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TRIBOLOGICAL PROPERTIES OF SPUTTERED MoS_2 FILMS IN RELATION TO FILM MORPHOLOGY

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TRIBOLOGICAL PROPERTIES OF SPUTTERED MoS_2 FILMS IN RELATION TO FILM MORPHOLOGY

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INTRODUCTION

It is well established that sputtered MoS_2 films (2000 - 6000 Å) have displayed excellent lubricating properties when used under sliding or rotating conditions in dry air, inert gas or in vacuum. The tribological properties such as the low coefficient of friction 0.04 and the long endurance lives (> million cycles) are directly influended by the sputtering parameters (rf power density, biasing, argon pressure, etc.) and substrate temperature, chemistry and topography. To obtain sputtered MoS_2 films which not only exhibit effective lubricating properties but also a high degree of reproducibility, it is of fundamental importance to properly select and precisely control sputtering parameters and substrate conditions.

Considerable progress has already been achieved as a result of studies of sputtered films deposited under various conditions (refs. 1-5). It is known, for example, that: (1) the substrate temperature strongly influences the crystalline-amorphous structure (refs. 6, 7), (2) biasing during sputtering depletes the sulfur concentration and changes the film's stoichiometry (refs. 2, 3), (3) composition of the substrate material such as copper or silver chemically reacts with the sulfur in the plasma and forms chemical compounds which display poor adherence (ref. 8), and (4) surface finish is responsible for defect growth features in the coating.

Since sputtered MoS_2 films are being more widely used for industrial applications and consequently finding more extensive uses to solve many practical lubrication problems, it is important to inspect and determine the integrity of the as-sputtered MoS_2 film. Inconsistent results in terms of the coefficient of friction and wear life can be avoided, if the as-sputtered MoS_2 film is screened by visual inspection and slight rubbing. This is of concern because the fact remains that sputtered MoS_2 films can exhibit a low coefficient of friction of 0.04 and effective lubrication. The friction coefficient can also be as high as 0.4 and act more like an abrasive if the sputtering parameters and substrate conditions are not properly selected and precisely controlled.

The objective of this paper is to correlate the morphological and compositional properties of sputtered MoS_2 films with the coefficient of friction and propose a visual screening for identifying the integrity of an effective lubricating film.

APPARATUS AND PROCEDURE

The sputtering apparatus used was an rf-diode system with a superimposed dc-bias which has been previously described (ref. 1).

The planar MoS_2 sputtering target was 12.7 cm-diameter and had a 75 percent theoretical density. Before sputter deposition the target was cleaned and outgassed by pre-sputtering until the pressure stabilized. Stable plasma conditions before sputter deposition have to be established. This can be detected by the color of the glow discharge.

The sputtering conditions were 3.5 w/cm^2, at a frequency of 13.56 MH_z, argon pressure 2×10^{-2} torr, and target to substrate distance of approximately 2.5 cm. The average sputtering rate of MoS_2 was about 250 Å/min. Before sputter depositing MoS_2, the substrate surfaces were sputter cleaned. In the case of 304 stainless steel the cleaning was continued for 10 minutes.

RESULTS AND DISCUSSION

Two requirements have to be met for sputtered MoS_2 film lubrication: (1) intercrystalline slip and, (2) adhesion to the substrate. The degree of adherence and the mode of the morphological nucleation and growth directly affect the quality of the sputtered film as a lubricant. Based on the selection of the substrate, the sputtered films can display excellent adherence. The real criterion of the lubricating properties of the film depends strongly on the morphology, grain size and their related distributions, and stoichiometry. Very precise control of the sputtering parameters and substrate condition is required to obtain high reproducibility. In many instances the integrity of the as-sputtered film can be easily identified by visual screening and gentle rubbing of the film as reflected by distinct color changes and the appearance of rub marks.

Substrate Temperature and Film Morphology

Variation of the substrate temperature during MoS_2 sputtering results in changes in the nucleation and growth characteristics as well as in particle size. The nucleation and growth characteristics in the temperature range of -195° to 320° C have been investigated by electron transmission micrographs and diffractograms and are summarized in Fig. 1. The substrate temperature had a profound effect on the film structure in the nucleation and growth stages. At cryogenic temperatures, the film was amorphous with a grain size about 10 Å while at the ambient and higher temperature it was crystalline with a particle size of 50 Å and increased to 110 Å at 320° C.

The substrate temperature above ambient temperatures did not affect the orientation perceptibly, only the diffraction patterns became sharper due to a larger grain size. The amorphous MoS_2 film has no lubricating characteristics, whereas the crystalline film is an effective lubricant with a low coefficient of friction. The transition region is not well established, and is not of any significant importance in practical lubrication. This region, depending on the substrate temperature, consists of the crystalline and amorphous states and the coefficient of friction responds to the volume of the crystalline and amorphous material present.

When the thickness of sputtered MoS_2 film is increased to a micrometer at ambient and at cryogenic temperatures and examined topographically and in cross sections by scanning electron microscopy (SEM), distinct differences in film morphology can be identified as shown in Fig. 2. The film sputtered at ambient temperatures has a typical "feathery" lamellar structure and is soft, whereas films sputtered at cryogenic temperatures have a highly dense structure and the film is hard and brittle.

Substrate Biasing and Film Stoichiometry

It has been established that the friction coefficient is very sensitive to the amount of bias applied to the substrate during MoS_2 sputter deposition. The friction coefficient of the film increases steeply with a bias over -150 v dc and the lubricating properties of the film are completely lost at a bias of -350 v dc as shown in Fig. 3. This increase in friction is due to the depletion of sulfur in the film. Since the composition of MoS_2 is strongly affected by bias voltage it is advisable to perform MoS_2 sputtering at zero bias voltage.

Screening of Surface Layers

The integrity of the as-sputtered MoS_2 film generally can be identified by visual appearance and gentle rubbing or wiping across the surface. Basically, an acceptable MoS_2 film as-sputtered displays a black-sooty surface appearance whereas an unacceptable film has a highly reflective mirror type surface. When the reflective surface is slightly wiped or rubbed unidirectionally no rub-marks are left since the film has lost its lubricating properties. However, upon wiping slightly with an absorbent cotton, the black-sooty surface displayed an immediate surface change in color. The color changes from black to grey and the wipe marks can be easily identified as shown in Fig. 4. It is interesting to note that after wiping across the film there is no residue left on the absorbent cotton. The color change occurs without tearing loose any of the surface platelets. The surface morphology of the as-sputtered black-sooty film, the same film after wiping, and the highly reflective non-lubricating film are shown by SEM micrographs in Fig. 5.

To identify the black-sooty surface layers Auger Electron Spectroscopy (AES) was used. This technique can detect all elements except hydrogen and helium and is sensitive to a depth of three to four atomic layers (5 to 6 Å). For reference purposes an Auger spectrum was obtained for the molybdenite MoS_2 crystal and is presented in Fig. 6. Two specimens, one as-sputtered MoS_2 black-sooty and a second one after rubbing, were installed in the spectrometer and their respective Auger spectra taken. In addition, each of the above films were also neon sputter cleaned for 15 seconds and their respective spectra again taken. The corresponding Auger spectra are shown in Fig. 7. The Mo and S Auger peaks of the sputtered MoS_2 film are identical to the original MoS_2 crystal. Consequently, no changes in film stoichiometry have occurred as a result of sputter deposition of the MoS_2 film. In addition, the as-sputtered MoS_2 film which gives an appearance of a black-sooty layer, and the gray surface appearance after wiping do not reveal any chemical changes when the two AES spectra are compared. The black-sooty appearance before wiping and the gray appearance after wiping are explained by stereo-micrographs. The black appearance is due to the crystallites growing on edge, with the basal planes perpendicular to the plane of the film. Upon slight rubbing these platelets easily reorient horizontally and the color changes from mat-black to a reflective gray. It has been observed that the sputtered MoS_2 films which display the black appearance exhibit effective lubricating properties. However, when the as-sputtered MoS_2 film has a highly reflective gray surface appearance the film is brittle and does not have the typical lamellar structure. As a result it does not exhibit acceptable lubricating properties.

A typical wear track for an effective lubricating sputtered MoS_2 film is shown in Fig. 8 after an incomplete first traverse. The plowed, displaced film ahead of the rider tends to agglomerate in a spherical build-up, possibly due to a polar nature of certain crystallographic faces.

SUMMARY OF RESULTS

The lubricating properties of sputtered MoS_2 films are strongly influenced by the sputtering parameters and substrate conditions.

The substrate temperature determines the particle size, resulting in a film which is crystalline having lubricating properties or one that is amorphous having no lubricating properties. Substrate biasing depletes the sulfur concentration in the film which also deteriorates the lubricating properties. Effective lubricating properties can be determined by visual screening and slight wiping of the film. A black sooty surface appearance displays excellent lubricating properties, whereas slightly reflective film with a gray surface has no lubricating properties.

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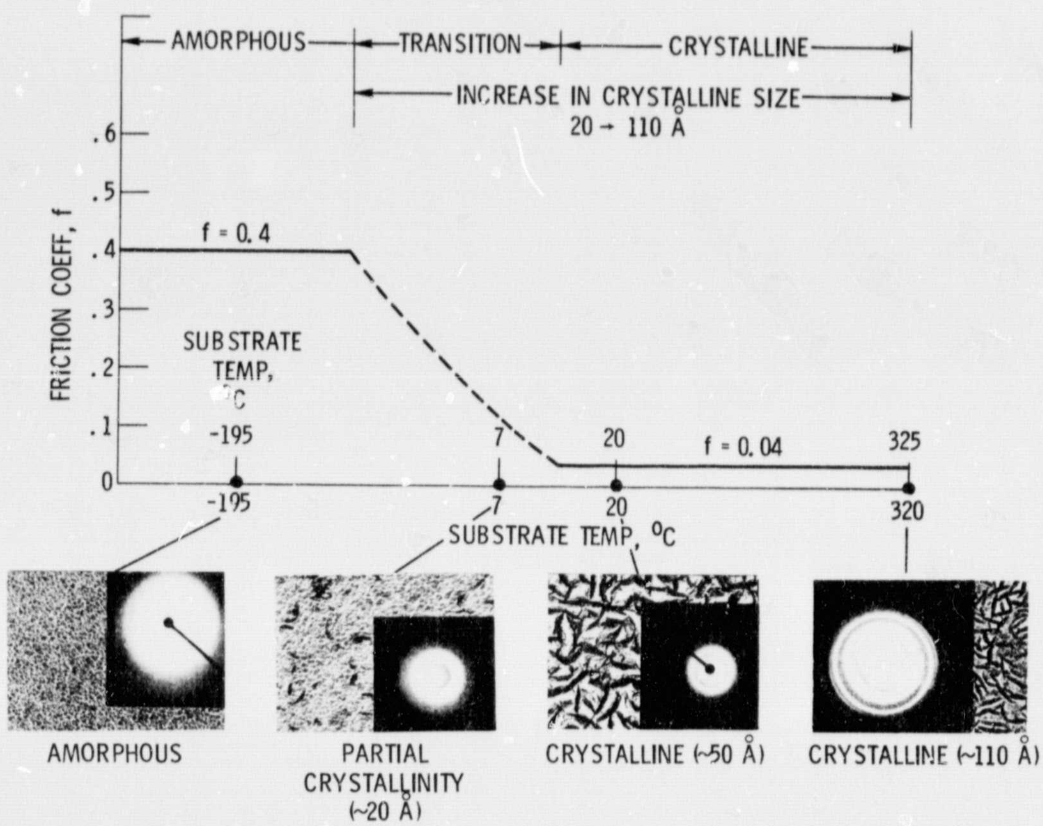
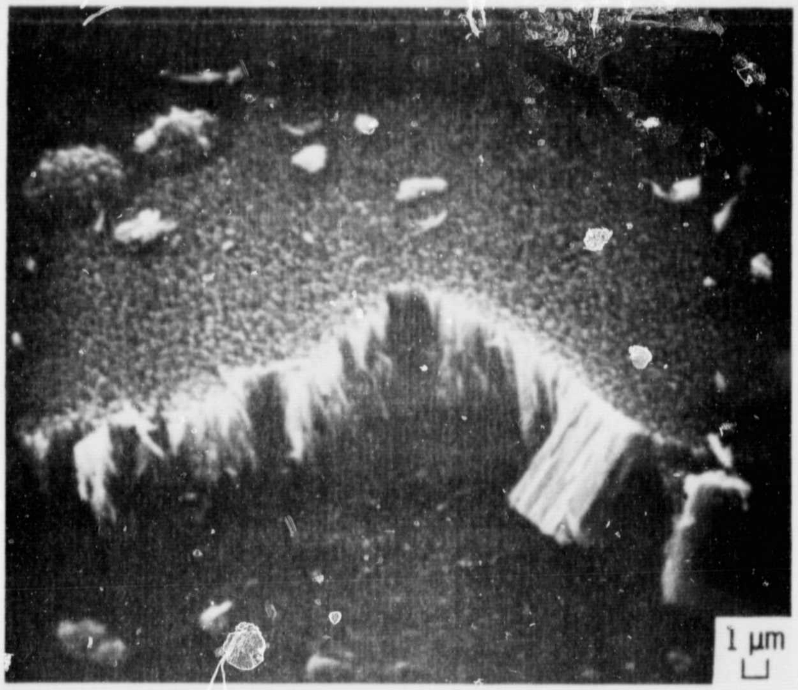


Figure 1. - Substrate temperature effects on MoS_2 film morphology and friction coefficient.



(a) AT AMBIENT TEMPERATURE.

(b) AT CRYOGENIC TEMPERATURE (-195° C).

Figure 2. - Surface and cross sectional structure of sputtered MoS_2 on steel.

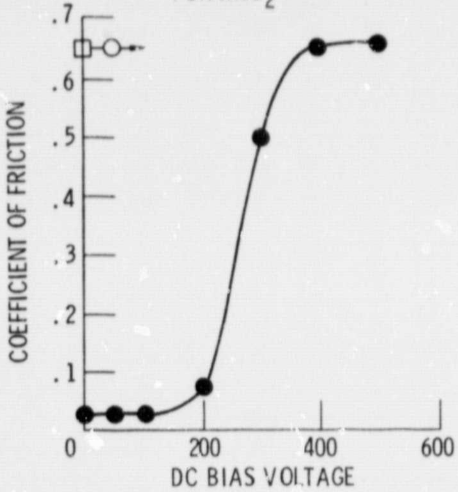


Figure 3. - Effect of negative DC bias on coefficient of sliding friction for sputtered MoS_2. Load, 250 grams; speed, 40 rpm; substrate/rider, 440C/440C at 1×10^{-3} torr.

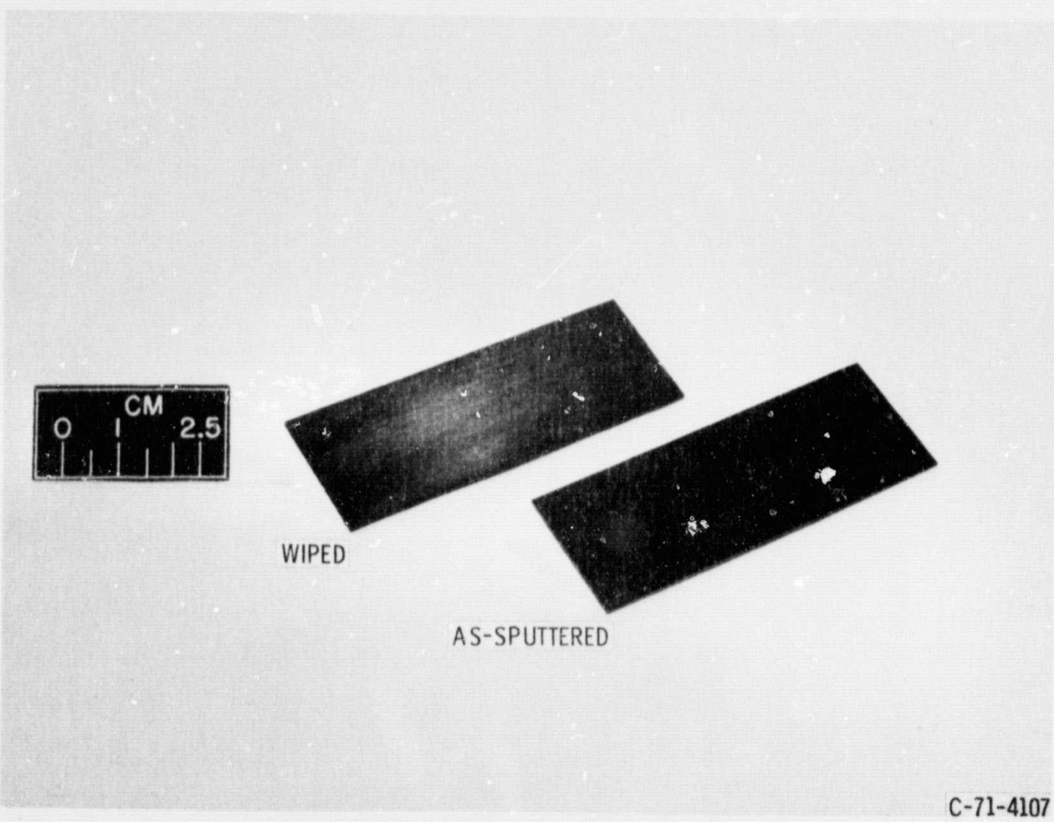
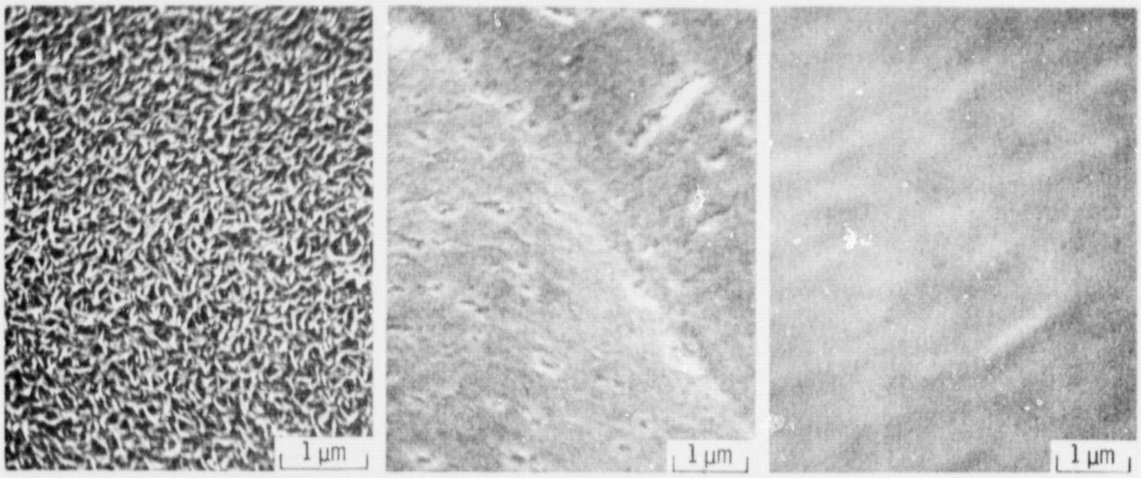


Figure 4. - Sputtered MoS_2 film on glass slides.



(a) AS SPUTTERED BLACK-SOOTY. (b) AFTER WIPING. (b) REFLECTIVE, GREY, NON-LUBRICATING.

Figure 5. - Surface layer morphology of sputtered MoS_2 films.

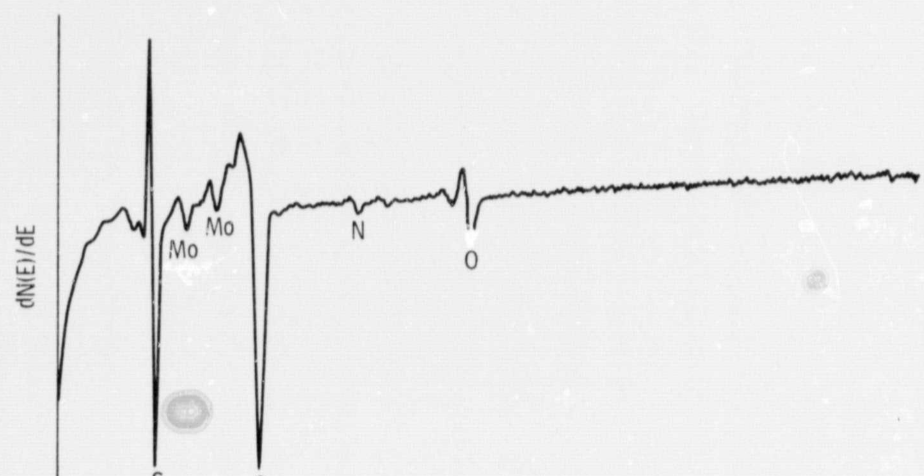


Figure 6. - Auger spectrum of MoS_2 molybdenite crystal.

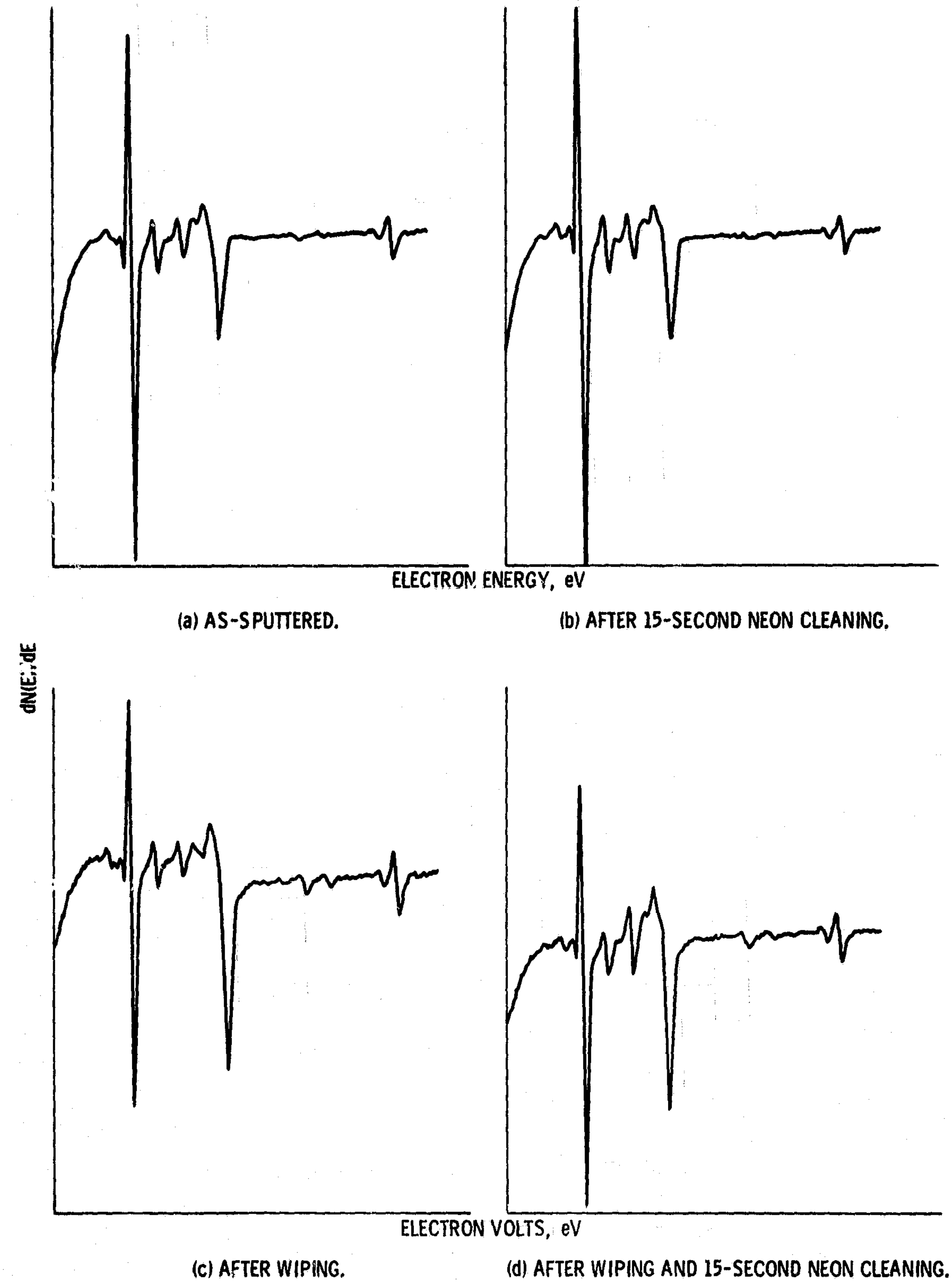


Figure 7. - Auger spectra of sputtered MoS_2 films.

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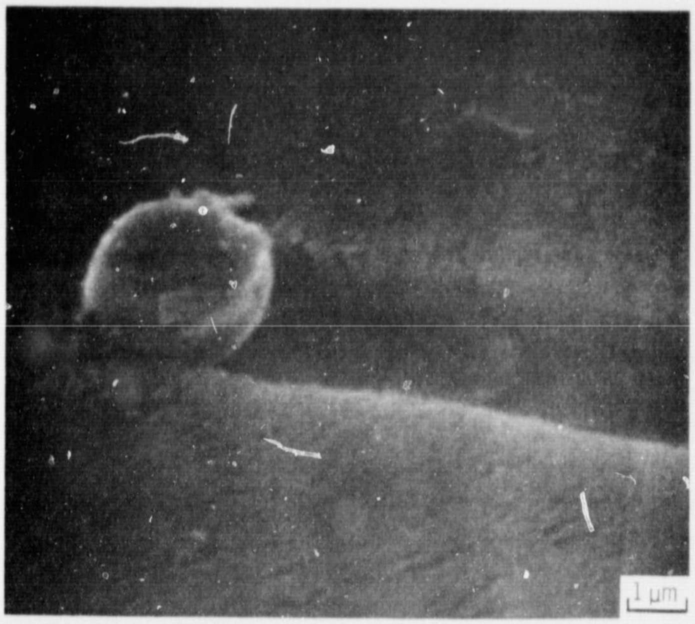

Figure 8. - Wear track and film displacement of a lubricating MoS_2 sputtered film.

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16. Abstract

Thin sputter deposited MoS_2 films in the 2000 to 6000 Å thickness range have shown excellent lubricating properties, when sputtering parameters and substrate conditions are properly selected and precisely controlled. The lubricating properties of sputtered MoS_2 films are strongly influenced by their crystalline-amorphous structure, morphology and composition. The coefficient of friction can range from 0.04 which is effective lubrication to 0.4 which reflects an absence of lubricating properties. Visual screening and slight wiping of the as-sputtered MoS_2 film can identify the integrity of the film. An acceptable film displays a black-sooty surface appearance whereas an unacceptable film has a highly reflective, gray surface and the film is hard and brittle.

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