Available online at www.sciencedirect.com

ScienceDirect

Ceramics International 40 (2014) 465–470

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

A study of the oxidation behavior of multilayered tungsten nitride/amorphous tungsten oxide film prepared in a planar magnetron sputtering system

S. Khamseh*

Department of Nanomaterials and Nanocoatings, Institute for Color Science and Technology, Tehran, Iran

Received 30 April 2013; received in revised form 4 June 2013; accepted 10 June 2013
Available online 17 June 2013

Abstract

Tungsten nitride and tungsten nitride/amorphous tungsten oxide multilayered films were produced by a planar type reactive sputtering system on glass and stainless steel substrates. The effect of amorphous tungsten oxide top layer on oxidation behavior of tungsten nitride film has been characterized by thermal analysis using TGA and DTA. The structure of the film at different thermal-annealing temperatures was investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM). The mechanical properties of the films at different heat-annealing states were measured by nano-indentation. It was found that the tungsten nitride film oxidized in air at 600 °C by the dissociation of face center cubic (fcc)–W_2N to WO_3 and $WO_{2.92}$ and showed low hardness of 6 GPa. The addition of 500 nm thick amorphous tungsten oxide top layer to tungsten nitride film can further improve the oxidation resistance. Multilayered film oxidized in air at 800 °C by the dissociation of face center cubic (fcc)–W_2N to WO_3 and $WO_{2.92}$. The film retained a hardness of 24 GPa after annealing at 600 °C for 10 h. This indicates that this film is a good candidate for high temperature applications.

Keywords: Tungsten nitride; Amorphous tungsten oxide; Oxidation resistance; Magnetron sputtering

1. Introduction

Transition metal nitrides or carbides are the most widely used films for high performance applications such as hard and wear protective films. Tungsten nitride films are well-known for their outstanding properties such as excellent hardness, chemical inertness, high melting point and high conductivity [1]. These properties make tungsten nitride a suitable material for many applications such as diffusion barriers in microelectronic devices [2–8], and hard wear resistant protective films [9–11]. Over recent years a general approach aimed at improving the hardness, wear, and corrosion resistance of tungsten nitride films by process optimization, such as substrate temperature, partial pressure of nitrogen, substrate bias, etc. [9–13].

It is well known that coated tools not only have to possess extreme mechanical properties, but also have to resist potentially aggressive operating environments such as lubricant, cooling solutions and high temperatures in dry machining. For instance in dry machining, the temperature at the cutting edge can reach 1000 °C [14,15]. Consequently, the applied protective film must be able to withstand such extreme conditions. Polcar et al. showed that complete oxidation of the tungsten nitride occurs at 600 °C and the hardness value of the films decreases gradually with annealing temperature [11]. It was found that, some of the atmospheric oxygen atoms replace nitrogen atoms on the surface of tungsten nitride film for annealing temperatures higher than 400 °C [16]. Since W–O bond is more stable than the W–N bond, thereby making thin tungsten oxide top layer. Some of the oxygen atoms move towards the bulk of the film through the grain boundaries and replace some nitrogen atoms at the lattice sites at higher annealing temperatures. Eventually, the loss of nitrogen during

*Tel.: +98 2122969777; fax: +98 2122947537.
E-mail address: khamseh-sa@icrc.ac.ir

0272-8842/$ - see front matter © 2013 Elsevier Ltd and Techna Group S.r.l. All rights reserved.
http://dx.doi.org/10.1016/j.ceramint.2013.06.025

the annealing process will lead to the transformation of the tungsten nitride to tungsten oxide. It has been shown that presence of an amorphous and dense oxide layer on the top surface of transition metal nitride films can reacts as a diffusion barrier against inwards diffusion of oxygen at high temperatures and improves oxidation resistance of the films at high temperatures [17,18].

Since oxidation of tungsten nitride film is interrelated with the inward diffusion of oxygen into the surface of the film, the insertion of chemically stable amorphous tungsten oxide top layer may decrease the inward diffusion of the oxygen at high temperatures, which therefore enhances the oxidation resistance of tungsten nitride film. In the present work, we studied microstructure, thermal stability and oxidation resistance of tungsten oxide/amorphous tungsten nitride multilayered thin film. We expect that the disruption of the film's nanostructure caused by thermal oxide growth will be reduced by amorphous tungsten oxide top layer.

2. Experimental

Films were prepared in a planar type magnetron sputtering apparatus, (Yarenikane saleh-DRS320) on mirror-polished 304 stainless steel wafers and microscopic glass slides 20 mm^2. All the substrates were cleaned ultrasonically with acetone and ethanol, before sputtering deposition.

Oxidation of the sample coupons was carried out using a temperature controlled standard box furnace operated in air, with no additional features to control humidity or air flow rate. Samples were placed horizontally on a ceramic holder with the coated face upwards at the center of the furnace. The furnace temperature was controlled electronically and was raised to the desired temperature at the rate of 10 °C/min. Annealing time was controlled to give total oxidation period of ten hours. After each increment of oxidation time, the furnace was cooled to ambient temperature slowly.

The hardness was measured by a Hysitron Inc. TriboScope® Nanomechanical Test Instrument with a Berkovich diamond indenter at room temperature. The load was selected to keep an impression depth not more than 10% of the film thickness, so that the influence of the substrate could be neglected.

The crystal structure of the films was assigned using X-ray diffractometery (Cu Kα radiation) (Phillips PW-1800).

A scanning electron microscopy (FE-SEM, Hitachi S4160) was used to provide a high resolution scan on the plane view of the films.

3. Results and discussion

Details of the deposition parameters, chemical compositions and thickness of the as-deposited films are summarized in Table 1. The oxygen content of tungsten nitride film originating from the residual atmosphere and the chamber leaks was lower than 2.7 at%.

3.1. Tungsten nitride film oxidation behavior

Fig. 1 shows the XRD investigations performed on tungsten nitride film annealed at different temperatures in ambient air for 10 h. As shown in Fig. 1 (a), the as-deposited tungsten nitride film contains face center cubic W_2N phase with (111) orientation. The fcc-W_2N diffractions are retained on increasing the annealing temperature to 400 °C. When the annealing temperature reaches 600 °C, the fcc-W_2N peaks are difficult to be detected in the XRD pattern, while most of the XRD reflections are attributed to WO_3 and $WO_{2.92}$ phases (see Fig. 1). Absence of nitride phases demonstrates the complete oxidation of the film.

Variation of N/W and O/W ratios (measured using EPMA) of tungsten nitride film on annealing temperature is shown in Fig. 2. It can be seen that N/W ratio of the film decreased on increasing temperature and no nitrogen detected at 600 °C. In contrast O/W ratio of tungsten nitride film increased continuously on annealing temperature. It means that the nitrogen content in the film degraded rapidly on increasing annealing temperature accompanied by a significant coalescence of the surface oxide as shown in Fig. 4b.

The simultaneously recorded TGA and DTA thermograms of the powdered tungsten nitride film are shown in Fig.3. It is clear from Fig. 3 (a) that the adsorbed water and gases in the sample and the crucible are removed below 520 °C [16]. The weight loss increases gradually with increasing temperature up to 520 °C. However, a sharp increase in weight started for the temperatures higher than 520 °C. This sharp increase in weight is attributed to the oxidation of tungsten nitride film. After that, the oxidation slows down and an overweight region from what is expected to complete oxidation of tungsten nitride into tungsten oxide is observed [16] as confirmed by XRD measurement of the film (Fig.1). The DTA curves (Fig. 3 (b)) reveal a typical exothermic reaction. There is a sharp exothermal peak between 580 °C and 650 °C with a maximum value at 600 °C. Considering the TGA result together with its corresponding DTA curve, the large mass gain with a sharp exothermal peak at 580–650 °C is mainly due to the oxidation of tungsten nitride film to tungsten oxide.

Table 1
Details of deposition parameters thickness and chemical composition of the films.

Sample name	Sputtering pressure (Pa)	N_2/Ar	O_2/Ar	Sputtering current (A)	Sputtering voltage (V)	film thickness	N (at%)	W (at%)	O (at%)
W_2N	1.5×10^{-2}	1	–	8–10	608	1 μm	48.7	48.6	2.7
WO	4.5×10^{-2}	–	0.25	10–12	620	500 nm	–	49.1	50.9
W_2N/WO	–	–	–	–	–	1500 nm	30.2	49.1	10.7