Growth properties and resistive switching effects of diamond-like carbon films deposited using a linear ion source

Wei Dai(a)
Korea Institute of Science and Technology, Seoul 130-650, South Korea and Ningbo Key Laboratory of Marine Protection Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People’s Republic of China

Peiling Ke and Aiying Wang
Ningbo Key Laboratory of Marine Protection Materials, Ningbo Institute of Materials Technology and Engineering, Chinese Academy of Sciences, Ningbo 315201, People’s Republic of China

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Diamond-like carbon (DLC) films were prepared using an anode-layer linear ion beam source with C₂H₂ as the precursor and various negative bias voltages. The growth properties, microstructures, mechanical properties, and the resistive switching behaviors of the as-deposited DLC films were investigated as a function of bias voltage. The results showed that adjusting the bias voltage could vary the carbon atomic bonding structure (sp³/sp² carbon hybridized bonding) of the films. The sp³/sp² ratio initially increased as bias voltage increased and then decreased once the bias voltage exceeded −100 V. The variations in the film hardness and residual stress at different bias voltages were similar in profile to the sp³ bond fractions, indicating that both the residual stress and the mechanical properties of the DLC films were highly dependent on sp³-C bonding structures. The resistive switching characteristics of the DLC films were studied via a Cu/DLC/Pt cell structure. It was found that the bias voltages had a significant influence on the resistive switching behaviors of the DLC films. The film deposited with a bias voltage of 0 V showed excellent resistive switching effects with an ON/OFF ratio higher than 70 and device yield of about 90%, while the films deposited with higher bias voltages presented poor resistive switching effects. The sp²/sp³ ratio of the films was believed to account for the favorable resistive switching performances.

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I. INTRODUCTION

Diamond-like carbon (DLC) is a metastable carbon form, which consists mainly of graphite sp²-C hybridized bonds and diamond sp³-C hybridized bonds. It is well known that the sp² bonding structure controls the electronic properties and the optical gaps of DLC, while the sp³ bonding structure controls the mechanical properties. Due to the special diamond sp³-C structure, DLC films exhibit many favorable properties, including high hardness and wear resistance, low friction coefficients, and chemical inertness. Accordingly, DLC films have been widely used in many industries, such as magnetic and optical disk in data storage, microelectromechanical devices, and biomedical coatings. In addition, DLC films have very controllable preparation processes compared to diamond and other carbon nanostructures, and present various structures when the sp² and sp³ hybridized bonds in the DLC matrix are tuned. Therefore, DLC films are being targeted as suitable candidates for application in carbon-based electronic devices, such as nonvolatile memory devices.

The key process in DLC deposition is the formation of sp³-C hybridized bonds, which is believed to significantly depend on the energy of the carbon ions, and the optimum energy for sp³-C formation is thought to be between 100 and 150 eV per carbon atom. Different deposition techniques and process parameters would generate carbon ions with different energies and subsequently produce various DLC films with varied carbon structures (sp³/sp² ratios). So far, numerous techniques including magnetron sputtering, chemical vapor deposition, the cathodic arc technique, and ion beam deposition have been proposed for the synthesis of DLC films. An anode-layer linear ion source (LIS) is of the closed-drift anode-layer design and can operate without an electron emitter and accelerating grids, and thus can readily be scaled to any desired length and applied in industry for large-area surface processes and DLC film deposition.

In this paper, a LIS was employed to prepare DLC films with a negative bias voltage, which was used to vary the carbon ion energy. The microstructure, mechanical properties, and resistive switching behaviors of the as-deposited DLC films were studied systematically as a function of the bias voltage. The relationships between growth, carbon structure, and mechanical properties, as well as resistive switching behaviors of the DLC films, are discussed in detail.

II. EXPERIMENT

DLC films were deposited using the LIS with C₂H₂ as the precursor. P-type silicon (100) wafers of thickness 290 ± 5 μm and 545 ± 15 μm were used as the substrate materials to measure the residual stress and other properties, respectively. All substrate materials were cleaned ultrasonically in acetone for 10 min and then dried in air. Before the deposition process, the substrates were sputter-cleaned for...
10 min using Ar\(^+\) ion. During deposition, the typical discharge voltage and current were 1100 ± 100 V and 0.2 A, respectively. The substrate holder was biased by an asymmetrically bipolar pulsed power (Pinnacle Plus 5 kW, Advanced Energy), which supplied a square wave pulsed bias with a frequency of 350 kHz and a reversal time of 1.1 \(\mu\)s, and the bias voltage ranged from 0 to \(-300\) V. The details of the experimental parameters are shown in Table I. The deposition time was adjusted to obtain a film thickness of 740 ± 40 nm for all the samples.

The thicknesses of the films were measured using a surface profiler (Alpha-step IQ). A micro-Raman spectroscopy was used to characterize the carbon bond structure of the DLC films using a 514.5 nm Ar\(^+\) laser. Surface morphologies of the films were studied by an atomic force microscopy (AFM) (Dimension 3100 V, Veeco, USA) at a scan rate of 1.5 Hz. The root-mean-square roughness \(R_q\) of film surfaces was calculated from 512 × 512 surface height data points obtained from 2 \(\mu\)m × 2 \(\mu\)m scan area. High-resolution transmission electron microscopy (HRTEM) was performed on the films using a Tecnai F20 electron microscope operated at 200 KeV with a point-to-point resolution of 0.24 nm. TEM specimens were prepared by peeling off films from the NaCl crystalline substrates, which were dissolved in DI water. Residual stress of the DLC films coated on the Si wafers with thickness of 290 ± 5 \(\mu\)m was calculated from the curvature of the film/substrate composite using Stoney’s equation, where the curvature of the film/substrate composite was determined by a laser tester. The mechanical properties were determined using the nanoindentation technique with a continuous stiffness measurement mode. The maximum indentation depth was about 500 nm, and the characteristic hardness of the films was chosen to be that which was measured at a depth of around 1/10th of the film thickness to minimize the substrate contribution. Six replicate indentations were made on each sample in the present experiments.

In order to measure the electrical properties, DLC films with thicknesses of about 120 nm were deposited on Pt/Ti/ SiO\(_2\)/Si substrates followed by copper top electrodes (array) of about 100 \(\mu\)m in diameter deposited at RT using an electron-beam evaporation with an \textit{in-situ} metal shadow mask. \(I-V\) characteristics of the Cu/DLC/Pt structure cells were measured at RT in air using a semiconductor parameter analyzer (Keithley 4200). During the measurement in voltage sweeping mode, the positive bias was defined by the current flowing from the top to the bottom electrode, and the negative bias was defined as the opposite direction. The resistances of the Cu/DLC/Pt cells were measured by a physical property measurement system (Quantum Design).

### Table I. Deposition conditions of the DLC films by LIS.

<table>
<thead>
<tr>
<th>Deposition parameters</th>
<th>Condition (value)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Base pressure (Torr)</td>
<td>(2 \times 10^{-5})</td>
</tr>
<tr>
<td>Coating pressure (Torr)</td>
<td>(3 \times 10^{-3})</td>
</tr>
<tr>
<td>Deposition temp (°C)</td>
<td>50–80</td>
</tr>
<tr>
<td>(C_2H_2) flow (scpm)</td>
<td>40</td>
</tr>
<tr>
<td>LIS power (W)</td>
<td>200–250</td>
</tr>
<tr>
<td>Discharge voltage (V)</td>
<td>1000–1200</td>
</tr>
<tr>
<td>Film thickness (nm)</td>
<td>700–780</td>
</tr>
<tr>
<td>Negative bias voltage (V)</td>
<td>0 to (-300)</td>
</tr>
</tbody>
</table>

**FIG. 1.** (Color online) Growth rate of the films deposited by LIS as a function of bias voltage.
results illustrate that the as-deposited DLC films exhibited a typical amorphous structure.

More elaborate carbon bond analysis was performed by Raman spectroscopy, which is a reliable tool for characterizing carbon bonds in DLC films. Figure 4(a) shows a representative Raman spectrum for the DLC films deposited with various bias voltages. Note that there is a broad asymmetric Raman scattering band in the range of 1000–1700 cm$^{-1}$, representing the typical amorphous carbon structure. Generally, the Raman spectrum of DLC films can be fitted into two Gaussian peaks: the D-peak around 1350 cm$^{-1}$ and G-peak around 1550 cm$^{-1}$ [see Fig. 4(a)]. The D-peak originates from the breathing modes of only those $sp^2$ atoms that are in aromatic rings, while the G-peak is derived from the bond stretching of all pairs of $sp^2$ atoms in both aromatic rings and chains. Therefore, the intensity ratios of the D-peak to G-peak ($I_D/I_G$) and the position of G-peaks can be used to characterize carbon bond structures in DLC films. As the graphitic component ($sp^2$-C) decreases (or the $sp^3$-C bond fraction increases), the G-peak position will shift down and the $I_D/I_G$ ratio will decrease in hydrogenated DLC films.

The G-peak position and the ratio of $I_D/I_G$ are shown in Fig. 4(b) as a function of the bias voltage. It can be seen that the position of the G-peak and the ratio $I_D/I_G$ dropped slightly as the bias voltage increased from 0 to $-100$ V, and then reached their lowest points followed by a dramatic increase when the bias voltage exceeded $-100$ V. The variations in the G-peak position and $I_D/I_G$ ratio indicate that the $sp^3$ bond fractions of the films deposited at the low bias range of 0 to $-100$ V were higher than for films deposited at high biases ($>-100$ V), and the maximum value of the $sp^3$ bond fraction was obtained around $-100$ V.

It is clear that the formation of $sp^3$ bonds correlated with specific bias voltages. The “subplant” model by Robertson et al. can be employed to explain the relationship between bias voltage and $sp^3$ bond formation. At low bias voltages, the ion energy is too low to penetrate into the growing surface, so the ion species just sticks to the growing surface and remains in its lowest energy state of $sp^2$ bond. When the bias voltage increases, the ion species have sufficient energy to penetrate into the subsurface, resulting in the increase of the local density and formation of the $sp^3$ bond. When the ion energy exceeds the penetration threshold, however, the excess energy is dissipated as in other processes, and therefore causes the $sp^3$ fraction to decrease.

FIG. 2. (Color online) AFM images of the films deposited at a bias voltage of (a) 0 V, (b) $-100$ V, and (d) $-200$ V. (d) Roughness of the films as a function of bias voltage.

FIG. 3. Typical TEM micrograph and corresponding diffraction pattern of the DLC films deposited at a bias of $-100$ V.
The optimum energy for sp³-C formation is thought to be between 100 and 150 eV per carbon atom. In our case, at the discharge voltage of 1000–1200 V, the average initial energy of the ions was about 300 eV. For the acetylene ions, this energy was divided among two carbon atoms and two hydrogen atoms, so it was estimated that each carbon atom had an initial energy of about 140 eV. The ions were also accelerated by the negative bias voltage applied on the substrates. Since most of the ions produced by LIS are singly charged (C₂H₂/CO for acetylene), the energy supported by the bias voltage should also be divided among two carbon atoms and two hydrogen atoms. In addition, the pulse duty cycle of the bias (about 61.5%) should be taken into account. As a result, the effective value of the bias per carbon atom may only be about 28%. Accordingly, the carbon ions generated by LIS with low bias (0 to −100 V) had energies ranging from 140 to 168 eV, which favored formation of sp³-C bonds, while the carbon ions accelerated with high bias (>−100 V) had high energy exceeding the penetration threshold resulting in graphitization (the sp² fraction increased).

Figure 4(c) shows residual stress of the DLC films as a function of bias voltage. In the low bias voltage range, the magnitude of the films’ residual stress showed a small increase with increasing negative bias voltage, reaching a maximum value at about −100 V and then monotonically decreasing when the bias voltage was increased further (>−100 V). Figure 4(d) presents average hardness and elastic modulus values for the films. It should be noted that the hardness and residual stress profiles were similar. The maximum hardness value was also observed at a bias voltage of −100 V. It was found that the variations in the mechanical properties and residual stress against bias voltage had almost the same behaviors as the sp³-C bond fractions.

Previous works indicate that the residual compressive stress arises from ion bombardment, along with the formation of the metastable sp³-C bond. Accordingly, the residual stress has a proportional relationship with the sp³-C bond fraction. On the other hand, the DLC matrix is defined dominantly by the connectivity of the sp³-C structure, which determines the mechanical properties of a DLC film. Therefore, both the residual stress and mechanical properties of DLC films depend on sp³-C bond fraction.

Figure 5 depicts the I-V curves of the Cu/DLC/Pt structure cells obtained by DC voltage sweep measurements to evaluate the resistive switching effects of the films deposited at different negative bias voltages (the higher figs. and lower ones are linear and semilogarithmic scales, respectively). The activation of the Cu/DLC/Pt memory cell requires a forming process with a current compliance of 10 mA as well as a forming voltage of ∼10 V. It can be seen that the Cu/DLC/Pt cells of the DLC film deposited at a bias voltage of 0 V [Fig. 5(a)] exhibited a conspicuous I-V hysteresis by sweeping the voltage (0→−1→0→−1→0 V) after the initial forming process, implying that the Cu/DLC/Pt structures had resistive switching memory effects. The switching from the high resistance state (HRS, OFF state) to the low resistance state (LRS, ON state) could be achieved by applying positive electric voltage above a critical value (1 V) at a top gate electrode, corresponding to the “SET” process and the corresponding voltage is called “V_SET.” By applying a negative
gate voltage (−1 V), we could switch back to the original high resistance state, corresponding to the “RE-SET” process and the corresponding voltage is called “VRESET.”

The endurance characteristics of the Cu/DLC/Pt cell are shown in Fig. 6. It can be seen that two stable resistance states could be maintained during 110 cycles with the ON/OFF-resistance ratio >70. The cell also showed little degradation after repeating sweep cycles, although the resistances of the HRS and LRS scattered to a certain extent during cycling. Furthermore, we also found that the Cu/DLC/Pt structure cell exhibited a high device yield of about 90%. This indicates that the switching between LRS/ON and HRS/OFF states was stable, reversible, and reproducible. I-V hysteresis was also noted for the DLC film deposited at a negative bias voltage of −100 V [Fig. 5(b)]. However, the resistive switching was neither stable nor reproducible, and the device yield was very low. For the film deposited at the bias voltage of −300 V, we did not observe the resistive switching phenomenon at all, and the Cu/DLC/Pt structure just presented an ohmic performance [as shown in Fig. 5(c)].

It is evident that the resistive switching behaviors of the DLC films significantly correlated with the carbon atomic structure (sp3 and sp2-C), which was changed by the negative bias voltages. Within the DLC matrix, the sp2 sites tend to be arranged in planar, σ bonded clusters (conducting graphite-like phase) embedded in a sp3 bond matrix that has a wide \( \sigma-\sigma^* \) gap. Indeed, the sp3 matrix acts as a tunnel barrier between each sp2 cluster, and therefore, the arrangement of the sp2 clusters greatly controls the electronic properties. On the other hand, it has been reported that by applying high electric voltage to carbon based devices, an electrical conducting graphitic channel is formed in DLC films due to a local heating process induced by the high current flow. This flow in turn promotes the transformation of the sp3 phase into a more conductive sp2 phase between each sp2 cluster. Accordingly, the Cu/DLC/Pt structure exhibited a resistive switching behavior.

However, for the DLC film deposited at a bias voltage of −100 V, the sp3 fraction was very high. In other words, the magnitude of sp2 clusters in the film was very small. As a result, the mean distance between the two sp2 clusters was very large, which means that it would be very difficult to form a conducting channel in the films. Thus, the resistive switch effect was hard to observe in this case. The DLC film deposited at a bias voltage of −300 V, however, consisted of a conducting graphite-like sp2 matrix with sp3 phase inclusions (low value of the sp3/sp2 phase ratio). Consequently, it exhibited conductor characteristics like graphite without the resistive switching phenomenon.

![Fig. 5](http://example.com/fig5.png)

**Fig. 5.** (Color online) Typical I-V curves (the higher and lower are linear and semilogarithmic scales, respectively) of the Cu/DLC/Pt structure cells at (a) 0 V, (b) −100 V, and (c) −300 V.

![Fig. 6](http://example.com/fig6.png)

**Fig. 6.** (Color online) Endurance performance of the Cu/DLC/Pt structure cell. More than 100 write-erase cycles were demonstrated. The resistance values of HRS and LRS vs the switching cycles at 0.1 V reading voltage.
IV. SUMMARY AND CONCLUSIONS

DLC films were deposited using a LIS at various bias voltages. It was found that the bias voltage significantly influenced the growth properties and the resistive switching behaviors of the DLC films. The sp³ bond fraction of the DLC films exhibited a maximum value at −100 V and then tended to decrease at all other bias voltages. Hardness and residual stress exhibited similar performance to the sp³ bond fraction at various bias voltages, implying that the mechanical properties of the DLC films were mainly depended on the sp³ bond structure. Only the film deposited at 0 V showed excellent resistive switching characteristics with high stability and device yield. Proper magnitude of the sp² bond was believed to be very important for favorable resistive switching. A higher fraction of sp² bonds caused the DLC film to present as a graphite-like conductor without any resistive switching phenomenon, and the lower fraction of sp² bonds made formation of the conducting channel difficult and degraded the resistive switching performance.

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22See: www.advanced-energy.com