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Lubrication With Sputtered MoS_2 Films: Principles, Operation, Limitations

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LUBRICATION WITH SPUTTERED MoS_2 FILMS: PRINCIPLES, OPERATION, LIMITATIONS

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ABSTRACT

This paper 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.

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, 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 the above 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) which operate under high vacuum, high and low temperatures, and space radiation. These films are also used for terrestrial vacuum systems which house surface analytical instruments, thin film deposition devices and related instrumentation which 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 upon the sputtering conditions which in turn influence the film's microstructural properties such as crystallinity, morphology, and composition (Refs. 1-4). The objective of this review is to describe the current understanding of the process-property-performance interrelationships of sputtered MoS_2 films.

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 lubricant's shear strength, 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 it is the case with sputtered MoS_2 films, the load is supported primarily by the substrate. Increasing the substrate modulus, decreases the contact area for a given load as shown in Fig. 2 (Ref. 5). For low friction and acceptable wear life, the desirable film thickness has been found to be between 0.2 and 0.6 μm.

CRYSTAL STRUCTURE OF MoS_2

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 Mo atoms arranged in hexagonal array situated between two hexagonal layers of S 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 Mo and S atoms within the lamellae are covalent and, therefore, strong giving MoS_2 films 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. Further, 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 results in low friction.

CHARACTERISTICS OF SPUTTERED MoS_2 FILMS

Since 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 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.

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 most widely investigated, and these substrates display excellent adhesion (Refs. 6,7). Many extensive studies are currently underway to investigate the interfacial modifications (chemical or mechanical bonding) which 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_3Sri_2, BN, TiN prior to the deposition of MoS_2 (Fig. 5) (Refs. 8-11). 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 the surface hardness through case hardening (nitriding, carburizing) or by ion implantation with nitrogen or carbonaceous materials as shown in Fig. 5.

Crystallinity/Orientation, 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 (Ref. 12). These 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 as shown in Fig. 6. It is still unclear whether shear during sliding occurs between the basal planes within the crystallites or between the crystallites themselves. Previous studies (Refs. 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 in the order of 0.2 μm thick is left behind. This thin, residual film is essentially responsible for the lubrication. The film fracture mechanism is schematically illustrated in Fig. 7. The columnar morphology during sliding or rolling contact leads to film fracture and the formation of undesirable wear debris. 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 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 employed sputtering changes which 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) cosputtering with alloy dopants (Au, Ni) and (4) multilayer deposition. All of these techniques attempt to improve a film either by modifying the film density, adhesion or structure and are used depending upon the particular application.

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 (S/Mo ratios from 1.1 to 2.2). It should be noted that the basic molybdenite structure prevails even for films with S to Mo ratios as low as 1.1 (Ref. 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 (Refs. 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, since it is an inferior lubricant. It has been also proposed that "O" can substitute for "S" or it can even form a new phase $MoS_{2-x}O_x$ (Refs. 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 S to Mo ratio of about 1.8.

THE 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. 9). 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 (Ref. 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 (R.H. 70 percent) the friction coefficient starts at 0.15 and has a very limited endurance life (Ref. 22). Thus, in humid environment the initial friction coefficient can be a magnitude higher as compared in vacuum. This moisture sensitivity is also of importance if MoS_2 sputter-coated components for example, which have been assembled in a space mechanism which 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 start 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.

Since the edge sites readily oxidize this contributes to the degradation of the film's lubricating properties. Further, the columnar-tapered crystallites do not have a full density structure, but contain longitudinal porosity with 100 Å width between the tapered crystallites. Therefore, MoS_2 films should not be used in tribo-systems which 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.

SUMMARY REMARKS

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, substrate temperature) the resultant film properties adherence, crystallinity/

morphology and stoichiometry can be achieved in their most desirable state. Figure 8 summarizes sputtered film's properties as they affect 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 lubricous sputtered MoS_2 films, the sputtering conditions have to be optimized, since the resultant film properties are very dependent upon the selected sputtering conditions. The three primary sputtered MoS_2 film properties: adhesion, chemical composition, and crystallite/morphological structure are the dominant factors which affect the tribological behavior: 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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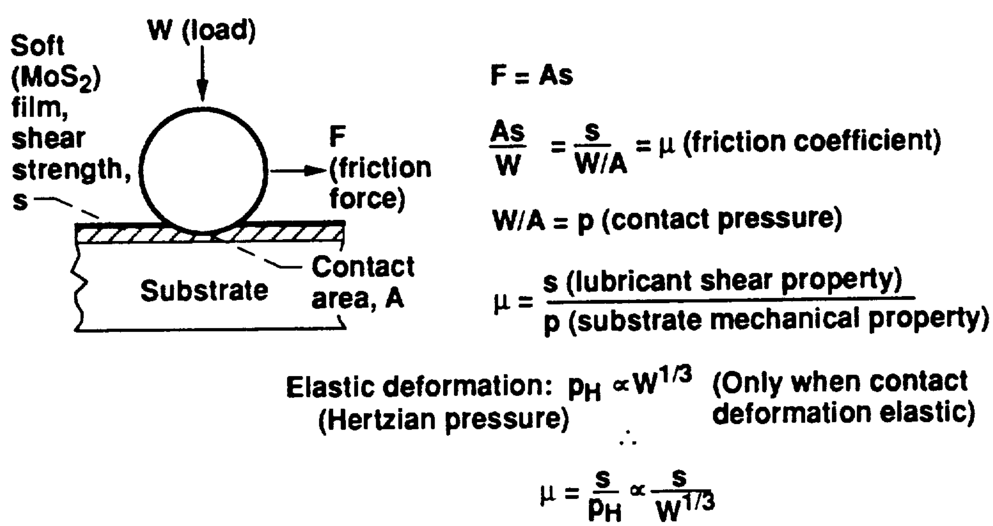

Figure 1.—Principles of solid film friction (lubrication).

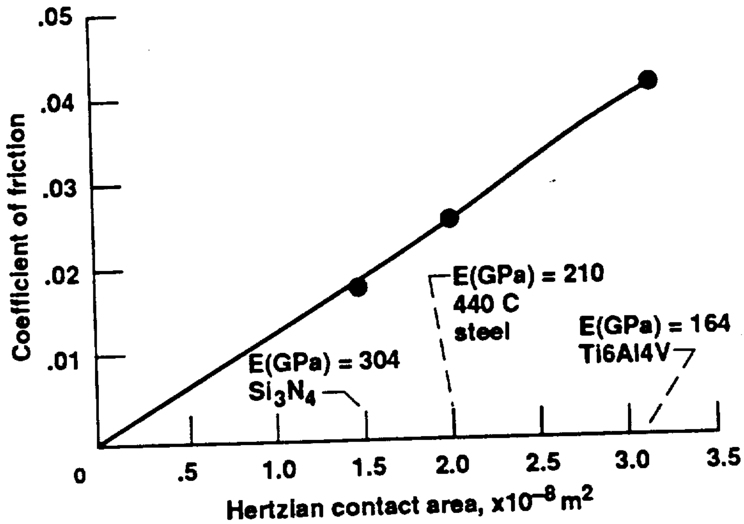

Figure 2.—Coefficient of friction as a function of contact area. Sputtered MoS_2 film.

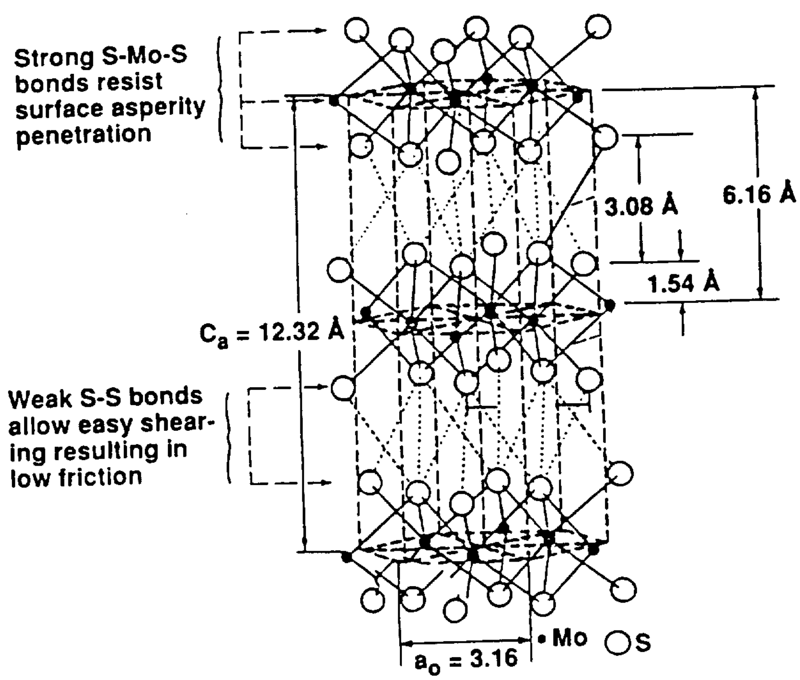

Figure 3.—Structure of MoS_2.

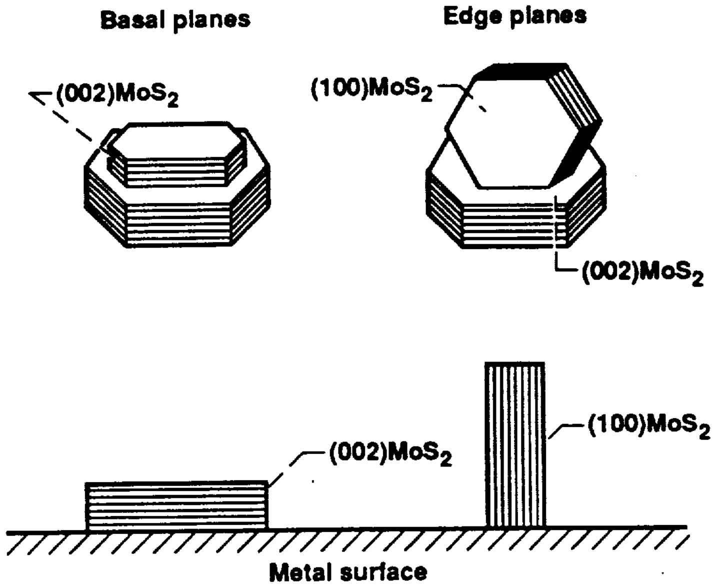

Figure 4.—Basic orientations of MoS_2 crystallites.

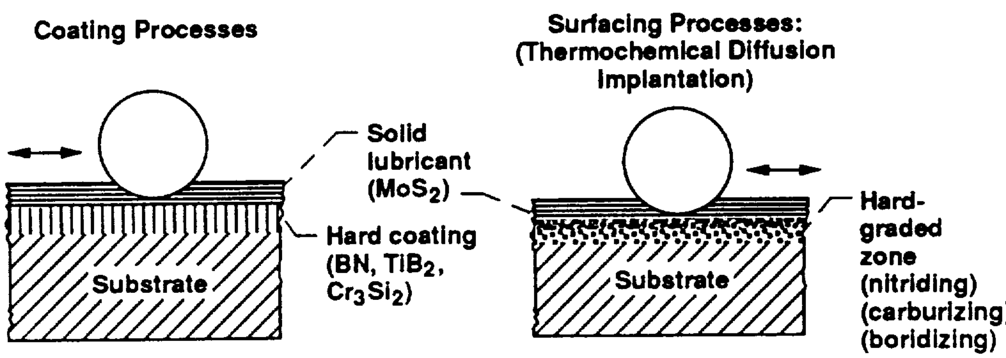

Figure 5.—Duplex surface modifications.

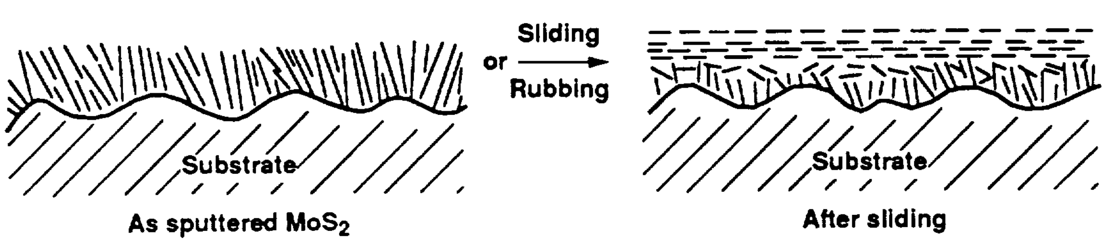

Figure 6.—Schematic of sputtered MoS_2 crystallite orientation before and after sliding.

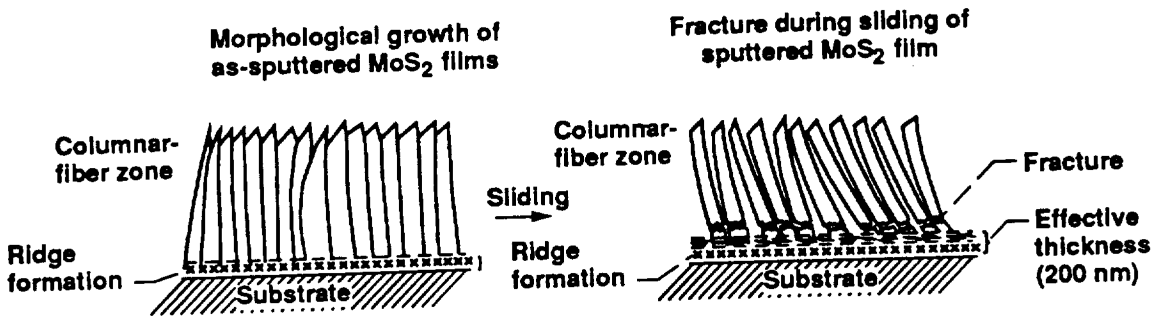

Figure 7.—Film structure before and during sliding.

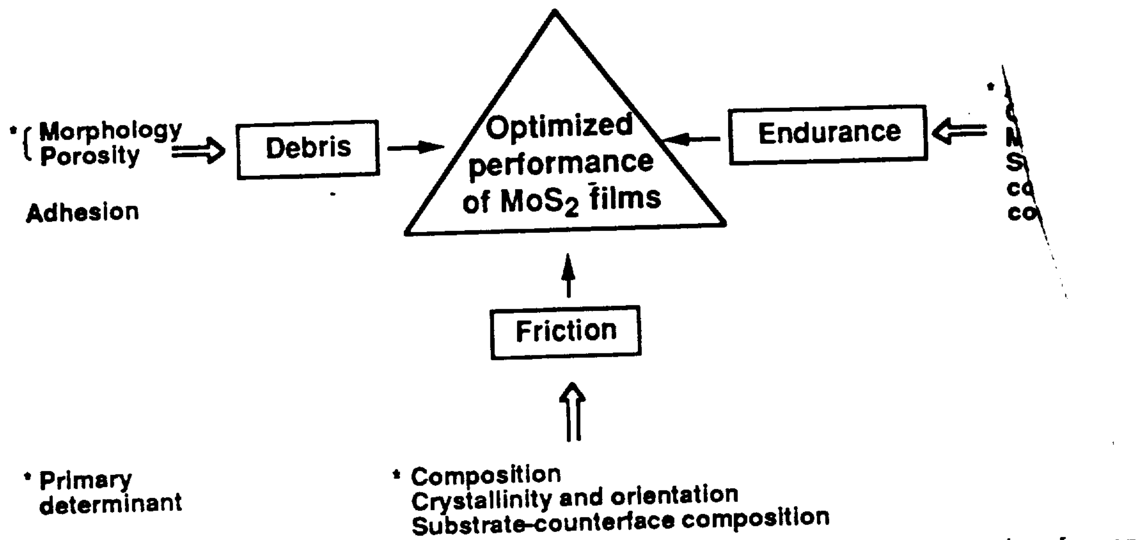

Figure 8.—Sputtered MoS2 film properties which determine the tribo-parameters and performanc

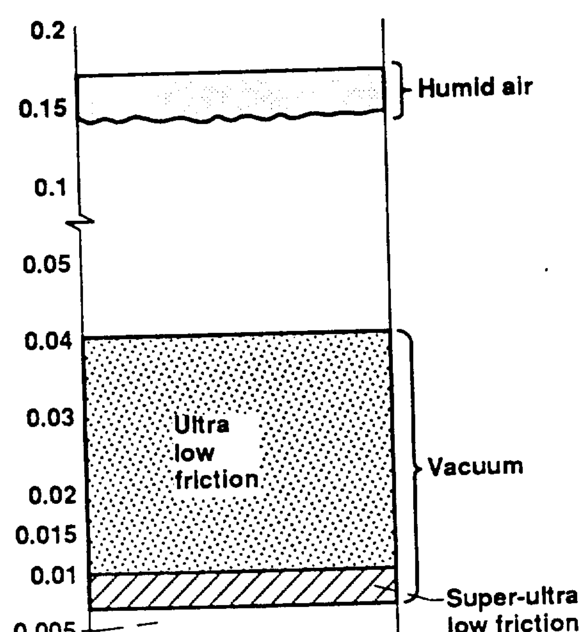

Figure 9.—Frictional variation of sputtered MoS_2 films.

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