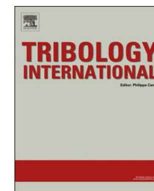
Tribology International 114 (2017) 478–484

Contents lists available at ScienceDirect

Tribology International

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



Tribological performance of a tungsten disulfide lubricant film prepared by atomic layer deposition using tungsten hexacarbonyl and hydrogen sulfide as precursors

Yongfeng Sun[a], Zhimin Chai[a], Xinchun Lu[a,*], Jing Lu[b]

[a] State Key Laboratory of Tribology, Tsinghua University, Beijing 100084, China
[b] National Engineering Research Center for Nanotechnology, Shanghai 200241, China

ARTICLE INFO

Keywords:
Tungsten disulfide
Atomic layer deposition
Low friction
Reorientation

ABSTRACT

The tribological properties of a tungsten disulfide solid lubricant film prepared by atomic layer deposition were investigated. The WS_2 film was deposited using tungsten hexacarbonyl and hydrogen sulfide as precursors. The results showed that due to the incomplete reaction of tungsten hexacarbonyl, steady atomic concentrations of carbon and oxygen were detected throughout the WS_2 film. The friction tests showed that in humid air the WS_2 film exhibited good environmental robustness, and in dry nitrogen it exhibited a low friction coefficient, which decreased to 0.035 at a steady lubrication state. The formation of a transfer film on the counterface of a Si_3N_4 ball, and the reorientation with a few top (002) basal planes in the wear track were revealed.

1. Introduction

Microelectromechanical systems (MEMS) have advanced significantly over the last decades based on the success of the semiconductor manufacturing [1]. In the recent years, a number of MEMS devices were commercially used, such as pressure transducers, accelerometers, temperature/humidity sensors and so on [2]. As an important building material, silicon (Si) substrate has been widely used in the MEMS devices due to its merit of well-established design and fabrication. However, direct use of bare Si mays lead to some problems. For example, when MEMS devices have contacting or rubbing structures, such as micro gears and motors [3,4], Si exhibits severe wear by producing contaminating particles in the contacting structures [5,6], resulting in fast failure. In order to reduce friction and wear of these devices, several methods have been explored. So far, vapor phase lubrication (VPL) using alcohol is the most effective method to decrease friction and wear of the MEMS devices [7,8]. However, packaging the MEMS devices and the in-situ vapor feed system together is a challenging problem. Another efficient way to reduce friction and wear is covering the contacting surfaces with proper lubricating films, such as tungsten (W) [9], titanium dioxide (TiO_2) [10], alumina (Al_2O_3) [10,11], zinc oxide (ZnO) [12] and tungsten disulfide (WS_2) [13].

Several deposition technologies have been adopted to grow solid lubricating films, including pulsed laser ablation [14,15], ion beam deposition [16] and chemical vapor deposition (CVD) [17]. However, it is difficult to uniformly cover shadowed surfaces and high-aspect-ratio structures via these methods (except CVD) [11]. Although the CVD technology is suitable for structures with shadowed surfaces, the temperatures required for the surface chemical reactions are pretty high, which limits its application [13]. Recently, atomic layer deposition (ALD) has received much attention as an advanced technology for the deposition of ultra-thin films. Due to its self-limiting character, it facilitates the growth of thin films at low temperatures and ensures excellent step coverage, accurate thickness control, and conformal deposition on high-aspect-ratio structures [18–20]. Thus, ALD is ideally suited for the fabrication of MEMS devices with three-dimensional microstructures [11–13]. Previous results have shown that Al_2O_3 and ZnO lubricating films can be uniformly deposited on MEMS devices by ALD [11,21,22]. However, the friction coefficient of those films is high and there still remains a great demand for films with lower friction coefficient.

Transition metal dichalcogenides (TMD), especially tungsten disulfide (WS_2) and molybdenum disulfide (MoS_2), are well-known for their excellent lubrication performance [23]. These materials exhibit extremely low friction coefficients (< 0.05) in a dry inert gas or ultrahigh vacuum environment [24,25]. Recently, some studies have revealed that ALD can be used to grow MoS_2 and WS_2 films. For example, a MoS_2 thin film with a nanocrystalline microstructure was grown by ALD using $Mo(CO)_6$ and H_2S as the precursors with a 75%

* Corresponding author.
E-mail address: xclu@tsinghua.edu.cn (X. Lu).

http://dx.doi.org/10.1016/j.triboint.2017.04.047
Received 6 March 2017; Received in revised form 17 April 2017; Accepted 26 April 2017
Available online 26 April 2017
0301-679X/ © 2017 Elsevier Ltd. All rights reserved.

step coverage on a nanoscale trench [26]. In comparison with MoS_2, WS_2 has higher thermally stability [27]. The tribological performance of ALD-WS_2 film was reported in a few studies [13,28]. One such study reported the ALD growth of a WS_2 film deposited on MEMS devices using WF_6 and H_2S gases as the precursors with a zinc catalyst. The WS_2 film grown by this method had ZnS impurity which arose from reaction between zinc catalyst and H_2S. The ZnS impurity may deteriorate the tribological performance of the WS_2 film. Moreover, hydrofluoric vapor was produced in this method, which was toxic and not eco-friendly [13]. Therefore, WS_2 film prepared by other ALD method should be explored.

In this paper, WS_2 film was prepared by ALD using $W(CO)_6$ and H_2S as the precursors. No toxic by-product was produced in this method. Detailed film deposition process and film characterization can be found in our previous paper [29]. The objective of this study was to gain an insight into the tribological performance of prepared WS_2 film.

2. Experimental

Prior to film deposition, a Si (100) substrate was cleaned in ultrasonic baths containing acetone, absolute alcohol, and deionized water for 30 min, respectively, and dried with high purity nitrogen (purity > 99.99%). In order to promote the growth of WS_2, a ZnS layer was deposited on the Si (100) substrate firstly using a Picosun SUNALE R-150 ALD reactor. Diethylzinc (DEZ) and H_2S were used as precursors and N_2 was a carrier gas. For one ALD cycle, the substrate was exposed to DEZ/N_2, N_2, H_2S/N_2, and N_2 for 0.1 s, 4 s, 10 s, and 20 s, respectively. A total of 50 ALD cycles was conducted and the chamber temperature was kept at 150 °C.

The WS_2 film was then deposited by using tungsten hexacarbonyl ($W(CO)_6$, 99%) and hydrogen sulfide (H_2S, 10%, mixed with nitrogen) as precursors. The base pressure of the reaction chamber was maintained at ~ 1000 Pa by an oil pump (EDWARDS, E2M80), and the deposition temperature was set to 400 °C. $W(CO)_6$ was first evaporated in a bubbler at a temperature of 60 °C for adequate vapor pressure, and then the vaporized $W(CO)_6$ and H_2S gases were alternately transported into the chamber with nitrogen carrier gas in 500 ALD cycles. The flow rate of the carrier gas and H_2S gas was 150 standard cubic centimeters per minute (sccm) and 50 sccm, respectively. The ALD of WS_2 involved 0.1 s, 20 s, 10 s, and 20 s of exposure of the substrate to $W(CO)_6$/N_2, N_2, H_2S/N_2 and N_2, respectively.

The ball-on-disk dry sliding friction test was performed using a Universal Micro-Tribotester (UMT-3, Bruker) under reciprocating mode. The friction test was carried out in the humid air (40% humidity) and the dry nitrogen conditions (N_2 ≥99.99%, O_2 ≤0.005%, H_2O ≤0.0015%) using a Si_3N_4 ball (4.763 mm diameter, ~ 15 nm surface roughness (Ra), and 310 GPa elastic modulus) as a counterface. The normal loads applied were 0.5 N, 1 N, 2 N, and 4 N, which corresponded to the initial maximum Hertzian contact stresses of 350 MPa, 440 MPa, 560 MPa, and 700 MPa, respectively. The reciprocating frequency was set to 1 Hz, and the sliding distance was set to 1 mm. All the data shown in this work were the average of three replicate experimental results, and all the tests were performed at the temperature of 15–20 °C.

The cross-sectional morphology of the WS_2 film was observed by transmission electron microscopy (TEM, JEOL 2011 operated at 200 keV). The chemical composition of the WS_2 film was analyzed by an auger electron spectrum (AES, PHI-700, ULVAC-PHI) using a pressure $< 3.9\times10^{-9}$ Torr for depth profiling. The sputtering rate for the calibration specimen (SiO_2 film) was 6 nm/min. The composition of the WS_2 film was also measured by an X-ray photoelectron spectroscopy (XPS, 250XI). In order to avoid the influence of surface contamination, the WS_2 film was sputtered 60 s by Ar ions prior to the XPS analysis. The wear track was analyzed by Raman spectroscopy (LabRAM HR Evolution, 532 nm) and a scanning electron microscope with an energy dispersive X-ray spectrometer (EDXS, LYRA 3 FEG – SEM). The transfer film formed on the Si_3N_4 ball was investigated by optical microscope, and energy dispersive X-ray spectrometry (EDXS, LYRA 3 FEG – SEM). Pristine and worn surfaces (after the friction test) of the WS_2 film were analyzed by an X-ray diffractometer (XRD, D/max 2500 Rigaku diffractometer equipped with a Silicon Drift Detector) with a Cu K α source at the same glancing angle. In order to record the XRD spectrum of the worn surface, the friction test was repeated 250 times to obtain a 5×6 mm^2 worn area. The cross section of the worn surface near the sliding contact interface was observed by a high-resolution transmission electron microscopy (HRTEM, JEOL 2011 operated at 200 keV) to detect changes in its crystal microstructure. Cross-sectional specimens to measure and observe the film thickness and interface structure, respectively, were prepared using a focused ion beam instrument (FIB, LYRA 3 FEG – SEM×FIB).

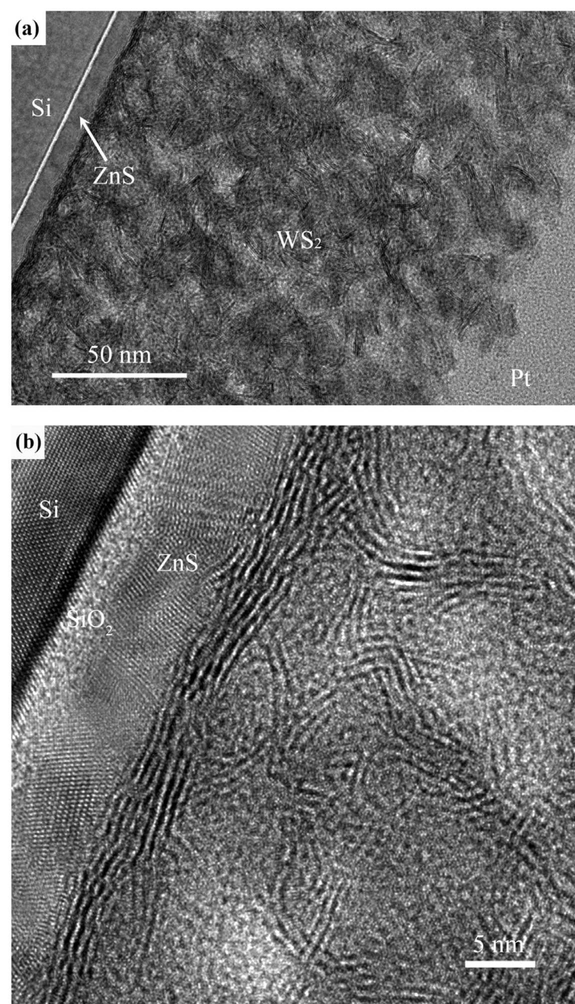


Fig. 1. (a) Cross-sectional TEM image of the WS_2 film grown on the ZnS-coated Si (100) substrate and (b) HRTEM image of the WS_2/ZnS/Si interface.

3. Results and discussion

3.1. Film characterization

The thickness and microstructure of the WS_2 film was characterized using cross-sectional TEM. Fig. 1(a) shows the cross-sectional TEM image of the WS_2 film and Fig. 1(b) shows the HRTEM image of the WS_2/ZnS/Si interface. The thickness of the WS_2 film is approximately 175 nm, and the calculated growth rate is 0.36 nm per ALD cycle, which is larger than the growth rate reported in previous studies [13,30]. Fig. 1(b) shows that the 50 ALD cycles ZnS layer deposited on

Download English Version:

https://daneshyari.com/en/article/4986020

Download Persian Version:

https://daneshyari.com/article/4986020

Daneshyari.com