Impact of nitrogen doping on growth and hydrogen impurity incorporation of thick nanocrystalline diamond films*

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A much larger amount of bonded hydrogen was found in thick nanocrystalline diamond (NCD) films produced by only adding 0.24% N_2 into 4% CH_4/H_2 plasma, as compared to the high quality transparent microcrystalline diamond (MCD) films, grown using the same growth parameters except for nitrogen. These experimental results clearly evidence that defect formation and impurity incorporation (for example, N and H) impeding diamond grain growth is the main formation mechanism of NCD upon nitrogen doping and strongly support the model proposed in the literature that nitrogen competes with CH_x $(x = 1, 2, 3)$ growth species for adsorption sites.

Keywords: thick nanocrystalline diamond films, nitrogen doping, crystalline quality

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1. Introduction

Recently, nanocrystalline diamond (NCD) films[1−3] have shown their strong potential for MEMS/NEMS and bio-sensor applications, because of the biocompatibility of diamond and the smooth surface benefiting from the nanometer size. Meanwhile, due to the huge potential application of nitrogen vacancy centre in diamond for quantum computers,[4] studies on nitrogen related defects in diamond, for example single nitrogen vacancy centres in chemical vapour deposited (CVD) diamond nanocrystals,[5] and the doping effect of nitrogen on diamond growth (by CVD technique,[6] and by high pressure high temperature (HPHT) method,[7]) have also attracted the attention of many researchers in the world.

The significant variation induced by nitrogen addition on morphology, quality and growth rate of large-grained polycrystalline diamond (nowadays more popular as microcrystalline diamond (MCD)) films or of homoepitaxial CVD diamond has been investigated for more than two decades and a substantial literature can be found on this subject. In contrast, so far only a few reports can be found on the effect of nitrogen additive on the growth and the properties of ultrananocrystalline diamond (UNCD)[8,9] and NCD films.[10,11]

Inspired by the experimental work of catalysed growth of preferentially {100} faceted diamond by nitrogen,[12] Kaukonen *et al.*[13] have proposed an alternative growth pathway upon nitrogen doping, the so-called zipper growth mechanism, which is a modification of the standard model of CH_x growth species dominated CVD diamond growth mechanism.[14] Recently, Dunst *et al.*[6] have studied the catalytic effect of growth rate enhancement by nitrogen in CVD diamond using laser reflection interferometry and proposed a model in which nitrogen catalyses diamond growth and competes with CH_3 species for radical adsorption sites and then enhances catalytically the incorporation of hydrocarbon growth species into the diamond lattice. However, no direct experimental work has been performed to study how nitrogen additive influences hydrogen impurity incorporation in CVD diamond films specially NCD during the growth process, and to provide experimental evidences for clarifying the diamond growth mechanism upon nitrogen doping.

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It is well-known that hydrogen is very important for CVD diamond. On one hand, hydrogen atoms in the gas source play a key role in conventional growth of diamond by CVD using hydrogen dominated gas mixtures.[14,15] On the other hand, hydrogen is incorporated as a ubiquitous impurity into CVD diamond during the growth process,[16] and thus affects many properties of CVD diamond films, for example dielectric properties.[17] Therefore, it is important to study how each of the growth parameters including nitrogen addition influences hydrogen incorporation, so that deep understanding of the CVD diamond growth mechanism and tailored growth of a diamond film with the desired morphology and properties can be achieved.

For this purpose, in the present work, we investigate the role of nitrogen additive on hydrogen impurity incorporation in NCD films using Fourier-transform infrared (FTIR) spectroscopy. In the literature, thin NCD films were produced by using large amount of nitrogen addition (up to about 4% N_2) into methane-hydrogen plasma (up to 15% CH_4/H_2).[9,10] However, in our case, thick NCD films were produced by only adding a small amount of N_2 into a standard condition used for the growth of high quality transparent large grained polycrystalline diamond film. The drastic production shift from transparent MCD (under standard model of CVD diamond growth mechanism) to NCD caused by a small amount of nitrogen addition, provides a good example for studying the specific growth mechanism of CVD diamond upon a perturbation of hydrogen/hydrocarbon chemistries by nitrogen, since all the other growth parameters are kept the same, the role of nitrogen can be clarified exclusively.

2. Experiment

The diamond samples were prepared on (100) silicon wafers of ∼50 mm in diameter and 3-mm thick using a 5-kW ASTeX PDS-18 microwave plasma CVD system. The growth parameters were microwave power 3 kW, pressure 1.4×10^4 Pa, substrate temperature about 750 °C and H_2 (400 SCCM)/CH_4 (16 SCCM) without or with 1 SCCM N_2 addition. Without nitrogen addition, namely using CH_4/H_2 plasma only, a high quality transparent large-grained polycrystalline diamond film was obtained after a deposition time of 30 h and represented as PD sample. With nitrogen additive (i.e., using 0.24 vol.% N_2 into 4 vol.% CH_4/H_2 plasma), a NCD film was grown for 25 h and labeled as ND for comparison. In the following, we analyse the morphology, crystalline quality, optical quality and bonded hydrogen content of the representative samples PD and ND in details.

3. Results and discussion

3.1. Morphology characterization

The drastic changes induced by nitrogen addition on morphology, grain size, crystalline quality and shape of crystallites are clearly demonstrated in Fig. 1

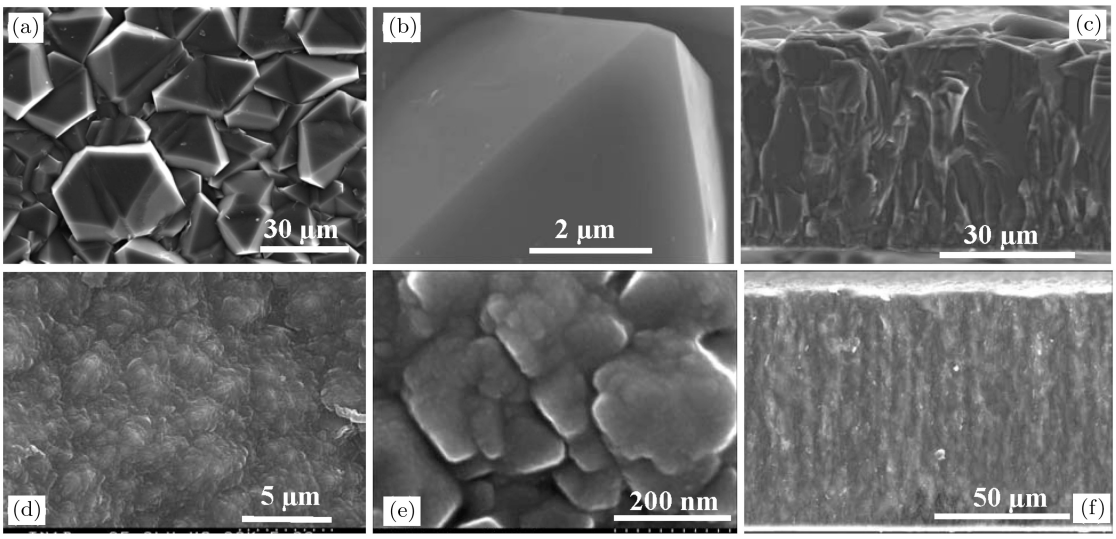


Fig. 1. SEM micrographs showing the top morphology and cross-sectional view of both samples: film PD (a), (b), (c) and film ND (d), (e), (f).

by the plane-view and cross-sectional view of the samples using conventional and high-resolution scanning electron microscope (SEM). From Fig. 1(a), one can see that film PD consists of smooth {111} facet dominated pyramid-like large crystallites of about 15 μm in size with an average grain size around 12 μm. The high-magnified SEM image (Fig. 1(b)) clearly evidences the high smoothness (namely no steps or terraces) and sharp edges of well-defined square {100} and triangular {111} facets, evidencing the high crystalline quality of the sample PD. The cross-sectional SEM micrograph (Fig. 1(c)) of film PD illustrates the typical columnar growth commonly found in large-grained PCD films and the rough growth surface due to columnar growth and large grains at the growth surfaces.

In contrast, cauliflower-like clusters made by fine grains are found in the large scale SEM image of film ND (Fig. 1(d)). The high-resolution SEM micrograph (Fig. 1(e)) further evidences the nanocrystalline nature of film ND consisting of fine grains smaller than 100 nm. It is interesting to note that large clusters (smaller than 200 nm) composed of fine grains show square-like or triangle-like sharp edges, in a manner similar to large {100} or {111} facets found in PD. The cross-sectional micrograph of film ND (Fig. 1(f)) also demonstrates slight columnar growth, but the grain size and surface roughness do not obviously increase or vary with film thickness. Hence, the growth surface of film ND is much smoother (because of its nanometre grain size) than that of film PD. The RMS roughness of the growth surface of film ND of 87 μm thick is 63 nm over 4 μm measured by atomic force microscopy (AFM), while that of film PD is larger than 3 μm measured by using a profile meter. The average grain size of film ND is calculated to be about 46 nm using the well-known Scherer equation based on synchrotron single crystal x-ray diffraction (XRD) measurement (not shown here).

From the cross-sectional SEM images, we can measure the film thickness, namely 47 μm for PD and 87 μm for ND. Therefore, their growth rates are 1.6 μm/h for PD and 3.5 μm/h for ND. The double growth rate of film ND compared to that of PD can be ascribed to the catalytic effect of nitrogen addition on growth rate enhancement,[6] and is consistent with other works in the literature.

The diamond nature of both samples was confirmed by their Raman spectra (Fig. 2). The drastic degradation of crystalline quality and phase purity of film ND induced by nitrogen addition is clearly demonstrated by the much weaker and broader diamond Raman peak around 1332 cm^{-1} and strong broad band around 1500 cm^{-1}, compared with the sharp diamond Raman peak of film PD. The full width at half maximum (FWHM) of the diamond Raman peak is 6.0 cm^{-1} for PD and 13.1 cm^{-1} for ND. In addition, the small peak around 1140 cm^{-1} commonly found in NCD films also gives additional support to the nanocrystalline nature of film ND. It is worth to note that the origin of 1140 cm^{-1} peak was under debate for a while and now it is generally accepted that it does not come from diamond and was assigned to trans-polyacetylene.[18]

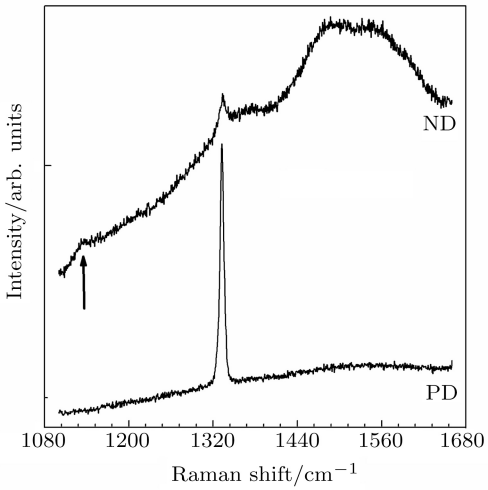


Fig. 2. Raman spectra of the samples PD and ND taken from the growth surfaces.

3.2. Infrared spectroscopy study of N impurity and hydrogen incorporation in CVD diamond films

The FTIR absorbance spectra of the two samples are shown in Fig. 3 for comparison. The strong increase of absorption background in the absorbance spectrum of film PD is mainly due to absorption caused by the silicon substrate and scattering caused by the rough growth surface. Anyway, for sample PD, the intrinsic well-defined diamond two-phonon absorption features in the region between 1700 cm^{-1} and 2650 cm^{-1} shown in Fig. 3(a), clearly evidence the diamond nature and high crystalline quality of the sample as the Raman spectrum does. In contrast, for sample ND, from Fig. 3(b), one can see that the intrinsic diamond two-phonon absorption band is only roughly discernable, while two strong absorption bands appear in the one-phonon region below 1332 cm^{-1} and in the three-phonon region, namely the CH stretching band between 2800 cm^{-1} and 3100 cm^{-1}.

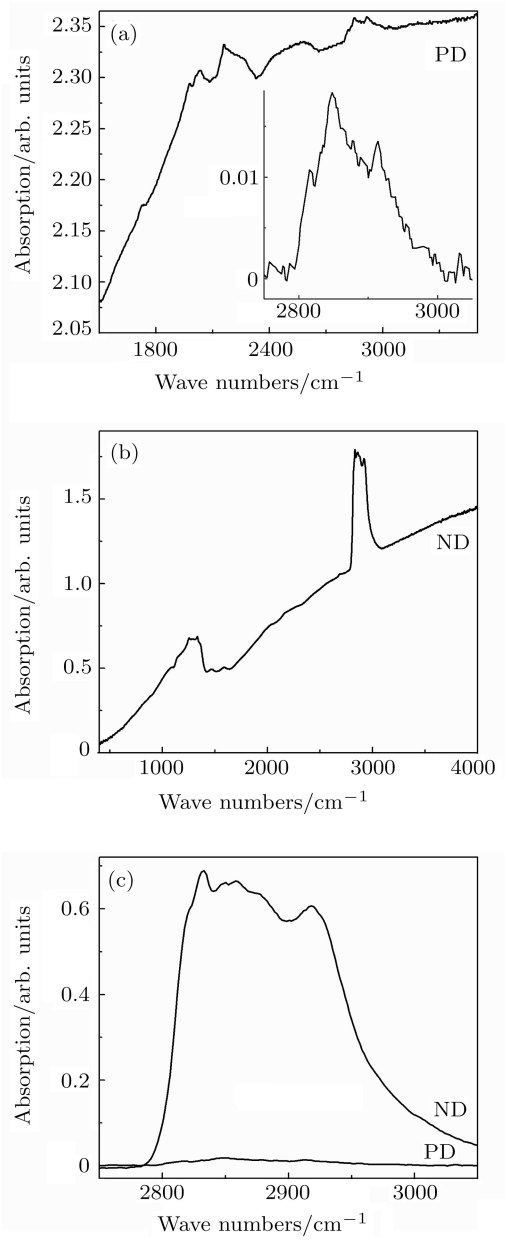


Fig. 3. FTIR spectra of films PD (a) and ND (b), and enlargement of the CH stretching bands of films PD and ND (c). The enlargement of the film PD spectrum is given in the insert.

These features are very similar to that observed for NCD films of 200 μm thick grown with 0.19% nitrogen and 0.05% oxygen addition under different growth conditions reported in detail in our previous work.[19] The common FTIR features found in NCD samples grown with nitrogen (with or without oxygen) under different conditions not only demonstrate the reproducibility of the NCD growth upon nitrogen addition but also confirm the existence of H and N impurity incorporated in NCD films grown with nitrogen doping.[20] The peaks at 1140, 1250 and 1332 cm^{-1} come from nitrogen related defects. Based on the intensity of the 1332 cm^{-1} peak in the one-phonon region of ND by normalization of the diamond two-phonon absorption coefficient to be 12.3 cm^{-1} at 2000 cm^{-1} and using the formula, namely the content of positively charged single-substitutional N^+ equal to 5.5 atomic ppm per cm^{-1} of the 1332 cm^{-1} absorption,[21] we calculate the single substitutional N impurity in film ND which is about 338 ppm. Note that the total amount of N impurity in film ND should be much higher than this, because single substitutional N is just one possible form of nitrogen impurity in diamond. The existence of N impurity in sample ND is also confirmed by energy disperse spectroscopy (EDS) measurements during SEM morphology observation.

The drastic increase of hydrogen impurity in ND sample is clearly demonstrated by its huge CH stretching band in comparison to that of film PD, which almost looks like a baseline, as shown in Fig. 3(c). The bonded hydrogen content of both films is calculated to be 11508 cm^{-2} for ND and 416 cm^{-2} for ND based on the integrated area of the CH stretching band A_{CH} divided by the film thickness d.[22] Therefore, the infrared active bonded hydrogen content of film ND is about 28 times that of film PD. Note that the average grain size of sample PD (12 μm) is more than two orders greater in magnitude than that of film ND (46 nm). TEM observation has shown that there are a high density of lattice defects, mainly stacking faults and twin boundaries in diamond nanocrystals grown by CVD besides the high density of grain boundaries.[23] In future work we shall focus on where hydrogen is incorporated in NCD films.

In short, by comparison of samples of PD and ND, one can see that a small amount of nitrogen addition (0.24 vol.%) drastically turns the conventional condition for growth of high quality PCD to favour the growth of NCD, significantly degrades the crystalline quality of the diamond films by defect formation (evidenced by SEM morphology observation and Raman spectra) and strongly provokes a large amount of hydrogen impurity incorporation (measured by FTIR spectra).

Based on our experimental results, we discuss the growth mechanism of NCD by CVD upon the perturbation of a small amount of nitrogen doping in the following. In this work, all the controllable growth parameters such as microwave power, pressure, flow

(concentration) of CH_4 and H_2 and substrate surface temperature, are kept unvaried, except the small amount of N_2. Because of the use of high power (3 kW) and high pressure (1.4×10^4 Pa), the gas temperature in the plasma should be above 3000 K according to the simulation work of Lombardi *et al.*,[24] and thus the dissociation of the feeding gases H_2, CH_4 and N_2 are very effective, compared to low power ($\leq$1.5 kW) MPCVD and HFCVD systems. Hence, the H atomic concentration and the number density of CH_y ($y = 3$–0) growth species in the gas phase can be considered more or less the same even with the presence of a small amount of nitrogen (in this work 0.24%). The production of high quality transparent large-grained PD film from CH_4/H_2 plasma only evidences that CH_x growth species dominated 'standard model' of CVD diamond growth mechanism[14,25] can be accounted for the employed condition.

When a small amount of N_2 is introduced into the CH_4/H_2 plasma, due to the high gas temperature, N_2 immediately dissociates and many additional reaction paths are introduced and new intermediate reaction species, for example N atom, CN and NH radicals can be created, which slightly modify the gas phase chemistry, but certainly influence the surface reactions. In the case of films PD and ND, the surface temperature of Si substrate was kept constant, hence the influence of temperature on reaction rates was kept constant. The presence of N containing species influences or varies the adsorption rate of CH_x species, thus changes the consequence of diamond growth. Many simulation works reported in the literature support this idea. For example, theoretical simulation works have shown that in the presence of N, a CH_3 group attached to a surface dangling bond site is severely suppressed due to steric hindrance and a CH_2 can be directly inserted into the bridging position of a dimer bond at the diamond (100): H(2×1) surface[13] and in the presence of NH, the CH_2 adsorption reaction is always significantly favoured in the two types of monatomic step edges on the diamond (100) surface,[26,27] and thus requires less H abstraction reactions. The effect of substitutional N on CVD diamond growth was also theoretically studied and it was found that the CH_3 adsorption was always strongly disfavoured with N in the second carbon layer.[28] Therefore, our result, i.e. the formation of NCD with a large amount of bonded H and N impurities requires only a small amount of N_2 doping, strongly supports the model that N containing species compete with CH_x growth species for adsorption sites.[6]

Then we briefly analyse the incorporation mechanism of hydrogen impurity into CVD diamond films during the growth process. Since H atom (through abstraction) and C1 hydrocarbon radicals CH_x ($x = 0, 1, 2, 3$) as growth species (by adsorption) are key elements for CVD diamond growth, it is easy to understand that the concentration of H impurity in CVD diamond films would strongly depend on the concentration of H atom near the substrate surface and the concentration of CH_x radicals attached to the diamond surface. With nitrogen doping, the created N containing species compete with CH_x growth species, modify the concentration of CH_x adsorbed to diamond surface, for example suppress the adsorption of CH_3 but enhance the attachment of CH_2. Since one N may stimulate the growth of a whole layer and less H abstraction reactions are required,[13] the fast growth rate will also increase the chance for N and H being buried as impurity into growing diamond. The incorporation of H and N impurities in ND as evidenced by FTIR measurement will further increase twinning and the renucleation rate and lead to form other structural defects, which prevent the diamond grains growing larger upon nitrogen doping, as illustrated by SEM morphological observations. The circulation of this process will result in the remaining of small grains and the formation of NCD upon nitrogen doping. Since direct etching of surface sp^3-bonded CH_2 or CH_3 groups is negligible,[25] we believe that the 2850 and 2920 cm^{-1} peaks (originates from sp^3CH_2) dominated feature in the FTIR spectra of CVD diamond films from microcrystalline to nanocrystalline also give indirect support to the CH_3 growth species dominated standard model CVD diamond growth and N enhanced CH_2 adsorption upon nitrogen doping.

4. Conclusion

In summary, thick NCD films of high growth rate 3.5 μm/h and of 46 nm in averaged grain size are produced by only adding a small amount of N_2 (0.24% here) into a standard high power condition using 4% CH_4/H_2 mixtures for the growth of high quality transparent large-grained MCD films. FTIR measurement shows that 28 times larger amount of bonded hydro-

gen impurities are found in NCD grown with N_2 than MCD grown without nitrogen, while keeping all the other parameters constant. These results clearly evidence the effects of nitrogen catalysed growth, nitrogen induced nanocrystallinity by strong reduction of grain size from tens of micron down to below 100 nm and nitrogen provoked large amount of hydrogen impurity incorporation in NCD. Based on these results, we conclude that defect formation and impurity incorporation (for example, N and H) are the main mechanisms for degradation of crystalline quality, reduction of grain size and formation of NCD upon nitrogen addition. These findings also provide direct experimental evidence for the model proposed in the literature that nitrogen containing species competes with the hydrocarbon growth species for adsorption sites.

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