Applied Surface Science 465 (2019) 564–574

Contents lists available at ScienceDirect

Applied Surface Science

journal homepage: www.elsevier.com/locate/apsusc

Full Length Article

Structure, properties and growth mechanism of a self-assembled nanocylindrical MoS_2/Mo-S-C composite film

Zewen Duan[a,b], Li Qiao[a,b], Liqiang Chai[a,b], Jiao Xu[a,*], Peng Wang[a,*], Weimin Liu[a]

[a] State Key Laboratory of Solid Lubrication, Lanzhou Institute of Chemical Physics, Chinese Academy of Sciences, Lanzhou 730000, China
[b] University of Chinese Academy of Science, Beijing 100049, China

ARTICLE INFO

Keywords:
Nanocylindrical Mo-S-C film
Nanostructure characterizations
Friction
Hardness
Growth mechanism

ABSTRACT

A self-assembled nanocylindrical MoS_2/M-S-C composite film with excellent tribological properties was synthesized by simultaneously sputtering of MoS_2 and graphite targets. The HRTEM observation of the polished surface and cross-sections reveals that this nanocylindrical structure with MoS_2-rich phase encircled by carbon matrix arranging alternately in vertical patterns is initiated from the film-substrate interface and continues to the film surface. The XRD results show that this film exhibits dominant (1 0 0) basal planes. In comparison with pure MoS_2 film, this nanocylindrical MoS_2/Mo-S-C composite film exhibits largely enhanced hardness and higher elastic recovery ratio ($d_{elastic}/d_{max}$) under the same load. Surprisingly, the pin-on-disk tribotests in vacuum on it display a low friction-coefficient and long wear lives (up to 5×10^5 revolutions). The HRTEM observation of wear tracks finds that the MoS_2 texture was reassembled on the film surface, and a tribofilm with preferential (0 0 2) basal planes in thickness about 100 nm is quickly formed in sliding. Based on the XRD results and TEM images of this film, this clear nanocylindrical structure was attributed to atomic transport occurring preferentially along the edge sites of MoS_2 crystallites.

1. Introduction

Nanomultilayer film has attracted much attention in recent years due to its extraordinary mechanical properties and potential applications in wear-resistant protective coatings. For example, a nanomultilayer TiAlCrSiYN/TiAlCrN film [1] with hardness has been reported recently. This nanomultilayer composite film formed self-adaptive protective tribofilm during friction, which largely enhanced the film wear lives in serve climatic conditions. Recently, Pogrebnjak [2] prepared one set of nanomultilayer TiN/SiC films with excellent mechanical properties by controlling the growth temperature, which provides new wear-resistant protective coatings. Bagdasaryan [3] also prepared (TiZrNbTaHf)N/MoN multilayered nanocomposite coatings, a protective material, by vacuum-arc deposition under different energy conditions.

Transition metal dichalcogenides compounds (TMD), MoS_2, a typical 2-dimensional lamellar materials with layers of metals atoms sandwiched between layers of chalcogen atom, has been widely used as solid lubricant extensively in moving mechanical assembles of spacecraft such as holding and release mechanisms of solar array, gimbal bearings and precision bearings [4,5]. Unfortunately, solid lubricant films prepared by sputtering exhibit columnar structures, which leads to shorter wear lives in industrial application. However, like the nanomultilayer TiAlCrSiYN/TiAlCrN, TiN/SiC and (TiZrNbTaHf)N/MoN films, excellent mechanical and wear-resistant properties have been proved for the nanomultilayer alloyed MoS_2 film, where the multilayered film consists of nanomultilayered MoS_2-riched domain layers with preferential (0 0 2) basal planes, and amorphous layers in nanoperiodicities. Particularly, C-doped TMD films with nanomultilayer structure have been widely investigated in recent years because of its enhanced hardness and longer wear lives. For example, a self-assembled multilayer structure with 1–2 nm sub-layer thickness had been observed in co-sputtered WS_2/a-C composite films as once reported by Noshiro et al. [6] Besides, a similar nanostructure was also seen in MoS_2/a-C composite films as mentioned in Ref. [6,7]. Recently, Xu and Wang again prepared highly ordered MoS_2/Mo-S-C and MoS_2/Mo-S-C-N multilayer films by r.f. co-sputtering of MoS_2, graphite targets, and N_2 onto non-biased substrates [8–10]. In comparison with the pure MoS_2 films, these nanomultilayer composite films exhibit dominant (0 0 2) texture, and HRTEM tests on wear track showed that an adaptive tribofilm was formed in large parts of sliding area, both of which are the key mechanism of low friction performance of deposited film with long wear life. Significant attentions have been focused on fabricating nanomultilayer composite film in recent years due to its extraordinary

---

* Corresponding authors. Address: No. 18, Tianshui middle road, Lanzhou 730000, China.
E-mail addresses: xujiao@licp.cas.cn (J. Xu), pengwang@licp.cas.cn (P. Wang).

https://doi.org/10.1016/j.apsusc.2018.09.076
Received 25 June 2018; Received in revised form 7 August 2018; Accepted 8 September 2018

mechanical properties and self-adaptive feature during friction. However, the tribological properties, structure characterizations, self-adaptive characterizations and growth mechanism of nanocylindrical composite film have less been studied in the field of tribology.

In this study, based on the previous experiments in our group [8], a self-assembled nanocylindrical MoS_2/Mo-S-C composite film with excellent tribological properties in vacuum was fabricated for the first time by r.f. co-sputtering of MoS_2 and graphite targets onto non-biased substrates. Contrary to the MoS_2/Mo-S-C composite film with highly ordered nanoperiod multilayers [8], this nanocylindrical MoS_2/Mo-S-C composite film we prepared exhibits no preferential orientation of sputtered MoS_2 in (1 0 0) basal planes. Our studies were focused on the nanostructure characterizations, the self-adaptive properties and the tribofilm formation of this nanocylindrical MoS_2/Mo-S-C film. Meanwhile, based on the observations of X-ray diffraction spectroscopy (XRD) and images of high resolution transmission electron spectroscopy (HRTEM), we make clear the atomic mechanism of self-assembling process, micro-structural evolution and the driving force of the MoS_2/Mo-S-C composite films with different nanostructure (nanomultilayer structure or nanocylindrical structure), which may provide theoretical basis for fabricating different nanostructure materials with diverse functions.

2. Experimental details

2.1. Deposition of Mo-S-C composite films

The MoS_2/Mo-S-C composite films were deposited by sputtering MoS_2 and graphite targets simultaneously in argon atmosphere. The substrates were cleaned by in alcohol for 20 min, and then were assembled in the substrate holder which is 60 mm away from the targets. During deposition, the rotation speed of sample stage was driven to keep at 0.15 rev./s, and sample holder was heated to 150 °C. Before deposition, the chamber was evacuated to 1.3×10^{-3} Pa, and then the substrates were etched by Ar^+ ions 10 min to remove native oxides at the surface. During deposition, the gas flow was kept at 40 sccm and the corresponding pressure was 0.65 Pa. The r. f. sputtering power applied to the MoS_2 target was 250 W. To fabricate Mo-S-C composite films with different contents of carbon, the r. f. sputtering power applied to C targets varied from 200 W to 400 W. Prior to the deposition, a 200 nm Ti interlayer was first deposited to enhance the adhesion.

2.2. Characterization of film structure

The morphology, cross-sectional nanostructures and thickness of deposited films were investigated by using field-emission scanning electron microscopy (FESEM, JSM-6701F, JEOL, and Japan) and the high-angle annular dark-field scanning and high revolution transmission electron microscopy (HAADF-HRTEM, TECNAI G2 S-TWIN F20, FEI, USA; accelerating voltage 200 kV), respectively. The composition and crystallographic phases of sputtered films were studied by using Energy dispersive spectroscopy (EDS, JSM-5601LV, JEOL, Japan), grazing incidence X-ray diffraction (GIXRD, Rigaku RINT2400), and Raman spectroscopy (Horiba LabRam HR800), respectively. GIXRD measurements were carried out using Cu Kα radiation $\lambda = 1.54056$ and the diffractograms were acquired from 10° to 90°. The Raman spectra was measured by a 532 nm wavelength excitation, using a low laser power of D2 filter and one acquisition cycle for 120 s to avoid film damage.

2.3. Mechanical and tribological properties characterizations

The tribological behavior was tested on a pin-on-disk tribometer equipped with a vacuum chamber. For vacuum tests, a pressure of 9.0×10^{-3} Pa was achieved at room temperature. Sliding tests of the films against steel ball counterpart (GCr15, radius 3 mm) were run at a normal load of 3 N, which created a Hertz contact pressure about 1.5 GPa. A sliding speed of 1000 rev/min produced wear tracks in radius of 3 mm on tested films. All tests were performed in high vacuum successively under the same loading conditions. The nanoindented hardness and Young's modulus for deposited films were determined by using a Nano Indenter DCM nano-mechnical system ((MTS, America) with Berkovich diamond indenter, and the maximum indentation depth was set to be less than 10% of film thickness to avoid the problems of substrate deformation [11]. Five repeated indentations were made in different regions of each sample for an average evaluation.

Table 1
The deposition parameters and chemical composition of pure sputtered MoS_2 film and Mo-S-C composite films.

Process		Target power (W)		Chemical composition (at.%)		Thickness (um)
T (°C)	P_{Ar} (Pa)	C target	MoS_2 target	C	S/Mo	
150	0.65	–	250	2	1.83	2.51
150	0.65	200	250	19	1.78	1.78
150	0.65	300	250	30	1.81	1.63
150	0.65	400	250	40.	1.71	1.59

3. Results and discussion

3.1. Structure and chemical composition

The deposition parameters and the corresponding composition of MoS_2 and Mo-S-C films measured by EDS are listed in Table 1. The listed film thickness was measured by SEM cross-sectional images. For all the films, the S/Mo ratios obtained by EDS of all films are less than 2. As reported before [12,13], the sub-stoicheiometry of S and Mo in films is attributed to the reaction of sulfur with residual atmosphere (particularly with H_2 and O_2), plus the preferential sputtering effects of sulfur due to the bombardment of neutral argon atoms reflected on the target during sputtering process. Besides, a clear tendency can be seen that in comparison with the pure sputtered MoS_2 films, the Mo-S-C composite films thickness reduces with the increase of graphite sputtering power from 200 W to 400 W, a phenomenon usually noticed in Mo-S-C films [8–10,14,15] (the doping of a-C phase may block the growth of nanocylindrical structure of pure sputtered TMD phase, so the composite films were more compacted and the deposition rate calculated in terms of film thickness reduced clearly).

The chemical bonds of Mo-S-C films were characterized by XPS and the resulting spectra were fitted by XPSPEAK41 software, using a shirley background and Guassian-Lorentian function in ratio of 80%:20%. Fig. 1 shows that C 1s, S 2p and Mo 3d spectra of Mo-S-C films deposited at different power applied on graphite target. In Fig. 1(a1), the C 1s spectra are deconvolved into two components, representing the C—C and C—C bonds (284.4 eV and 285.2 eV [9]). With increasing power applied on the graphite target from 200 W to 400 W, the shape and area of C 1s have no significantly changing, and there are no C-Mo related chemical bonding in C 1s spectra eventhough power applier to graphite target up to 400 W, as shown in Fig. 1(b1, b2), which means no obviously chemical reaction occurring in deposition. The S 2p spectra (Fig. 2a2–c2) shows a doublet binding energy of 162.6 and 163.8 eV, which represents the S $2p^{2/3}$ and S $2p^{1/2}$ spectral lines of S^{2-} in MoS_2 [9,16]. And the deconvolution of S 2p spectra suggests that the S 2p peaks at 161.9 and 163.1 eV are identified corresponding to the standard S $2p^{3/2}$ and S $2p^{1/2}$ lines in S^{x-2}, which agrees with the analysis by Kedong Shang [16]. In Fig. 1(b2) and (c2), with the carbon contents, no new sulfide was formed, such as CS_2. As shown in Fig. 1(a3), the Mo 3d spectra at the binding energy of 228.9 and 232 eV corresponds to the standard spectral line of Mo $3d_{5/2}$ and Mo $3d_{3/2}$ in