A long-lifetime MoS$_2$/a-C:H nanoscale multilayer film with extremely low internal stress

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ABSTRACT

A series of MoS$_2$/a-C:H multilayer films with different bilayer periods were deposited by medium frequency unbalanced magnetron sputtering. The morphology, microstructure, mechanical and tribological properties of the films were investigated. It was found that all the films have relatively low hardness and internal stress. Furthermore, the nanoscale multilayer film with a bilayer period of 97.8 nm shows highly dense and well defined interfaces. Tribological tests indicated that the MoS$_2$/a-C:H nanoscale multilayer film has low friction coefficient and extremely long sliding distance in vacuum, under high sliding speed and the initial Hertzian contact pressure of the sliding surface closed to its hardness. In addition, the film exhibits excellent tribological properties in both N$_2$ and air, which is associated with the oxidation of MoS$_2$ and the graphitization of a-C:H. The result indicates that the nanoscale multilayer combined soft and hard phase is continuously a design methodology for developing the vacuum solid lubricating materials.

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1. Introduction

Using the moving mechanical assemblies in vacuum is a challenging issue for many applications. In such environment, direct contact between the metallic surfaces would result in high friction and severe wear through seizure and even 'cold welding' [1]. Therefore, the use of lubricant is important. However, the use of liquid lubricants is problematic because of the losses by evaporation or creep, and consequent possibility of contamination [2,3]. Thus, the solid lubricant appears as an interesting alternative for the lubrication in vacuum environment, which includes polymers, soft metals, the transition metal dichalcogenides (TMD-sulfides, selenides or tellurides of tungsten, molybdenum and niobium) and the diamond-like carbon (DLC) films [4]. Among them, TMDs and DLC films are investigated mostly.

TMDs have the advantage of presenting extremely low friction coefficient in vacuum and dry environments. The main drawbacks of them are their low load bearing capacity, low adhesion to the substrate, low hardness and poor performance in H$_2$O containing atmospheres [5,6]. As the most popular member of the TMDs family, sputter-deposited MoS$_2$ which has been explained on an atomic scale in terms of its lamellar crystal structure [7] is widely used for vacuum and space lubricant [8]. Nevertheless, it is rather more restricted in terrestrial applications since performance of the film falls in the presence of oxygen and water vapor. Either by co-deposition a dopant [9] or fabricating a multilayer, such as MoS$_X$/metal [7,10], MoS$_2$/WS$_2$ [11], MoS$_2$/a-C [12], can reduce the humidity and oxidation sensitivity of the sputtered MoS$_2$ film. However, the film still suffers from poor adhesion and load bearing capacity during the friction process. The DLC film and its derivatives have been emerged during the last 20 years for conventional applications, which exhibit low friction and high wear resistance in many environments [13,14]. These DLC films are widely known as a-C and a-C:H films. The two films show inverse friction and wear behavior in some environments (dry N$_2$, dry air, humid air) [15]. However, when concerning the vacuum under heavily loaded, and/or high sliding speed, both of the films maintain extremely short wear lives which greatly limit their applications [16,17]. The a-C film shows high wear rate of 10^{-4} mm^3/m, and the a-C:H film cannot maintain long durations due to hydrogen depletion after about 10^4 cycles [17–19]. Adaptive tribological films by various dopants in a-C matrix can overcome the poor tribological properties of a-C film in vacuum [20]. Unfortunately, the improvements on the wear life of a-C:H film in vacuum are merely reported [21].

During the last two decades, multilayer films combined with hard and soft layer have been proved successful in various applications, especially for wear protection [22,23]. They usually maintain moderate residential stress, good adherence and proper hardness [24]. However, the mechanical and tribological properties of the multilayer films are related to the composition, bilayer period and the number of interfaces [25,26]. As the bilayer period decreases, the internal stress of the multilayer film will increase since there are more hard/soft layers in the fixed film at small bilayer period [27]. Meanwhile, the interfaces are postulated to act as barriers against dislocation motion, and as the

bilayer period and crystallite size approach nanometer dimension, dislocation generation becomes energetically unfavorable. Both factors make the multilayer film maintain good mechanical and tribological properties [28].

Bearing those perspectives in mind and viewing that few reports are currently available about the tribological study of multilayer MoS_2/a-C:H film, we fabricated MoS_2/a-C:H films by unbalanced magnetron sputtering in this study. This design of multilayer film can not only enhance the MoS_2 film adhesion due to the excessive ion bombardment induced by escaped electrons [12,29], but also increase the load bearing capability by the a-C:H film and thus reduce the abrasive wear and prolong sliding lifetime of the film in various environments. The microstructure, morphology and tribological properties of the films are investigated as well as the friction and wear mechanism of the multilayer films in various test environments.

2. Experimental details

2.1. Deposition of the MoS_2/a-C:H multilayer films

A series of MoS_2/a-C:H multilayer films with different bilayer periods were prepared by medium frequency unbalanced magnetron sputtering (SP-0806SI) using Ar (purity 99.9%) and CH_4 (purity 99.9%, for a-C:H sublayer deposition) as sputtering gases of two graphite targets (size 94×300 mm^2, purity 99.9%) and one molybdenum-disulfide target (purity 99.9%). A Si target (99.99%) was connected to pulsed DC power supply to deposit a Si interlayer. Details of the deposition system were reported before [30]. The multilayer film deposited on the stainless steel substrate (1Cr18Mn8Ni5N) was used for friction and wear tests, and that deposited on Si p(111) was used for characterizations. The substrates were cleaned ultrasonically in an acetone bath and dried in air followed by plasma etching with Ar^+ ions in a vacuum chamber to remove the native oxide on the substrates' surface. Then they were placed on the substrate holder which is 20 cm away from the sputtering targets. The substrate holder with pulse bias voltage of -200 V and duty cycle of 20% kept revolving (5 rev/min) during the deposition process, which would be beneficial to improve the uniformity of the multilayer films. Prior to the film deposition, silicon interlayer, about 200 nm thick, was deposited on substrates by magnetron sputtering (a target current of 8 A) to improve the adhesion between the substrate and film. Then multilayer film was deposited by sputtering graphite target current of 14 A and MoS_2 target current of 0.4 A alternately for each sublayer's deposition times of 90 min, 45 min, 30 min, 15 min, 5 min, respectively. The corresponding bilayer periods of the as-deposited films are 2053 nm (S1), 1124 nm (S2), 628 nm (S3), 334 nm (S4) and 97.8 nm (S5), while the corresponding total bilayers of each film are 1, 2, 3, 6 and 18, respectively. Furthermore, the total deposition time of every film is fixed at 180 min and the thicknesses of them was 1.8–2.0 μm. The work pressure during the deposition of a-C:H film was about 0.53 Pa with Ar/CH_4 flow ratio of 65/45 (sccm/sccm), while 0.30 Pa for the deposition of MoS_2 film with pure Ar flow ratio of 65 sccm. The chamber temperature during the deposition is about 90 °C.

2.2. Characterization of the MoS_2/a-C:H multilayer films

Fourier transformation infrared (FTIR) spectra of the typical MoS_2/a-C:H films were recorded on a FTS165 spectrometer to detect the bonded hydrogen. The bonding structure information of the multilayer films and the film after tests in various environments was obtained by Jobin-Yvon HR-800 Raman spectrometer. An argon-ion laser source power density of 0.3 mW/m^2, having wavelength of 532 nm was used for this study. The composition of the nanoscale multilayer film was analyzed on a Perkin-Elmer PHI-5702 multifunctional X-ray photo-electron spectrometer (XPS), and Al-Kα was used as the exciting source

with binding energy of Au (1s) as the reference. For depth profiling, ion sputtering was carried out with 3 keV Ar^+ ions. A digital instrument Nanoscope IIIa multimode atomic force microscope (AFM) in tapping mode was performed in tapping mode to observe the surface morphology of the nanoscale multilayer film. The average surface roughness of the film over an area of 3.0 μm $\times 3.0$ μm was calculated using the software attached to AFM. A JSM-6701F type FESEM was used to observe the cross-sectional morphologies of nanoscale multilayer film. A JEOL 2010 transmission electron microscope (TEM) was performed at an accelerating voltage of 300 kV to record high resolution TEM images (HRTEM) of cross-section of the nanoscale multilayer film. The thin foils from film cross-section were prepared by mechanical polishing and then Ar ion-milling (Gatan 691) at a small angle with respect to the milled surface. The wear debris on the counter ball in vacuum was dissolved to ethyl alcohol for the HRTEM observation.

The hardness value of the multilayer films was determined using a NanoTest 600 nanomechanical system (MicroMaterials Ltd, UK), where the maximum indentation depth was controlled to be about 170 nm (less than 10% of film thickness) so as to minimize the effect of the substrate. The curvature radii of the films were measured using a MicroXAM surface mapping microscope (ADE shift, America) and the internal stress was calculated based on the Stoney equation [31]:

$$\sigma = \frac{E_s}{6(1-\nu_s)}\left(\frac{t_s{}^2}{t_f}\right)\left(\frac{1}{R_2} - \frac{1}{R_1}\right)$$

Where σ is the internal stress, R_1 and R_2 are the substrate curvature radii before and after film deposition, The ν_s and E_s are Poisson ratio and Young modulus of the substrate, t_s and t_f are the thickness of the substrate and film [32], respectively. Silicon p(111) over an area of 2.0 cm $\times 2.0$ cm is used for calculating internal stress. The curvature of the Si flat wafers (R_1) before the deposition of film is assumed to tend to infinite, and that after deposition is measured by MicroXAM-3D surface profiler. Young's modulus of 131 GPa and the Poisson ratio of 0.278 are adopted for Si p(111) substrates, respectively. The thickness of the Si substrate (t_s) is 620 nm and the thickness of the film (t_f) could be measured by MicroXAM-3D surface profiler.

2.3. Ball-on-disk tribological testing

The tribological properties of the films were evaluated with a tribo-meter equipped with a frictional force sensor with rated output of 1.0 mV/V and accuracy rating of 0.01%, using a pin-on-disk mode. Briefly, sliding tests of the film against steel ball (GCr15, Φ 6 mm) counterpart were run at a normal load of 5 N, corresponding to a theoretical initial Hertzian contact pressure of 1.0 GPa. The wear track radius was fixed at 6 mm at room temperature about 20 °C. For the test in vacuum (1.0×10^{-3} Pa), the rotational speed was 0.6 m/s with a sliding distance of 10,000 m. Then a rotational speed of 0.2 m/s with a sliding distance of 720 m in various environments was performed to gain the wear rate of the film. In N_2 environment, the chamber was pumped to 1.7×10^{-4} Pa and then charged with dry pure N_2 to maintain a pressure of 1.0×10^5 Pa. The test in air was maintained at relative humidity of 45% at 1.0×10^5 Pa. Upon completion of the friction and wear tests under each experimental condition, the frictional pair was disassembled and ultrasonically cleaned with acetone. Friction experiments were conducted thrice under each experimental condition. The wear volumes of the film in various test environments were measured by the MicroXAM-3D surface profiler, and the wear rate was calculated using the followed formula: $k = V/(F \times S)$, where k is wear rate, V is the wear volume (mm^3), F is the normal applied load (N), and S is the sliding distance (m).