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

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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.
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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

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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

Fig. 4 shows the SEM micrographs of the surface of the as-deposited and annealed films. For as-deposited tungsten nitride film a pebble-like microstructure can be seen (Fig. 4(a)) while the film annealed at 600 °C shows formation of a coarse structure with large grains (Fig. 4(b)).

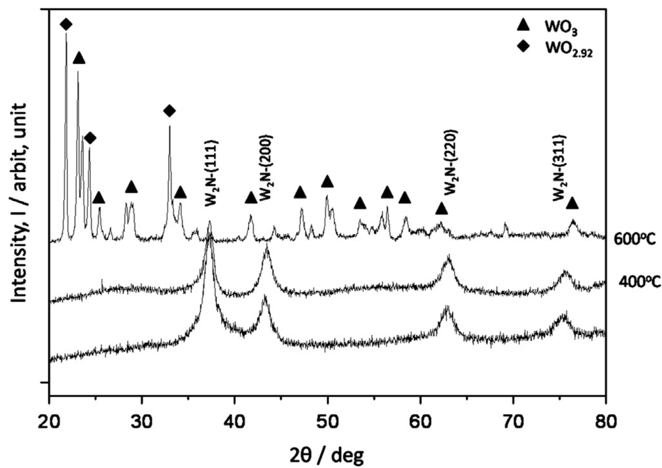

Fig. 1. X-ray diffraction patterns of tungsten nitride films, as-deposited and after annealing at varying Tox measured by thin film mode.

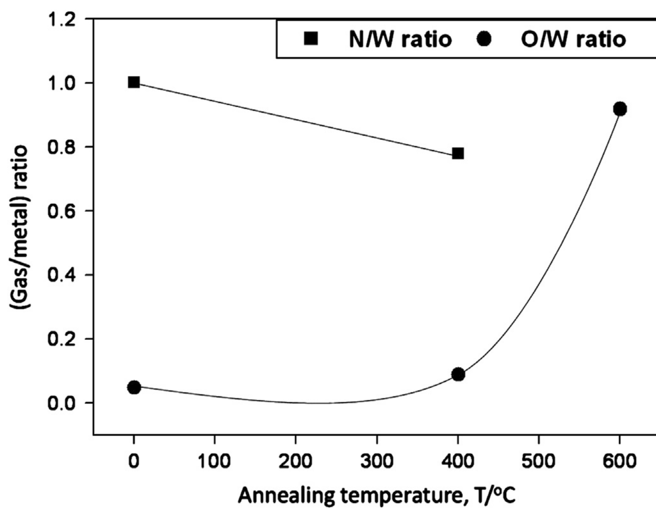

Fig. 2. Variation of N/W and O/W ratios of tungsten nitride film on annealing temperature.

The combined XRD, EPMA, TGA, DTA and SEM analyses revealed that the tungsten nitride film was oxidized at temperature around 520 °C, which corresponds to the onset of the weight increase in the TG curve, and the main oxidation temperature is at 600 °C, which is related to the oxidation in Fig. 3. It has been shown that the tungsten nitrides decompose around 600–700 °C [19,20] and N atoms release from the film. Inward oxygen diffusion proceeds through channels remaining after the N release. Free tungsten atoms react very easily with ambient oxygen to form volatile WO_x, which escapes from the film.

3.2. Multilayered tungsten nitride/amorphous tungsten oxide film oxidation behavior

Fig. 5 shows the XRD investigations performed on multilayered tungsten nitride/amorphous tungsten oxide films annealed at different temperatures in the ambient air for ten hours. Variation of N/W and O/W ratios of multilayered tungsten nitride/amorphous tungsten oxide film on annealing temperature is shown in Fig. 6. Fig. 7 presents the TGA and DTA curves for the samples heated from room temperature to 900 °C. Fig. 8 shows the SEM micrographs of the films after annealed in ambient air at 800 °C for 10 h.

The XRD spectra of multilayered films annealed at 400, 600, 800 and 900 °C in Fig. 5 show that fcc–W_2N phases were well maintained up to 800 °C. The peaks at 400 °C grew in intensity and became sharper than that in the as-deposited state, indicating increased grain size at the evaluated temperature and film recovery process. The recovery process corresponds to the annealing of the deposition-induced lattice defects and residual stress due to the increased diffusivity at elevated temperatures and the growth of the grains [21,22]. However, peak intensity of fcc–W_2N phases were decreased at 600 °C which can be attributed to the formation of amorphous or small fractions of tungsten oxide phase in the film which cannot be detected by XRD. A phase transformation to a mixed structure of WO_3 and $WO_{2.92}$ phases was observed on annealing at 800 °C [16]. Absence of nitride phases at 800 and 900 °C demonstrates the complete oxidation of the film. It was

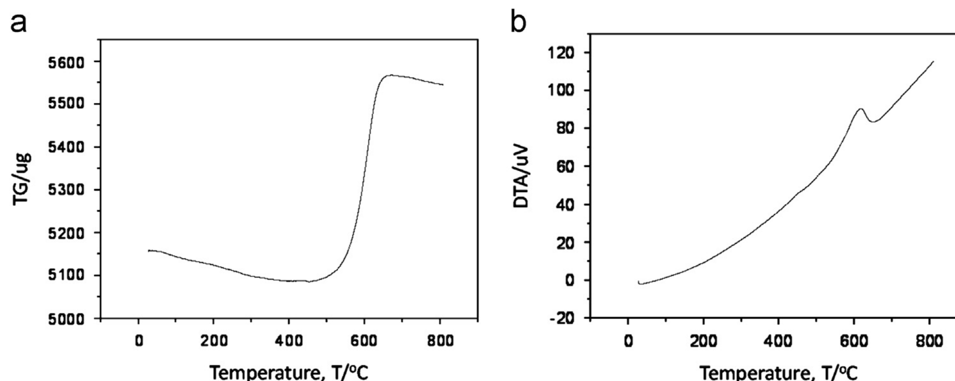

Fig. 3. TGA and DTA thermograms of tungsten nitride film.

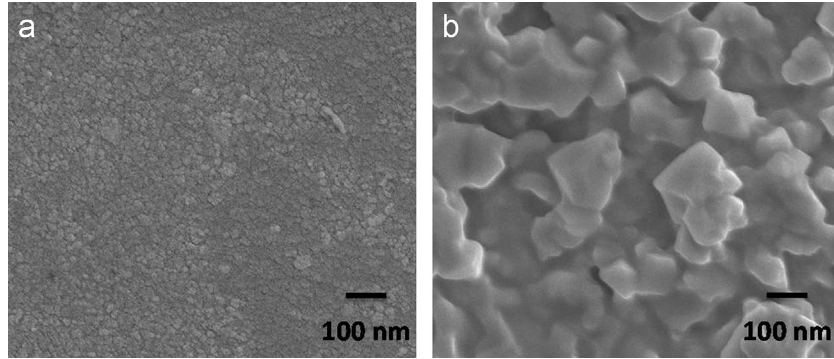

Fig. 4. Plane-view FE-SEM images of tungsten nitride film (a) as-deposited and (b) annealed at 600 °C.

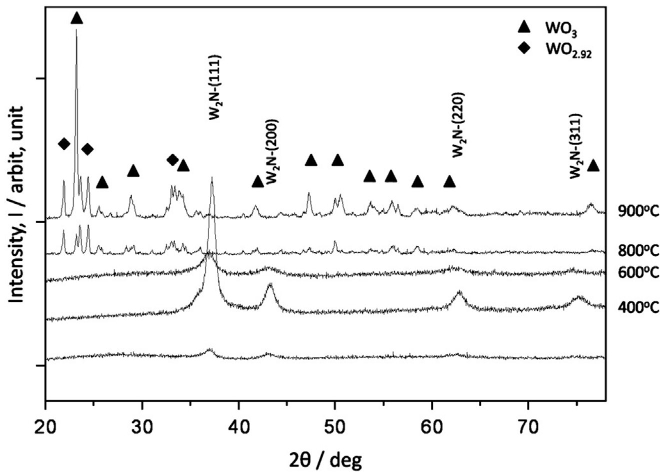

Fig. 5. X-ray diffraction patterns of tungsten nitride/amorphous tungsten oxide film, as-deposited and after annealing at varying Tox measured by thin film mode.

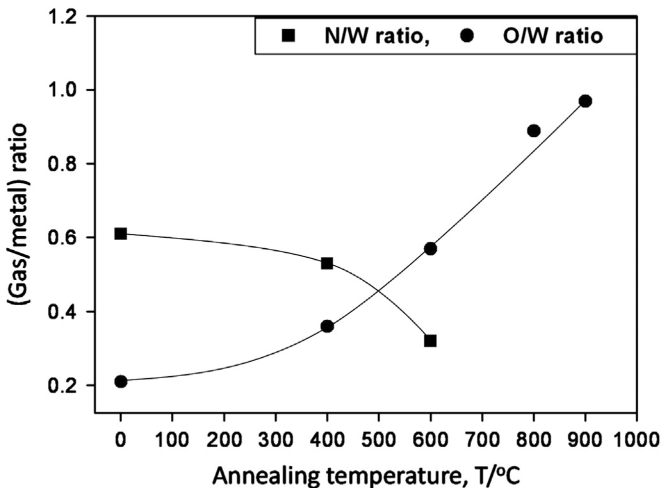

Fig. 6. Variation of N/W and O/W ratios of tungsten nitride/amorphous tungsten oxide film on annealing temperature.

also found that the film received certain degree of oxidation attack at 900 °C, which is also confirmed by an increase in the O/W ratio in the film from the EPMA analysis (Fig. 6) and the surface morphology change of the film in the SEM micrograph (Fig. 8b).

The simultaneously recorded TGA and DTA thermograms of the powdered film are shown in Fig. 7. From this figure it is clearly seen that no mass gain corresponding to oxidation is observed up to 650 °C where a sharp increase in weight started. This sharp increase in weight is attributed to the oxidation of tungsten nitride film with the peak temperature at 780 °C. Moreover, from Fig. 7 it can be clearly seen that the coated samples demonstrate a slight mass loss from 780 °C, which was resulted from the volatilization of tungsten oxide phases from the samples. This main decomposition and oxidation process is also confirmed from EPMA analysis of film shown in Fig. 6. EPMA measurements yield significantly decreased nitrogen contents compared with the films annealed at lower 800 °C. The DTA curves (Fig. 7 (b)) reveal a typical exothermic reaction. There is a small exothermal peak between 750 °C and 800 °C with a maximum value at 780 °C. Simultaneously, the TGA curve (Fig. 7) reveals a decrease in the mass gain for higher than 780 °C, which is possibly because of the reduction of nitrogen in the film.

Fig. 8 shows the SEM surface morphologies of multilayered tungsten nitride/amorphous tungsten oxide film as-deposited and annealed at 800 °C. A dense and fine grained structure observed in as-deposited sample (Fig. 8 (a)). This can be attributed to the existence of amorphous tungsten oxide top layer. The SEM micrograph of the film annealed at 800 °C shows formation of a coarse structure with large grains (Fig. 8 (b)).

Compared with the tungsten nitride oxidation study, it was found that the incorporation of amorphous tungsten nitride top layer has a significant influence on the film oxidation behavior. The onset temperature of the tungsten nitride film oxidation can be increased from 600 °C to 800 °C (based on the XRD and TGA observations). The temperature of the significant reduction of nitrogen will be increased from 400 °C to 600 °C, while the temperature for the main oxidation reaction was increased from 600 °C to 900 °C. It is well known that the species transport during oxidation is much faster in grain boundaries of crystalline materials than in amorphous materials without such diffusion paths [20]. In summary, we can conclude that the amorphous glassy-like microstructure of

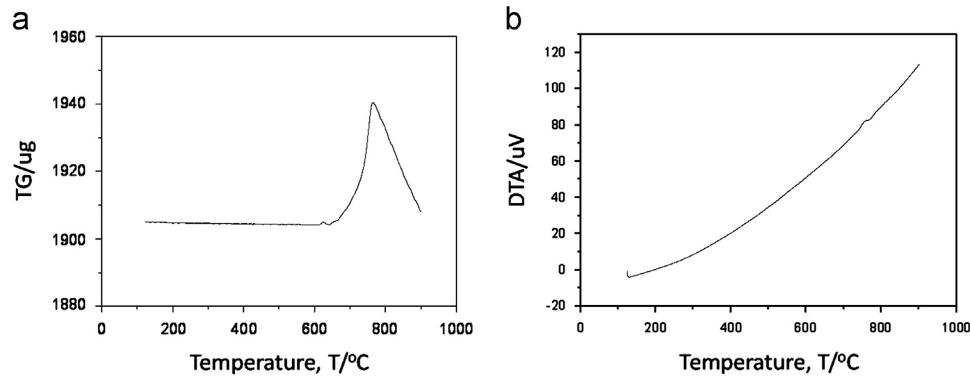

Fig. 7. TGA and DTA thermograms of tungsten nitride/amorphous tungsten oxide film.

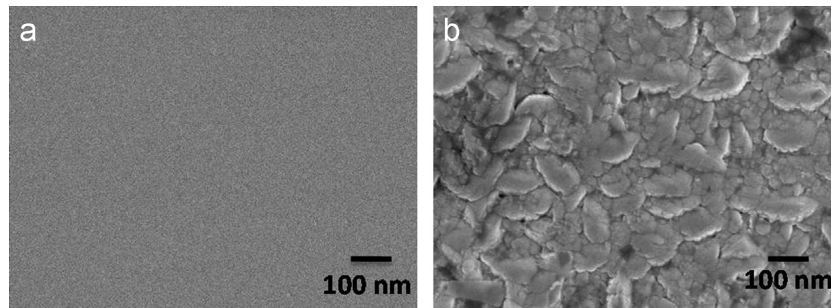

Fig. 8. Plane-view FE-SEM images of tungsten nitride/amorphous tungsten oxide film on varying annealing temperature (a) as-deposited and (b) annealed at 800 °C.

tungsten oxide top layer without grain boundaries preventing inward oxygen diffusion is a decisive factor enabling to achieve the better oxidation resistance of multilayered film.

3.3. Mechanical properties of annealed films

Fig. 9 illustrates the variation of plastic hardness of the films with annealing temperature. The plastic hardness of tungsten nitride film decreased gradually with increasing the annealing temperature. In contrast, the plastic hardness of multilayered tungsten nitride/amorphous tungsten oxide film decreased slowly on annealing temperature up to 600 °C. Since no oxidation was observed, the hardness decrease in temperature can be attributed to a decrease of the compressive stress, which is closely related to the stress relaxation and decrease of defect density induced by the heating. However, plastic hardness of the film decreased sharply in 800 and 900 °C. Since, the films were fully oxidized at 900 °C; the hardness reaches 6 GPa, a value typical for tungsten trioxide [11,19]. The evolution of the hardness with the increasing annealing temperature in these films follows the general observations in typical binary and ternary nitrides, that is, the hardness of the films decreases due to a decrease in the defect density and compressive stress and an increase in the grain size during the thermal annealing process [18]. According to the relatively good oxidation resistance (600 °C) and high hardness of multilayered tungsten nitride/amorphous tungsten oxide film up to 600 °C, this film is a good candidate for high temperature applications.

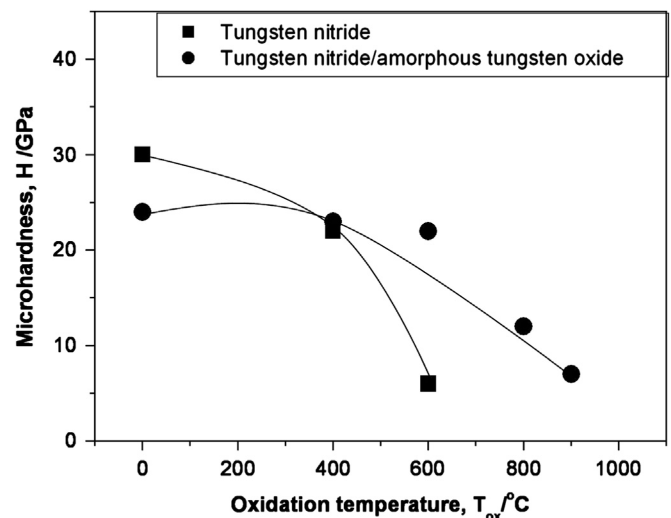

Fig. 9. Influence of annealing temperature on the plastic hardness of the films.

4. Conclusions

Tungsten nitride and tungsten nitride/amorphous tungsten oxide multilayered films were produced by a planar type reactive sputtering system. Oxidation resistance and thermal stability of the films were investigated using XRD; TGA, DTA and SEM. Amorphous tungsten oxide top layer improved thermal stability of tungsten nitride films and increased the oxidation temperature of the film from 600 °C to 800 °C. The amorphous glassy-like microstructure of tungsten oxide top

layer without grain boundaries acts as a diffusion barrier and prevents inward oxygen diffusion, enabling to achieve the better oxidation resistance of multilayered film.

The plastic hardness of tungsten nitride film decreased gradually with increasing the annealing temperature. In contrast, the plastic hardness of multilayered tungsten nitride/amorphous tungsten oxide film decreased slowly on annealing temperature up to 600 °C. The relatively good oxidation resistance (600 °C) and high hardness of the film with tungsten oxide top layer up to 600 °C indicates that this film is a good candidate for high temperature applications. Finally, it can be concluded that amorphous tungsten oxide top layer can reduce disruption of the film's nanostructure and improve thermal stability and oxidation resistance of tungsten nitride films.

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