

Growth and Characterization of Polycrystalline CVD Diamond Films Obtained by MWPACVD at High Power 2,45GHz Microwave Discharge

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Among all the allotropic forms of carbon, diamond has attracted a broad scientific and technological interest for its extreme and unique properties rarely matched by other materials in nature. In a rapid rise from a technological point of view, much has been achieved in the study of obtaining this material through CVD technique. Studies of CVD diamond growth parameters of monocrystalline structure, underway in the team, are very expensive and time-consuming requiring in-depth studies of CVD diamond growth parameters of polycrystalline structure. So, this work presents an analysis focused on obtaining CVD diamond films with polycrystalline structure through the 2.45 GHz microwave plasma activation method (MWPACVD) in high power regime using a modified substrate holder to find a set of parameters appropriated for getting uniform quality and growth rate of thick films. The films were characterized using Raman scattering spectroscopy and scanning electron microscopy. The results point to optimized conditions for depositing films with growth rates of up to 20 $\mu\text{m}/\text{h}$ with low levels of intrinsic stress, good structural quality and uniform microcrystalline morphology along the deposition surface.

Keywords: *Polycrystalline, CVD diamond, Raman spectroscopy, MWPACVD, Plasma, Characterization.*

1. Introduction

Diamond as the most studied and perhaps the most widely known forms of carbon, is a material that has extreme properties such as its high hardness, low friction coefficient, transparency over a wide spectrum of wavelengths, high breakdown voltage, high bandgap, high mobility of charge carriers, high thermal conductivity, among others^{1,2}. These properties make diamond a promising candidate for use in innovative technologies such as anti-wear or anti-friction coating to increase the life of cutting tools or for its use in difficult-to-work materials^{3,4}, high-power electronic devices⁵⁻⁷, and more recently, its use as a charge accumulation device in nuclear batteries has been in evidence^{8,9}.

Many of these applications, however, are impractical using naturally available diamond, primarily for its scarcity, but also because its natural form is limited in terms of shape, size, and purity. Thus, around the 50s, a search for the production of this material in the laboratory began¹⁰, both for studies and for immediate applications. The first way to obtain diamonds in the laboratory was mimicking its natural formation through the use of high pressure and high temperature, a method known as HPHT¹¹. A short time later it was reported the obtaining of it under conditions in which diamond is a metastable phase of carbon, using still high temperatures but at pressures below atmospheric, through chemical vapor deposition (CVD)¹²⁻¹⁴.

Diamond deposition via CVD technique has some advantages such as the possibility of homogeneously covering

surfaces following their geometry, obtaining diamond films a few centimeters wide, which is particularly useful for emerging applications, and even increasing the size of diamond single crystals. To grow diamond through CVD, it is necessary the dissociation of a mixture of reacting gases in a controlled atmosphere environment, which is usually performed by the use of heated refractory metal filaments, known as HFCVD (hot filament chemical vapor deposition) method, or through microwave resonance in a cavity, known as MWPACVD (microwave plasma assisted chemical vapor deposition)^{12,13}.

In the course of its history, the CVD diamond has been continuously improved either by the better understanding of growth kinetics or the development of better machines as technology advanced through the years¹⁵⁻¹⁷. MWPACVD has been of particular interest in this context once it is the most used and suitable technique to grow industrial scale large single crystal diamonds^{18,19} and also high quality polycrystalline diamond coatings and wafers of different sizes and thicknesses²⁰⁻²². MWPACVD has been the better system of choice due to its capacity of creating very high densities of atomic hydrogen and the absence of contaminants such filament materials when compared to HFCVD, for example.

The method consists in applying microwaves into a resonating circuit generally composed of a cylindrical resonant cavity, rectangular waveguides, and a mode converter to couple the electromagnetic waves in the correct mode to achieve resonance inside the cavity. This resonant cavity is designed in a way it is possible to achieve a degree of high vacuum to control pressures in levels below atmospheric

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pressure, in which diamond is grown¹². The resonance of the electromagnetic waves creates a region of very high concentration of electric field, strong enough to excite atoms and electrons when gases are inserted into the chamber creating a plasma.

The gases involved in this process are methane and hydrogen, which have distinct but essential roles in the creation of polycrystalline and single crystal CVD diamond films. Methane provides carbon for the deposition layer by layer, this molecule is of particular interest for diamond growth by CVD because it is tetrahedrally coordinated easing the process for carbon atoms binding to the growth surface. Hydrogen is converted into atomic hydrogen that has a preferential etching for sp^2 bonded carbon enabling faster growth of better quality diamond material and also provides the abstraction of hydrogen from growth surface exposing dangling bonds for the maintenance of growth process¹³. Other process gases are also studied for different purposes, nitrogen for example is known to provide better growth rates for [100] oriented diamond films and single crystals²³, oxygen is often used as a strategy to enhance quality of the crystals²⁴⁻²⁶.

Driven by the growing interest on the application of the electronic properties of diamond, many research have already been made for the production of large area diamond freestanding wafers, Popovich et al.²⁰ were able to deposit a 100 mm-diameter and 660 μm thick polycrystalline diamond onto silicon substrates using a 915 MHz, 15 kW reactor, Mallik et al.²¹ also reported growth over 100 mm-diameter substrate area with thickness reaching 130 μm . Bolshakov et al.²² deposited polycrystalline diamond over polycrystalline diamond substrates with samples varying from 5x5 mm^2 and 6x6 mm^2 and reported growth rates of about 30 to 36 $\mu\text{m}/\text{h}$ employing a 2,45 GHz, 6 kW reactor. It is also an unrivaled choice as heat management device due to the very high thermal conductivity of diamond. Grown films can be placed directly over heat generating electronic devices or even diamond layers can be directly deposited over semiconducting components so the heat is promptly spread out of the hot spots²⁷.

Much of the process is determined by the substrate holder inside the chamber, the exposure of the sample to the plasma and the heat exchange between substrate, holder and cooling or heating components, are examples of parameters related to it.

In the search for the development of deposition of single crystal CVD diamond for long periods of time, researchers often adopted the strategy of implementing a pocket shape substrate holder, that consists in a recess in the surface of substrate holder, where the seed crystal is placed. This procedure prevents the formation of polycrystalline diamond on the edges of the single crystal but also to improve surface quality²⁸⁻³⁰.

In a recent study for the effects of substrate holder geometry on growth of polycrystalline diamond, three types of holder were employed in order to improve thickness homogeneity and stress reduction of polycrystalline diamond films of 100 μm thick over 2-inch silicon substrates, and a particular substrate holder design reduced the stress of the grown film in 1.1-1.4 GPa ³¹.

However, the effects of adopting a different shape of substrate holder could have in the formation of polycrystalline diamond films is not well known, a study of these aspects could help to enlighten how it could impact growth.

In this work, we employ a modified MWPACVD technique using an adapted substrate holder, to deposit polycrystalline CVD diamond films and evaluate growth parameters as growth rates, crystal morphology, structure film quality and the presence of non-diamond carbon phases in the bulk of the film correlating these results to the variations in deposition temperature and pressure. The objective is to study the effects of the deposition of polycrystalline diamond under higher pressures and higher temperatures than usual. In fact, these parameters are close to that is required for CVD single crystal growth and establish better parameterization for obtaining the best balance between growth rate and film quality, for deposition of polycrystalline diamond allowing to extrapolate growth conditions to obtain good quality single crystalline CVD diamond films.

The structural quality of a diamond can be studied in different ways, one of them is the Raman scattering spectroscopy which, by means of the excitation of the material with light at specific wavelengths, results in a spectrum related to light scattering by Raman effect of the atomic bonding of that material^{32,33}. The information provided from Raman spectra was to quantify film purity, as the ratio between diamond and non-diamond phases, and to calculate film stress using the displacement of diamond peak position³⁴⁻³⁶.

The results obtained by both the analysis of Raman spectra and scanning electron microscopy allowed the definition of optimized growth conditions for the growth of polycrystalline diamond films through MWPACVD in a regime of high power.

2. Material and Method

2.1. Materials

A set of 12 samples of 3.0 x 3.0 x 0.3 mm^3 cut from 2-inch diameter p-type silicon wafers oriented in the (100) plane (Wafer World Inc.) was used as substrate for growth in a diamond deposition reactor through CVD technique activated by high power 2.45 GHz microwave plasma.

2.1.1. Substrate holder

Our conventional substrate holder for our microwave-activated plasma reactor do not have the ledge present in this modified version, which contributes to the sample heating and allows higher temperature levels for the same applied power. The modified substrate holder along with the plasma shape formed is shown in Figure 1.

2.2. Methodology

The substrates were subjected to a cleaning procedure to remove organic residues and particles adhered to the surface. Then, a seeding procedure with diamond nanoparticles was performed by the ESND method in order to increase the diamond nucleation rate, as described elsewhere³⁷. The CVD diamond films were deposited using microwave power of 3.6 kW, a 2% of CH_4 in H_2 , and varying the pressure and

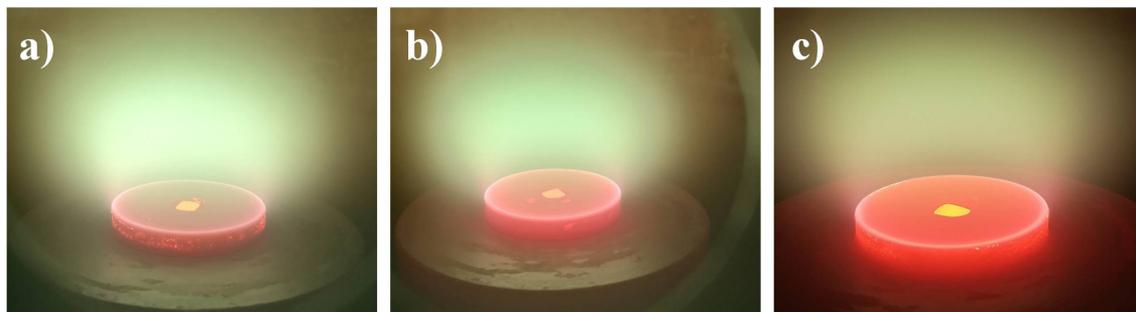


Figure 1. Images of the plasma formed on the substrate holder with a sample during the growth process from left to right: a) sample at 950 °C, b) at 1000 °C and c) at 1040 °C.

temperature parameters from 125 to 200 Torr and from 950 to 1040 °C, respectively. The groups of samples and their growth conditions are described in Table 1 and growth time for all samples was 2h. The obtained films were evaluated by FEG-SEM conducted in a Tescan MIRA3 electron microscope for film morphology. Thickness was measured directly in the microscope imaging software using micrographs of the cross section of the samples, taking at least three measurements for each sample. Raman spectroscopy was performed in a HORIBA LabRAM spectrometer with a 532 nm excitation wavelength in the range of 800 to 1800 cm^{-1} . The resulting Raman spectra were then studied by curve fitting method to find diamond and non-diamond phases that were used for calculate the quality factor and residual stress.

3. Results and Discussion

3.1. Morphology and thickness

The morphology of all grown samples presents in its majority, characteristics of microcrystalline CVD diamond films, with grains varying in size in the micrometer scale. Figure 2 shows the surface morphology and thickness of all samples.

Despite of visible differences in surface morphology of the films, none of them presented a clear preferential growth orientation. However, it is possible to determine that for some films secondary nucleation had a significant impact on morphology, while for others individual grain size was the dominant contribution for growth as seen by the surface features.

Considering the narrow variation of tested temperatures, little changes on orientation of the films could be observed as consequence of this variation, based on observations of Wild et al.^{38,39} and others^{40,41}, significant changes occur from the range of 700 to 1000 °C, also impacted by pressure and methane concentration but in a less critical manner.

As pressure increases, secondary nucleation starts to be relatively strong, once nucleation increases with pressure and methane concentration^{25,42} so that the growing crystals do not form facets completely, they are suppressed by new layers of crystals in the early stages of formation, the facets that survive are those favored by growth conditions.

Film morphology does not seem to have a direct influence or correlation with the resulting thickness but it is important to emphasize that the conditions used in its majority favored

Table 1. Growth conditions for each sample.

Sample	Pressure (Torr)	Temperature (°C)
B2W	125	950
B3W	125	1000
B4W	125	1040
B2X	150	950
B3X	150	1000
B4X	150	1040
B2Y	175	950
B3Y	175	1000
B4Y	175	1040
B2Z	200	950
B3Z	200	1000
B4Z	200	1040

the same film orientation, with more or less crystal defects and enabled specific growth mechanisms in each experiment, therefore when the growth conditions were most appropriate for that orientation, growth rate was maximized and this could be observed in samples B3X, B3Y and B3Z.

Film thickness measurements were obtained through cross sectional FEG-SEM micrographs, these results are summarized in Table 2 and plotted in Figure 3. For samples B2Y, B2Z and B4Z, although diamond crystals grew in a similar rate throughout the entire sample surface, it were not uniformly covered as seen in top morphology micrographs.

In a general manner growth rate is favored with the increase of surface temperature⁴³, however, it is possible to observe that for the pressures from 150 to 200 Torr, film thickness presented a maximum at the temperature of 1000 °C and a further increase to 1040 °C caused a perceivable reduction in growth rate, that was more pronounced for the sample grown at 200 Torr pressure.

We observed that for samples grown at 125 Torr pressure, the trend was always a reduction in growth rate, despite of temperature increase. It is noteworthy to recognize that, regardless of growth method, CVD polycrystalline films are usually grown at much lower pressures, in the range of 10 to 100 Torr, that is a well-established and studied pressure range²⁵. However, it is clear the growth rate is higher for temperature around 1000 °C specially for higher pressure.

3.2. Raman spectroscopy

Raman spectra for all CVD Diamond films are shown in Figure 4. It is possible to observe in all films only a slight

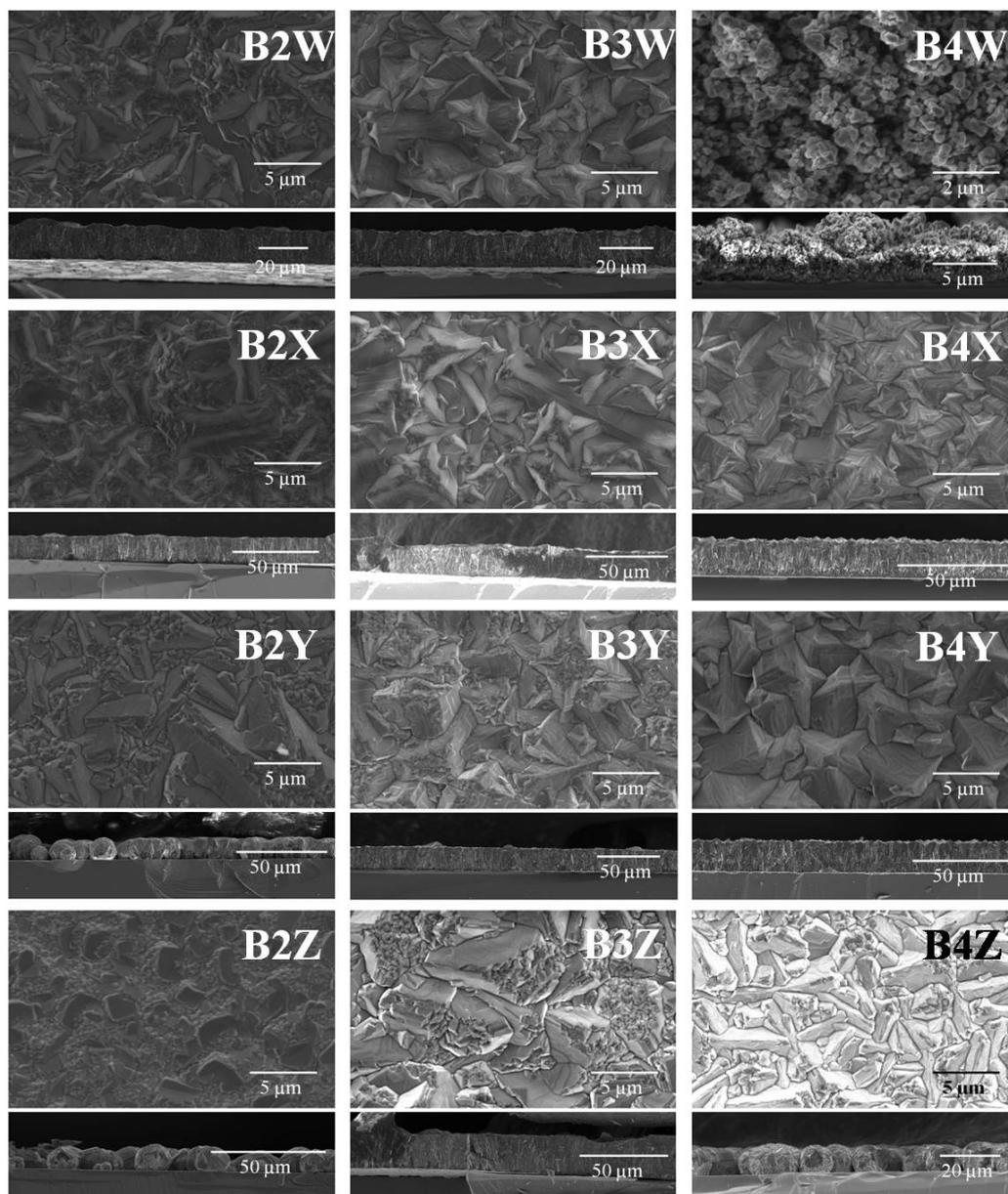


Figure 2. FEG-SEM micrographs of top morphology and cross section of all grown samples.

Table 2. Thickness measurements for each grown sample.

Sample	Thickness (μm)
B2W	$14,66 \pm 1,01$
B3W	$13,99 \pm 0,81$
B4W	$4,21 \pm 0,98$
B2X	$14,66 \pm 0,97$
B3X	$19,11 \pm 0,68$
B4X	$16,13 \pm 1,92$
B2Y	$11,94 \pm 1,21$
B3Y	$19,62 \pm 0,58$
B4Y	$17,56 \pm 0,46$
B2Z	$10,94 \pm 0,83$
B3Z	$20,23 \pm 2,41$
B4Z	$12,12 \pm 2,11$

luminescence, identified from the rise of the spectra baseline, and also the characteristic peak of diamond centered around 1332 cm^{-1} .

All samples presented features around 1340 cm^{-1} and 1580 cm^{-1} , D and G bands respectively, that are characteristic bands for graphite. The maximum diamond peak position variation was from 1332.65 cm^{-1} to 1333.51 cm^{-1} for samples B4X and B2Y respectively. Observing the spectrum for B4W sample there is a more prominent band centered at 1560 cm^{-1} that refers to the presence of monocrystalline graphite⁴⁴ this band is not clearly seen in the other samples spectra. The samples B2X, B2Z, B3X and B4W presented broader D bands around 1340 cm^{-1} and a band at 1150 cm^{-1} which is associated to trans-polyacetylene⁴⁵.

Using the relationship between the displacement of the characteristic diamond peak compared to its naturally occurring position one can obtain an estimate of residual stresses in the film as follows in Equation 1³⁴.

$$\sigma(\text{GPa}) = -0,567 \times \Delta v_m \quad (1)$$

Where σ is the total residual stress present in the film, and Δv is the difference between the measured position for the center of the diamond peak in the Raman spectrum and its natural occurrence position at 1332 cm^{-1} . The result obtained from calculations by this methodology can be either positive or negative representing traction or compression stress on the film, respectively.

Furthermore, it is possible to obtain a film quality factor from the relationship between the characteristic peak intensities of diamond and D (disordered) and G (graphite) bands related to non-diamond carbon present in its structure as shown in Equation 2^{35,36}.

$$Q_{[514nm]} = \frac{I_{\text{diamond}}}{\left(I_{\text{diamond}} + \frac{I_G}{233} \right)} \times 100 \quad (2)$$

Where Q is the quality factor of the analyzed sample, I_{diamond} is the intensity of diamond peak in the Raman spectrum and I_G is the total intensity of non-diamond carbon identified in the Raman spectrum.

Table 3 provides a compilation of calculations performed using Equations 1 and 2 to estimate the stress and quality factor (Q) of the films and also FWHM values for diamond peak of each sample.

An overview of all data collected from Raman spectroscopy investigation of the samples is shown in Figure 5a, b and c.

Diamond can be assessed regarding its structural quality and anisotropic stress by looking at FWHM of the characteristic peak^{44,46}, a lower value of FWHM indicates that the grown film has lower density of defects, once it is inversely proportional to phonon lifetime⁴⁷. Not only FWHM is related to the density of defects in diamond films but it is also affected by the presence of non diamond phases^{48,49},

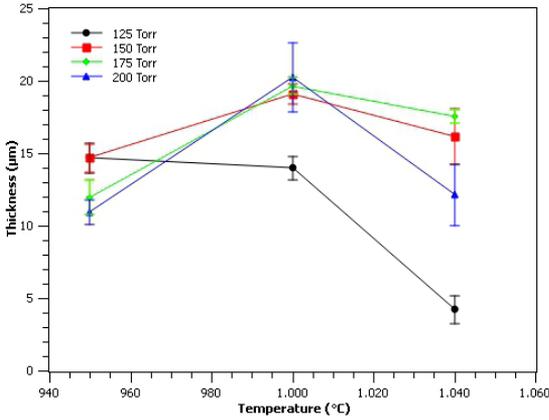


Figure 3. Relationship between film thickness and deposition temperature observed at different growth pressures.

Table 3. Results of stress and quality factor calculations for the obtained films.

Sample	Stress (GPa)	Q (%)	FWHM (cm^{-1})
B2W	-0,640	99,87	5,22
B3W	-0,595	99,95	4,29
B4W	-0,776	99,88	4,11
B2X	-0,657	99,85	5,52
B3X	-0,527	99,92	4,81
B4X	-0,368	99,98	3,18
B2Y	-0,856	99,90	5,81
B3Y	-0,402	99,94	4,77
B4Y	-0,368	99,98	3,53
B2Z	-0,782	99,88	5,71
B3Z	-0,413	99,91	4,81
B4Z	-0,663	99,94	3,55

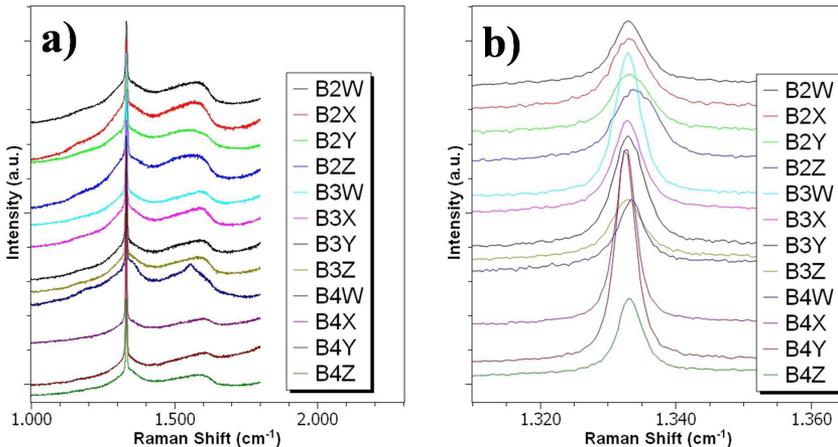


Figure 4. a) Raman spectra for each grown sample. The typical position for the diamond peak at 1332 cm^{-1} , graphite D band at 1340 cm^{-1} and G band at 1580 cm^{-1} are represented by markers (i), (ii) and (iii) respectively. b) Magnification of diamond peak in the spectra.

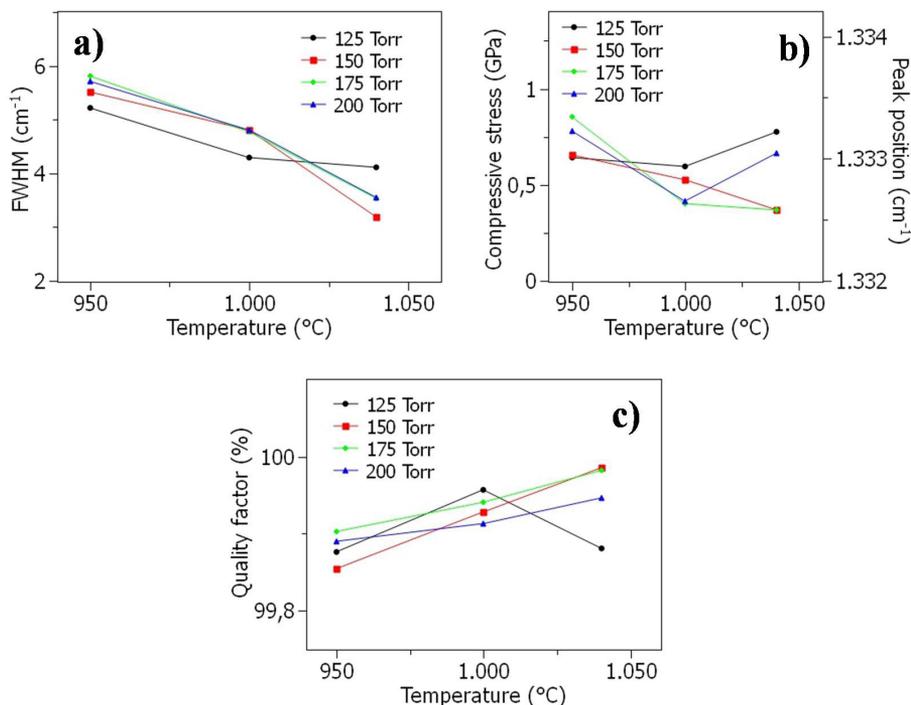


Figure 5. a) Relationship between diamond peak FWHM and growth temperature for each deposition pressure. b) Relationship between film stress, diamond peak position and growth temperature for each deposition pressure. c) Relationship between quality factor and growth temperature for each deposition pressure.

what is particularly consistent with the results presented in this work, films with lower quality factors, i.e. more prominent bands of sp^2 bonded carbon, also bear higher values for FWHM.

Observing FWHM values as a function of deposition temperature in Figure 5a, it is clear that the film quality tends to enhance as deposition temperature is increased, and this trend is valid for all deposition pressure levels, although changes were less significant to the group of samples grown at 125 Torr, they are still perceivable.

Interestingly higher temperatures also lead to the deposition of less stressed films as seen in Figure 5b. For those grown under 150 and 175 Torr of pressure, the stress levels kept this reduction trend as temperature was increased, which is not observed for samples grown at 1040 °C at 125 and 200 Torr. These results suggest that there probably is an optimum pressure value for growth in the range of 150 to 175 Torr, for the experimental setup proposed in this work.

According to Figure 5c, samples grown under higher temperatures presented better quality factor and for those grown at the same pressure levels, as temperature increases so does the quality factor, except for the sample grown at 1040 °C and 125 Torr with very small grained diamond crystals and considerable amounts of non-diamond material. Actually, its quality factor remained similar to those of samples grown at 125 and 150 Torr at lower temperature, although those samples presented much more faceted and bigger crystals in the film. A probable cause is that even presenting high quality for diamond, the amounts of non-diamond phases embedded in the crystals and grain boundaries are significantly high, that can be supported by the findings of Tang et al.⁵⁰, a

comparison between different grain sizes of diamond films obtained by different experimental parameters, nanocrystalline films presented higher amounts of non-diamond carbon. Furthermore, it was the only sample to present the peak for monocrystalline graphite, besides the broader D and G bands. It is also noteworthy that all the samples presented a sharp diamond peak with similar FWHM values, what indicates that the diamond material deposited presents good quality in all samples, however what makes the film a better or worse material is the amount of non-diamond phases incorporated in the coating. The increase of pressure or reduction of temperature is a widely used procedure for controlling grain size of diamond crystals produced by CVD, reported in some of our previous works⁵¹⁻⁵³ and from others⁵⁴⁻⁵⁶.

Previous studies used different ways to evaluate diamond quality using different equations and analysis methods of Raman spectra. In a work by Silva et al.⁴⁰ diamond films were produced by MWPACVD aiming to control film morphology by changes in crystalline orientation, these films reached quality factors in the range of 70 to 90 percent. Other work approached the problem using a similar methodology to that hereby reported, for thin diamond films produced using HFCVD method, their quality assessment rendered a quality factor ranging from 95.56 to 99.71 percent, however, it is noteworthy to compare the stress levels of the samples, that varied from -0.84 to -4.29 GPa³⁶ while values for stress reported in this work remained below -1 GPa. Veillère et al.³⁵, obtained good quality diamond films over WC-Co using a laser-assisted combustion flame method, reaching a quality factor higher than 99.9 percent for all produced samples, the stress was also studied by the authors and yielded

values from about -1 to -3 GPa, considering the significant difference between thermal expansion coefficients of the diamond films and the WC-Co substrates, higher levels of stress are expected.

It is known that higher temperatures promote the growth of better quality films⁵⁷. This is confirmed in the carried out experiments, since the samples obtained at higher temperatures have better quality indexes for all groups, except for the sample grown at 125 Torr and 1040 °C which was possibly caused by the presence of more significant amounts of non-diamond phases including monocrystalline graphite that was not present in other samples.

Higher pressures tend to increase renucleation rates, forming film layers more quickly, however, this accelerated process induces the occurrence of greater amounts of graphite among the diamond grains^{58,59}, which can be observed in our films by the presence of the graphite G-band more evident in samples grown at higher pressures and lower temperatures.

The stress levels observed in all films varied considerably and this variation is due to two main factors, one is the intrinsic stress of the film, caused by inclusions of non-diamond phases and which has a less significant contribution to the final result, another one is the extrinsic stress of the film, mainly caused by the thermal accommodation of the diamond film as a whole on the substrate material which cannot be neglected. A more in-depth study of the contribution of each of these stress components would be adequate to determine the real impact of impurities on the total stress.

4. Conclusions

This work had as main scope the definition of parameters to obtain good quality diamond films in a higher power regime of CVD activated in 2.45 GHz microwave plasma. It was possible to estimate ranges of temperature and pressure to obtain high quality films. Specially for the identification of combinations of pressure and temperature that promotes higher levels of secondary nucleation.

Thus, the experiments demonstrate through Raman spectroscopy that the quality of the films was substantially impacted by the pressure and temperature levels tested, which help us to understand better the MWPACVD discharge behavior.

Also, as a final conclusion the results showed that for the condition of higher plasma concentration obtained by the modification carried out in the substrate holder of our reactor, the temperature range above 1000 °C is more suitable for obtaining better quality films, using pressures in the range of 150 to 175 Torr, where there was a gain in the growth rate of films without significantly compromising their structure. So, the current study also helps us to establish the best set of parameters for single crystal CVD diamond growth, that will be very useful to shorten the time of studies in CVD single crystal diamond growth, as this kind of experiments are usually more expensive.

5. Acknowledgments

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