

High pressure high power microwave plasma chemical vapor deposition of large area diamond films

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Abstract

Uniform, large area, smooth, and chemically clean diamond films having low residual stress are important for many applications such as electronic packaging, metallurgical and optical coatings, and X-ray lithography masks. Uniform diamond films were deposited on 75 mm diameter p-type (100) silicon substrates using a Wavemat Inc. microwave plasma disc reactor (MPDR) which was modified for high pressure and high power operations. These high pressure high power deposited films yielded much better quality even though the deposition rate increased by more than 50% when compared to films deposited under low pressures and powers. A dry abrasive seeding technique was used that was simple but offered very high nucleation density. The CH_4 concentration was varied over 0.5–3.0% and the deposition pressure and power were set at 67 Torr and 3500 W, respectively. Deposited films were characterized by SEM, AFM, Raman, and X-ray diffraction (XRD) techniques. For increasing CH_4 flow from 0.5 to 3%, the deposition rate increased by four times without much reduction in the film quality, as observed by Raman spectroscopy. For CH_4 flow rate of up to 2%, the film texture was (111) whereas it changed to $\langle 220 \rangle$ for films deposited at 3% CH_4 . The macro- and micro-stress in the films were measured by XRD $d\text{-sin}^2\psi$ technique and diffraction peak broadening, respectively. All the deposited films showed moderate compressive macro-stress; the micro-stress values for these samples were much less than observed for films deposited in low-pressure low power regime. © 1997 Elsevier Science S.A.

Keywords: Diamond films; High pressure; High power; Microwave plasma; Chemical vapour deposition

1. Introduction

Diamond is a technologically important material. Immediately after the discovery of the chemical vapor deposition technique to grow diamond [1,2], it got considerable attention for its utilization in optical, electronic, abrasive, cutting tool, and thermal management applications. So far, several techniques have been successfully used for diamond deposition [3]. However, the microwave plasma chemical vapor deposition (MPCVD) technique has emerged as a method of choice for depositing relatively smooth, defect free diamond films for optical windows and X-ray lithography mask applications [4,5]. For diamond growth, the deposition temperature window is narrow (700–1100°C). By increasing the plasma density and, consequently, the concentration of active species, the deposition rate could be increased. This can be achieved in the MPCVD technique by exciting the plasma at high pressures and powers. Since the three body recombination of electrons with ions becomes dominant at higher pressures, a high power is required to sustain the

plasma [6]. At this high pressure and power conditions, a substrate cooling mechanism is required to keep the substrate temperature in the diamond growth regime.

Diamond does not nucleate easily on non-diamond substrates making diamond nucleation a critical issue. Diamond nucleation strongly depends on the seeding technique and the substrate material. Understanding and control of diamond nucleation is very important as it influences the final film properties like surface morphology, film stress, micro-cavity formation etc. However, the understanding of the nucleation process is complicated by its metastable growth mechanism. Conventionally, single crystal silicon is used as a substrate for diamond deposition and different pretreatment techniques are used to enhance the nucleation density. In this study a dry abrasion technique was used that provided efficient diamond nucleation on single crystal silicon substrates. Deposited diamond film morphology also strongly depends on the deposition conditions like CH_4 flow, deposition pressure, and applied microwave power. Thus, by increasing nucleation density and optimizing deposition parameters, diamond films with desirable properties can be achieved. In this work we will present the results

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of good quality diamond deposition at high pressure and power conditions with relatively high CH_4 flow rates on the above mentioned substrates.

2. Experimental

Seventy-five millimeter diameter, p-type, (100) oriented silicon substrates of 1 mm thickness were used as substrates for diamond deposition. The silicon substrates were cleaned in piranha solution (7 parts H_2SO_4 , 3 parts H_2O_2) followed by a HF dip to remove native oxide. The cleaned substrates were dried by blowing nitrogen. Then, they were rubbed uniformly by a lint free paper containing 4 nm size diamond particles for 15 min. The extra diamond powder was blown away with dry nitrogen. Thus, a mirror polished seeded substrate was achieved.

Diamond films were deposited in a Wavemat Inc. microwave plasma disc reactor (MPDR) operating at 2.45 GHz, using a cylindrical cavity tuned to excite TM_{012} mode. The gases were introduced and the plasma was excited inside a bell jar located within the microwave cavity. Initially the system did not have a substrate cooling facility and a moderate flow of forced N_2 heat removal technique was utilized to cool the bell jar. The substrate was loaded on a graphite susceptor resting on a quartz ring inside the bell jar, so that the substrate temperature was solely dependent on the plasma heating. This system was modified for high pressure and power applications. A substrate cooling stage was installed to reduce overheating during high pressure and power operations. The substrate was placed on a stack of suitable susceptor materials (Mo, graphite, quartz etc.) which was placed on the stainless steel cooling stage. Water jet cooling was used to keep the substrate temperature in the diamond deposition temperature range. Before

doing the modification, the system could operate at a maximum power of 2400 W and a pressure of 50 Torr which yielded a substrate temperature range suitable for diamond deposition. After installing the substrate cooling stage and an improved bell jar cooling mechanism, the system could be operated at up to 3800 W and 90 Torr.

A Hitachi Model S-2300 scanning electron microscope (SEM) and a Digital Instruments Model Nanoscope-III scanning probe microscope (SPM) were used to observe surface morphology and roughness. An ISA Model U1000 Raman spectroscopy system using an Ar ion laser operating at 514.5 nm was used to take the macro Raman spectra over a 0.5 mm diameter spot size. A Phillips Model X'pert system using a PW 3710 diffractometer control unit was used for XRD measurements. Cu K_α radiation from an X-ray source operating at 45 kV and 40 mA was used. Macro-stress measurement was performed using XRD $d\text{-sin}^2\psi$ technique. The measurements were performed using the highest 2θ peak ((331) peak) to ensure high accuracy in the d -spacing measurement. The micro-stress was measured from the peak broadening of different diamond diffraction peaks. $\text{K}_\alpha 2$ peaks were stripped off before analyzing the peak broadening.

3. Results and discussion

Deposited diamond film quality strongly depends on the nucleation density. Fig. 1a shows the SEM taken near the center of a diamond film deposited for 1 h on the substrates seeded by the dry polishing technique. From Fig. 1 it is clear that the seeding technique used in this study gave a very high nucleation density. However, the nucleation density was found to be less at the edge of the substrate so that it took longer deposition time for the individual diamond par-

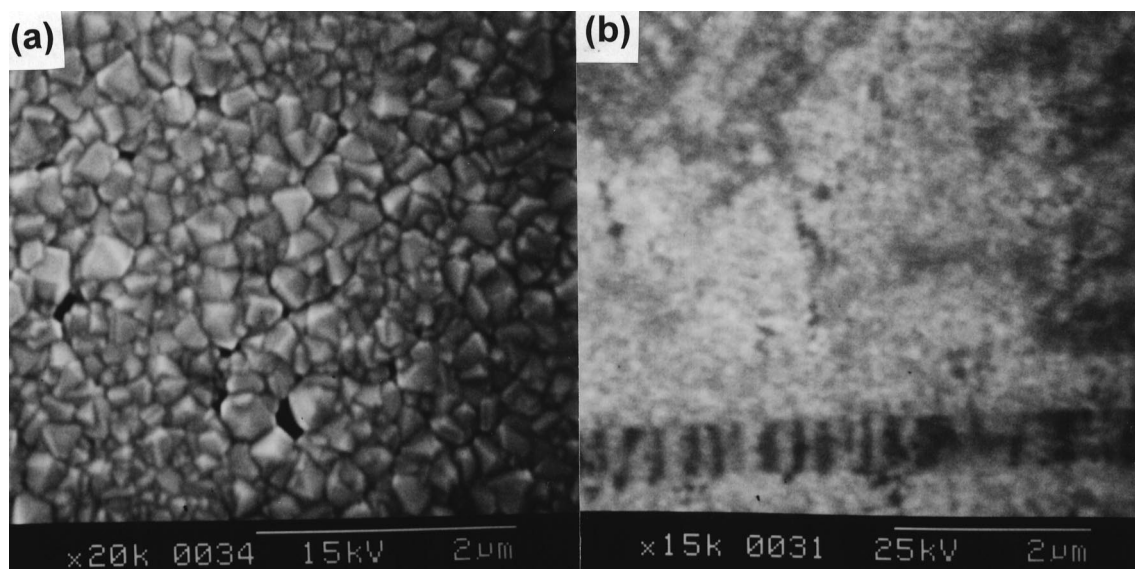


Fig. 1. Uniform nucleation density achieved by the dry polishing technique as observed the SEMs of (a) 1-h deposited film surface (b) backside of the deposited diamond film.

ticles to form a continuous film near the outer edge of the substrate when compared with the rest of the sample. This, despite the fact that the whole wafer was polished uniformly to create the nucleation sites. It should be noted that at high pressure and power it becomes more difficult to have a uniform plasma density and substrate temperature across the 75 mm diameter substrate. The above discrepancy in nucleation density clearly suggests that the plasma density and/or substrate temperature have a profound effect on nucleation. Fig. 1b shows an SEM of the backside of the deposited diamond film. It is clear that the backside is very smooth and only in some areas, submicron size scratches on the silicon substrate (created during nucleation) are visible on substrate side of the diamond film. This smooth back surface clearly indicates that the film became continuous early on in the deposition process.

Diamond films were deposited with varying CH_4 concen-

trations (0.5–3%). The pressure and power could not be varied independently for a particular susceptor stack because of the necessity to maintain the temperature in the diamond deposition temperature range. More important is the fact that to achieve a large area uniform plasma, chamber pressure could not be varied much for a certain power condition and vice versa. Thus, a systematic study of pressure and power variation could not be done. A parametric study under low pressure and power conditions was done earlier using the same system before modifying it for high pressure operations. Those results have been published elsewhere [7].

The films were deposited at a pressure and power of 67 Torr and 3400 W, respectively. Substrate temperature at the center under these conditions was $800 \pm 20^\circ\text{C}$. The maximum temperature variation from edge to center of the substrate was 60°C . Fig. 2a,b,c,d present the SEMs showing

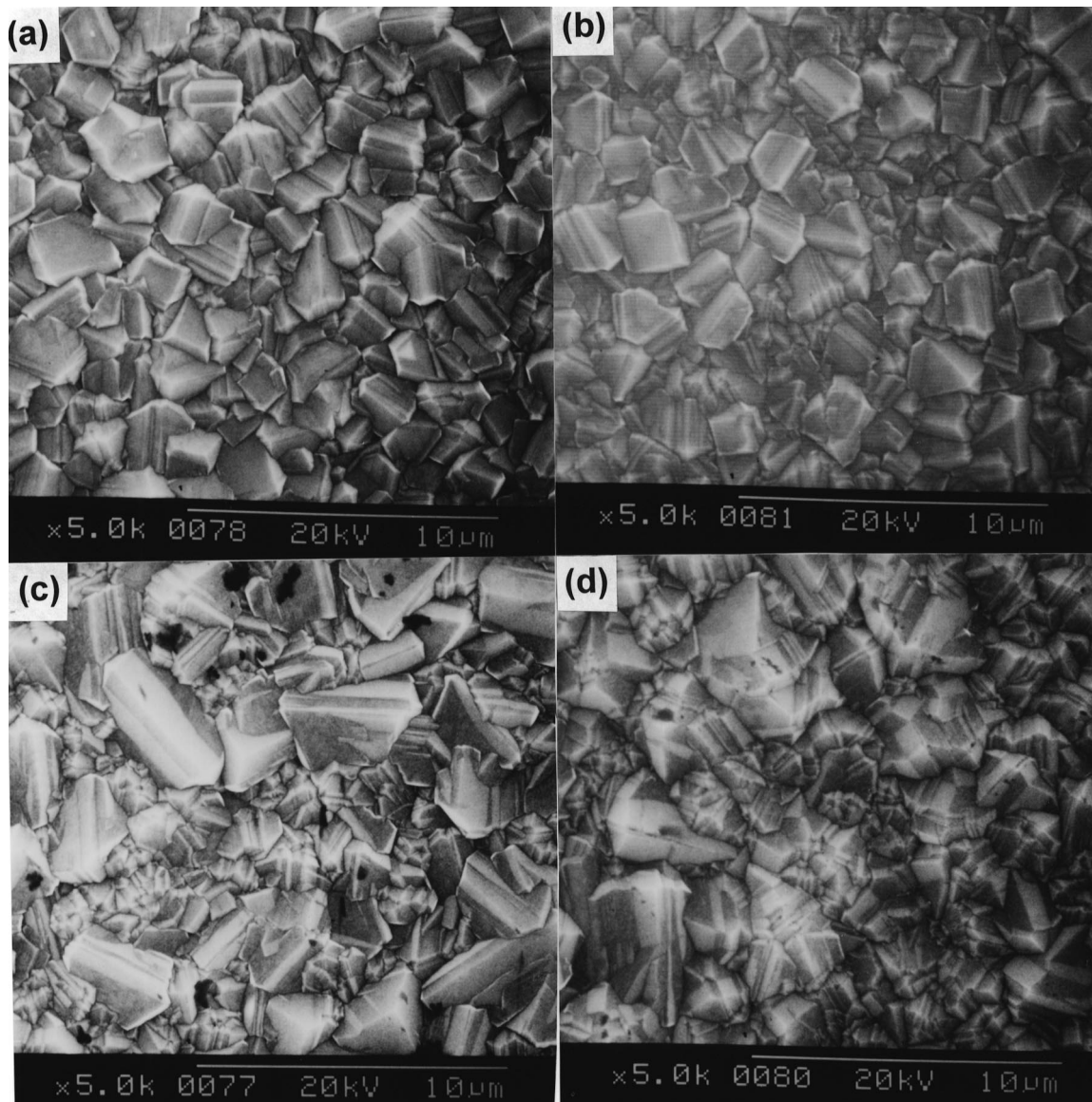


Fig. 2. SEM of diamond films deposited under four different CH_4 flow conditions (a) 0.5, (b) 1, (c) 2, and (d) 3%.

morphology of the diamond films deposited with four different CH_4 concentrations. The deposition time for the 0.5% CH_4 case was 20 h and for each of the other three films were 12 h. The deposited films weighed 55, 51, 83, and 140 mg, respectively, on a 75 mm diameter substrate. Assuming density of diamond of 3.5 g cm^{-3} , the respective film thicknesses calculated were 4, 3.7, 6.5, and $11 \mu\text{m}$. Not much change in the facet size and shape in the surface morphology was observed for increasing CH_4 flow up to 3%. An increase in grain size observed for the film deposited with 2 and 3% CH_4 could be related to higher film thickness. It is observed that for the 0.5 and 1% CH_4 concentrations, the crystal sizes are more or less uniform. Whereas, for the 2 and 3% case, the crystal sizes are non-uniform which may be related to secondary nucleation. Secondary nucleation increases the density of grain boundary surface and would favor non-diamond carbon incorporation in the film under higher CH_4 flow conditions.

Even though films deposited with the lowest CH_4 concentration showed very strong (111) orientation as revealed by XRD, the SEM did not show any triangular facets. These results will be discussed later. The average surface roughness of the diamond films deposited with four different increasing CH_4 flow conditions were measured by AFM over a $25 \mu\text{m}$ square area and the values were 141, 168, 150, and 288 nm, respectively. Usually, the surface roughness of diamond films increases with increase in film thickness. Keeping this information in mind it is clear that the observed difference in film roughness simply correlated with film thickness. Thus, the surface roughness seems insensitive to CH_4 flow rate in the parameter range studied.

Fig. 3 shows the Raman spectra of the diamond films deposited under four different CH_4 concentrations. A measure of the diamond film quality can be obtained from the FWHM of the diamond Raman peak at 1333 cm^{-1} and the intensity of the non-diamond broad hump at around 1560 cm^{-1} [8]. Better the quality, smaller the FWHM of the Raman diamond peak and smaller the intensity of the non-diamond hump. The FWHM values of the Raman diamond peak were 5.25, 5.25, 5.5, and 6.5 cm^{-1} , respectively, for the CH_4 flows varying from 0.5 to 3%. It is further observed that even for 3% CH_4 , not much non-diamond phase is incorporated in the sample whereas at low pressure and power conditions, even the films deposited with 2% CH_4 showed very strong non-diamond hump. The spectra for a sample deposited for 40 h at 40 Torr and 1600 W with 2% CH_4 is shown in Fig. 3 for comparison. The FWHM values of the Raman diamond peak for the low pressure and low power case with a CH_4 flow of 0.5, 1 and 2% were 5.5, 10, and 15 cm^{-1} , respectively.

Increasing CH_4 flow gives more carbon species available near the surface. During deposition carbon supersaturation provides the driving force for the condensation of various forms of solid carbon, including diamond. The atomic hydrogen provides a reactive environment for the removal of the non-diamond species by etching and/or converting sp^2

bonded sites to sp^3 sites. For CH_4/H_2 gas ratio above a certain value, atomic hydrogen concentration near the depositing surface has been observed to decrease [9]. Thus, at higher CH_4 concentrations there is an increasing chance for non-diamond species incorporation in the film. It should be noted that in the same deposition chamber under low pressure and power conditions (40 Torr, 1600 W), changing CH_4 flow from 1 to 2% caused the deposited film morphology to change dramatically [7]. The changes were reflected in high non-diamond carbon band in Raman spectra, orientation change (from (111) to (220)) and increase in tensile macro-stress as determined by XRD. For the present high power and high pressure case even at 3% CH_4 , we got very good quality films. The quality, as detected by the above mentioned techniques, did not get adversely affected as the CH_4 concentration in the feed gas was increased. Recently, two other groups have also reported diamond film deposition at higher pressure and powers under high CH_4 concentrations. Chein and Tzeng reported diamond deposition at high pressure (130 Torr) and temperatures ($>1300^\circ\text{C}$) even with 13% CH_4 in the presence of 1.6% O_2 on 0.5 inch diameter Mo substrates [10]. Kuo and Asmussen studied diamond deposition in a plasma disc reactor in the 80–150 Torr and 3000–4500 W range on 2 inch diameter silicon substrates. They also reported deposition of good quality diamond films with up to 5% CH_4 under the high pressure and power conditions. However, for their case the deposition temperature was higher (1100°C) and the deposited film had a (220) preferred orientation [11].

For a constant CH_4 flow, with increasing pressure and

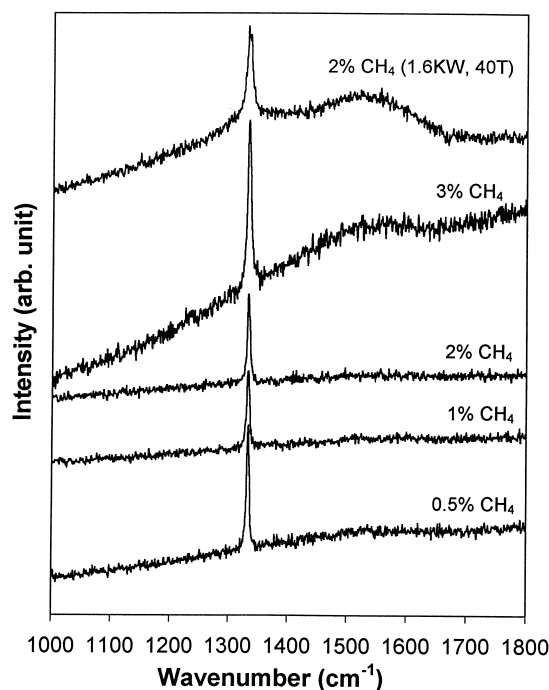


Fig. 3. Raman spectra of diamond films deposited under high pressure and high power conditions with four different CH_4 flows. Raman spectra for a diamond film deposited at 1600 Watts and 40 Torr with 2% CH_4 is shown for comparison.

power, a considerable increase in deposition rate was observed. For an increase in pressure and power from 40 Torr and 1600 W to 67 Torr and 3400 W with other parameters same (same CH_4 flow, same substrate temperature maintained by cooling stage, and same substrate of 75 mm diameter silicon wafer), the deposition rate increased from 0.21 to 0.33 $\mu\text{m/h}$. Anthony explained the increase in deposition rate at high pressure-power conditions as follows [12]. In a low pressure plasma, due to higher mean free path of electron, energy redistribution between the electrons and molecules are not expected to occur and the gas molecules remain relatively cooler. Only the high energy electrons whose concentration is less contribute to the generation of atomic hydrogen and reactive carbon species. At higher pressures the electron mean free path decreases and a redistribution of energy between electron and molecules is expected. Any excess energy absorbed by the electrons from the electric field will be quickly transferred to molecular species by electron-molecule collision. Thus, the temperatures of both the gas molecules and electrons are high and both are expected to participate in the collisions that generate atomic hydrogen and reactive carbon species. Because of the higher concentration of reactive species and atomic hydrogen in the plasma, the growth rate increases with increasing pressure.

From the Raman spectroscopy results, it was also observed that the non-diamond phase incorporation is much less in high pressure high power deposited films as compared to the low pressure low power case. For the same CH_4 flow ratio, the deposition rate increases considerably and the film quality improves. It should be noted that the total gas flow rates were the same for both high and low pressure deposition cases. The higher non-diamond carbon incorporation in the film with decreasing pressure and power can be explained as follows. For a constant flow rate, with a decrease in pressure, the residence time of the gas species decreases. Since heavy hydrogen dilution is used during diamond deposition, the atomic hydrogen to methyl radical concentration remains the same on the surface, whereas the concentration of atomic hydrogen reacting with the surface decreases. This has two effects—less non-diamond species will be etched from the film during deposition and the substrate temperature will be lower. Both of these effects favor more non-diamond phase incorporation in the film. Furthermore, as discussed earlier, at low pressure and power conditions gas temperature is less and the concentration of reactive species and atomic hydrogen are also less. All these factors should lead to higher non-diamond phase incorporation in the film.

XRD θ - 2θ scans of diamond films deposited under four different CH_4 concentrations were taken. It was observed that for changing CH_4 flow from 0.5 to 2%, the preferred orientation changed from very strong (111) to moderate (111). At 3% CH_4 , the orientation changed to (220). Fig. 4 presents the XRD scans for films deposited with 1 and 3% CH_4 flow showing the drastic change in film texture. How-

ever, looking at the SEM, the grain boundary density did not change much and there was not much extra non-diamond carbon incorporation. This fact is clear from the Raman spectra also.

The macro- and micro-stress in the diamond films were measured. All the deposited films showed moderate compressive macro-stress. For 0.5, 1, 2, and 3% CH_4 flow cases, the respective macro-stress values obtained were -112 , -150 , -164 , and -92 MPa, respectively. As the stress values are very small and not much different, no strong conclusion about the effect of CH_4 flow on film stress could be drawn. The micro-stress for all these films were in the range of 700 to 1000 MPa, and increased with increasing CH_4 flow. It should be noted that for the low power, low pressure regime the stress was found to vary from compressive to tensile (from -275 to 425 MPa) by increasing CH_4 flow from 0.5 to 2% [13]. Also, the micro-stress values were much higher for these films (900–3000 MPa range). The reason behind this wide range of stress values was reflected in the Raman and SEM results. With increase in CH_4 concentration, incorporation of non-diamond carbon increased drastically and so did the density of grain boundary for those films. However, for the high power high pressure deposited films, up to 3% CH_4 , none of these changes were observed.

The pole figure plots for deposited diamond films were also studied. For all the films, the orientation distribution for the (111) texture will be discussed. For the (111) and (220) oriented films, the maximum intensity occurs at the center ($\chi = 0$) and at $\chi = 35^\circ$, respectively, as expected. For CH_4 flow up to 2%, the maximum intensity was at the center

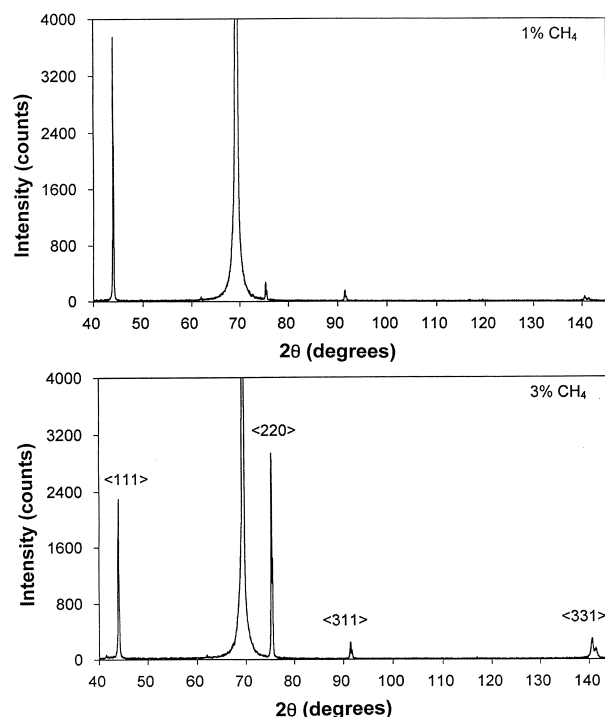


Fig. 4. XRD θ - 2θ plots of diamond films deposited with four different CH_4 flow conditions.

indicating (111) oriented film. It should be noted that the intensity was the same for any ϕ value (0–360°) indicating that these oriented grains were not aligned in-plane. Similar results were obtained from the SEM study. Also even though XRD showed very strong (111) orientation, not much triangular facets were observed. For the 3% CH₄ case, the maximum intensity was at $\chi = 20^\circ$ indicating a switch to (220) preferred orientation. The orientation distribution of other textures ((220), (311) etc.) could not be obtained due to the reason that the data were contaminated by signal from the (100) silicon substrate at different χ angles.

4. Conclusions

High quality polycrystalline diamond films were deposited at high pressure and high power conditions in a Wave-mat microwave plasma disc reactor. An efficient seeding technique was used that resulted in a continuous film over the 75 mm diameter surface within an hour to yield relatively smooth films. A considerable increase in deposition rate was achieved as compared to low pressure and power case. The deposition rate could still be increased further by using higher CH₄ concentrations without having a detrimental effect on the film quality. The film quality did not degrade much for increasing CH₄ flow up to 3%. For CH₄ flow up to 2%, the films showed (111) preferred orientation whereas at 3% the preferred orientation changed to (220). All the deposited films showed very low compressive stress. The stress in the films were less sensitive to CH₄ flow rates unlike what was found in the case of films deposited under low pressure and power conditions.

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