Property mapping of polycrystalline diamond coatings over large area

Awadesh Kumar MALLIK^{a,*}, Sandip BYSAKH^a, Monjoy SREEMANY^a,
Sudakshina ROY^a, Jiten GHOSH^a, Soumyendu ROY^b,
Joana Catarina MENDES^c, Jose GRACIO^d, Someswar DATTA^a

^aCSIR -Central Glass & Ceramic Research Institute, Kolkata 700032, West Bengal, India

^bDepartment of Physics, Indian Institute of Technology Bombay, Powai, Mumbai 400076, Maharashtra, India

^cInstituto de Telecomunicações, Campus Universitário de Santiago, 3810-193, Portugal

^dNanotechnology Research Division, Centre for Mechanical Technology and Automation,
University of Aveiro, 3810-193, Portugal

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Abstract: Large-area polycrystalline diamond (PCD) coatings are important for fields such as thermal management, optical windows, tribological moving mechanical assemblies, harsh chemical environments, biological sensors, etc. Microwave plasma chemical vapor deposition (MPCVD) is a standard technique to grow high-quality PCD films over large area due to the absence of contact between the reactive species and the filament or the chamber wall. However, the existence of temperature gradients during growth may compromise the desired uniformity of the final diamond coatings. In the present work, a thick PCD coating was deposited on a 100-mm silicon substrate inside a 915-MHz reactor; the temperature gradient resulted in a non-uniform diamond coating. An attempt was made to relate the local temperature variation during deposition and the different properties of the final coating. It was found that there was large instability inside the system, in terms of substrate temperature (as high as $\Delta T = 212$ °C), that resulted in a large dispersion of the diamond coating's final properties: residual stress (−15.8 GPa to +6.2 GPa), surface morphology (octahedral pyramids with (111) planes to cubo-octahedrals with (100) flat top surfaces), thickness (190 μm to 245 μm), columnar growth of diamond (with appearance of variety of nanostructures), nucleation side hardness (17 GPa to 48 GPa), quality (Raman peak FWHM varying from 5.1 cm^{-1} to 12.4 cm^{-1} with occasional splitting). This random variation in properties over large-area PCD coating may hamper reproducible diamond growth for any meaningful technological application.

Keywords: plasma-enhanced chemical vapor deposition (CVD); diamond film; mechanical properties; nanostructures

1 Introduction

Large-area polycrystalline diamond (PCD) coatings

have a wide range of technological applications, from micro-electromechanical systems to gyrotron windows for mm-wave transmissions and electrochemical sensors under harsh environments. Due to their high thermal conductivity and biocompatibility, PCD coatings are also used as heat sink substrates and

* Corresponding author.
E-mail: amallik@cgcri.res.in

bio-sensors. For all these applications, the uniformity of the coatings is a major requirement, i.e., the point variation of the properties of the coatings should be as low as possible. For example, the loss tangent of large-area diamond gyrotron windows [1] and strip particle detectors [2,3] should be as uniform as possible. Large-area PCD coatings have various industrial applications; as an example, we can mention “Diafilm”, a freestanding diamond disc manufactured by DeBeers Industrial Diamond Division since the early 1990s. The optical, thermal and dielectric properties of the discs are very uniform [4], and researchers all over the world use them as windows in high-power electron tubes.

Several authors have evaluated the growth [5–14] and nucleation [15] sides of large-area PCD coatings deposited by chemical vapor deposition (CVD). Sussmann *et al.* [4] mapped the $\tan\delta$ loss over a 120-mm-diameter freestanding PCD disc. Yokota *et al.* [7] reported that {100}-faceted crystals can be deposited with high uniformity on a 150-mm-diameter silicon substrate using 915-MHz and 60-kW ASTeX reactor when the parameter α (the ratio of growth velocities along {100} and {111} directions, $\alpha = v_{100}/v_{111}$) is 1. Schelz *et al.* [8] evaluated the radial variation of the Raman peak shift, roughness, nucleation density and thickness of PCD films deposited on a 75-mm-diameter substrate in a 915-MHz reactor. Vikharev *et al.* [9] deposited PCD films on 60–90-mm-diameter substrates with large growth rate (9 $\mu\text{m/h}$) in a 10-kW and 30-GHz system, but did not comment the uniformity of the properties. Zuo *et al.* [11] outlined the thickness uniformity of a PCD film deposited on a 75-mm-diameter substrate in a 2.45-GHz system, but did not analyze other properties. Tsai and Kuo [13] studied the properties of PCD films deposited on a 4-inch-diameter silicon substrate with addition of nitrogen, and reported the center-to-edge variation in microstructure, texture, thickness, and Raman and X-ray diffraction (XRD) peak patterns. Meykens *et al.* [16] evaluated the optical absorption coefficient of diamond infrared (IR) windows by quasi-parallel collinear photothermal deflection (PTD) of a 10.6-mm CO_2 laser [17]. Low- and high-power mm-wave diamond gyrotron windows have thoroughly been investigated [18,19], but no report about the variation of properties over the large-area coatings was made. 2-inch-diameter PCD optical lenses were fabricated in large quantities with consistent quality and characteristics over the whole

area [20]. The flexural strength of the nucleation and growth sides was evaluated by ring-on-ring method for 50 17–19-mm-diameter PCD disks deposited by microwave plasma CVD (MPCVD), with thicknesses ranging from 0.1 mm to 0.7 mm, for potential missile dome application in supersonic jets [21]. All the cited studies reported the investigation of large-area PCD coatings; however, to date, there is no systematic study of point-to-point variation of different physical properties like microstructure, thickness, crystallinity, quality, etc.

Substrate temperature is a key parameter in the deposition of diamond by CVD [22–30]. CVD diamond grows between 700 °C and 1100 °C at sub-atmospheric pressure of 20–130 Torr; to deposit high-quality diamond with well-faceted morphology, the substrate temperature has to be on the higher side of 900 °C, whereas substrate temperature lower than 700 °C produces cauliflower nanocrystalline morphology [31–34]. The growth rate initially increases with temperature, and after attaining maximum slowly decreases down.

Zimmer *et al.* [35] reported a lower-than-20 °C variation of the substrate surface temperature during deposition of diamond on a 300-mm-diameter silicon wafer by hot filament CVD (HFCVD) under nominal substrate temperature of 895 °C. They reported left-to-right, front-to-back and circular temperature variations, with corresponding non-uniformity in thickness, bowing, warping and Raman spectra of the diamond coating. However, even though the thermal management of the wafer substrate plays a major role in maintaining the diamond coating uniformity over large area, thorough temperature distribution studies are still lacking for MPCVD reactors. Authors have already addressed the issue of thermal management for large-area PCD deposition in their previously published work [36], but that study did not have thorough physical characterizations of the grown PCD coatings, which are necessary to better understand the influence of substrate temperature variation on the properties of the grown coatings. In addition to the systematic characterization of large-area PCD coating, the influence of CH_4/H_2 ratio on the uniformity of such coating is now fully understood through the present work, where a 100-mm-diameter silicon wafer is coated with diamond inside a 915-MHz low-power MPCVD reactor. Special care is taken to minimize the temperature gradient across the substrate during

growth [36]. Nevertheless, the properties of the PCD coating (quality, morphology, thickness, stress, crystallinity and hardness) differ from place to place, reflecting non-uniformity in the plasma that causes a temperature gradient on the silicon substrate during the diamond deposition. Diamond nanostructures also appear in some places of the freestanding diamond wafer. To get a further insight on these effects, a thick PCD wafer is grown with a high CH_4/H_2 ratio; the sample is fully characterized by scanning electron microscopy (SEM), Raman, XRD and high-resolution transmission electron microscopy (HRTEM). The results are then compared with samples deposited with a lower CH_4/H_2 ratio [36] and suggest that the increase in the methane content not only decreases the overall diamond quality (as will be seen from the Raman spectra) but also increases the temperature distribution gradient, leading to a film with a large dispersion of the characteristics.

2 Materials and methods

2.1 Substrate seeding and diamond growth

PCD was deposited on a (100) 100-mm-diameter and 6-mm-thick p-type single crystal silicon wafer with a 915-MHz and 9-kW MPCVD reactor (DIAMOTEK 1800, Lambda Technologies Inc. USA) [37] (Fig. 1(a)). The silicon substrate was previously seeded with a mixture of detonation nano-diamond (DND) suspension [38] and methanol of 1:3 ratio for 15 min. The substrate was placed inside the chamber with a stage height of -0.1 cm. The chamber was initially evacuated down to 10^{-3} Torr, and the microwave power and pressure were slowly increased till the final growth conditions were reached (9 kW and 110 Torr). Diamond growth proceeded for 95 h with a hydrogen flow rate of 1000 sccm and an initial methane flow rate of 40 sccm. After 4 h, this value was decreased to 35 sccm; after 8.5 h, the stage height was changed to $+0.1$ cm.

2.2 Thermal management of the wafer substrate

To minimize the temperature gradient during diamond growth, the silicon wafer was placed on top of a quartz plate. The diameter of the quartz plate was smaller than the diameter of the silicon substrate, and cold water was circulated through the molybdenum substrate

Fig. 1 (a) Schematic of the MPCVD reactor. (b) (100) 100-mm-diameter silicon wafer sitting on a structured quartz plate, depicting the positions of the nine different “zones” studied in the present work.

holder stage, as described in Fig. 1(b) [36]. At the beginning of the deposition, the hemispherical plasma ball was centered in the middle of the substrate.

The substrate temperature was measured with a double-wavelength optical pyrometer (Williamson, USA, Model: PRO 82-40-C). The pyrometer was focused at the center of the substrate throughout the 95-h long run. The temperature was monitored from time to time at nine different spots (a few millimeters in area), identified in Fig. 1(b). These spots were located 40 mm away from the center of the substrate and were separated from each other by other 40 mm. For each reading, the maximum temperature difference between the spots was determined as

$$\Delta T = T_{\max} - T_{\min} \quad (1)$$

where $T_{\max}$ and $T_{\min}$ are the maximum and

minimum temperature readings, respectively.

2.3 Physical characterization of the PCD coating

The silicon substrate was etched with a solution of hydrofluoric acid, nitric acid and acetic acid in 1:1:1 ratio; the freestanding PCD coating was then broken into pieces to collect specimens A to H from the sites described in Fig. 1(b). An extra sample M was collected in the middle region of the 100-mm-diameter area. The samples A to H were characterized in detail. The roughness of the nucleation and growth sides of the samples was measured by coherence scanning interferometry (CSI, Contour GT-K, Bruker Nano GmbH, Germany). Each scan was performed on a surface area of $0.8\text{ mm} \times 0.6\text{ mm}$, generating millions of data points. A $10\times$ objective lens was used, with back scan and length parameter of $35\text{ }\mu\text{m}$ and $70\text{ }\mu\text{m}$ respectively for the rough side, and $15\text{ }\mu\text{m}$ and $20\text{ }\mu\text{m}$ for the nucleation side. The micro and nanostructural features of the samples were evaluated by SEM (LEO 430i STEROSCAN, UK), and the thickness was measured by cross-section SEM. The nucleation surface morphology of the MPCVD diamond films was characterized by field-emission SEM (FESEM, Supra 35VP, Carl Zeiss, Germany). The structural characterization of the samples was done with XRD technique. The XRD patterns of the samples were recorded in an X'pert Pro MPD diffractometer (PANalytical) with an X'Celerator operating at 40 kV and 30 mA using Cu K α radiation with step size of 0.05° (2θ) and step time of 30 s from 20° to 90° . The weight percentages of the crystalline phases were estimated using Rietveld analysis of the XRD line profiles [39,40] by X'pert high score plus software (PANalytical)^①. In addition, the quality of the diamond films was examined by Raman spectroscopy (HR-800, HORIBA JOBIN YVON, Japan) with a 514-nm Ar⁺ laser with 10-mW laser power and 50- μm spot size. The micro hardness of the nucleation side was measured by applying 1-kgf load for 60 s of duration using a Vickers indenter (model Leica VMHT-microsystem GmbH, Australia).

3 Results and discussion

3.1 Substrate temperature

Figure 2(a) shows the temperature distribution pattern and ΔT values recorded at the different surface during the first 24 h of diamond deposition. After 4 h, ΔT rises up to 160°C and the methane flow rate is decreased from 40 sccm to 35 sccm; after 5.5 h, ΔT decreases to 114°C , reaching a minimum value of 100°C after 7 h of diamond deposition. After 8.5 h, the stage height is increased from -0.1 cm to $+0.1\text{ cm}$ and the effect is immediate, and ΔT decreases down to 90°C , stabilizing at 71°C after 24 h of deposition. With this new set of parameters (35-sccm methane flow rate and $+0.1\text{-cm}$ stage height), the coating is grown unattended over four days. At the end of the fourth day, the temperature distribution has become very non-uniform, with ΔT as high as 212°C . Throughout the initial 24 h of deposition, the temperature at the center of the wafer is always the highest, in and around 1050°C , but after 95 h, the center temperature rises to 1127°C and

Fig. 2 (a) Substrate temperature distribution during the first 24 h of deposition. (b) XRD patterns on the growth side (zoom-in: presence of trace amounts of trigonal phase).

① <http://www.PANalytical.com> (last accessed on November 14, 2013).

the points marked as H, G and E—the opposite ends of the wafer cut marks (I and F)—become hotter than the center of the wafer; the temperature of region E is as high as 1180 °C, higher than the initial value of 1022 °C. After 95 h of deposition, points H and G have become red hot and the deposition is stopped to prevent the cracking of the wafer. This temperature gradient over 95 h of deposition is clearly reflected in the characteristics of the PCD coating.

3.2 Growth rate

The samples were mounted vertically on the holder and the cross sections were observed under SEM. The thicknesses are listed in Table 1. The differences on the thickness, and consequently on the local growth rate, reflect the temperature gradient across the 100-mm wafer during diamond growth. Samples I and F are the thinnest (190 µm thick and 192 µm thick, respectively). All other thicknesses are above 200 µm; samples B, C and D are about 210 µm thick, samples A and E have comparable thicknesses of 219 µm and 220 µm, and samples G and H are widely different with thicknesses of 233 µm and 245 µm respectively. The growth rate across the 100-mm wafer ranges from 2 µm/h for sample I up to 2.57 µm/h for sample H.

Different parameters, like pressure, substrate temperature, methane percentage, hydrogen flow rate, etc., are known to affect the growth rate [41]. Axial and radial distributions of gas species and temperatures inside an MPCVD reactor were elaborately discussed by Ma in his thesis [42]; he showed that there is a wide variation in the species concentration and gas temperature away from the discharge core and the substrate. However, even though the hemispherical

plasma symmetrically covers the whole 100-mm-diameter substrate surface, the temperature distribution is not radial. In fact, experimental data shows evidence of a strong temperature gradient across the substrate, probably due to the asymmetry that the wafer cuts introduce in the circular shape of the substrate (Table 1).

The temperature distribution also changes as diamond growth proceeds. At the beginning of deposition, the temperature of the substrate center is 1010 °C, increasing to 1063 °C after the methane gas flow rate is reduced to 35 sccm and the stage position adjusts from −0.1 cm to +0.1 cm (Fig. 2(a)). After 24 h of deposition, the temperature at point C decreases further to 1037 °C and ΔT reaches its minimum recorded value (71 °C). The temperatures at points G and H are 1024 °C and 1034 °C, respectively, still lower than that at point C. However, after 95 h of deposition, this area has become red hot.

This temperature evolution suggests the stability of the plasma at the core of the discharge. However, as the coatings become thicker and thicker with time, the heat distribution becomes more and more non-uniform. The values of thickness and growth rate at the center of the wafer (214 µm and 2.25 µm/h, respectively) are found to be essentially the average values of the two extreme thicknesses and growth rates at points H and I. These points correspond to two opposite positions of the substrate: point I is near the substrate cut mark and is at lower temperature values throughout the four-day long run (mostly below 1000 °C) in comparison to point H (always above 1000 °C). It can be concluded that, in spite of the quartz plate that improves the temperature homogeneity of the substrate, the

Table 1 Substrate temperature, mechanical properties and SEM analysis results (G: growth side; N: nucleation side)

Sample	Substrate temperature after 24 h (°C)	Mechanical property				SEM			
		Hardness N (GPa)	Roughness		Top surface microstructure	Grain size		Thickness (µm)	Growth rate (µm/h)
			G (µm)	N (nm)		G (µm)	N (nm)		
A	1000	19.50 ± 2.79	5.86	23.4	(111)+octahedral	6.23 ± 0.71	63	219	2.30
B	999	17.07 ± 1.14	6.87	16.3	(110)+cubo-octahedral	9.76 ± 1.69	49	210	2.21
C	1037	18.22 ± 1.27	5.84	17.1	(110)+(100)+cubo-octahedral	10.52 ± 1.68	282	214	2.25
D	972	35.00 ± 3.83	7.39	12.9	(111)+octahedral	21.43 ± 1.86	—	211	2.22
E	1022	30.03 ± 6.05	6.45	11.7	(100)+(110)+cubo-octahedral	18.58 ± 0.86	1450	220	2.31
F	966	24.21 ± 3.70	3.59	11.4	(111)+octahedral	10.02 ± 0.44	280	192	2.02
G	1024	29.90 ± 7.85	7.52	9.54	(100)+(110)+cubo-octahedral	21.29 ± 1.76	68	233	2.45
H	1034	48.07 ± 3.16	5.56	18.8	(110)+(100)+cubo-octahedral	10.82 ± 2.15	—	245	2.57
I	995	18.72 ± 3.42	6.15	27.1	(111) + octahedral	10.19 ± 1.17	—	190	2.00

existence of a discontinuity in the shape of the wafer (the wafer cut close to point I) induces the loss of the plasma radial symmetry, thereby causing a temperature gradient through the substrate that is reflected, for instance, in the difference of the growth rates that are measured across the diamond coating. The temperature gradient can be reduced to some extent by adjusting the process parameters (such as methane flow rate and stage height), but cannot be completely avoided, and deteriorates the uniformity of the diamond film deposited on the wafer. As growth proceeds and the diamond film thickens, the temperature gradient increases, suggesting that the plasma radial symmetry is further reduced as growth proceeds.

3.3 Surface roughness

The roughness of the nucleation side of the diamond coating (Table 1) is comparable to the roughness of the mirror-polished silicon surface and varies from 9.5 nm to 27 nm. The roughness of the growth surface is much higher, ranging from 3.5 μm to 7.5 μm , depending on the point of measurement. Figure 3 shows typical 0.8 mm $\times$ 0.6 mm CSI scans of the growth and nucleation sides and bare silicon substrate.

3.4 Surface morphology

3.4.1 Growth side

Figure 4 shows SEM micrographs of the growth

Fig. 3 0.8 mm $\times$ 0.6 mm CSI scans of the (a) grown and (b) nucleation sides of the PCD coating and (c) bare silicon substrate.

Fig. 4 SEM images of growth surface points as described in Fig. 1(b).

surface of the different regions of the wafer (labeling corresponds to positions depicted in Fig. 1(b)). The microstructure can be classified in terms of crystal size, shape and noticeable crystal facets on the top surface of the diamond coating. The grain sizes, calculated following ASTM line intercept method (ASTM Standard E 112-88), vary from 6 μm to 21 μm (Table 1). Based on the grain size, the nine surface regions can be divided into three groups, namely 10- μm -sized region, about-20- μm -sized region and region A with the smallest 6- μm grain size.

One can notice an expected tendency: larger grains correspond to higher roughness values due to the presence of bigger diamond octahedral pyramids in the microstructure. For instance, the average grain size is approximately three times larger than the roughness of regions G, E and D. However, this tendency is not a rule, since the R_a roughness and grain size of region A, for instance, are of the same magnitude.

The octahedral pyramids found in region A suggest the parameter α near or equal to 3. Similar near-perfect octahedral diamond pyramids can be seen in the regions D and F and also to some extent in region I. In regions B, C, E, G and H, cubo-octahedral pyramids with distinguishable flat top surfaces are clearly visible. These top surfaces are rectangular, which imply the appearance of (110) planes. The presence of (100)

planes would translate in perfect square top surfaces. XRD peaks (Fig. 2(b)) reveal the presence of (220) planes at 74.3° , but there is no diffraction peak corresponding to (100) plane. The reason can be explained on the basis of XRD “extinction rules”. It is known that for successful diffraction to occur in the diamond cubic crystal structure, the Miller indices h , k and l should meet the following criteria: (i) all odd, (ii) all even or (iii) $(h+k+l)$ divisible by 4 [43]. Following such argument, it can be concluded from the XRD data that (100), (200) and (300) peaks will be missing, although one could have detected the (400) plane peak at 2θ value of 119° ; however, in the present study, the scan was performed from 20° to 90° due to physical limitations of the goniometers. The XRD peaks from most regions indicate the presence of 100% intensity peaks corresponding to (111) planes in comparison to 17% relative intensity peaks for (220) set of planes; these planes can be correlated to the appearance of cubo-octahedral surface morphological features revealed under SEM.

3.4.2 Nucleation side

While the growth side is populated with cubo-octahedral pyramids, the nucleation side consists of agglomerated colonies/grains (Fig. 5). These individual colonies are separated by distinguishable

Fig. 5 FESEM images of nucleation surface points as described in Fig. 1(b).

grain boundaries (Figs. 5(C)–5(F) and 5(I)). The size of the colonies varies from 0.28 μm (points C and F) to 1.45 μm (point E), depending on the location of the substrate.

Higher-magnification images of these colonies reveal nanocrystalline agglomerations of diamond crystals (more clearly in Figs. 5(A), 5(B) and 5(G)). Typical sizes of these diamond nanocrystals vary from 49 nm (point B) to 68 nm (point G). It is interesting to notice that the initial temperature at these regions is in-between 940 $^{\circ}\text{C}$ (Fig. 5(B)) and 955 $^{\circ}\text{C}$ (Fig. 5(G)). These agglomerations are visible neither in spot C (higher initial temperature) nor in spots D, E or F (lower initial temperatures).

Energy dispersive X-ray analysis (EDAX) signals of the boundaries and the colonial features are shown in Figs. 6(a) and 6(b), respectively. The scans taken on the colonial features (Fig. 6(b)) produce only carbon peaks, whereas signals from the boundaries (Fig. 6(a)) show silicon and to some extent oxygen peaks, in addition to the normal carbon peaks. Silicon is present as SiC and SiO₂ compounds.

3.4.3 Diamond nanostructure

The cross sections of the different surface points (not shown) reveal the traditional columnar growth of diamond crystals along the z -direction from the substrate side. However, sample collected from point B has a whitish 40–50- μm -thick layer at the middle of

the cross section (Fig. 7(a)). This white layer runs parallel to the substrate and through the entire length of the sample, while the characteristic columnar diamond growth is apparent in the growth direction (z). From the growth rate at this point (2.21 $\mu\text{m}/\text{h}$), it can be estimated that this layer is deposited during 20 h, after the initial 55 h of deposition.

The double-arrows (Fig. 7(a)) indicate that the microscopic columnar growth is kept at the nanostructured whitish layer of sample B. However, when this layer is magnified, nanostructures become evident: the region is filled with elongated nano-features which are either oriented randomly (Fig. 7(b) nanoworms) or in particular directions (Fig. 7(c) nanoplates). The high aspect ratio plates are 30–80 nm thick and 0.5–2 μm long. They run parallel along two directions separated by an angle slightly greater than 70 $^{\circ}$ (Fig. 7(c)). Literature suggests that the angle between (311) and (100) planes is equal to 72.4 $^{\circ}$, so we raise the hypothesis that these plates correspond to (311) and (100) diamond planes formed during CVD growth, forming square and rectangular grids as shown in Fig. 7(c). Such diamond nanogrids can have futuristic application of “nano-shelf” for storing different materials.

MPCVD of diamond nanoplate arrays on (111) planes was reported in a recent paper in the view of field-emission applications [44]. The authors attributed the high aspect ratio growth to the extension of

Fig. 6 EDAX signals from (a) the boundaries and (b) the colonial features of the freestanding coating.

Fig. 7 (a) Cross section of the white layer of sample B showing typical microcrystalline-columnar growth; (b) higher-magnification SEM image showing nanoworms; (c) higher-magnification SEM image revealing a mesh of nanoplates forming square and rectangular grids, with plates running parallel along two directions separated by angle greater than 70° .

penetration $\{111\}$ twins from underlying diamond grains. But such structures are selectively grown in 20-nm-thick layers. There have been several reports about reactive ion etching (RIE) fabrication techniques of diamond nanorods/nanowires/whiskers of 50–400 nm thick and several microns long [45–49]. Moreover, it has been shown that CVD diamond can be grown into solid or hollow fiber-, wire- or tube-like structures by using suitable templates^②. One, two and three dimensional nanodiamond structures have been discussed in detail by Shenderova and McGuire [50], who reported the occurrence of diamond crystallites embedded in amorphous carbon clusters, nanocrystalline diamond (NCD)–carbon nanotube (CNT) composites grown by CVD, diamond filament structures obtained by laser ablation of pellets of pressed ultra-nanocrystalline diamond (UNCD) particle, etc. But none of the reported nanostructures resemble the presently obtained diamond nanoplates along the cross section of the freestanding PCD. The closest structure was deposited by MPCVD on a Ni-coated HFCVD-grown PCD substrate [51]. The nanoplates grown by Chen and Chang are single crystalline and 30–70 nm thick. The plates are triangular or parallelogram-like with top and bottom

surfaces parallel to (111) planes, whereas the edges are along the $\langle 110 \rangle$ directions. There is no more report on such nanoplates maybe because of their limited application/repeatability. The thicknesses of the nanoplates obtained in the present study are of similar dimension, but they are not (111) planes as shown by Ref. [51]. Very recently, the CVD diamond group at Bristol University published some SEM micrographs of diamond oddities and unusual structures (rod, plate, star or spaghetti like carbon/diamond structures) without confirming their repeatability and standard method of deposition^③.

Similar whitish layers with different nanocrystalline features are also present in samples A, C and G (Fig. 8). Other than well-aligned nanoplates, the whitish region of sample A consists of a unique nanoporous structure (Fig. 8(a))—here termed as nanosieves—typical sintered ceramic structures. The pore size varies from 30 nm to 130 nm. There are reports of PCD sintered at 5–10 GPa and 1300–1800 °C during 5–60 min [52,53]. The appearance of this nanosieve structure suggests that under MPCVD growth environment, there may exist a pressure–temperature regime where diamond particles are melted/sintered, forming a granular network with open pores. In fact, the pressure rise due

② <http://www.chm.bris.ac.uk/pt/diamond/semwires.htm> (last accessed on November 14, 2013).

③ <http://www.chm.bris.ac.uk/pt/diamond/semoddities.htm> (last accessed on November 14, 2013).

Fig. 8 SEM images of nanostructural features found in samples A, B, C and G.

to nanosize may push the meta-stable CVD growth environment into the stable diamond phase region in nanocarbon-phase diagram [54,55]. In addition, gas temperature may reach 1400–3300 °C under typical MPCVD pressure of 105 Torr (≈ 14 kPa) [41]. It is possible that, under the present growth conditions, the nanosize-induced pressure rises up to several GPa; this effect, together with the high plasma temperature, may have induced sintering of the diamond grains/crystals from secondary nucleation sites, forming the nanosieve network.

A similar sintered/melted porous microstructure is found in the cross section of sample H (not shown); however, the grains here are elongated and bent with less porosity.

Wavy nanocrystalline features (nanoworms) are found at some locations of the cross section of sample G (Fig. 8(G3)). On some regions of sample C, the diamond crystals form curved nanopetals (Fig. 8(C1)). These nanopetals are folded or bent in nature but are not fused together, like in the case of sample G (Fig. 8(G3)) and H (not shown); instead, this nanostructure resembles bent onion structures. The cross section of sample C also has regions with grids of nanoplates or randomly dispersed nanoworms.

Figures 8(C2), 8(C1) and 8(G4) show the transition region between the whitish layer and the as-grown diamond surface. The top surface of sample C (Fig. 8(C2)) consists of typical diamond cubo-octahedral pyramids with (111) planar side surfaces and flat top surfaces (either (100) or (110), as found in Fig. 4(C)). The base size of the pyramids is around 30 μm ; 8 μm down from the pyramid base, the texture changes from smooth to rough. A similar transition from microcrystalline grains into nanostructures is also observed below the growth surface of sample G (Fig. 8(G1)). The surface is densely populated with diamond cubo-octahedral pyramids (Fig. 4(G)), with different top and bottom surface textures. A whitish layer, 10–20 μm below the top surface, is also present; upon higher magnification (Fig. 8(G4)), the interface between this whitish layer and the remaining film reveals a gradual skin transformation: diamond crystals, with initial smooth texture, seem to be broken down into smaller fragments. These bug-like fragments are less than 1 μm long, and as the distance from the top surface increases, they disappear with emergence of elongated worms/plates, initially running randomly with respect to each other but gradually forming a mesh/grid-like nanostructure (Fig. 7(c)) throughout the

outer skin of the typical diamond columns. The other end of this whitish layer (Fig. 8(G2)) also contains similar elongated plates or worms. A higher magnification of the encircled portion of Fig. 8(G2) (Fig. 8(G3)) reveals somewhat molten nanoworm structures randomly oriented.

3.5 Quality

Figure 9 shows the Raman spectra collected from both sides of the nine different surface regions. Since the spot size of the 514.5-nm laser was 50 μm , it can be assumed that the Raman spectra are generated from several grains. Both signals corresponding to diamond (I_d) and graphite-like-carbon (I_{glc}) are present in all spectra.

The FWHM (full width at half maximum) of the diamond peaks (Table 2) vary between 5 cm^{-1} (point G) and 12.39 cm^{-1} (point A) on the growth surface, and between 9.33 cm^{-1} (points A, B, C and E) and 11.79 cm^{-1} (point G) on the nucleation surface. Generally speaking, the broadening of the peaks is higher on the nucleation surface, since it contains more grain boundaries and defect sites. The dispersion is higher on the growth surface, reflecting once again the non-homogeneity of the growth side. Raman peak broadening can be due to two reasons: (i) homogeneous lifetime broadening and (ii) size effect of crystal. Scattering of phonons at grain boundaries and defect sites shortens their lifetime, increasing the FWHM. The Raman peaks are symmetrical, so peak broadening due to phonon confinement in small domain size might not have occurred in the present study.

The quality factor, a semi-quantitative estimation of the diamond phase ratio

Fig. 9 Raman spectra taken on the (a) growth and (b) nucleation sides of the different samples.

$$Q = \frac{I_d}{I_d + I_{glc}} \times 100\% \quad (2)$$

was calculated for the growth and nucleation surfaces, considering the 1332 cm^{-1} diamond peak and 1500–1600 cm^{-1} graphite-like carbon band (Table 2). For the nucleation side, Q varies between 50% and 51%. The Q values for the growth surface vary between 50% (point H) and 79% (point G). This high dispersion is a consequence of the poor homogeneity of the thick

Table 2 Raman and XRD results

Sample	Raman spectroscopy								Rietveld refinements of XRD patterns					
	1332 cm^{-1} peak shift (cm^{-1})		FWHM (cm^{-1})		Q (%)		Stress (GPa)		Crystalline phases (%)		Cell parameter ($\text{\AA}$)	Unit cell volume ($\text{\AA}^3$)	Average crystallite size (nm)	Average lattice strain (%)
	G	N	G	N	G	N	G	N	Cubic	Trigonal				
A	-1.37	0.58	12.39	9.33	57	50	0.7	-0.33	90.9	9.1	$a=b=c=3.56742$	45.400	40.38	0.046
B	0.58	-0.39	9.40	9.33	53	51	-0.3	0.22	90.1	9.9	$a=b=c=3.56749$	45.403	41.64	0.041
C	-2.36	0.09	8.36	9.33	56	51	1.33	-0.05	99.6	0.4	$a=b=c=3.57043$	45.515	39.23	0.039
D	-0.88	-0.88	7.68	10.81	52	51	0.5	0.50	98.3	1.7	$a=b=c=3.56628$	45.357	41.74	0.043
E	-0.88	0.09	7.91	9.33	54	50	0.5	-0.05	99.3	0.7	$a=b=c=3.56725$	45.394	41.25	0.039
F	-0.88	1.08	8.17	9.82	52	51	0.5	-0.60	96.1	3.9	$a=b=c=3.56547$	45.326	41.87	0.040
G	5.99	0.09	5.07	11.79	79	50	-3.3	-0.05	98.0	2.0	$a=b=c=3.56910$	45.465	41.55	0.040
H	1.57	-1.37	11.84	10.32	50	50	-0.9	0.78	82.2	17.8	$a=b=c=3.57003$	45.500	39.20	0.038
I	-0.88	-1.37	7.38	9.82	53	51	0.5	0.78	99.0	1.0	$a=b=c=3.56377$	45.261	39.62	0.041

PCD coating due to the large temperature gradient during deposition. The Q values are in general very low, due in one hand to the high CH_4/H_2 ratio used (3.5%) and on the other hand to the high Raman scattering efficiency of non-diamond phase [56].

3.6 Stress

CVD diamond film can have extrinsic and intrinsic stresses. The extrinsic stress arises from thermal expansion mismatch and lattice parameter mismatch between the substrate and the diamond coating. In this study, the silicon substrate was etched, so the extrinsic stress component was removed.

The intrinsic internal stress arises from defects present within the PCD coating and leads to a diamond peak shift. The intrinsic stress (hydrostatic stress symmetrically distorts the diamond lattice and hence also its optical modes phonon) can be compressive leading to up-lift of the peak shift, or tensile leading to down-shift of the diamond peak in the Raman spectrum. Further, due to the presence of biaxial stress, the diamond peak can split into two or three maxima, depending on the degeneracy of the phonon [57,58]. Factors like temperature, grain domain size, hydrostatic stress, have a strong influence on the peak shifting [59–61].

The residual stress (γ) is calculated in GPa using

$$\gamma = -0.567 \times \Delta\nu \quad (3)$$

where $\Delta\nu$ is the peak shift in cm^{-1} [62] (Table 2). The minus and plus signs are assigned to compressive and tensile stresses, respectively.

On the growth surface, stress varies from highly compressive (3.3 GPa at point G) to highly tensile (1.33 GPa at point C). The residual stress on the nucleation side is considerably lower and varies from tensile (0.78 GPa at points H and I) to compressive (0.6 GPa at point F). The Raman spectra taken on the growth surface of samples B, C, E, H and G show a diamond peak splitting, indicating an inhomogeneous stress distribution.

The stress level variation is wider on the growth side. Tensile stress arises from voids, dislocations and grain boundaries in the diamond crystal lattice, whereas impurities or hydrogen clusters introduce compressive stress in the PCD. Growth defects (twins, dislocations, stacking faults, etc.) are present more on the growth surface, producing tensile stress. The possibility of contamination is lower for the growth surface, and this is reflected in less points under compression on this

surface; on the contrary, the nucleation side has many non-carbon phases such as silicon and oxygen (maybe in the form of amorphous silica, as evidenced from the EDAX signals, Fig. 6), which are responsible for the compressive stress on the nucleation side after the etching of the silicon substrate. In spite of the large stress variation on the growth surface, no observable trend could be established between these values and the temperature distribution pattern.

3.7 Hardness

The hardness of CVD diamond films is beyond 60 GPa [63], high enough to cause damage to the indenter tip used for Vickers microhardness testing. CSI surface scans (Fig. 3(a)) reveal a very high surface roughness ($Ra=6.87\text{ }\mu\text{m}$) due to the presence of very big diamond cubo-octahedral pyramids on the growth surface, which produce peak ($Rp=23.9\text{ }\mu\text{m}$) to valley ($Rv=-30.7\text{ }\mu\text{m}$) distance as high as $56\text{ }\mu\text{m}$. These high values prevent reliable microhardness measurements. On the contrary, the nucleation side (Fig. 3(b)) has a very low surface roughness ($Ra=16\text{ nm}$) with peak ($Rp=0.67\text{ }\mu\text{m}$) to valley ($Rv=-0.35\text{ }\mu\text{m}$) distance as low as $1\text{ }\mu\text{m}$; this result is supported by FESEM images (Fig. 5) of the smooth nucleation side that reveal the existence of diamond colonies with nanocrystalline agglomeration (expected to be softer than the growth surface).

Taking into account the experimental limitations, the hardness measurements with Vickers indenter were performed only on the nucleation side (Table 1). It can be observed that, although the hardness values are very high in comparison to any other known hard ceramic materials, they are much lower than the theoretical value of natural diamond (100 GPa), varying from 17 GPa (point B) to 48 GPa (point H). The reason behind this fact may be the existence of agglomerates of diamond nanocrystals (Fig. 5); these agglomerates are $0.3\text{--}1.5\text{ }\mu\text{m}$ in size, and are formed by $50\text{--}70\text{-nm}$ -sized particles and separated by an intergranular region which contains silicon and oxygen. The diameter of the indentation marks varies from $6\text{ }\mu\text{m}$ to $10\text{ }\mu\text{m}$; if the indenter probe penetrates these agglomerates, the local hardness value will be lowered. However, this local lowering cannot account for the large difference in the measurements (the lowest and highest measured values differ by a factor of almost 3). This large variation can be explained on the basis of the different percentages of crystalline phases present,

as measured by XRD peak broadening. Rietveld analysis of the XRD profiles (inset of Fig. 2(b)) of the samples reveals that all the samples contain variable percentages of cubic carbon phase having space group Fd-3ms (227) as a major phase and trigonal carbon phase having space group R-3mH (166) as a minor or trace phase (Table 2). The values of crystal size, average crystal strain, cell parameters and cell volume are also shown in Table 2. In particular, sample H has a considerable amount of trigonal phase (17.8%), which may be responsible for the high hardness value (48 GPa) measured at that region.

4 Conclusions

A thick PCD coating was deposited on a 100-mm-diameter silicon wafer during four days. The thick PCD coating was cut into smaller pieces, further investigated through SEM, Raman, and Vickers indentation. The temperature of the substrate during deposition was not uniform; in fact, the existence of a temperature gradient, that was reduced to some extent by adjusting the process parameters (such as methane flow rate and stage height), deteriorated the uniformity of the diamond film deposited.

The temperature gradient was kept stable after 24 h of deposition ($\Delta T = 71^\circ\text{C}$) but further increased with increasing deposition time, reaching the value $\Delta T = 212^\circ\text{C}$ at the end of deposition; the growth rate, and hence film thickness, followed this gradient; lower substrate temperatures corresponded to perfect octahedra, and higher substrate temperatures corresponded to cubo-octahedral morphology; other properties varied in a somewhat random way. Raman spectra of the growth surface also differed considerably; the FWHM varied between 7.32 cm^{-1} and 5.07 cm^{-1} . There was no correlation with temperature distribution, morphology or growth rate patterns. Raman spectra of nucleation surface had a little variance of $\pm 1\text{ cm}^{-1}$ with a high average value of 10 cm^{-1} . Most of the surface points were under tension, while the others were under compressive residual stress; most of the nucleation side points were under compression with little variance and without any apparent reason. No correlation could be established between the presence of trigonal phase and the corresponding hardness values among different surface points.

Colonies or micron-sized agglomerations of 50–

70 nm diamond nanocrystals were identified on the nucleation surface. Different nanostructures, random in nature, were also found on the cross section of five samples. They consisted of elongated nanoflake-like structures, sometimes randomly dispersed (nanoworms), sometimes running parallel in definite directions (nanoplates), sometimes bent and flat (nanopetals), and sometimes fused/sintered together to form nanoporous microstructure (nanosieves). It seemed apparent that regions deposited at lower growth rates didn't develop nanostructures, whereas higher growth rate regions had varied nanodiamond features across the thickness.

As a general conclusion, it could be said that there is no general trend in the physical properties of the PCD coating, although the deposition was carried out uninterruptedly in a controlled way, and special care was taken in order to minimize the temperature gradient during deposition; only growth rates and octahedral morphologies could be correlated with substrate surface temperatures; other physical parameters varied in a random way.

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