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EFFECT OF MOLYBDENUM CONTENT ON THE STRUCTURE AND TRIBOLOGICAL PROPERTIES OF DIAMOND-LIKE CARBON FILMS

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Abstract: Molybdenum doped amorphous diamond-like carbon thin films (Mo-DLC) were deposited on Si (100) substrates by magnetron sputtering. The graphite and the molybdenum cathode current were fixed at 1 A and 0.25 A, respectively. The deposition duration was 600 s, and the distance was 6 cm. During the deposition the Mo content was changed by increasing the opening of a shield mounted above the Mo target from 4 mm to 32 mm and at the end without shield. The elemental composition, surface morphology, structure, and friction forces of the films were investigated by energy dispersive X-ray spectroscopy (EDS) and atomic force microscopy (multimode 8 Bruker) and Raman spectroscopy. The EDS results indicated that the Mo content increased with the opening of the shield above the Mo target. Additionally, the Raman spectra of the films indicated that the sp^2 carbon sites fraction increased, and graphitization was induced. The average surface roughness R_a slightly increased from 1.3 to 2.7 nm with the rise of Mo content. The friction coefficient of the Mo doped DLC films depended on the structure and composition of the films.

Keywords: Molybdenum, morphology, roughness, friction, AFM, tribology.

1. INTRODUCTION

Nowadays, various metals such as Mo, Ag, Ti, Ni, Cr, Ag as well the non-metals elements Si, O, N, F were remarkably used as doped materials in the diamond-like carbon (DLC) films. Each dopant has unique role in modifying the film structure and as consequence enhancing a desirable property for different DLC film types and in several application domains [1-5]. The doping process of DLC films with molybdenum (Mo) has demonstrated its enhancing role for the tribological and mechanical characteristics, like reducing the compressive stress, friction coefficient and enhancing the corrosion and wear resistance as well improving the hardness [1, 6].

Recently various research was reported in the literature on molybdenum doped DLC films (Mo-DLC) [1 ,2, 6-8]. It has been observed that the DLC coatings exposed to failures on substrates, usually due to intrinsic stress [9], however this issue is generally overcome by deposit metal interlayer or metal doping in a carbon matrix which significantly improved the coating adhesion on several substrates [10]. It was reported that molybdenum could enhance the toughness of the material, due to its ability to form carbides in the film's matrix. As well like other metals, the incorporation of nanoparticles metals in the film results in more graphitization and subsequently provides more stable films at low dopants amount [11].

In this work, we investigated the characteristics of DLC and Mo-DLC films prepared by direct current (DC) magnetron sputtering system. The objective of this study was to synthesize and characterize the microstructure and tribological properties of DLC films with various Mo content, focusing on nanotribological property scale using atomic force microscopy (AFM).

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2. EXPERIMENT

In this work, the direct current magnetron sputtering technique was used to deposit the DLC and Mo-DLC thin films using graphite and molybdenum cathodes. The deposition was done on two copies of silicon (100) substrates. Prior to formation, an argon plasma cleaning was used to the surface for 10 minutes to remove the contaminations and activate the surface. Argon was used as sputtering gas and the distance between the Si substrate and targets was set to 6 cm and the deposition time was 600 s for all samples. For the DLC film the discharge current of the graphite target was fixed at 1.5 A, while the Mo-DLC samples the discharge current of the graphite and molybdenum targets were fixed at 1.5 and 0.25 A, respectively. A shield mounted above the Mo target was used to change the molybdenum amount in the Mo-DLC films by changing the opening of a rectangular slot in this shield. The slot opening started with 4 mm until 32 mm. The deposition system used for the formation of films is shown in Figure 1, where the substrate was moving above the targets back and forth at the same altitude.

Figure 1. The photo of magnetron deposition system, control panel with the main elements (left) and deposition chamber (right).

The Bruker Quad 5040 spectrometer, AXS Microanalysis GmbH XPS, was used to measure the thin film's elemental composition. The measurements were done using the following parameters: 15 kV, magnification of 100, surface area of ~1.15 mm^2, 3-5 different spots. The average values of the elemental composition were calculated. The structure of the deposited films was characterized at room temperature using Raman scattering spectroscopy. The technical data of this Raman spectroscopy are as follows: excitation wavelength: 532 nm; semiconductor laser power: 45 mW; stokes lines range: 100 to 8000 cm^{-1}; resolution: < 1 cm^{-1}; The measurement was done several times on different spots for each sample. The measurement parameters were selected as follows: exposure time 10 s, accumulations number 3, laser power 0,3 mW, range from 100 to 2000 cm^{-1}, spot size ~10 µm. The Atomic force microscopy (AFM) is a widely used technique to investigate at an extremely low scale the height profile of surfaces with different materials. This property distinguishes the AFM from the conventional microscopes such as the optical and electron, where the vertical dimension at the wanted scale cannot be measured using them. The notable distinction in the function principle overall the traditional microscopes is that the AFM does not rely on the electromagnetic radiation as the measurement means, but instead it uses the mechanical contact to provide three-dimension topography images. In this work the multimode 8 Bruker AFM was used. The contact mode was used to investigate the surface morphology and the friction at nanoscale with the sharp standard cantilever HQ:CSC17/ALBS, and its technical properties provided by the manufacturer are listed in Table 1.

Table 1. HQ:CSC17/ALBS cantilever, manufacturer technical properties [12].

Cantilever	Resonance frequency KHz			Force constant N/m			Length l ± 5 µm	Width w ± 3 µm	Thickness t ± 0.5 µm
17 Series	min	nominal	max	min	nominal	max	450	50	2
	10	13	17	0.06	0.18	0.4			

3. RESULTS AND DISCUSSION

In Table 2. EDS results indicated that the elemental composition of DLC film was carbon and oxygen. The presence of silicon content is expected as the substrate is made from silicon. The values in this table reveals as expected that the atomic percentage of the molybdenum increased from 0.32 at.% to 6.61 at. %, respectively with the increase of opening slit above the molybdenum target from 4 to 32 mm, respectively. The Mo content in samples increased proportionally with the widening of slot from 4 and 32 mm. Since more sputtered Mo atoms will be able to deposit on the substrate.

Table 2. The average values of the elemental composition of samples.

Samples \ Elements	Silicon, at. %	Carbon, at. %	Oxygen, at. %	Molybdenum, at. %
DLC	68.60	29.33	2.07	---
Mo-DLC1	71.02	26.80	1.86	0.32
Mo-DLC2	61.95	27.70	3.74	6.61

Meanwhile the carbon content slightly decreased from 29.33 at. % to 27.70 at. %. Contrarily and as expected, the oxygen content increased from 1.86 at. % to 3.74 at. %. This slight decrease in the carbon content is reasonable as the more oxygen and molybdenum atoms are deposited, so the carbon share was reduced. The increase of oxygen amount is due to the high reactivity of the molybdenum with the oxygen. This increase of oxygen indicates the formation oxide phases incorporated into the DLC films [1, 6]. The reason for having this high oxygen amount is that before the deposition of coating, the sputter-cleaning of the molybdenum target was done. Therefore, during the cleaning process, some of the oxygen residues in the chamber were united with the molybdenum target before deposited on the films.

The Raman spectra of DLC and Mo-DLC films were plotted using Origin software. The G and D peaks positions, the intensity ratio of D and G peaks were obtained. The Raman spectra parameters values were calculated from the average of three different spots taken during the measurements and the Raman spectra were well fitted with the Gaussian function. The intensity of the Raman spectra was reduced with the increase of the molybdenum content in the film, which was observed [1, 6]. When the Mo content increased from 0.32 to 6.61 at. %, the intensity peak ratio I(D)/I(G) was increased from 0.85 to 1.07 and the G peak full width at half maximum (FWHM) became narrower from 133 cm^{-1} to 117 cm^{-1}, respectively. These two parameter trends are well fitted with the results of other studies. Similar trends were observed in DLC films doped with different metals, especially in the chromium doped DLC films. Also, this study indicates that the increase in the I(D)/I(G) demonstrates a higher disorder in the coating, formation of more aromatic disorder rings, or increase in the fraction of sp^2 carbon sites [1]. Many other authors obtained a similar trend when the concentration of metal was enhanced in the DLC film [2,13, 14]. However, the G peak position shifted to a higher position from ~1565 cm^{-1} to ~1571 cm^{-1} with increasing of Mo content. The reason for having this trend could be due to the oxygen amount, and this is what was proving the W. Liu et al. [14] study, where a similar trend was noticed. It was demonstrated that oxygen's presence leads to modifying the coating's structure. Also, a large amount of oxygen causes the sp^2/sp^3 ratio to be increased radically and heightens the presence of carboxyl (O–C=O) groups and carbonyl (C=O) groups. M. Evaristo et al. [15] found that the existence of oxygen is responsible for augmenting graphitic clusters and the sp^2 content. The D peak shifted from 1390 cm^{-1} to 1393 cm^{-1} with the increase of Mo content. This result agreed with the previously mentioned studies. Thus, the Raman results indicated that the addition of Mo (and increase of oxygen) stipulates the formation of DLC films with a higher fraction of sp^2 bonds.

The statistical quantities of the roughness parameters were extracted from the AFM images with the scale (10μm*10μm) from 3 different spots measured on the sample's surfaces (fig. 2. The surface roughness was the lowest for the DLC films with average surface (R_a) and root mean square (RMS) values of about 3.1 nm and 4.9 nm, respectively. Skewness and kurtosis were 2.3 and 13.4 and the lateral force was 0.49 nN. For the Mo-DLC films R_a and RMS values were slightly increased from 1.3 to 2.7 nm and from 2.2 to 4.2 nm, respectively with the increasing of Mo content from 0.32 at. % to 6.61 at. %. The skewness slightly changed from 3.8 to 1.7 and kurtosis from 53 to 38 respectively. A similar observation was made in the work of D.B.Padmanaban et al. [1], where the surface roughness values of Mo-DLC films rose from 0.7 to 1.2 nm as the Mo amount increased from 3.9 at.% to 16.2 at.%. The enhancement in Mo content led to the formation of a higher fraction of the molybdenum carbide phase, thus increasing the metallicity of the film, as stated by the authors. Another reason could be the graphitization of the DLC films due to doping with Mo, while the sp^2 fraction sites grow and the fraction of sp^3 carbon sites reduces [16]. D. Zhao et al [17] found that the adatoms with higher energy would promote the migration of small grains into larger agglomerates and increase the density of DLC film. However, when the highest flux of Mo atoms was used, the agglomeration of larger granules began to dominate and resulted in the highest surface roughness.

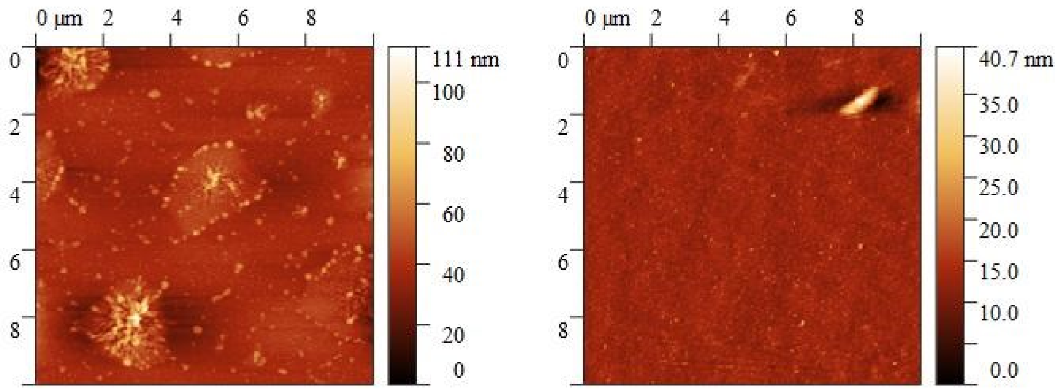

Figure 2. Topography surface of the DLC (right) and Mo-DLC (left) films.

The AFM measurements indicated that the lateral force slightly decreased from 0.13 to 0.07 nN with the increase of the Mo concentration in the films. Also, by measuring the lateral force at different applied force from 10-40 nN, the friction coefficient was possible to calculated. The results show that the DLC and Mo-DLC1 films have friction coefficient of 1.16 and 0.97, respectively. It is expected for Mo-DLC2 the friction coefficient value should be lower as the lateral force is lower. Similar results were obtained by D.B. Padmanaban et al. [1] where possible formation of nanoaggregate features enhanced the surface roughness of the Mo-DLC films. This could be due to the existence of a higher fraction of molybdenum carbide phase and increased metallicity of the coating. Tomala et al. [18] noticed that the friction coefficient is lower if the content of sp^2 bonds is higher. In addition, Kolodziejczyk et al. [9] carried out a broad range of friction coefficient measurements on Ag- and Si-doped DLC films using AFM tips coated with DLC and Si [19]. It was found that the lateral force was affected by two factors: firstly, the affinity of the AFM tip, and secondly, the amount of hydrogen in the Ag-DLC and Si-DLC coatings that limits the adhesive interaction with oxygen species, water vapor, and the AFM tip surface. The results revealed that the friction coefficient of Mo-DLC films depends not only on the Mo dopant, but also on the oxygen content, sp^2/sp^3 ratio, and the films bonding state.

CONCLUSIONS

The Raman spectroscopy measurements demonstrate that the Mo doped DLC films contained a high fraction of sp^2 carbon sites compared to DLC films. The fraction of sp^2 carbon and oxygen content increased with the increase of the molybdenum amount in the DLC films from 0.32 at. % to 6.61 at. %, respectively. The sp^2/sp^3 carbon sites ratio (graphitization) in the films increased with increase of Mo concentrations. The morphology was measured using Bruker AFM multimode 8 with sharp cantilever HQ:CSC17/ALBS. The average surface roughness of the films slightly increased from 1.3 to 2.7 nm. The results indicated that lateral force decreased from ~0.5 nN to 0.07 nN with the enhancement of Mo content in the films. The friction coefficient was reduced by 17% with addition of 0.32 at. % of Mo, further increasing in the Mo content might lead to a greater decrease in the friction coefficient value. As the results revealed from the literature works, the interpretation of the tribological data require a deeper investigation especially for the bonding states of the films with equipment such as XPS.

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