, Ecole Centrale de Lyon, Ecully F-69134, France
[f] MATEIS Laboratory-INSA de Lyon, Bât. B. Pascal, 7 Avenue Jean Capelle, 69621 Villeurbanne Cedex, France
[g] Center of Physics, University of Minho, Campus de Gualtar, 4710-057 Braga, Portugal

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ABSTRACT

Tantalum oxynitride thin films were produced by magnetron sputtering. The films were deposited using a pure Ta target and a working atmosphere with a constant N_2/O_2 ratio. The choice of this constant ratio limits the study concerning the influence of each reactive gas, but allows a deeper understanding of the aspects related to the affinity of Ta to the non-metallic elements and it is economically advantageous. This work begins by analysing the data obtained directly from the film deposition stage, followed by the analysis of the morphology, composition and structure. For a better understanding regarding the influence of the deposition parameters, the analyses are presented by using the following criterion: the films were divided into two sets, one of them produced with grounded substrate holder and the other with a polarization of −50 V. Each one of these sets was produced with different partial pressure of the reactive gases $P(N_2+O_2)$. All the films exhibited a O/N ratio higher than the N/O ratio in the deposition chamber atmosphere. In the case of the films produced with grounded substrate holder, a strong increase of the O content is observed, associated to the strong decrease of the N content, when $P(N_2+O_2)$ is higher than 0.13 Pa. The higher Ta affinity for O strongly influences the structural evolution of the films. Grazing incidence X-ray diffraction showed that the lower partial pressure films were crystalline, while X-ray reflectivity studies found out that the density of the films depended on the deposition conditions: the higher the gas pressure, the lower the density. Firstly, a dominant β-Ta structure is observed, for low $P(N_2+O_2)$; secondly a fcc-Ta(N,O) structure, for intermediate $P(N_2+O_2)$; thirdly, the films are amorphous for the highest partial pressures. The comparison of the characteristics of both sets of produced TaN_xO_y films are explained, with detail, in the text.

1. Introduction

Transition metal oxynitrides (TM-O-N) are ceramic materials that recently have been extensively investigated, not only because of their attractive properties for different applications, but also because the properties may gradually be changed by controllably varying the concentration of the constituents during processing, along with the variation of other deposition parameters, such as the polarization of the substrate holder. Transition metal oxynitrides demonstrate to have capabilities, in general, in a much larger domain, in relation to the corresponding metallic nitrides and oxides [1]. As a consequence, TM-O-N thin films may be prepared for different applications, such as biocompatible and electronic materials, solar absorbers, optical, decorative, and photocatalytic materials, etc. [2–8]. Particularly in the case of sputtered TM-O-N films, the multifunctional characteristics are strongly dependent on the composition, morphology and structure, which can be controlled by the deposition parameters. Besides the control of the reactive gases, target parameters, and deposition temperature, the negative substrate bias voltage applied to the substrate holder is a critical parameter, because it allows controlling the energy of the ions arriving on the substrate (and consequently, on the growing film) and can significantly affect the characteristics of the produced films [9–11].

* Corresponding author.
E-mail address: lcunha@fisica.uminho.pt (L. Cunha).

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Table 1
Characteristics and variable deposition conditions of the produced TaN_xO_y films: $V_{subst.}$ – substrate bias; Φ ($N_2 + O_2$) – reactive gases flow; $P(N_2 + O_2)$ – reactive gases partial pressure; t_f – thickness of the films, σ – residual stress of the films.

Set	Sample	$V_{subst.}$ [V]	$\Phi(N_2+O_2)$ [sccm]	$P(N_2+O_2)$ [Pa]	t_f [µm]	σ [GPa]
A	A1	−50	4.5	0.05	1.21 ± 0.06	−1.12 ± 0.28
	A2		10	0.08	0.98 ± 0.05	–
	A3		15	0.10	1.04 ± 0.05	−0.62 ± 0.09
	A4		25	0.15	1.04 ± 0.05	+0.10 ± 0.06
	A5		35	0.19	1.17 ± 0.06	+0.03 ± 0.10
B	B0	GND	0.0	0	1.42 ± 0.07	–
	B1		2.5	0.02	1.15 ± 0.10	−0.30 ± 0.05
	B2		5	0.04	1.26 ± 0.07	−0.75 ± 0.10
	B3		10	0.08	1.30 ± 0.08	+0.27 ± 0.11
	B4		15	0.13	1.34 ± 0.09	−0.64 ± 0.08
	B5		20	0.17	1.37 ± 0.08	−0.91 ± 0.11
	B6		22.5	0.20	1.31 ± 0.10	−0.11 ± 0.09
	B7		25	0.22	1.21 ± 0.04	−0.05 ± 0.03
	B8		30	0.24	1.13 ± 0.08	−0.26 ± 0.12

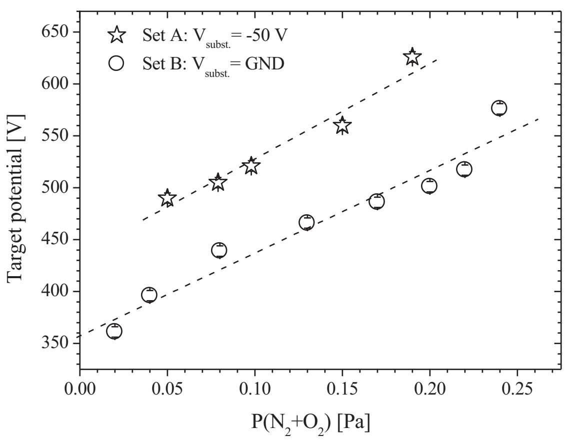

Fig. 1. Target potential during the production of TaN_xO_y films, as function of the reactive gases partial pressure.

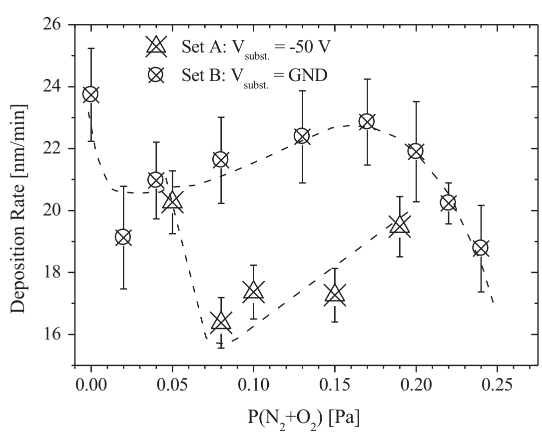

Fig. 2. Deposition rate of TaN_xO_y films, as function of the reactive gases partial pressure.

The use of a negative bias voltage applied to the growing film allows modifying its morphology and structure. Consequently the properties of the produced films can be altered. Some of these changes may include: improved film adhesion to the substrate, substantial improvement in step coverage, increased film density, changes in electrical resistivity of metallic films, changes in the dielectric constant of dielectric films, variation of hardness and residual stress, removal of contaminants, modification of surface chemistry, enhancement of nucleation and re-nucleation and the elimination of interfacial voids and subsurface porosity (caused by argon entrapment) [12].

There are several references concerning the effect of substrate bias on the properties of the coatings but, to this day, there are no extensive works published concerning the consequences of this parameter on the properties exhibited by sputtered tantalum oxynitride thin films. However, some points of interest might be extracted from the literature concerning other oxynitride systems (CrN_xO_y, NbN_xO_y, TiN_xO_y, ZrN_xO_y). These studies may help to understand the influence of this parameter on tantalum oxynitride thin films structures and properties. According to Savisalo et al. [13], the variation of the substrate bias voltage during the deposition of multilayer structures of chromium oxynitride and niobium oxynitride causes a significant effect on the microstructure: at lower bias voltages the microstructure is columnar, while at higher bias voltages the density of the coatings is increased and the column boundaries are less distinct. The higher ion bombardment on the surface of TiO_xN_y samples, due to the substrate polarization, may cause the enhancement of phase segregation and the formation of TiN polycrystalline grains, while the absence of substrate bias leads to the formation of the Ti–O–N phase, where some of the oxygen atoms are occupying nitrogen positions in the fcc-TiN lattice [14]. Moreover, the grounded samples (no potential on the substrate holder) exhibit a much lower degree of compressive stress than the biased samples. Again, discussing about the TiO_xN_y system, it was found that the bias voltage influences the deposition rate, reaching its maximum at an applied substrate bias of −40 V, in a range of values between 0 V and −60 V [15]. It was also found that the surface roughness decreases slightly with the raise of substrate bias. As expected, the ion bombardment increases the density of the TiO_xN_y films [16]. The content of oxygen evidences a tendency to decrease when a polarization voltage is applied, leading to a possible relation between the energy of the impinging ions on the surface and the oxygen incorporation. The discussion concerning ZrO_xN_y thin films evidences several effects of the bias voltage: a smoothing of the surface roughness up to a certain value of bias voltage followed by an increase of roughness for higher values, which causes a variation of the optical brilliance; a structural texturing phenomenon, possibly promoted by the ion bombardment; an increase of the residual compressive stress with the raise of the substrate bias [17]. Ariza et al. [18] showed that the corrosion resistance at ambient temperature of the substrate/coating system (AISI M2/ZrN_xO_y), in an artificial sweat solution with pH = 4.5, seems to not be influenced by the substrate bias.

Another important factor is the variation of the properties of oxynitrides depending on the oxygen/nitrogen ratio. The control of this ratio allows tuning the structure, the electric, mechanical and optical properties and the photocatalytic behaviour of this class of materials.