Growth of mirror-like ultra-nanocrystalline diamond (UNCD) films by a facile hybrid CVD approach*

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Received 11 November 2016, revised 1 December 2016
Accepted for publication 19 December 2016
Published 31 March 2017

Abstract
In this study, growth of mirror-like ultra-nanocrystalline diamond (UNCD) films by a facile hybrid CVD approach was presented. The nucleation and deposition of UNCD films were conducted in microwave plasma CVD (MPCVD) and direct current glow discharge CVD (DC GD CVD) on silicon substrates, respectively. A very high nucleation density (about $1 \times 10^{11}$ nuclei cm$^{-2}$) was obtained after plasma pretreatment. Furthermore, large area mirror-like UNCD films of Φ 50 mm were synthesized by DC GD CVD. The thickness and grain size of the UNCD films are 24 μm and 7.1 nm, respectively. In addition, the deposition mechanism of the UNCD films was discussed.

Keywords: plasma pretreatment, microwave plasma CVD, direct current glow discharge CVD, ultra-nanocrystalline diamond films

(Some figures may appear in colour only in the online journal)

1. Introduction

Ultra-nanocrystalline diamond (UNCD) films have attracted great interest because of their unique outstanding characteristics [1]. Besides their original properties, which are the same as microcrystalline diamond (MCD) films and nanocrystalline diamond (NCD) films, UNCD films possess a smoother surface and lower cost.

A high-density nucleation rate is crucial for synthesizing UNCD films, which can avoid the appearance of large grains and defects. Pre-synthesizing diamond nanoparticles on the surface of substrates is the mainstream way to get a high-density nucleation rate. There are different kinds of effective substrate pretreatment means to enhance nucleation, such as ultrasonic agitation or mechanical scratching with nanodiamond powders [2, 3], bias-enhanced nucleation (BEN) [4], additional carbide interlayer [5, 6]. The nucleation density of ultrasonic agitation and mechanical scratching was reported in the range from $10^{9}$ to $10^{10}$ nuclei cm$^{-2}$ [7]. Such low nucleation density is not suitable for long-time deposition of micro-scale thickness UNCD films. BEN is an effective method that provides a high nucleation density ($10^{10}$–$10^{11}$ nuclei cm$^{-2}$) and does not cause any mechanical damage to the substrate [4]. However, the BEN process cannot be applied to porous or dielectric substrates. A carbide interlayer would lead to poor nucleation and non-uniformity when depositing on steel, copper, or non-carbon affinity materials [5].

A new nucleation process (NNP) which provides extremely high diamond nucleation density ($10^{11}$–$10^{12}$ nuclei cm$^{-2}$)
and causes no damage to substrates has been developed in recent years [6, 8]. There are two steps in the NNP; pretreating substrates with plasma is the first step. Second, ultrasonicating substrates in an ethanol solution that contains nanodiamond powders. In the previous reports, the NNP and the deposition of UNCD films were generally completed in only one chemical vapor deposition (CVD) reactor, such as microwave plasma CVD (MPCVD). MPCVD, which contains a denser plasma density than other plasma enhanced CVD (PECVD) methods [9–11], is always used to deposit high quality diamond films. Meanwhile, MPCVD could provide more nuclei even on a mirror-like surface due to the denser plasma density. Although MPCVD has a denser plasma energy, the edge effect [12–14] is the biggest impediment in depositing large area substrates. The edge effect, which originates from the point discharge in an electromagnetic field, will cause an apparent temperature rise and grain enlargement in the edge region of the substrate. On account of the advantages and disadvantages, MPCVD is suitable for long-time deposition of a small sample (e.g. single crystalline diamond homoepitaxy) or short-time treatment of large sample (e.g. rapid pre-nucleation on silicon). The spherical plasma ball of MPCVD is shown in figure 1(a). A unique feature of DC GD CVD is the large volume of the positive column in the interelectrode plasma space, which provides a uniform and stable plasma region above substrates (a schematic diagram is shown in figure 1(b)). The disc-shaped cathode and anode (as the substrate holder) in DC GD CVD are made of molybdenum. This is in contrast to MPCVD, suitable for the long-time deposition of micro-scale thickness UNCD films. Although several studies of large-area UNCD films using only DC GD CVD have been reported in recent years [15–17], the possible impact of the combination of MPCVD and DC GD CVD processes in UNCD films deposition is interesting. However, so far, no such research has been conducted.

In this study, experiments combining two different CVD methods (MPCVD and DC GD CVD) were performed in order to investigate the effects of a combination method in depositing UNCD films. Mirror-like UNCD films with micro-scale thickness were deposited by the modified hybrid approach combining MPCVD and DC GD CVD methods.

2. Experimental

In the first step of the pre-nucleation process, mirror-polished p-type (100) oriented Si substrates (Φ 50 mm) were subjected to plasma treatment in a 2.45 GHz MPCVD system for 30 min. The microwave power, deposition pressure, H2/CH4 reacting flow rate and substrate temperature are 1.6 kW, 50 Torr, 500/25 sccm and 720 °C, respectively. In the second step, the substrates were taken out of the CVD chamber and then ultrasonicated with an ethanol solution containing 5 nm crystallite size diamond powders for 30 min (ultrasonic power is 200 W). After two steps of pre-treatment as described above, the substrates were rinsed with ethanol and then immediately dried with N2. The pre-nucleated substrates were then put into a DC GD CVD system. Growth was carried out for 30 min with parameters same as the first pre-nucleation step, except for a different DC supply power 4.9 kW (current: 7.0 A, voltage: 700 V). Another three similar experiments were conducted to obtain the preferred process. These four experiments are listed in table 1, and samples from those four experiments were named #1, #2, #3 and #4, respectively.

### Table 1. Experiments of the combination of two CVD methods.

<table>
<thead>
<tr>
<th>Experiments</th>
<th>Process</th>
<th>#1</th>
<th>#2</th>
<th>#3</th>
<th>#4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pre-nucleation</td>
<td>MPCVD</td>
<td>DC GD CVD</td>
<td>MPCVD</td>
<td>DC GD CVD</td>
<td>(all the same)</td>
</tr>
<tr>
<td>Ultrasonic bath</td>
<td></td>
<td>DC GD CVD</td>
<td>MPCVD</td>
<td>DC GD CVD</td>
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<tr>
<td>Growth</td>
<td>DC GD CVD</td>
<td>MPCVD</td>
<td>MPCVD</td>
<td>DC GD CVD</td>
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</table>

![Figure 1. Schematic diagram of the plasma ball in: (a) MPCVD method, (b) DC GD CVD method.](image)
The parameters for the MPCVD and DC GD CVD processes are listed in table 2.

The surface morphology of samples was examined with a field emission scanning electron microscope (FESEM, Hitchi S4800). The crystal quality of the UNCD films was investigated by x-ray diffraction (XRD, Bruker D8Discover) and Raman spectroscopy with a 532 nm argon laser beam (Renishaw in Via-reflex). Surface topography and roughness were measured with atomic force microscopy (AFM, VeecoDimension 3100 V).

### 3. Results and discussion

#### 3.1. Pre-nucleation process

Figure 2 shows SEM images of the four samples after deposition for 30 min by different methods. Samples #1 and #4 have a fairly high nucleation density of ∼1×10^{11} nuclei cm^{-2} and ∼4×10^{10} nuclei cm^{-2}, respectively. Compared to the other two samples, however, the crystal particles of samples #2 and #3 are too large to estimate nucleation rate (grain size: about 50–200 nm). Owing to such sub-micron grain size, it is impossible to deposit UNCD films on these samples in the next stage (long-time deposition). Moreover, the grains deposited by DC GD CVD in the third process (no matter what the first process) were spherical diamond nuclei, as shown in figure 2 (#1 and #4), whereas grains deposited by MPCVD in the third process (no matter what the first process) show a faceted shape, as shown in figure 2 (#2 and #3).

According to the mechanism of different plasma ignition, MPCVD has a higher plasma energy density and faster growth rate, compared with DC GD CVD. In appropriate MPCVD conditions, a dense nucleation layer on the untreated substrate would be formed in a few minutes, but the nuclei would rapidly grow large in the following long-time growth. Hence, MPCVD and DC GD CVD were chosen for the prenucleation and growth processes in this study, respectively.

#### 3.2. UNCD films growth

The mirror-like UNCD film is illustrated in figure 3. It is clear that the reverse words ‘UNCD diamond films’ are reflected directly on the surface of the UNCD films. The reflection indicates that the UNCD film is smooth enough to be mirror-like.

Figure 4 shows the surface morphology of the UNCD films after deposition for 42 h using method #1. It can be seen that the UNCD films are uniform and dense. Every separated grain is an aggregation of smaller nanodiamond grains by virtue of the effect of second nucleation [18]. The aggregation grain size is about 10–15 nm and the actual grain size could be even smaller.

The UNCD films were separated by immersing the sample into a HF/HNO_3 solution to dissolve the silicon substrate. The cross-section image of the separated UNCD films is shown in figure 5. It is obvious that the cross-section of this UNCD films has a dense and uniform structure without any columnar structure, which is always observed in MCD films [19]. The unique structure of these UNCD films indicates that the films have a conformable quality from bottom to top, and provides reliability and stability in practical applications. The thickness (24 μm) of the UNCD films is marked in figure 5. Therefore, the calculated growth rate is approximately 0.56 μm·h^{-1}.

The UNCD films show a uniform distribution from bottom to top according to the results of SEM images. The detailed morphology was studied using AFM to evaluate the surface roughness. Figure 6 shows, for the 42 h-deposited UNCD films, densely and uniformly distributed nano-scale particles spreading on the substrate. The surface roughness R_s value is as small as 36.1 nm in a measured area of 5 × 5 μm².

Figure 7 shows Raman spectra of the UNCD films, which are consistent with the typical Raman spectra of UNCD deposited on silicon substrates [6, 20]. The four dominant resonance peaks in the spectra are located at around 1140 cm^{-1} (υ_1), 1350 cm^{-1} (D), 1470 cm^{-1} (υ_2), 1550 cm^{-1} (G), respectively. The 1350 cm^{-1} and 1550 cm^{-1} can be ascribed to the graphite D and G bands (sp^2-bonded carbon), while the 1140 cm^{-1} and 1470 cm^{-1} are the two typical peaks assigned to trans-polyacetylene (TPA, υ_1 and υ_2). The TPA Raman peaks are usually observed in the Raman spectra of NCD or UNCD films [21], and always considered as a marker of NCD or UNCD formation. The 1332 cm^{-1} (D*) is always assigned to diamond (sp^3-bonded carbon), but the peak at 1332 cm^{-1} in figure 7 is broadened and hardly visible as the Raman signal is much more sensitive to sp^2-bonded carbon than to sp^3-bonded carbon. The broadened 1332 cm^{-1} is always considered as evidence of the grain size decreasing from micrometer to nanometer scale [21, 22].
nanocrystalline nature and the full width at half maximum (FWHM) of the films. The (111), (220) and (311) diamond peaks are obvious in figure 8, and the (220) peak at 75.4° is the dominant peak. The (111) diamond peak in the diffraction patterns of the films is broadened as a result of the nanocrystalline structure of these films. The average grain size of the sample could be evaluated by the Scherrer formula.
\[ d = \frac{0.89 \lambda}{B \cos \theta} \]  

where \( \lambda = 0.1541 \) nm is the x-ray wavelength, \( B \) is the FWHM of the diffraction peak, and \( \theta \) is the Bragg angle. The instrumental peak width was subtracted from the measured \( B \) values. According to the specialized XRD analysis software Jade, the grain size was estimated to be approximately 7.1 nm. This is in agreement with the analysis of actual grain size, shown in the SEM image (figure 4).

### 4. Conclusions

The impact of a hybrid CVD approach combining MPCVD and DC GD CVD for depositing UNCD films has been studied. A high nucleation density of about \( 1 \times 10^{11} \) nuclei \( \text{cm}^{-2} \) was obtained after plasma pretreatment. A \( 50 \) mm and \( 24 \) \( \mu \)m thickness UNCD films with 7.1 nm average grain size have been deposited on Si substrates by the modified hybrid CVD approach. This process consists of nucleation and growth using the MPCVD and DC GD CVD method, respectively. The unique characteristics of the UNCD films were confirmed by SEM, Raman spectroscopy, XRD, and AFM. The deposition of larger and thicker UNCD films is in progress.

### Acknowledgments

This work was supported by the program of international S&T cooperation (Agreement No. S2015ZR1100).

### References