Structure and growth of basal and random oriented MoS_x coatings deposited by magnetron sputtering

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Detailed information on the topography and microstructure of sulfur deficient MoS_x coatings deposited by magnetron sputtering at a different argon pressure, is presented. Hereto, a transmission electron microscopy investigation was done on cross sections from the interface between substrate and coating up to the outer part of 1.6 to 3 μm thick coatings. The evolution in structure and crystallographic orientation across these coatings is presented. In this way, the growth modes of MoS_x coatings with different crystallographic orientation are clarified, and the reasons why different crystallographic orientations are obtained, are explained. This clarifies also the wear dependence of some of these coatings on relative humidity. © 2003 American Vacuum Society.

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I. INTRODUCTION

The tribological properties of MoS_x coatings depend on their structure,¹ S/Mo ratio,^{1,2} thickness,^{3,4} impurity content,^{1,3,5} density and bonding strength.^{5,6} All these characteristics were linked to the deposition parameters, such as substrate temperature, argon pressure, power density, gas purity, ion bombardment, and so on. MoS_x coatings may have an amorphous or crystalline structure with different crystallographic orientations, depending strongly on the substrate temperature during deposition.^{7,8} As-deposited amorphous MoS₂ coatings possess poor lubrication properties, with a coefficient of friction up to 0.4.^{9,10} However, good lubrication is obtained when the amorphous MoS₂ structure was achieved by ion bombardment.¹¹ Crystalline MoS_x coatings may grow with a predominant orientation of the basal planes or can be random oriented. The crystallographic orientation appeared to be the most important factor that influences the tribological behavior of such MoS_x coatings. The tribological properties of basal or random oriented MoS_x coatings were investigated in uni- and bidirectional sliding tests performed in ambient air of different relative humidity.^{1–3,7,12} A basal oriented coating, with the easy-sliding (002) basal planes parallel to the substrate surface, is preferred. However such coatings have been obtained only in a few cases.^{1,2,7,13} In

addition, transmission electron microscopy (TEM) analysis on the structure and growth of such coatings has not been reported yet.

Dense and basal oriented MoS_x coatings are achieved by adjusting deposition parameters such as lowering gas pressures,² ion bombardment during growth,⁷ or doping with other elements.^{3,12,14} Chemical modification or insertion of a passive interlayer at the substrate surface can eliminate chemical sites that activate the edge facets and promote a preferential basal orientation growth over edge planes.¹⁵ Different opinions about the effect of surface roughness of the substrate on the crystallographic orientation of the coatings have been published. Bertrand¹⁵ reported that the roughness alone did not yield perpendicular orientation unless the surface was chemically active and retained OH[−] and H₂O after presputtering heating. Other authors^{10,15–17} believed that within the initial range of 100–200 nm thickness, the crystallographic orientation was independent of the roughness of the substrate, and that only the upper part of the film grew with a perpendicular orientation. Buck showed that rough substrates led to the formation of a cluster structure and resulting in poor lubrication.¹⁸ However, Roberts *et al.*¹⁹ showed that an increase of the substrate roughness from 0.04 to 0.12 microns (central line average values) could result in a lower coefficient of friction and a higher wear resistance. Similar results were also reported on burnished MoS₂ coatings.²⁰

The importance of reducing the H₂O pressure in the plasma to obtain a basal orientation was emphasized by Buck.¹ On the contrary, Mikkelsen *et al.*²¹ stated that the presence of H₂O in the plasma had no influence on the crys-

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tallographic orientation of the deposited film.

Sulfur deficient MoS_x coatings are normally produced under sputtering conditions, the preferential sputtering and the ion irradiation on the growing coating leading to the reduction of sulfur content. Dimigen *et al.*²² studied the effect of argon pressure, substrate bias potential, substrate material, and substrate temperature on the composition of MoS_x coatings. They found that the S/Mo ratio of the deposited coatings changed on a large scale, and that the crystalline structure of 2H-MoS₂ can be kept within the range of $0.95 < \text{S/Mo} < 2.17$. The lowest coefficient of friction was found for MoS_{1.5-1.7} coatings.²³ Basal oriented coatings were obtained in a range of 1.2–1.4 S/Mo ratio,² and Aubert *et al.*²⁴ obtained a similar result, i.e., $1.3 < \text{S/Mo} < 1.7$. However, Buck¹ showed that basal oriented coatings could only be produced when the S/Mo ratio was higher than 2. These results showed that the S/Mo ratio of the coatings might not be very crucial for the structure of MoS_x coatings.

In this article, the topography, the surface roughness, the cross-sectional structure, and the crystallographic orientation of MoS_x coatings deposited at different argon pressures by magnetron sputtering is discussed. The growth mode of MoS_x coatings with different crystallographic orientation is investigated along the cross section by TEM.

II. EXPERIMENT

MoS_x coatings were deposited by planar magnetron sputtering (WTCM, Diepenbeek, Belgium).²⁵ The hot-pressed MoS₂ target (Target Materials, Inc.) with diameter 75 mm had a purity of 99% and a density of 77%. A bipolar pulsed power supply type Magplus QP-100/6/15 (Magtron GmbH, Germany) was used with long duration negative pulses (40 μ s) for sputtering and short duration positive pulses (5 μ s) in order to prevent charging of the target. A turbomolecular pump (360 l/s) connected to a roots and rotary pumping unit as forepump, was used to evacuate the deposition chamber. The chamber was typically pumped down to a base pressure of about 1×10^{-3} Pa. Before deposition, the substrate surface was cleaned by sputter etching and the target was pre-sputtered with a shutter in front of the substrate. Hardened and polished ($R_a = 0.05 \mu\text{m}$) 440C stainless-steel disks were used as substrates. The deposition was mostly performed at a substrate temperature of about 80 °C. Some samples have been deposited using higher substrate temperatures up to 300 °C. The distance between the substrate and the target was kept at 65 mm, the deposition time was 14 min. the target power was set at 8 W/cm², and the argon pressure was varied between 0.2 and 2.4 Pa.

The crystallographic orientation and structure of the coatings were investigated by x-ray diffraction (XRD), using Cu K α radiation at an incident beam angle of 3° (Siemens D500 diffractometer). The morphology and roughness of the coatings were analyzed using a Nano-Scope III atomic force microscope (NanoScope III AFM, Digital Instruments Inc.), and a scanning white light/optical phase-shifting interferometer [Wyko NT 3300, resolution in *x*, *y*, and *z* (depth) direction of 4.0 μm , 4.0 μm , and 1.0 nm, respectively]. The TEM

FIG. 1. XRD spectra of MoS_x coatings deposited at different argon pressures.

samples were prepared by embedding the MoS_x coating in epoxy. They were then trimmed and cut by ultrafine microtomy²⁶ at a cutting speed of 1 mm/s, into 100 nm thick slices using a RMC MT-XL and a 45° diamond cutter (Diatom, CH) operated at an inclination angle of 6°. The thin sections were collected on copper grids, and investigated in a Philips CM 200 FEG. In this way, the growth of the coatings was investigated along their whole cross sections. The diffraction patterns were matched with a Powder Diffraction Database. The composition of the MoS_x coatings was obtained from energy dispersive analysis by x ray and x-ray photoelectron spectroscopy (XPS).

III. RESULTS AND DISCUSSION

XRD analyses of MoS_x coatings deposited at different argon pressures, showed that only the diffraction peak of basal planes was exhibited for coatings deposited at an argon pressure of 0.4 Pa and below (Fig. 1). This indicates that the basal planes are parallel to the substrate surface. These coatings are referred to as “basal oriented coatings.” Upon increasing the argon pressure from 0.6 to 2.4 Pa, the diffraction peaks related to edge planes become stronger (Fig. 1). Such coatings are referred to as “random oriented coatings.”²⁸ Upon increasing the deposition temperature from 100 to 300 °C, it was noticed that the content of edge oriented crystals in the coatings increased, and a sharpening of all the MoS_x diffraction peaks was noticed due to the increasing crystal size. The formation of basal oriented MoS_x coatings was enhanced by high-energy bombardment achieved by applying a negative bias on the substrate (−100 V).

The composition and thickness of MoS_x coatings deposited at different argon pressures are shown in Table I. Low argon pressure results in a decrease of the sulfur content, an increase of the argon content, and a decrease of the deposition rate of MoS_x coatings. XPS measurements revealed the presence of 3 to 5 at.% oxygen and 5 to 8 at.% carbon contaminants. A depth profiling indicates that the contamination level is constant throughout the whole coatings. This contamination level is frequently reported in literature.²⁷ The addition of liquid nitrogen in the pumping system was found to be vital to reduce the contamination level in the coatings.

TABLE I. Composition and thickness of bipolar magnetron sputtered MoS_x coatings deposited at different argon pressures.

Ar pressure (Pa)	0.2	0.4	1.2	1.5	2.4
S/Mo ratio	0.69	0.9	1.2	1.29	1.27
Ar content (at. %)	4.99	4.59	1.34	0.55	<0.2 ^a
Coating thickness (μm)	1.5	1.6	2.0	3.0	2.7

^aDetection limit.

Almost no oxygen or carbon was detected in MoS_x coatings deposited in the presence of a liquid-nitrogen trap, except at the surface of the coating due to postoxidation and surface contamination.

The AFM topography of basal and random oriented MoS_x coatings deposited at 0.4 and 1.5 Pa argon is shown in Fig. 2. The surface of basal oriented coating shows a clusterlike feature [Fig. 2(a)], whereas a rigid and edge feature is no-

TABLE II. Roughness data recorded in an area of 600×800 μm² on basal and random oriented MoS_x coatings by scanning white light/optical phase-shifting interferometer. σ represents the standard deviation.

MoS _x coatings	R_a (nm)	σ_{R_a} (nm)	R_t (nm)	σ_{R_t} (nm)	R_{sk}	$\sigma_{R_{sk}}$
Basal oriented coating (0.4 Pa argon)	15	2	175	92	-0.7	1.4
Random oriented coating (1.5 Pa argon)	16	8	404	465	-2.7	3.7

ticed as topography on random oriented coatings [Fig. 2(b)]. Roughness values (R_a , R_t , and R_{sk}) were determined by scanning white light/optical phase-shifting interferometer analyses performed on a large sample area of 600 × 800 μm² (Table II). Comparable R_a values for these two types of MoS_x coatings were recorded by AFM on a small sample area of typically 2 × 2 μm², namely 16 nm for basal oriented coatings and 18 nm for random oriented ones. It appears thus that the roughness value, R_a , of basal and random oriented MoS_x coatings are almost the same, while R_t , R_{sk} , and their standard deviations of the profile data of random oriented MoS_x coating are higher than those for basal oriented ones (Table II). This indicates that the roughness of a random oriented MoS_x coating is higher than a basal oriented MoS_x coating. The negative value of R_{sk} in Table II shows that the surface of both coatings consists more of valleys than of peaks, and that the valleys in random oriented coatings occur more frequently than in basal oriented MoS_x coatings.

The whole cross sections of basal and random oriented MoS_x coatings deposited at 0.4 and 1.5 Pa argon pressure, are shown in Figs. 3(a) and 3(b), respectively. The long arrow, starting at the coating/substrate interface, indicates the direction of growth of these coatings. The structure of basal oriented coatings is quite uniform with some clusterlike features [Fig. 3(a)]. A substructure, as indicated by the small arrows "1" in Fig. 3(a), consisting of strips parallel to the substrate surface, is also noticed. The cross-sectional TEM sample of this basal oriented coating is curved along the substrate/coating interface [see from lower left- to upper right-hand side in Fig. 3(a)]. In the outer part of that coating, cracks are noticed after microtomy, pointed out by the small arrows "2" in Fig. 3(a). These cracks seem to result from the bending of the samples on microtomy. Both facts indicate that a high residual stress is present in these basal oriented MoS_x coatings. In random oriented MoS_x coatings, such facts were not noticed, indicating lower residual stress in such coatings. The contrast in Fig. 3(a) is small because of the uniform basal orientation and the dense structure of the basal oriented coatings. On the contrary, random oriented MoS_x coatings show a columnar feature and the contrast of the TEM picture is larger than that of basal oriented ones. This can be attributed to the random orientation and the porous structure of the coatings. The size of the columnar crystals varies, and reaches sometimes up to about 500 nm [Fig.

FIG. 2. AFM analyses of (a) basal (0.4 Pa argon) and (b) random oriented (1.5 Pa argon) as-deposited MoS_x coatings.

FIG. 3. Complete cross section by TEM of (a) basal (0.4 Pa argon) and (b) random (1.5 Pa argon) oriented MoS_x coatings. The big arrows start from the substrate/coating interface and point out in the direction of growth of the coatings.

3 (b)]. This columnar shape shows that the growth along the edge plane direction is much faster than along the basal plane direction. This is supported by the grow out of isolated needlelike crystals at the outer surface of the MoS_x coatings [see small arrows in Fig. 3(b)], that was in fact the growth frontier of the coatings. This finding can be linked to the fact that, for an identical deposition time, the thickness of the random oriented coating ($3.0\ \mu\text{m}$) is much larger than for basal oriented ones ($1.6\ \mu\text{m}$) (see Fig. 3), revealing a higher deposition rate in cases where random oriented coatings are deposited. The fact that random oriented coatings are more vulnerable to moisture than basal oriented ones,^{13,28} can be linked to this columnar structure which provides an easy path for moisture to penetrate into the coatings.

Fringes corresponding to (002) planes of MoS_2 crystal are visible in Figs. 4 and 5 for basal and random oriented MoS_x coatings, respectively. In Figs. 4 and 5, the arrows also start at the substrate/coating interface and point out in the direction of the growth of the coating. Although there are some local disturbances, the basal planes in basal oriented MoS_x coatings are mainly parallel to the substrate surface right from the interface (Fig. 4). Such fringes were detected throughout the whole cross section. On the contrary, the growth of random oriented MoS_x coatings is not uniform

FIG. 4. Cross section by TEM of basal oriented MoS_x coatings at an early growth stage. The arrow starts at the substrate/coating interface and points out in the direction of the growth of the coating. Insert: diffraction patterns of (002), (102), and (107) planes of MoS_2 crystals.

throughout the coating thickness but is divided into three stages. At the first stage, basal oriented crystals nucleate and grow onto the substrate. When the thickness of the coating increases to more than 30 to 45 nm (as shown in the bottom part of Fig. 5), a second growth stage is reached. Edge oriented crystals appear and grow competitively with basal oriented crystals (as in the main part of Fig. 5). Finally, at the third stage, the growth of edge oriented crystals dominates. This can be clearly seen from Fig. 6 in which a TEM picture taken in the middle of the coating is shown. The thickness at which the growth of MoS_x coatings evolves from the initial basal orientation into a random orientation, has been reported in literature but a large scatter in values is noticed. Indeed, 100 to 200 nm was reported by Bertrand,¹⁵ while Hilton *et al.*²⁹ mentioned 5 to 10 nm. In our tests, this initial stage last for about 30 to 45 nm. The different thickness of the initial stage is probably related to the different deposition conditions used by different researchers, such as substrate temperature and deposition rate.

FIG. 5. Cross section by TEM of random oriented MoS_x coatings at the early growth stage. The arrow starts from the substrate/coating interface and points out in the direction of the growth of the coating

FIG. 6. Cross section by TEM of random oriented MoS_x coatings in the middle of the coating far beyond the interface area. The arrow indicates the direction of growth of the coating. Insert: diffraction patterns of the (002), (102), and (107) planes of MoS₂ crystals.

From a scanning electron microscopy analysis, Spalvins suggested three structural growth morphologies in MoS₂ coatings with a thickness of 0.02 to 2 μm .³⁰ The sequence from bottom to top consisted of a ridge formation zone, an equiaxial transition zone, and a dense packed columnar zone.³⁰ Based on TEM analysis in this work, these three stages can now be related to different growth modes. The first stage is the initial nucleation and growth of basal oriented crystals; the next one is the transition stage corresponding to the competitive growth between basal and edge oriented crystals; and, finally, the third one is linked to the growth of mainly edge oriented crystals. Due to the difference in surface energy and kinetic approach, the edge planes tend to grow faster than the basal plane. On edge planes, both S and Mo atoms are exposed at the growth frontier, the deposited atoms of these two species can easily find the proper sites to attach. But a sequential order of atom species is required and the growth is slowed down in the basal direction.³¹ This work shows that the formation of basal or random oriented coatings resulted from the competitive growth between basal and edge oriented crystals. The deposition parameter, especially argon pressure, is crucial in controlling the growth in basal orientation. First, the mean-free path is larger and the sputtered species are less thermalized when reaching the substrate. Second, the bombarding of the growing coating is stronger at a low argon pressure. As a result, the growth of basal oriented crystals is enhanced at decreasing argon pressure. In the meantime, the deposition rate and the sulfur content of the coatings are reduced.

The fringe distances for both basal (Fig. 4) and random (Figs. 5 and 6) oriented MoS_x coatings are about 0.7 nm. That value is larger than the distance between (002) basal planes in MoS₂ crystal, namely 0.6 nm. This is in accordance with XRD results where it was noticed that the diffraction peak of the (002) plane is shifted to lower angles. This might result either from the deficient sulfur content or from the residual stresses present in the MoS_x coatings.

IV. CONCLUSIONS

MoS_x coatings with different crystallographic orientation can be deposited by adjusting the deposition conditions, mainly the argon pressure. This investigation demonstrates that dense and basal oriented MoS_x coatings with the basal planes parallel to the substrate are obtained at an argon pressure of 0.4 Pa or below. These coatings contain high internal stresses and exhibit a basal orientation right from the start of the deposition process. The growth of basal oriented crystals is enhanced, as the sputtered species have a larger mean-free path to move, and the bombardment of the growing coating is stronger at low argon pressure. At argon pressures above 0.4 Pa, the ratio of edge to basal oriented crystals in the coatings increases, and that results in random oriented MoS_x coatings with a columnar structure and low internal stresses. A major difference in the roughness parameters R_t and R_{sk} is noticed for these two types of MoS_x coatings, indicating different growth modes.

Based on a TEM analysis, the growth of random oriented coating could be divided into three stages related to different growth modes. The first stage is the nucleation and growth of basal oriented crystals; followed by a transition stage where a competitive growth between basal and edge oriented crystals takes place; and finally, the third stage characterized mainly by the growth of edge oriented crystals.

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