

# Mechanical evaluation of unbiased W–O–N coatings deposited by d.c. reactive magnetron sputtering

N.M.G. Parreira<sup>a</sup>, N.J.M. Carvalho<sup>a</sup>, F. Vaz<sup>b</sup>, A. Cavaleiro<sup>a,\*</sup>

<sup>a</sup> ICEMS, Grupo de Materiais e Engenharia de Superfícies, Faculdade de Ciências e Tecnologia da Universidade de Coimbra, Pólo II, 3030-201 Coimbra, Portugal

<sup>b</sup> Departamento de Física, Universidade do Minho, Campus de Azurém, 4800-058 Guimarães, Portugal

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## Abstract

Tungsten nitride (WN<sub>y</sub>) and tungsten oxynitride films (WO<sub>x</sub>N<sub>y</sub>) were prepared with chemical compositions in the range 0 < x < 1 and 0 < y < 1. Besides the detection of amorphous features, the following crystalline phases were identified and related with the amount of the non-metal elements: α-W, β-W and β-W<sub>2</sub>N. All coatings exhibited compressive residual stresses between 1.5 and 5 GPa. Generally, the lower values were concerned with either O-containing coatings or the presence of amorphous phase. The values of the hardness varied from 20 to 40 and 15 to 33 GPa in W–N and W–O–N coatings, respectively. Very good correlation was detected between the residual stress and the hardness values. Moreover, a linear relationship between the hardness and the Young's modulus of the coatings was found. The scratch-test values for W–N coatings decreased from 70 to 15 N with nitrogen increase, whereas W–O–N coatings showed very low values (<15 N) in all range of compositions.

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## 1. Introduction

Transition metal (TM) nitrides (like tungsten nitride) are known for the unique combination of excellent mechanical properties (hardness and Young's modulus), high melting point, good chemical stability and high conductivity [1]. The first studies of tungsten nitride thin films were performed, basically, for electronic applications such as semiconductors [2] or diffusion barriers [3]. In the 1990s, W–N coatings were started to be studied for mechanical applications [4] and further studies were performed on the addition of different elements (e.g. W–Ti–N [5,6] and W–Si–N [7]) on the improvement of the mechanical properties of these coatings.

In order to improve the performance of TM nitrides, a new generation of coatings was recently started to be developed by combining oxygen with nitrogen as reactive gases using a transition metal as target. An example of this procedure is the work of Vaz et al. [8,9] in Ti–O–N or Zr–O–N coatings deposited by r.f. reactive magnetron sputtering. The scope is to combine the optical characteristics and the corrosion resistance

of the oxides with the mechanical properties of the nitrides. These coatings can be deposited by controlling the oxygen and nitrogen ratio, and thereby crossing over a wide range of compositions. Therefore, numerous industrial applications including coatings for decorative purposes, cutting tools, micro- and optoelectronics can now be envisaged.

In this work, the main objective was to study the mechanical properties of W–N and W–O–N thin films deposited from a pure tungsten target by d.c. reactive magnetron sputtering in an Ar–N<sub>2</sub> or Ar–O<sub>2</sub>–N<sub>2</sub> atmosphere. The mechanical properties (residual stress, hardness and Young's modulus) were analysed, as a function of the chemical composition and the structure of the coatings.

## 2. Experimental details

Tungsten nitride and tungsten oxynitride coatings were deposited by conventional d.c. reactive magnetron sputtering from a tungsten target (150 × 150 mm) using a reactive atmosphere Ar–N<sub>2</sub> or Ar–N<sub>2</sub>–O<sub>2</sub>, respectively. Tool steel substrates (AISI M2) were thermal treated to reach a final hardness close to 9 GPa prior to deposition. For stress measurements, disks of stainless steel (AISI 304) were used.

\* Corresponding author. Tel.: +351 239 790745; fax: +351 239 790701.

E-mail address: [albano.cavaleiro@dem.uc.pt](mailto:albano.cavaleiro@dem.uc.pt) (A. Cavaleiro).

The deposition runs were performed by keeping constant the following parameters: total working pressure (0.3 Pa), target current density ( $10 \text{ mA} \cdot \text{cm}^{-2}$ ), substrate at floating potential, no substrate rotation, inter-electrode distance (65 mm) and substrate temperature ( $<350 \text{ }^\circ\text{C}$ , with no external heating). Before deposition, an ultimate vacuum pressure of  $5 \times 10^{-4}$  Pa was reached and the substrate's surface was ion cleaned with an ion gun following the procedure described somewhere else [10].

A Cameca SX-50 electron probe microanalysis apparatus (EPMA) was used for determination of the chemical composition of the coatings. The structure of the films was analysed by X-ray diffraction (XRD) using a Philips diffractometer with Co  $K\alpha$  radiation ( $\lambda=0.178897 \text{ nm}$ ) in Bragg–Brentano configuration.

The residual stress value is determined by deflection method from the Stoney's equation [11] using substrate curvature radii, both before and after coating deposition [12].

The hardness and Young's modulus of the coatings were evaluated by depth-sensing indentation technique using a Fischer Instruments-Fischerscope. The load  $P$  was increased in 60 steps until the indentation load of 50 mN was reached and the same steps were used during unloading. The testing procedure includes the correction of the experimental results for geometrical defects in the tip of the indenter, thermal drift of the equipment, and uncertainty in the initial contact; for more details see Ref. [13].

The adhesion/cohesion of the coatings was evaluated by scratch-testing technique using a Revetest, CSM Instruments. The load was increased linearly from 0 to 50 N (Rockwell C 200  $\mu\text{m}$  radius indenter tip, loading rate of 100 N/min, and scratch speed of 10 mm/min). The  $L_c$  values corresponding to the different failure mechanisms (adhesive/cohesive) were measured by analyzing the failure events in the scratch track by optical microscopy.

### 3. Results and discussion

#### 3.1. Chemical composition

The evolution of the chemical composition of the deposited coatings (measured by EPMA) is shown in Table 1, as a function of the partial pressure of the reactive gas. Increasing the nitrogen partial pressure from 0 to 0.225 Pa led to an increase of the nitrogen content in the films from 0 to 55 at.%. The nitrogen content increased almost linearly with the nitrogen partial pressure, showing that a progressive poisoning of the target occurred.

In the case of W–O–N coatings, the argon pressure was kept constant at 0.15 Pa and the quantity of nitrogen and oxygen partial pressure was tuning from 0 to 0.145 and from 0 to 0.075 Pa, respectively. The higher reactivity of oxygen comparatively with nitrogen was confirmed as it is evident in the coating deposited with the same partial pressure of  $\text{N}_2$  and  $\text{O}_2$  (0.075 Pa), in which 35 at.% of O could be measured while almost no N ( $<1$  at.%) was detected. According to the chemical composition, two series of  $\text{WO}_x\text{N}_y$  coatings will be considered from now on: series I with  $x=0\text{--}30$  and  $y \approx 40$  at.% ( $f_{\text{O}_2} \leq 0.46$ )

Table 1

Chemical composition of W–N and W–O–N coatings as a function of the reactive gases partial pressures

	Sample	Partial pressure of reactive gases		Chemical composition (at.%)			
		$p_{\text{N}_2}$ (Pa)	$p_{\text{O}_2}$ (Pa)	W	O	N	$f_{\text{O}_2}$
System W–N	W <sub>100</sub>	0.000	–	98.58	1.42	0.00	–
	W <sub>95</sub> N <sub>05</sub>	0.050	–	93.05	1.78	5.17	–
	W <sub>90</sub> N <sub>10</sub>	0.075	–	88.36	2.20	9.44	–
	W <sub>88</sub> N <sub>12</sub>	0.100	–	84.21	3.96	11.93	–
	W <sub>84</sub> N <sub>16</sub>	0.125	–	80.17	5.07	14.77	–
	W <sub>66</sub> N <sub>34</sub>	0.150	–	65.20	1.75	33.05	–
	W <sub>64</sub> N <sub>36</sub>	0.175	–	62.76	2.03	35.21	–
	W <sub>58</sub> N <sub>42</sub>	0.200	–	57.60	0.27	42.13	–
	W <sub>45</sub> N <sub>55</sub>	0.225	–	44.81	0.41	54.78	–
System W–O–N	W <sub>59</sub> O <sub>02</sub> N <sub>39</sub>	0.145	0.005	59.24	1.46	39.30	0.04
	W <sub>48</sub> O <sub>11</sub> N <sub>41</sub>	0.140	0.010	48.44	11.09	40.47	0.22
	W <sub>44</sub> O <sub>19</sub> N <sub>37</sub>	0.135	0.015	43.70	18.91	37.39	0.34
	W <sub>35</sub> O <sub>30</sub> N <sub>35</sub>	0.130	0.020	34.91	30.17	34.92	0.46
	W <sub>58</sub> O <sub>32</sub> N <sub>10</sub>	0.120	0.030	58.50	31.59	9.91	0.76
	W <sub>64</sub> O <sub>35</sub> N <sub>01</sub>	0.075	0.075	64.44	34.65	0.91	0.97

and series II with,  $x \approx 30$  and  $y=0\text{--}35$  at.% ( $f_{\text{O}_2} \geq 0.46$ ),  $f_{\text{O}_2}$  being the oxygen fraction determined by the ratio of the oxygen content and the sum of oxygen and nitrogen content:  $f_{\text{O}_2} = C_{\text{O}} / (C_{\text{O}} + C_{\text{N}})$ .

#### 3.2. Residual stress and structure

The evolution of the residual stress values of tungsten nitride and tungsten oxynitride was shown in Figs. 1(a) and 2(a) as a function of either the nitrogen content or the oxygen fraction, respectively. The first important conclusion is that all coatings display a compressive residual stress state, result which should be expected due to the low working pressure, 0.3 Pa. In these conditions the bombardment of the growing film by energetic particles, such as sputtered atoms or reflected Ar neutrals, could induce the well-known atomic peening effect which promotes the compressive residual stress state [14]. Moreover, as the coatings were deposited at  $\sim 350 \text{ }^\circ\text{C}$ , during the cooling down to room temperature, a compressive thermal stress component is introduced in the films, due to the higher thermal expansion coefficient of the steel substrate ( $\sim 13.2 \times 10^{-6} \text{ K}^{-1}$ ) in comparison to W-based films ( $<5 \times 10^{-6} \text{ K}^{-1}$ ) if the bulk materials' values of W and W–N are considered. The structural evolution of W–N and W–O–N coatings was already studied in detail [10]; however, due to the correlation that will be established between structure and stress results, the X-ray diffraction patterns of W–N (Fig. 1(b), (c), and (d)) and W–O–N (Fig. 2(b) and (c)) coatings are also shown.

The evolution of the residual stress of tungsten nitride coatings as a function of nitrogen content can be divided in three groups according to their structure. The coatings with low nitrogen content ( $\text{N} \leq 10$  at.%) — group I — display the  $\alpha$ -W phase as it is shown in Fig. 1(b). The increasing nitrogen incorporation in the coatings promotes a shift in the  $\alpha$ -W (110) peak position to lower diffraction angles, suggesting that nitrogen is being placed in interstitial positions in the lattice, giving rise to the dilatation of the

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