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ABSTRACT

Sputtered MoS_2 films from 300 Å to 20,000 Å thick were deposited on metal and glass surfaces. The substrate effects such as surface temperature, finish, pretreatment and chemistry as they affect the film formation characteristics were investigated by optical, electron transmission, electron diffraction and scanning electron microscopy. Substrate temperature and surface chemistry were found to be the prime variables as to the formation of a crystalline or amorphous film. The friction characteristics are strictly influenced by the type of film formed. Surface chemistry and surface pretreatment account for compound formation and corresponding grain growth, which directly affect the adhesion characteristics, resulting in poor adherence. The type of surface finish (topography) as related to scratches, impurities, inhomogeneities, etc., are favorable nucleation sites for the growth of isolated and complex nodules within the film, and various complex surface overgrowths on the film. These nodular growth features have progressively more undesirable effects on the film behavior as the film thickness increases.

INTRODUCTION

Interrelation between film formation, structure and properties is strictly controlled by the parameters of sputter-deposition and the substrate conditions. The objective is always to obtain an adherent, coherent film with a homogeneous growth morphology. Factors which generally affect the film morphology during sputtering are the sputtering parameters (power input, argon pressure, etc.) and the substrate conditions (temperature, surface chemistry, surface finish, etc.).

Thin sputtered MoS_2 films (>2000 Å) generally exhibit superior lubricating properties in vacuum and dry air during the lubrication cycle in terms of low coefficients of friction, low wear and long endurance lives (ref. 1). However, in certain instances the same films have not fulfilled their expected goals. Some of the deficiencies can be eliminated by selecting the desirable sputtering parameters and the substrate conditions. The understanding of the reasons which contribute to the beneficial as well as the deleterious effects during the lubrication cycle can be established by evaluating the morphological growth of the film in terms of substrate temperature, surface chemistry, surface pretreatment, and surface finish. Recent studies of sputtered MoS_2 films show distinct morphological changes as affected by temperature (refs. 2, 3), surface chemistry (ref. 4), and surface finish. These morphological changes affect the lubricating properties of the film.

The objective of this paper is to illustrate and evaluate by optical, electron transmission, electron diffraction and scanning electron micrographs how change in substrate temperature, surface chemistry and surface topography affect the growth morphology of the sputtered MoS_2 films. The morphological growth pattern formed is directly responsible for the resultant properties of the lubricating film.

APPARATUS AND SPECIMEN PREPARATION

The sputtering apparatus used in these studies is an rf-diode mode with superimposed dc bias for sputter etching or biasing purposes. This apparatus has been previously described in reference 1. The sputtering parameters that were used in this investigation were the same as those used in all previous studies and are as follows: rf power density 3.5 w/cm^2 at a frequency of 7 MH$_z$, argon pressure 18x10^{-2} Torr, distance from substrate to target about 2.5 cm, the sputtering rate about 300 Å/min. The substrate surfaces were cleaned in all instances by sputter etching at -200 v dc for about 10 minutes prior to sputter deposition.

Substrates used for determining the temperature effects on MoS_2 film formation were aluminum foils. The substrate temperatures during MoS_2 sputtering were kept at 320°C, 150°C, at ambient, at cold water temperature (7°C), and at liquid-nitrogen temperature (-195°C). The metal foils were placed on a stainless steel stage and the heating was performed by direct current ion bombardment until the desired temperature was reached. During the heating process, a shutter was positioned between the target and the substrate. The substrate temperature was monitored by a chromel-alumel thermocouple. During cold water and cryogenic cooling, the corresponding liquids were circulated continuously through the substrate stage. In all instances the average sputtering rate was 300 Å/min. For electron transmission microscopy and electron diffraction, the film was removed by dissolving the substrates in suitable solutions.

The substrates used for the investigation of chemical effects on MoS_2 film formation were copper, silver, gold and bronze circular disks.

In one instance MoS_2 was sputtered directly on highly polished single crystals of copper, silver and gold. The surfaces were mechanically polished and sputter etched before MoS_2 sputter-deposition.

Specimens which were utilized for determining the topographical effects on sputtered MoS_2 film formation were 304 stainless steel sheets (2.2x0.25 cm) with 2 types of surface finishes and microscopic glass slides. The surface finishes for 304 stainless steel were: 1) ground on a 600 grit energy paper with a resultant surface finish of 22.5×10^{-2} µm and 2) lapped on a polishing wheel with a resultant surface finish of 5×10^{-2} µm. Prior to sputter deposition, all metal surfaces were cleaned by dc-sputter etching. The coating thickness was maintained at about 2.5 µm.

RESULTS AND DISCUSSION

Substrate Temperature Effects on Sputtered MoS_2 Film Formation

Preliminary studies of substrate temperature effects on the initial film formation (nucleation) of sputtered MoS_2 have been reported (ref. 2). Additional studies were pursued of sputtering MoS_2 films 300-400 Å thick onto aluminum foils in the temperature range from liquid nitrogen -195°C to 320°C to determine the change in particle size.

The previous and new results are illustrated by micrographs and diffractograms in Figures 1, 2, 3 and 4. Molybdenum disulfide films sputtered on aluminum at liquid nitrogen temperatures (-195°C) in Figure 1 show a homogeneous structure and are characterized by broad, diffuse diffraction rings which indicate an amorphous structure. Figure 2 shows a micrograph and a diffractogram where MoS_2 was sputtered on aluminum at cold water temperature about 7°C. At this temperature, the formation of a few dispersed ridges are starting to appear in the matrix. The corresponding diffractogram has still a diffused ring structure. The mean particle size was estimated to be about 20 Å.

At ambient sputtering temperatures (no external cooling or heating) distinct ridge formation is observed in the matrix film and the diffractogram is characterized by sharp diffraction rings as shown in Figure 3. The mean particle size was estimated to be about 50 Å. When MoS_2 was sputtered on aluminum which was preheated to 320°C, pronounced ridge formation is again observed and the diffractograms have sharp diffraction rings. The mean particle size was about 110 Å. The increased surface temperature gave rise to a further increase in particle size.

The micrographs indicate a threshold temperature of about 7°C. Below the threshold temperature the film is continuous and amorphous, above the threshold temperature ridges are formed in the matrix (nucleation) and the film has a crystalline structure. The substrate temperature controls the surface mobility and growth of the sputtered species and determines thereby the degree of disorder of the growing film. At the cryogenic temperatures, the surface mobility of the sputtered species is retarded since these temperatures have essentially a severe quenching affect on the sputtered material. As a consequence, continuous, amorphous films are formed during the initial nucleation stages.

At substrate temperatures above 7°C, pronounced ridge formation is observed with an increase in particle size. In essence, nucleation theory states that a substrate surface has barriers to the condensation of a permanent film. If there are nucleation barriers, the film will show an island (ridge) structure in the initial stages of growth. With increasing substrate temperatures, above the threshold temperature, structural reordering occurs by forming a network of ridges which are essentially build-ups of preferentially agglomerated sputtered particles.

These morphological changes observed during the early stages of sputtered MoS_2 film growth have very pronounced affects when these films >2000 Å thick are tested in friction experiments as shown by the corresponding friction curves in figure 5. MoS_2 sputtered on metal surfaces at ambient and elevated temperatures formed a soft, gray, "greasy" film and this film exhibited good lubricating properties, gave a low coefficient of friction 0.04 and long endurance lives over 250,000 million cycles. MoS_2 sputtered on metal surfaces at cryogenic temperatures formed a hard, brittle, shiny film. When this film was friction tested, it acted like an abrasive starting with coefficient of friction of 0.4 and did not display any lubricating properties.

Chemical Effects on Sputtered MoS_2 Film Formation

MoS_2 was sputtered onto a set of highly polished, single crystal surfaces of copper, silver and gold. The results on these surfaces are shown in figure 6. Film flaking and peeling occurred on copper and silver surfaces, but there was a strong adherence to the gold surface.

In the following discussion all substrates used such as copper, silver, gold and bronze were polycrystalline. The surface preparation was either by mechanical polishing or sputter etching. When MoS_2 was sputtered on a polished copper surface, figure 7 shows the sulfur reaction islands in the initial stages of film formation. With further MoS_2 sputtering, as the film thickness increases isolated film reaction islands which have lifted from the surface, tend to interact by joining, and finally complete film lifting occurs. Similar effects were also observed with silver and bronze surfaces.

Electron transmission micrograms and diffractograms were taken of 300-500 Å thick films which were sputtered on copper foils as shown in figure 8. The large, white areas in the micrographs are voids where particles or grains of copper-sulfide or copper-molybdenum sulfide reaction compounds were leached out during the dissolution of the copper substrate. The leached out grains can be distinctly identified. The crystallite size of the MoS_2 reaction product becomes apparent, measuring between 100-200 Å. The diffractogram shows distinct, sharp diffraction rings. MoS_2 sputtered under the same conditions on steel, nickel and glass surfaces had a mean particle size of about 50 Å.

The sputtered, flakey MoS_2 films on copper and silver surfaces, and the adherent MoS_2 films on gold surfaces were analyzed by energy dispersive X-ray analysis. X-ray spectrum of the flakey MoS_2 film showed pronounced peaks due to the presence of copper and silver, respectively. The adherent MoS_2 film on gold surfaces when examined showed no gold peaks. This analysis indicates that a chemical reaction has occurred between the flakey MoS_2 film and the copper and silver surfaces. This analysis also complements the observation in the electron micrographs that copper-sulfur and silver-sulfur compounds are formed during the sputtering process. The exact sulfides formed were not identified.

It is generally agreed that during sputtering the sputtered material is in a highly energetic state and is very prone to chemical reaction and adsorption, which normally leads to increased adherence to substrate. It should be remembered that during sputtering of MoS_2 the film is believed to be deposited in the atomic state. The energetic sputtered atoms (sulfur) which strike the substrate with high velocity have a certain activation energy for reacting with the substrate. However, in the above cases the generally considered favorable energetic effects proved to be detrimental for film adherence.

When MoS_2 films are deposited, the selection of the substrate material becomes of paramount importance. When copper and bronze surfaces were specially oxidized to form an oxide film 1200 to 1500 Å thick, and subsequently sputtered with MoS_2 film a strong adherence was formed. It is believed that the oxide film was thick enough to function as a barrier to prevent sulfide formation on the copper or bronze surfaces.

Topographical Effects on Sputtered MoS_2 Film Formation

Various unusual crystallographic defect growth features are formed in the matrix of the sputtered MoS_2 films. The most commonly observed features are those of the nodular growth. These nodules can grow individually, together, or overlap forming complex aggregates. Also, extreme, complex surface overgrowths can be formed.

The scanning electron micrographs in figures 9, 10, 11 and 12 show randomly selected surface sites with the defect growth structures. The MoS_2 films investigated were about 2.5 μm thick sputtered on 304 stainless steel surfaces and also on microscopic glass slides. Figure 9 shows a surface view of sputtered MoS_2 on stainless steel surface with surface finish of 22.5×10^{-2} μm. As shown, nodules have the tendency to grow preferentially in high concentrations along the edge boundaries of polishing marks. A high degree of overlapping and fusion of these nodules are seen in figure 9. Previous studies (refs. 5, 6) with sputtered metal and alloy films showed similar effects. Surface topographical effects as related to surface scratches, inhomogeneities, impurities, etc., are favorable nucleation sites for the growth of isolated or fused nodules and extreme surface overgrowths.

Surface irregularities or imperfections are the high points with a high energy concentration for preferential nucleation and growth. At these points an accelerated growth occurs relative to the matrix growth; as a consequence the crystallographic defect features extend above the matrix surface. Figure 10 shows a randomly selected site of individual and overlapping nodules on a highly polished stainless steel surface ($5 \times 10^{-2} \mu m$).

A typical surface morphology of the nodule is seen at a higher magnification in figure 11, with a pronounced "feathery" lamella-like structure. The nodular growth or cone type structures shown above are predominantly a result of outward growth. Surface irregularities such as scratches, ridges or steps seem to lead to a nodular growth of the typical parabolic (conical) type. The exact configuration and dimensions of the nodules, whether they are individual, fused, overlapping, etc., depend on the size and spacing of the various nucleation sites. The above micrographs show a distinct separation or mismatch boundaries between the nodules and the matrix. These distinct boundaries are the weakest areas in the film and will have a tendency to break around the nodule edges. As a result, the nodule can simply be ejected from its place and leave an empty cavity as shown in figure 12. It is important to recognize that the diameter of these nodules increases as the film thickness increases. As a result, larger diameter cavities in the film can be expected. A high concentration of these cavities creates porosity and eventually weakening of the film structure.

On the other hand, it was observed that surface impurities, inclusions or other foreign matter (possibly from grinding or polishing) settled on the surface may also lead to extreme localized surface outgrowths of unusual geometrical configurations as seen in figure 13. These crystallographic structures generally have a lateral growth in nature and they stretch over the surface. These features are very weakly bonded in the matrix and they have a tendency to fall out especially under stress conditions.

SUMMARY OF RESULTS

The morphological growth of sputtered MoS_2 films as evaluated by electron transmission, scanning electron micrographs and electron diffractograms revealed the following results:

1. The particle size and the initial growth (nucleation) of 300-400 Å thick MoS_2 films depend on the substrate temperature.

2. A threshold substrate temperature at about 7°C was determined. Below 7°C the particle size is amorphous and film morphology is continuous. Above 7°C the particle size increases to a crystalline structure and pronounced ridge formation (nucleation) is obserbed.

3. MoS_2 films with crystalline structure have good lubricating properties. Films with amorphous structure act like abrasives.

4. Sputtered MoS_2 had poor adherence on copper, silver and bronze surfaces.

5. Sputtered sulfur reacts with copper, silver and bronze surfaces forming the corresponding sulfides, which contribute to poor film adherence.

6. Sputtered MoS_2 had strong adherence to a go.. substrate.

7. Surface defects such as surface irregularities and contaminants are responsible for nodular and extreme surface outgrowths in the film matrix.

8. Crystallographic defect growth features are loosely bonded in the film matrix, thus creating porosity in the film when ejected.

9. Crystallographic defect features can be eliminated by perfection of the surface finish.

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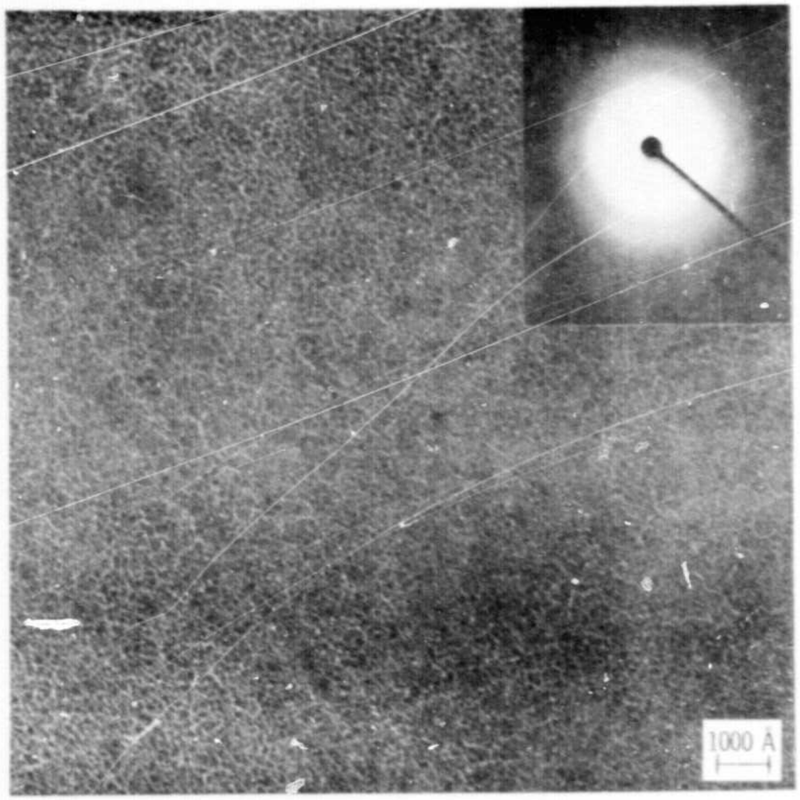

Figure 1. - Electron transmission micrograph and diffractogram of sputtered MoS_2 on aluminum at -195° C.

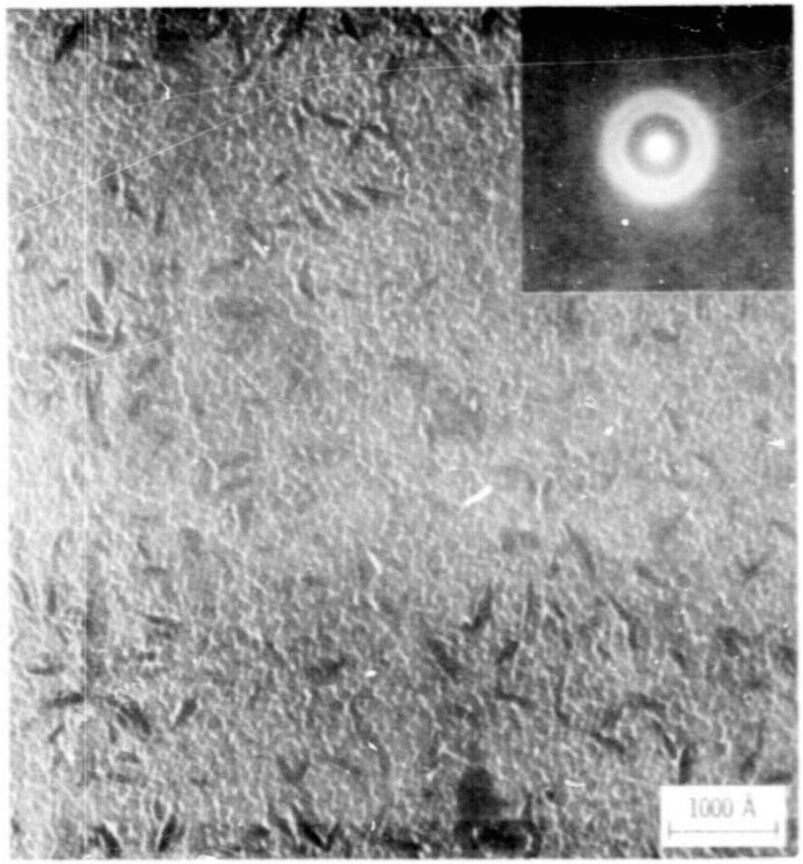

Figure 2. - Electron transmission micrograph and diffractogram of sputtered MoS_2 on aluminum at 7° C.

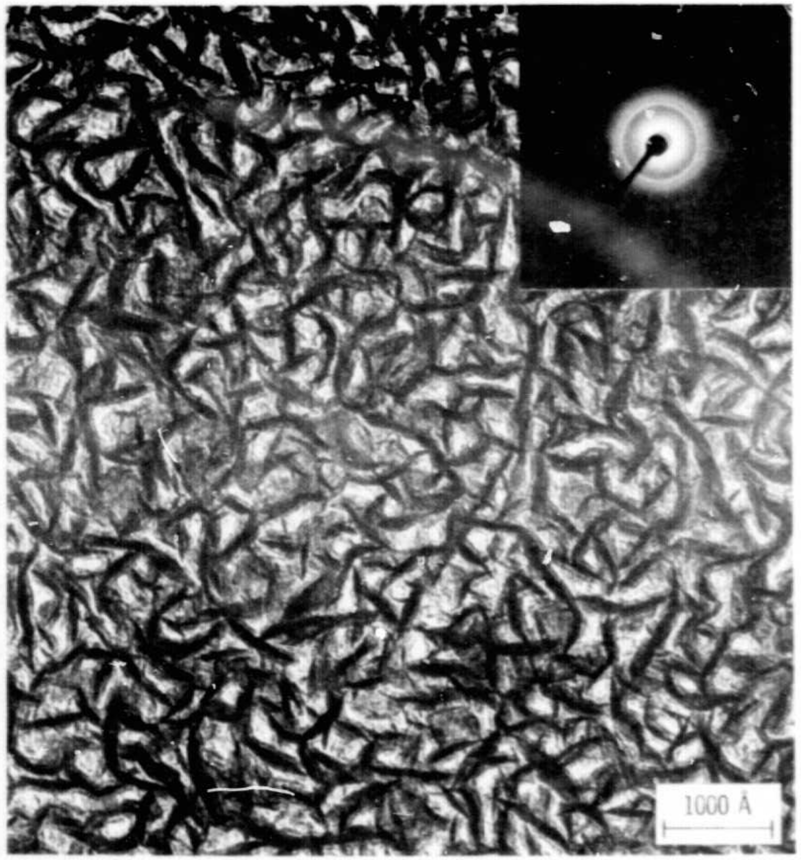

Figure 3. - Electron transmission micrograph and diffractogram of sputtered MoS_2 on aluminum at ambient temperature.

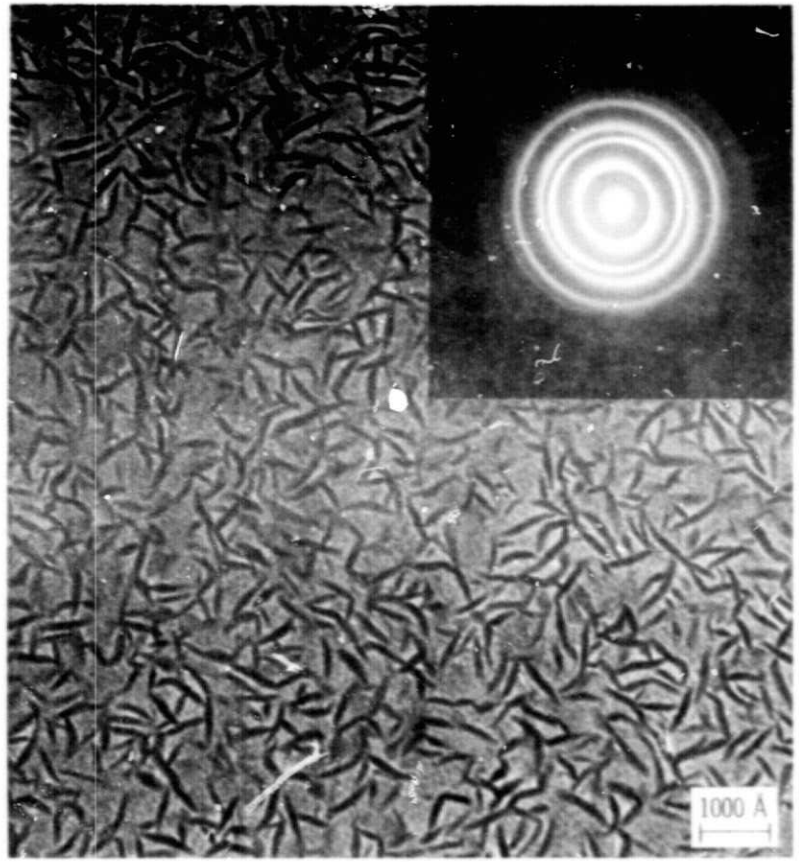

Figure 4. - Electron transmission micrograph and diffractogram of sputtered MoS_2 on aluminum at 320^0 C.

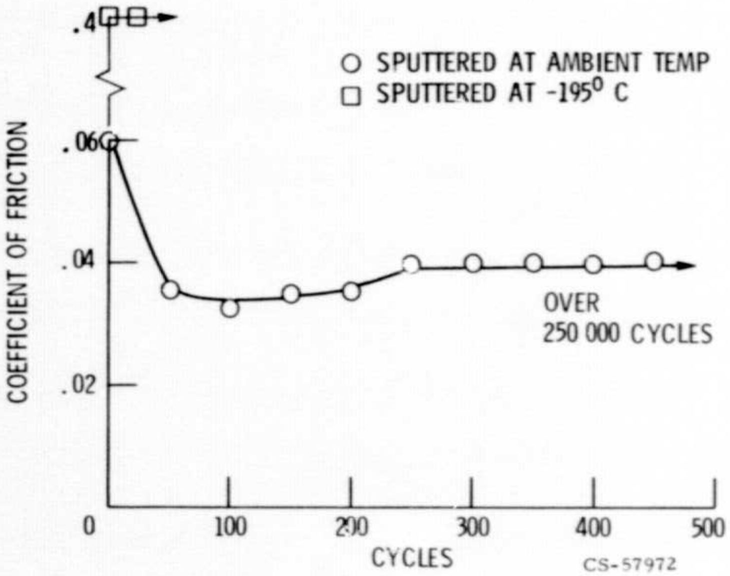

Figure 5. - Initial coefficient of friction of 440 C rider sliding on 440 C disk coated with rf sputtered MoS_2 (2000 Å) in vacuum (10^{-9} torr); load, 250 gms; speed 50 rpm, at ambient temperature.

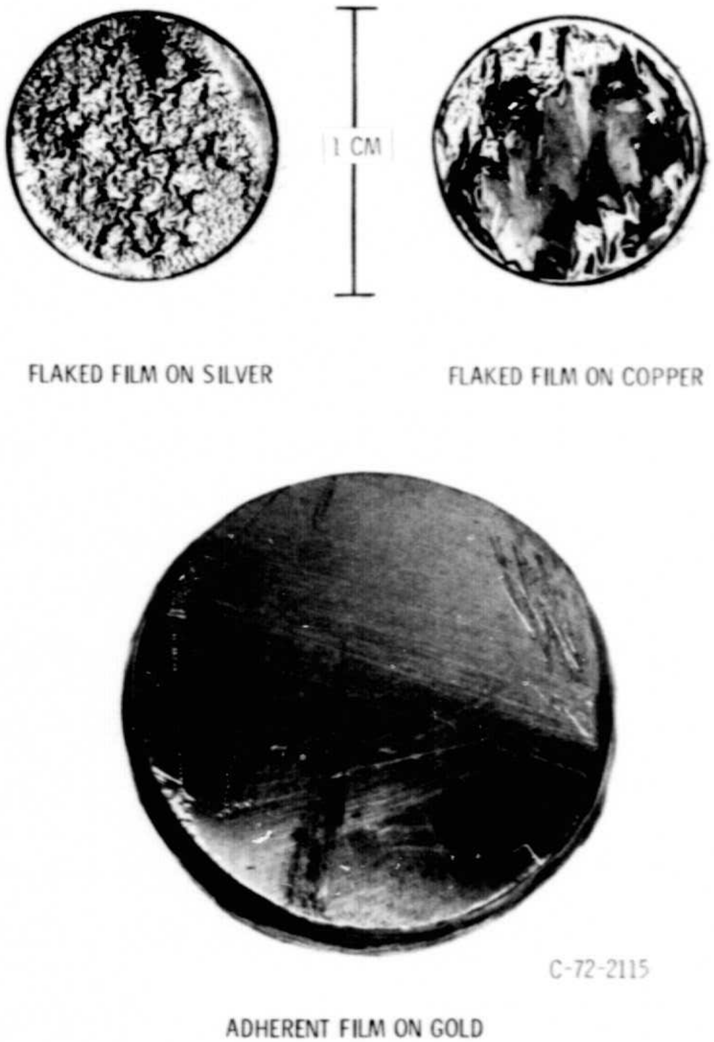

Figure 6. - Sputtered molybdenum disulfide film on single crystals of silver, copper, and gold.

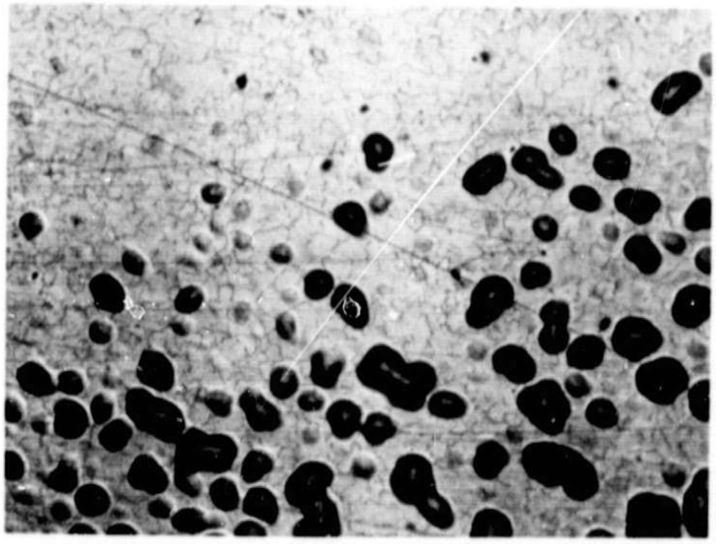

Figure 7. - Sputtered molybdenum disulfide on polycrystalline copper in the initial state of film formation. X80.

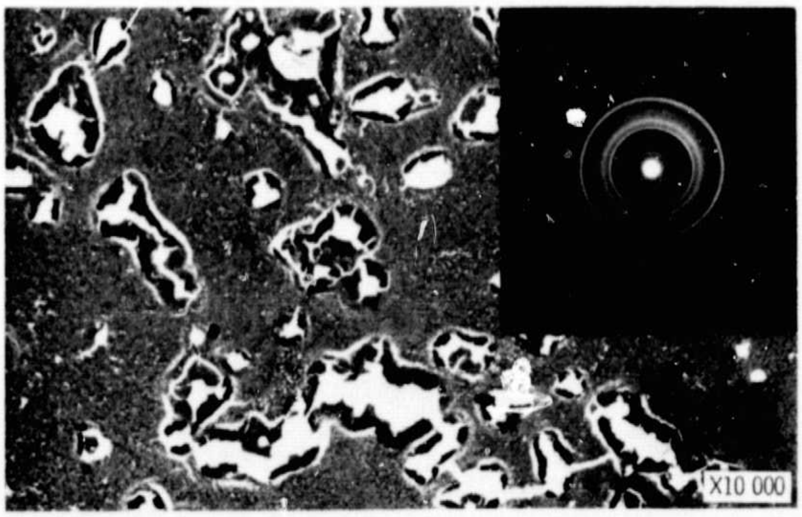

Figure 8. - Electron transmission micrograph and diffractogram of sputtered molybdenum disulfide on copper.

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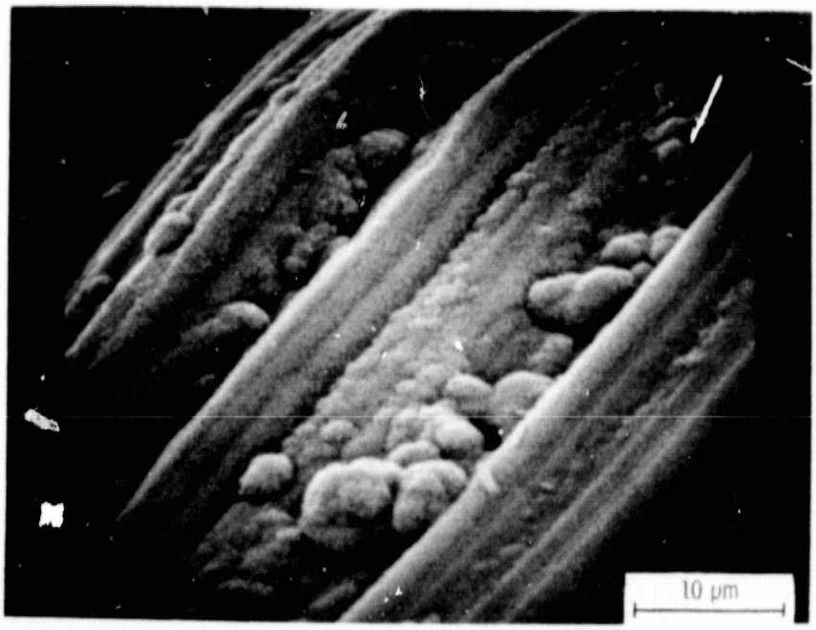

Figure 9. - Surface of sputtered MoS_2 on 304 stainless steel sanded to 22.5×10^{-2} μm finish.

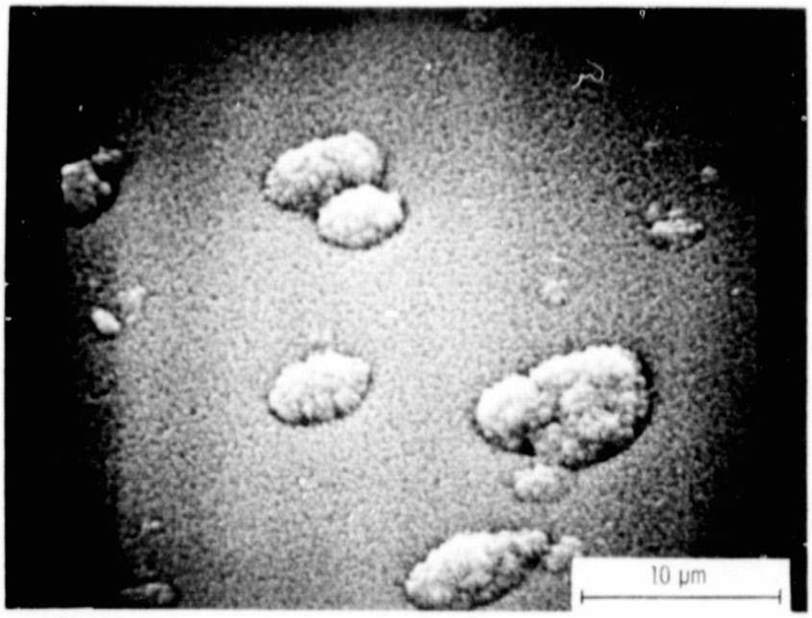

Figure 10. - Surface structure of sputtered MoS_2 on glass.

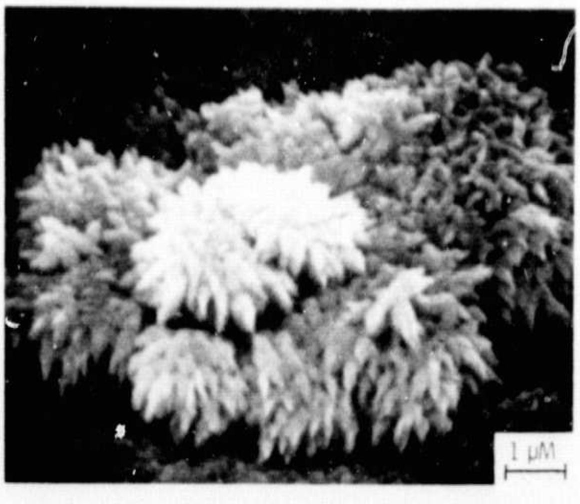

Figure 11. - Surface structure of a nodule of sputtered MoS_2 on 304 stainless steel with $5x10^{-2}$ μm finish.

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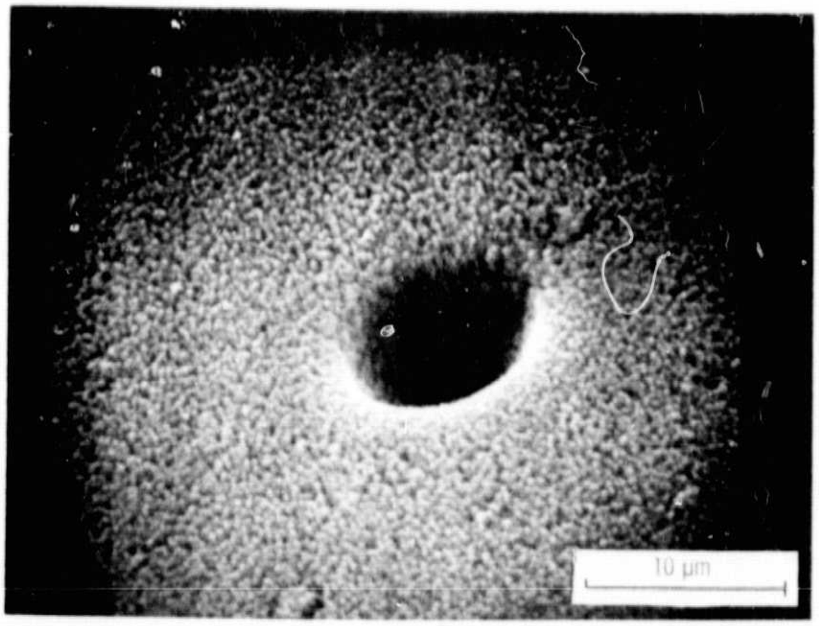

Figure 12. - Cavity on sputtered MoS_2 left by ejected nodule.

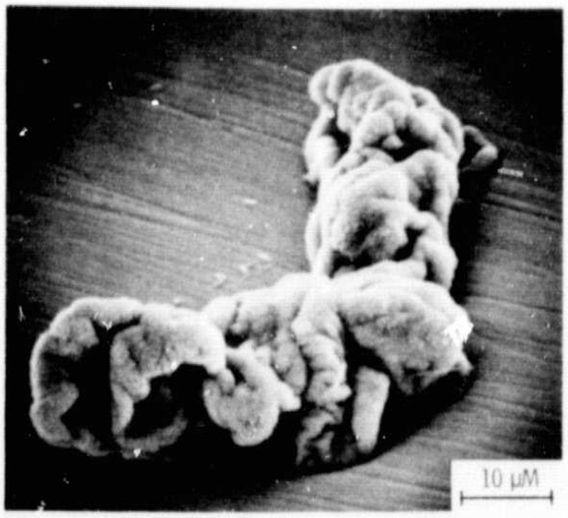

Figure 13. - Extreme surface outgrowths in sputtered MoS_2 on 304 stainless steel with $5x10^{-2}$ μm finish.