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EFFECT OF NITROGEN CONTENT ON PHYSICAL AND MECHANICAL PROPERTIES OF TUNGSTEN FILMS DEPOSITED BY COMBINED MAGNETRON SPUTTERING AND ION IMPLANTATION

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Abstract. Tungsten films with various nitrogen content (WN_x with $x = 1.25$, 2.00 and 2.47 at%), intended for use as hard coatings were deposited by Combined Magnetron Sputtering and Ion Implantation method. A study was performed to assess the correlations between the nitrogen flow rate and physical and mechanical properties of the films.

Key words: hard coatings, magnetron sputtering, tungsten films.

1. INTRODUCTION

Transition metal nitrides represent a class of materials with outstanding characteristics concerning mechanical properties (microhardness, Young's modulus), chemical stability and high melting point. Representative for this class of materials is titanium nitride (TiN), a compound that attracted a large scientific and technological interest for a long period of time. In recent years, a large variety of thin film deposition techniques have been used to obtain TiN, such as, chemical vapour deposition (CVD) [1], laser ablation [2–4], ion beam sputtering [5, 6], DC and RF reactive sputtering [7, 8], etc. It was observed that the microstructure, stoichiometry and the properties of the films depends on the deposition technique with its associated parameters.

Combined magnetron sputtering and ion-implantation (CMSII) is a hybrid deposition technique, consisting in using a periodical high energy ion bombardment of the growing layer, with a magnetron discharge used as plasma source for ion implantation [9]. The technique was successfully used for producing dense and uniform nanostructured titanium-nitride coatings on various substrates [10].

Unlike titanium nitride, tungsten nitride is much less studied. Initially, studies on this compound were focused on its use in the field of electronic applications or diffusion barriers [11]. There are also reports related to mechanical applications as standalone coatings [12–14] or in combination with other elements (Si, Ti etc.) [15].

Here we report our results on the effects of nitrogen content on the physical properties of tungsten-nitrogen coatings with relatively small nitrogen concentrations (WN_x with x = 1.25, 2.00 and 2.47 at%), deposited on plain carbon steel and titanium substrates. Coatings were deposited by CMSII, a definite correlation between the nitrogen flow rate admitted in the deposition chamber and the physical properties (structure, microhardness) being observed.

2. EXPERIMENTAL METHODS

During the magnetron discharge, high voltage pulses (30–70 kV typically, with pulse duration of 20 μs and frequency of 10–50 Hz) are applied to the negatively biased substrates, accelerating the ions from plasma to the surface of the growing layer. The technique proved to be very effective for the deposition of well-adhered layers, with controlled mechanical properties [16]. Prior to introduction in the deposition chamber the substrates were ultrasonically cleaned in acetone bath and dried in air.

The deposition chamber was evacuated initially to a base pressure of 10^{-6} mbar. The working gas flow rate (Ar, 5.0 sccm), the working pressure (3.0 mbar), the power applied to the magnetron (700 W) and the temperature of the substrate were kept constant during deposition. Several layers were deposited, the only variable parameter being the nitrogen (N_2) flow rate, varied in the range 0–3 sccm. The target-to-substrate distance was 10 cm, the thickness of the deposited layers was in the range of 12–14 μm. Two types of substrates were used, titanium (Ti) plates and steel (OL45) plates.

The crystalline structure of the deposited layers was characterized by X-ray diffraction (XRD), using a Bruker D2 Phaser diffractometer with a CuK_a radiation. Chemical characterizations were performed by Glow Discharge Optical Emission Spectrometry (GDOES). Mechanical properties were evaluated by microhardness measurements and wear resistance investigations using a pin-on-disc tribometer.

3. RESULTS AND DISCUSSIONS

Figures 1 and 2 show GDOES depth profiles of WN_x films deposited on Ti and steel (OL45) substrates, respectively. In the case of OL45 substrate, a molybdenum (Mo) buffer layer (~5 μm) was deposited by DC sputtering to increase WN_x adhesion to OL45, otherwise poor. For both types of substrates, the concentration profile of nitrogen is relatively uniform throughout the film depth. Variation of nitrogen concentration against the flow rate, plotted in Fig. 3, is quasi-linear in the flow rates range used here. The thickness of WN_x coatings was in the range 10–14 μm (see Table 1).

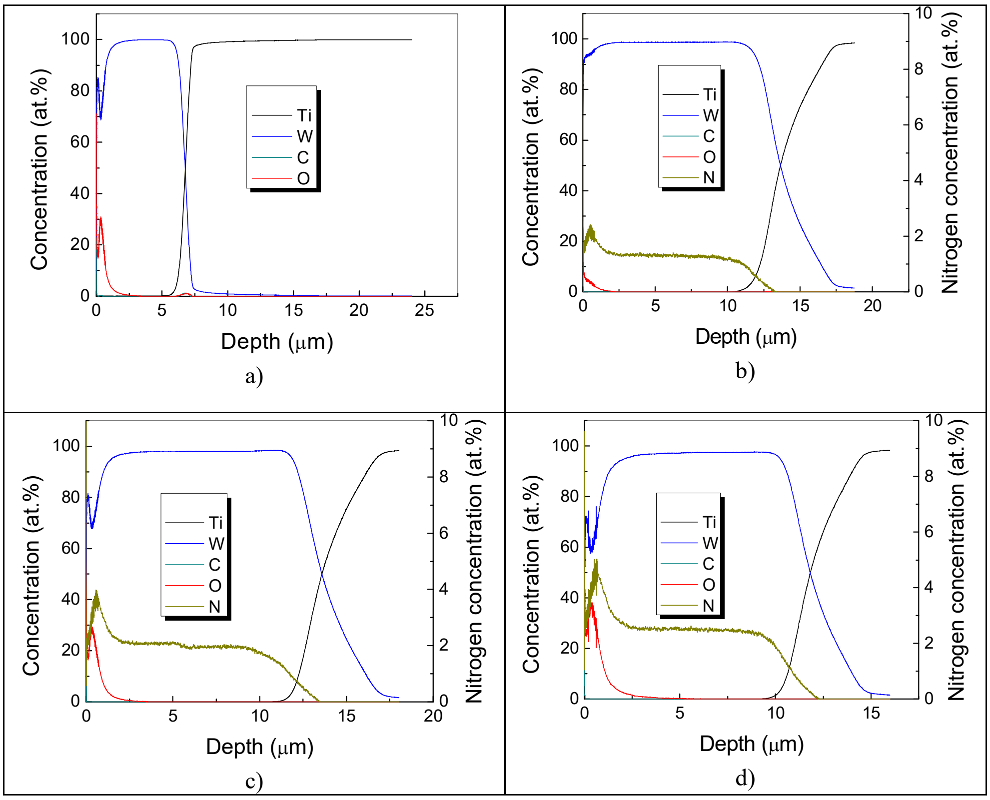

Fig. 1 – GDOES depth profiles for the W (a) and WN_x (b, c, d) coated samples.

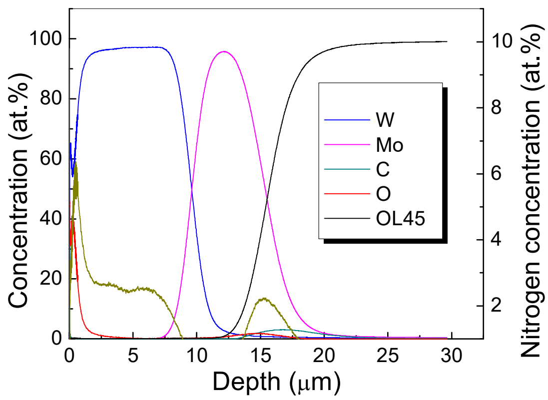

Fig. 2 – GDOES depth profile for the WN_x layer, deposited on OL45 substrate.

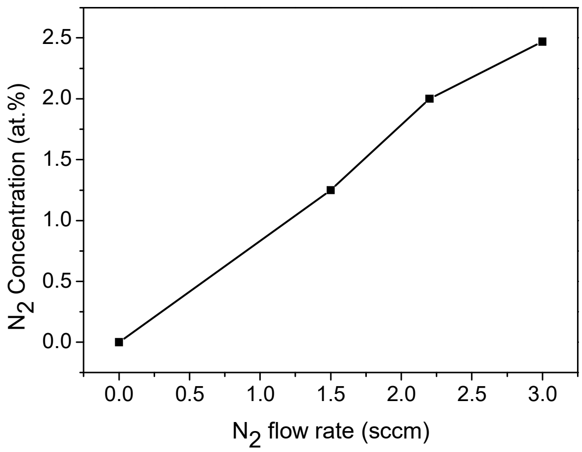

Fig. 3 – Variation of nitrogen concentration in WN_x layers deposited on Ti substrate at various nitrogen gas flow rates used during growth.

XRD patterns scanned in Bragg-Brentano theta-theta geometry show that all WN_x films are polycrystalline and contain the body centered cubic phase (Im-3m space group) of tungsten (W) (Fig. 4). Within detection limits of the method, no tungsten nitride compound was observed; nitrogen atoms are dissolved in the crystalline lattice of W. Williamson-Hall plots were used to extract crystalline parameters of the films:

$$\beta\cos\theta = \frac{0.9\lambda}{D_{ef}} + 2\sqrt{2\pi}\left\langle\varepsilon^2\right\rangle^{1/2}\sin\theta. \quad (1)$$

where β and θ are integral breadth and Bragg angle of the diffraction peaks, λ is the wavelength of X-rays, D_{ef} is the crystalline coherence length and $\left\langle\varepsilon^2\right\rangle^{1/2}$ is the averaged microstrain contributing to the broadening of the peaks. Williamson-Hall plots obtained for all analyzed films are shown in Fig. 5 and crystalline parameters extracted from Williamson-Hall analysis are collected in Table 1.

A slight distortion of the W lattice is observed, the lattice constant increasing with the nitrogen concentration (as determined from GDOES results, presented above). When a large nitrogen content is introduced in tungsten lattice, the mechanical macroscopic stress of the structure (measured by $\Delta a / a_0$) increases. Also crystalline disorder is more pronounced with increasing N_2 concentration, as suggested by the decrease of the crystalline coherence length and by the increasing trend of the averaged microstrain (except for the film with 1.25 at% N_2).

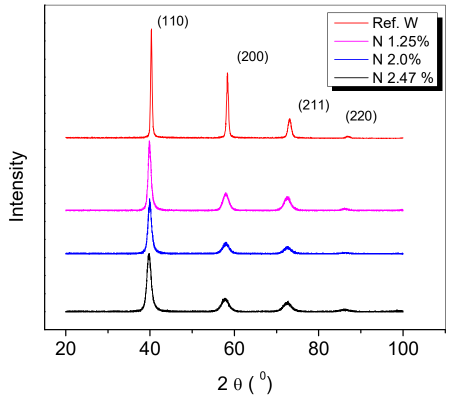

Fig. 4 – X-ray diffraction spectra of WN_x / Ti films scanned in Bragg-Brentano theta-theta geometry.

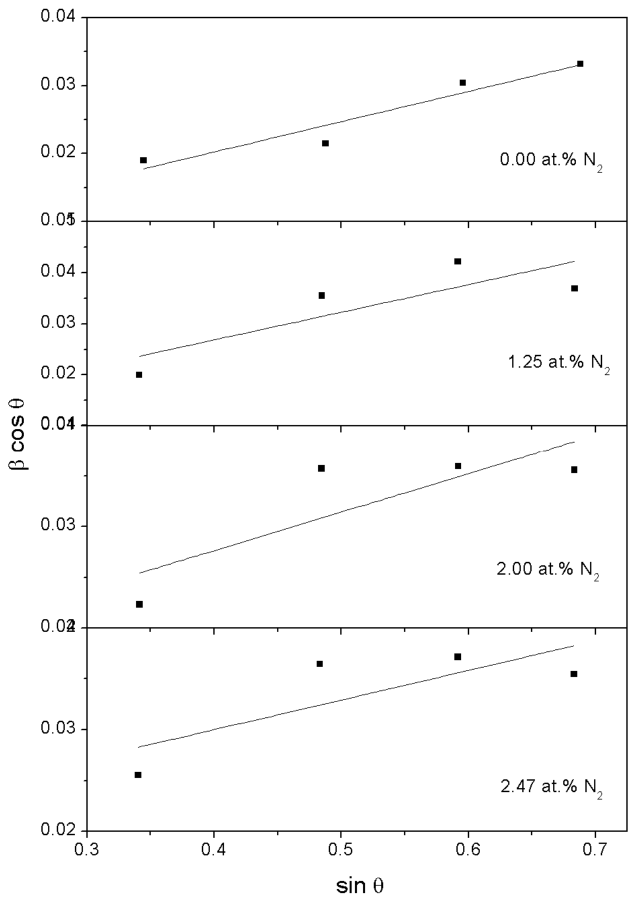

Fig. 5 – Williamson-Hall plots obtained for WN_x / Ti films.

Table 1

Crystalline parameters of WN_x / Ti films

N_2 concentration (at.%)	Lattice constant (Å)	Crystalline coherence length (nm)	Averaged microstrain	$\Delta a / a_0$
0.00	3.165	86.4	4.5×10^{-3}	-1.8×10^{-4}
1.25	3.196	31.0	1.1×10^{-2}	9.8×10^{-3}
2.00	3.193	21.1	7.5×10^{-3}	8.7×10^{-3}
2.47	3.205	10.0	8.8×10^{-3}	1.23×10^{-2}

Tribological properties were assesed by performing pin-on-disc measurements. A tungsten carbide ball has been used to obtain the wear rate profile of the WN_x layers. The test was performed with a load of 6 N for a sliding distance of 300 m at room temperature and in the absence of a lubricating element. The specific wear rates of the coatings were calculated as [17]:

$$\text{specific wear rate} = \frac{\text{wear volume}}{\text{friction mechanical work}} = \frac{V_w}{F_n a}, \qquad (2)$$

where V_w is the worn material volume, F_n is the normal load and a is the sliding distance.

Specific wear rate variation with nitrogen flow rate is presented in Fig. 6 for WN_x/OL45 films. The smallest specific wear rate corresponds to the layer with 1.25 at% N.

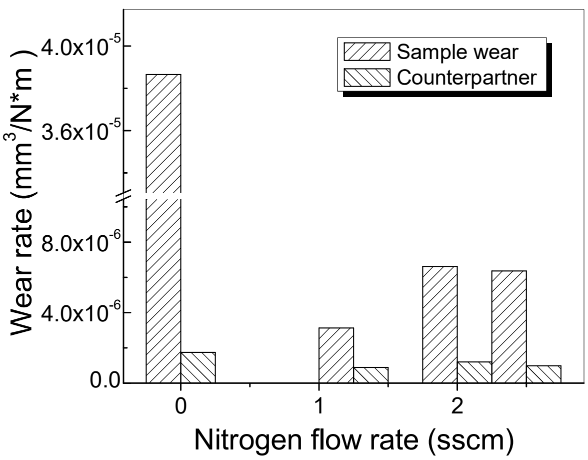

Fig. 6 – Specific wear rate variation against N_2 flow rate for WN_x / OL45 films.

Table 2

Effect of nitrogen content on averaged hardness values

N_2 content (at.%)	Hardness HV 0.05 (OL45 substrates)	Hardness HV 0.05 (Ti substrates)
0.00	1325.8	1210.0
1.25	1821.7	1881.4
2.00	2013.3	1928.6
2.47	2229.1	2260.2

Averaged hardness values were determined and a definite increase of the hardness with the nitrogen concentration was observed for both types of coatings (Table 2).

4. CONCLUSIONS

CMSII was successfully used for WN_x coatings of Ti and steel substrates. At small nitrogen flow rates used here (below 3 sccm), the layers consist of W body centered cubic phase, N atoms being dissolved in the crystalline lattice of W. N concentration profile is relatively uniform in all analyzed layers, as proved by GDOES experiments, being in the range 1.25–2.5 at%.

With increasing N concentration the crystalline coherence length decreases while the macro- and micro- strain increases. Microhardness of WN_x layers increases monotonically with N concentration in the investigated concentration range, for both types of substrates.

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