TITLE: CHARACTERIZATION AND PERFORMANCE OF DLC FILMS SYNTHESIZED BY PLASMA AND ION BEAM TECHNIQUES

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CHARACTERIZATION AND PERFORMANCE OF DLC FILMS SYNTHESIZED BY PLASMA AND ION BEAM BASED TECHNIQUES

Abstract

Diamond-like carbon (DLC) films have been deposited on dissimilar substrates using three different deposition processes. Two well-studied deposition methods, employing cathodic arcs and rf-plasma self-bias, have been used. These two processes differ in that cathodic arc processes use gas pressures less than 1 mtorr and deposit atomic ions with energies less than 100 eV, while rf-plasma self-bias processes use gas pressures greater than 1 mtorr and deposit molecular ions with energies greater than 100 eV. In addition, DLC films have been deposited using a new plasma-based, pulsed-bias process. The pulsed-bias process uses gas pressures greater than 1 mtorr and deposits molecular ions with energies greater than 1000 eV. Both the self-bias and pulsed-bias processes utilized hydrocarbon gases as the carbon source. Cathodic arc processes generally rely on the arc between two graphite electrodes as the carbon source. Deposited films from all three processes have been characterized using ion backscattering techniques, Elastic Recoil Spectrometry (ERS), Transmission Electron Microscopy (TEM) and Selected Area Diffraction (SAD). Films deposited using the cathodic arc process are virtually hydrogen free while the self-bias and pulse-bias films contain up to 40% hydrogen. TEM results indicated the films are homogeneous and amorphous. The hardness, elastic modulus, coefficient of friction and wear rate of the films are also reported.

Introduction

A number of methods have been devised to deposit DLC films since the first reported fabrication of DLC [1,2]. Deposition methods and corresponding film properties have been reviewed by Robertson [3,4], Angus et al. [5], Geis and Tamor [6], and Catherine [7].
general, DLC films are technologically interesting due to their high hardness [4], low coefficients of friction and wear rates against a number of materials [8-16] and chemical inertness [5,12,16]. This work compares the film composition, mechanical properties (hardness and elastic modulus) and tribological behavior of DLC films deposited using two familiar techniques, namely deposition using cathodic arc and a self-bias in a rf-plasma, and a newer technique using a pulse-bias [17]. The goal of this work was to compare the tribological behavior of the three DLC films and illustrate any correlation between tribological behavior, film properties, film composition and synthesis route. Similar comparisons [18] between hydrogenated and hydrogen free DLC films have been made but the comparison did not include DLC films made using the pulse-bias method.

**Experimental Procedures**

DLC deposition using cathodic arc processes has been described elsewhere [19]. Briefly, the deposition utilized a pulsed 60 eV, $^{12}\text{C}^+$ beam extracted from a cathodic arc discharge between graphite electrodes. The D3 tool steel substrate temperature was less than 60°C during deposition. The final film thickness is 0.8 μm. The DLC film extracted from an 13.56 MHz rf-generated CH$_4$ (4.6 mtorr) plasma was deposited onto silicon using a self-bias of 450 volts. The final film thickness is 0.5 μm. The DLC film deposited using a pulse-biased method used a 1.2 mtorr C$_2$H$_2$ plasma, a pulse-bias of 21 kV, a pulse frequency of 2 kHz, and a pulse width of 20 μs. The final film thickness, also on silicon, was 0.7 μm.

Non-Rutherford resonant ion back-scattering to determine the carbon atom content of the films was accomplished using a NEC Pellantron accelerator to produce a 3.55 MeV $^4\text{He}^+$ beam. The 70-90 nA beam current was normal to the surface with a scattering angle of 166° and the collected charge was 20μC. A graphite sample (100 at% C) was used as a standard when analyzing the spectra. Elastic Recoil Spectrometry (ERS) analysis was accomplished using identical beam parameters except the beam was incident on the surface at an angle of 75° with a scattering angle of 30°, the beam current was 4-7 nA and the collected charge was 4μ
C. The back-scattered and ERS spectra were quantitatively analyzed using conventional computer-aided techniques [20].

Nanoindentation tests were conducted using a Nano Indenter® II [21]. The hardness and elastic modulus of the DLC films was calculated from load/displacement curves at depths of approximately 45, 85 and 165 nm. Elastic corrections were taken into account. The hardness and elastic modulus values are averages of ten measurements at each of three indentation depths. The error bars are simple standard deviations of the ten measurements.

Pin-on-disk (POD) tribological tests were conducted using a computer controlled apparatus, in air, a 6mm diameter 440C stainless steel pin and a load of 0.81 gm (0.80 N). Using the elastic modulus of the films measured from the nanoindentation tests, the maximum Hertzian contact pressure was 829 MPa, 539 MPa and 457 MPa respectively for the cathodic arc, self-bias, and pulse-bias films. The yield stress of 440C is 450 MPa. The yield stress of the films (see Discussion Section) was not exceeded so, disregarding the increased contact stress on small asperities, plastic deformation did not play a role in the wear rate measurements. The pin was polished with 0.25µm diamond paste and ultrasonically cleaned in acetone for one minute, followed by ultrasonic cleaning in methanol for one minute. The track diameter was about 3 mm and the sliding speed was approximately 35 mm/sec. The sliding distance was about 1.1 km. The frictional force was measured using a calibrated load cell and the coefficient of friction was calculated and recorded electronically. After testing, the wear track cross-sectional area was measured using a Sloan Dektak II surface profilometer at four positions along the track, each about 90° apart. The largest observed cross-sectional area was used to calculate the wear track volume. Wear rates, $K$, were then calculated using the following formula [22]

$$K \left[ \frac{mm^3}{Nm} \right] = \frac{V}{Ld}\quad (1)$$

where $V$ is the wear volume, $L$ is the load, and $d$ is the total sliding distance.

**Results**
The 3.55 MeV resonant $^{12}\text{C}(\alpha,\alpha)^{12}\text{C}$ ion back-scattered spectra for a graphite (100 at% C) and the three DLC films are shown in Fig. 1. The ERS spectra for the three DLC films is shown in Fig. 2. A simple qualitative comparison of the back-scattered spectra for graphite and the cathodic arc film indicates the cathodic arc film to be nearly 100 at% carbon, as expected. The back-scattered spectra from the self-bias and pulse-bias films contain less carbon, with the self-bias film containing the least carbon. A similar qualitative comparison of the ERS spectra indicate the cathodic arc film to be virtually hydrogen free (<0.5 at%) and the self-bias film to contain the most hydrogen. The small amount of hydrogen on the surface of the cathodic arc film is due to water on the surface [23]. A similar observations was made on the graphite standard (not shown). The results of quantitative analysis of the spectra in Figs. 1 and 2 to determine carbon and hydrogen concentrations are shown in Table I. Film thickness, from surface profilometry measurements, and composition information were combined to calculate mass density and the gram-atom number density [5] for each of the films.

The films were further characterized in cross-section using TEM. The films were observed to be featureless and homogeneous. SAD patterns exhibited diffuse halos consistent with diffraction from an amorphous phase. The micrographs and SAD patterns were otherwise uninformative and are not included here.

Nanoindentation results are shown in Fig. 3-4. The cathodic arc DLC film has a hardness of 42 GPa which is approximately 40% of the hardness of single-crystal diamond [4]. The self-bias DLC and the pulse-bias DLC are softer at 11 GPa and 9 GPa, respectively. The elastic modulus of the cathodic arc DLC is about 430 GPa which is again approximately 40% of the elastic modulus of single crystal diamond [4]. The elastic moduli of the self-bias and pulse-bias DLC is lower at 100 GPa and 80 GPa respectively.

The results of the tribological tests are shown in Figs. 5-6. Fig. 5 indicates the coefficient of friction is virtually independent of the film process and varies slightly between 0.08 and 0.14 during testing. However, the wear rates differ significantly as seen in Fig. 6.
The cathodic arc DLC film wears at only ~20% of the wear rate of the self-bias and pulse-bias DLC films.

**Discussion**

It is worth noting that DLC films have compositions and physical properties that span a wide range [3]. For instance, hard amorphous DLC films deposited using hydrocarbon, plasma-based processes have reported mass densities ranging between 1.6 and 2.2 g/cm³, hardness values between 10 and 20 GPa, and hydrogen contents between 10 and 40 at%. Amorphous DLC films deposited from mass selected ion beams, such as cathodic arc deposition processes, have mass densities as high as 3.0 g/cm³ (3.5 g/cm³ for diamond), hardness values ranging between 30 and 130 GPa, and hydrogen contents less than 9 at%, depending on what type of ion (C⁺ or CHₙ⁺) is used for the deposition. In each case, the carbon films fabricated for this work have compositions and properties in or near the specified ranges of density, hardness and hydrogen content and therefore meet the qualifications necessary to be called DLC films. In addition, the gram-atom number density of DLC films is required to be greater than 0.2 [5].

For the hydrogen-containing DLC films, a higher hydrogen content correlates with a slight increase in hardness. Since hydrogen in the film converts sp² bonds (softer) to sp³ bonds (harder) [3], the increased hydrogen content may play a role in increasing the hardness of the self-bias deposited DLC film. In addition, it is speculated the DLC film deposited using the pulse-bias method is softest due to graphitization of the film, due to radiation damage within the collision cascade, by the 21 kV incident ions during deposition. [3,24]. As previously mentioned, cathodic arc DLC films are generally harder than DLC films produced using plasma-based processes.

The friction coefficient measured for this work is in good agreement with the friction coefficients measured for similar cathodic arc DLC films and tested under similar conditions [8]. The friction values reported in this study are within the range of values, 0.02-0.25, reported for DLC films deposited using several different methods and relative humidity values...
between 1% and 100% [9-16]. Generally speaking, increasing relative humidity tends to increase the coefficient of friction and tends to lower the wear rate [12]. The general trend of the wear rate decreasing with film hardness is also consistent with the tribological behavior of other materials [25].

The relationship between the hardness, H, and elastic modulus, E, shown in Fig. 7, is in good agreement with that pointed out by Roberston [4]. The relationship $H/E=0.1$ is in agrees well with $H/E=0.10638$ for this work. The correlation allows the calculation of the yield stress, Y, of the deposited DLC films using the relationship [4] $H/Y\approx1.8$. Thus, the calculated yield stresses of the cathodic arc DLC film, the self-bias film and the pulse-bias film are 23 GPa, 6 GPa and 5 GPa, respectively. To put these values in perspective, the yield stress of the cathodic arc film is between that of SiC (10 GPa) [26] and diamond (59 GPa) [4]. The self-bias film has a yield stress equivalent to that of WC (6 GPa) [26]. The yield stress of the pulse-bias film is equivalent to that of Al$_2$O$_3$ (5 GPa) [26].

**Conclusions**

A variety of deposition techniques utilizing a surprisingly wide range of deposition energies can be used to deposit DLC films. These DLC films can vary over a wide range in composition and mechanical properties, such as hardness and elastic modulus. The wide range of properties does not affect the coefficient of friction, but can have a significant effect on the wear rate. Since DLC films with various physical properties and compositions have very similar coefficients of friction under a wide variety of testing conditions, each tribological application of DLC should be evaluated carefully and a wear rate criteria established. The choice of deposition method should be made on the basis of the wear rate criteria.

**Acknowledgments**

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Bibliography


Figure Captions

Fig. 1. $^{12}$C($\alpha$, $\alpha$)$^{12}$C ion backscattering spectra, indicating carbon content, for the carbon standard and the DLC films.

Fig. 2. Elastic recoil spectra, indicating hydrogen content, of the DLC films.

Fig. 3. Nanohardness results for the DLC films measured at three different depths. The error bars for the self-bias and pulse-bias films are within the plot symbols.

Fig. 4. Elastic moduli of the DLC films measured at three different depths. The error bars for the self-bias and pulse-bias films are within the plot symbols.

Fig. 5. Coefficient of friction, measured using a pin-on-disk apparatus, for a 440C stainless steel pin riding against the DLC films.

Fig. 6. Bar graph comparing the wear rates, measured using a pin-on-disk apparatus, of the DLC films.

Fig. 7. Graph of the DLC film hardness versus the DLC film elastic modulus. The linear fit, which was forced to include zero, gives a slope nearly identical to the expected value of 0.1. The symbol assignment is the same as in Fig. 3. The error bars for the self-bias and pulse-bias films are within the plot symbols.
Figure 3: Graph showing hardness (GPa) vs. contact displacement (nm) for different biasing methods:
- Cathodic arc
- Self-bias
- Pulse-bias
Wear Rate ($x10^{-6}$ mm$^3$/Nm)

- Cathodic arc
- Self-bias
- Pulse-bias
H/E = 0.10638
TABLE I. Deposition details and film composition, thickness, and density.

<table>
<thead>
<tr>
<th>Deposition Process</th>
<th>Beam Energy or Bias</th>
<th>Beam or Source Gas</th>
<th>at% C ± 3 at%</th>
<th>at% H ± 3 at%</th>
<th>Thickness (μm)</th>
<th>Mass Density (g/cm³)</th>
<th>Gram-atom Density (g-at/cm³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cathodic Arc</td>
<td>60 eV</td>
<td>$^{12}$C⁺</td>
<td>&gt; 99.5</td>
<td>&lt; 0.5</td>
<td>0.80</td>
<td>2.5</td>
<td>0.21</td>
</tr>
<tr>
<td>Self-bias</td>
<td>450 V</td>
<td>CH₄</td>
<td>61</td>
<td>39</td>
<td>0.52</td>
<td>2.5</td>
<td>0.30</td>
</tr>
<tr>
<td>Pulse-bias</td>
<td>21000 V</td>
<td>C₂H₂</td>
<td>74</td>
<td>26</td>
<td>0.66</td>
<td>2.7</td>
<td>0.32</td>
</tr>
</tbody>
</table>

Gram-atom density = (mass density)/ $\Sigma x_i A_i$, where $x_i$ is the atomic fraction and $A_i$ is the atomic mass of element i.
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