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Lubrication with Sputtered MoS_2 Films: Principles,Operation, and Limitations

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This article reviews the present practices, limitations, and understanding of thin sputtered MoS_2 films. Sputtered MoS_2 films can exhibit remarkable tribological properties such as ultra-low friction coefficients (0.01) and enhanced wear lives (millions of cycles) when used in vacuum or dry air. To achieve these favorable tribological characteristics, the sputtering conditions during deposition must be optimized for adequate film adherence and appropriate structure (morphology) and composition.

1. Introduction

SPUTTERED MoS_2 thin films display remarkable lubrication properties. Friction coefficients on the order of 0.01 or less can be achieved. This represents an uncommonly low level of friction for a solid film lubricant. For instance, most solid lubricating films such as the soft metallic (Au, Ag, and Pb) and the PTFE (Teflon) films display coefficients of friction of 0.1 and 0.05, respectively. In nature, a friction coefficient of 0.025 is achieved during the rubbing of ice on ice at 0 °C. Thus, optimized MoS_2 films formed by sputtering can, under favorable operating conditions, achieve some of the lowest friction coefficients of any solid material known today.

In vacuum (*e.g.*, a space environment), sputtered MoS_2 films display ultra-low friction, but in humid air the friction properties are degraded. For these reasons, sputtered MoS_2 films are primarily used for spacecraft and satellite moving mechanical assemblies and components (solar array drives, antenna pointing and control systems, despin mechanisms, and rack and pinion gears) that operate under high vacuum, high and low temperatures, and space radiation. These films are also used for terrestrial vacuum systems that house surface analytical instruments, thin-film deposition devices, and related instrumentation that requires the use of vacuum chambers.

A common deposition technique used today is sputtering. The sputtering process is ideally suited to coat precision mechanical components with thin, uniform films. It also permits tailoring the structural/morphological and chemical properties of the films. The tribological performance of sputtered MoS_2 films is critically dependent on sputtering conditions, which in turn influence the microstructural properties of the film, such as crystallinity, morphology, and composition.[1-4] The objective of this review is to describe the current understanding of the process-property-performance interrelationships of sputtered MoS_2 films.

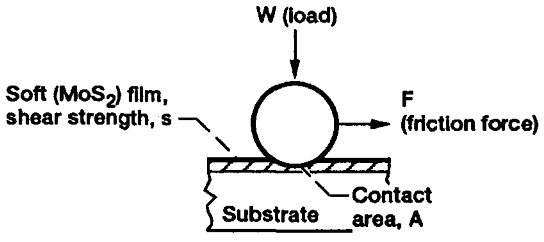
2. Principles of Solid Film Lubrication

The basic concept of thin solid film lubrication follows the principle that, if a low shear strength material is placed between sliding surfaces in contact, the friction force during sliding will be reduced. The friction force, F, is related to the shear strength of the lubricant, s, and the contact area, A; therefore $F = sA$. According to Fig. 1, the friction coefficient, μ, can be arrived at in terms of the lubricant shear strength, the contact area, and the normal load, W. Thus, $\mu = sA/W$. For friction to be low, s and A should have low values; s is strictly a property of the lubricant film itself, and A is determined by the deformation properties of the contact (bearing) materials, namely the hardness or elastic modulus of the substrates.

It follows that $\mu = sA/W = s/(W/A)$, where $W/A = p$, which is the contact pressure. Therefore, $\mu = s/p$.

If the contacts are under elastic deformation, which is normally the situation in bearing technology, the load dependence is determined from the Hertzian pressure, p_H, where $p_H \propto W^{1/3}$. Therefore, the friction coefficient, μ, can be expressed as $\mu = s/p_H \propto s/W^{1/3}$.

According to the above relationships, the friction coefficient, μ, for elastically loaded contacts should decrease as the load increases. If the film is thin, as is the case with sputtered



$$F = As$$

$$\frac{As}{W} = \frac{s}{W/A} = \mu \text{ (friction coefficient)}$$

$$W/A = p \text{ (contact pressure)}$$

$$\mu = \frac{s \text{ (lubricant shear property)}}{p \text{ (substrate mechanical property)}}$$

Elastic deformation: $p_H \, \alpha W^{1/3}$ (Only when contact deformation elastic)
(Hertzian pressure)

$$\therefore$$

$$\mu = \frac{s}{p_H} \, \alpha \, \frac{s}{W^{1/3}}$$

Fig. 1 Principles of solid film friction (lubrication).

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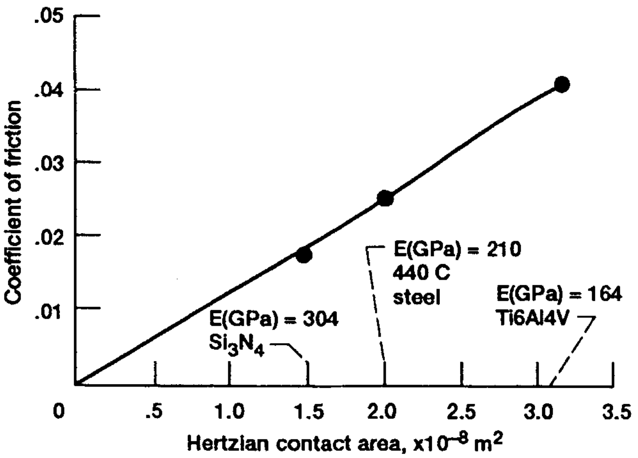

Fig. 2 Coefficient of friction as a function of contact area. Sputtered MoS_2 film.

MoS_2 films, the load is supported by the substrate. Increasing the substrate modulus decreases the contact area for a given load, as shown in Fig. 2.[5] For low friction and acceptable wear life, the desirable film thickness has been found to be between 0.2 and 0.6 μm.

3. Crystal Structure of MoS2

The unique characteristic of MoS_2 (natural molybdenite) is its highly anisotropic crystal layer structure. It is composed of "sandwich" layers, each of which comprises a plane of molybdenum atoms arranged in a hexagonal array situated between two layers of sulfur atoms, as shown in Fig. 3. The interlamellar (layer) attractions between the adjacent lamellae are weak and consist basically of weak van der Walls forces. However, the bonds between molybdenum and sulfur atoms within the lamellae are covalent and therefore strong, thus imparting MoS_2 films with excellent load capacity. As a result, the weak interlamellar bonding contributes to the low shear strength during sliding in the [0001] crystallographic direction, *i.e.*, in the direction parallel to its basal planes. The easy shear in the basal plane direction contributes to the low coefficient of friction and the excellent lubrication properties. Furthermore, the MoS_2 layer structure can exhibit two types of crystallite orientation—either the basal planes are parallel or perpendicular to the substrate, as shown in Fig. 4. The basal planes, when in parallel orientation as shown in Fig. 4, provide the lowest shear strength and result in low friction.

4. Selection of Optimum Sputtering Conditions

By varying the sputtering conditions such as radiofrequency (RF) power and the argon pressure, MoS_x films of various stoichiometry, density, morphology, and adhesion are produced. As a result, these sputtering MoS_x films vary in their tribological performance. Therefore, it is essential to determine the optimum sputtering conditions to produce an optimized film for each specific sputtering system. For example, for MoS_2 films sputtered in an MRC 8667 RF magnetron sputtering system in which the sputtering conditions were varied from 5 to 50 mtorr and the RF power from 150 to 1000 W, the optimum conditions of argon pressure of 20 mtorr and an RF power of 900 W were selected to produce the desired film density, stoichiometry, morphology, and adhesion. These optimized films displayed ultra-low friction coefficients on the order of 0.01 to 0.04 in a pin-on-disk tribotester under vacuum conditions.

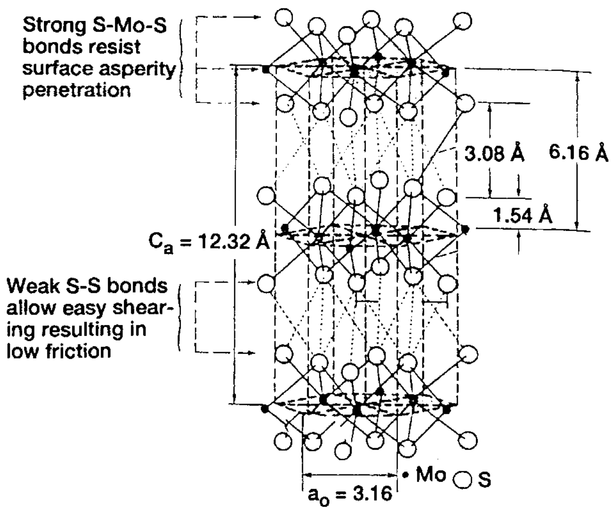

Fig. 3 Structure of MoS_2.

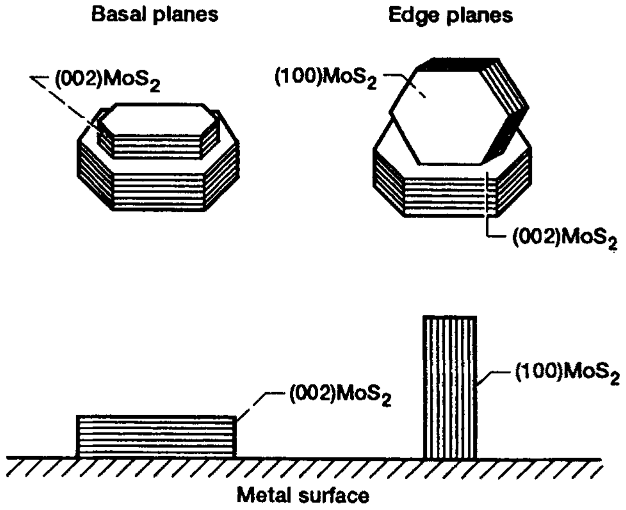

Fig. 4 Basic orientations of MoS_2 crystallites.

5. Characteristics of Sputtered MoS2 Films

Because very thin (0.2 to 0.6 μm) MoS_2 lubricating films are used for tribological control, it is important to understand the relationship between the sputtering conditions, the resultant film properties, and their friction and wear behavior. To obtain

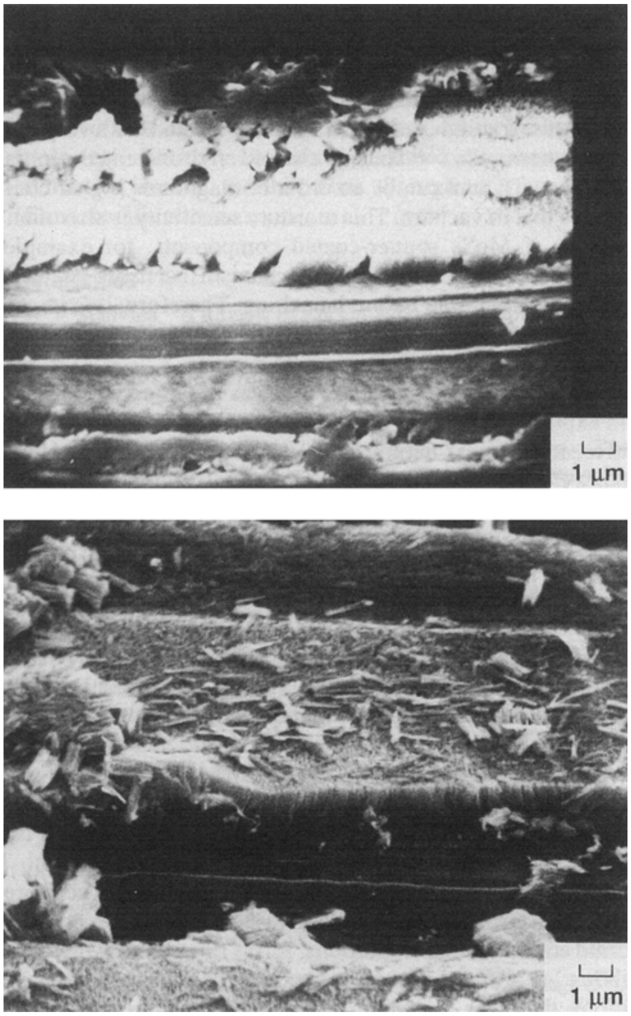

Fig. 5 Sputtered MoS_2 film after a single-pass sliding.

optimized sputtered MoS_2 films with ultra-low friction, it is essential to understand how adherence, structure, and chemical composition affect the friction and wear behavior.

5.1 *Adherence and Interface Modification*

Strong film adherence is the key to achieving extended endurance lives; therefore, the preparation of the substrate surface prior to film deposition has a major effect on the degree of adhesion. To some extent, it can also influence the nucleation and growth characteristics of the film, which determine the packing density of the columnar film structure. The most commonly used surface pretreatment prior to deposition is sputter-etch cleaning. This is accomplished by negatively biasing the substrate in the presence of the glow discharge for a preselected time. Sputtered MoS_2 films on 440C or 52100 bearing steel surfaces have been widely investigated, and these substrates display excellent adhesion.[6,7] The surface pretreatments that increase the density and chemical reactivity of nucleation sites on the substrate surface generally increase film-to-substrate adhesion. Many extensive studies are currently underway to investigate the interfacial modifications (chemical or mechanical bonding) that determine the degree of adherence.

A remarkable feature in interface modification has been observed by the deposition of thin (1000 Å) hard refractory compound layers such as Cr_3Si_2, BN, and TiN prior to the deposition of MoS_2 (Fig. 5).[8-11] The thin, hard interlayer serves to contour the surface asperities and acts as a barrier layer during asperity deformation. Thus, direct metal-to-metal contact, which leads to seizure, would be hindered. When used in rolling element contacts, these duplex films have shown a dramatic increase in endurance life. A feasible explanation of the improved endurance life may be attributed to the smaller Hertzian contact area as previously described. Similar benefit can be obtained by increasing surface hardness through case hardening (nitriding or carburizing), or by ion implantation with nitrogen or carbonaceous materials.

5.2 *Crystallinity/Orientation and Morphology*

The structure of sputtered MoS_2 films can change from crystalline to amorphous by simply changing the substrate temperature during sputtering. When MoS_2 is sputtered on cold substrates from 7 °C down to the cryogenic temperature of -195 °C, an amorphous structure is formed.[12] The amorphous films are very brittle and do not display any lubricating properties and are essentially abrasive. Most sputtered MoS_2 films deposited at ambient or elevated temperatures exhibit the characteristic columnar structure corresponding to crystallite growth, in which the low shear basal planes are aligned perpendicular to the substrate surface. The density of the columnar-type films is normally less than that of the original molybdenite, which is 4.8 g/cm^3.

Upon sliding, reorientation of the basal planes to a parallel alignment with the substrate occurs in the sliding direction. It is still unclear whether shear during sliding occurs between the basal planes within the crystallites or between the crystallites themselves. Previous studies[13,14] have shown that during sliding the columnar structure easily fractures and most of the film is worn away. Only a residual, adherent, coherent film on the order of 0.2 µm thick is left behind. This thin, residual film remaining after fracture determines the effectiveness of lubrication. Sputtered MoS_2 films have the tendency to fracture within the columnar region, as shown by the scanning electron micrographs (SEM) in Fig. 5. Because the film fracture occurs in the columnar region and generates undesirable wear debris, the film thickness during sputtering should be maintained in the thickness range before the distinct columnar structure forms. Also, the columnar structure contributes to accelerated oxidation when the films are exposed to or stored in humid air. To overcome the structural limitations (columnar growth and low density), numerous sputtering modifications have been and are presently being investigated to modify the film growth.

Most sputtered MoS_2 films with a columnar morphology are not fully dense, but exhibit various degrees of porosity. Typically used sputtering changes that modify the film behavior can yield higher film densifications and can be classified as follows: (1) low-pressure deposition, (2) ion beam bombardment during film growth, (3) co-sputtering with alloy dopants (Au or Ni), and (4) multilayer deposition. All of these techniques attempt to improve a film by modifying the film density, adhe-

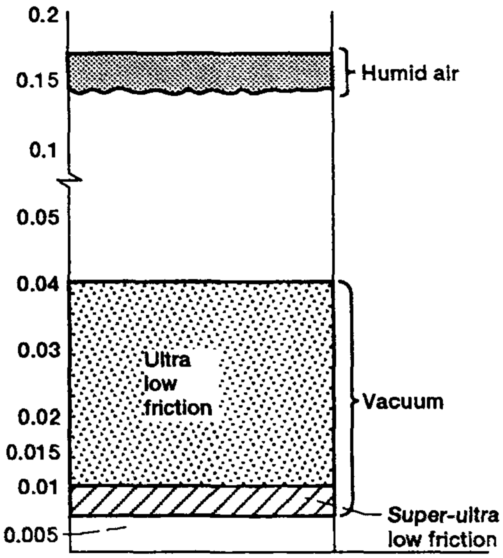

Fig. 6 Frictional variation of sputtered MoS_2 films.

sion, or structure and are used depending on the particular application.

5.3 *Stoichiometry*

Depending on the selection of the sputtering conditions, the stoichiometry of sputtered MoS_2 films can vary widely, from being sulfur deficient to sulfur rich (sulfur/molybdenum ratios from 1.1 to 2.2). It should be noted that the basic molybdenite structure prevails even for films with sulfur to molybdenum ratios as low as 1.1.[15]

Recent investigations have shown that the presence of small amounts of water vapor during sputtering can have major effects on the crystallinity/morphology and stoichiometry of the films.[16,17] MoS_2 films are highly sensitive to moisture and oxidize easily. Oxygen can be present in a variety of chemical states; however, oxidation products such as MoO_3, when formed, are detrimental to triboperformance, because it is an inferior lubricant. It has also been proposed that O can substitute for S, or it can even form a new phase $MoS_{2-x}O_x$.[18-20] Friction, however, is very sensitive to these stoichiometric changes. Most sputtered films when optimized for their tribological properties and used commercially are substoichiometric with the sulfur to molybdenum ratio of about 1.8.

6. Influence of Environmental Conditions

The environment has by far the greatest influence of the friction of sputtered MoS_2 films. Under vacuum conditions, optimized, sputtered MoS_2 films display ultra-low friction (Fig. 6). Optimized, sputtered MoS_2 films tested in vacuum generally fall into the friction range of 0.01 to 0.04, with very low wear and endurance lives of several million cycles.[21] The existing friction variation from 0.01 to 0.04 cannot be precisely explained; however, it has been observed that small amounts of oxygen incorporated into the film during sputter deposition, predominantly in the form of H_2O, can affect the chemical and structural properties of the film.

When films are friction tested in humid air (70% relative humidity), the friction coefficient starts at 0.15 and has a very limited endurance life.[22] Thus, in a humid environment, the initial friction coefficient can be an order of magnitude higher compared to that in vacuum. This moisture sensitivity is also of importance if MoS_2 sputter-coated components, for example, have been assembled in a space mechanism that has to be stored for an extended time before launching. Therefore, it is important to recognize that the storage should be in dry, inert gas or vacuum environment.

The anisotropic crystal structure, as previously discussed, can exhibit two types of crystallite orientation. As a result, the different chemical nature of the basal and edge sites of the planes contribute to the anisotropic gas adsorption-reaction behavior. The adsorption-reaction characteristics of water vapor are strongly affected by the particular crystallite orientation. The basal planes are basically inert to gas adsorption or chemical interaction, whereas their edge planes are chemically reactive to oxidation. As a result, the deterioration of MoS_2 films starts from the edge and progresses toward the center. This effect is accelerated if the MoS_2 films have a perpendicular orientation to the substrate and are maintained at a high relative humidity.

Because the edge sites readily oxidize, this contributes to the degradation of the lubricating properties of the film. Furthermore, the columnar-tapered crystallites do not have a full density structure, but contain longitudinal porosity, with a width of 100 Å between the tapered crystallites. Therefore, MoS_2 films should not be used in systems that are exposed to humid environmental conditions. MoS_2 films exhibit their best lubricating properties under vacuum or dry environmental conditions; therefore, they are of great interest and are the primary candidate materials for space tribology applications. These two crystallographic features of MoS_2—namely, the weak interlamellar bonding for easy shear and the anisotropic preferential crystallite gas adsorption—are the basis for the quality of MoS_2 lubrication.

7. Summary

In thin-film lubrication where films in the 0.2 to 0.6 µm range are used, it is important to understand the relationships between the sputtering conditions, the resultant film properties, and the friction and wear behavior. By optimizing the sputtering conditions (power input, chamber pressure, and substrate temperature), the resultant film properties, adherence, crystallinity/morphology, and stoichiometry can be achieved in their most desirable state, which is reflected in the tribological control in terms of friction, endurance, and wear debris formation.

MoS_2 is a layered material, whose crystallographic anisotropy controls both shear behavior and reactivity of the film to the environment. It has been shown that sputtered MoS_2 films can display ultra-low friction only when the sliding or rolling contact is performed in vacuum or in dry, inert gases. To obtain effective lubricious sputtered MoS_2 films, the sputtering conditions have to be optimized, because the resultant film properties are very dependent on the selected sputtering conditions. The three primary sputtered MoS_2 film properties—adhesion, chemical composition, and crystallite/morphological structure—are the dominant factors that affect the tribological behavior of endurance, friction, and wear debris generation, respectively. Current research is aimed at extending the endurance lives of the thin films through interface and bulk (film) modifications.

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