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The microstructure and tribological properties at elevated temperatures of tungsten silicon nitride films

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ABSTRACT

W-Si-N films with various Si contents were deposited using a reactive magnetron system, and the film with the highest hardness, the lowest average friction coefficient (μ) and wear rate at room temperature (RT) was chosen to study the tribological properties at elevated temperature. Tribological properties of the film were performed using un-lubricated sliding tests against an alumina counterpart. Elevating the testing temperature from RT to 100 °C induced an intense skin plastic deformation, as a result, the μ increased rapidly and the wear rate decreased significantly. As the testing temperature was in the range of 100–200 °C, the surface deformation strengthening was induced furtherly, μ was further increased and the wear rate could not be calculated due the adhesive wear debris on the wear track. From 200 to 600 °C, the main wear mechanism changed to oxidation wear and the a lot of WO_3 tribo-film led to the decrease of μ. Wear rate increased gradually due to the accelerated oxidation of the film and the disappearance of surface deformation strengthening.

1. Introduction

Since ancient times, surface modification and tribology research has played vital roles in the processing and manufacturing industry. The main traditional method of reducing friction coefficient and improving the service life of machinery components is through liquid lubrication. With the advancement of manufacturing technology, higher requirements especially in the pollution prevention and reduction in weight of structures has necessitated the exploration of an efficient replacement for liquid lubricants. As reported [1], the solution to this problem is by designing hard solid lubricated films. Transition metal nitride (TMN) films with excellent mechanical and tribological properties are widely applied in the tribological industry [2–5].

Cutting tool engineers and material scientist have turned their attentions to the recently reported tungsten nitride film which exhibits low coefficient of friction and forms a Magnéli phase during wear test [3]. There is a significant improvement in the mechanical properties of TMN with the incorporation of Si as a result of the formation of a nanocomposite structure [2]. An ultra-high hardness was achieved when Si was incorporated into a Ti-N to form a Ti-Si-N nanocomposite film [6]. There are lots of reports on the W-Si-N film using physical vapor deposition. The microstructure [7,8], mechanical [7], thermal stability [9], electrical properties [10] of the film have been widely studied. Our group deposited a series of W-Si-N films with different silicon contents and the effects of silicon content on the crystal structure, mechanical properties and the friction coefficient and wear rate at room temperature were discussed [3]. The friction and wear rate are affected by both the intrinsic properties and the testing environment. A classic example is the molybdenum disulfide films, which were reported to exhibit excellent tribological properties in vacuum, but it is easy to be worn out in a moist testing environment [11,12]. Testing temperature is an important factor which influences the tribological behavior of TMN-based films [3,13,14]. For example, W. Tillmann and Dildrop [15] synthesized a series of Ti-Al-Si-N films using a magnetron sputtering system and investigated the influence of silicon contents on the tribological properties of the films at elevated temperatures. They found that the combination of lower silicon (<7.9 at.%) into Ti-Al-N based films could reduce the friction coefficient at 500 °C, while the films with higher silicon content (>7.9 at.%) exhibited an improved wear resistance at 800 °C [15]. K. Yalamanchili et al. [16] reported that the Zr-Si-N films with high Si content best combine hardness, toughness, and oxidation resistance to yield superior macroscale wear resistance both at room temperature and high temperature. However, there are not too many reports on the tribological properties of W-Si-N films, especially on the tribological properties at elevated temperatures. In our paper, W-Si-N films with different Si contents were deposited by reactive magnetron sputtering and the film with excellent mechanical and tribological properties at room temperature was chosen to study the tribological behavior under a wide range testing temperature (from RT to 600 °C) using un-lubricated sliding tests against an alumina counterpart. The aim of the tribo-test design was to solve the following: (1) mechanism of the friction and wear behaviors of W-Si-N film with varying testing temperatures; (2) reason causing generation of tribo-

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film Magnéli phase at different testing temperatures; (3) besides the tribo-films, factors such as surface deformation effect on the tribological performance will also be investigated.

2. Experimental details

Deposition of various amounts of W, Si and N onto both mirror polished stainless steel (AISI 304 SS, 15 mm × 15 mm × 2.5 mm) and silicon (100) wafer substrates was done using a multi-target magnetron sputtering system in the mixture of argon and nitrogen. The substrates were successively cleaned with acetone and alcohol in an ultrasonic environment for a period of 10 min each. And then the substrates were blown dry with a hot air and were mounted on the substrate holder. When the base pressure reached to 6.0×10^{-4} Pa, surface contaminant of tungsten (99.9%, Ø 75 mm) and silicon (99.9%, Ø 75 mm) targets was removed through argon bombardment with the target powers of 40 W for 5 min. And then the tungsten target power was increased to 150 W with a substrate temperature 200 °C for the deposition of a 100 nm tungsten adhesion layer on the substrates. Various W-Si-N films with a thickness of ~2 μm were deposited by fixing the tungsten target power of 280 W and adjusting the silicon target power from 0 to 210 W while constantly maintaining the working pressure at 0.3 Pa and the partial nitrogen pressure of 0.15 Pa. The deposition time is ~2 h. The substrates were not biased. The W-Si-N deposited on the AISI 304 SS substrates were used to test for the wear rate of the film, while film's compositional, structural, thermal stability and mechanical properties were evaluated using the film on the silicon (100) wafer substrates.

The elemental compositions of the film were characterized by X-ray photoelectron spectroscopy (XPS) with Al Kα irradiation at a pass energy of 160 eV. Before the acquisition of the spectra, the surface contaminants on the films were removed using Ar^+ ion beam sputtering at a primary energy of 3 keV for 3 min. The microstructure of the films was evaluated using a Siemens X-ray diffractometer using Cu Kα radiation, operated at 40 kV, 35 mA. High resolution transmission electron microscopy (HRTEM) was performed using a JEOL JEM-2010F microscope operated at an accelerating voltage of 200 kV. The oxidation resistance of the films was measured by a TG system (SDT-2960, TA Instrument) equipped with thermogravimetric (TG) unit. The samples were heated from 250 °C to 1000 °C at a heating rate of 15 °C/min and 60 ml/min of air to maintain an oxidative atmosphere for the thermal decomposition. A Berkovich indenter, which tip geometry was calibrated using fused silica, was employed to measure the hardness of the films using CPX + NHT + MST nano-indentation tester (CSM instruments, Switzerland). A minimum of nine (9) indentations were made for each sample and the mean value taken. The maximum load of 5 mN was used. A 30 min wear test was carried out along a circular track of 8 mm diameter against a 9 mm diameter Al_2O_3 counterpart at 50 rpm under a constant normal load of 3 N in the atmosphere (the relative humidity of about 25–30%) at room temperature (about 25 °C) and elevated temperatures using a UTM-2 CETR tribometer. Raman spectroscopy using the 514.5 nm Ar^+ laser with a backscattering optical configuration was used to study the tribo-film on the surface of wear track. The spot size of the Raman spectroscopy is ~1 μm. After the wear tests, the wear tracks were examined using a profilometer (Bruker DEKTAK-XT) to measure the wear loss of the films (V). The wear rate of the films (W) was calculated by Archard's wear equation:

$$W = \frac{V}{S \times L} \tag{1}$$

where

S is the total sliding distance;
L is the applied load.

3. Results and discussion

3.1. Microstructure, hardness and tribological properties at room temperature

The elemental compositions of W-Si-N films with different Si target powers are shown in Table 1. As shown in Table 1, Si content and Si/(W + Si) atomic ratio rise with the rising of Si target power. The O content in the films is stable and its value is in the range of 3.4–3.8 at.%.

Fig. 1 illustrates the XRD patterns of W-Si-N films with various Si content. As shown in Fig. 1, the binary tungsten nitride film exhibits a single fcc structure. Three diffraction peaks appear at ~36°, ~43° and ~62° respectively, and can be referred to fcc-W_2N (111), (200) and (311) [3]. For the W-Si-N film at 2.6 at.% Si, the XRD pattern also shows three peaks corresponding to fcc-W_2N, but does not show peaks corresponding to some other crystal phases such as the tungsten silicide and silicon nitride. Rising silicon content to 23.5 at.%, The XRD pattern of the film shows two broadening peaks corresponding to fcc-W_2N (111) and (200) respectively. Further rising silicon content to 43.4 at.% induces the disappearance of XRD peaks. Besides this, the addition of silicon into tungsten nitride matrix also leads to the peak shift phenomenon to higher diffraction angle, which is attributed to the drop of the lattice constant induced by the solution of silicon into the tungsten nitride lattice [3].

Fig. 2 shows the high resolution transmission electron microscopy (HRTEM) images and their corresponding selected area electron diffraction (SAED) patterns of W-Si-N films with various Si content. As shown in Fig. 1(a), the HRTEM image of binary tungsten nitride film presents the clear lattice fringe with a lattice spacing of 0.2401 nm, which is corresponding to the face-center cubic (fcc) W_2N [3]. Dislocations are also detected in the HRTEM image. According to the SAED pattern of the tungsten nitride film, the diffraction rings can be referred to as the lattice planes of fcc-W_2N (111), (200), (220) and (311). As shown in Fig. 2(b), the HRTEM image of the W-Si-N film at 2.6 at.% Si exhibits a nanocomposite structure, and the film is consisted of crystalline and amorphous phase. Doping silicon into fcc-W_2N matrix induces the grain refinement. There are three different lattice fringes with a lattice spacing of about 0.2076, 0.1420 and 0.1225 nm. The standard lattice spacing of fcc-W_2N (200), (220) and (311) is 0.2086, 0.1453 and 0.1244 nm respectively. Therefore, the three different lattice fringes correspond to fcc-W_2N (200), (220) and (311), respectively. For all the above lattice fringes, the value of lattice spacing is smaller than that of standard lattice spacing, which suggests that the film lattice is influenced by the solution of Si. As shown in the SEAD pattern as an

Table 1
Elemental compositions, hardness, average friction coefficient (μ) and wear rate against a alumina counterpart under a constant normal load of 3 N in the atmosphere (the relative humidity of about 25–30%) at room temperature (about 25 °C) of W-Si-N films with different Si target powers.

Si target power (W)	Elemental compositions (at.%)					Hardness (GPa)	Average friction coefficient (μ)	Wear rate (mm^3/N·mm)
	W	Si	N	O	Si/(W + Si)			
0	66.8 ± 3.4	0.0	29.4 ± 1.5	3.8 ± 0.2	0	26 ± 2	0.44 ± 0.02	$(7.3 \pm 0.4) \times 10^{-8}$
50	64.0 ± 3.4	2.6 ± 0.1	29.9 ± 1.5	3.5 ± 0.2	2.8 ± 0.1	28 ± 2	0.43 ± 0.02	$(4.6 \pm 0.3) \times 10^{-8}$
120	41.2 ± 2.1	23.5 ± 1.2	31.9 ± 1.6	3.4 ± 0.2	32.1 ± 1.6	40 ± 2	0.30 ± 0.01	$(8.7 \pm 0.5) \times 10^{-9}$
210	17.5 ± 0.9	43.4 ± 2.2	35.6 ± 1.8	3.5 ± 0.2	71.3 ± 3.6	22 ± 2	0.60 ± 0.03	Worn out