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# Characterization of chemical vapour deposited diamond films: correlation between hydrogen incorporation and film morphology and quality

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## Abstract

In order to tailor diamond synthesized through chemical vapour deposition (CVD) for different applications, many diamond films of different colours and variable quality were deposited by a 5 kW microwave plasma CVD reactor under different growth conditions. The morphology, quality and hydrogen incorporation of these films were characterized using scanning electron microscopy (SEM), Raman and Fourier-transform infrared (FTIR) spectroscopy, respectively. From this study, a general trend between hydrogen incorporation and film colour, morphology and quality was found. That is, as the films sorted by colour gradually become darker, ranging from white through grey to black, high magnification SEM images illustrate that the smoothness of the well defined crystalline facet gradually decreases and second nucleation starts to appear on it, indicating gradual degradation of the crystalline quality. Correspondingly, Raman spectra evidence that the diamond Raman peak at  $1332\text{ cm}^{-1}$  becomes broader and the non-diamond carbon band around  $1500\text{ cm}^{-1}$  starts to appear and becomes stronger, confirming increase of the non-diamond component and decrease of the phase purity of the film, while FTIR spectra show that the CH stretching band and the two CVD diamond specific peaks around  $2830\text{ cm}^{-1}$  rise rapidly, and this indicates that the total amount of hydrogen incorporated into the film increases significantly.

## 1. Introduction

High quality large area diamond synthesized by chemical vapour deposition (CVD) is an excellent material for many applications, especially for electronic applications. Since the growth rate of a conventional hot filament CVD (HFCVD), 1 or 1.5 kW microwave plasma CVD (MPCVD) deposition system is low, only in the order of  $1\text{ }\mu\text{m h}^{-1}$ , in recent years high power 5 kW, 8 kW or even higher 60 kW MPCVD reactors have been widely used to

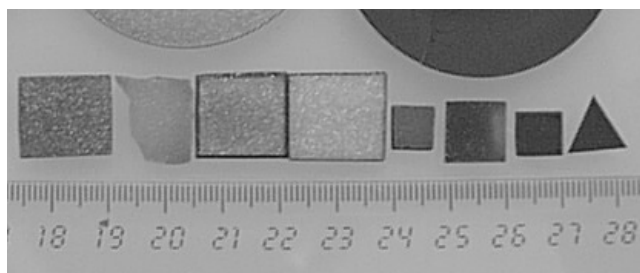
prepare large area (say diameter 2 inch) diamond films with high quality and high growth rates ranging from about 3.0 up to 42  $\mu\text{m h}^{-1}$  [1–8]. It is a well known fact that each deposition system, for example HFCVD, DC-arc jet plasma CVD, lower power ( $\leq 1.5$  kW) or high power ( $\geq 5$  kW) MPCVD has its own specific parameter windows for growth of diamond. Similar to the numerous investigations on the relationship between film quality and growth conditions for HFCVD and low power MPCVD techniques in the last decade, many efforts were focused on the relationship between growth parameters and film quality, growth rate and texture for high power ( $\geq 5$  kW) MPCVD reactors too [1–8]. Hydrogen is a ubiquitous impurity in CVD diamond films due to rich hydrogen in the growth atmosphere. Since defects and impurities represent a limitation for many applications, for example electronic properties deteriorate with increasing defect densities [9], it is important to investigate the relationship between impurity incorporation, for example hydrogen, and film morphology and quality, in order to tailor CVD diamond for electronic applications. However, so far no such study has been performed for diamond films deposited using the high power MPCVD technique.

In this work, the relationship between the crystalline quality (morphology), phase quality and impurity incorporation, namely hydrogen, in CVD diamond films prepared using a high power 5 kW MPCVD reactor is studied. For this purpose, scanning electron microscopy (SEM), Raman spectroscopy and Fourier-transform infrared (FTIR) spectroscopy were explored to characterize CVD diamond films. SEM allows the characterization of crystalline defects [10], and is the most common technique used to identify the morphology of CVD diamonds. Raman spectroscopy is another most commonly used investigative technique to determine the quality and characteristics of diamond films due to its cheap, fast and non-destructive advantage [11–15]. Usually, micro-Raman is employed preferentially to diagnose the quality difference of CVD diamond films, because it has con-focal ability and in most laboratories an  $\text{Ar}^+$  laser is employed for this purpose. FTIR spectroscopy is a powerful tool for study of hydrogen in CVD diamond films [16–19], because it is a convenient non-destructive technique used for detecting the bonded hydrogen type and its amount in diamond films since the integrated intensity of the C–H stretch region correlates linearly with hydrogen concentrations obtained by the sophisticated technique of nuclear magnetic resonance (NMR) [20, 21]. By combining the three most common and convenient techniques, especially using high magnification SEM, a general trend between crystalline quality (morphology), Raman quality and hydrogen content of CVD diamond films is established from this work.

## 2. Experimental details

A 5 kW ASTeX PDS-18 MPCVD deposition system was used to deposit polycrystalline diamond films on (100) silicon substrates. Numerous thick polycrystalline diamond films of variable quality ranging from white colour to black colour were synthesized by adjusting the growth parameters, namely, substrate temperature, microwave power, pressure, methane concentration in hydrogen, and nucleation density. Variable nucleation density was achieved by controlling either the nucleation conditions or the substrate pre-treatment (i.e. with or without scratching the silicon substrate with diamond powder of grain size 0.5  $\mu\text{m}$ ). Some of the samples prepared in our system and used for this study are shown in figure 1 through an optical photograph taken by a CCD camera. The process conditions were microwave power 3–4.5 kW, 3–5 vol%  $\text{CH}_4$  diluted in  $\text{H}_2$  (flow 400–500 sccm) with or without  $\text{O}_2$  addition ( $\text{CH}_4:\text{O}_2 = 10:1$ ), pressure 100–110 Torr and temperatures between 700 and 1000 °C. The thickness of the films ranges from 100 to 400  $\mu\text{m}$ .

SEM, Raman and FTIR spectroscopy were used to characterize the morphology, quality and hydrogen incorporation of these samples, respectively. Both macro- and micro-Raman



**Figure 1.** An optical photograph of many CVD diamond films of different quality synthesized in our 5 kW MPCVD deposition system.

**Table 1.** Some characteristic parameters such as colour, FWHM and H content (represented by the area of the CH stretching band) of the representative samples.

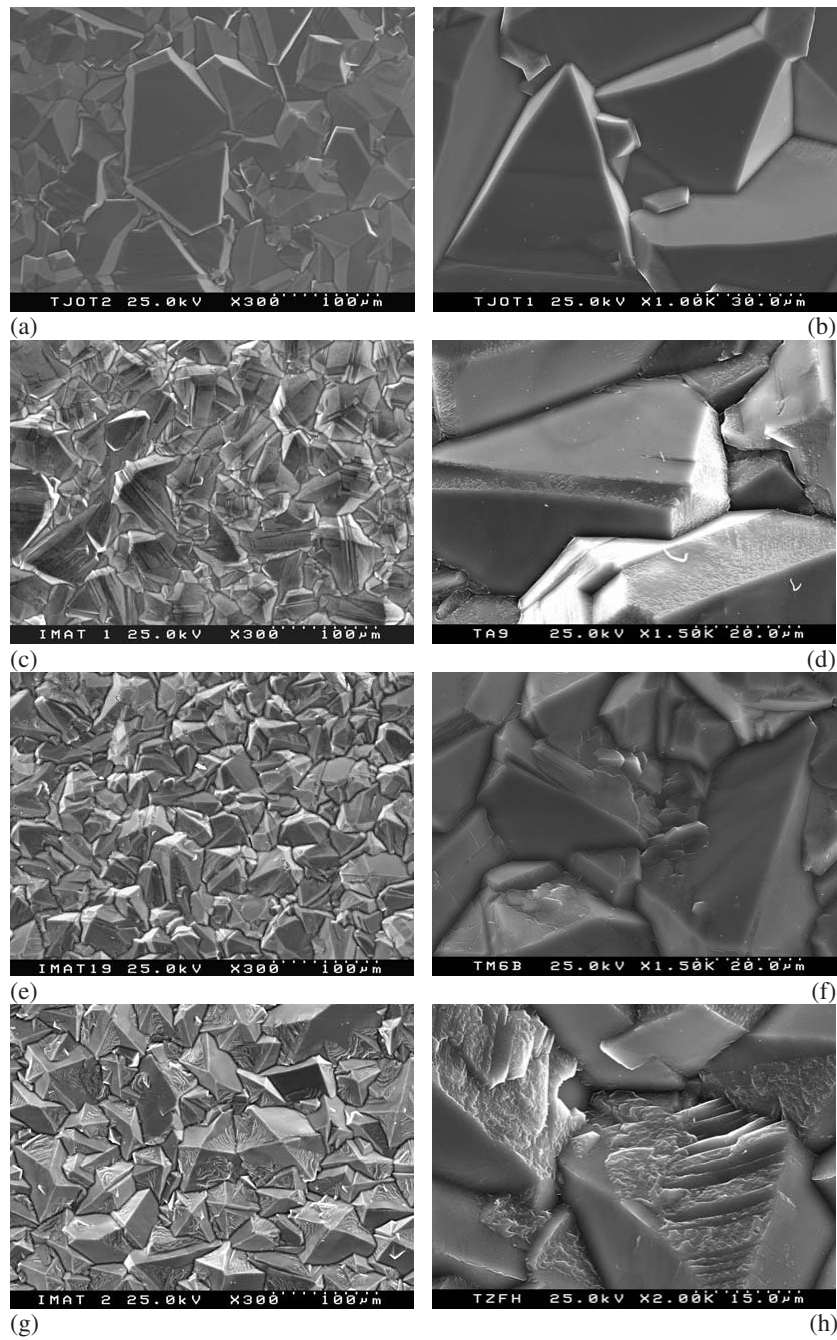
Sample	Colour	Micro-Raman FWHM ( $\text{cm}^{-1}$ )	Macro-Raman FWHM ( $\text{cm}^{-1}$ )	H content ( $\text{cm}^{-2}$ )
I-1	White	2.2	2.3	20
II-1	Light grey	5.4	5.5	173
II-2	Grey	7.6	8.0	307
III-1	Black	11.9	/	380

spectra were taken for the representative samples using a Jobin Yvon T64000 Raman spectrometer with a 514.5 nm  $\text{Ar}^+$  laser operating at a beam power of 2 mW on a spot size of 1.4  $\mu\text{m}$  in diameter for micro-Raman and on a spot size of 1 mm in diameter for macro-Raman. The Raman spectra were decomposed into the diamond peak around 1332  $\text{cm}^{-1}$ , one broad non-diamond carbon band around 1500  $\text{cm}^{-1}$  and a luminescence band as background. For the measurement of the full width at half maximum (FWHM), the diamond Raman peak was fitted with Lorentzian curve after subtraction of the luminescence background. The FTIR spectra were recorded at room temperature on an IFS 66V FTIR spectrometer with KBr beamsplitter using a resolution of 4  $\text{cm}^{-1}$  in the middle IR region (400–4000  $\text{cm}^{-1}$ ).

### 3. Results and discussion

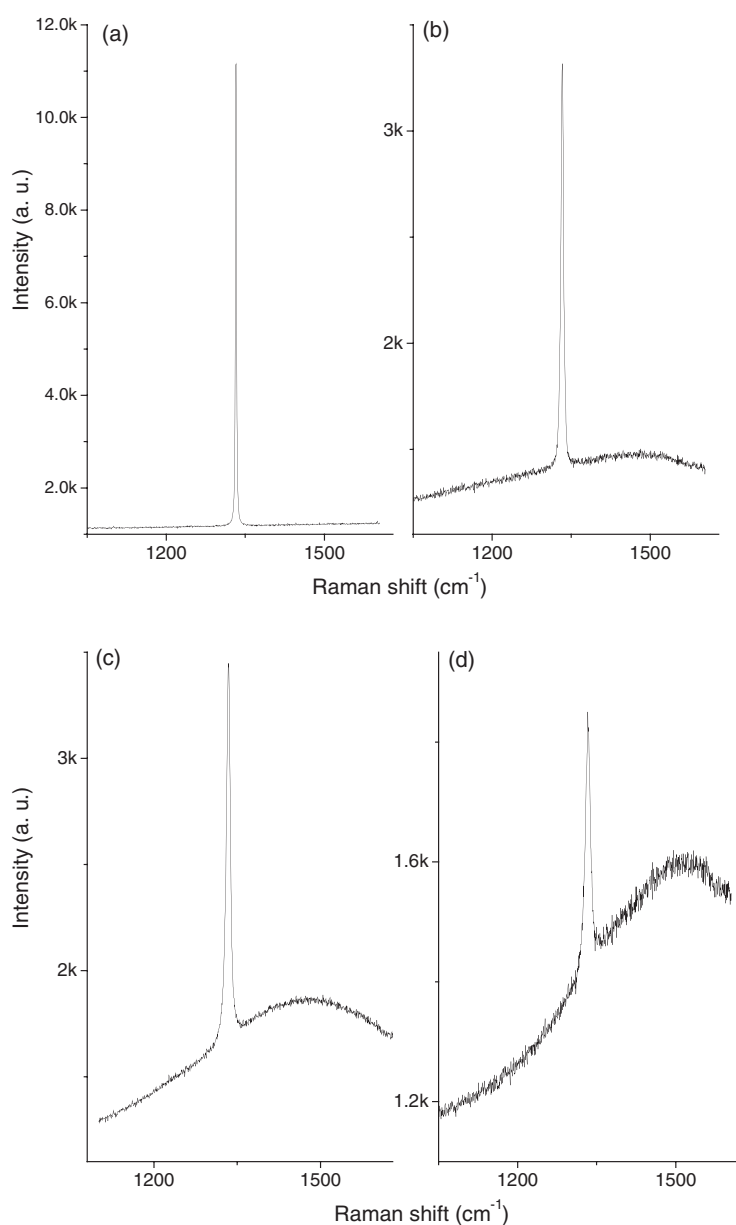
As evident in figure 1, polycrystalline CVD diamond films can be divided into three types by the colour, i.e. films of white colour (type I), films of light grey to grey (type II) and films of dark grey to black (type III). After characterization of all the samples (more than 30) we obtained by SEM, Raman spectroscopy and FTIR spectroscopy for film morphology, quality and impurity incorporation, namely hydrogen, we found that there are some links between the characterization represented by these three techniques and the colour type of the films. For the sake of clarity and comparison, we choose four representative samples from the three types of films in terms of colour i.e. films I-1, II-1, II-2 and III-1, and present the corresponding characterization of these four samples by the three techniques as follows. Table 1 itemizes some characteristic parameters such as colour, FWHM, growth rate, and H content of the representative samples for better comparison.

Figures 2 and 3 give the SEM micrographs and Raman spectra of the four representative films of different colours, respectively. Film I-1 is white in colour; SEM micrographs (figures 2(a) and (b)) illustrate that the film is composed by well defined crystallites with smooth (100) and (111) facet. Especially the high magnification SEM image (figure 2(b))



**Figure 2.** Low and high magnification SEM micrographs of the four representative films I-1 (a), (b), II-1 (c), (d), II-2 (e), (f) and III-1 (g), (h), the left column corresponding to low magnification and the right column corresponding to high magnification.

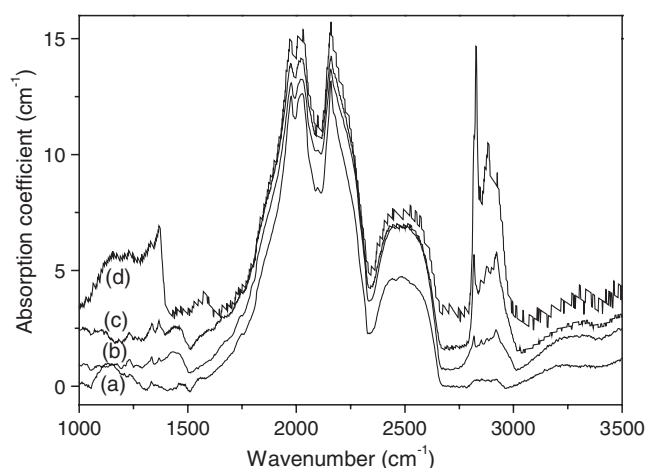
shows that both (100) and (111) crystalline surfaces including for very small crystallites are very smooth within the resolution of the SEM and free of micro-twins. It is well known that CVD diamond grown on {100} contains far fewer structural defects than {111} growth



**Figure 3.** Raman spectra of the four representative films: (a) I-1, (b) II-1, (c) II-2 and (d) III-1.

sectors [22] and TEM observations show that most CVD diamond films contain a high density of defects, predominantly twins and stacking faults on  $\{111\}$  planes [22, 23]. Therefore, the high smoothness of (111) facets of film I-1 evidences the very high crystalline quality of the film and is consistent with its high transparency. The Raman spectrum (figure 3(a)) confirms the quite high phase purity of the film from the point of view of optical scattering, since it shows only a very strong and narrow diamond peak at  $1332\text{ cm}^{-1}$  (the FWHM is  $2.2\text{ cm}^{-1}$ , as narrow as that of IIa natural diamond) with a linear background, indicating no non-diamond component can be detected by the Raman spectrometer used.





**Figure 4.** FTIR absorption spectra of the four representative films: (a) I-1, (b) II-1, (c) II-2 and (d) III-1.

For film II-1, light grey in colour, SEM micrographs (figures 2(c) and (d)) show that the film is composed by well defined crystallites, but the high magnification SEM image (figure 2(d)) illustrates that (100) and (111) crystalline surfaces are not so smooth with some planar steps and defects or micro-twins, which indicates degradation of the crystalline quality. Meanwhile, the Raman spectrum (figure 3(b)) shows that the diamond peak at  $1332\text{ cm}^{-1}$  becomes broad (FWHM  $5.4\text{ cm}^{-1}$ ) with increasing luminescence background, which also confirms the crystalline quality of the diamond is decreasing and is consistent with the SEM morphology observation. For film II-2, grey in colour, the low magnification SEM image (figure 2(e)) indicates that the film is composed by well defined crystallites similar to the case of film II-1, whereas the high magnification SEM micrograph (figure 2(f)) highlights that (100) and (111) crystalline surfaces become rough and second nucleation appears, indicating further decrease of the crystalline quality. Accompanying this change of crystalline quality through morphology observation, the diamond Raman peak (figure 3(c)) becomes broader (FWHM  $7.6\text{ cm}^{-1}$ ) and the non-diamond band around  $1500\text{ cm}^{-1}$  appears more apparent with continuously increasing luminescence background, which indicates that the phase purity decreases further.

Now for film III-1, black in colour, the low magnification SEM micrograph (figure 2(g)) emphasizes that the film is still composed by large crystallites with sharp edges, but powder-like rough (100) and (111) crystalline surfaces as clearly evident in the high magnification SEM micrograph (figure 2(h)) and second nucleation occurs frequently on the crystallite facets, which evidences that the crystalline quality degrades significantly. Now, the Raman spectrum (figure 3(d)) shows that the diamond peak at  $1332\text{ cm}^{-1}$  becomes much broader (FWHM  $11.6\text{ cm}^{-1}$ ) and the broad band centred at around  $1500\text{ cm}^{-1}$  appears stronger with a very high luminescence background. It is important to note that for the first three films both micro- and macro-Raman give more or less the same FWHM of the diamond Raman peak, while for film III-1 macro-Raman spectroscopy is not able to detect the diamond Raman peak due to strong absorption from the non-diamond component in the film since the macro-Raman sample area is much larger than that of micro-Raman. So, corresponding to the SEM morphology observation, the Raman spectrum confirms that both the crystalline quality and phase purity of diamond in film III-1 is the worst among the four types of films.

Now we address the FTIR spectra of the four films (figure 4), which can be divided into three regions, i.e. the one-phonon region below  $1330\text{ cm}^{-1}$ , the two-phonon region between  $1332$  and  $2667\text{ cm}^{-1}$ , and the three-phonon region from  $2667$  to  $3996\text{ cm}^{-1}$ . Theoretically one-phonon absorption is forbidden for pure diamond due to lattice symmetry; however, CVD diamond may contain some defects and impurities, which break the selection rules based on symmetry and cause absorption in the one-phonon region. Here we will not further discuss this part. For all the four representative films, the FTIR spectra show the well defined intrinsic two-phonon absorption feature of diamond, especially the sharp peaks at  $1970$ ,  $2044$  and  $2156\text{ cm}^{-1}$  which come from two-phonon absorption accruing at the high symmetry critical point in the Brillouin zone [24]. This is consistent with the common feature that all the four films have large diamond crystallites as indicated by the SEM observation and confirmed by the Raman spectra. The major difference is in the three-phonon region. The absorption band between  $2800$  and  $3000\text{ cm}^{-1}$  is the well known C–H stretching band [25, 26], which lies in the three-phonon region. It is obvious that from film I-1 through II-1 and II-2 to III-1, the CH stretching band increases rapidly in area; for example, film I-1 has only a very small CH absorption band, while film III-1 has the largest CH band among the films, indicating the amount of H incorporated increases drastically. Since the integrated intensity or area of the CH stretching band is proportional to the total amount of bonded hydrogen in the films [20, 21], the hydrogen content of our films is represented by the area of the CH stretching band and is listed in table 1 for comparison. In addition, peaks around  $2818$  and  $2828\text{ cm}^{-1}$  start to appear in film II-2 and become strong and sharp in film III-3, and rapidly increase in intensity from III-3 to IV-4. These two peaks are CVD diamond specific [17, 25], since they are observed neither in natural diamond nor amorphous carbon. In our previous work the peak at  $2828\text{ cm}^{-1}$  was assigned to hydrogen bonded to a structural defect of CVD diamond [26]. A study on the origin of the peak at about  $2818\text{ cm}^{-1}$  is under the way. Other peaks originate from the C–H bond in the form of  $\text{sp}^3\text{ CH}_x$  ( $x = 1, 2, 3$ ), for example peaks at  $2850$  and  $2920\text{ cm}^{-1}$  are the symmetry and anti-symmetry stretching vibrations of the  $\text{sp}^3$  bonded  $\text{CH}_2$  group [17, 25].

The above-described observations are summarized below. Generally, low magnification SEM micrographs indicate that the morphologies or microstructures of these films are different; however, it is not easy to distinguish the fine difference in crystalline quality. In contrast, from the high magnification SEM images, we can easily distinguish the difference in crystalline quality; the smoothness of the crystalline facet gradually decreases while second nucleation starts to appear and becomes more serious as the films gradually become darker, ranging from white through grey to black in colour. Accompanying the change in colour and morphology, the diamond Raman peak becomes broader and broader and the non-diamond carbon band around  $1500\text{ cm}^{-1}$  begins to show up and becomes stronger with further darkening of the colour, indicating an increase of the non-diamond component and a decrease of the phase purity of the film. Meanwhile, FTIR spectra show the total amount of incorporated hydrogen and the two peaks at  $2818$  and  $2828\text{ cm}^{-1}$ , especially the latter, rise rapidly with decreasing film quality and darkening film colour. Haque *et al* [19] have investigated six thick industrial DC arc-jet diamond films and observed that the higher the hydrogen content (determined by FTIR), the darker the colour of the film, the larger the non-diamond  $1560\text{ cm}^{-1}$  peak intensity, and the larger the FWHM of the diamond Raman peak at  $1332\text{ cm}^{-1}$ . Their observation is in harmony with our findings for diamond films grown using the MPCVD technique, which implies that the quality of CVD diamond films generally correlates well with the colour, independent of the specific growth techniques.

Comparing film colour, Raman quality and hydrogen content, a general trend between film quality and hydrogen incorporation is obtained and summarized in table 2. That is, when the colour of CVD diamond films gradually becomes darker, both crystalline quality and phase



**Table 2.** A general trend between film quality (colour and FWHM of the diamond Raman peak) and bonded hydrogen content (represented by the area of the CH stretching band).

Film colour type	Quality	FWHM (cm <sup>-1</sup> )	H content (cm <sup>-2</sup> )
White	Very good	<4.3	Low (<125)
Light grey to grey	Good	4.3–8.0	Medium (60–300)
Dark grey to black	Poor	>7.2	High (>300)

quality decreases, while second nucleation becomes serious and hydrogen content increases significantly.

#### 4. Conclusions

Many diamond films of variable quality ranging from high quality transparent to poor quality opaque were prepared using a 5 kW MPCVD reactor. These films can be roughly divided into three types by colour, i.e. white colour film, light grey to grey colour film, and dark grey to black colour film. These films were characterized by combining the three commonly used techniques of SEM, Raman and FTIR spectroscopy and a general trend between hydrogen incorporation and film colour, morphology and quality was found. Generally, with darkening colour, the crystalline quality decreases as evidenced by decrease of the smoothness of the crystalline facet and increase of second nucleation on it; the diamond Raman peak around 1332 cm<sup>-1</sup> becomes broad (i.e. larger FWHM and lower intensity); meanwhile, the non-diamond carbon band centred about 1500 cm<sup>-1</sup> rises, indicating increase of the non-diamond component; whereas the total amount of hydrogen incorporated into the film increases significantly. Generally speaking, the quality of CVD diamond films evidenced by different characterization techniques is consistent with the type sorted by the colour, or in other words a film of darker colour has lower quality and a larger amount of hydrogen impurity.

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