Synthesis and Characterization of Microcrystalline Diamond to Ultrananocrystalline Diamond Films via Hot Filament Chemical Vapor Deposition for Scaling to Large Area Applications

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Abstract.

This paper focuses on reporting systematic studies on the effect of the precursor gas chemistry ratio between hydrogen/methane (H_2/CH_4) and argon (Ar) to tailor control of the grain size, morphology and roughness of large area diamond films. Films ranging from a microcrystalline diamond structure (MCD 1-3 μm grain size) all the way to an ultrananocrystalline diamond (UNCD 3-7 nm grain size) structure were grown over 100 mm diameter areas, as a pathway for scaling diamond film growth processes by hot filament chemical vapor deposition (HFCVD) to large areas (≥ 150 mm in diameter). H_2 -rich/ CH_4 chemistry was used to synthesize the MCD films, while Ar-rich/ CH_4/H_2 chemistry was used to grow the UNCD films. The synthesis of the diamond films using the HFCVD process indicate that the Ar content is critical to achieve the characteristic UNCD film structure with roughness, chemical bonding and thickness uniformity in the range of 5% across large areas. The ratio of Ar/ H_2 in the range 70/30 sccm to 90/10 sccm, all with 2 sccm of CH_4 gas, yields films with grain size from 10-50 nm for nanocrystalline diamond (NCD) films to 3-7 nm for the UNCD films, respectively. The extremely smooth UNCD films (~ 3 -5 nm rms) are achieved using Ar (90 sccm)/ H_2 (10 sccm)/ CH_4 (2 sccm) gas flows.

Keywords: Microcrystalline, nanocrystalline, ultrananocrystalline, diamond, thin films, large area deposition

1. Introduction.

Diamond films have been attracting the interest of the research and technology-oriented communities because they exhibit a unique combination of properties such as high wear resistance, highest hardness

relative to any other film, lowest friction coefficient among known coatings, chemical inertness, excellent thermal conductivity for microcrystalline diamond ($\geq$ several micro-meter grain size), tunable electronic properties by doping, and biocompatible properties. Extensive fundamental and applied science on diamond film growth has resulted in a broad range of application to devices. [1-4]

Hot Filament Chemical Vapor Deposition (HFCVD) and Microwave Plasma Chemical Vapor Deposition (MPCVD) are the two main techniques being used to grow diamond films with various microstructures, from microcrystalline diamond (MCD, $\geq 1 \mu\text{m}$ grain size) to both nanocrystalline diamond (NCD, ~ 6 to hundreds of nm grain size) and ultrananocrystalline diamond (UNCD, 3-7 nm grain size). [1-3, 5, 6] UNCD films properties are similar to those of single crystal diamond. UNCD films exhibit outstanding mechanical properties such as Young's Modulus (998 GPa) and hardness (98 GPa) [1] close to single crystal diamond (1100 GPa and 100 GPa, respectively) and the lowest coefficient of friction ($\sim 0.02 - 0.04$) with respect to other materials [1], including MCD and NCD films. UNCD films also exhibit high electrical conductivity with either nitrogen incorporated in grain boundaries [1] or boron doping via substitution of B for C atoms in the diamond lattice. Furthermore, UNCD also exhibits outstanding biocompatibility. All the UNCD film properties mentioned above enable broad range of applications to a new generation of mechanical, [1, 4, 7-9] electronic [1] and biomedical devices. [1, 7]

One of the main challenges of diamond film technology is the challenge to grow films on large areas with uniform thickness and structure for technological applications and product development. MPCVD has been used to grow uniform MCD and NCD [1, 10, 11] and UNCD [1] films on small to medium size areas [1, 12]. Alternatively, HFCVD is capable to grow films on substrates with up to 300 mm in diameter.

The chemistry to grow MCD, NCD, and UNCD films has been previously demonstrated to depend on gas composition with a H_2 – rich (80-99%) $/\text{CH}_4$ chemistry for the case of growing MCD and NCD films, and Ar-rich (99%) $/\text{CH}_4$ (1%) chemistry for growing UNCD films. [1, 13] The growth of diamond films using the HFCVD technique has been reported for optimization in small substrates, [14] with most of them presenting grain size in the NCD range. In addition, no systematic analysis of the uniformity in

structure and film thickness across the area of the grown diamond films has been reported. Table 1 summarizes some of the works reported in the literature.

Table 1. Film growth parameters, diamond film structural and characterization techniques for films grown by HFCVD reported in literature.

Gas Mixt. (%)	Filament Material/ Geometry	Fil/Sub Temp (K)	Fil-Sub Distan (mm)	Seeds size (μm)	Gas Press (kPa)	Diam. Grains (μm)	Analysis Technique	Ref
H ₂ -98 CH ₄ -2	W(Array filament)	2424/1074 -1124	6	0.5 on Si	2.6-2.2	0.5-1	SEM/ Raman	[14]
H ₂ -99 CH ₄ -1	Ta(20 filament)	2594/1074 -1124	20	Carbide Rods	0.3-4.8	0.3-1	SEM/AFM/Raman	[15]
H ₂ -99 CH ₄ -1	W (Grid filament)	2274/724-824 Anneal. at 650	5	20-40	0.9	0.04-0.07	SEM/AFM/Raman/ XRD/IR	[16]
H ₂ -99 CH ₄ -1	W (4 filament)	2374/1124	8	40	0.1-4.8	0.2-0.3	SEM/AFM/XRD/ Raman/	[17]
H ₂ +CH ₄ -1-100% Ar-0-100%	Ta (coil filament)	2674/1124 -1174	5	No info	13.3	0.05	SEM/ Raman	[18]
CH ₄ -1% H ₂ -1-5% Ar-Rich	Ru (helix filament)	2374-2674/674-1074	5	1	2.6-4	0.01-0.05	SEM/ Raman	[19]
CH ₄ -1% H ₂ -9% Ar-90%	W (5 filament)	2474/824-1124	5	0.250	4	0.0045-0.0068	SEM/XRD/ Raman	[20]
CH ₄ -0.25,0.5, 1, 1.5 , 2% H ₂ -9.75, 9.5, 9, 8.5, 8% Ar-90%	W (5 filament)	2474/1024	5	0.250	4	No reported	SEM/XRD/ XPS/ Raman	[21]

The information presented in Table 1 indicates that there has not been an effort to systematically investigate the effect of the gas chemistry ratio between hydrogen/methane (H₂/CH₄) and argon (Ar), filaments distribution and gas flow to tailor the growth of diamond films using the HFCVD technique towards scaling growth of MCD to UNCD large area applications. Most recent reports have focused on the doping of UNCD for small areas with specific applications, such as bio and field emission. [22-24] Tailoring of diamond films from MCD (~1 μm grain size) to UNCD (~3-7 nm grain size) has been achieved on small areas. [1, 13] The role of Ar gas to achieve UNCD films is explained in detail based on a systematic analysis using High-Resolution Transmission Electron Microscopy (HRTEM) and supported by X-Ray Diffraction (XRD) and Atomic Force Microscopy (AFM) to determine the grain

size, roughness and uniformity of the UNCD films across substrate with 100 mm in diameter. Scanning Electron Microscopy (SEM) and Raman analysis, using both a visible (523 nm) and a far UV (244 nm) analyzing laser wavelength, were used to characterize the films' surface morphologies and C atoms' chemical bonds, respectively.

2. Experimental

For the synthesis of diamond films, tungsten (W) layers (40 nm thick) were grown on the surface of SiO₂/Si substrates, using RF-magnetron sputtering, to provide a template layer, which has been proven to induce the growth of densest diamond films. [1, 22] The substrate surface temperature was calibrated using a K-type thermocouple in direct contact with the substrate surface's previous deposition. A calibration curve correlating the substrate and sample holder temperatures was plotted to enable the accurate measurement of the substrate surface temperature during film growth. Optimization of the number of filaments and the distance between filaments and substrate were necessary for a better heat distribution. The optimized parameters were found to be an array of 9 parallel W filaments ($\phi = 0.25$ mm, length ~ 14.2 cm) held on a Molybdenum (Mo) frame positioned above the substrate holder at a distance of 3 cm as shown in **Figure 1**. Computer simulation as well as experimental result for large area diamond coating deposition were recently reported by Shen et al. [25]. Filaments diameter, length and separation between parallel filaments used in this work were similar to those reported by Shen et al. [25]. However, one of the main differences in this work is the substrate rotation. In the HFCVD process described here, rotation of the substrate holder was used to provide a better temperature and carbon radical species distribution arriving to the substrate surface, allowing the diamond film to grow over large areas with optimum thickness uniformity. The substrate was positioned on a Mo disk that was rotated during film growth to induce film thickness uniformity on up to a 100 mm diameter. The filaments were heated to 2474K by passing an AC current during the film growth. Several gas ratios were investigated for diamond film growth, i.e., (a) 200 sccm H₂, (b) 50 sccm H₂ /50 sccm Ar, (c) 30 sccm H₂ /70 sccm Ar, (d) 20 sccm H₂ /80 sccm Ar, (e) 15 sccm H₂/85 sccm Ar, and (f) 10 sccm H₂/90 sccm Ar, with fixed CH₄ gas flow of 2 sccm at a total pressure of 1.3 kPa.

Before the deposition process, the substrates were pretreated with a solution for diamond nucleation enhancement (20% of diamond nanoparticles-stock solution in methanol), such that 3-5 nm diamond particles were immersed on the surface of the substrate by sonication. The pretreatment step was followed by sequential substrate cleaning with methanol, isopropanol and acetone. Afterwards, the substrates were placed inside the HFCVD chamber (Blue Wave Semiconductor HFCVD) with the deposition geometry and conditions described above (**Fig. 1**). The W filaments were then carburized. The carburization step consisted of increasing the filaments' temperature by passing current through them, reaching temperatures of 2474 to 2574K in an atmosphere of 100 sccm of H₂ and 20 sccm of CH₄ for about 2 hrs.

The surface roughness of the films was measured using atomic force microscopy with a scan size of 1 µm in tapping mode (AFM, Veeco, 3100 Dimension V atomic force microscope). The surface morphology of the films and film thickness were characterized by plain view and cross-section scanning SEM using a ZEISS SUPRA-40 SEM system, respectively. High-Resolution Transmission Electron Microscopy (HRTEM), using an aberration correction JEOL 2100F TEM and Rigaku Ultima III X-Ray Diffraction (XRD), was used to characterize the grain size of the films across the wafer. The samples for the HRTEM were prepared using a Focused Ion Beam (FIB, FEI Nova 200). Characterization of the atomic chemical bonds in the diamond films was done by Raman spectroscopy, using a Thermo nicolet micro and macro almega XR Raman spectrometer, with a laser beam wavelength of 532 nm, and a near resonance Raman scattering Horiba-Jobin T64000 micro-Raman system, with a laser beam wavelength of 244 nm.

3. Results and Discussion

Knowing that tungsten (W) forms a good interface for diamond film growth, [1, 26] the SiO₂/Si substrates were coated with 40 nm W layers. It is important to mention that a good interphase is necessary for diamond growth, even when is not a detailed topic in this manuscript. Interphase materials for diamond growth were previously studied and reported by one of the members in our group. [1, 26] **Figure 2** shows SEM images of diamond films deposited with different Ar and H₂ gas flow ratios, keeping the CH₄ constant at 2 sccm. MCD films (grain sizes of 1-3 µm) were grown using a mixture of

2 sccm CH₄ and 200 sccm H₂ flow (**Fig 2a**). An increment in Ar concentration was necessary to reduce the grain size. Large grain NCD (~300 nm grain size) films were produced, using a gas ratio of 2 sccm CH₄: 50 sccm H₂: 50 sccm Ar (**Fig. 2b**). NCD films with even smaller grain sizes of 9-25 nm, were obtained with 2 sccm CH₄: 70 sccm Ar: 30 sccm H₂ (**Fig. 2c**) and UNCD (3-7 nm) films were produced with 2 sccm CH₄: 90 sccm Ar: 10 sccm H₂ for which the electron scattering spectra showed as an inset correspondent to UNCD films (**Fig. 2d**). [1] AFM analysis was performed to measure the film surface roughness and uniformity across the substrate. These measurements showed approximately 60% surface roughness reduction by changing gas flow ratios from 70sccmAr/30sccmH₂ to 90sccmAr/10sccmH₂. HRTEM and XRD analysis were used as complementary techniques to determine the film grain size. **Figure 2e** shows the variation of film surface roughness and thickness as a function of diamond grain size, where the error bars represent the main distribution across the 100 mm diameter substrate.

Table 2 summarizes the deposition conditions, gas ratio, growth rate, grain size and film surface roughness for MCD, NCD, and UNCD films produced by the HFCVD technique implemented in this work.

Table 2. Deposition parameters, average roughness, grain size, and growth rate of diamond films deposited by HFCVD as a function of various CH₄, H₂, Ar gas flow ratios.

Purpose: CH ₄ ;H ₂ ;Ar (sccm) Total pressure; 1.3 kPa	Grain Size (nm)	Average Surface roughness (nm)	Growth Rate (nm/h)
<i>Carburization: 20;100;0</i>	-	-	-
<i>Micro-crystalline Diamond: 2;200;0</i>	~ 3,800	250	1,044
<i>Nano-crystalline Diamond: 2;50;50</i>	~ 335	12.6	600
<i>Nano-crystalline Diamond: 2;30;70</i>	9-25	5.7	249
<i>Nano-crystalline Diamond: 2;20;80</i>	10-25	3.42	155
<i>Nano-crystalline Diamond: 2;15;85</i>	6-10	2.5	140
<i>Ultrananocrystalline Diamond: 2;10;90</i>	3-9	2.0	80

Raman analysis, using a 532 nm wavelength laser beam, was done to compare the C atoms chemical bonding between the MCD, NCD, and UNCD films grown by HFCVD, as shown in **Figure 3**.

1 The most notorious difference in the Raman spectra between the MCD, NCD, and UNCD films is the
2 1332 cm^{-1} peak, which is not observed for the UNCD film, due to the D band signal at 1350 cm^{-1} . The D
3 band superimposes the 1332 cm^{-1} peak due to the smaller grain size of the UNCD film with a relatively
4 larger band gap. Also, the peak at 1550 cm^{-1} , produced by the sp^2 C atom's bond, is stronger in UNCD
5 than in MCD and NCD due to the substantial increase in grain boundaries, concurrently with the
6 substantial reduction in grain size. UNCD films, as analyzed by visible Raman (532 nm wavelength), are
7 characterized by the appearance of the sp^2 peaks at 1550 cm^{-1} (G band) and at 1350 cm^{-1} (D band).
8 Others peaks can also be observed such as 1150 cm^{-1} which are related to trans-polyacetylene. To study
9 in greater detail, the effect Ar / H_2 ratio near the UNCD growth regime, the gas flow ratios were changed
10 as follows: (a) 30 sccm H_2 /70 sccm Ar, (b) 20 sccm H_2 /80 sccm Ar, (c) 15 sccm H_2 /85 sccm Ar, and (d)
11 10 sccm H_2 /90 sccm Ar with fixed flow rate of 2 sccm of CH_4 . Roughness was a parameter also
12 characterized across the 100 mm films; **Figure 4** shows SEM pictures of the surface morphology and
13 thickness of the film with different gas ratios after 1 hour of growth. **Figure 4e** shows a plot with the
14 main distribution of thickness and roughness of the films' surface across the entire 100 mm diameter
15 substrate, with an average variation of $\pm 5\%$.

16 HRTEM analysis was performed to precisely measure the grain size of each film. XRD analysis was
17 performed to measure the uniformity of the grain size across the 100 mm diameter films grown under
18 reduced H_2 concentrations, as shown in **Figure 5**. HRTEM analysis of films grown with 70 sccm Ar/30
19 sccm H_2 and 80 sccm Ar/20 sccm H_2 flow ratios revealed average grain sizes of 17 nm and 18 nm,
20 respectively, classifying both of them in the NCD range. On the other hand, films grown with 85 sccm
21 Ar/15 sccm H_2 had an average grain size of 8 nm, positioning this ratio in the UNCD size limit. Films
22 grown with 90 sccm Ar/10 sccm H_2 flow ratio presented the minimum grain size obtained (3-6 nm),
23 corresponding to the grain size characteristic of UNCD films (**Fig. 5d**). Fast Fourier transform
24 diffractograms (FFTs) (insets in **Figure 5a-d**) and Selected Area Electron Diffraction (SAED) were
25 performed on the samples. An inter-planar distance d of 0.19 nm corresponding to a crystalline plane of
26 (2,2,0) was observed. For better appreciation of grains and grain boundaries in the samples, a Fourier
27 transformed image is also presented as an inset in **Figure 5(a)**. The grain size uniformity across 100 mm
28 in diameter films grown on Si substrates were measured by XRD. Diamond films grown with Ar/ H_2 gas

flow ratios (in sccm) 70/30, 80/20, 85/15 and 90/10, all with CH₄ gas flow of 2 sccm, show an average grain size of, 11, 11.8, 8.3 and 5.6 nm, respectively. [1, 27, 28] The XRD grain size was calculated using Scherrer's Equation, where the full width at half maximum (FWHM) was 1.57604, the Bragg angle (2θ) equal to 43.65, the shape factor (K) 0.94 and the X-Ray wavelength (λ) of 1.5406 Å (**Fig. 5e**). The remnant peaks not labeled in the spectra are due to the substrate.

Further lowering of the H₂ gas flow below 10 sccm was attempted, even eliminating flow of H₂ gas, which resulted in no film growth. Measurements of the diamond film surface revealed a substantial reduction in roughness correlating with the substantial reduction of H₂ gas flow (**Fig. 4e**). This behavior was uniform across the entire 100 mm diameter length for all films. Deposition rate was also reduced by the increase of Ar in the mixture.

Because of the limitations of the visible Raman analysis in identifying the diamond peaks in NCD and UNCD films, UV-Raman (244 nm wavelength laser beam) was performed, as well as on single crystal diamond for comparison, as presented in **Figure 6**. In NCD and UNCD films, the phonon confinement could activate zone boundary phonons that appear in the Raman spectra. In this case, $q \neq 0$ and phonons can contribute to the Raman spectra. [17, 28-31] Raman spectra in the UV range were used to study this phenomenon. It is clear that the UV Raman spectra for NCD and UNCD films (**Fig. 6**) are significantly different than that of visible Raman for similar films shown in **Figure 3**. Two distinct features can be identified: (1) the sharp peak at 1332 cm⁻¹, which is the fingerprint of diamond, can be seen for the NCD films produced with 70 sccm Ar/30 sccm H₂ and 80 sccm Ar/20 sccm H₂. The 1332 cm⁻¹ peak is much smaller as H concentration is reduced further to 85 sccm Ar/15 sccm H₂ and 90 sccm Ar/10 sccm H₂ for UNCD films; (2) the peaks at 1150 and 1480 cm⁻¹ which were very sharp and distinct in **Figure 3** (532 nm laser) now can hardly be observed. The reduction of diamond peak intensity as H₂ concentration decreases suggests a reduction of nanoparticle size with a relatively larger band gap due to quantum confinement, which is in agreement with the grain size measured by HRTEM. [29] Furthermore, the disappearance of the additional peaks at 1150 and 1458 cm⁻¹ indicates that these peaks are not the consequence of phonon confinement. [31] Even when it has been reported that these peaks are associated with trans-polyacetylene, those peaks are often found in NCD films. Raman analyses were

done on the diamond films across the entire 100 mm diameter substrates, with no changes observed, thus verifying the uniformity of the UNCD film.

The research reported in this paper focused on studying two of the three main ways to reduce grain size that have been observed and reported in the last decade. A summary of these studies previously reported is presented below.

(1) The increment of the methane (CH_4) concentration, which results in the reduction of grain size, but with an associated increase in graphitic phase (not studied in this paper).

(2) The increment of Ar concentration and reduction of H_2 concentration contributes to the enhanced production of C_2 dimers, [6] that may help to the formation of secondary nuclei. [32] As shown previously for MPCVD growth of UNCD films [1, 32-34] and later for HFCVD growth of NCD and UNCD films [35], Ar collisions with CH_x species in the gas phase helps to the production of C_2 dimers. The C_2 dimers, observed via optical emission spectroscopy, [1] contribute to the continuous formation of secondary nuclei, and jointly with CH_x radicals to the growth of UNCD film with grain dimensions in the 3-5 nm ranges. [1, 32-34]

(3) In addition, the effect of Ar species and electrons bombardment emitted from the hot filament to the substrate may contribute to a uniform distribution of the C-based species responsible for the diamond film growth with grain sizes in the ultranano-range, and the related smooth surface characteristic of UNCD films. [18, 33-38] The increased bombardment on the substrate may provide added energy for C atoms displacement via collision cascades on the surface, enhancing the continuous nucleation of nano-grains as shown by modeling. [37, 39]

The increase of secondary nuclei by the increment of Ar and reduction of H_2 concentrations, as well as Ar bombardment, leads to the formation of more but smaller grains, helping the formation of the UNCD film.

4. Conclusions.

Systematic studies on the effect of the gas chemistry e.g., ratio between hydrogen/methane and argon gases flow during growth of diamond films by the HFCVD technique have shown that the grain size can be tailored by the gas chemistry, controlling the grain size of diamond films from MCD ($\geq 1\mu\text{m}$ grain size) all the way to UNCD ($\sim 3\text{-}5\text{ nm}$ grain size) in areas of at least 100 mm in diameter. The systematic studies reported in this paper used a combination of complementary electron microscopy (SEM and HRTEM), XRD, AFM, and Raman analysis, which revealed that the combined gas composition and proper substrate material interface during film growth are critical to determine surface morphology and roughness, chemical bonding of C atoms, grain size, and growth rate on areas of up to 100 mm in diameter. The increment of Ar flow along with the reduction of H_2 flow, reaching the 2 sccm CH_4 : 90 sccm Ar/10 sccm H_2 chemistry enables the growth of UNCD films with grain size in the range $\sim 5.6\text{ nm}$ and a surface roughness of about 3 nm. UNCD films were grown with excellent uniformity in thickness, nanostructure and surface roughness ($\pm 5\%$ average variation) across substrates with 100 mm in diameter. The optimization of the HFCVD process for UNCD films deposition with good uniformity on large areas represents promising implications to accelerate the practical applications of the UNCD films for the development of new technological and/or bio-medical devices and systems.

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1

2 **Figure Captions**

3 **Figure 1.** Schematics of the HFCVD deposition chamber-cross section (left panel), and top view of
4 filament array (right panel).

5 **Figure 2.** SEM images of diamond films deposited with different gas flow ratios: (a) MCD film grown
6 with 2 sccm CH₄ / 200 sccm H₂, (b) NCD film grown with 2 sccm CH₄ / 50 sccm H₂ / 50 sccm Ar, (c)
7 NCD film grown with 2 sccm CH₄ / 70 sccm Ar / 30 sccm H₂, and (d) UNCD film grown with 2 sccm
8 CH₄: 90 sccm Ar/10 sccm H₂. (e) Plot of the average grain size and roughness of the different diamond
9 films studied as a function of distance along the 100 mm diameter substrate.

10 **Figure 3.** Raman spectra from analysis of MCD (a), NCD (b and c) and UNCD (d) films, using a visible
11 532 nm wavelength laser beam.

12 **Figure 4.** SEM pictures of diamond films grown on W coated SiO₂/Si substrate using different gas flow
13 ratios: (a) 70 sccm Ar/30 sccm H₂, (b) 80 sccm Ar/20 sccm H₂, (c) 85 sccm Ar/15 sccm H₂, and d) 90
14 sccm Ar/10 sccm H₂, while keeping the CH₄ gas flow constant at 2 sccm. Top right small inset SEM
15 pictures show the cross-sections of the films, (e) Shows the mean distribution of the thickness and
16 roughness of NCD and UNCD films across 100 mm diameter substrates.

17 **Figure 5.** Cross-section HRTEM pictures of diamond films deposited on W coated SiO₂/Si substrate
18 under different gas flow ratios: (a) 70 sccm Ar/30 sccm H₂ (Fourier transformed image from
19 diffractogram is presented as upper right inset), (b) 80 sccm Ar/20 sccm H₂, (c) 85 sccm Ar/15 sccm H₂,
20 and d) 90 sccm Ar/10 sccm H₂, while keeping the CH₄ gas flow constant at 2 sccm; Fast Fourier
21 Transform (FFT) patterns as insets, (e right panel) XRD spectra used to determine the UNCD film grain
22 size across the 100 mm diameter substrate.

23 **Figure 6.** (a) Room temperature Raman spectra of the diamond films grown with 70 sccm Ar/30 sccm
24 H₂, 80 sccm Ar/20 sccm H₂, 85 sccm Ar/15 sccm H₂, and 90 sccm Ar/10 sccm H₂, using a 244 nm
25 wavelength laser beam. Notice that the diamond peak at 1332 cm⁻¹ is still visible for the UNCD films,
26 even if extremely small.

27

28 **Table Captions**

29 **Table 1.** Film growth parameters, diamond film structural and characterization techniques for films
30 grown by HFCVD reported in the literature.

31 **Table 2.** Growth parameters, average film surface roughness, grain size, and growth rate of diamond
32 films deposited by HFCVD as a function of various CH₄, H₂, Ar gas flow ratios.

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