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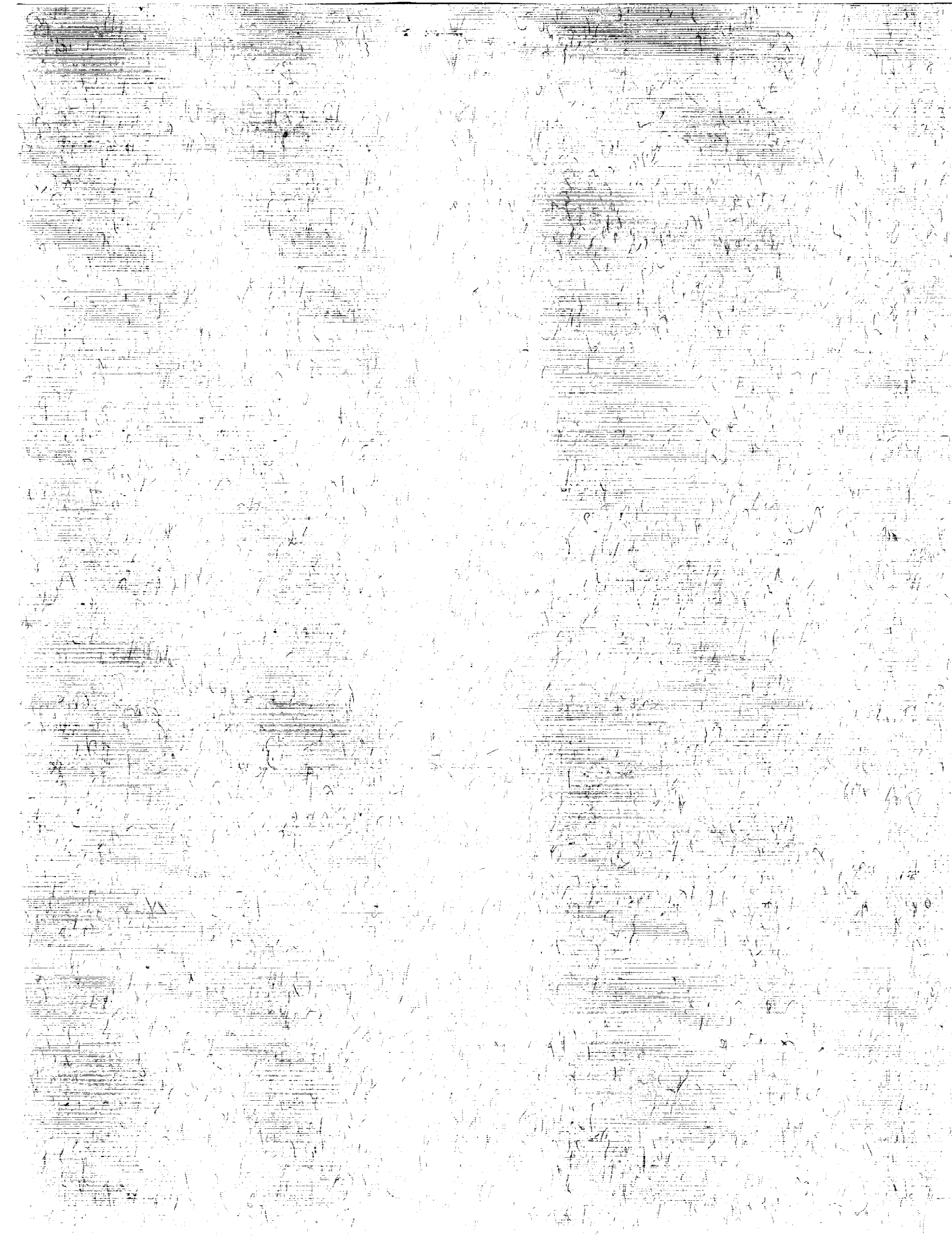
Influence of the Deposition Conditions on Radiofrequency Magnetron Sputtered MoS₂ Films

Pierre A. Steinmann
and Talivaldis Spalvins

DEPARTMENT OF AERONAUTICS AND SPACE ENGINEERING
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Pierre A. Steinmann
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*Lewis Research Center
Cleveland, Ohio*

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Summary

By varying the radiofrequency (rf) power, the Ar pressure, and the potential on the substrates, MoS_x films of various stoichiometry, density, adhesion, and morphology were produced. An increase of rf power increased the deposition rate and density of the MoS_2 films as well as improved adhesion. However, the stoichiometry remained constant. An increase of Ar pressure increased the deposition rate but decreased the density, whereas both stoichiometry and adhesion were maximized at around 20 mtorr Ar pressure. Furthermore, a transition from compact film growth to columnar film growth was observed when the pressure was varied from 5 to 15 mtorr. Substoichiometric films were grown when a negative (bias) voltage was applied to the substrates.

Introduction

Sputtered MoS_2 films are often used to lubricate spacecraft mechanisms since they offer ultra-low coefficients of friction and long endurance lives. Many investigators have documented the strong dependence of the useful tribological properties of sputtered MoS_2 films on the sputtering parameters selected (refs. 1 to 7). However, many contradictory results are reported in the literature. Therefore, the purpose of this study is to vary deposition parameters to produce films of various properties and then identify those properties (and, thus, the deposition conditions) that are desirable. In this study, the following sputtering parameters—Ar pressure, rf power, and substrate bias—were varied, and their influences on properties such as density, stoichiometry, adhesion, and morphology are discussed.

Note that although the starting material was a dense target of stoichiometric MoS_2 , the sputter-deposited films were generally substoichiometric and are designated as MoS_x .

Experimental Procedure and Conditions

The films were deposited in an MRC 8667 rf magnetron sputtering system (Materials Research Corporation). The chamber had an approximate volume of 115 liters and was composed of three 16.5-mm-diameter targets, one heater, and one rotating table where the substrates could be sputter etched

or biased. The distance between the MoS_2 target (MRC) and the steel substrates to be coated was always 60 mm.

The system was diffusion pumped to an ultimate pressure on the order of 1×10^{-7} to 2×10^{-7} torr. The base pressure was always lower than 5×10^{-7} torr before the chamber was backfilled with Ar for sputtering.

Before placing the 440C steel disks in the chamber, they were polished (1- μm paste finish) and cleaned with alcohol and acetone. Then these substrates were sputter etched in situ for 10 min (20 mtorr; 100 W), and the target was sputter cleaned, under the conditions selected for the deposition to follow, for at least 30 min.

For each experiment, the thickness of a weighed microscope glass slide partially covered with a small, thin glass mask was measured along with the thickness of the steel substrates. After deposition, the mask was removed and the microscope slide was weighed. The film density was calculated from the weight differences, the dimensions of the nonmasked area, and the thickness of the MoS_2 film measured by stylus profilometry.

The stoichiometry (S/Mo ratio) of the films deposited on steel was measured by a wavelength dispersive x-ray spectroscope (WDS) installed on a scanning electron microscope (SEM) at a beam energy of 5 keV. This particular method was able to clearly resolve the sulfur and molybdenum peaks, whereas energy dispersive x-ray spectroscopy (EDS) was not able to because of the overlap of the adjacent Mo- $L\alpha$ and S- $K\alpha$ x-ray energies. A typical WDS spectrum of a sputtered MoS_x film is shown in figure 1(a). The stoichiometry of the film was determined by the ratio x_0 of the sulfur peak height to the molybdenum peak height. Quantitative results were obtained by measuring a monocrystal of natural molybdenite (MoS_2) as a standard (fig. 1(b)). In this case, the WDS peak-heights ratio x_0 was normalized to 2 (by definition). Therefore, it was possible to determine an x value for each sputtered film by means of the simple relation

$$x = 2 \frac{x_0 \text{ (sputtered film)}}{x_0 \text{ (molybdenite)}} \quad (1)$$

The interfacial adhesion was measured by a CSEM-REVETEST Automatic Scratch Tester (Centre Suisse d'Electronique et de Microtechnique) using a stylus with a 800- μm tip radius (ref. 8). For this test, the hemispherically tipped stylus applied a continuously increasing load on the coated surface while the sample was displaced at a constant

speed. The stylus produced an increasing elastic and plastic deformation of the coating-substrate system until a critical load was reached. The critical load was defined as the minimum load at which evidence of adhesive failure occurred. By taking into account various test-related and sample-related parameters (ref. 9), we could use the critical load to characterize the adhesion of the coating. Finally, the morphology was assessed by SEM observation of transverse fractures of coated glass microscope slides.

The deposition conditions (rf power, argon pressure, and substrate bias) were varied to produce films of different density, stoichiometry, adhesion, and morphology. The rf power was varied from 150 to 1000 W, the argon pressure was varied from 5 to 50 mtorr, and the bias was varied from 0 to -100 V.

Experimental Results and Discussion

The experimental results are presented in table I and in figures 2 to 9. Figure 2 shows the effect of the rf power. For a 20-mtorr Ar pressure, the influence of the applied rf power on the deposition rate was also a function of the sputtering time—the longer the deposition time, the higher the rate. The density dependence on power, for 20-mtorr Ar pressure, is shown in figure 3. Note that for a variation of the power from 150 to 900 W, the density ranges from 2.7 to 4.4 g/cm³, which is in every case lower than the theoretical density of 4.9 for bulk MoS₂. From figures 2 to 4 it can be concluded that the deposition rate increases with the sputtering time (fig. 4). Therefore, if the sputtering rate is constant, higher density films will be formed at the beginning of the process, and it can be concluded that the lower the deposition rate, the higher the density. This supposition is supported by the experimental results shown in figure 4, where longer sputtering at 900 W led to a significant decrease of the overall density. This is in good agreement with previous work by Spalvins (ref. 1), although the film's morphology, (as observed by SEM on fractured MoS₂ films deposited on glass slides) does not exactly match the morphology reported by Spalvins. In the present study, a columnar structure was observed to grow readily from the surface of the substrate.

The experimental results shown in figure 3 also indicate that the films grown at low rf power are not as dense as the ones grown at higher power. This is in apparent contradiction with the previous conclusion since, according to figure 2, a low deposition rate was measured on films deposited at low rf power. However, the previous conclusion did not take into account the effect of the higher energy of impinging particles occurring at the high rf power, which probably contributes to the film densification.

Figure 5 shows, for a 20-mtorr Ar pressure, the results of the film stoichiometry versus the applied rf power. The variation of rf power from 150 to 900 W did not affect the stoichiometry of the films. On the other hand, films deposited

with a -30 V bias on the substrate were deficient in sulphur, confirming previously published data (refs. 2 to 7). The application of a -100 V bias led to a stoichiometry of MoS_{1.09} (which is not represented in fig. 5). This significant loss of sulfur was probably caused by Ar ions preferentially resputtering the sulfur atoms from the film.

Figures 6 to 9 show, for a 900-W rf power, the influence of the Ar pressure on the deposition rate (fig. 6), film density (fig. 7), stoichiometry (fig. 8), and adhesion (fig. 9).

The increase of the deposition rate as a function of pressure (fig. 6) was due to an increase in the number of ionized species bombarding the target. However, this increase leveled off at higher pressures since scattering of the sputtered species coincided with the reduction of their mean free path.

The film density was a function of the Ar pressure: higher pressures yielded higher film density (fig. 7). This behavior agrees with the Thornton model (ref. 10) as well as with experimental results reported by Mueller et al. (ref. 11) on dc magnetron deposited films of MoS₂.

The stoichiometry of MoS_x reached an average maximum of 1.8 at 15 to 20 mtorr pressure (fig. 8). At lower pressures, the sulfur content was much lower. At higher pressures, because of the high concentration of Ar ions, the film could resputter with preferential sputtering of sulfur. This preferential resputtering led to a loss of sulfur in the deposited film. The results for biased substrates are also shown in figure 8.

Figure 9 shows the film adhesion characterized by the scratch testing technique. It is known from previous work (ref. 9) that the critical load measured in this test increases with the thickness of the coating. This relation was observed for films deposited at 20 mtorr. Similar to the stoichiometry dependence, the film adhesion was maximum at about 20 mtorr; lower critical loads were measured for either lower or higher pressures as indicated by the open circles in figure 9.

As mentioned previously, the MoS₂ films showed columnar growth. This was true for films grown at any rf power, provided the Ar pressure was greater than or equal to 15 mtorr.

Increasing the rf power from 150 to 900 W corresponded to the growth of more densely packed columns in accordance with density measurements reported in figure 3. The effect of the Ar pressure on the morphology is shown in figure 10 for 900 W rf power. By varying the pressure from 5 to 50 mtorr the structural change could be observed. The film was column free and dense at 5 and 10 mtorr (fig. 10(a) and (b)). These films were brittle and had a shiny, metallic appearance. Such films do not perform well in tribological applications (ref. 12). At 15 mtorr, thin, closely packed columns grew (fig. 10(c)), giving the film a grayish appearance. These films were much softer than those produced at 5 and 10 mtorr and could be scratched very easily. Finally, at 30 and 50 mtorr (fig. 10(d) and (e)) larger columns grew, the structure was more open, and there were voids between the columns. This is in good agreement with results reported in figure 7.

Conclusions

This study has shown that a large range of MoS_x films can be prepared by radiofrequency (rf) magnetron sputtering. An Ar pressure of 20 mtorr and an rf power of 900 W with the substrate at plasma potential have been determined as the optimum conditions to produce the desired density, stoichiometry, and adhesion.

Lewis Research Center
National Aeronautics and Space Administration
Cleveland, Ohio, January 10, 1990

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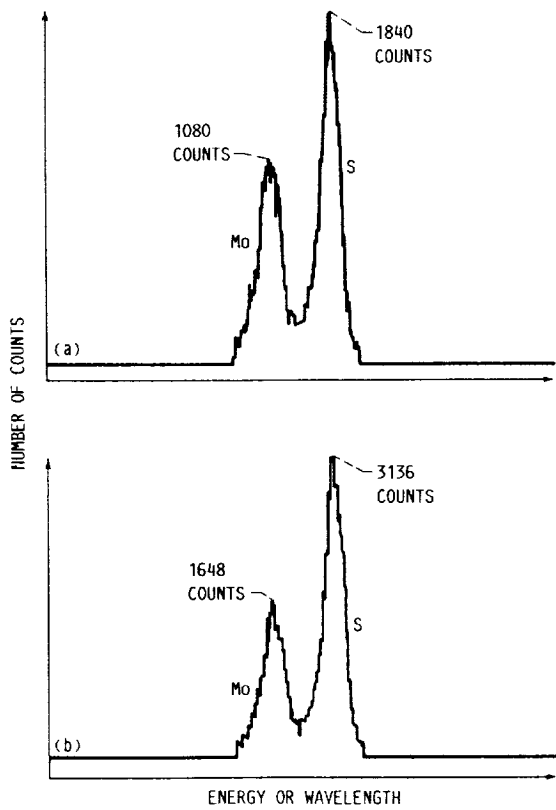
TABLE 1.—DEPOSITION CONDITIONS AND RESULTING PHYSICAL AND CHEMICAL PROPERTIES
[Flow rate, 12 sccm.]

Sample ^a	Pressure, mtorr	Power, W	Voltage, V	Thickness, Å	Time, min	Deposition rate, Å/min	Density, g/cm ³	Stoichiometry, S/Mo
787082-1	5	900	375	4 960	4	1240	3.98	1.45
787070-1	10	↓	400	15 940	10	1594	----	1.37
783040-1	15	↓	460	16 166	↓	1617	3.83	1.80
786062-1	30	↓	445	22 840	↓	2284	3.01	1.54
786062-2	50	↓	455	23 150	↓	2315	2.67	1.28
785081-1	20	150	135	7 914	30	264	2.74	1.72
788011-1	↓	200	165	2 540	9	280	2.83	1.81
782132-1	↓	275	200	3 650	7	520	3.77	1.79
783002-1	↓	300	230	10 543	15	703	3.14	1.76
781152-3	↓	600	340	6 670	5	1335	3.83	1.64
785041-2	↓	630	370	8 138	5.5	1480	3.50	1.76
781140-1	↓	900	435	2 570	1.5	1715	4.39	----
788011-2	↓	↓	440	4 250	2.5	1700	3.80	1.74
788002-2	↓	↓	435	5 300	3	1770	3.93	1.79
788002-3	↓	↓	435	9 200	5	1840	3.81	1.68
783002-2	↓	↓	465	20 983	10	2098	3.33	1.74
787031-1	↓	↓	335 ^b	2 370	2.25	1050	3.77	1.42
784020-2	↓	↓	370 ^b	15 808	10	1581	3.38	1.28
781152-2	↓	1000	340 ^c	5 630	5	1130	4.38	1.09

^aNumbers are given for samples shown in figure 10 photomicrographs.

^bBias voltage, 30 V.

^cBias voltage, 100 V.



(a) MoS_x sputtered film; $\text{S}/\text{Mo} = x_0 = 1.7$.
 (b) Natural molybdenite MoS_2 ; $\text{S}/\text{Mo} = x_0 = 1.9$.
 Figure 1.—Wavelength dispersive x-ray spectra.

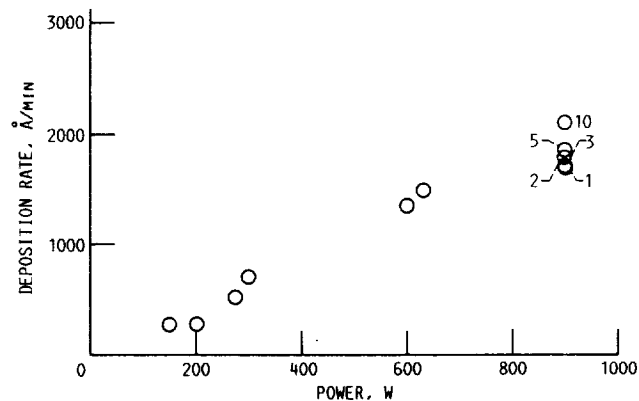


Figure 2.—Effect of radiofrequency power on the deposition rate of magnetron sputtered MoS_2 films on floated substrates (plasma potential) at 20-mtorr Ar pressure. For the 900-W data points, the numbers indicate the duration of the deposition (in minutes).

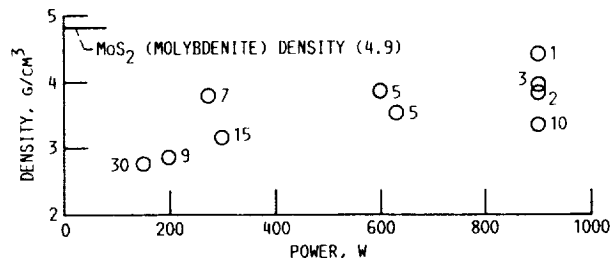


Figure 3.—Effect of radiofrequency power on the density of magnetron sputtered MoS_2 films on floated substrates (plasma potential) at 20-mtorr Ar pressure. The numbers on each data point indicate the duration of the deposition in minutes.

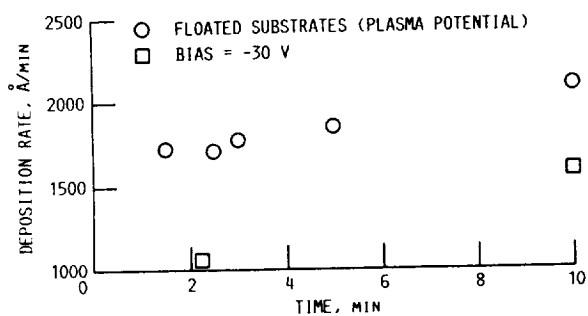


Figure 4.—Effect of sputtering time on the deposition rate of MoS₂ at 900 W and 20-mtorr pressure.

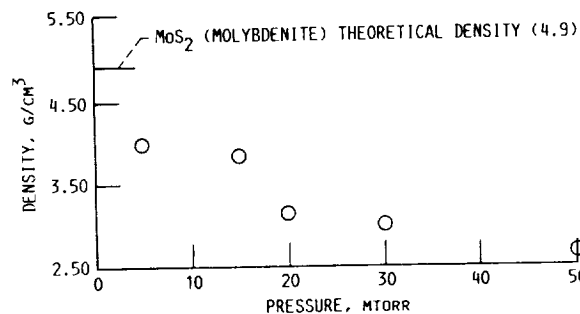


Figure 7.—Effect of Ar pressure on the density of radiofrequency magnetron sputtered MoS₂ films at 900 W. The deposition time is equal to 10 min except for the 5-mtorr data point (4 min).

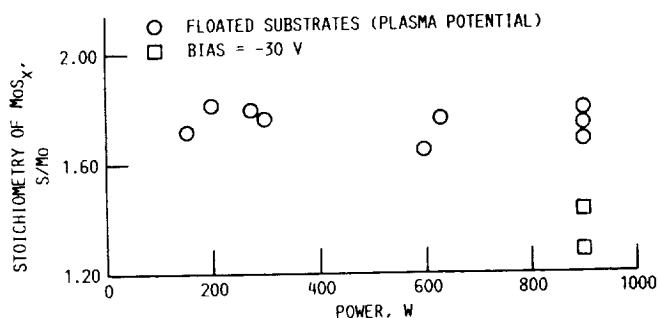


Figure 5.—Effect of radiofrequency power on the stoichiometry of magnetron sputtered MoS₂ films at 20-mtorr Ar pressure.

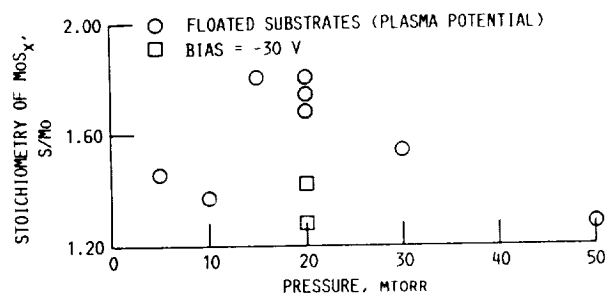


Figure 8.—Effect of Ar pressure on the stoichiometry of radiofrequency magnetron sputtered MoS₂ films at 900 W.

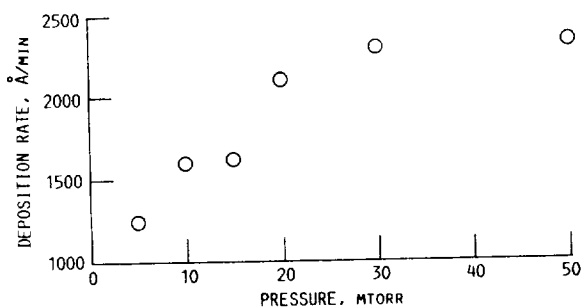


Figure 6.—Effect of Ar pressure on the deposition rate of radiofrequency magnetron sputtered MoS₂ films on floated substrates (plasma potential) at 900 W. The deposition time is equal to 10 min except for the 5-mtorr data point (4 min).

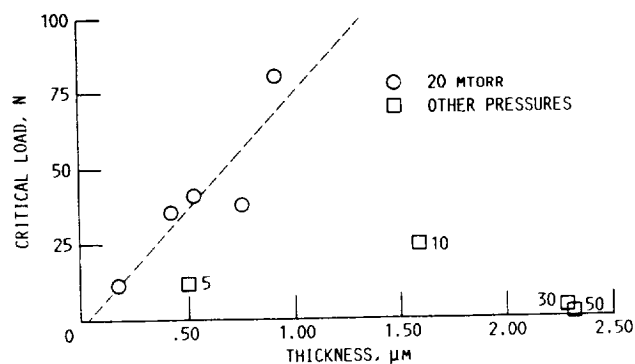
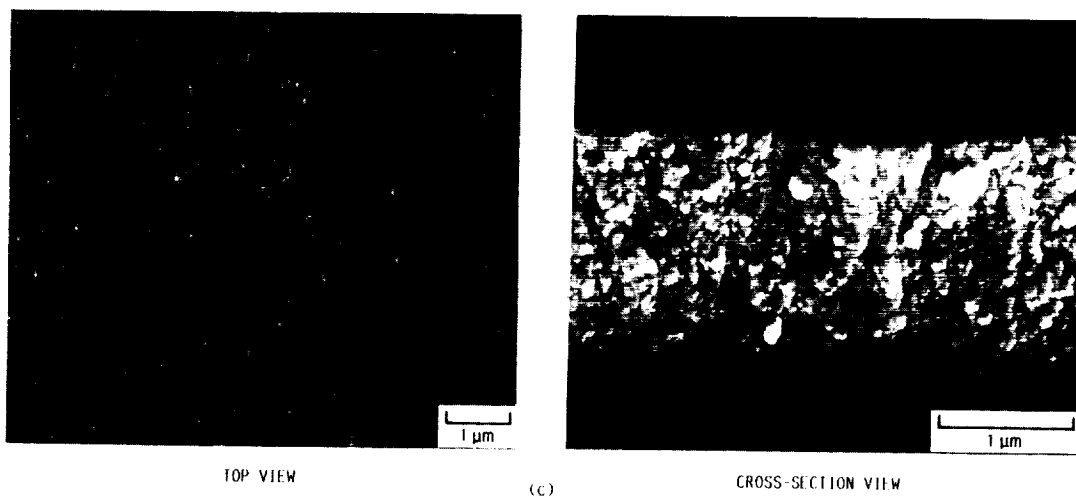
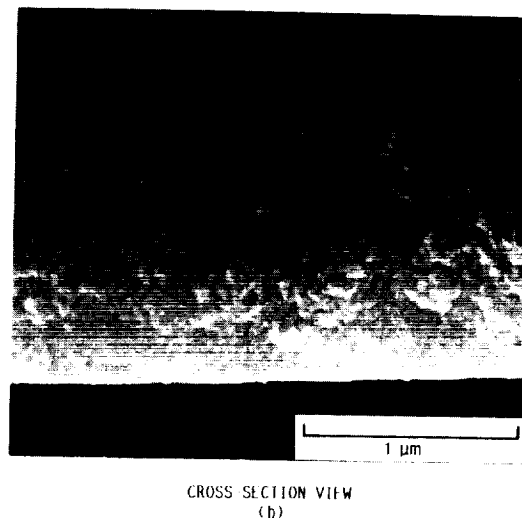
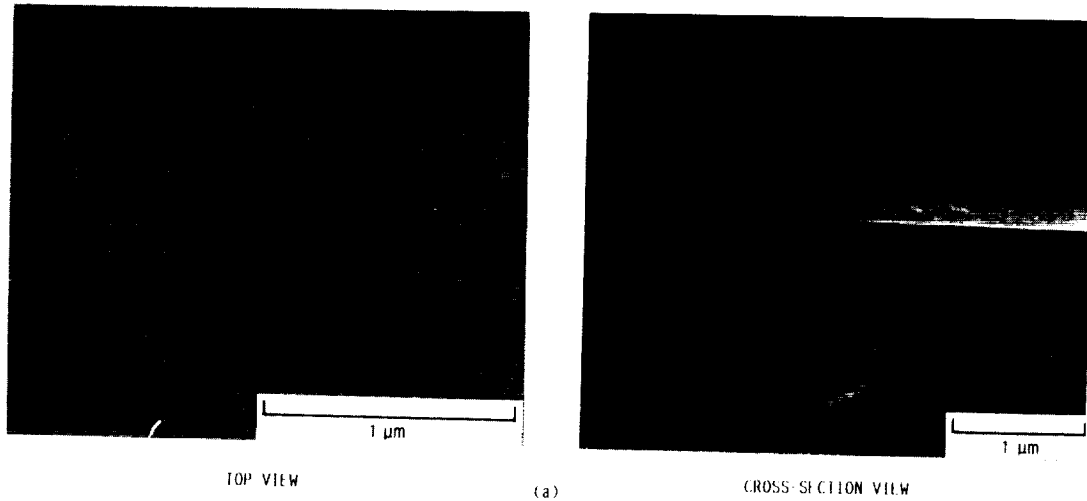


Figure 9.—Effect of Ar pressure on the adhesion of radiofrequency magnetron sputtered MoS₂ films on floated substrates (plasma potential) at 900 W. The number on each data point indicates the Ar pressure in millitorrs.

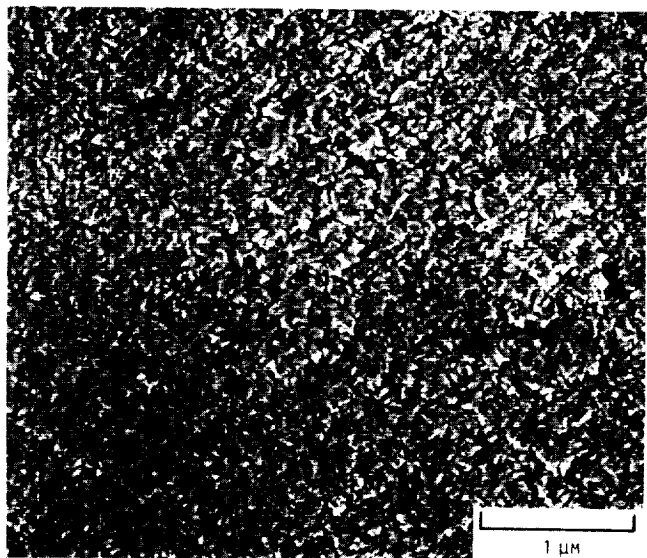


(a) Sample 787082-1; top and cross-section views of a film deposited at 5 mtorr.
(b) Sample 787070-1; cross-section view of a film deposited at 10 mtorr.
(c) Sample 783040-1; top and cross-section views of a film deposited at 15 mtorr.

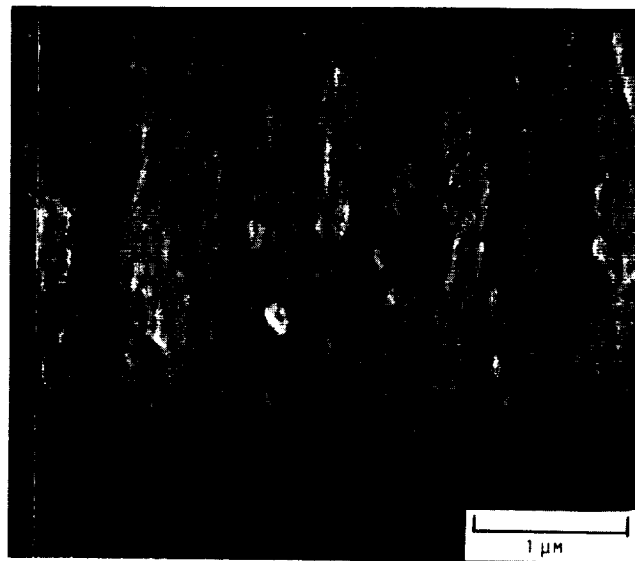
Figure 10.—Effect of Ar pressure on the morphology of radiofrequency magnetron sputtered MoS₂ films at 900 W.

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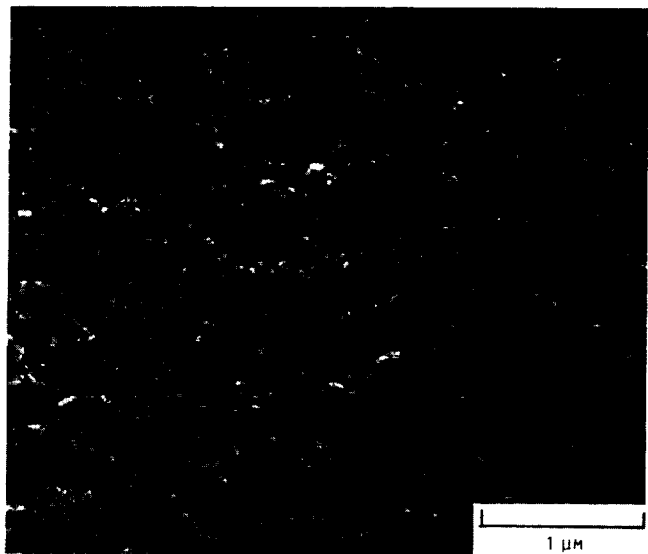


TOP VIEW

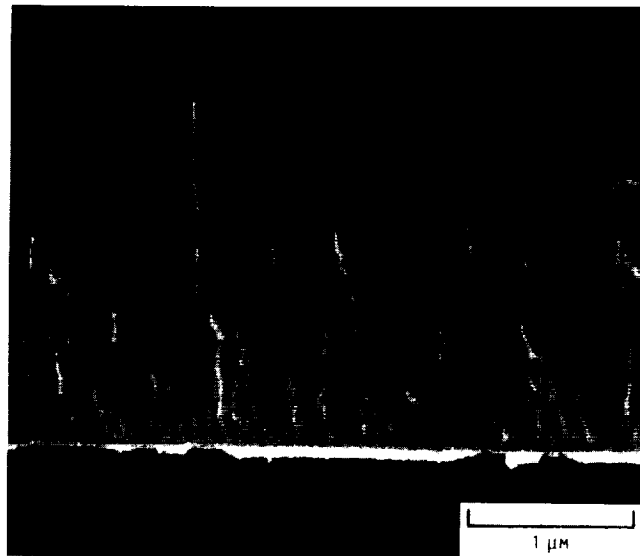


CROSS-SECTION VIEW

(d)



TOP VIEW



CROSS SECTION VIEW

(e)

- (d) Sample 786062-1; top and cross-section views of a film deposited at 30 mtorr.
(e) Sample 786062-1; top and cross-section views of a film deposited at 50 mtorr.

Figure 10.—Concluded.



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