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Synthesis and Characterization

Hydrogen-free diamond-like carbon films prepared by microwave electron cyclotron resonance plasma-enhanced direct current magnetron sputtering

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A B S T R A C T

Hydrogen-free diamond-like carbon (DLC) films were prepared by means of microwave electron cyclotron resonance plasma enhanced direct current magnetron sputtering. To study the influence of enhanced plasma on film fabrication and properties, the structures as well as mechanical and electrical properties of these films were studied as a function of applied microwave power. Results showed that higher microwave power could induce higher plasma density and electron temperature. The hardness increased from 3.5 GPa to 13 GPa with a variation of microwave power from 0 W to 1000 W. The resistivity showed a drastic increase from 4.5×10^4 Ωcm at 0 W to 1.3×10^{10} Ωcm at 1000 W. The variation of the intensity ratio I(D)/I(G) and the position of the G-peak of the DLC films with respect to changes in microwave power were also investigated by Raman spectroscopy.

1. Introduction

Diamond-like carbon (DLC) film has attracted considerable attention in research and applications for its many advantages: high hardness, high resistivity, high optical transparency, low friction and excellent chemical inertness [1–6]. Many different deposition techniques have been used to prepare DLC film, such as ion beam deposition, cathodic arc deposition, pulsed laser deposition, chemical vapor deposition and magnetron sputtering [7–12]. Among these prevalent techniques, magnetron sputtering has become the most popular one not only for its high efficiency and ease of control, but also because it can be used in synthesis on large area substrates [10–13]. And magnetron sputtering can produce hydrogen-free DLC film, which has enhanced hardness compared to hydrogenated DLC film [14].

DLC film is a metastable form of amorphous carbon containing a mixture of sp^2 and sp^3 hybridized bonds [15]. The electronic structure of amorphous carbon has been investigated in detail by Robertson and O'Reilly [16], who showed that a mixture of sp^2 and sp^3 carbon sites would tend to segregate into sp^2-bonded graphitic clusters embedded in a sp^3-bonded matrix. The sp^2 clusters were found to control the electronic properties while the connectivity of the sp^3 matrix largely controls the mechanical properties. Subsequently, using experiment and electronic structure calculations, Robertson [17] proposed a two-phase model in which he suggested that sp^2 sites contribute no rigidity if they form graphitic clusters, and can even lower the hardness of amorphous carbons. Hence, how to improve the content of sp^3 bonds has been the focus of the current study on DLC films. So far, many technologies have been used together with magnetron sputtering to improve the properties of DLC films [18–20].

In this work, a method of utilising microwave electron cyclotron resonance plasma (MECRP) enhanced direct current (DC) magnetron sputtering to deposit hydrogen-free DLC films is presented. The MECRP system is a non-electrode discharge which can generate plasma with higher density and purity [21–23], and it can also be used to control independently the plasma density and the bombardment energy of the ions [24]. We also report the changes caused by plasma enhancement to the hardness as well as resistivity and nanoparticle size for DLC films. We find that the electrical and mechanical properties both depend on the microwave power.

2. Experimental setup

The experimental device used to deposit hydrogen-free DLC films at room temperature, which includes a DC sputtering system, MECRP and a probe detection system, is sketched in Fig. 1. The MECRP consists of a microwave generator, a directional coupler and an electron cyclotron resonance chamber, as shown in Fig. 1. The working gas was argon with a purity of 99.99%. High purity graphite (99.99%) with a diameter of 74.8 mm served as the target. P-type (100) silicon wafers with resistivity 0.01 Ωcm were employed as the substrates. The target-substrate distance was about 8 cm. The substrates were ultrasonically cleaned for 10 min in acetone followed by 10 min cleaning in ethanol. Before deposition, the substrates were degassed at 300 °C for 30 min to prevent the incorporation of water desorbed from the sample holder and deposition chamber walls during deposition. The base pressure was 3.5×10^{-4} Pa, the gas flow

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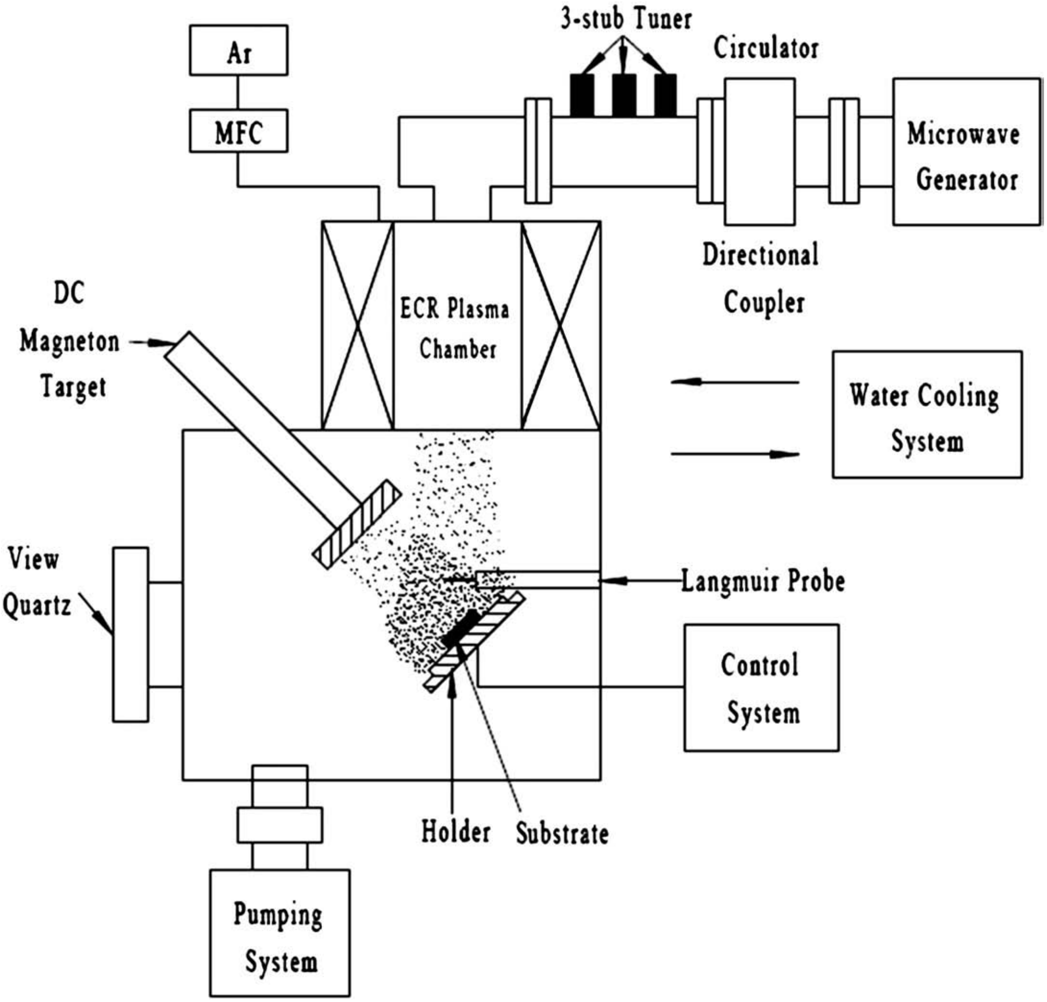

Fig. 1. A schematic of the MECRP system with a plasma source.

rate was 40 sccm and the working pressure was 0.5 Pa. DLC films were deposited at room temperature with a 200 W DC sputtering power and the microwave power was set at 0, 300, 600 and 1000 W respectively. In each deposition with different microwave power, the plasma density and electron temperature were all diagnosed by a Langmuir double probe system to study the influence of microwaves.

The electrical structure and chemical bonding of the hydrogen-free DLC thin films was characterized by visible Raman spectroscopy. The Raman spectrum was obtained in a backscattering arrangement for 514.5 nm light from an Ar ion laser (Renishaw inVia reflex) with a resolution of 1 cm^{-1}. The surface morphology and root mean square (RMS) surface roughness analysis of the thin films were performed by atomic force microscopy (AFM, CSPM5000). A four-point probe station (KEITHLEY2400) measurement gives the electrical resistivity of hydrogen-free DLC films. The hardness of the thin films was estimated by a nanomechanics comprehensive test system (CSM OPX) with the maximal load of 100 mN and a loading rate of 200 mN/min. All the data given in the following chapters are the mean value of five measurements for each parameter.

3. Results and discussion

3.1. Structural properties

The typical characteristic of Raman spectra for DLC films is two broad peaks with different intensity near 1370 cm^{-1} and 1580 cm^{-1}, which are known as the disorder D peak and G peak respectively. The G peak corresponds to the stretching vibration mode of any pair of sp^2 sites, whether in sp^2 chains or in aromatic and odd-membered rings, while the D peak is attributed to the breathing mode of sp^2 sites only in aromatic rings [25]. According to the three-stage model of Ferrari and Robertson [26], the visible Raman parameters can be used to derive the sp^3 fraction.

In Fig. 2, a series of visible Raman spectra of hydrogen-free DLC films deposited by enhanced plasma at various microwave power levels are shown. The D peak and G peak are clearly located at the two positions mentioned above. As the microwave power increases, the intensities of the D and G peaks both increase. The G peak position was also found to shift to higher wave numbers with increasing microwave power. This can be attributed to the reduction of sp2 sites of aromatic rings in hydrogen-free DLC films as the microwave power increases. Secondly, it can also be determined that the I(D)/I(G) ratio decreases from 0.98 to 0.94, 0.81 and then to 0.58, corresponding to the microwave power at 0 W, 300 W, 600 W, 1000 W, respectively. The increase of G peak wave number and the decrease of I(D)/I(G) ratio indicate the formation of aromatic bonds and an increase in the size of sp^2-C clusters, which means that the increase of sp^3 content changes the sp^2 configuration from mainly rings to short chains [26]. By all the features shown in the Raman spectra, we can conclude that the sp^3 content is improved by the MECRP.

As reported in the two-phase model [17], the connectivity of the sp^3 matrix largely controls the mechanical properties, while the electronic properties are controlled by the sp^2 content. Hence, the hardness and the resistivity of the films are measured to prove the

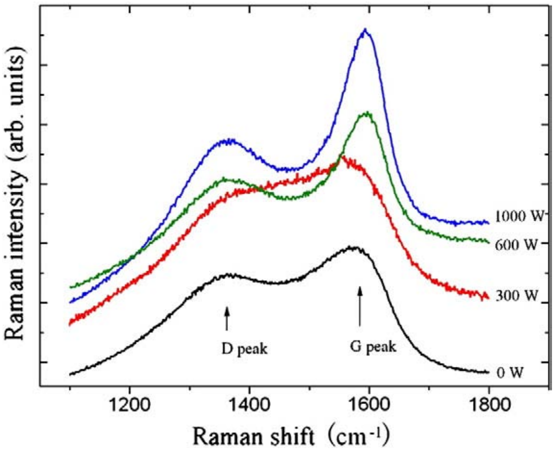

Fig. 2. Raman spectra of DLC films deposited under different microwave power with argon gas.

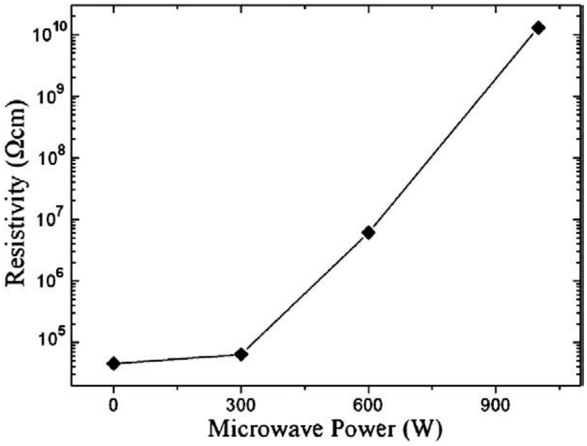

Fig. 4. The resistivity under varying microwave power.

validity of the former conclusion. The evolution of hardness with microwave power is plotted in Fig. 3. From this graph, we can see the hardness is enhanced with increasing microwave power. The hardness of the hydrogen-free DLC film was only about 3.5 GPa at 0 W, but over 13 GPa at 1000 W, which was four times as great as that of the film made by magnetron sputtering. It can be noted that the hardness achieved at 1000 W microwave power is high compared to the hardness obtained in other devices as such as 5 GPa in Plasma Enhanced Chemical Vapor Deposition [27] and about 10 GPa in unbalanced magnetron sputtering [19]. The measurement of hardness shows that the content of sp^3 bond increases with increasing microwave power.

The electrical sheet resistance R_s is determined by the four-point probe method, and the resistivity ρ is obtained using $\rho = 2\pi S R_s$ where S is the distance between two adjacent probes. Fig. 4 shows the trend of the resistivity against the microwave power. A mild increase from 4.5×10^4 Ωcm at 0 W to 6.4×10^4 Ωcm at 300 W and a drastic increase from 6.1×10^6 Ωcm at 600 W to 1.3×10^{10} Ωcm at 1000 W are shown. The resistivity of hydrogen-free DLC films almost exponentially increases with the microwave power. This also can be attributed to the microwave enhanced plasma improving the sp3 content in these films. If we regard DLC films as an insulator–conductor-system [28], a quantitative analysis on the microwave power and the sp3 content of DLC films would be given.

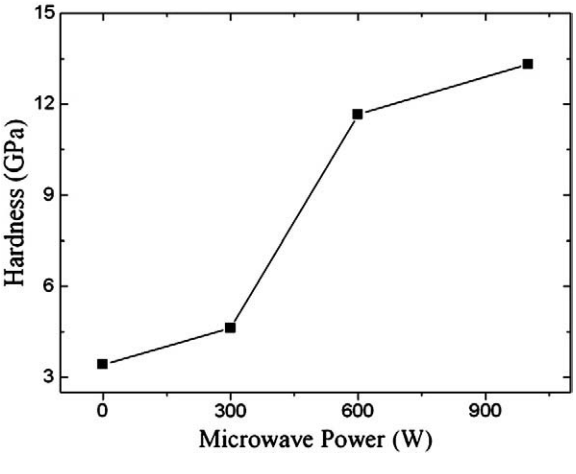

Fig. 3. The hardness of DLC films prepared under varying microwave power.

3.2. Surface morphology

To investigate the effect of microwave power on the surface morphology and the RMS surface roughness of hydrogen-free DLC films, AFM analysis was implemented, as shown in Figs. 5 and 6. The disordered structures of the films were obtained and look like many arrayed nanoparticles on the surface. Comparing the four images in Fig. 5, we can see clearly that the nanoparticle size increases with increasing microwave power. At the same time, the RMS surface roughness which ranges from 3.6 nm to 2.06 nm is a monotonic decreasing function of the microwave power, as shown in Fig. 6. The reason is thought to be as follows. The growth of nanoparticles during the deposition depends on the plasma density and ion energy, which is affected by the microwave power to a large extent. Colliding with more energetic ions, the carbon ions deposited on the surface are inclined to form stronger and closer bonds with each other. If the density of energetic carbon ions is higher at the time, the grains in the films will become larger. Hence, the film surface becomes more smooth and compact than that of films without MECRP enhancement.

3.3. Plasma density and electron temperature

To reveal the role of microwaves in the formation of hydrogen-free DLC films, the parameters of MECRP were diagnosed by a Langmuir double probe. The plasma density and the electron temperature go up steadily with increasing microwave power as shown in Fig. 7. This is because, as the microwave power increases, the electric field gets stronger and transfers much more energy to electrons than ions between collisions due to their very different masses. Electrons are heated and their velocities are increased to form energetic electrons while ions haven't been taken in consideration. These energetic electrons collide with the neutral particles and make more of them excited and ionized. Hence, by such pyrogenation and collisions, the plasma density and the electron temperature rise.

As we know, the ion density and energy are related to the plasma density and electron temperature. The raised ion energy which causes weaker bonds to be broken can supply sufficient energy for the forming of stronger bonds. In other words, the σ bonds which are stronger than π bonds and are the infrastructure of sp^3 bonds could be formed. Simultaneously, on the film surface dangling bonds are created through the ion bombardment process [29], whose density also increases with the increasing plasma density. The production of these bonds has a great impact on sp^2 and sp^3 sites, in the respect that sp^3 hybridized carbon atoms can transform into sp^2 hybridized carbon atoms (graphite) by recombination of two dangling bonds [30]. This recombination will only happen provided that two adjacent dangling

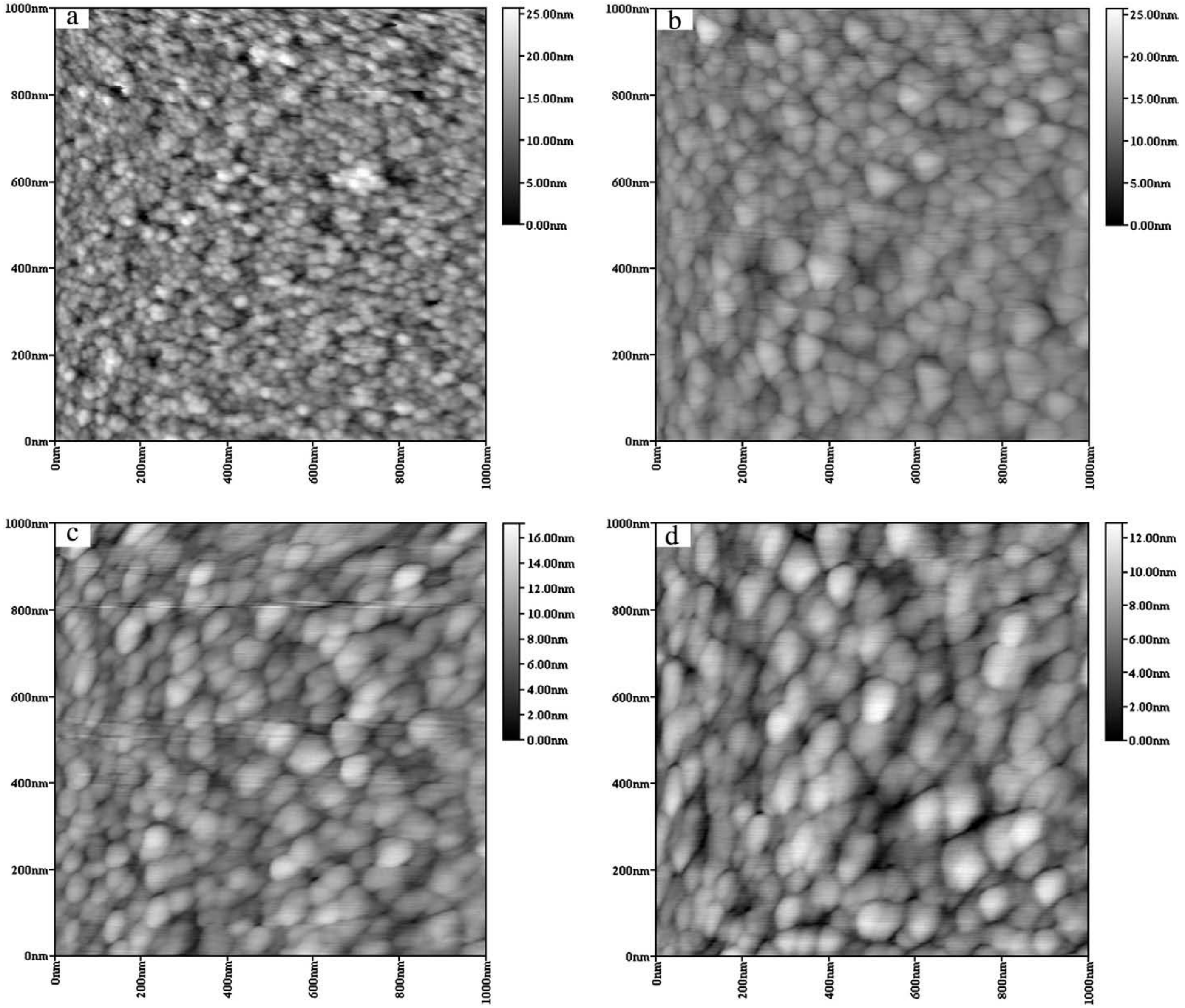

Fig. 5. AFM images of DLC films prepared under microwave power of (a) 0 W, (b) 300 W, (c) 600 W and (d) 1000 W.

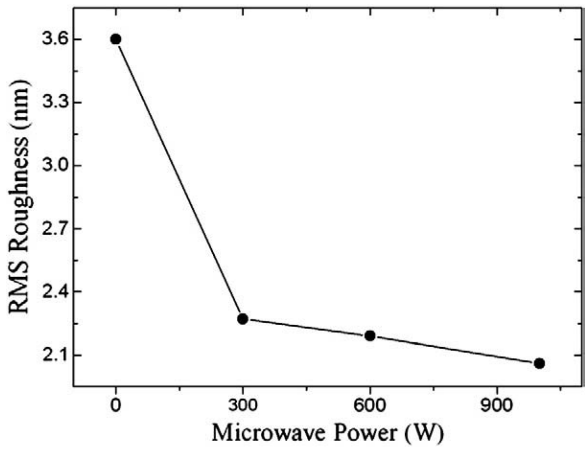

Fig. 6. The roughness of DLC films as a function of microwave power.

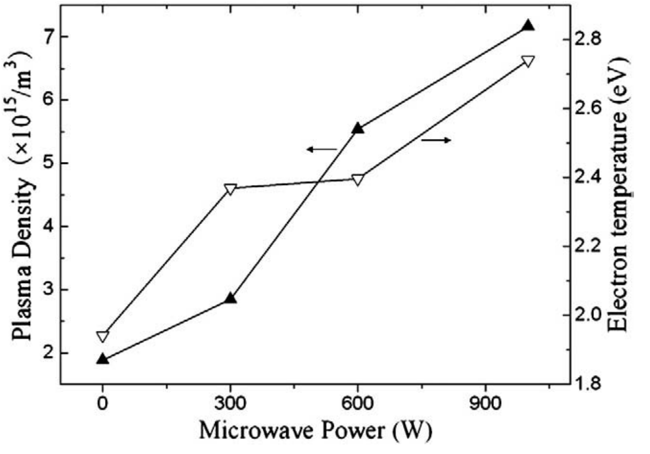

Fig. 7. Variation of plasma density and electron temperature as a function of microwave power.

bond sites exist simultaneously [31]. However, as Figs. 3 and 4 show, the films become more diamond-like following the increase in microwave power. Therefore we can deduce that, under conditions where the increase of dangling bond density follows the increase in plasma density, the recombination rate of dangling bonds is not increased. Furthermore, the fact is that the total dangling bond density increases following the increase in ion density, but the probability of the existence of two adjacent dangling bond sites is not increased (this result, which is different from that of S. F. Yoon et al. [31], is limited to the discussion in this paper). However, the deposition rate of diamond phase in the film is different from that of graphite phase at different microwave powers. As the increase of ion energy and deposition temperature with increasing microwave power provides the necessary formation energy to σ bonds and contributes to the formation of σ bonds, the deposition of diamond phase is accelerated which results in the increase of hardness and resistivity. This can also explain the observations in Figs. 3 and 4. In the same way, as shown in Figs. 5 and 6, at high ion energy, the sputtered ions have sufficient surface diffusion energy to form large nanoparticles and to make the film surface more smooth and compact.

Form the discussions above, under conditions where the ion density and energy are increased, it can be concluded that enhanced plasma is helpful for film growth and is capable of increasing the content of sp^3 hybridized bonds in hydrogen-free DLC films. Unfortunately, because of the complexity of the formation process during the deposition, we can not determine the quantitative dependence of sp^3 content on microwave power from these data. Not withstanding its limitation, this study does suggest that MECRP is an effective method to improve the properties of DLC films.

4. Conclusions

Hydrogen-free DLC films are prepared by the method of MECRP-enhanced DC magnetron sputtering in argon atmosphere under different microwave powers. It is found that the plasma density and electron temperature of the enhanced plasma, which decide the ion density and energy during the deposition of the films, are improved. Simultaneously, the electrical and mechanical properties of the films are both strengthened by the MECRP enhancement. The sp^3 content in hydrogen-free DLC films is increased by this deposition technology. It is believed that this method will be helpful for the quantitative study of DLC films.

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