



Substrate temperature influence on W/WCN_x bilayers grown by pulsed vacuum arc discharge

R. Ospina, D. Escobar, E. Restrepo-Parra*, P.J. Arango, J.F. Jurado

Universidad Nacional de Colombia Sede Manizales, Km. 9 vía al Magdalena, Manizales, Colombia

ARTICLE INFO

Article history:

Received 6 November 2011

Received in revised form 21 January 2012

Accepted 24 January 2012

Available online 2 February 2012

Keywords:

Tungsten

EDS

XRD

Structure

Raman

Morphology

ABSTRACT

W/WCN_x coatings were produced by using a repetitive pulsed vacuum arc discharge on stainless-steel 304 substrates, varying the substrate temperature from room temperature to 200 °C. Energy dispersive spectroscopy (EDS) was used for determining W, C and N concentrations dependence on the substrate temperature. A competition between C and N can be observed. Atomic force microscopy was employed for obtaining the thickness and grain size that present similar tendencies as a function of the temperature. X-ray diffraction characterization showed phases of W and α-WCN (hexagonal). Raman spectra for all substrate temperatures were obtained, presenting two peaks corresponding to D (disorder) and G (graphite) bands in the region of 1100–1700 cm⁻¹ due to the amorphous carbon. As an important conclusion, it was stated that substrate temperature has strong influence on the structure, chemical composition and morphology of W/WCN_x bilayers, caused by the competition between carbon and nitrogen.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Tungsten coatings are widely used in the microelectronics industry, and the incorporation of carbon [1] and nitrogen [2] in tungsten coatings has been studied as diffusion barriers in surface modification processes [3] and many other applications. Since there appears to be a gap in the knowledge about coatings between tungsten and tungsten carbide and nitrides, it seems reasonable trying to understand effects of a non-metallic element when it is interstitially incorporated in a tungsten matrix. Pauleau and Gouy-Pailler [4] concluded that the increase in coatings hardness with tungsten and small amounts of carbon was due to the isotropic dilatation of the α-W structure. More recently, Quesnel et al. [5] developed W layers containing small amounts of carbon to be used in W/WC multilayers as erosion resistant coatings. Regarding to WCN_x, it has been produced not only by chemical vapor deposition techniques [6–8] but also by physical vapor deposition [9–11]. The structural characterization of WCN_x coatings has been normally carried out by means of X-ray diffraction (XRD) [6,12], Auger spectroscopy [13,14] and X-photoelectron spectroscopy (XPS) techniques [15,16]; on the other hand, Raman spectroscopy is a suitable tool for characterizing carbon based materials. Different Raman modes for diamond, graphite and amorphous carbon have been studied by several groups [17–19]. Moreover, Raman analysis can complement results

obtained by other techniques such as XRD and XPS, because it allows identifying D (disorder) and G (Graphite) bands. In the literature, no many reports about Raman studies of WCN_x coatings can be found. One work was presented by Lee et al. [20] who studied the gas-phase decomposition pathways of the tungsten dimethylhydrazido complexes as precursors for single source deposition of W/WCN_x. Nevertheless, a depth analysis of the coating is not carried out.

In this study, Raman spectroscopy in combination with electron dispersive spectroscopy (EDS) and X-ray diffraction have been employed for obtaining structural information of the carbon fraction in the WCN_x coatings produced by the pulsed vacuum arc technique.

2. Experimental set up

The W and WCN_x layers were deposited by using a repetitive pulsed vacuum arc discharge in a reaction chamber made of stainless steel. In this chamber there are two-faced electrodes, the cathode with targets of W (6N) and WC (6N) for the W and WCN_x layers respectively, and the anode which contains substrates of stainless-steel 304. Coatings were produced at 4 pulses. Substrates were polished and deeply cleaned with an ultrasonic cube. A high-power source designed to generate pulses with different active and passive times was used in order to produce the discharge between electrodes. By means of this power supply it was possible to carry out variations of the inter-electrode voltage from 0 to 280 V_{rms} (root medium square voltage), with 100 A as maximum current of

* Corresponding author. Tel.: +57 6 8879495; fax: +57 6 8879495.

E-mail address: erestrepopa@unal.edu.co (E. Restrepo-Parra).

work. The active time is limited to the minimum value necessary for the arc formation process, under a given conditions of work such as, target material, working gas and pressure. The inactive arc time can take any theoretical value; nevertheless it is necessary to take into account that the minimum value is subjected to the arc extinction time under the given working conditions (mainly the target material and the working gas). Initially, the reaction chamber was evacuated up to 10^{-3} Pa; then, the W and WCN_x layers were deposited on substrates using as gas of work argon for the W layer and a mixture of argon and nitrogen (1:1) for the WCN_x layer at 300 Pa and 280 V between the electrodes. Both layers were grown at 1 s and 2 s as passive and active time respectively. The substrate temperature (T_s) was varied taking values of room temperature (RT), 50, 100, 150 and 200 °C. The system is widely described in previous work [21,22].

Semi-quantitative elemental analysis was carried out with energy dispersive spectrometry (EDS) in a Philips XL 30 FEG with a standard probe EDAX. D8 Bruker AXS Diffractometer was used for X-ray diffraction characterization. It has an X-ray source of Cu K α , with $\lambda = 1.5406$ Å and a secondary monochromator of graphite. For films structure characterization, grazing incidence was used. To obtain films topographic images, a scanning probe microscopy (SPM) in the atomic force microscopy (AFM) mode, using a cantilever probe of silicon nitride (Si₃N₄), with a spring constant of 0.16 N/m, a scanning speed of 1 Hz, and image resolution of 256×256 pixels, in environmental conditions was employed. Measurements were obtained at 60% of relative humidity and 24 °C. These analyses were done taking five images from different positions of each coating and averaging them. Moreover, Raman spectra of W/WCN_x coatings were obtained by means of a μ -RAMAN Lab Ram HR 800 Horiba Jovin Yvon equipment with a monochromatic radiation source of 473 nm DPSS (diode pulsed solid state) and a laser power of 100 mW, objective of 50 $\times$; the signals were collected by using a CCD type detector electrically refrigerated (Peltier effect) and configuration of backscattering measurement.

3. Results and analysis

W/WCN_x thin films elemental composition was studied by using EDS technique as a function of T_s . The main elements in W/WCN_x bilayers are W, C and N coming from the electrode, and Co and Fe that are due to the stainless steel substrate. For having a general outlook of the elemental composition evolution, Table 1 shows W, C and N concentrations dependence on T_s , presenting a competition between C and N. Initially, an increase in the carbon concentration with the temperature is observed, producing C–C, C–N, C=C and C=N bonds. It causes the sample amorphization as is reported by Kukielka et al. [23]. They presented a study of

Table 1

Atomic percentages of W, C and N present in the W/WCN_x bilayers as a function of T_s .

T_s (°C)	W (wt%)	C (wt%)	N (wt%)
RT	69 $\pm$ 1	15 $\pm$ 2	5.7 $\pm$ 0.5
50	62 $\pm$ 2	22 $\pm$ 1	2.2 $\pm$ 0.2
100	59 $\pm$ 1	25 $\pm$ 1	3.3 $\pm$ 0.1
150	64 $\pm$ 2	18 $\pm$ 1	6.2 $\pm$ 0.3
200	55 $\pm$ 2	30 $\pm$ 2	2.4 $\pm$ 0.1

amorphous hydrogenated Ni/C. In this study, as the C percentage increases, the sample structure tends to be amorphous. Films deposited at RT and 150 °C showed lower carbon percentage. Since nitrogen presents higher concentration at these two temperatures, the WCN_x phase formation is favored as will be shown by XRD analysis.

Fig. 1 shows 3D AFM images presenting the W/WCN_x coating surface morphology (Fig. 1(a)) and the step (Fig. 1(b)) that allows determining the thickness of sample grown at 150 °C. According to Fig. 2(a) and (b), the grain size and thickness present similar tendencies as a function of T_s . In all physical processes, there is an equilibrium point, where the system could present a greater efficiency. In the thin films deposition process, many growth mechanisms occur, such as adsorption, nucleation, coalescence and resputtering [24]. The initial decrease of thickness as T_s increases has been reported in previous work by Pal and Jacob [25]. They produced WO₃ films on silicon substrates concluding that this behavior is caused by the increase in the vapor pressure of the deposited material. It also can be attributed to the importance of the resputtering process at this stage, since the adatoms gain enough energy from T_s , returning then to the plasma. It causes less material deposition, as is reported by Beena et al. [26]. On the other hand, several authors report a direct relationship between thickness and grain size. Savaloni and Player [27,28] found that by increasing the film thickness the grain size increases, while the morphology and crystal structure also change. It is usually accepted that defects in thin films structure are accumulated during the deposition and they are the cause of voids formation in low adatoms mobility. Therefore, they should form with the same rate as described by Messier et al. [29], i.e., column size is increased by a factor of three relative to the previous level, with increasing film thickness and then grains normally grow as conic columns [30].

On the other hand, surface morphology can be described through different parameters. Roughness average (R_a) and root-mean square (rms) roughness (R_q) are the most widely used surface parameters in the industry [31]. Surface roughness of the films decreases as T_s increases. The enhancement in surface smoothness with T_s can be attributed to the higher surface atoms diffusion

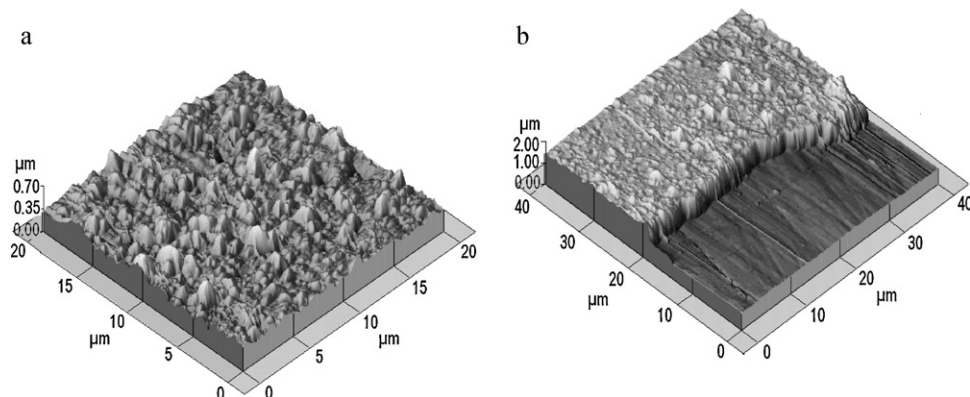


Fig. 1. 3D AFM image for W/WCN_x bilayers grown at 150 °C: (a) morphology and (b) step for measuring the bilayer thickness.

Download English Version:

<https://daneshyari.com/en/article/5365910>

Download Persian Version:

<https://daneshyari.com/article/5365910>

[Daneshyari.com](https://daneshyari.com)