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Structural, mechanical and tribological properties of Mo–S–N solid lubricant films

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ABSTRACT

In this paper, the composite Mo-S-N solid lubricant films are synthesized by magnetron sputtering of molybdenum disulphide (MoS_2) target in nitrogen and argon atmosphere. With the increase of the nitrogen content, the nitrogen concentration in the deposited films increases from 0 to 35 at.%, and the corresponding S/Mo atomic ratio reduces to below 0.70. X-ray diffraction (XRD) and Raman spectroscopy analyses reveal that introducing nitrogen into films leads to the formation of amorphous structure and chemical bonds between nitrogen and molybdenum were detected by X-ray photoelectron spectroscopy. The hardness and elastic modulus of Mo–S–N films increase more than one order of magnitude higher than that of pure MoS_2 films with increasing the N_2 flow rate (i.e., with increasing N content), reaching to the maximum of 9.59 and 113.12 GPa, respectively. The tribological properties of the prepared films tested by a ball-on-disc tribometer under a low-pressure vacuum exhibit that the incorporation of a suitable content of N dopant could significantly reduce the wear rate, however, both friction coefficient and wear rate increase dramatically in excess a certain amount of N dopant.

1. Introduction

Transition metal dichalcogenides (TMDS) compounds, such as MoS_2 and WS_2 have a hexagonal layer structure like graphite and make them very successful as solid lubricants in inert gas environments and vacuum [1,2]. Sputter-deposited MoS_2 films as an excellent solid lubricant is one of the major ways in interface engineering surface modification [3]. However, sputtered pure MoS_2 films normally exhibit porous structure, low load-bearing capacities and high wear resistance even in vacuum [4]. Moreover the porosity structure of the sputtered films will also speed up the oxidation of MoS_2 films as a result of tribochemical reactions. These factors will result in the deterioration of their tribological properties [5,6]. In order to improve the mechanical and tribological properties of MoS_2 films, the alloying of TMDs with the other elements is a common solution. The additional element (such as Ti [7–12], C [13–16], Cr [17–19]) were found to disrupt the microstructure and increase the hardness of the films. Later studies have demonstrated that the addition of metallic element can have a detrimental effect on tribofilms formed during sliding for the composite thin films reported by Nyberg et al. [20] for a W–S–C–Ti low-friction coatings.

Recently, Polcar et al. [21] reported that magnetron sputtered amorphous W-S-N films exhibited low coefficient of friction, high load-bearing capacities and good wear resistance. The atomic-level structure and bonding arrangements in amorphous W–S–N have been described in a recent study by Isaeva et al. [22]. Furthermore, the doped-N element is easily removed in the form of the gaseous oxides of N, thus avoiding the detrimental effects seen for metal addition. Unlike the W-S-N films, the investigation of the structural and tribological performances of Mo-S-N films was rarely reported previously. Huiwen Liu et al. [23] have studied the effect of N^+ implantation on the microstructural and tribological properties of sputtered MoS_2 films. The N^+-modified MoS_2 films exhibit fairly good lubrication properties and are denser than pure MoS_2. So far, systematic studies on the variation of the structure and tribological performance of Mo-S-N composite films have not been reported. In this work, a new set of nitrogen-doped Mo–S–N films deposited by magnetron sputtering by varying the flow rate of N_2. The core objective of this study is thus to identify the influence of nitrogen content on the structures and properties of magnetron sputtered Mo-S-N films.

2. Experimental details

2.1. Film deposition

Mo-S-N films were deposited on a silicon substrate by radio frequency (RF) reactive magnetron sputtering of MoS_2 target (75 mm in diameter, 99.9% in purity) in a N_2/Ar mixture atmosphere. The substrates were mounted parallel to the surface of target. Before deposition, the silicon substrates were cleaned twice ultrasonically in alcohol for 20 min to remove the dust and impurities on the surface and then mounted on the sample holder. The vacuum chamber was pumped

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down to a background vacuum of less than 1×10^{-3} Pa. Prior to deposition all substrates were sputter-cleaned in Argon plasma for 5 min at bias voltage of 550 V. During deposition the substrate temperature was maintained at 150 °C. The RF power applied on target was kept as a constant at 275 W. Argon and nitrogen were introduced into vacuum chamber simultaneously with fixed Argon flow rate at 40 sccm, and the flow rate of N_2 gas was varied from 0 to 50 sccm (0, 2, 3.5, 5, 20, 30 and 50 sccm). The work pressure was kept at 0.75 Pa during deposition process.

2.2. Film characterization

The morphologies and film cross-sections of the prepared films were investigated by field-emission scanning electron microscopy (FESEM) (JSM-6701F, JEOL, Japan). The cross-section images of the films were obtained by breaking the silicon substrate after film deposition. Crystallographic phases and composition of samples were examined by grazing incident X-ray diffraction (XRD) at 2° incident angle in parallel beam geometry. XRD measurements were performed on a Rigaku RINT2400 X-ray diffract meter using Cu Kα radiation $\lambda = 1.54056$ Å. Diffractograms were acquired from 10° to 70°. Raman spectra were measured by a LabRam HR800 spectrometer with a 532 nm-wavelength excitation.

Films composition was determined by energy-dispersive X-ray spectroscopy (EDS) and X-ray photoelectron spectroscopy. XPS was carried out on a PHI5072 system using a monochromatic Al Kα source, the photoelectron spectra were measured with a hemispherical analyzer operating at a pass energy of 29.4 eV. The XPS spectra were referenced with respect to C1 s line at 284.8 eV. Prior to the measurement an Ar^+ ion beam at the acceleration voltage of 2 kV was used to clean the oxidation surface due to air exposure.

The mechanical properties of Mo-S-N films were determined by the depth-sensing indentation technique using a Nano Indenter DCM nanomechanical system (MTS, USA) equipped with a Berkovich diamond tip. The maximum indentation depth was controlled to be around 100 nm so as to reduce the substrate effect [24]. Five repeated indentations were made for each sample. The tribological properties of these Mo-S-N films were tested using a ball-on-disc tribometer with 3 mm diameter 100Cr6 balls as count partner. The friction tests were performed at room temperature under a low-pressure vacuum of 0.08 Pa condition at a normal load of 3 N, a sliding velocity of about 1000 r/min, to a maximum sliding time of 60 min. After the friction test, the wear track on film was evaluated using white light interference profilometry (AD Corporation). Optical micrographs of the wear scars on the balls were acquired using an BX51 microscope (Olympus). The wear rate was achieved using the relationship of $K = V / (LS)$, where V is the wear volume loss in mm^3, L corresponds to the normal load applied in N and S represents the sliding distance in meters.

3. Results and discussion

3.1. Microstructure and composition characterization

The surface morphologies of Mo-S-N films prepared at the different N_2 flow rates are shown in Fig. 1. It can be seen that the pure MoS_2 film exhibit an acicular and porous microstructure (confirmed by cross-sectional FESEM studies). Obviously, introducing N into deposition process strongly influences the microstructure of deposited Mo-S-N films. For example, for Mo-S-N films prepared at a N_2 flow rate of 2 sccm (Fig. 1(b1)), the film displays a fiber-like structure characterized by reduced porosity comparing to pure MoS_2. With the increase in N_2 flow rate to 5 sccm (Fig. 1(c1)) the film exhibits a cauliflower-like morphology. At very high N_2 flow rates (Fig. 1(d1)), the film microstructure becomes a smooth, featureless and dense morphology which is the characteristic of an amorphous structure. From the FESEM micrographs of the fractured cross-sections of Mo-S-N films, the composite films deposited at low (2 sccm) nitrogen flow rate (Fig. 1(b2), (c2)) also shows the loose columnar microstructure, where the gaps between the columns are still visible, even though a certain amount of N contents had been incorporated into the MoS_2 films. As the increase of N_2 flow rate, the growth of columnar microstructure is completely suppressed, and a fully compact and featureless microstructure is formed, as evidently demonstrated in Fig. 1(d2). Overall, the incorporation of nitrogen into MoS_2 can suppress the growth of columnar structure and results in the formation of a more compact and featureless microstructure. This result agrees with the conclusion that achieved in W-S-N films [22,25,26].

The dependence of the deposition rate with the flow rate of N_2 is plotted in Fig. 2. It is clear from the Fig. 2 that the increase of N_2 flow rate from 0 to 5 sccm leads to the reduction of the deposition rate by a factor of nearly 3 from 27.92 to 11.10 nm/min. However, with the further increase of N_2 flow rates, the deposition rate is almost unchanged.

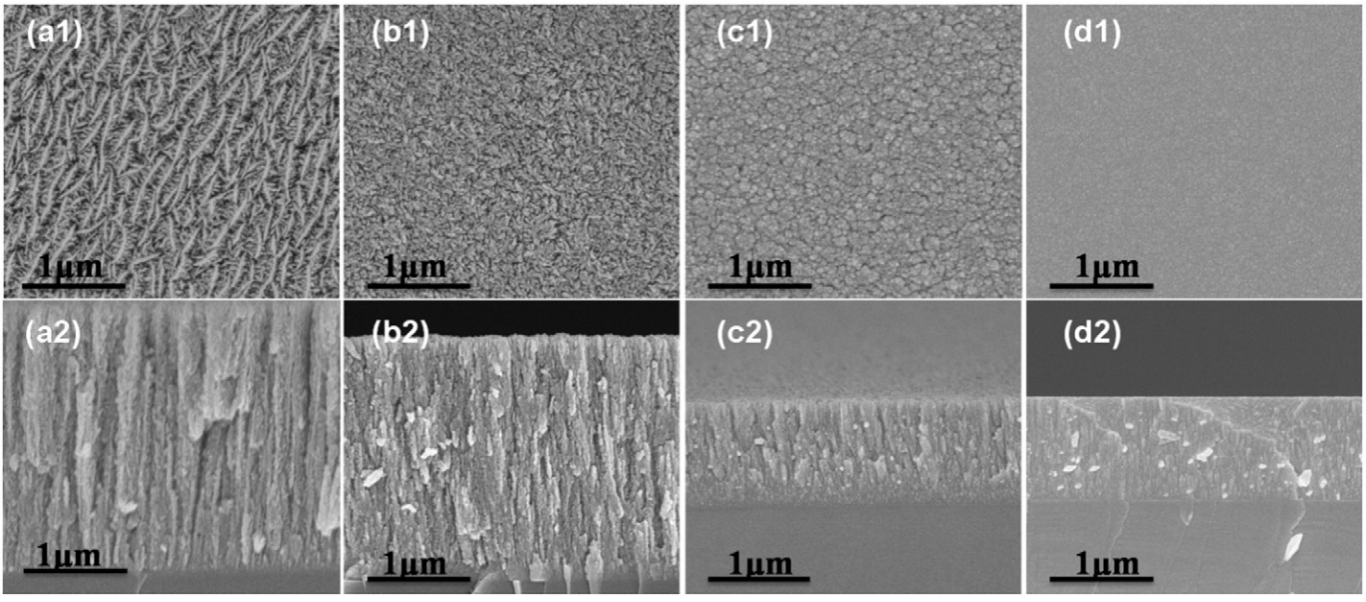

Fig. 1. Surface (*a*1, *b*1, *c*1 *and d*1) and cross-sectional (*a*2, *b*2, *c*2 *and d*2) FESEM images of the Mo-S-N films deposited in various N_2 flow rates: (a) 0 sccm, (b) 2 sccm, (c) 5 sccm and (d) 30 sccm.