

# Investigation of the effect of the total pressure and methane concentration on the growth rate and quality of diamond thin films grown by MPCVD

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## Abstract

The influence of total gas pressure (50–125 Torr) and methane concentration (0.75%–10%) on diamond growth by microwave plasma chemical vapor deposition (MPCVD) was investigated. Within the regimes studied, the growth rate was proportional to the methane concentration in the source gas while it exhibited a super-linear dependence on total pressure. For a fixed methane concentration, characterization by Raman spectroscopy, scanning electron microscopy and X-ray diffraction indicated there was a minimum pressure required for the growth of large grain diamond, and conversely, for a fixed pressure, there was a maximum methane concentration that yielded diamond deposition. Higher pressures and higher carbon concentrations yielded diamond growth rates more than 10 times higher than achieved by the conventional low pressure MPCVD process.

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**Keywords:** Diamond growth; High growth rate; Pressure dependence; Methane concentration dependence

## 1. Introduction

Diamond possesses many technically useful properties: excellent thermal conductivity, high dielectric strength, optical transparency down to the deep UV part of the spectrum, and chemical inertness. However, to date, the impact of CVD grown diamond is still limited. A part of the reason is high quality CVD grown crystalline diamond films are not cost effective. Therefore, the growth of diamond films at a high growth rate on economical substrates, such as silicon, is desired.

It has been shown that the growth rate of homoepitaxial diamond by chemical vapor deposition (CVD) in the presence of nitrogen exceeded 100  $\mu\text{m}/\text{h}$  [1] and reached 50  $\mu\text{m}/\text{h}$  in processes without nitrogen [2]. In these two cases, higher methane concentrations and higher pressures than those of traditional processes were utilized. Nevertheless, there was very limited research on heteroepitaxial diamond growth at high growth rates. Most experimental data for heteroepitaxial diamond growth on silicon substrates were available for pressures in the range 25–30 Torr with methane concentrations below 2% [3,4].

In this work, a study of polycrystalline diamond growth on (100) silicon substrates at higher pressures (up to 125 Torr) and higher methane concentrations (up to 10%) was reported. The substrates employed in this study were templates for highly oriented diamond (HOD). While this study was focused mainly on growth rate and minimizing non-diamond carbon in the films, future studies will focus on obtaining high growth HOD films. The following sections provided experimental details and results of films analyzed by scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy. The conclusions gave general guidelines to trends in growth rate and diamond quality as a function of total pressure and methane concentration.

## 2. Experimental

All experiments were carried out using an AsTeX<sup>TM</sup> plasma chemical vapor deposition system with a 1.5 kW microwave source and a vertically confined plasma excited at 2.45 GHz. The substrate holder was made of molybdenum. The substrate was heated by the plasma; no auxiliary heating was necessary. During the deposition, the temperature of the growth surface was monitored with a single-color pyrometer (Mikron M190) by focusing it on the substrate edge.

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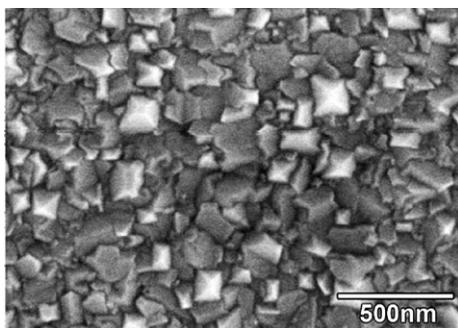


Fig. 1. Template film morphology nucleated by bias-enhanced nucleation and grown to a thickness of 0.5  $\mu\text{m}$  in the octahedral growth mode. Approximately 50% of grains have (100) orientation.

In all experiments, diamond template layers grown on  $10 \times 10 \times 1 \text{ mm}^3$  (100) single crystal silicon were used as substrates. The diamond template layer was nucleated by bias-enhanced nucleation and grown to a thickness of 0.5  $\mu\text{m}$  in the octahedral growth mode at 25 Torr and 1.6% of  $\text{CH}_4$  in hydrogen [5,6]. During this process, the growth rate was only 0.16  $\mu\text{m}/\text{h}$ . The SEM image in Fig. 1 showed the morphology of the template film. The film was well-faceted and approximately 50% of the facets had (100) orientation.

Diamond layers grown at higher growth rates were deposited on top of these templates. Higher growth rates were realized by using higher methane concentrations (0.75–10%) and higher pressures (50–125 Torr) than those used in more conventional processes [3,4]. With the increase in pressure from 25 Torr to 125 Torr, the size of the plasma ball, at the same power input ( $\sim 1000 \text{ W}$ ), was reduced from 6 cm down to 2.5 cm in diameter.

High purity methane (5.5 N) and ultra-high purity hydrogen (6 N) were used as the source gases. The morphology of diamond films was controlled by adding 25 ppm of nitrogen to the source gases. All growth runs were performed at 1150  $^\circ\text{C}$  and a hydrogen gas flow of 300 sccm; the growth time for all samples was 4 h.

The growth rate, morphology and crystal quality of films were assessed by scanning electron microscopy (SEM), Raman spectroscopy and X-ray diffraction (XRD). The SEM images were obtained using a JEOL 6400F microscope with beam energy of 5 kV. The Raman spectroscopy was carried out using 514.5 nm excitation and a 1 m double spectrometer (ISA JY U-1000). The light was collected in  $45^\circ$  backscattering geometry. XRD measurements were done using a Rigaku diffractometer with  $\text{Cu-K}\alpha$  radiation. The diffractometer was operated in the standard theta/2-theta geometry with a  $3^\circ$  offset between the detector and sample axis to reduce the intensity of the Si substrate peak. The sample thickness was measured by SEM of cleaved samples.

In a typical Raman spectrum of pure diamond, a characteristic diamond peak at  $1332 \text{ cm}^{-1}$  is observed. Any deviation from the diamond structure results in additional, broader peaks, associated with disordered carbon deposits. The most common are the D peak around  $1350 \text{ cm}^{-1}$  and the G peak around  $1580$ – $1600 \text{ cm}^{-1}$ . Depending on the actual bonding, these two peaks vary in intensity, position, and width. Following the work of

Ferrari and Robertson, the position of the G peak and the ratio of the intensity between the two peaks were used to identify the nature of carbon deposits by Raman spectroscopy [7].

Diamond quality was also assessed by studying the surface morphology of deposits: diamond structure usually showed a well-faceted topography while all graphitic deposits were flake-like.

### 3. Results and discussion

#### 3.1. The effect of methane concentration on diamond growth

In the first set of experiments, the methane concentration dependence in the source gas was determined by varying the methane flow while keeping the total pressure at 100 Torr and all other parameters constant as described above. A linear relationship between the growth rate and methane concentration was observed, indicated in Fig. 2. It has been reported that a similar linear relationship can be found at methane concentrations as high as 20% [8].

Diamond growth by CVD constituted a delicate balance between diamond deposition and etching of graphite by hydrogen. At a constant pressure, the hydrogen-etching rate remained approximately constant regardless of the methane concentration. As such, any change in the net growth rate was due to increased diamond deposition and not due to decreased etching. Because the density of active surface sites was high at high pressure, the limiting factor for the growth was the availability of carbon precursors, i.e., the deposition process was in a mass transfer limited regime. At constant temperature and pressure, the number of carbon radicals arriving at the growth surface depended only on the methane concentration (partial pressure) in the source gas and, as a consequence, the growth rate increased linearly with carbon concentration.

As a function of increasing methane concentration at constant pressure, the intensity of the characteristic diamond peak decreased until it was not detectable while the intensity of the D and G bands increased (Fig. 3). The ratio of the intensity between the D and G peaks was  $\sim 2$  and the G peak was positioned at

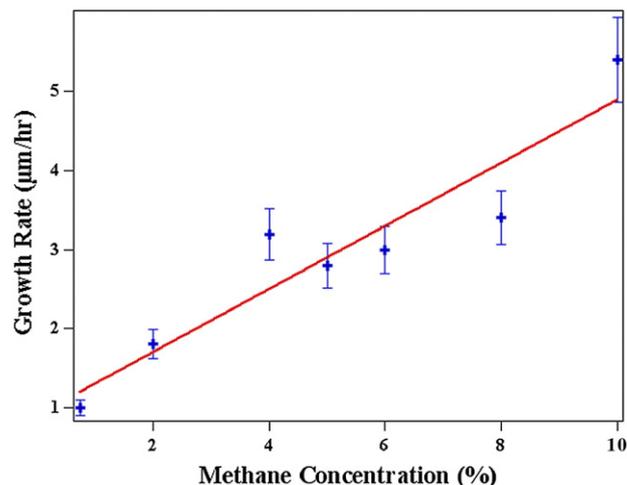


Fig. 2. Dependence of methane concentration on the growth rate at a fixed pressure of 100 Torr.

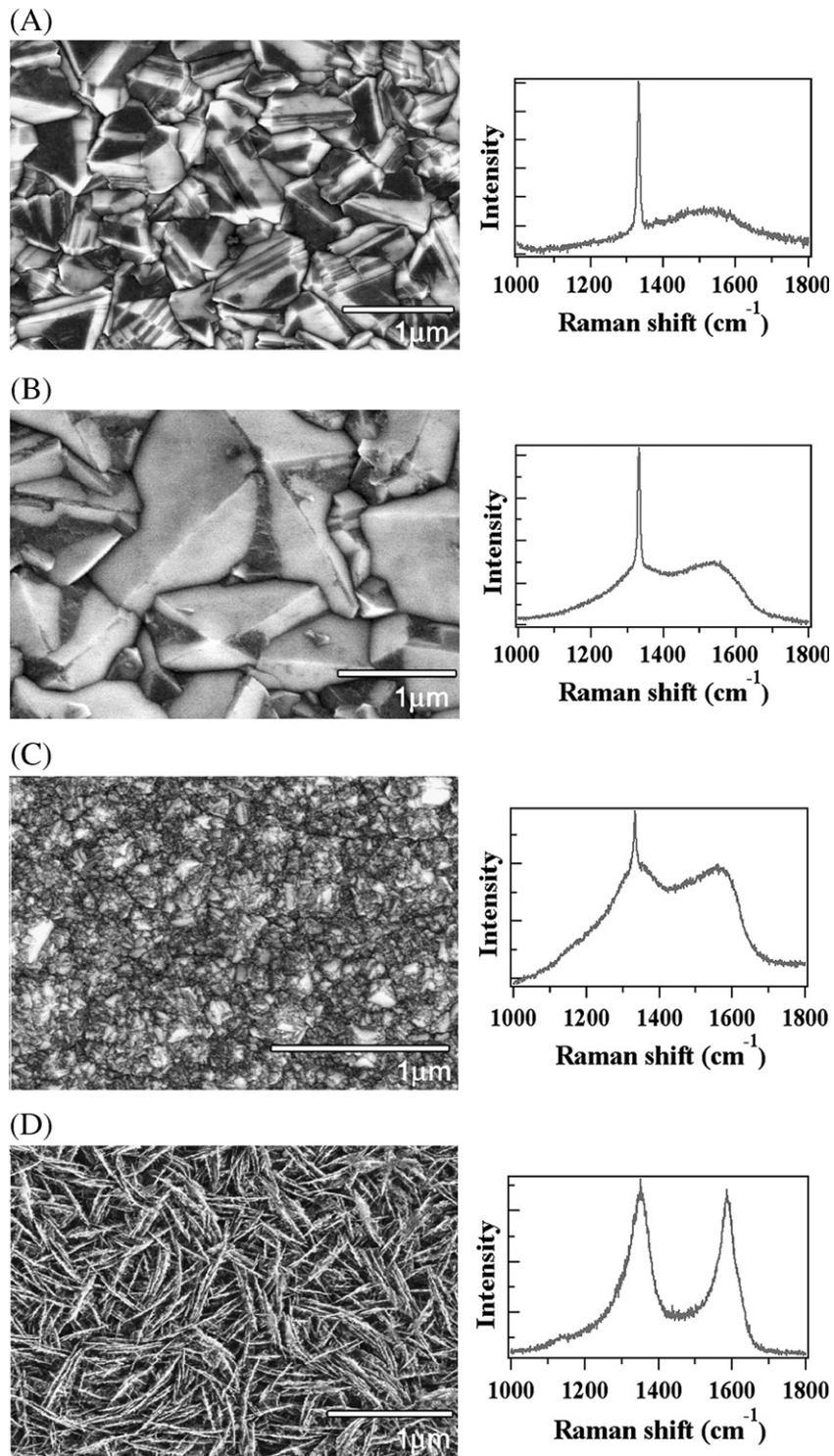


Fig. 3. SEM images and Raman spectra showing the effect of methane concentration on diamond crystal quality at a fixed pressure of 100 Torr: (A) 0.75%, (B) 5%, (C) 6%, (D) 10%. Film changes from diamond to nano-crystalline graphite.

$1600\text{ cm}^{-1}$ . According to Ref. [7], the film exhibited predominantly a nano-crystalline graphite structure. This behavior indicated that the film changed from diamond to nano-crystalline graphite. The SEM images and XRD spectra shown in Figs. 3 and 4, respectively, corroborated this transition. The methane concentration at which the transition occurs depended on pres-

sure and was higher at higher pressures. Growth at a pressure of 100 Torr and  $1150\text{ }^{\circ}\text{C}$  was limited to about 5% of methane, which yielded a growth rate of about  $3\text{ }\mu\text{m/h}$ . From these findings, it was concluded that for a given pressure, there was a maximum methane concentration that still allowed the growth of diamond.

### 3.2. The effect of total pressure on diamond growth

In the second set of experiments, the effect of total pressure (50–125 Torr) on the growth rate was studied, while keeping the methane concentration at 5% and all other parameters constant as described above. As seen in Fig. 5, the growth rate showed a super-linear dependence on pressure. This may not have been expected since plasma density decreases as a function of pressure, and the arrival rate of radicals at the growth surface is slower. Higher pressure may have promoted the formation of carbon dimers in the gas phase, which were precursors for diamond growth [8], however, a spectroscopic analysis of the plasma was required to confirm this hypothesis.

As seen in Fig. 6, diamond quality, at a fixed methane concentration, increased with increasing pressure, as indicated by the sharp characteristic diamond peak in Raman Spectra. At lower pressures, only broad D and G bands existed, as shown in Fig. 6 A and B. The ratio of the intensity between the D and G peaks was  $\sim 2$ , and the G peak as positioned at  $\sim 1600\text{ cm}^{-1}$ , again indicating a nano-crystalline graphite structure.

SEM results shown in Fig. 6 also indicated two distinct morphologies, which corroborated the results from the Raman spectra. At higher pressures, the films showed well-faceted diamond morphology with facets larger than  $1\text{ }\mu\text{m}$ . In contrast, growth at lower pressures and high methane concentration yielded only graphitic-flakes.

From these experiments, it was concluded that for any fixed methane concentration, there was a minimum pressure requirement for growth of diamond, as indicated in Fig. 6.

### 4. Conclusion and outlook

In this work, the growth rate and quality of diamond film were investigated with pressure up to 125 Torr and methane concentration up to 10%. At a fixed pressure, the growth rate was proportional to the methane concentration in the source gas, while it exhibited a super-linear dependence on total pressure at a fixed methane concentration. Diamond quality depended strongly on pressure and methane concentration and at a certain combination of the two parameters. There was a relatively sharp transition from diamond to nano-crystalline graphite. At a fixed methane concentration, diamond growth was achieved only above a minimum pressure, while at a fixed pressure, diamond growth

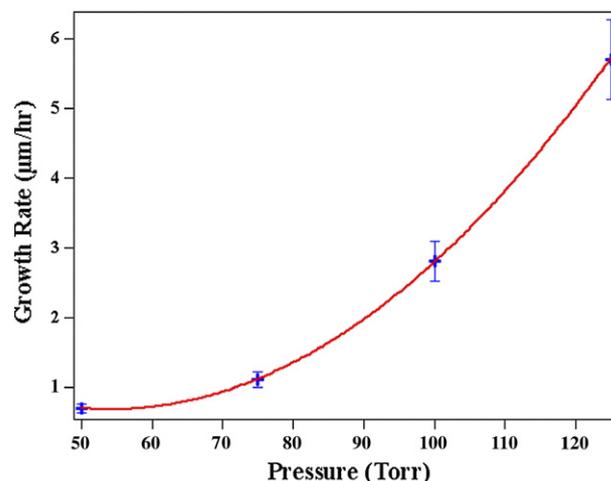


Fig. 5. Super-linear dependence of total pressure on the growth rate at a fixed  $\text{CH}_4$  concentration of 5%.

was only below a maximum methane concentration. Both parameters were interdependent; the maximum allowed methane concentration to increase with pressure, thus allowing higher growth rates.

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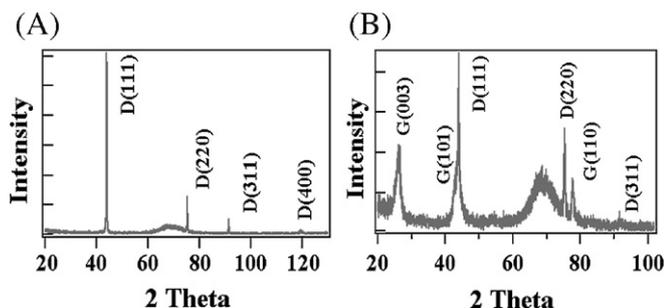


Fig. 4. XRD spectra corroborate the transition from diamond to nano-crystalline graphite with increasing methane concentration: (A) 0.75% methane concentration; (B) 10% methane concentration.

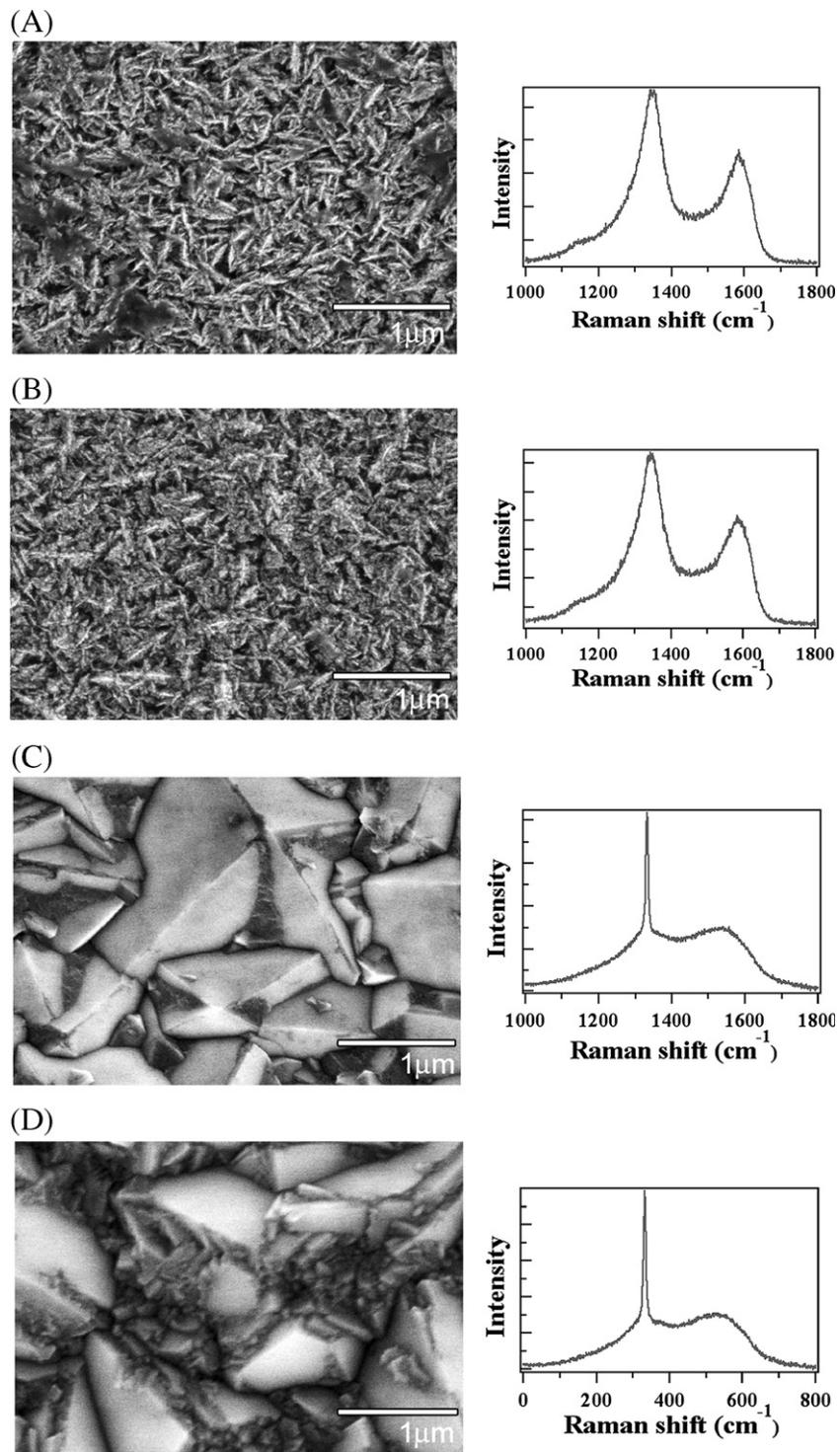


Fig. 6. SEM images and Raman spectra show the effect of total pressure on diamond crystal quality at a fixed methane concentration of 5%: (A) 50 Torr, (B) 75 Torr, (C) 100 Torr, (D) 125 Torr. Films change from nano-crystalline graphite (lower pressure) to diamond (higher pressure).