VACUUM ARC DEPOSITED DLC BASED COATINGS

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The great interest in the use of diamond-like carbon (DLC) films as a coating material is justified by the superior wear resistance and hardness, chemical inertness, and very low friction coefficients of these coatings. Vacuum arc deposition is well suited to prepare superhard films with high sp^3/sp^2 ratios. However, the high level of internal stresses originating during growth prevents the deposition of thick films, and their hardness makes it difficult for DLC layers to comply with substrate deformations. In order to overcome these limitations, different approaches are possible. Multilayer structures are one means to maintain the surface mechanical properties of the DLC while relieving the internal stresses. Another possibility is to dope the DLC films in order to reduce the internal stress and to stabilize the desirable sp^3 bonds to higher temperatures. At higher doses of dopants, the formation of nanocrystals is possible and the properties of the coatings change drastically. All these approaches were investigated on films prepared by cathodic arc and a synthesis of the results is presented here.

I. Introduction

In response to the challenges of implementing diamond-like carbon (DLC) into several applications, different strategies have been developed in order to enhance their performances. Addition of alloying elements such as refractory metals [1], silicon [2-4], nitrogen and fluorine was extensively investigated. Incorporation of such elements typically leads to improvements in some properties at the expense of others.

The formation and properties of nanocomposite, functionally graded layers and multilayers involving DLC has also been the subject of extensive work [5-6]. The results are very promising [7].

Stresses can reach values higher than 10 GPa in pure non-hydrogenated DLC [8], and about 3 GPa in hydrogenated DLC [2]. If there is a general acceptance in the literature on the effect of alloying elements on the reduction of internal stress, the results

concerning other properties are not as generally accepted. For example, reports on the influence of the silicon concentration on the hardness of the DLC doped films are contradictory [2, 9, 10]. Most of the work on silicon additions to DLC has involved hydrogenated films. The effect of tungsten and titanium additions on the mechanical is highly dependent on the concentration of the alloying element that induces changes in the structure of the films.

Many parameters such as proportion of the different layers, the structure of the interfaces control the properties of multilayers. A comparison of the properties of coatings prepared by different techniques is thus rather difficult.

The work presented here focuses on non-hydrogenated DLC based coatings prepared by filtered cathodic arc and will briefly summarize results on mechanical properties and structure of silicon and tungsten doped layers, TiC-DLC nanocomposites and TiC-DLC multilayers.

II. Experimental procedure

II.1. DEPOSITION

The various coatings were prepared using two filtered cathodic plasma sources and a pulsed bias voltage applied to the substrate. Depending on the desired structure of the coatings (doped DLC, multilayers, nanocomposite), the two sources were triggered simultaneously or successively. In all cases, one source was fitted with a graphite cathode and the other with the addition element cathode: Silicon, titanium or tungsten. For the doped and nanocomposite layers, the composition was controlled by varying the duration of the pulses in each source. During each plasma pulse a fraction of a monolayer was deposited. No layering was observed in these conditions. For the multilayers, the carbon source was working by itself for the deposition of the pure DLC components. The titanium source was added for the synthesis of the TiC_x component of the multilayers.

A pulsed bias voltage was applied to the substrate during each arc pulse. The pulse duration of the sources varied between 0.5 and 10 ms. The arc frequency was 1 Hz and pulsed bias voltage of -100 V was applied to the substrate with alternating on-periods of $2\text{ }\mu\text{s}$ and off-periods of $6\text{ }\mu\text{s}$. To obtain a diffuse interface between the substrate and the coatings or between the different layers composing the coatings, a higher bias voltage of -2000 V was imposed for a short period before switching to -100 V.

II.2. CHEMICAL AND STRUCTURAL CHARACTERIZATION

Quantitative chemical composition of the deposited coatings was obtained by Rutherford Backscattering Spectroscopy using a 1.8 keV He^+ beam. X-Ray photoelectron spectroscopy (XPS) and Auger Electron Spectroscopy (AES) were used to characterize the bonding in the films and the depth distribution. Transmission

electron microscopy was used to characterize the morphology and structure of the films, TEM was carried out in a Phillips CM200 with a PEELS system and a Topcon 002B with point resolution of 0.19 nm at 200 kV.

II.3. MECHANICAL AND TRIBOLOGICAL CHARACTERIZATION

Hardness and elastic modulus of the films were determined by nanoindentation using a Hysitron Picoindenter. The hardness was evaluated from the residual impression of the indenter whereas the modulus was evaluated from the slope of the load-unload curve at the beginning of the unloading process [11]. A Hysitron Triboscope was used to determine the friction coefficient. It was determined using a single-pass scratch test. Ball on disk wear tests were performed to evaluate the macroscopic wear resistance of the layers using a CSEM apparatus. The tests were performed in 50% relative humidity, with a 2N load, a 6mm in diameter alumina ball at 0.2 m/s speed.

III. Results and discussions

III.1. SILICON DOPED AND TUNGSTEN DOPED LAYERS

The Si-content of the DLC:Si films used in this work are 3 at%, 5 at% and 6 at% as determined by RBS. The W-content of the DLC-W films varied between 1 and 10 at%. The film composition and structure result from a balance between the incident ion currents from the two plasma sources and the sputtering rates of the individual elements due to the incident energetic Si^{n+} or W^{n+} and C^+ ions. The mean charge state of the Si^{n+} ions generated by the cathodic arc source is 1.4 while the mean charge state of the W^{n+} ions is higher than 3. This is extremely important for the mean energy transferred to the growing film. It is dependent on the proportion of the elements incorporated in the films all other conditions remaining constant. It is known that the properties of undoped DLC depend strongly on the energetics of the deposition. However, for low ratio of addition element in the mixed plasma stream the final effect of the difference in energy transfer should be relatively small especially in the case of silicon.

For both systems, the films are totally amorphous in the range of concentration considered here. The sp^3 content increases with the incorporation of silicon in the films [10], the highest ratio being obtained for 3 at%. The hardness values of DLC/Si films obtained at several loads are shown in figure 1. The values given in this figure are not corrected for the deformation of the diamond indenter. The “real” hardness is probably slightly lower than the values that are quoted. The hardness of undoped DLC films prepared in similar conditions is of the order of 72 GPa. The addition of silicon induces a hardness decrease but it is accompanied by a large decrease of internal stress.

A similar behavior is observed for W:DLC films as shown in figure 2 a and b. The addition of 1at% of tungsten reduces the stress by a factor of three but decreases the hardness only by 15%. In both systems, the best compromise between reduced stresses and hardness is obtained at low concentration of the addition element. The weaker Si-C

and W-C bonds could be responsible of the reduction of the stress and of the hardness. These bonds also stabilize the sp^3 configuration of the carbon atoms. The very strong effect of tungsten could also be related at high concentration to the modification of the sp^3/sp^2 ratio resulting from the large energy input per W atom.

figure 1: Hardness of the DLC:Si films obtained at several loads

Figure 2: variation of (a) internal stress and (b) hardness with the W-content in DLC:Z films

III.2. TiC_x -DLC MULTILAYERS

Figure 3 presents the structure of three multilayers based on TiC_x and pure DLC components. Each interface was deposited at a bias voltage of $-2000V$ while the bulk is deposited at -100 V for ensuring a good adhesion between the different components of the film. Figure 4 gives the hardness and elastic modulus of the same layers at different loads. None of these values was corrected for the deformation of the indenter tip. This deformation is responsible of the abnormally high value of the registered hardness. The decrease of hardness as a function of load reflects the hardness variation

with indentation depth. The contribution of TiC_x layers, having a lower hardness than pure DLC, increases with the indentation depth and thus reduces the total hardness of the system.

figure 3: TEM of multilayers (a) DLC-TiC_x-DLC-Si, (b) DLC-TiC_x-DLC-TiC_x-DLC-Si and (c) DLC-TiC_x-DLC-TiC_x-DLC-TiC_x-DLC-Si

Figure 4: variation of the (a) elastic modulus and (b) hardness of the multilayers: triangle = DLC-TiC_x-DLC-Si, dots = DLC-TiC_x-DLC-TiC_x-DLC-Si and squares = DLC-TiC_x-DLC-TiC_x-DLC-TiC_x-DLC-Si

The elastic modulus follows a similar trend. The strong reduction of the hardness and modulus for the 7 layers film is due to the high proportion of interfaces in this film. The interfaces are soft because the sp^2 content is high for films deposited with a -2000V bias. The friction coefficient measured during a single-pass nanoscratch reflects the penetration of the indenter in the different layers when the load is increased as shown on figure 5. The step noticed when the normal load reach a value of $100\text{ }\mu\text{N}$ is probably due to the penetration of the indenter in the second layer. This layer is softer and has another composition. The friction coefficient of TiC is higher than for DLC. The step increase in partially due to the change of contact nature but also to an increase of the plowing contribution to the friction coefficient.

The value of the friction coefficient obtained at the nanometric scale is similar to those measured during macroscopic wear tests. In those tests, a step-like variation of the

Figure 5: variation of the friction coefficient during a single-pass nanoscratch in the DLC-TiC_x-DLC film .
The normal load increases linearly from left to right

friction coefficient is also observed as the number of rotations is increasing. The contact of the alumina ball with the TiC_x layer is probably also responsible of this sudden increase. In this conditions, the normal load is constant but the top DLC layer is progressively wearing out with the TiC_x layer showing up in the center of the track. For the TiC_x-DLC system studied here, the best compromise seems to be a 5 layer films. The hardness and elastic modulus of this film are high and its wear behavior is excellent.

IV. Conclusions

By doping, forming nanocomposite layers or alternating DLC and carbide containing layers, it is possible to tune the mechanical properties of DLC based coatings and to overcome the main disadvantages of pure DLC films. The proportion of the alloying element is critical for the structure of the coatings and for their properties. At low concentrations, the amorphous structure is mainly maintained, the stress reduction is significant and the hardness remains relatively high. At higher concentrations, attention must be paid to the mean charge state of the alloying element because it can modify the energy transferred to the growing film and thus indirectly change the sp³ to sp² ratio. The alloying element can form a separate phase giving rise to a nanocomposite structure. The parameters controlling the mechanical properties in those films differ from those observed in the doped layers.

The proportion of “soft” interface and the relative thickness of the DLC and TiC_x layers are the key factors for the mechanical properties of the multilayers.

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