# The Formation of Films of MoS<sub>2</sub> By Sputtering and Sulfidizing

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A thin, dense, and durable solid film of molybdenum disulfide was obtained by plasma sputtering and chemical sulfidizing in two steps; first, pure metallic molybdenum was sputtered from a molybdenum target and deposited onto a substrate (glass or quartz slide)' in the chamber of a radio-frequency (rf) sputtering system in an argon atmosphere. The coated substrate was then sulfidized at temperatures between 200 and 800° C by introducing a gas mixture of H<sub>2</sub>S, H<sub>2</sub> and Ar into the sputtering chamber for a period of 10 to 30 min. The deposition efficiency of molybdenum was influenced by the distance from target to substrate, by the argon pressure of sputtering and by the sputtering rf power. The sulfidation rate of molybdenum increased with increasing temperature from 200 to 800° C, using a gas mixture of H, to H,S in a 10:1 molal ratio, and also with decreasing ratio of H, to H,S from 10:0.5 to 10:2.5. In addition to the distance of target to substrate, and the chamber pressure in the sputtering process, the temperature of the reaction between Mo and H,S is also an important factor affecting the wear life of the MoS, film.

olybdenum disulfide can be used as a solid lubricant because it has a layer-lattice structure (Fig. 1) similar to that of graphite.' Each layer of molybdenum atoms occurs between two layers of sulfur atoms. The bonds between molybdenum and sulfur layers are strongly bound by covalent chemical bonds; however, the two layers of sulfur atoms between two molybdenum disulfide elements are joined by weak Van der Waals bonds.<sup>12</sup> Therefore, the crystal can be split readily along the cleavage faces between molybdenum disulfide layers without breaking the bonds between molybdenum substrate, can be produced.



and sulfur. As a result, MoS, is one of the best solid lubricants available for use with two material surfaces in moving contact. Because MoS, is chemically very stable and does not decompose to molvbdenum and sulfur below 1100° C, is resistant to most acids, and is insensitive to radioactive radiation, it is widely used in space technology. It is effective under conditions of heavy load, high speed, and high temperature, and in precision mechanical equipment which can tolerate only low start-up friction with no contamination by lubricating oils or greases.<sup>37 4</sup>

Additionally, MoS, is an n-type semiconductor. It can be used for solar energy conversion or for energy storage because it has high absorptivities and high corrosion resistance, and because its band-gaps lie in the optimum range." 'Currently, there is interest in coating the surface of magnetic recording heads and disks with molybdenum disulfide because of its lubricity and diamagnetic properties. However, detailed information is not readily available.

Methods for forming MoS<sub>2</sub> on surface layers of materials include rubbing, dipping, sputtering and metal-organic chemical vapor deposition.<sup>2, 5</sup>However, a thin  $MoS_2$  film which has good durability, homogeneity and strong adhesion is not readily and economically coated on surfaces of materials. Though sputtering of MoS<sub>2</sub> from a MoS<sub>2</sub> target onto surfaces of materials is an important coating method, it is not widely used because of difficulties in obtaining this target material. A new method for depositing a thin layer of MoS<sub>2</sub> on the surface of a substrate (glass or quartz slide) by sputtering molybdenum and then sulfidizing the substrate has been tested and is reported in this paper. The experimental results indicate that a thin, uniform MoS, film, which has long durability and good adhesion characteristics between the MoS, film and the



Fig. 1-Schematic diagram of layered structure of molybdenum disulfide. Fig. 2-Schematic diagram of plasma sputtering chamber.

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Fig. 3—Schematic diagram of sulfidizing apparatus.

## **Experimental Studies**

A radio-frequency sputtering system with a superimposed dc bias, \* was employed for the deposition of pure molybdenum on the surface of a substrate. A schematic diagram of the sputtering system is shown in Fig. 2. The chamber of this system consists of three electrodes: 1) the target, which is connected to the output of a power supply (rf); 2) the substrate holder, which is at a negative dc potential relative to ground; and 3) the shutter, which is grounded. The water-cooled metal target is a circular disk 0.63 cm in thickness and 12.7 cm in diameter, to which the rough, pure Mo sheet was bonded. The substrates (glass or quartz slides, 2 x 2 cm) were cleaned with acetone. They were then placed on the holder in the chamber and were baked at a temperature of 100° C by applying 110 V for 10 min. before sputtering. When the vacuum system was evacuated to a pressure range of 1.33 x 10<sup>4</sup> to 10<sup>5</sup> Pa, argon was then introduced at a pressure range of 2.00 to 2.30 Pa. Finally, the rf power was supplied, under the following conditions: frequency, 13.6 MHz; argon pressure, 2.13 Pa; power input, 400 watts; reflective power, 2 watts; target negative bias voltage, between 1.2 and 1.3 kV; target-tospecimen distance, 2-5 cm.; and sputtering time, 40 to 50 min. depending on the thickness required.

A horizontal electrical furnace was used with a quartz tube of 5 cm I.D. to heat a glass (or quartz) substrate coated by the sputtered molybdenum. The temperature of the furnace was controlled automatically. A glass capillary flowmeter and two rotor flowmeters were employed to adjust the volume of flow of the gases (H,S, H, and Ar). During the entire process, argon, as a carrier gas and protecting atmosphere, was passed into the furnace. Hz and H,S were each dried and purified using two tubes in parallel packed with copper turnings at 200° C and silica gel, respectively, in order to remove oxygen and water vapor. The offgas was passed through a solution of CuSO<sub>4</sub>to absorb any residual hydrogen sulfide. The substrate which was coated by a film of metallic molybdenum was placed into the center of the tube furnace and heated to the reaction temperature in a hydrogen atmosphere for 5 min. in order to avoid formation of molybdenum oxide. A schematic diagram of the apparatus is shown in Figure 3. Gas mixtures of H, (99.9% H,) and H,S (99.5% H,S) were used in the following ratios: 10:0.5,10:1, and 10:2.5 (H/H,S) by volume respectively. Samples were exposed to these gas atmospheres at temperatures ranging from 200 to 800° C for times ranging from 10 to 30 min.. Then the samples were rapidly cooled to room temperature in an argon atmosphere. The test conditions and results are shown in Table 1.



Fig. 4—Phase stability diagram for Mo-S system. (After Stubbles, Richardson and Suzuki, et al.,<sup>89</sup> as presented by Lee and Rapp.)

		Table 1		
Sulfidizing	Test	Conditions	and	Results

Temp	Time.		Cher Anal		
°C	min	H <sub>2</sub> / H <sub>2</sub> S	Мо%	S %	X-ray
200	20	100.5	99.20	0.08	Мо
200	20	101.0	99.02	0.81	Мо
200	20	102.5	99.01	0.86	Мо
350	25	101.0	99.0	0.93	Мo
500	20	101.0	97.40	2.05	Мо
500	20	102.5	97.40	2.10	Мо
600	15	10:1.0	96.80	3.05	Мo
600	25	101.0	96.05	3.83	Мо
600	20	10:2.5	95.62	4.03	Мо
700	15	101.0	88.75	11.00	Mo,
					MoS <sub>2</sub>
750	15	10:0.5	65.64	34.06	Mo,
					MoS <sub>2</sub>
750	15	10:1.0	63.07	36.60	Mo,
					MoS₂
750	25	10:1.0	62.62	37.07	Mo₁
					MoS₂
750	15	102.5	62.45	37.30	Mo,
					M o S₂
800	15	100.5	60.65	39.03	MoS₂
600	10	101.0	59.60	40.00	MoS₂
800	10	102.5	59.51	40.05	M o S₂

# Table 2 Sputtering Yield of Molybdenum

Energy/ Gas	,	He	N	Ne	Ar	Kr	Xe
500 eV	o\/	0.03	-	0.48	0.80	0.87	0.87
1000	ev	_	0.06	0.49	1.13	1.27	1.60

<sup>\*</sup>R.D. Mathis, (Model sp-310)

The thickness of Mo film sputtered onto the substrate was measured by an alpha-step<sup>\*\*</sup> surface profile measurement unit. The MoS<sub>2</sub>films were tested by friction and wear test apparatus, which consisted of a hemispherical rider sliding against a rotating flat. The rider was loaded against the rotating flat. Friction experiments were conducted at various speeds from 1 to 100 rpm using loads of 10 to 20 g. The samples were weighed using a precision balance, and analyzed by chemical analysis, X-ray diffraction, and scanning electron microscopy.

## **Results and Discussion**

When argon gas is ionized to form a glow discharge with a given rf power supply and given argon pressures, positive ions are accelerated by an applied strong electric field, and strike the target plate of molybdenum metal to remove mainly neutral molybdenum atoms from the target due to momentum transfer by the positive ions of argon. Then, some of the impacted molybdenum atoms are deposited onto the surface of the substrate to condense as a thin film. The sputtering yield, defined as the number of atoms ejected from a target surface per incident ion, is the most fundamental parameter of the sputtering process. Table 2<sup>7</sup> indicates that argon is a good sputtering gas which provides a reasonable sputtering yield. Therefore, pure argon was introduced into the chamber in which a glow discharge could be initiated and maintained during sputtering. In the energy range of 10 to 5,000 eV for the sputtering processes, the sputtering yield increased with incident ion energy.' The incident ion energy is related mainly to the rf power and the argon pressure. Generally, the incident ion energy increases with increasing rf power;



Fig. 5—Scanning electron micrographs showing MoS formed (a) at 700° C, (b) at 750°C and (c) at 800°C in an atmosphere of  $H_2$  and  $H_2$ S In a ratio of 101.

however, there is a practical upper limit, since 75 percent of the energy is wasted in heating the target, which can be easily destroyed by overheating. However, Christy reported that as the rf wattage to the target is increased, the wear life of the film is probably decreased.'

Increasing argon pressure increases the argon ion concentration but reduces the incident ion energy. Our tests indicate that the optimum conditions for deposition were obtained on the Mathis equipment at an rf power of 400 watts and an argon pressure of 2.13 Pa. The pressure of the chamber was in the range of  $1.33 \times 10^3$  to  $10^4$  Pa before introducing argon, avoiding contamination of the molybdenum. A dense, uniform film of molybdenum between 0.2 and 0.3 µm thick was condensed at a sputtering rate of about 0.9 x  $10^2$ µm/min. The smooth surface and dense composition of the film was confirmed by optical microscopy.

When sulfidizing tests were conducted at temperatures between 700 and 800° C, in atmospheres of  $H_2$  and  $H_2$ S and in the ratios of 10:0.5, 101, and 10:2.5, the films which formed consisted only of molybdenum disulfide as confirmed by X-ray diffraction, scanning electron microscopy, and chemical analysis.

Some investigators" have confirmed a narrow band of stability for the sesquisulfide phase in contact with molybdenum under equilibrium conditions. Also Young et al. have reported both the sesquisulfide and the sulfide forming at 700° C on a Ni-Mo alloy;10 however, others" indicate that the sesquisulfide is not stable below 1400° C. In a recent study of the sulfidation kinetics, the presence of the sesquisulfide in a thin layer immediately adjacent to the molybdenum metal surface was reported after an initial period when only the disulfide was formed.<sup>12</sup>The rate of formation of the disulfide phase (at the gas/sulfide interface) was more rapid than the formation of the sesquisulfide phase. This observation, coupled with the incubation period associated with the formation of the sesquisulfide, means that it should be possible to inhibit or minimize the formation of the non-lubricating sesquisulfide by control of time of exposure and scale thickness. Even though the sesquisulfide is temporarily formed at this temperature range and in a given ratio of H<sub>2</sub>/H<sub>2</sub>S, it reacts rapidly, according to the following reaction:

# $Mo_{2}S_{3(s)} + H_{2}S_{(g)} = 2MoS_{2(s)} + H_{2(g)}$

The conditions under which the molybdenum sulfide phase was formed in our investigation were neither isothermal nor slow enough to be considered under equilibrium. Also the MoS<sub>2</sub>film was rapidly quenched to room temperature since oxidation of MoS<sub>2</sub>could be expected to occur even with relatively pure argon overpressures.

X-ray diffraction analysis of the product of the reaction in the temperature range of 700 to 800° C showed no evidence of the sesquisulfide; although minor traces (less than 1 percent, depending on crystal system) could have escaped detection because they would have been below the detection limits. The monoclinic crystal structure of the sesquisulfide<sup>13</sup> is not that of a lubricant; its presence would have been observed in the lubricity tests that exhibited friction coefficients ranging only from 0.03 to 0.04. The phase stability diagram for this system was developed from the data of references 8 and 9, as plotted by Lee and Rapp<sup>1</sup>

<sup>\*\*</sup>Pencor Instruments (Model 0-00020)

and is reproduced here in Fig. 4. The region of possible stability of the sesquisulfide is shown.

Lee and Rapp<sup>12</sup> have explored the kinetics of sulfide scale growth on pure molybdenum and observed linear kinetics of sulfide formation below about 800° C with a transition to parabolic rates above that temperature. They reported that the disulfide forms directly on the molybdenum metal substrate until the scale reaches a critical thickness, after which the sesquisulfide forms. The scales formed in the present investigation were about 0.25 µm thick, which appears to be approximately optimum to achieve high lubricity without conversion to the non-lubricating sesquisulfide phase.

In all tests, the MoS<sub>2</sub>film was quickly cooled to a temperature below 200° C in an argon atmosphere because  $MoS_2$  begins to oxidize to  $MoO_3$  (as determined by X-ray diffraction analysis) at temperatures above 350° C in air. The oxidation of molybdenum sulfide was also confirmed by Shigegaki et al.<sup>13</sup>

The sulfidation of molybdenum is a solid-gas reaction, with the following steps:

(1) the adsorption of  $H_2S$  onto the surface of the molybdenum film,

(2) the diffusion of  $H_2S$  along microcracks or capillaries,

(3) initiation of the reaction between Mo and  $H_2S$ ,

(4) the formation of  $MoS_2$  crystallite, and the desorption of the produced H<sub>2</sub>, and

(5) the nucleation of new crystallite after crystalline impingement has locally halted crystallite growth.

When a molybdenum film is exposed to an atmosphere of  $H_2/H_2S$ , only a fraction of the  $H_2S$  gas can be adsorbed onto the surface of the molybdenum atoms by virtue of the Van der Waals forces of its surface atoms. <sup>14</sup> This adsorption is related to the gas pressure. At lower temperatures, as the gas pressure is increased, the amount of adsorption increases rapidly at first, then more slowly as the surface becomes saturated with adsorbed molecules. Therefore, during the first 5 min. of reaction, a slight excess of stoichiometric  $H_2S$  was admitted into the furnace, then reduced to a lower ratio of  $H_2/H_2S$  by adjusting the flowmeters.

The H<sub>2</sub>S gas should diffuse along microcracks to the molybdenum scale by collision between the gas molecules, and via collision of gas molecules with the microcrack walls. Since molybdenum films deposited by sputtering are uniform and dense, it is proposed that the mean free path of the H<sub>2</sub>S molecules is of a length comparable to the radius of capillary tubes in the molybdenum film. Based on this assumption, the diffusion of H<sub>2</sub>S follows Knudsen's equation: <sup>15,16</sup>

 $D_{k} = 2/3V r = 9.7 \times 10^{3} r (T/M)^{1/2}$ 

where  $D_k$  is the diffusion coefficient, M is the molecular weight of the diffusing species, T is the temperature, and r is the radius of the capillary tube in centimeters. The above equation suggests that the diffusivity is related to temperature. Thermodynamic data indicate that the formation of MoS<sub>2</sub>at low temperatures (100-600° C) is feasible; however, MoS<sub>2</sub>was not found in the products sulfidized in this temperature range, probably because of a low diffusion rate. Based on this observation, it is proposed that the diffusion in this sulfidizing process is the ratecontrolling step. The micrographs (Fig. 5) show that crystalline grain size of MoS<sub>2</sub>increased with increasing



Fig. 6—X-ray diffraction pattern of (a) MoS<sub>2</sub>+ Mo formed at 750" C and (b) MoS<sub>2</sub> formed at 800°.

temperatures from 700 to 800° C. Analogously, according to chemical analysis, the sulfidation rate of the film produced at the same ratio of 10:1  $H_2/H_2S$  increased with increasing temperature (Table 1).

When H<sub>2</sub>S gas diffuses to the molybdenum surface, the chemical reaction between Mo and H<sub>2</sub>S should occur rapidly. Meanwhile, the crystallite of MoS<sub>2</sub> in a hexagonal lattice are sequentially formed. According to the X-ray diffraction patterns and scanning electron microscopy (Figs. 5 and 6), the MoS<sub>2</sub> crystallite, formed at 750 or 800° C and in an atmosphere having a ratio of 10:1 H<sub>2</sub>/H<sub>2</sub>S, exhibited the highest peak for (002) planes at 20 =14.40° for the hexagonal layered structure. Meanwhile, the hydrogen produced from the sulfidation reaction was desorbed from the Mo/MoS<sub>2</sub> interface. Finally, nucleation of crystallite occurs by internal diffusion of hydrogen sulfide.

Sliding friction tests with the MoS<sub>2</sub> films formed by sputtering and sulfidizing indicated that the films can provide very effective lubrication compared with oils and greases. The friction coefficient of (approx.) 0.25-µm-thick films in the sliding contact was 0.03 to 0.04 (Fig. 7). Wear



Fig. 7—Coefficient of friction of  $MoS_2$  as a function of rotating cycles at a load of 20g and a speed of 50 rpm.

tests indicated that as the film was deposited at the shorter target-to-substrate distance of 2.5 cm and in the lower chamber pressure (such as 2.13 Pa), and sulfidized at the higher temperature (750-800° C), a long wear life, over 10<sup>5</sup> cycles before failure, was obtained. During the sputtering process, the shorter distance of target to substrate and lower argon pressure are favorable for the deposition of Mo atoms and for the incident ion energy; during the sulfidizing process, higher temperatures assist the diffusion of H<sub>s</sub>S gas into inner layers. The wear test confirmed that the thicker the MoS<sub>3</sub>film, the longer the wear life.

One important requirement to achieve effective lubrication is that there be strong adhesion between film and substrate. However, it is difficult to measure adhesion quantitatively, hence the MoS films were tested for shear damage only. The results indicated that these films of molybdenum disulfide were not readily spalled by an inserted knife or by shearing. Therefore, strong filmsubstrate adhesion was observed by this simple test.

## Conclusions

MoS<sub>2</sub> films were formed by a two-step process of sputtering and sulfidizing. The metallic molybdenum films deposited on the surface of glass (or quartz) slides by plasma sputtering under an argon pressure of about 2.13 Pa, at a frequency of 13.6 MHz, with a power input of 400 watts, a target voltage (de) of 1.3 kV, and a distance between the target and the sample of 2.5 cm, had good homogeneity and density. The MoS, film formed by chemical sulfidizing at temperatures 700° C to 800" C, and under an atmosphere consisting of H, and H,S in a ratio of 10:1, had a lattice layer structure favorable for lubrication (friction coefficient 0.03 to 0.04), strong film-substrate adhesion, and long wear. The sulfidation rate of molybdenum increased with increasing temperature of the reaction between Mo and H<sub>2</sub>S, with decreasing ratio of H<sub>2</sub>/H<sub>2</sub>S. Wear tests indicated that wear life depended on the distance of target to substrate, the chamber pressure during the sputtering process, the reaction temperature of the sulfidizing process, and strongly on the thickness of the film. Long wear life was found when a 0.25-µm-thick MoS, film was formed under the above conditions.

The MoS<sub>2</sub>, as a solid lubricant, can be coated onto the surface of different shaped materials by this two-step process, This method could potentially be used to deposit MoS, onto surfaces of machine parts. It is difficult to form MoS, film at low temperatures, 200 to 600° C, probably because of a low rate of H<sub>2</sub>S gas diffusion in this temperature range.

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