High rate deposition of diamond-like carbon films by magnetically enhanced plasma CVD

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Abstract

A magnetically enhanced plasma chemical vapor deposition (MEPCVD) system has been developed for the deposition of DLC film without deterioration of the film quality. A perpendicular magnetic field (B) to the electric field was applied in the RF capacitively coupled plasma enhanced (PE) CVD system. Significantly higher levels of ionization are achieved in the MEPCVD system, resulting in much lower self-bias voltage and higher deposition rate. The deposition rate of DLC film can be increased by about one order of magnitude (B at 200 Gauss) by MEPCVD, comparing with the non-magnetic field case. The properties of the DLC film deposited by MEPCVD system were also improved; there is a higher hardness and Young’s modulus, and lower surface roughness, compared with that of the DLC film deposited by the conventional PECVD system.

Keywords: Diamond-like carbon; Magnetic field; Plasma; Chemical vapor deposition

1. Introduction

Diamond-like carbon (DLC) films have some interesting properties such as high mechanical hardness, dielectric strength, chemical inerterness, low wear and friction and optical transparency in the infrared range. These properties are promising for a wide range of mechanical, optical, electronic and medical applications. DLC films can be deposited by various methods. Radio frequency (RF) diodes (capacitively coupled RF discharge) are widely used for materials processing more than any other type of plasma discharge. RF diodes offer significant advantages over other types of discharges. They are simple and their operation is reasonably well understood; asymmetric discharges yield inherently uniform plasmas that can be scaled over large areas; asymmetric discharges where the chamber wall is a large grounded electrode offer large processing volume; RF diodes yield ion-bombarding energies that are sufficient for most processes. However, RF diodes also present significant limitations: the ion flux and ion energy are coupled, and cannot be varied independently, which leads to narrow processing windows; the high sheath voltages can cause substrate damage and loss of line width control. The low plasma densities ($10^9$ to $10^{10}$/cm$^3$) result in low processing rates and low gas utilization.

RF-PECVD has become the most common technique for depositing DLC films or coatings from a hydrocarbon precursor gas. Plasma-assisted gas decomposition reduces the substrate temperature required for the deposition process. This lower substrate temperature makes it possible for sufficient hydrogen to be incorporated during the deposition. Under certain conditions, plasma-induced ion bombardment of the film during deposition tends to improve the quality of the film. Using conventional PECVD, the deposition rate is usually low. DLC film is typically produced at a deposition rate of 1–5 nm/min in the low pressure range (10–100 mTorr) at the power density of 1 W/cm$^2$. Increasing the deposition rate is believed to be one way to reduce manufacturing time and, hence, manufacturing cost. There are various potential approaches to increasing the deposition rate for good quality material. Increasing the plasma density to enhance the deposition rate is a most effective way. In a conventional PECVD system, the plasma density is increased by increasing the RF input power. However, increasing the RF input power results in a high sheath voltage (DC self bias voltage) and deteriorates the film quality due to the high ion energy, which can make the film more graphite-like. So increasing the RF power to enhance the plasma density in a given system is of limited use. A magnetic field can be used to confine the plasma, influence the plasma density and ion energy, and modify the glow discharge deposition process without changing other deposition parameters. Plasma confinement by magnetic fields minimizes film contamination from the walls, reduces film deposition on walls, and can provide a more uniform...
electric field. Increasing the applied magnetic field parallel to the substrate surface during RF glow discharge has been shown to enhance plasma density effectively, which has been used in reactive ion etching [1], the deposition of high quality a-Si:H film at high rate [2], and the deposition of c-BN [3]. For DLC film deposition, only magnetically confined (permanent magnet) PECVD (capacitatively coupled) [4], and inductively coupled MEP-CVD [5] has been reported. However, the deposition and properties of DLC films by MEP-CVD are not well known. In this work, the deposition process and the properties of the DLC films deposited by a modified MEP-CVD system under various conditions will be described.

2. Experiment details

A schematic diagram of the deposition system is shown in Fig. 1. The system is asymmetric and capacitively-coupled with a generator, which is composed of a deposition chamber and one set magnetic coils. The base pressure is less than $5 \times 10^{-5}$ Torr maintained by a turbo-molecular pump. The deposition chamber consists of a cross shaped stainless-steel cylinder (20 cm in diameter and 40 cm in length). The substrate electrode (14 cm in diameter) is water cooled, and is coupled to a RF generator (RF excited frequency is 13.56 MHz) by an impedance-matching network and a blocking capacitor. The RF power is applied between the ground and substrate electrode which is placed at the center of the chamber. The substrate electrode is subject to a negative DC self-bias voltage $V_b$, which was controlled by changing the RF input power. The negative self-bias voltage increases as the RF power increases; this is due to increased ionization in the plasma with increasing input power. When a magnetic field was applied, $V_b$ dropped for the same condition. The variation of $V_b$ versus RF input power in non-magnetic field and magnetic field is shown in Fig. 2. The magnitude of the self-bias voltage decrease in the magnetic field is about 100 V when the magnetic field is about 100 Gauss. This is due to the higher dissociation of ions in the magnetic enhanced plasma that gives rise to a large ion current, and decreases the negative DC self-bias voltage.

At a fixed RF input power, $V_b$ decreased with the magnetic field increase, whilst the deposition rate of DLC film increased. The $V_b$ and deposition rate dependence on deposition. During the deposition, the methane pressure was kept at 20 mTorr. The substrate temperature was kept at room temperature (about 25°C) during the deposition process. After deposition, the thickness of the DLC films was measured using a surface profilometer (Tencor P10). The hardness and Young’s modulus were characterized by a nanoindenter (Nanoindenter® II, Nano Instruments); the continuous stiffness option was used, and the maximum load was 10 mN. The morphological features of DLC films deposited under various RF plasma deposition conditions were observed by atomic force microscopy (AFM) (DimensionTM 3000, Digital Instruments) using a tapping mode, because the roughness depended on the thickness of the DLC film under different deposition conditions. In order to make a reasonable comparison, the thickness of the films was kept to about 200 nm by controlling the deposition time. The root mean square (RMS) roughness of the DLC films was evaluated by AFM measurements made on a $1 \mu m \times 1 \mu m$ area.

3. Results and discussion

The substrate electrode is subject to a negative DC self-bias voltage $V_b$, which was controlled by changing the RF input power. The negative self-bias voltage increases as the RF power increases; this is due to increased ionization in the plasma with increasing input power. When a magnetic field was applied, $V_b$ dropped for the same condition. The variation of $V_b$ versus RF input power in non-magnetic field and magnetic field is shown in Fig. 2. The magnitude of the self-bias voltage decrease in the magnetic field is about 100 V when the magnetic field is about 100 Gauss. This is due to the higher dissociation of ions in the magnetic enhanced plasma that gives rise to a large ion current, and decreases the negative DC self-bias voltage.

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the magnetic field at the RF input power of 40 W is shown in Fig. 3. Without a magnetic field, the $V_b$ is 180 V, and deposition rate is 2.4 nm/min. After applying a magnetic field, the $V_b$ dropped to 65 V and deposition rate increased to 23 nm/min at the magnetic field of 200 Gauss. The deposition rate is varied nearly ten times.

In order to compare the deposition and properties of DLC films with magnetic field and without magnetic field, two series of samples were prepared. The $V_b$ was changed from 100 to 500 V by controlling the RF input power. One series of samples were deposited at various $V_b$ without applying a magnetic field. Another series of samples were prepared at various $V_b$ with a magnetic field of 100 Gauss. The deposition rate, RMS roughness, hardness and Young’s modulus of the DLC films as a function of the bias voltage are shown in Fig. 4. There is an increase in the deposition rate with increasing power. When the magnetic field was applied, the deposition rates significantly increased, whilst the surface roughness of DLC film decreased, compared with the non-magnetic field case. At the same deposition conditions, the deposition rate increased about 5–10 times by applying the magnetic field, and the film surface is smoother, comparing with the non-magnetic field case. The results show that the deposition rate was enhanced significantly when the magnetic field was applied in the system.

The roughness of the DLC films decreases greatly with an increase in the bias voltage in the low bias voltage range (below 200 V). This is due to nano particles being embedded in the film. In the high bias voltage range, the roughness of the film is slightly decreased with increased bias voltage. After applying the magnetic field, the roughness of the DLC films decreased at the same bias voltage. Fig. 5a,b shows AFM images of films deposited without magnetic field and with magnetic field (100 Gauss), respectively; the $V_b$ was fixed at 120 V. Without magnetic field, some nano particles about 20–60 nm in size can be observed, and the roughness is 0.169 nm. After applying the magnetic field, the film is particle free and the roughness becomes smaller; as shown in Fig. 5b, the roughness of the film is 0.111 nm.

The hardness and Young’s modulus of the film increases with the bias voltage increase; at about 200–250 V, the hardness and modulus reach to a maximum (20 and 190 GPa, respectively), then decrease at higher bias voltage. The dependence of the hardness and Young’s modulus of the DLC films on the bias voltage under magnetic field conditions are similar to that under no magnetic field; which is slightly improved by applying magnetic fields. The maximum hardness and modulus is about 22 GPa and 200 GPa at the bias voltage around 200 V, respectively.

If the magnetic field ($B$) is oriented parallel to the cathode surface, and hence vertical to the electric field ($E$), $E \times B$ effects will be observed. Secondary electrons produced at the cathode surface will drift vertically because of the electric field, and horizontally because of the $E \times B$ drift. Eventually, the electrons will tend to pile up at one side of the plasma and will probably be lost. Orienting the magnetic field parallel to the cathode results in a significant reduction in the mobility of the secondary electrons emitted from the cathode; rather than being rapidly lost as they travel across the plasma to the counter-electrode, the electrons are constrained near the cathode. The result is that significantly higher levels of ionization are achieved in these plasmas, compared to the non-magnetic case. The higher plasma densities result in much lower plasma impedance, and hence a much lower discharge voltage, than the comparable non-magnetic case [6]. However, the $E \times B$ drift will lead to
a non-uniformity in the plasma, and as a result a non-uniformity in the deposition process. In the case of no magnetic field, the DLC films deposited under various conditions are quite uniform. When a transverse magnetic field was applied, the growth rate of the film increased remarkably, however, the film becomes non-uniform. One means of correcting this lateral non-uniformity caused by the \( E \times B \) drift is to change the direction of the magnetic field with time [6]. This technique results in a significant increase in the plasma density and a reduction in the DC bias voltage compared to a non-magnetic case.

The properties of the DLC films deposited by the glow discharge depend primarily on the bias voltage and thus on the mean ion energy. This dependence arises from the variation of the \( sp^3 \) and the \( H \) content with the bias voltage. The process of DLC film deposition by glow discharge is actually a balance of etching and deposition, which mainly depends on the plasma density and ion energy. In addition to the effects of physical sputtering by energetic ions, chemical etching occurring at the surface of the film during growth can also affect the film quality. In the system, higher self-bias voltages are achieved by an increase in RF power leading to an increase in the ion density in the plasma. The enhancement in ionization is accompanied by a higher degree of dissociation in the plasma leading to an increase of atomic hydrogen and methyl radicals [7], enhancing the deposition rate of the DLC films. With an increase in the bias voltage, both plasma density and ion energy will increase; the etching effect becomes stronger and results in smooth growing surface.

With an increase in the power, the higher accelerating voltage across the sheath space increases the energy of the film-forming ions that impinge on the substrate surface, thus results in a film which is more diamond-like in nature. It has been shown that the certain carbon ion energy region (30–300 eV) is beneficial to deposit amorphous carbon films possessing diamond-like properties. Lower or higher than this range, the properties of the film become polymer-like or graphite-like [8–11]. However, a very high bias voltage can cause substrate damage and make the film more graphite-like. After applying a magnetic field, the bias voltage can be decreased into this desirable range, whilst the plasma density can be enhanced, making the film more diamond-like. The increase in the magnetic field led primarily to an enhancement in plasma density and ion current density, resulting in more \( sp^3 \) and less hydrogen contents in the film which possesses high hardness [5].

4. Conclusion

A magnetically enhanced plasma CVD system has been developed for deposition of DLC films. A perpendicular magnetic field to the electric field was applied in a RF capacitively coupled plasma enhanced CVD system. Significantly higher levels of ionization are achieved in the system, resulting in much lower self-bias voltage and higher deposition rates, compared with the non-magnetic field case. The self-bias voltage decreased with an increase in the magnetic field, and the deposition rate of DLC film was increased. The properties of the DLC films deposited by applying the magnetic field were also improved. There is a higher hardness and Young’s modulus and lower surface roughness, compared with that of the DLC films deposited without applying a magnetic field. However, the \( E \times B \) drift leads to a non-uniformity in the plasma, resulting in a non-uniformity in the deposition process.

References


