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Structural, surface and mechanical characterization of spray-deposited molybdenum disulfide thin films

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ABSTRACT

Molybdenum disulfide (MoS_2) was deposited with the precursor salt of ammonium molybdate tetrahydrate and thiourea on glass substrate at various precursor solution volume (10–50 mL) using the spray pyrolysis technique. The X-ray diffraction pattern indicates the polycrystalline nature of the film with a hexagonal structure and the occurrence of peak shift due to stacking fault. The field-emission scanning electron micrograph shows the increment in grain growth with increase in the precursor solution volume, leading to the conversion of grains to nanoflakes. Energy dispersive spectrum confirms the presence of molybdenum and sulfur. Vickers microhardness shows increament in microhardness with decrease in the precursor solution volume. The mechanical properties related to microhardness were analyzed. Raman analysis confirms the hexagonal structure of MoS_2 with the presence of vibrational modes.

1. Introduction

Layered materials such as metal oxychlorides [1], graphite [2], transition metal dichalcogenides (TMDs) [3,4] and quasi ternary systems [5,6] have tribological properties because of their anisotropic nature [7]. MoS_2, $MoSe_2$, WS_2, and WSe_2 are the most commonly used TMDs in various applications, such as tunnel field effect transistor [8], photovoltaic devices [9], tutelage of industrial surfaces [10] and aviation [11]. This wide range of applications is due to their adjustable bandgap, high optical absorption and shearing property towards the load. Being non-toxic and cost effective, MoS_2 and WS_2 are preferred over other layered structures [7]. The crystal structure of MoS_2 is mostly hexagonal, in which each layer of molybdenum atoms is sandwiched between two layers of sulfur atoms. The layers of molybdenum atoms and sulfur atoms are held together by covalent bond, and the (S–Mo–S) layers are held together by weak van-der-Waals interaction [12]. The triple layer (S–Mo–S) can be arranged in three ways: the hexagonal (2H-MoS_2), the rhombohedral (3R-MoS_2) and the trigonal (1T-MoS_2) [7]. Among these, 2H-MoS_2 stipulates a basal plane parallel to the substrate and hence exhibits low frictional co-efficient [13]. The frictional co-efficient relies on the ratio of shear stress, which occurs parallel to the layers, and yield stress. Therefore, it can withstand heavy loads that can be placed at right angle to the layers [13]. Other properties of MoS_2 are: the ability to adhere strongly to the bearing surface, the tendency to prevent contamination or erosion, being chemically inert, stability against radioactive agents, and its non dependency on the adsorbed vapors for lubrication [13].

Apart from tribological application, MoS_2 is also used in opto-electronic devices, to its direct band gap that causes photoluminescence of optical wavelength and exhibits variation of intensity through electric gating [14]. Because of its stratum structure, MoS_2 has the ability to intercalate lithium so as to enhance the electrical conductivity, and is therefore

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used in lithium based batteries [15]. Based upon the structure, the application of MoS_2 changes. Nano- particles of MoS_2 have been used in the applications of selective coatings and photoconductors [16]. Nanosheets of MoS_2 have been applied in the field of spintronics and nanodevices [17]. A MoS_2 ionic nanofluid exhibits excellent lubrication in microelectromechanical systems/nanoelectromechanical systems [18]. A MoS_2 nanoribbon exhibits highly stable magnetic and electronic properties, which is a significant advantage in the applications of nanotechnology [19]. MoS_2 thin films can be deposited using various techniques, namely, chemical bath deposition [7], electrodeposition [20], sputtering technique [21], mechanochemical method [22], novel two-step method [23], pulsed laser deposition [24], spin coating technique [25], dip technique [26] high-power power impulse magnetron sputtering (HIPIMS) [27] and chemical vapor deposition [28].

Depositing protective coatings to the interior parts of bearings [29], blades and vanes of turbine engine [30], internal combustion engines [31], HCCI engine [32], aircraft engine [33] and actuator of rocket engine [34] is hard to achieve through the above mentioned techniques. Spray pyrolysis techniques can be used for interior protective coatings in a controlled manner owing to its outstanding features. That includes: protection from high operating temperature, thermal radiation, oxidation, ablation, corrosion and wear resistance, simplicity in operation, low equipment cost, and minimal raw material requirements. Much work has not been reported on MoS_2 thin film preparation through spray pyrolysis technique. Very few works have been reported on MoS_2 thin film formation from the precursor solution of pyrolyzed aerosol using ultrasonic spray pyrolysis [35]. In this work, MoS_2 thin films were prepared through spray pyrolysis technique and were found to exhibit a layered structure (2H-MoS_2) that could be used as solid lubricant.

2. Experimental

2.1. Preparation of precursor solution

To deposit Molybdenum disulfide (MoS_2) thin films on chemically cleaned glass substrate, an aqueous precursor solution containing salt of ammonium molybdate tetrahydrate ($(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ Sigma-Aldrich, 99.98% purity) and thiourea (SC $(NH_2)_2$ Sigma-Aldrich, 99.0% purity) was prepared. To get the 50 mL volume of precursor solution 0.61 g of ammonium molybdate tetrahydrate and 0.19 g of thiourea were dissolved in 25 mL of deionized water separately and were mixed at room temperature ($\sim$30 °C).

2.2. Thin film preparation

A homemade spraying system as reported earlier [36] was used to obtain MoS_2 thin films. The substrates were heated to 230 °C and the temperature was monitored and controlled using K-type thermocouple and thermostat, respectively with an accuracy of ± 1 °C. The precursor solution was then sprayed at an angle of 45° on to the preheated glass substrates. Compressed dry air was used as carrier gas with a flow rate of 3 mL/min. Excessive cooling of substrates was avoided by successive spraying process, with a time interval of 15 s. The MoS_2 film formation is given in the following equation as:

$$(NH_4)_6Mo_7\cdot 4H_2O + 14SC(NH_2)_2 + 24H_2O \rightarrow 7MoS_2 + 34NH_3\uparrow + 14CO_2\uparrow + 17H_2\uparrow \quad (1)$$

2.3. Characterization

The structural details of the prepared MoS_2 thin films were studied using X-ray diffractometer (XPERT-PRO Model) of CuKα_1 radiation with a wavelength (λ) of 1.5406 Å. The surface morphology of the films was studied using field-emission scanning electron microscope (FE-SEM, JEOL-6701F). The chemical composition of the deposited films was obtained from energy dispersive spectroscopy (EDS). Microhardness tests were performed using a (SHINADZU, Japan) type Vickers Microhardness tester by applying load from 245.16 mN to 4903.32 mN. The vibrational properties of the MoS_2 thin films were determined using Raman spectroscopy (LabRAM HR, Horiba Jobin Yvon, France).

3. Results and discussion

3.1. Structural studies

Fig. 1(a) shows the X-ray diffraction (XRD) spectra of MoS_2 thin film obtained from different precursor solution volumes. The spectrum obtained from 10 mL precursor solution volume shows the amorphous nature of the film. As the volume of the precursor solution increases, crystallinity improves and results in a polycrystalline nature. The intensity of the peaks improves gradually as precursor solution volume increases, indicating improvement in the crystallinity of the film. The diffraction peaks at 12.70°, 29.026° and 38.88° were indexed to (002), (004) and (103) planes respectively according to the standard of the Joint Committee on Power Diffraction Standards (card no: 73-1508). The peaks at 12.70° and 38.88° confirm the hexagonal structure (2H-MoS_2). But the X-ray diffraction peak at 29.026 is of molybdenum trioxide phase. The formation of MoO_3 may be due to the presence of oxygen in the carrier gas. Texture co-efficient determines the highly preferential peaks and is obtained using the following equation [36]:

$$TC = \frac{I_{(hkl)}/I_{o(hkl)}}{(1/N)\left(\sum_N I_{(hkl)}/I_{o(hkl)}\right)} \quad (2)$$

where I is the intensity of the observed value, I_o is the intensity of the standard JCPDS value, N is the number of diffraction peaks. Table 1 shows the texture co-efficient with respect to the precursor solution volume. It indicates the preferential peaks at (0 0 4) plane irrespective of precursor solution volume. The presence of (002), (004) and (103) planes reveals that the basal plane of MoS_2 thin film parallel to the substrate is significant for tribological application [37]. The Williamson–Hall (W–H) method [38] was used to find microstrain and grain size from the following equation:

$$\beta \cos\theta = \frac{k\lambda}{D} + 4\varepsilon \sin\theta \quad (3)$$