Nanoindentation investigation of amorphous hydrogenated carbon thin films deposited by ECR-MPCVD

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Abstract

Nanomechanical properties of amorphous hydrogenated carbon thin films are performed by nanoindentation technique. The amorphous hydrogenated carbon films are produced on silicon substrate by electron cyclotron resonance microwave plasma chemical vapor deposition (ECR-MPCVD). The effect of negative bias voltage on amorphous hydrogenated carbon films is examined by Raman spectroscopy and the results showed that the intensity ratio of D-peak to G-peak (I_D/I_G) of amorphous hydrogenated carbon films at various bias voltages, increased as the bias voltage increased. The results also showed that Young’s modulus and hardness both decreased as the indentation depth increased.

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1. Introduction

Amorphous hydrogenated carbon (a-C:H) films, also known as diamond-like carbon (DLC) films, have desirable performance due to their physical and chemical properties, such as optical transparency, high electronic resistivity, chemical inertness, high hardness and low surface energy [1–4]. Amorphous hydrogenated carbon thin films are a candidate for a wide range of applications as protective coatings in areas such as magnetic storage disks, biomedical coatings and micro-electromechanical system (MEMS) [5–8].

Many deposition methods have been developed, including ion-beam sputtering, direct current and radio frequency (RF) magnetron sputtering, cathode arc deposition and plasma enhanced chemical vapor deposition [9–13]. Each method has its relative advantages for certain applications. Among them, electron cyclotron resonance microwave plasma chemical vapor deposition (ECR-MPCVD) is an excellent technique because of the superior plasma species production rate and low substrate temperature during deposition [14–17].

Nanoindentation testing is the most frequently used technique for measuring thin film properties such as Young’s modulus and hardness within a sub-micron scale [18–20]. Therefore, this technique is expected to be useful for measurement of mechanical properties of thin films. Research in this area is partially summarized in references [21–24].

The aim of this study is to investigate the nanomechanical properties of amorphous hydrogenated carbon thin films deposited by the ECR-MPCVD at various substrate biases. Additionally, discussion of indentation mechanisms on a nanometer-scale and the influence of bias voltage on the deposited films are presented.

2. Experimental details and methodology

Amorphous hydrogenated carbon thin films are produced on silicon substrates by ECR-MPCVD, with RF bias being applied to the substrate holder. The films are prepared in an ECR-MPCVD system, with a mixture of methane and hydrogen reactant gases. A 13.56 MHz RF with a negative bias voltage is coupled to the substrate holder. The chamber is first evacuated to
Table 1
Growth conditions of amorphous hydrogenated carbon thin films

<table>
<thead>
<tr>
<th>Substrate</th>
<th>Silicon</th>
</tr>
</thead>
<tbody>
<tr>
<td>Gas</td>
<td>H\textsubscript{2}, CH\textsubscript{4}</td>
</tr>
<tr>
<td>Pressure (Pa)</td>
<td>10\textsuperscript{-3}</td>
</tr>
<tr>
<td>Flow rate (sccm)</td>
<td>H\textsubscript{2}: 30, CH\textsubscript{4}: 30</td>
</tr>
<tr>
<td>Deposition time (min)</td>
<td>180</td>
</tr>
<tr>
<td>Microwave power (W)</td>
<td>70</td>
</tr>
<tr>
<td>RF bias (V)</td>
<td>−30, −50, −70</td>
</tr>
</tbody>
</table>

10\textsuperscript{-3} Pa, and then the methane/H\textsubscript{2} mixture is introduced for film deposition. The amorphous hydrogenated carbon thin films growth conditions are listed in Table 1. Further details of the deposition process can be found in Refs. [5,25].

The surface morphology of amorphous hydrogenated carbon thin films was examined using atomic force microscopy (AFM) under ambient conditions. AFM scanning uses only the two vertical quadrants to measure vertical deflection of the cantilever, and thus the surface profile of the specimen, i.e. topography. The surface roughness was measured using the same device in contact mode. Nanomechanical properties such as Young’s modulus and hardness of amorphous hydrogenated carbon thin films were obtained by nanoindentation. Load controlled indentation testing followed a trapezoidal loading profile with a hold time of typically 10 s at peak loads. Peak loads ranged from 100 to 1000 µN at loading rate of 10 µN/s. The diamond indenter was a Berkovich tip with a tip radius of 100 nm [19].

Amorphous hydrogenated carbon thin films were subjected to a depth-sensing nanoindentation, which is a reliable method [26,27] for measuring the mechanical properties of thin films. The typical continuous load-displacement curves are obtained from a Berkovich indenter. The area and the depth relationship of the displacement curves are obtained from a Berkovich indenter. The area and the depth relationship of the displacement curves are obtained from a Berkovich indenter.

Here \( v \) and \( E \) represent Poisson’s ratio and Young’s modulus, respectively. The subscripts \( i \) and \( m \) refer to the indenter and test material. The indentation properties used in this study’s calculations were \( E_i = 1140 \) GPa and \( v_i = 0.07 \) and assumed that Poisson’s ratio was \( v_m = 0.3 \) for the amorphous hydrogenated carbon thin films.

The hardness of a material is defined as its resistance to local plastic deformation. Thus, the hardness, \( H \), is determined from maximum indentation load \( P_{\text{max}} \) divided by the projected contact area [19]:

\[
H = \frac{P_{\text{max}}}{A_c}.
\]

To better understand the mechanism of plastic deformation on amorphous hydrogenated carbon thin films, the radius \( a \), of the contact area to determine the stress is calculated by using the Hertzian equation [28]:

\[
a = \left( \frac{3PR}{4E^*} \right)^{1/3}.
\]

The contact stress-strain analysis revealed that the local strain on the thin film can be very useful to improving the quality of the films and also recognized the deformation mechanisms at a nanoscale under the micro-Newton level loads.

3. Results

The first-order Raman spectrum of single-crystalline graphite shows a sharp intense peak at 1581 cm\textsuperscript{-1}. This peak is assigned to the E\textsubscript{2g} C-C stretching mode and is referred to as the G-peak [29]. In contrast, for polycrystalline graphite the peak is centered at 1350 cm\textsuperscript{-1} and is referred to as the D-peak [29]. It has been suggested that an additional type of diamond-like carbon exists, with a frequency of 1540 ± 20 cm\textsuperscript{-1} depending on the distortion from the graphite structure and the vibrational mode is mainly represented by C-C stretching [30]. Raman spectral analysis of the films grown with different substrate negative bias voltages reveals a diamond-like structure with a peak centered at approximately 1540 ± 20 cm\textsuperscript{-1} and a shoulder peak at approximately 1350 cm\textsuperscript{-1}, as shown in Fig. 1. On the whole, the films displayed the same typical Raman spectra of the DLC thin films presented in other reports [5,31].

From the fitting parameters, the peak position, peak width and integrated intensity ratio \( I_D/I_G \) is obtained. The intensity ratio of the D- and G-peaks, \( I_D/I_G \), has been shown to correlate inversely with both the size and the density of the graphite crystallites. In Fig. 2, the \( I_D/I_G \) ratio increased as the negative bias was increased and the results showed that this phenomena lead to the formation of carbon films with less diamond-like structures. Therefore, increasing the negative bias volt-
Age will make the G-peak shift towards a higher frequency and decrease the sp³-bonded in the DLC thin films.

Fig. 3(a)–(c) show that the surface topography for the amorphous hydrogenated carbon thin films, grown at the different bias voltages of −30, −50 and −70 V. The corresponding surface roughness \( R_a \) for −30, −50 and −70 V are 0.23, 0.28 and 0.29 nm, respectively. In addition, Fig. 4 shows the load–displacement curve and indent mark. The load–displacement curve on the amorphous hydrogenated carbon thin film was −50 V and a triangle indent can be observed in the indent mark having shallow depths. In addition to that, the amorphous hydrogenated carbon thin films have cracked due to their plastic behavior, which caused the atoms to ‘pile-up’ on either side of the indentation. This ‘pile-up’ phenomenon is found to be anisotropic and the
magnitude of the pile-up increases as the indentation load was increased. This phenomenon gives evidence of the plastic behavior on amorphous hydrogenated carbon thin films.

The Young’s modulus of the amorphous hydrogenated carbon thin films can be derived during nanoindentation process by Eqs. (2) and (3) as above-mentioned. Young’s modulus was obtained from the nanoindentation process at different applied loads and is shown in Fig. 5. The experiment results showed that the Young’s modulus was 166.47±1.53 to 173.82±1.95, 168.61±1.39 to 180.56±3.44 and 175.34±1.16 to 187.45±2.55 GPa for the bias voltages of −30, −50 and −70 V, respectively. A plot of the estimated hardness as a function of plastic penetration depth for the three different bias voltages substrates is shown in Fig. 6. It is apparent that the hardness decreases as the applied load was increased. In addition, the corresponding hardness was 17.68±0.22 to 18.96±0.54, 18.82±0.29 to 20.12±0.58 and 19.52±0.23 to 21.56±0.64 GPa for −30, −50 and −70 V, respectively. This indicated that the Young’s modulus and hardness increased as the bias voltage was increased and the highest value being obtained at a bias of −70 V.

The contact stress and contact strain relationships were deduced from the above-calculated data at the bias voltages shown in Fig. 7. The larger the stress, the larger the strain and therefore the deformation of the thin films subsequently lead to a yielding behavior. It can be seen that when the substrate bias voltage was increased it causes a larger contact stress and contact strain on the deposited films. In other words, the higher the negative bias voltage the more stress the deposited films could bear.

### 4. Discussion

The Raman spectra measurement showed that the sp³-bonding carbon clusters increased as the negative bias voltage was increased, which is consistent with the results in Ref. [32]. The properties of the amorphous hydrogenated carbon thin films deposited by ECR-MPCVD were improved by the effects of negative bias voltages.

The structure of the amorphous hydrogenated carbon thin films has a strong dependence on the ion energy, because the ion energy is proportional to the bias voltage of the cathode and the ions in the capacitive coupled RF plasma were accelerated by the negative bias voltage. The results indicated that the different bias voltages caused the bias energies bombarding the surface of the growing films, to have had a major influence on the amorphous hydrogenated carbon films. The increased quantity of
sp$^3$-bonded carbon and the increased number of areas of high strain caused by the increased bias voltages and thereby increased ion energy had a beneficial effect on the amorphous hydrogenated carbon thin films. Also when looking at the amorphous hydrogenated carbon thin films microstructures, the number of small islands decreased as the increasing bias voltage was increased. So, as the bias voltage was increased, more sp$^3$-bonded carbon was created. The sp$^3$-bonded carbon exhibits the properties of diamond, such as a lower friction coefficient and higher harnesses [33]. Nanoscale mechanism was mainly caused by the interaction of the surface atoms and the sub-surface atoms, including the stretching or breaking of interatomic bonds. Hence the nanoscale characteristics and mechanisms were clearly shown with the aid of nanoindentation measurements.

5. Conclusion

In summary, it was demonstrated that the nanomechanical properties of amorphous hydrogenated carbon thin films that were deposited by ECR-MPCVD at different substrate biases had improved microstructure and nanomechanical properties. The Raman spectra showed that all the deposited films, regardless of the substrate bias, exhibit two characteristic peaks centered at 1350 and 1580 cm$^{-1}$. In addition, it was found that increasing the negative bias voltage caused the G-peak to shift towards a high frequency and the D-peak to shifts towards a lower frequency causing the ratio of $I_D/I_G$ to be increased. The nanoindentation experiment results showed that the presence and level of bias voltage on the substrate plays a significant role in the nanomechanical properties of amorphous hydrogenated carbon thin films deposited on silicon wafers.

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References