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STRUCTURE OF MOLYBDENUM DISULFIDE FILMS SPUTTERED ON SUBSTRATES AT VARIOUS TEMPERATURES

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16. Abstract

Molybdenum disulfide films (30 to 40 nm (300 to 400 Å)) thick were rf sputtered on aluminum and nickel surfaces at elevated, ambient, and liquid nitrogen temperatures. Electron transmission micrographs and electron diffraction patterns were taken to determine the structural growth. These transmission micrographs revealed that sputtered MoS_2 films at ambient and elevated temperatures (320° and 150° C) formed an irregular network of ridges. The electron diffraction patterns of these films showed relatively sharp diffraction rings, indicating crystallinity. The transmission micrographs of sputtered films at liquid nitrogen temperatures revealed a continuous featureless film. The electron diffraction patterns showed broad, diffused rings indicating an amorphous film. The transmission micrographs of a post-annealed (425° C) MoS_2 film sputtered at liquid-nitrogen temperature revealed the tendency for ridge formation. Electron diffraction patterns also showed increased sharpness of the diffraction rings. Friction tests showed that MoS_2 films deposited at ambient and elevated temperatures exhibited good lubricating properties. The MoS_2 films deposited at cryogenic temperatures had no lubricating characteristics.

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STRUCTURE OF MOLYBDENUM DISULFIDE FILMS SPUTTERED ON SUBSTRATES AT VARIOUS TEMPERATURES

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SUMMARY

A sputtered molybdenum disulfide (MoS_2) film (30 to 40 nm (300 to 400 Å)) thick was applied to aluminum and nickel surfaces at elevated, ambient, and liquid-nitrogen temperatures. These films were examined for structural growth by electron transmission microscopy and electron diffraction. Molybdenum disulfide films sputtered at ambient or elevated temperatures (320° and 150° C) revealed an irregular network of ridges by transmission micrographs. Electron diffraction patterns of these films showed relatively sharp diffraction rings, indicating film crystallinity. The MoS_2 films sputtered at liquid-nitrogen temperature revealed a continuous, featureless film. The electron diffraction patterns showed broad, diffuse rings indicating an amorphous film. The MoS_2 films that were sputtered at liquid-nitrogen temperature and afterwards post-annealed at 425° C revealed a tendency for ridge formation. Electron diffraction patterns also showed increased sharpness of the diffraction rings. Friction tests showed that MoS_2 films deposited at ambient and elevated temperatures exhibited good lubricating properties. The MoS_2 films deposited at cryogenic temperatures had no lubricating characteristics.

INTRODUCTION

When molybdenum disulfide (MoS_2) lubricating films are applied to bearing surfaces by radio-frequency sputtering, a high degree of film adherence and coherence is obtained. As a result, during the lubrication cycle, low coefficients of friction and long wear lives are obtained. The superior adherence of these thin films of 200 nanometers (2000 Å) is primarily responsible for the effective lubrication. Strong adherence is generally attributed to the high arrival energies (>10 eV) of the sputtered material and the submicroscopic particle size (5-nm (50-Å range)). Also, the film compactability and density, as well as the strength, are favorably affected during the sputtering process. For instance, strength is related to grain size: the smaller the grain, the stronger the film or the compact (ref. 1). The initial stages of film formation and subsequent growth of film are important and decisive to the effectiveness of sputtered MoS_2 as a lubricating film.

During the sputtering process, there is an interrelation between film formation characteristics, film structure and the resultant properties of these films. The formation of vacuum deposited films (sputtering and evaporation) occur in two steps: first nucleation, then growth. Nucleation is frequently the key to a detailed understanding of a physical process. It is, after all, the first step in coating deposition and as such often sets the pattern that follows. This study of nucleation attempts to examine the first step in film formation on an intimate atomic basis.

The nucleation and growth processes are principally responsible for the surface structure of the films. Since the sputtered particles are transported through a glow discharge, the particles are in an excitied state; the charge effects therefore have an influence on the nucleation and growth process. It is believed that the glow discharge itself is an effective nucleant (ref. 1).

Presently there is no information available relative to sputtered MoS_2 film formation characteristics in terms of nucleation and growth. It has been reported how various surface pretreatments on silver, gold, copper, and bronze affect the adherence of sputtered MoS_2 films (ref. 2). The objective of this study, therefore, was to illustrate the structural growth characteristics of MoS_2 films especially in the initial stages of formation (nucleation) at various substrate temperatures. Thin MoS_2 films 30 to 40 nanometers (300 to 400Å) thick were sputtered onto a aluminum or nickel foils, which were maintained at ambient (no deliberate heating or cooling), elevated, and liquid-nitrogen temperatures. The sputtered MoS_2 films were then examined by electron transmission microscopy and election diffraction to determine their structure.

APPARATUS AND PROCEDURE

The sputtering apparatus that was used in this study is an rf-diode mode with superimposed dc bias as schematically and photographically shown in figure 1. This apparatus has been previously described in references 3 and 4. The sputtering conditions that were used in this investigation were the same as those used in previous studies and are as follows: radio frequency (rf), 7 MH_z; argon pressure, 18 micrometers; radio-frequency power input, 440 watts; direct-current input, 500 volts; target voltage (ac), 1.30 kilovolts; target to specimen distance, about 2.5 centimeters; sputtering time, 60 to 70 seconds; and sputtering rate about 30 nanometers per minute (300 Å/min). The substrates used were aluminum and nickel foils. The substrate temperature during sputtering was kept at 320° and 150° C, at ambient, and at liquid-nitrogen temperature (-195° C). The metal foils were placed on aluminum blocks and the substrate heating was performed by direct current ion bombardment until the desired temperature is reached. During the heating process, a shutter is positioned between the target and the substrate. Before starting rf-sputtering, the shutter is maintained between the target and substrate for a few minutes for the sole purpose of cleaning the target surface and establishing steady-state sputtering conditions. The substrate temperature was monitored by a chromel-alumel thermocouple. During cryogenic cooling, the aluminum blocks with the substrate foils were placed on a copper cooling stage through which liquid nitrogen was continuously circulated. In all instances the sputtering time was kept between 60 to 70 seconds with an average sputtering rate of 30 nanometers per minute (300 Å/min). For the electron transmission microscopy and electron diffraction, the film was removed by dissolving the substrates in suitable solutions. For the aluminum substrates 30 percent HCl in water or saturated $HgCl_2$ was used, and for the nickel substrates $FeCl_2$-HCl, was used.

RESULTS AND DISCUSSION

Film Formation During Sputtering

The film formation process during vacuum deposition determines the growth structure. When films are deposited by thermal evaporation, the nucleation and growth mechanisms have been described in detail for a large number of metals (ref. 5). The nucleation theory is based on the atomistic approach, which considers the condensation and migration of individual atoms. It recognizes the critical nucleus size and the smallest stable atomic cluster-nuclei. The process of cluster formation is called nucleation. In the initial stages of film growth the clusters generally start to grow upwards before they join sideways, thus forming an island structure film. During the later stages of nucleation and growth the islands formed will sooner or later start to coalesce. This coalescence of the islands continues until finally the individually separated islands grow together and form a continous film.

During sputtering many additional factors are introduced that have certain effects on the nucleation process. The glow discharge itself is an effective nucleant, since charged particles have a tendency to initiate nucleation (ref. 6). The basic effects during sputtering, which have to be accounted for on the surface, are the relatively high kinetic energy (10 eV or greater) for the sputtered species (which arrive at the substrate in an excited state), the various energetic charged particles of the plasma (i.e., electrons, and ions) that strike the surface, and the increased surface temperature. It has been demonstrated that any surface exposed to a glow discharge will develop a small potential relative to the plasma, which may be of the order of a few volts (ref. 7).

In this study, the sputtering conditions were kept constant and were as already described. It has been acknowledged in the literature with materials other than MoS_2 (ref. 7) that the higher rates of deposition have a tendency to produce poorer quality films. In this study, therefore, the sputtering rate was selected on the basis of that previously used in sputtered MoS_2 films. These films have performed effectively during friction experiments (ref. 3). The only parameter that was varied, therefore, was substrate temperature. The surface mobility of the sputtered species is temperature dependent and thereby determines the degree of order of the growing film.

The surface temperature is also affected by the sputtering process, and it depends on the power input to the target and the duration of the sputtering cycle. Usually it takes 5 to 10 minutes to reach an equilibrium temperature, which is influenced solely by the input power. It is interesting to note that the plasma temperature itself during sputtering was measured to be 95° C. Since the duration of MoS_2 sputtering was very short (60 to 70 sec) and no noticeable temperature increase was measured by the thermocouple during sputtering, the possible outside specimen heating effects from the plasma were negligible.

Characterization of Sputtered Molybdenum Disulfide Films by Transmission Microscopy and Electron Diffraction

Electron transmission and diffraction micrographs were used to illustrate the film structure during the nucleation stage at ambient, elevated, and liquid-nitrogen temperatures. Figure 2 is a typical micrograph for sputtered MoS_2 on aluminum at 320° C; the corresponding electron diffraction pattern is shown in figure 3. The transmission micrograph shows the formation of a network of ridges, which are essentially buildups of preferentially agglomerated sputtered particles. The particle size was estimated to be from 7 to 14 nanometers (70 to 140 Å), and the electron diffraction pattern (fig. 3) reveals distinct crystallinity. Figures 4 and 5 show the micrographs of sputtered MoS_2 at 150° C with a particle size predominantly between 3 to 6 nanometers (30 to 60 Å). The electron diffraction pattern in figure 6 reveals again the crystalline type of formation. Figures 7 and 8 show the micrographs of sputtered MoS_2 at ambient temperature on nickel surfaces. The estimated particle size ranged from 3 to 8 nanometers (30 to 80 Å). Distinct ridge formation was observed in all instances. The corresponding electron diffraction pattern is shown in figure 9. The same nature of film formation was observed when MoS_2 is sputtered on aluminum at ambient temperature as shown in figure 10. When the substrate is cooled to liquid-nitrogen temperature (-195° C) for the sputtering process, the film structure on aluminum is as shown in figures 11 and 12. No ridge formations are observed. The film has a continuous nature. Also, the corresponding electron diffraction pattern (fig. 13) shows broad (diffuse) diffraction rings, which indicate an amorphous type of film.

At the cryogenic substrate temperatures, the surface mobility of the sputtered species is retarded, since these temperatures have essentially a quenching effect on the sputtered material. As a consequence, continuous films are formed during the nucleation stages.

In another experiment MoS_2 was sputtered at cryogenic temperatures on aluminum and subsequently postannealed in vacuum for one hour at 425° C. Figure 14 shows a typical structure after post annealing, and 15 shows the corresponding electron diffraction pattern. It should be noted that during the annealing process there is a tendency for agglomeration and formation of ridges. Also the electron diffraction patterns reveal that there is a considerable increase in sharpness of the diffraction rings, which indicates a higher degree of crystallinity.

CHARACTERISTICS OF THE SPUTTERED MOLYBDENUM DISULFIDE

The distinct difference in the film formation appearance as shown by the electron transmission micrographs and electron diffraction patterns of MoS_2 films sputtered on metal surfaces at ambient and elevated temperatures as compared with the cryogenic temperatures is reflected in a very pronounced way in the physical appearance and friction characteristics when the film thickness is increased to several thousands of angstroms. The MoS_2 sputtered on metal surfaces at ambient and elevated temperatures formed a soft, greasy film; this film exhibited good lubricating properties. A low coefficient of friction (0.04) and long endurance lives (over million cycles) were obtained, as previously reported (ref. 3). The MoS_2 sputtered on metal surfaces at cryogenic temperatures formed a hard brittle, dry, shiny film; when friction tested, acted like an abrasive and not as a lubricating film. The friction tests exhibited a high coefficient of friction and no useful endurance life for lubrication.

SUMMARY OF RESULTS

Electron transmission micrographs and diffraction patterns of sputtered molybdenum disulfide (MoS_2) film on aluminum and nickel surfaces at ambient, elevated, and liquid-nitrogen temperatures revealed the following results:

1. The film structure of 30- to 40-nanometer (300- to 400-Å) thick MoS_2 films during early stages of the nucleation process depends on the substrate temperature.

2. At elevated temperatures (320° and 150° C) and at ambient temperatures, distinct elongated ridge formation is observed. The film had a crystalline structure as revealed by electron diffraction patterns.

3. At cryogenic (liquid nitrogen, -195° C) temperatures, a continuous film is formed, and it had an amorphous structure as shown by electron diffraction patterns.

4. Postannealing MoS_2 films at 425° C for 1 hour after sputtering at liquid-nitrogen temperatures have a tendency to form the elongated ridges. Electron diffraction patterns exhibit some degree of crystallinity.

Lewis Research Center
National Aeronautics and Space Administration,
Cleveland, Ohio, November 22, 1972,
502-27.

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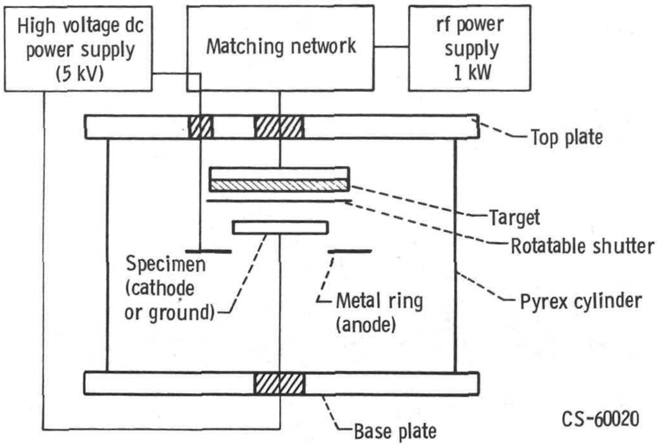
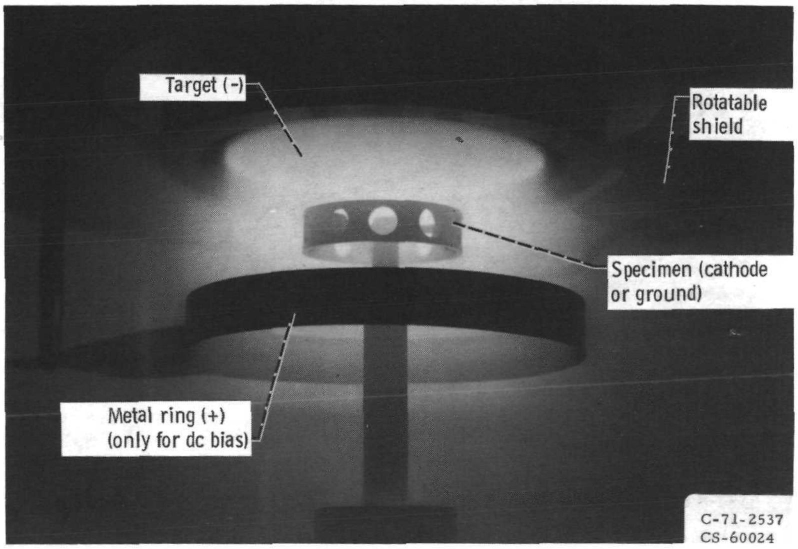


(a) Radiofrequency with direct-current bias sputtering system.



(b) Radiofrequency with direct-current during sputter coating of complex specimens.

Figure 1. - Schematic and photographic sputtering apparatus.

Figure 2. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at 320° C. X135 000.

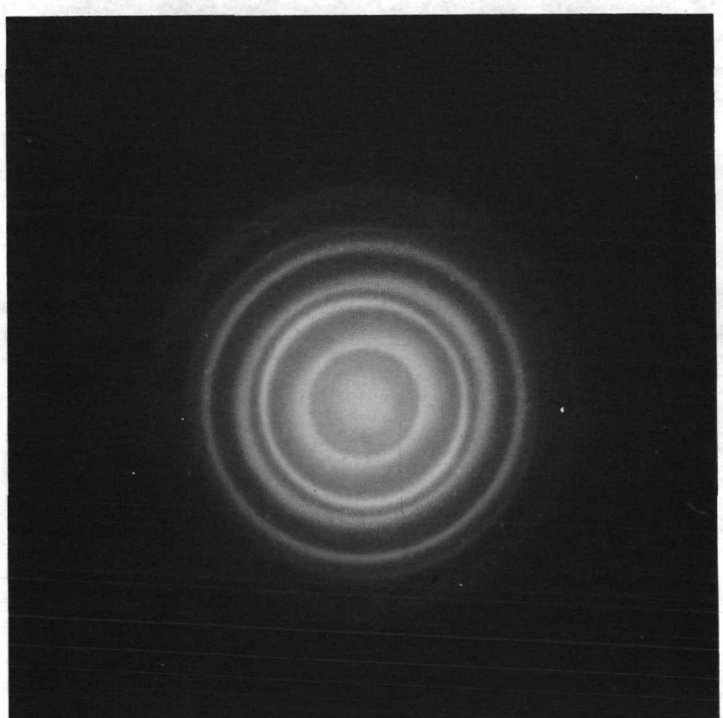


Figure 3. - Electron diffraction pattern of sputtered molybdenum disulfide on aluminum at 320° C.

Figure 4. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at 150° C. X200 000.

Figure 5. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at 150° C. X400 000.

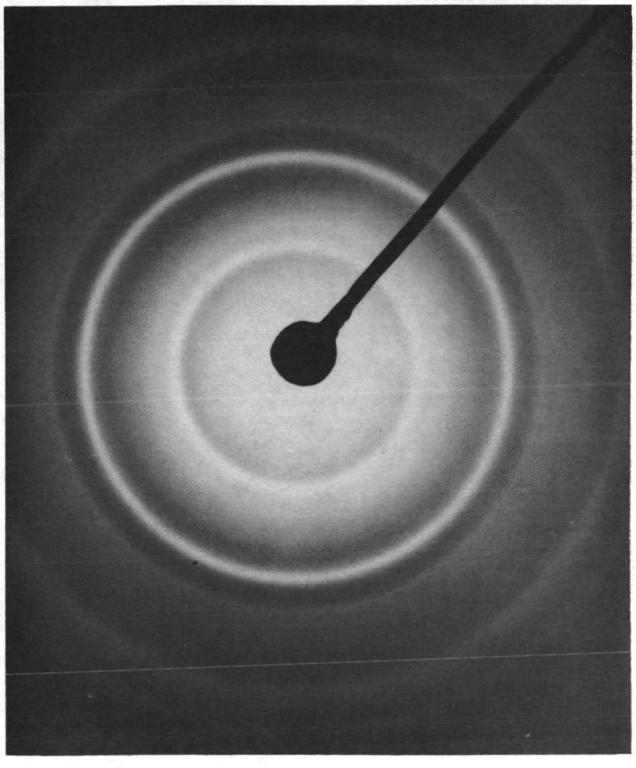


Figure 6. - Electron diffraction pattern of sputtered molybdenum disulfide on aluminum at 150° C.

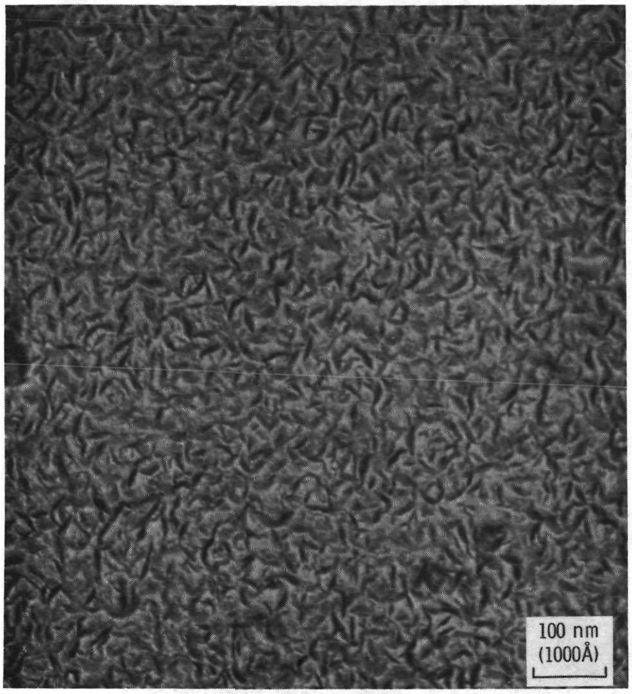


Figure 7. - Electron transmission micrograph of sputtered molybdenum disulfide on nickel at ambient temperature. X200 000.

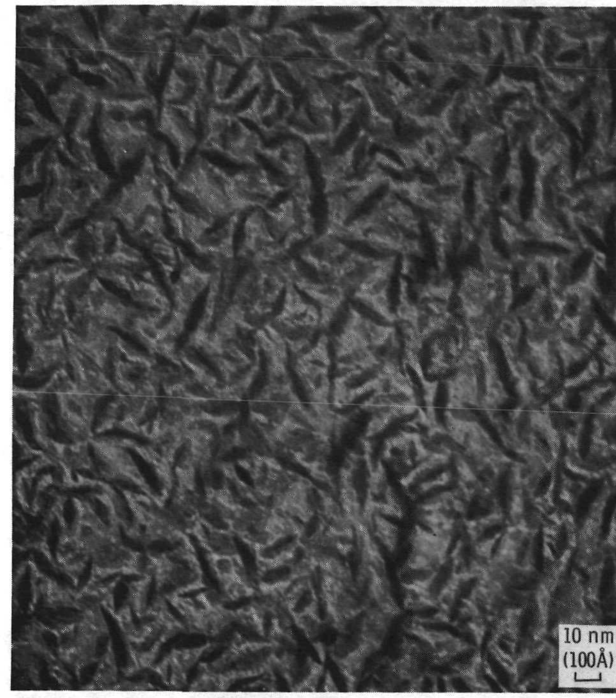


Figure 8. - Electron transmission micrograph of sputtered molybdenum disulfide on nickel at ambient temperature. X400 000.

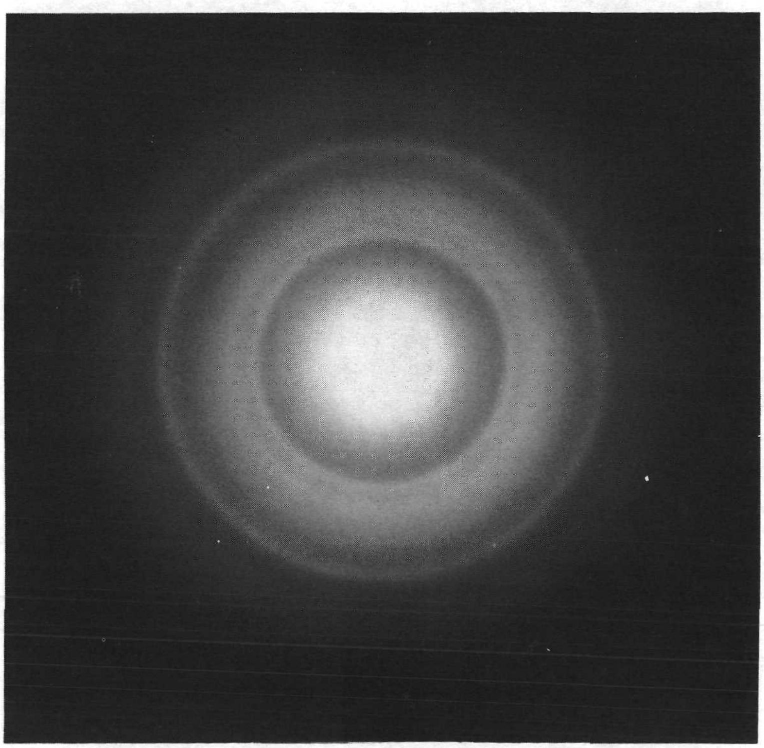


Figure 9. - Electron diffraction pattern of sputtered molybdenum disulfide on nickel at ambient temperature.

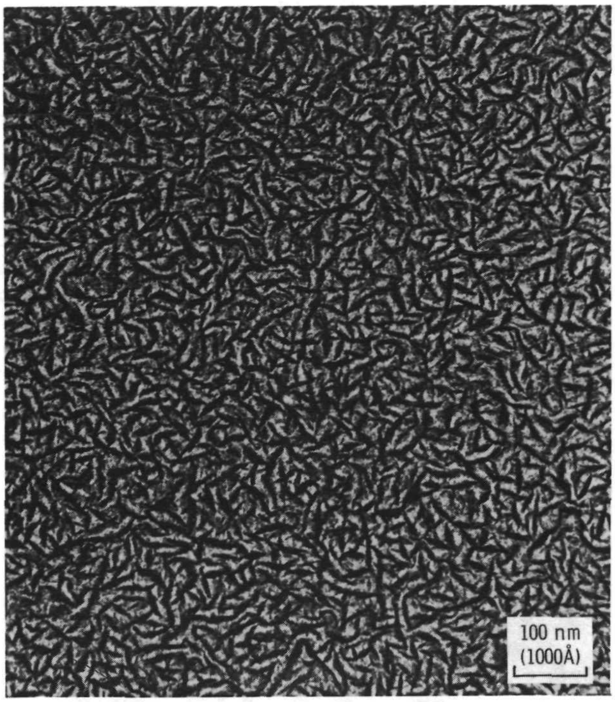


Figure 10. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at ambient temperature. X200 000.

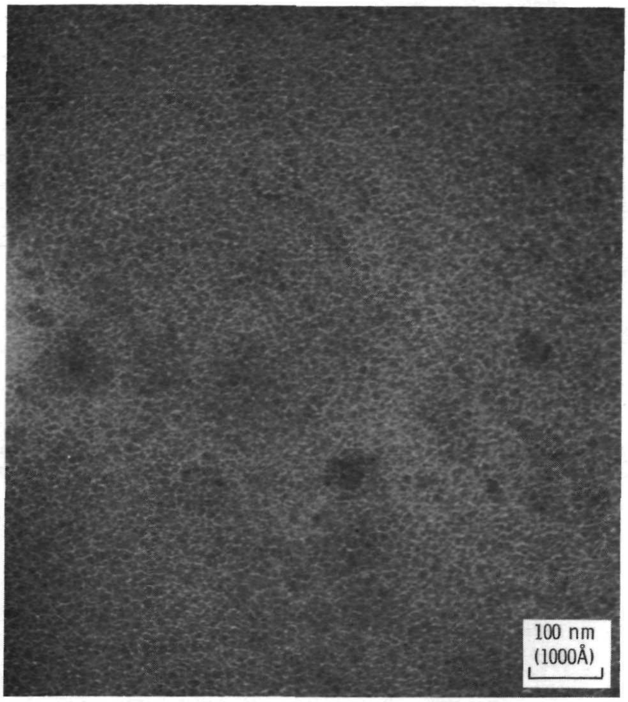


Figure 11. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at -195^{0} C. X200 000.

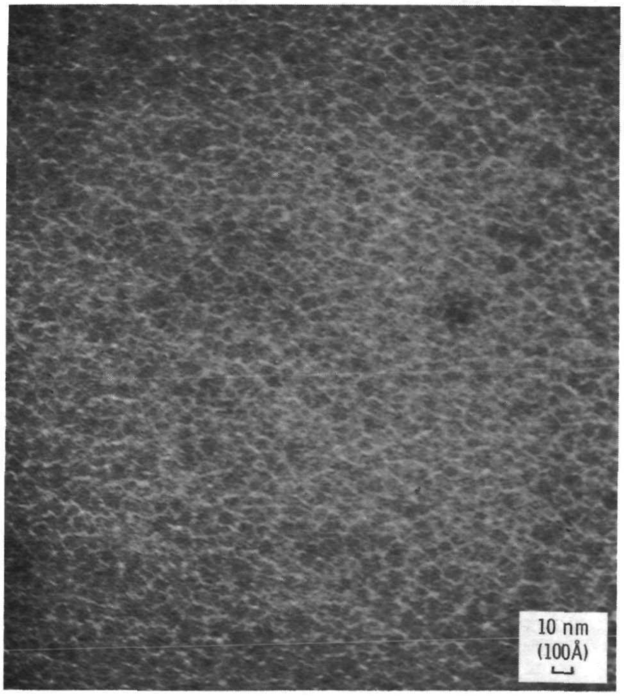


Figure 12. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at -195^{0} C. X400 000.

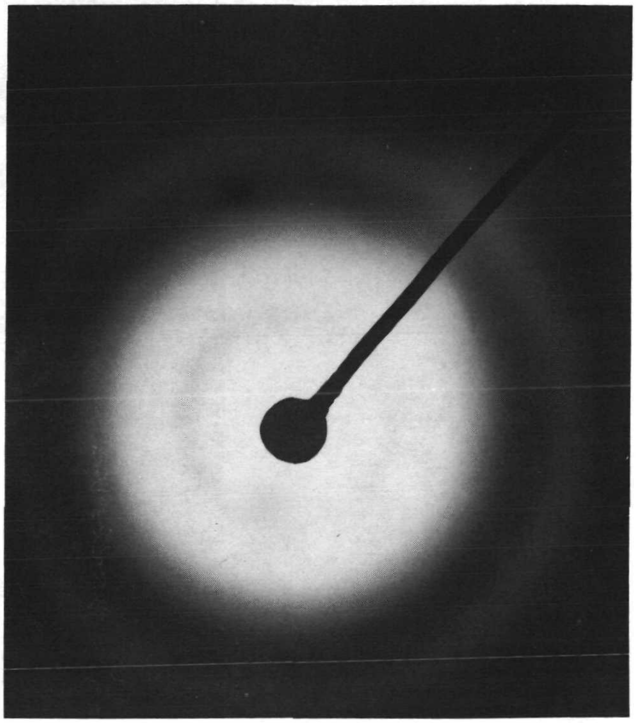


Figure 13. - Electron diffraction pattern of sputtered molybdenum disulfide on aluminum at -195^{0} C.

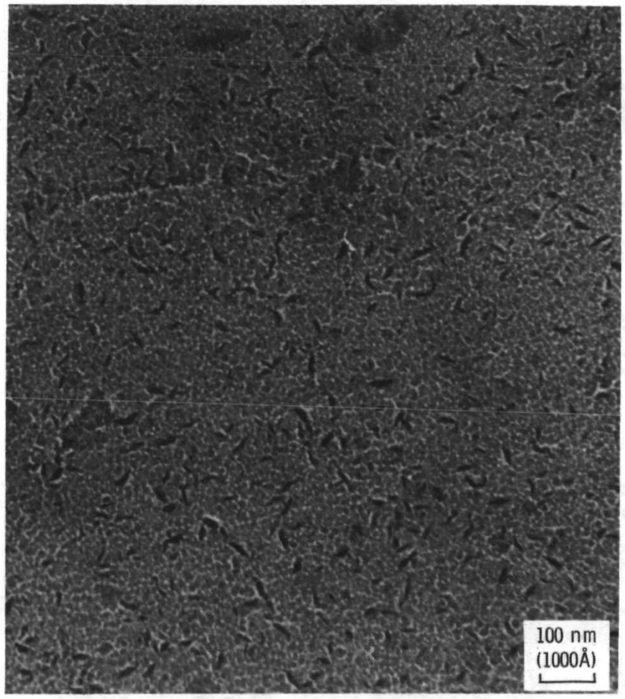


Figure 14. - Electron transmission micrograph of sputtered molybdenum disulfide on aluminum at -195° C and subsequently annealed at 425° C. X135 000.

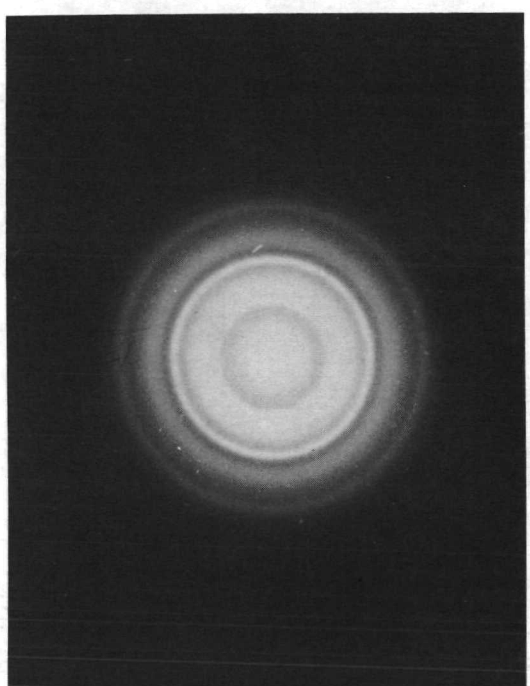


Figure 15. - Electron diffraction pattern of sputtered molybdenum disulfide on aluminum and postannealed at 425° C.

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