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SCIENCE DIRECT
Applied Surface Science 252 (2006) 5419–5423
applied surface science
www.elsevier.com/locate/apsusc

Characteristics of surface nano-structural modifications in nitrogen ion implanted W as a function of temperature

H. Savaloni [a,b,*], F. Modiri [b], H. Hajihosseini [b], A. Shokouhy [b]

[a] Department of Physics, University of Tehran, North-Kargar Street, Tehran, Iran
[b] Plasma Physics Research Center, Science and Research Campus of I.A. University, P.O. Box 14665-678, Tehran, Iran

Available online 3 February 2006

Abstract

The surface modifications of tungsten massive samples (0.5 mm foils) made by nitrogen ion (30 keV; 1×10^{18} N^+ cm^{-2}) implantation are studied by XRD, AFM, and SIMS. XRD patterns clearly showed WN_2 (0 1 8) (rhombohedral) very close to W (2 0 0) line. Crystallite sizes obtained from WN_2 (0 1 8) line, showed an increase with substrate temperature. AFM images showed the formation of grains on W samples, which grew in size with temperature. These morphological changes are similar to those observed for thin films by increasing substrate temperature (i.e. structure zone model (SZM)). Surface roughness variation with temperature, showed a decrease with increasing temperature. The density of implanted nitrogen ions, and the depth of nitrogen ion implantation in W are studied by SIMS. The results show a minimum for N^+ density at a certain temperature consistent with XRD results (i.e. $I_{W\ (2\ 0\ 0)}/I_{W\ (2\ 1\ 1)}$). This minimum in XRD results is again similar to that obtained for different thin films by Savaloni et al. [Physica B, 349 (2004) 44; Vacuum, 77 (2005) 245] and Shi and Player [Vacuum, 49 (1998) 257].

PACS: 68.55.Ln; 68.49.Sf; 82.80.Ms; 68.37.Ps

Keywords: SEM; AFM; XRD; SIMS; Ion implantation; Depth profile

1. Introduction

Ion implantation emerged during 1970, has found a wide usage in modifying the surface properties of existing materials and obtaining new ones, and meeting the requirements of modern engineering. The investigation of structural changes and the formation of chemical compounds due to ion implantation are of importance both from the scientific point of view and in practical applications [1–4]. The detailed metallurgical studies have elucidated the role played by the implanted nitrogen in enhancing the resistance to wear of broad range of alloys [5]. However, some nitrides, like those of chromium, molybdenum, and tungsten, are the most difficult to form [6], because they show the lowest reactivity with nitrogen and the respective compounds, the lowest stability and the narrowest region of existence in the phase diagrams [7,8].

The aim of this article is to investigate the nature of nitride formation in tungsten during nitrogen implantation, as a function of substrate temperature.

2. Experimental details

The samples used were cut in two different sizes of 3 mm × 3 mm (for SIMS analysis), 10 mm × 5 mm (for XRD and AFM analysis) from 0.5 mm thick polycrystalline W foil (Balzers; nr. 07049). Neither mechanical nor chemical polishing treatments were applied to the samples surfaces. The rms and average surface roughness, R_q and R_a of W surface was measured by AFM and are given in Table 1.

The nitrogen ion implantation of the samples was carried out at 30 keV and a dose of 1×10^{18} N^+ cm^{-2} for 1600 s. The base pressure of the chamber was 2×10^{-5} mbar, which during the implantation process increased to 6×10^{-5} mbar. Detailed description of the substrate holder is given in our earlier work [9]. On the copper disk substrate holder two of each size of the substrates can be fixed by a stainless steel mask. The substrate temperatures were controlled by programmed thermostats and

* Corresponding author. Tel.: +98 21 88635776; fax: +98 21 88004781.
E-mail addresses: savaloni@yahoo.com, savaloni@khayam.ut.ac.ir (H. Savaloni).

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doi:10.1016/j.apsusc.2005.12.063

Table 1
Details of tungsten samples investigated

Sample no.	Initial temperature (K)	Final temperature (K)	Surface roughness, rms (Å)	Surface roughness (R_a) (Å)	D (Å)	GS (Å)
W	RT	RT	12.3	9.54	–	–
W1	300	750	55.1	44.2	409	739
W2	423	775	21.9	17.1	670	940
W3	523	800	23.7	17.3	915	1967
W4	623	825	27.0	20.1	770	1750

thermocouples fixed inside a hole on the surface of copper disk substrate holder.

Just before use all W samples were ultrasonically cleaned in heated acetone then ethanol.

The crystallographic structure of the samples was obtained using a PTS 3003 diffractometer, while the surface morphology and roughness was obtained by means of AFM (Park Scientific). SIMS (Cameca, IMS 6F) analysis provided the density and depth profile of implanted N^+ ions in W samples. The details of W samples produced for investigation in this work, and the data obtained from different analysis are given in Table 1.

3. Results

3.1. X-ray diffraction (XRD)

In Fig. 1, (a) and (b–e) show X-ray diffraction patterns obtained from untreated and N^+ (30 keV) implanted W at four different temperatures, respectively. It should be mentioned that the initial temperature, which is given in column 2 of Table 1, was set before implantation and it changed during implantation process owing to heat transfer from ion beam to the samples. The final temperature of the samples at the end of implantation process is given in column 3 of Table 1, and the data were analyzed according to this temperature, as in fact this temperature effectively acts on the processes activated in the sample, until the sample cools down to room temperature in vacuum.

The comparison of the XRD patterns in Fig. 1 clearly shows the formation of WN_2 (0 1 8) (rhombohedral; $d = 1.5859$) and WH (1 1 1) (hexagonal; $d = 1.2946$) lines very close to W (2 0 0) (bcc; $d = 1.5820$) and W (2 1 1) (bcc; $d = 1.2920$) lines, respectively.

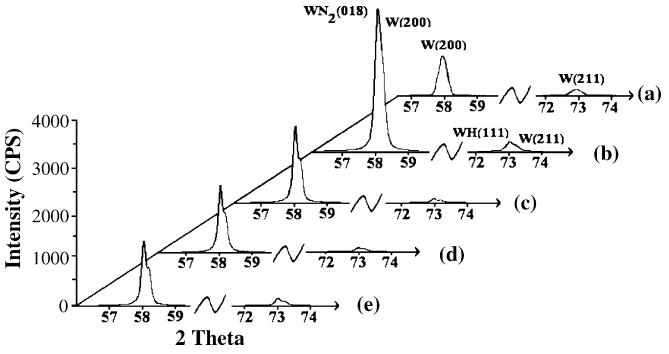

Fig. 1. XRD patterns of untreated and N^+ ion (30 keV) implanted tungsten at different temperatures. (a) Untreated W; (b) 750 K; (c) 775 K; (d) 800 K; (e) 825 K.

The crystallite size D (coherently diffracting domains), are obtained using the Scherrer formula [10]:

$$B = \frac{k\lambda}{D\cos\theta}, \tag{1}$$

where, λ is the wavelength of X-ray, θ is the Bragg angle, k is a dimensionless constant which is related to the shape and distribution of crystallites [11] (usually taken as unity). One has to include a correction for instrumental broadening in this calculation, which is usually known as full width half maximum (FWHM) measurement technique [12,13], therefore:

$$B = (W_0^2 - W_i^2)^{1/2}, \tag{2}$$

where, W_0 is the FWHM of the sample and W_i is the FWHM of stress free sample (annealed powder sample).

The grain size (coherently diffracting domains) variation with substrate temperature obtained from WN_2 (0 1 8) line is given in column 6 of Table 1. The general trend of the results is an increase with substrate temperature.

3.2. Surface morphologies obtained by AFM

Surface morphologies of untreated and N^+ ion implanted W samples were observed by AFM and the influence of substrate temperature on them has been studied. The surface morphology images of samples are shown in Fig. 2(a–e). Fig. 2(a) shows the surface morphology of unimplanted W, which shows no clear/ordered morphology. The surface roughness of all samples is given in Table 1.

Fig. 2(b) is the AFM image of N^+ implanted W with a final temperature of 750 K. Grains of column-like structure are formed on the surface. Fig. 2(c–e) shows the surface morphology pictures of N^+ implanted W at three higher final temperatures, given in Table 1. In Fig. 2(c), larger grains are formed and the difference between the large and small grains is still obvious. At higher temperatures (Fig. 2(d and e)), a distinct change in the surface morphology can be seen. In addition, the size of the grains increases dramatically. The grain sizes obtained from AFM images are given in Table 1, while the effective activation energy E_a may be estimated from Arrhenius plot, as in Fig. 3.

The rms and average roughness measurements of the samples (Table 1) support the AFM observations. Both rms and R_a follow similar trend and consistent with microscopic