Influence of ion energies on the surface morphology of carbon films

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Abstract

Diamond-like carbon (DLC) films were deposited using vacuum arc deposition (VAD) and plasma immersion ion implantation and deposition (PIII and D). The surface morphologies of these films were investigated using atom force microscopy (AFM). Raman spectroscopy results show that the films have different microstructures. Based on the AFM images and Raman spectra, the aromatic ring cluster diameters hardly affect the surface morphology of the films, but the surface growth and nucleation are all subjected to the ion energies and the substrate temperature determines the surface morphology of the films.

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1. Introduction

There have been a lot of interests in carbon films in the last two decades because they exhibit beneficial chemical and physical properties such as high chemical inertness, diamond-like physical properties and tribological properties suitable for industrial usage [1–3]. Their unique properties can be attributed to not only the special and interesting properties of the microstructures, but also their surface morphology. In our previous studies, we synthesized carbon films on Al alloy substrate by optimizing the deposition parameters in either vacuum arc deposition (VAD) or plasma immersion ion implantation and deposition (PIII and D). By monitoring the deposition process, very different growth phenomena were observed. In vacuum arc deposition, the growth of carbon films always began from the same spot, but in PIII and D, growth occurred on the entire surface without any preferred starting spots. Based on the statistical formation theory, the nucleation and growth models for VAD and PIII and D diamond-like carbon (DLC) films were proposed [4]. At the same time, very different DLC film morphologies which depended on the growth patterns were also observed. They can in turn affect the properties of the films such as friction coefficient, optical characteristics, as well as electronic properties. One of the key deposition parameters affecting the film structure and properties is the ion energy, and some results have been reported [5–7]. However, the specific influence of the ion energies on the surface morphology of DLC films has not been studied in details. In addition to the surface morphology of the original substrate, there are at least four other factors that may influence the DLC film morphology: nucleation, film growth, film thickness and film structure. All four factors depend on the ion energies, and so there is a need to investigate the relationship between the DLC film morphology and ion energies.

In the study described in this paper, the samples were prepared by VAD or PIII and D. The influence of the ion...
energies on the nucleation, growth and structure on the film morphology was investigated by atomic force microscopy (AFM) and Raman spectroscopy.

2. Experimental details

Two sets of samples were prepared by VAD and PIII-D, respectively. Detailed descriptions of the equipment and experimental methods can be found elsewhere [4, 8–10]. The deposition parameters are shown in Table 1. The substrates were LY12 aluminum alloy with a diameter of 40 mm and thickness of 5 mm. Before deposition, the substrates were sputter cleaned by 1 kV argon ions for 30 min. In VAD, a carbon cathodic arc plasma source was used and the samples were placed 250 mm from the exit of the arc source. The film growth rate is estimated to be about 160 nm/min. In PIII and D, a C2H2 plasma was sustained by 1 kW hot filament discharge. Negative pulses of 20 kV with a pulse width of 27 μs were applied to the substrates at a frequency of 128 Hz. The film growth rate is estimated to be approximately 2 nm/min. Previous studies [4] have shown that when the DLC film gets thicker, the film color changes from yellow, red and then to blue or black, and so a blue DLC film is thicker than a red one. To investigate the morphological differences on the same film with various

<table>
<thead>
<tr>
<th>Deposition method</th>
<th>Sample number</th>
<th>Deposition pressure</th>
<th>Gas</th>
<th>Time (min)</th>
<th>Specific parameters</th>
</tr>
</thead>
<tbody>
<tr>
<td>VAD</td>
<td>#1</td>
<td>3–4×10^{-2} Pa</td>
<td>Ar</td>
<td>4 min</td>
<td>Arc current 17–35A, Arc voltage 40–52 V, Bias voltage/bias current 0</td>
</tr>
<tr>
<td></td>
<td>#2a</td>
<td>6.4–7×10^{-2} Pa</td>
<td>Ar</td>
<td>3 min</td>
<td>66 A, 20–30 V, 300 V/150 mA</td>
</tr>
<tr>
<td></td>
<td>#2b</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>PIII-D</td>
<td>#3</td>
<td>2×10^{-1} Pa</td>
<td>C2H2</td>
<td>120 min</td>
<td>Pulse voltage/current 20 kV/4 mA, Pulse width 27 μs, Pulse frequency 128 Hz</td>
</tr>
</tbody>
</table>

Fig. 1. AFM images of DLC films: (a) sample #1, (b) sample #2a, (c) sample #2b, (d) sample #3.
thicknesses, samples #2a and #2b represent the red and blue areas of a same sample, respectively. Raman spectra were acquired by a SPEX 1403 Raman spectrometer employing a laser wavelength of 488 nm. The laser power was 30 mW and the spot size was 2 μm. The resolution was 2 cm\(^{-1}\).

3. Results and discussion

The ion energy is one of the crucial parameters that control the film structure as well as the mechanical, electrical and optical properties [5,7,11]. The ion energy adopted in the PIII and D experiments was much higher than that in VAD technique thereby giving rise to different surface morphologies. Fig. 1 depicts the AFM images over an area of 10×10 μm for these specimens. The surface morphologies of the DLC films are different from each other. However, it should be noted that the surface roughness is accentuated in the images because the z-axis is 200 nm per division while the x- and y-axes are 2 μm per division. The surface of sample #1 (Fig. 1a) shows many pits and buds distributed randomly on the film, whereas the surface morphology of sample #2a (Fig. 1b) resembles that of sample #2b (Fig. 1c). Therefore, the film color, that is, the film thickness, does not alter the surface morphology too much. Once the first layer is formed, subsequently, film growth will not alter the surface morphology significantly. On the surface of the sample #2 (Fig. 1b and c), the pits shown on the surface of sample #1 can still be observed. However, the buds are sparser. With the exception of the pits distribution, the morphology of sample #1 resembles that of sample #2 to some extent. Fig. 1d (sample #3) shows a surface morphology very different from those of sample #1 and #2, and so the growth mechanism or nucleation mode must be very different between samples #3 and #2.

Besides the surface morphology of the original substrate, there are at least four other factors that determine the DLC film morphology: nucleation, growth, thickness and structure. Fig. 1b and c shows that the effect of film thickness is negligible if the film thickness does not vary too much. The growth mechanism will determine the final structure of the films. For instance, various carbon and hydrogen arrangements during the growth will determine the final structure of the film.

Raman spectroscopy has been widely used to study the structure of DLC films. Fig. 2 depicts the Raman spectra acquired from the samples. As conventionally practiced, the Raman spectra are fitted by two Gaussian peaks: a G peak centered around 1550 cm\(^{-1}\) and a D peak centered at 1360 cm\(^{-1}\) [12]. The G peak is due to the bond stretching of all pairs of sp\(^2\) atoms in both rings and chains. This mode does not require the presence of sixfold rings, and so it occurs at all

![Fig. 2. Raman spectra of DLC films: (a) sample #1, (b) sample #2a, (c) sample #2b, (d) sample #3.](image)

sp² sites and not only those in rings. It always lies in the range of 1500–1630 cm⁻¹, and so is an indication of aromatic and olefinic carbon. The D peak is due to the vibrational modes of A₁₈ symmetry involving phonons near the K zone boundary. This mode is forbidden in perfect graphite and only becomes active in the presence of disorder [13,14].

By calculating the intensity ratio: $I(D)/I(G)$, the aromatic ring cluster diameter $L_a$ can be estimated by using the following relationship [13,15]:

$$I(D)/I(G) = C/L_a \quad \text{(when $L_a > 20$ Å)}$$

$$I(D)/I(G) = C' L_a^2 \quad \text{(when $L_a < 20$ Å)}$$

The G peak position, $I(D)/I(G)$, and $L_a$ estimated for each sample are summarized in Table 2. According to the three-stage model [13], the G peak positions of samples #1, #2a and #2b are in the range from 1561 to 1574, suggesting that the carbon films possess either an amorphous (a-C) or ta-C (tetrahedral carbon) structure. However, the values of $I(D)/I(G)$ are in the range of 0.15–0.37, and it can be deduced that samples #1, #2a and #2b consist of tetrahedral carbon films, and these have been confirmed elsewhere [10]. Similarly, we know that sample #3 is a-C.

The largest $L_a$ is obtained from sample #3 (41.9 Å). It is still much smaller than the size of the pits or buds shown in Fig. 1 and, therefore, the pits in the films may be independent of the aromatic ring clusters. To evaluate the microstructures of the films in more details, Fig. 3 displays the high resolution AFM images showing little buds with different sizes. Sample #1 has the highest number of buds and the size of the buds is the largest, whereas samples #2a and #2b have the least number of buds but the buds are larger. As for sample #3 (Fig. 3d), the buds are smallest and they can hardly be seen without careful observation and the cluster size of sample #3 is the largest. Therefore, the buds have no direct relationship with the clusters. During the deposition of sample #1, the substrate was grounded and so the ion energy should be on the same order as the arc voltage based on the assumption that the carbon charge state was +1. In the deposition of sample #2, an initial negative bias of 300 V was applied to the substrate. The

<table>
<thead>
<tr>
<th>Sample</th>
<th>G peak position (cm⁻¹)</th>
<th>$I(D)/I(G)$</th>
<th>$L_a$ (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>#1</td>
<td>1574.09</td>
<td>0.37</td>
<td>8.2</td>
</tr>
<tr>
<td>#2a</td>
<td>1562.62</td>
<td>0.203</td>
<td>6.1</td>
</tr>
<tr>
<td>#2b</td>
<td>1561</td>
<td>0.15</td>
<td>5.2</td>
</tr>
<tr>
<td>#3</td>
<td>1586.51</td>
<td>1.05</td>
<td>41.9</td>
</tr>
</tbody>
</table>

Fig. 3. High-resolution AFM images of DLC films: (a) sample #1, (b) sample #2a, (c) sample #2b, (d) sample #3.
bias dropped to nearly zero after the arc was ignited. Therefore, the ion energy was also determined by the arc voltage for sample #2. This may be the reason why the morphology of sample #2 is similar to that of sample #1.

For sample #1, the ion energy is relatively low, and so the adatoms have low energies and so the carbon atoms and buds are evenly distributed on the substrate surface. For sample #2, the ion energy is nearly the same as sample #1, but the substrate has a higher temperature due to the substrate bias thereby provide additional energies to the adatoms. As described in Ref. [4], other adatoms diffuse to the side and the film grows like a ripple, resulting in a mountain-like surface morphology. As for sample #3, the ion energy is very high. The implanted carbon ions and cluster ions land randomly onto the surface and provide nucleation sites. The growth thus starts randomly on the film and the diffusion of the carbon adatoms can be neglected. Hence, the buds on this film are very small and when the growth edges merge with each other, the morphology shown in Fig. 3 results.

4. Conclusion

DLC films were obtained by VAD and PIII and D. Though the AFM images show that all the DLC film surfaces are smooth, the surface morphologies change with the ion energies and substrate temperature. The Raman spectra show that samples #1 and #2 are ta-C films while sample #3 is a-C film. The aromatic ring clusters in the films do not determine the surface morphology. The nucleation, which is strongly influenced by the ion energies, plays an important role on the surface morphology. A higher temperature enhances diffusion of the adatoms and more nucleation sites can induce a pit-like morphology.

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