

CITY UNIVERSITY OF HONGKONG

香港城市大學

Study of Diamond Materials with Different Morphologies

多种表面形貌金刚石材料的研究

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Wu Yu

吳宇

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Abstract

This work steams from one of the most attractive and challenging goals in synthesis of heteroepitaxial diamond materials and is one of the milestones towards the growth of heteroepitaxial single crystal diamond films. The works herein were based on the synthesis of various diamond structures with different morphologies, studying of their epitaxial relationships with substrates and relevant physical properties. It demonstrates a high level of controlling the deposition parameters for synthesizing different diamond structures. More importantly, the originality of this work is in pioneering of novel conical diamond arrays and elucidating the Raman signature of nanodiamond materials.

In this work, microcrystalline and nanocrystalline diamond films were synthesized by using a commercial 1.5 kW microwave plasma enhanced chemical vapor deposition (CVD) system. Both types of materials were prepared by employing two steps deposition, i.e., nucleation and growth processes. The bias enhanced diamond nucleation and diamond seeding/scratching methods were adopted as the first step in the diamond synthesis. The nucleation was followed with selective textural growth to obtain the diamond films with desired morphologies and promote heteroepitaxial relationship between the films and substrates. Such processes were carried out by carefully tuning the deposition parameters including substrate temperature, composition of CVD gas mixture and microwave power supplied into plasma.

A part of this work aims at heteroepitaxial growth of diamond films which was performed on two types of substrates, silicon(001) and Ir(111)/CaF₂ (111)/Si(111) layered substrates employing either biased enhanced nucleation or nucleation induced from ultrasonic scratching and seeding. In the growth step, the alpha parameter associated with substrate temperature and concentration of hydrocarbon precursor in CVD gas phase controlled the

textural growth and coalescence of neighboring crystallites. The diamond synthesis at such conditions led to local heteroepitaxial relationships between the grown (001) diamond films and (001) silicon substrates as revealed by high-resolution transmission electron microscopy and no transition layer was detected at the diamond/silicon interface. High quality (111) textured diamond films with possibly partial epitaxial relationship respect to the iridium (111) substrate were deposited via using ultrasonic scratching/seeding nucleation method and were observed by scanning electron microscopy. In our best knowledge, the diamond synthesis on Ir(111)/CaF₂(111)/Si(111) layered substrates yielding textural growth with potential local heteroepitaxial relationship is the first work ever reported.

Far more exciting output of this work is in the development of conical arrays made of either single crystal diamond cones or cones composed of nanodiamond. These two different conical structures are prepared from the similar hydrogen reactive ion etching (RIE) process applied to structurally dissimilar materials - polycrystalline diamond and nanodiamond. The polycrystalline diamond films were prepared in hydrogen/methane CVD environment, which had abundance of CH₃ radicals. The best single crystalline diamond cones were produced by RIE on pyramidal textured diamond (001) films, which was prepared with alpha parameter close to the value of three. In contrast, nanodiamond cones resulted from hydrogen reactive ion etching of nanodiamond films, in which nanodiamond grains clustered into columns penetrating through the entire film. In general, nanodiamond films grown in CVD environments was dominated by C₂ dimers. The high aspect ratio, smoothness of the single crystal diamond cone surface, cone rigidity and possibility of doping indicates that these materials are the best choice of constructing the probes used for scanning probe microscopy (SPM) including atomic force microscopy (AFM), scanning tunneling microscopy (STM) and others. The investigation of the field electron

emission properties of the developed nanodiamond conical arrays showed a better performance and approach to the level of turn on field that is close to carbon nanotubes without optimizing their cone density. It is believed that the further improvement of field electron emission property of nanodiamond by optimizing the cone density will make it to be the potential materials for producing the field electron emission devices.

Another very important output with a scientific value reported here is the contribution of revealing the Raman spectral signature of nanodiamond structures. The extended analysis of nanodiamond films formed the base for elucidating bizarre peaks at 1140 and 1480 cm^{-1} , which often appeared in nanodiamond film Raman spectra. These peaks were incorrectly ascribed to nanodiamond structures. Such interpretation was accepted by scientific community and used for several years. However, our unique experiment in which deuterium substituted hydrogen and comparative work of Ferrari group in Cambridge University proved that the peak of our concern are associated with C-H (C-D) bonded sp^2 vibration modes of trans-polyacetylenes confined in the nanocrystalline diamond film surface but not with C-C bonded sp^3 nanocrystalline diamond crystals. This is well demonstrated by shifting the peaks down to 860 and 1430 cm^{-1} when deuterium substitutes hydrogen in CVD environment of nanodiamond synthesis.

Table of Contents

Figure List	i
Table List	vi
1. Overview of diamond materials	1
1.1 Brief history of chemical vapor deposited diamond	1
1.2 Properties of diamond materials	2
1.3 Applications of CVD diamond	6
2. CVD diamond synthesis and characterization	9
2.1 Introduction into the methods of diamond synthesis	9
2.1.1 Microwave plasma CVD diamond deposition	9
2.1.2 Hot filament chemical vapor deposition applied to diamond synthesis	13
2.1.3 Radio frequency plasma assisted CVD diamond deposition	15
2.1.4 Direct current plasma assisted CVD diamond deposition	15
2.1.5 Hot filament- direct current plasma assisted chemical vapor deposition	16
2.2 Diamond nucleation methods and controlling CVD diamond growth	18
2.2.1 Introduction into diamond nucleation	18
2.2.2 Diamond nucleation induced with mechanical abrasion of Substrates	18

2.2.3	Bias enhanced nucleation method	20
2.2.4	Growing polycrystalline diamond films with different textures	21
2.2.5	Nanodiamond and its classification	25
2.3	Diamond and nanodiamond properties and their characterization	26
2.3.1	Scanning electron microscopy	26
2.3.2	High resolution transmission electron microscopy	26
2.3.3	Raman spectroscopy	27
2.3.4	X-ray diffraction	29
2.3.5	Optical emission spectroscopy	31
3.	Heteroepitaxial of diamond films on Si (001) and Ir (111)/CaF₂ (111) /Si(111)	32
3.1	Introduction of current status of heteroepitaxial diamond growth	32
3.2	Experiments of the diamond heteroepitaxial growth	35
3.2.1	Synthesis and characterization of heteroepitaxial diamond films on Si (001) substrates	35
3.2.2	Synthesis and characterization of Ir (111)/CaF ₂ (111)/Si (111) layered substrates	36
3.2.3	Diamond films deposited on Ir (111)/CaF ₂ (111)/Si (111) layered substrates and their characterization	37
3.3	Diamond films deposited on different substrates	39
3.3.1	Assessment of heteroepitaxial diamond films grown on silicon (001) substrate	39
3.3.2	Analysis of Ir (111)/CaF ₂ (111)/Si (111) layered substrates	41

3.3.3	Analysis of diamond film on Ir (111)/CaF ₂ (111)/Si (111) layered substrates	44
4.	The arrays made of single crystalline and nanocrystalline diamond cones	52
4.1	The arrays made of single crystalline diamond cones	53
4.1.1	Growing textured diamond films for structuring the single crystalline diamond cones	53
4.1.2	Single diamond cones and their arrays structured from textured diamond films	55
4.2	The properties of single crystalline diamond cone arrays	57
4.2.1	The morphological structure of diamond cones and their arrays	57
4.2.2	Analysis of single crystalline diamond cones down to atomic resolution	58
4.2.3	Phase analysis of diamond single crystal cones with reference to polycrystalline diamond films	60
4.3	Synthesis of nanodiamond films for tailoring nanodiamond cones arrays	62
4.3.1	Deposition of nanodiamond films as a first step for structuring the nanodiamond cone arrays	62
4.3.2	Fundamental characterization of nanodiamond films	63
4.3.3	Nanodiamond film tailored to the arrays of nanodiamond cones	66
4.4	Characterization of nanodiamond cone arrays	
4.4.1	Morphology of nanodiamond cone arrays	68

4.4.2	Raman spectral signatures of nanodiamond films and the nanodiamond cone arrays	68
4.4.3	Electron field emission from nanodiamond and single crystal diamond conical structures	70
4.5	Discussion on diamond cones	72
4.5.1	Evolution mechanism of diamond based cone arrays	72
4.5.2	Diamond conical structure influenced by etching conditions	75
4.5.3	Electron field emission enhancement due to the diamond conical structure	77
5.	Revealing trans-polyacetylenes in nanodiamond films	81
5.1	Fundamental features of nanodiamond	81
5.1.1	Different nanodiamond films	82
5.1.2	Conventional characteristic criterion of nanodiamond from Raman spectroscopy characterization	83
5.1.3	Trans-polyacetylenes in nanodiamond films	84
5.2	Experimental: Nanodiamond grown in deuterium and hydrogen CVD environments	86
5.3	Discussion on nanodiamond	88
5.3.1	Diagnostic of different plasma CVD environments for nanodiamond growth	88
5.3.2	Morphological investigation of nanodiamond films prepared at different conditions	91

5.3.3	Nanodiamond films deposited at different conditions analyzed by Raman spectroscopy	92
6.	Conclusion	95
7.	References	100
8.	Appendices	114
8.1	List of publications	114
	8.1.1 Conference presentations	114
	8.1.2 Journal articles	115
8.2	Abstracts of publications	116

Figure List

1. Figure1.1, Carbon phase diagram.
2. Figure1.2, Diamond face-centered cubic crystal structure
3. Figure1.3, Crystal structure of cubic (a) and hexagonal (b) diamonds
4. Figure2.1, Microwave plasma enhanced chemical vapor deposition system
5. Figure2.2, Hot filament chemical vapor deposition system.
6. Figure2.3, Radio-frequency plasma assisted CVD diamond deposition.
7. Figure2.4, Hot filaments–direct current plasma assisted chemical vapor deposition.
8. Figure2.5, C/H/O diagram of CVD diamond deposition.
9. Figure2.6, Transition of crystal shape from cubic to octahedral as the growth parameter α is increased. The arrows indicate the direction of fast growth.
10. Figure3.1, Schematic of iridium/ calcium fluoride/ silicon layered substrates used for depositing heteroepitaxial diamond.
11. Figure3.2, Heteroepitaxial flat [001] textured diamond film deposited on a silicon (001) substrate:
 - (a) Surface morphology of flat (001) textured diamond film,
 - (b) Cross-sectional image of (001) textured diamond film on silicon.
12. Figure3.3, Raman spectrum collected from a (001) textured diamond film grown on a (001) silicon substrate.
13. Figure3.4, High-resolution TEM image taken from heteroepitaxially grown diamond on a silicon (001) substrate.

14. Figure3.5, XRD pattern collected from iridium (111)/CaF₂ (111)/silicon(111) layered substrate.
15. Figure3.6, The typical Ir (111) rocking curve shows a small FWHM of 0.6°.
16. Figure3.7, HRTEM cross-sectional image collected from Ir (111)/CaF₂ (111)/Si (111) layered substrate at the Ir-CaF₂ interface.
17. Figure3.8, SEM morphology of the diamond grains deposited on Ir (111) substrate using BEN at -150 V for 15 minutes and subsequent growth for (a) 0.5 hour and (b) 9 hours.
18. Figure3.9, Morphology of diamond films deposited on Ir (111) substrates pretreated by scratching/seeding of diamond fine powders using ultrasonic agitation:
 - (a) Preferential [111]-textured growth,
 - (b) Some grains with in-plane aligned orientation relationship.
19. Figure3.10, Raman spectrum of (111) textured diamond film deposited on (111) Ir substrate pretreated by diamond powder scratching/seeding using ultrasonic agitation.
20. Figure4.1, SEM images of [001] orientated diamond film with pyramidal crystallites.
21. Figure4.2, SEM image collected from an array of single crystal diamond cones the image shows the uniformity in cone density and apical angle.
22. Figure4.3, TEM image of a single crystal diamond cone with an inset of corresponding selected area diffraction pattern, the axis of the cone is oriented along the [001] crystal direction.

23. Figure 4.4, High-resolution TEM image collected from the tip of a single crystalline diamond cone.
24. Figure 4.5, Raman spectra collected from
 - (a) a polycrystalline diamond film, and
 - (b) an array of single crystalline diamond cones.
24. Figure 4.6, The SEM morphological image collected from a nanodiamond film deposited in hydrogen based plasma with high content of carbon precursor.
25. Figure 4.7, Cross-sectional SEM (a) and TEM (b) images of a nanodiamond film.
26. Figure 4.8, Typical Raman spectrum acquired from a nanodiamond film, the peaks at 1140 and 1470 cm^{-1} conventionally ascribed to nanodiamond are not associated with C-C sp^3 bonding.
27. Figure 4.9, The morphology of nanodiamond cone arrays:
 - (a) Density of $2 \times 10^8 / \text{cm}^2$, etched at -400 V and 40 Torr,
 - (b) Density of $3 \times 10^9 / \text{cm}^2$, etched at -400 V and 20 Torr.
28. Figure 4.10, Comparing structures based on Raman spectra collected from
 - (a) A flat nanodiamond film,
 - (b) An array of nanodiamond cones.
29. Figure 4.11, Plots of electron emission current density dependent on applied electric field with corresponding Fowler-Nordheim plots in the inset. The data were acquired from following structures:

- (a) A flat nanodiamond film,
 - (b) An array of nanodiamond cones with a low-density ($2 \times 10^8 \text{ cm}^{-2}$),
 - (c) An array of nanodiamond cones with a high-density ($3 \times 10^9 \text{ cm}^{-2}$),
 - (d) An array of single crystalline diamond cones.
30. Figure 4.12, SEM images of polycrystalline diamond films etched at: (a), (b) $-300\text{V}/ 40$ Torr and (c)/(d) $-300 \text{ V}/ 20$ Torr; the images (a) and (c) are acquired in plain-view whereas the images (b) and (d) were taken at a tilting angle of 45° towards the SEM detector.
31. Figure 5.1, Optical emission spectra obtained from different plasma growth environments with corresponding samples prepared:
- (a) $\text{CD}_4/\text{D}_2/\text{Ar}$ plasma for the sample W192,
 - (b) $\text{CD}_4/\text{H}_2/\text{Ar}$ plasma for the sample W194,
 - (c) $\text{CH}_4/\text{D}_2/\text{Ar}$ plasma for the sample W195,
 - (d) $\text{CH}_4/\text{H}_2/\text{Ar}$ plasma for the sample W196.
32. Figure 5.2, SEM images collected from nanodiamond films prepared in different plasma growth environments:
- (a) Sample W192 prepared in $\text{CD}_4/\text{D}_2/\text{Ar}$ plasma,
 - (b) Sample W194 grown in $\text{CD}_4/\text{H}_2/\text{Ar}$ plasma,
 - (c) Sample W195 synthesized in $\text{CH}_4/\text{D}_2/\text{Ar}$ plasma,
 - (d) Sample W196 deposited in $\text{CH}_4/\text{H}_2/\text{Ar}$ plasma.
33. Figure 5.3, Raman spectra collected from nanodiamond films prepared in different plasma growth environments:

- (a) Sample W192 prepared in CD₄/ D₂/Ar plasma for,
- (b) Sample W194 grown in CD₄/ H₂/Ar plasma,
- (c) Sample W195 synthesized in CH₄/ D₂/Ar plasma,
- (d) Sample W196 deposited in CH₄/ H₂/Ar plasma.

Table List

1. Table 1.1, Main properties of diamond.
2. Table 2.1, Raman peak positions from CVD diamond film.
3. Table 3.1, Materials might serve as substrate for the deposition of single-crystalline and highly oriented diamond films.
4. Table 3.2, Experimental parameters for BEN process.
5. Table 3.3, Experimental parameters for diamond growth.
6. Table 4.1, The parameters for growing [001] textured pyramidal diamond films.
7. Table 4.2, Nucleation and growth parameters used for the deposition of nanodiamond films.