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EXAMINATION OF MOLYBDENUM DISULFIDE WITH LEED AND AUGER EMISSION SPECTROSCOPY

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16. Abstract

LEED and Auger emission spectroscopy were used to examine the surface of molybdenite crystals, MoS_2 compacts, and sputtered films. Exposure of the molybdenite (0001) surface to 5000 Langmuirs of oxygen, ethylene, or ethylene oxide revealed no evidence of chemisorption of these gases. The Auger analysis revealed the presence of silicon and carbon in some of the specimens examined. Rubbing of the molybdenite crystal resulted in distortion of the surface layer which could be removed by heating of the crystal. The molybdenite crystals were cleaved in air yet no evidence for oxygen on the surface was observed.

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SUMMARY

Both LEED and Auger emission spectroscopy analysis were used in the examination of molybdenite natural crystals, MoS_2 compacts, and sputtered MoS_2 films. The basal orientation was examined with the molybdenite crystals. The crystal surface was exposed to the gases, oxygen, ethylene, and ethylene oxide. The molybdenite crystal surface was also rubbed with an iron single crystal flat.

At exposures to 5000 Langmuirs of each of the gases, oxygen, ethylene, and ethylene oxide, no evidence for the chemisorption of these gases to the molybdenite (0001) surface was observed. In some of the specimens examined, silicon and carbon were found to be present as impurities. Rubbing of the molybdenite surface resulted in lattice distortion which could be removed by heating. Although the molybdenite crystals were cleaved in air, no evidence for oxygen on the surface was observed.

INTRODUCTION

Molybdenum disulfide (MoS_2) has been very thoroughly studied through the years with respect to both its structure and lubricating properties (refs. 1 and 2). Two recently developed research tools, LEED (low energy electron diffraction) and Auger emission spectroscopy analysis, may lend to gaining a greater understanding of this material. LEED provides researchers with a device for examining the structural arrangement of atoms in the outermost atomic layer of a solid surface (ref. 3). Auger emission spectroscopy (AES) furnishes the capability of determining the elements present on a solid surface to hundredths of a monolayer (ref. 4). In addition, AES can penetrate the surficial layer to a depth of as much as four monolayers (ref. 5).

An examination of the literature indicates that only a short note has been published on the use of LEED in studying MoS_2 (ref. 6) and nothing has been published on the use of AES for examining MoS_2 surfaces. LEED can detect structural changes that take place as a result of rubbing contact and detect the structural arrangement of adsorbing species.

The objectives of this investigation were to (1) examine molybdenite crystals, MoS_2 compacts, and sputtered MoS_2 films with LEED and AES, (2) determine the ability of gases to adsorb on molybdenite crystal surfaces, and (3) ascertain the effect of rubbing contact on MoS_2 crystals, compacts, and films.

MATERIALS

The MoS_2 crystals were cleaved in air from a large piece of natural molybdenite. The crystals were supplied by the Climax Molybdenum Company. The MoS_2 used in compacts and for dc sputtering was a technical grade powder. Sample compacts were also pressed with the technical grade MoS_2 powder to which was added 5 weight percent purified feldspar.

APPARATUS

The apparatus used in these studies is shown schematically in figure 1. The specimen surface mounted in the center of the chamber could be rotated 350°. This rotatability allowed for the making of rubbing contact with the specimen surface shown in figure 1, and then rotating the specimen to obtain both an Auger analysis and a LEED pattern from the surface in the rubbed contact area. The specimen could also be moved in the lateral and vertical directions.

The MoS_2 specimens were supported in the chamber by means of two metal rods (insulated) and a tantalum holder which were used to resistance heat the specimen. A 100-ampere ac power supply was used for resistance heating.

A 3.0-millimeter-diameter flat-ended iron single crystal was used to contact the MoS_2 surfaces, and it was mounted in a stainless steel holder which was in turn mounted to a 1.5-millimeter-diameter stainless steel beam. The beam was mounted in a bearing containing yoke. At the end of the beam beyond the pivot point, and opposite the smaller cylindrical specimen, was a small permanent magnet. Outside the chamber wall were two electromagnets. The permanent magnet and electromagnets were positioned in such a manner as to have like poles facing each other. A variation in the current applied to the magnets could be used to move the beam.

The current applied to the electromagnets was calibrated in terms of the force applied in the rubbing experiments. Load applied to the surfaces in contact was measured

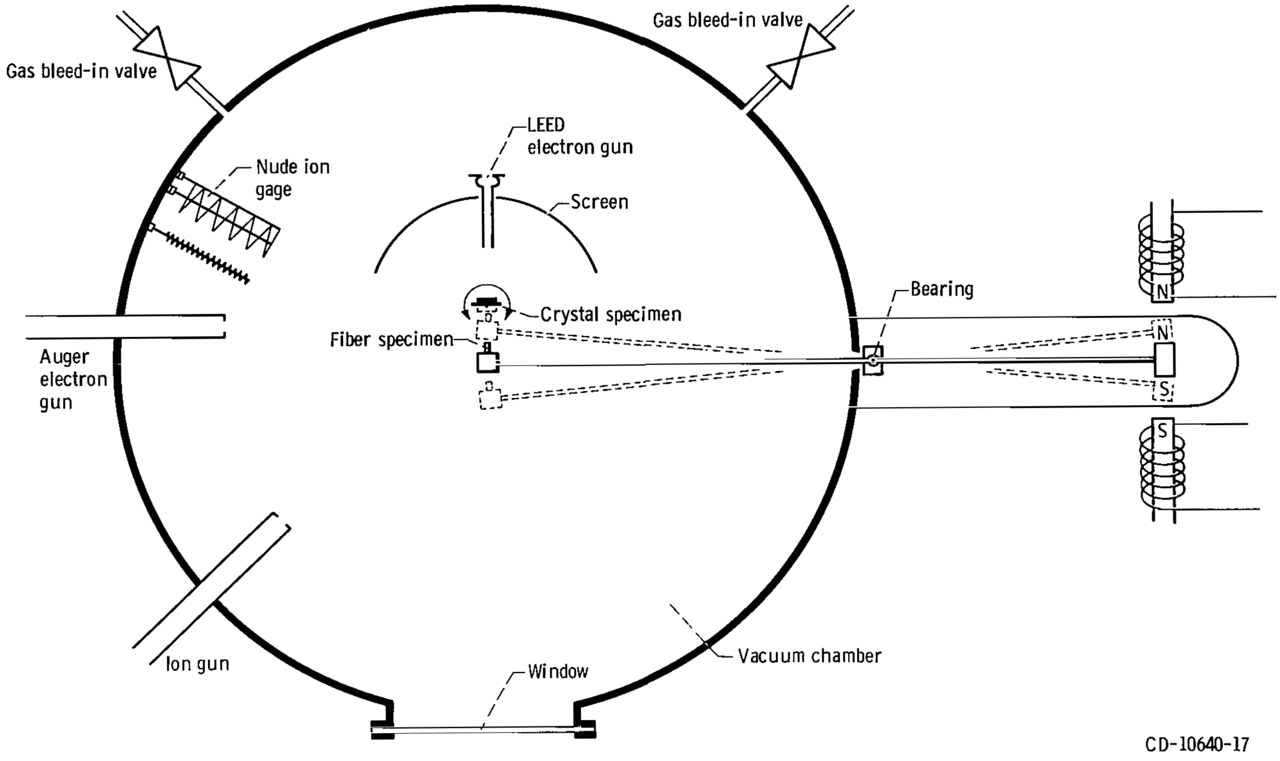


Figure 1. - Low-energy electron-diffraction (LEED) adhesion apparatus.

by current, as was the force required to separate the surfaces.

The basic LEED and Auger systems were obtained commercially. The LEED electron optics and the vacuum system were of the standard type used by those engaged in LEED studies. The Auger spectrometer gun was located at a position 90° from the LEED gun (see fig. 1). The electron optics of the LEED was of the Varian three grid type with a fourth grid added for Auger analysis. The LEED beam diameter was 0.6 millimeter. The vacuum system consisted of vacsorb pumps, an ion pump, and a sublimation pump. The system pressure was measured with a nude ion gage and all experiments were conducted with the vacuum system in the pressure range of 10^{-11} to 10^{-10} torr. No cryopumping was used.

EXPERIMENTAL PROCEDURE

A large piece of a single crystal of natural molybdenite was cleaved in air with a razor blade to produce the specimens. used in this study. They were then mounted to a tantalum holder and placed directly into the apparatus. No surface preparation was used.

The crystals were examined in the as-cleaved condition. The natural molybdenite crystals contained numerous wrinkles.

Molybdenum disulfide powder compacts were prepared by compressing powder into 1.25-centimeter-diameter tablets. The powder size was such that 88 percent passed through a 325 Fischer screen which indicates a particle size of less than 44 microns. The specimens like the single crystals were mounted into a tantalum holder and placed into the apparatus with no other surface preparation.

The sputtered MoS_2 film was prepared by dc-triode sputtering a powder compact onto a glass slide. The details of the sputtering process are described in reference 7. Small pieces of the slide were cut and mounted in a tantalum holder.

RESULTS AND DISCUSSION

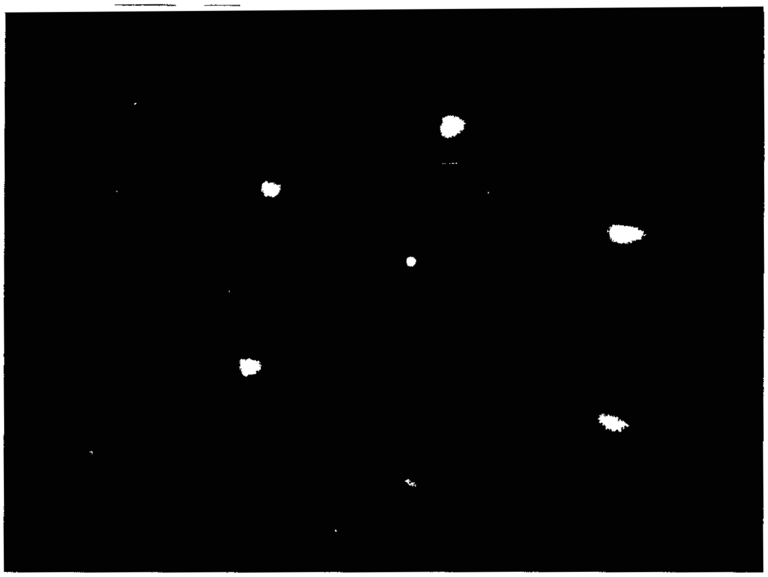
Single Crystal

It was possible to obtain LEED patterns of the molybdenite crystal surface after simply baking out the vacuum chamber at 250° C for 12 hours. Figure 2(a) is the LEED pattern for the (0001) surface of the crystal. The region where the pattern was obtained was not strain free. The diffraction spots rather than being sharp and circular are somewhat elongated. Earlier studies with metals indicate that the elongation of the diffraction spot is the result of strain in the outermost atomic layer (ref. 8). The very bright white spot in the central region of the LEED pattern of figure 2(a) was produced by the beam from the electron gun.

The natural molybdenite crystal contained wrinkles, and a diffraction pattern was obtained in one of these wrinkled areas in the crystal surface. The LEED pattern of figure 2(b) indicates how each diffraction spot was comprised of a series of smaller spots reflecting the variations in orientations seen by the incident or primary electron beam.

An AES analysis was made of the crystal surface. The results of the analysis are presented in figure 3. The element detected in addition to molybdenum (230 eV) and sulfur (164 eV) was silicon. The characteristic peaks associated with these elements are indicated in figure 3.

An iron (011) single crystal surface was rubbed against the molybdenite crystal surface with a force of 400 dynes on a 1.0-millimeter diameter apparent contact area. After three passes of the iron surface across the molybdenite crystal, the pattern of figure 4 was obtained. If the LEED pattern of figure 2(a) is compared with that of figure 4, it becomes evident that the structural arrangement of the atoms in the outermost layer have been distorted from their natural state by the rubbing contact.



(a) Crystal flat.

(b) Wrinkled region.

Figure 2. - LEED patterns for Basal (0001) orientation of molybdenite crystals.

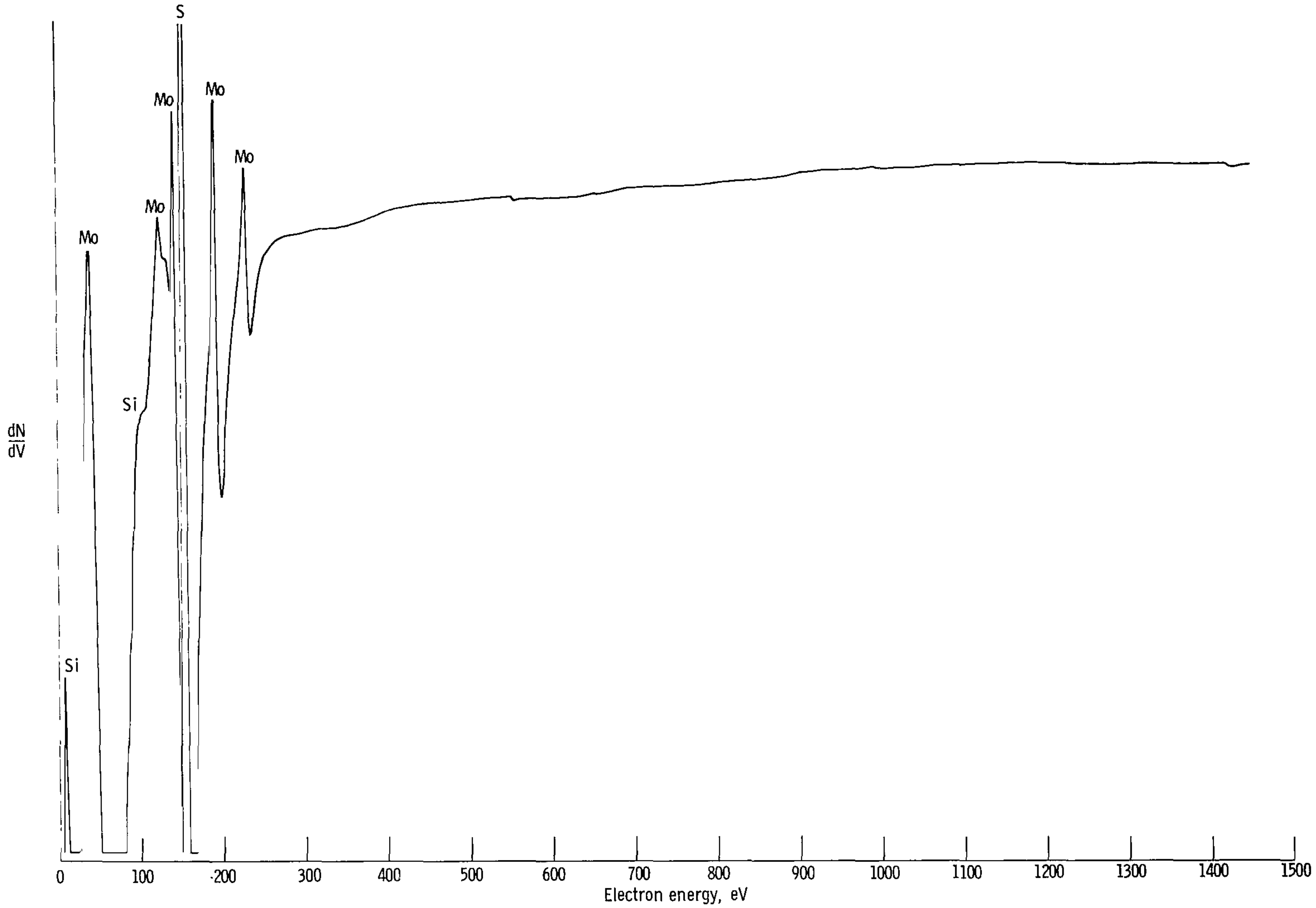


Figure 3. - Auger emission spectrometer trace of MoS_2 crystal.

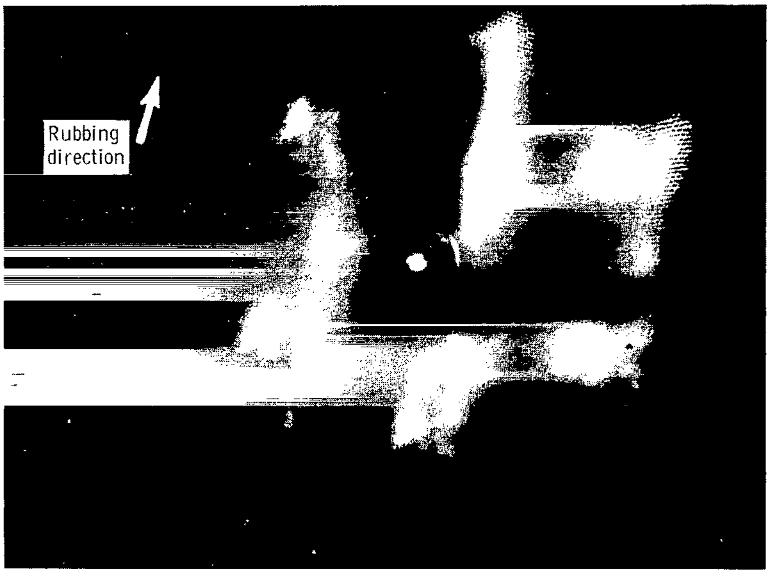


Figure 4. - LEED pattern for molybdenite crystal surface (0001) after three passes of an iron (011) single crystal slider.

Since the outermost layer of the molybdenite crystal is composed of a layer of sulfur ions, the changes observed are in this layer. It would appear that the preferred direction of distortion is near the ⟨10⟩. When the surface of figure 4 was heated to 600° C for 3 hours, the pattern of figure 2(a) was again obtained

It is of interest to note that the Auger trace of figure 3 taken before rubbing contact did not indicate the presence of any oxygen. The presence of oxygen on the MoS_2 surface has been observed under certain conditions (ref. 9). With Auger analysis, it is possible to detect oxygen surface coverage to less than 0.02 monolayer (ref. 4). It would appear therefore that there is an absence of oxygen on the surface before contact and rubbing does not expose any since an AES trace after rubbing yielded no oxygen peak. If oxygen were present on the surface, a peak should have been observed in figure 3 at an electron energy of 520 electron volts. The absence of the oxygen peak does not discount the possibility that oxygen may be present combined with some of the other impurity elements subsurface, or in the surface layer at sufficiently small concentrations to escape detection.

Most applications for the use of MoS_2 are in an air environment. Therefore, the ability of MoS_2 to chemisorb gases such as oxygen is of interest (ref. 1). The basal (0001) orientation of the natural molybdenite crystal was therefore exposed to various amounts of oxygen. At exposures to 5000 Langmuirs (1 Langmuir = 10^{-6} torr/sec) there was no evidence in either LEED patterns or AES traces for oxygen chemisorption (at

20° C) to the basal orientation. Figure 5 is an AES trace of the molybdenite surface after exposure to 5000 Langmuirs of oxygen. If oxygen had chemisorbed to any appreciable extent, a peak should have developed at 520 electron volts. In reference 10 an exposure of 1.0 Langmuir of oxygen was sufficient for it to be detected on an iron surface with LEED and AES.

There has developed in recent years considerable use of MoS_2 in organics (ref. 2). The question as to whether the hydrocarbons chemisorb to the basal planes of MoS_2 is as yet unanswered. The molybdenite surface of figure 2(a) was exposed to total exposures of to 5000 Langmuirs of ethylene and ethylene oxide. The unsaturated hydrocarbon ethylene will chemisorb more rapidly to a clean surface than its saturated parent ethane (ref. 11). Neither ethylene nor ethylene oxide were found to chemisorb to the molybdenite (0001) surface. With clean iron an exposure of 500 to 1000 Langmuirs of ethylene was sufficient to produce a 2 by 2 LEED structure and an AES carbon peak was readily detectable (ref. 11).

Figure 6 is an AES trace of the molybdenite surface after exposure to 5000 Langmuirs of ethylene oxide. If chemisorption had occurred, AES peaks would have been seen at electron energies of 270 electron volts for carbon and 520 electron volts for oxygen. These peaks are not detected in figure 6.

Compacts

LEED analysis of a MoS_2 compact gave no detectable diffraction spots. This resulted, in all probability, from the multitude of orientations normal to the surface because of the small particle size. While a diffraction pattern for a single crystal surface would not be anticipated, with a textured surface some diffraction spots might be expected.

The AES trace obtained on the powder compact is presented in figure 7. Examination of the trace indicates that all of the elements present in the molybdenite crystal are present in the powder compact. In addition, the compact contains carbon as indicated in figure 7. Commercial purity MoS_2 is known to contain carbon (refs. 1 and 12). Reference 1 indicates a carbon content of 0.7 to 1.0 percent and reference 12 a concentration of 1.22 percent. The presence of the very discernable carbon peak in figure 7 indicates the sensitivity of AES. The trace of figure 7 was obtained with a primary incident electron beam of 2000 volts and an amplifier sensitivity of 200 microvolts. The instrument has the capability of increasing the sensitivity by a factor of 20 if necessary for detection.

The MoS_2 compact surface was rubbed in the vacuum chamber with the iron crystal flat in the same manner as was the molybdenite crystal discussed earlier. The LEED

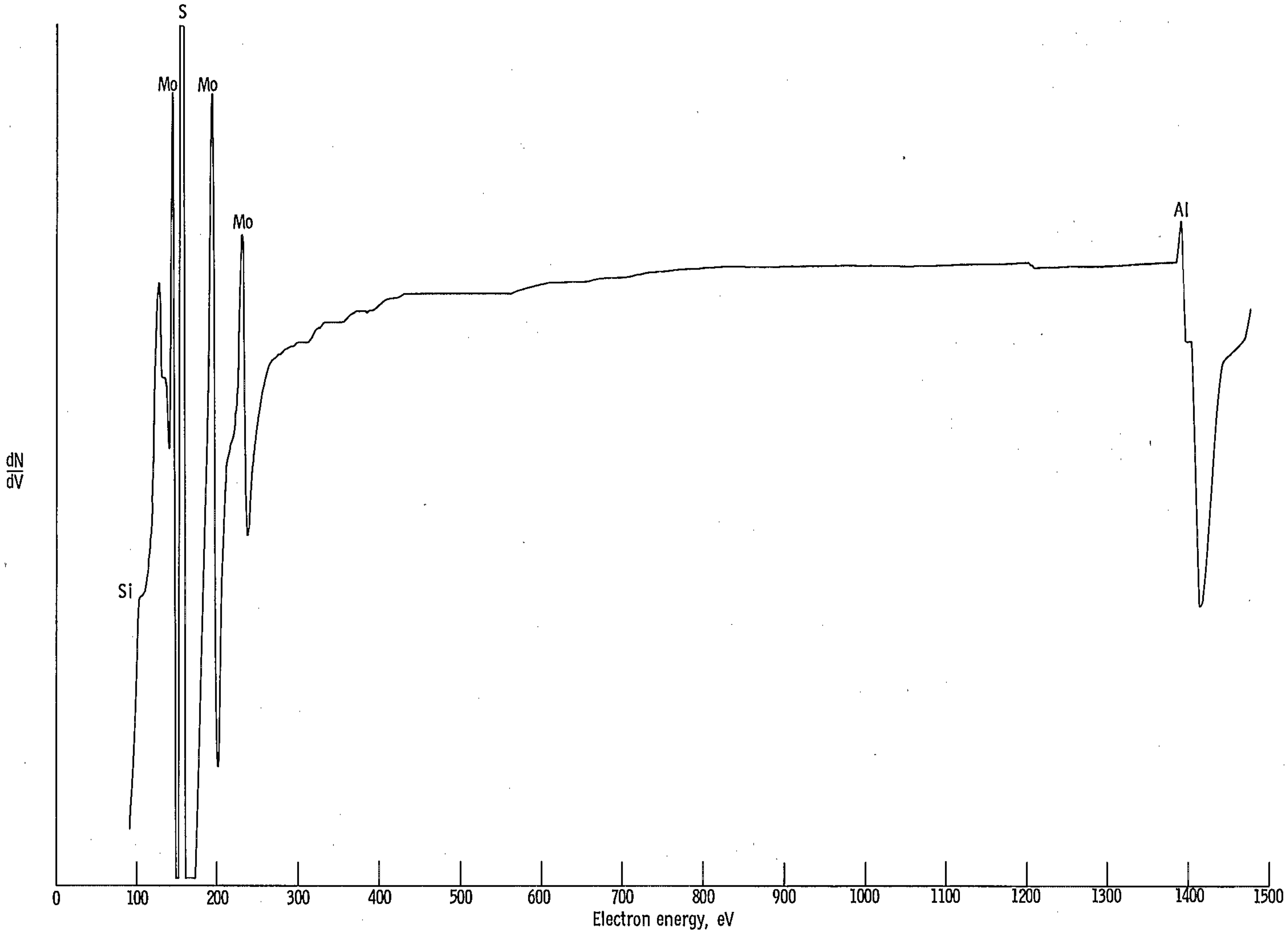


Figure 6. - Auger emission spectrometer trace or MoS_2 crystal after exposure to ethylene oxide.

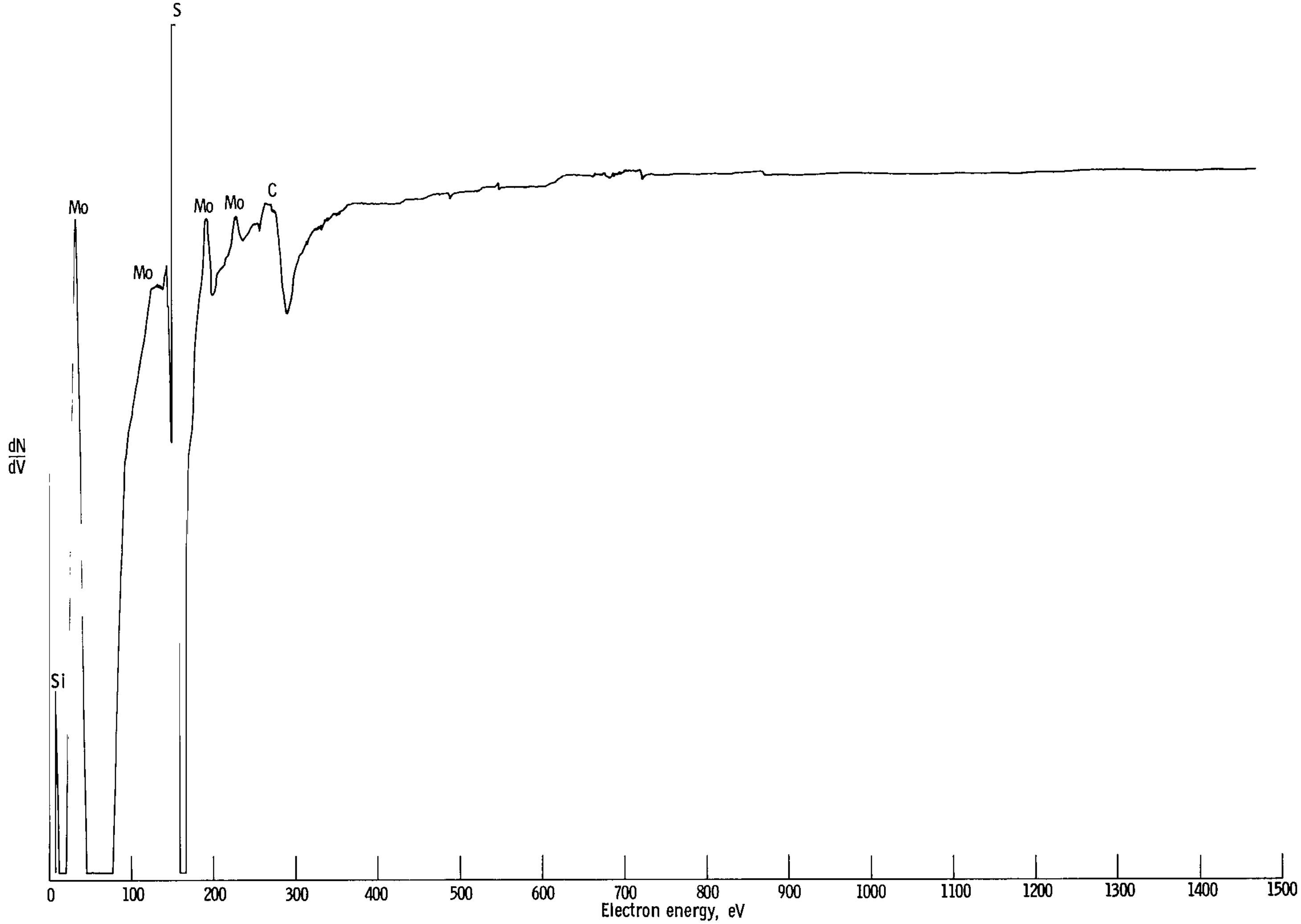


Figure 7. - Auger emission spectrometer trace of powder MoS_2 compact.

pattern and the AES trace of the rubbed surface were essentially the same as those obtained before rubbing. The loads applied were extremely light and may have been insufficient to result in the development of any surface texture.

Feldspar is one of the impurities found in naturally occurring molybdenite (ref. 1). A compact of MoS_2 powder containing 5.0 weight percent feldspar was made and analyzed with AES to determine if oxygen could be detected. Oxygen was in fact detected at 520 electron volts. Feldspar may contain any one of the following minerals: orthoclase $(KAlSi_3O_8)_3$, celsian $(BaAl_2Si_2O_8)$, plagioclase $(NaAlSi_3O_8)$, or anorthite $(CaAl_2Si_3O_8)$ (ref. 13). Thus, with 5.0 weight percent feldspar, the oxygen concentration is less than 5.0 percent and can still be detected.

Sputtered Film

A 9000 Å dc triode sputtered film on a glass substrate was examined with both LEED and AES. The film resulted from the sputtering of a compact of the powder already described. The reason for the examination was to determine if a structure developed with deposition and if the same impurity elements were present in the sputtered film as in the original compact. LEED analysis of the film revealed no evidence of any pattern as indicated in figure 8. This is the same result as was obtained with the compact from which the film came. Neither heating nor rubbing changed this pattern.

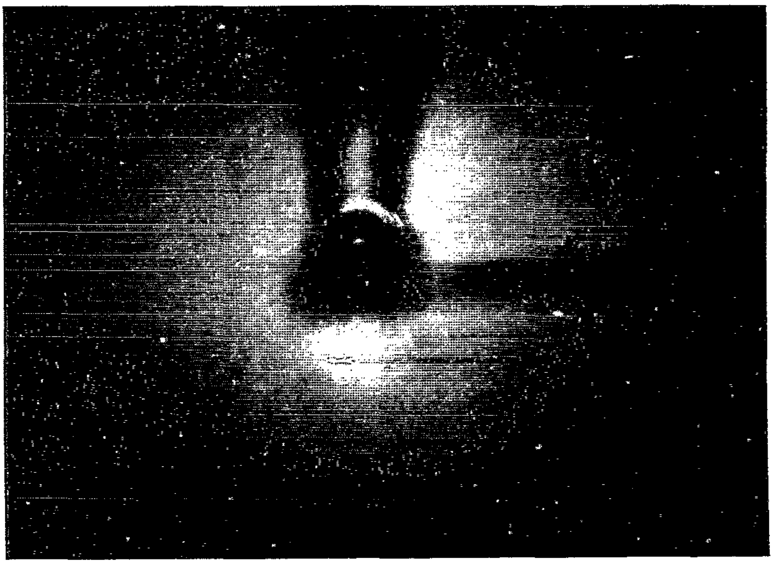


Figure 8. - LEED pattern for sputtered (DC) molybdenum disulfide film (9000 Å) on glass slide.

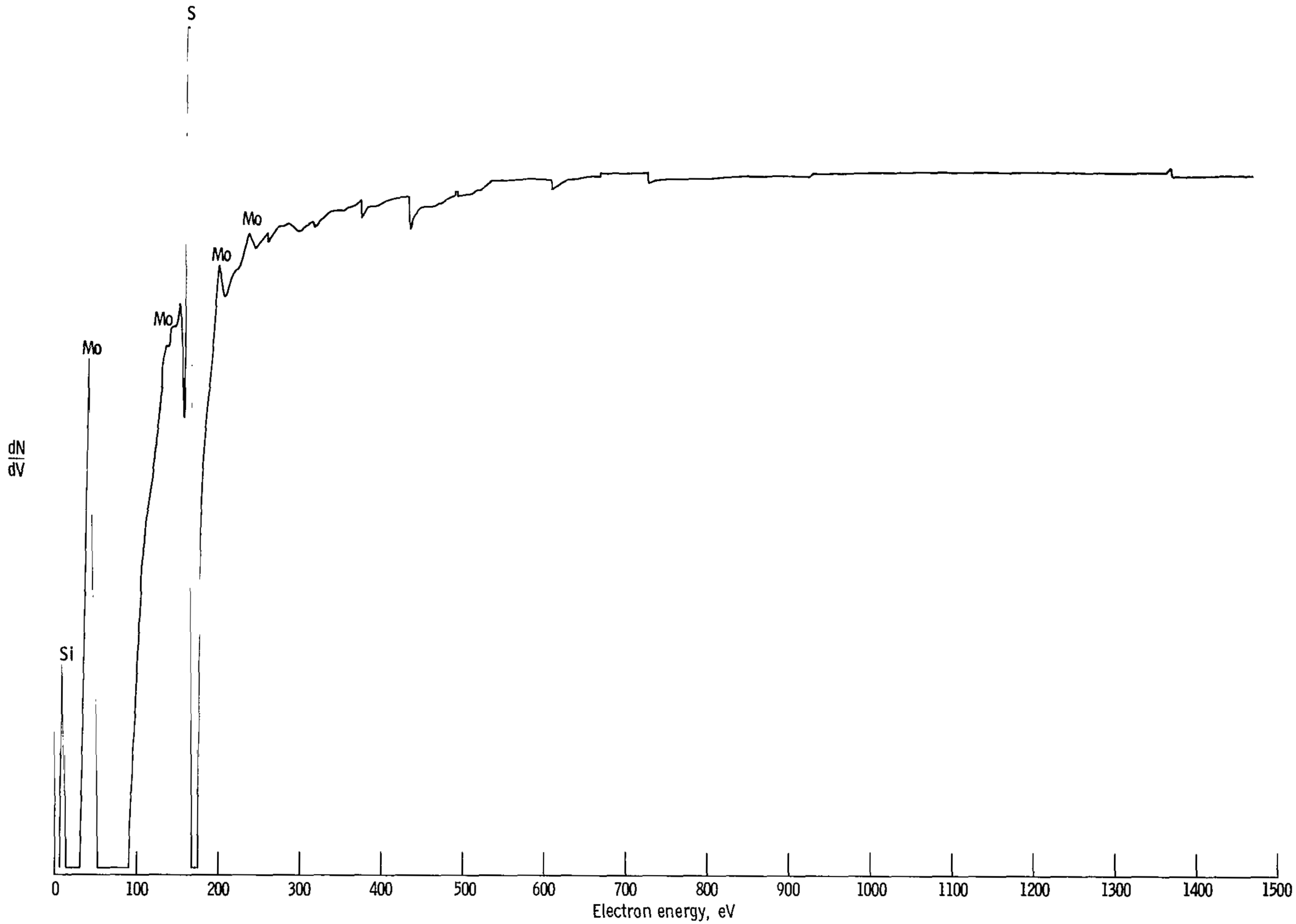


Figure 9. - Auger emission spectrometer trace of sputtered MoS_2 film.

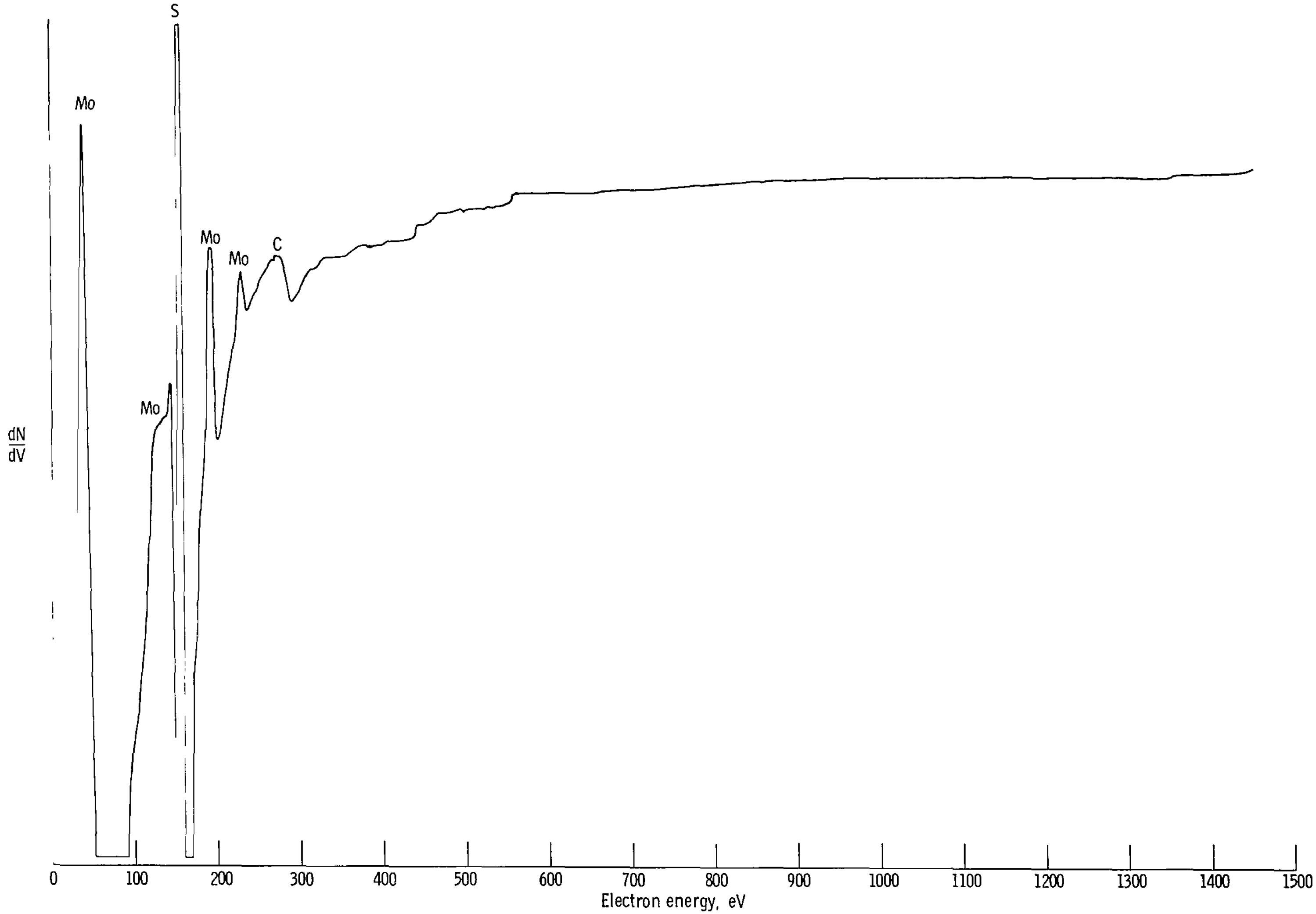


Figure 10. - Auger emission spectrometer tracer of sputtered MoS_2 film after sliding.

An AES analysis of the film indicates that the same elements are present in the sputtered film as in the original compact. A trace of the film is presented in figure 9. The sputtering process appears to carry the impurities in the MoS_2 target to the substrate to be coated along with the MoS_2 itself.

In figure 9 no readily discernable carbon peak was detected. After the surface was rubbed with the iron crystal, a carbon peak appeared. Figure 10 indicates the presence of carbon after rubbing the surface. Rubbing exposed the carbon present in the film as a contaminant.

CONCLUSIONS

Based on the LEED and Auger analysis of molybdenite, MoS_2 compacts, and MoS_2 sputtered films, the following conclusions are drawn:

1. At exposures to 5000 Langmuirs no evidence for the chemisorption of oxygen, ethylene, or ethylene oxide to the (0001) surface of molybdenite was detected.
2. AES analysis indicates that while carbon is present in the commercially purified MoS_2 powder it was not detected in the molybdenite crystal.
3. Rubbing of the molybdenite crystal surface with an (011) iron flat resulted in distortion of the (0001) diffraction pattern which could be eliminated by heating the molybdenite.
4. Although the molybdenite crystals were cleaved in air, no evidence was found for oxygen on the surface (0001).

Lewis Research Center,
National Aeronautics and Space Administration,
Cleveland, Ohio, August 27, 1970,
129-03.

REFERENCES

1. Winer, W. O.: Molybdenum Disulfide as a Lubricant: A Review of the Fundamental Knowledge. Wear, vol. 10, 1967, pp. 422-452.

2. Johnson, Robert L.: A Review of the Early Use of Molybdenum Disulfide as a Lubricant. Presented at the National Lubrication Grease Institute Annual Meeting, New Orleans, Lo., Oct. 29-Nov. 1, 1967.

3. May, J. W.: Electron Diffraction and Surface Chemistry. Ind. Eng. Chem., vol. 57, no. 7, July 1965, pp. 18-39.
4. Musket, Ronald G.; and Ferrante, John: Auger Electron Spectroscopy Study of Oxygen Adsorption on W(110). J. Vacuum Sci. Tech., vol. 7, no. 1, Jan.-Feb. 1970, pp. 14-17.
5. Palmberg, P. W.; and Rhodin, T. N.: Auger Electron Spectroscopy of FCC Metal Surfaces. J. Appl. Phys., vol. 39, no. 5, Apr. 1968, pp. 2425-2432.
6. Ino, Shozo; Ogawa, Shiro; Uchiyama, Masahiro; and Oda, Zenjiro: Low Energy Electron Diffraction Study of Molybdenite Cleavage Surface. Japan J. Appl. Phys., vol. 7, no. 3, Mar. 1968, pp. 308-309.
7. Spalvins, T.: Deposition of MoS_2 Films by Physical Sputtering and Their Lubricating Properties in Vacuum. ASLE Trans., vol. 12, no. 1, Jan 1969, pp. 36-43.
8. Buckley, Donald H.: LEED Study of the Adhesion of Various Materials to the (111) Surface of Nickel. NASA TN D-5247, 1969.
9. Ballou, E. V.; and Ross, Sydney: The Adsorption of Benzene and Water Vapor by Molybdenum Disulfide. J. Phys. Chem., vol. 57, no. 7, Oct, 1953, pp. 653-657.
10. Buckley, Donald H.: LEED and Auger Studies of Effect of Oxygen on Adhesion of Clean Iron (001) and (011) Surfaces. NASA TN D-5756, 1970.
11. Buckley, Donald H.: Interaction of Methane, Ethane, Ethylene, and Acetylene with an Iron (001) Surface and Their Influence on Adhesion Studied with LEED and Auger. NASA TN D-5822, 1970.
12. Tyler, J. C.; and Ku, P. M.: Compressive and Tensile Properties of Molybdenum Disulfide Compacts. ASLE Trans., vol. 10, no. 1, Jan. 1967, pp. 28-37.
13. Moeller, Therald: Inorganic Chemistry. John Wiley & Sons, Inc., 1952.

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