

Optical emission spectroscopic studies of microwave enhanced diamond CVD using CH₄/CO₂ plasmas

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Abstract

Diamond films have been grown using CH₄/CO₂ gas mixtures in a microwave plasma deposition reactor. Optimum growth of well-faceted polycrystalline diamond occurs at approximately 50% CO₂/50% CH₄ with a growth rate of approximately 1 μm h⁻¹ for a process pressure of 45 Torr and 1 kW applied power. Optical emission spectroscopic studies of CH₄/CO₂ microwave plasmas have been performed for a range of different process conditions, and the results correlated with diamond film quality and growth rate. Emission spectra (300–800 nm) are presented for gas compositions ranging from 100% CO₂ to 100% CH₄. Spectral peaks from electronically excited C₂, C₃, CH, CO, O and H have been observed, and maxima in the ratios of the CH:C₂, CH:C₃ and H:C₂ emission intensities are all found to correlate with process conditions for good quality diamond. By assuming that the rising spectral background at long wavelength can be attributed to blackbody radiation from macroscopic carbonaceous particles, we estimate the average gas temperature of the plasma to be 1925 K. For 100% CO₂ plasmas, emission peaks from atomic Mo are observed, indicating etching of the Mo substrate holder. © 2000 Elsevier Science S.A. All rights reserved.

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1. Introduction

Diamond films grown by chemical vapour deposition (CVD) have attracted much interest during recent years because of their outstanding mechanical, thermal, optical, electrical and chemical properties [1,2]. Well-established conditions for diamond growth include the use of a high substrate temperature (>700°C) and a carbon-containing precursor gas diluted in excess hydrogen (typically <5% CH₄ in H₂) [3]. A major goal for CVD diamond technology is the development of low temperature (<500°C) deposition processes, since this could permit the use of a wider range of substrate materials. The search for a suitable low temperature deposition process has led to the investigation of many gas mixtures, including those involving additions of halogens [4], as well as different combinations of H₂, CH₄, O₂, CO and CO₂ [5–12]. Bachmann et al. [13] collated the results of over 70 such deposition experiments to produce an atomic C–H–O phase diagram for diamond deposition

showing that low pressure diamond synthesis is only feasible within a well-defined domain centred on the H–CO tie line. Using a model of competitive deposition of diamond and non-diamond phases, Ford was able to rationalise this phenomenon [14]. An important conclusion was that the exact nature of the source gases was unimportant for most CVD diamond processes, and that it was only the relative ratios of C, H and O that controlled deposition.

Recently, there have been a number of reports suggesting that the use of CH₄ mixed with around 50% CO₂ or CO in microwave CVD plasmas offers a number of advantages over the more conventional gas mixtures [8,10,15]. The CO₂–CH₄ and CO–CH₄ systems are unusual in that they contain very little hydrogen compared to the excess needed in other processes. It is believed that the presence of O₂, O and OH species in the plasma [15] performs some of the role of the H atoms, such as etching of non-diamond carbon [10] and decreasing the concentration of gas phase unsaturated hydrocarbons [16]. As a result, diamond growth temperatures as low as 180°C have been reported for CO₂–CH₄ chemistries [12].

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Despite the high growth rates, good quality films and low deposition temperatures available with these newer gas mixtures, there has still been relatively little diagnostic work to understand how the chemistry differs from that in conventional CH_4/H_2 systems. Balestrino et al. [5] performed optical emission spectroscopy (OES) on CO_2/CH_4 and $\text{CO}_2/\text{C}_2\text{H}_2$ plasma systems and found a correlation between the quality of the diamond films and the ratio of the CH (431 nm) peak intensity to the C_2 (505–517 nm) band intensity, and suggested that this can even be used as a practical gauge to optimise diamond growth conditions. However, they did not investigate higher methane concentrations due to problems with graphite deposition in the chamber [17]. Mollart and Lewis [10] extended this work for a wide range of CH_4/CO_2 gas mixtures using higher pressures and microwave powers (140 Torr, 6 kW). They found that the ratio of the H_α (656 nm) and C_2 (516 nm) emission peaks varied with gas composition, but that this ratio had only a weak correlation with the diamond deposition domain.

However, the OES diagnostic work published to date has either been limited to a small wavelength range or only performed for a small number of gas compositions, usually close to the diamond growth domain. In this work, we report detailed OES measurements on a variety of CH_4/CO_2 and CH_4/CO plasmas over a wide composition range, extending well beyond the diamond domain.

2. Experimental

All deposition runs were performed using an ASTeX-style 2.45 GHz microwave plasma CVD reactor. The reactor chamber is water cooled, and contains a molybdenum substrate holder capable of being independently heated to 1000°C. Films were deposited on $\sim 2\text{ cm}^2$ single crystal (100) silicon wafers, manually pre-abraded with 1–3 μm diamond powder.

Most of the deposition runs did not require any additional substrate heating — temperatures of around $625 \pm 50^\circ\text{C}$ (as measured by two-colour optical pyrometer) were achieved solely by plasma heating. Films were grown for a duration of 8 h at a pressure of 45 Torr and 1 kW microwave power. The feedstock gas mixture contained varying ratios of CH_4 , CO_2 and CO with total flow rate $\sim 100\text{ sccm}$ with no additional hydrogen. We found that striking the plasma proved problematic when CH_4 was present in the chamber at concentrations $>10\%$, therefore plasmas were initially struck in pure CO_2 . The required concentration of CH_4 was then introduced after the operating temperature had been achieved ($\sim 10\text{ min}$) and the subsequent deposition performed for the allotted time.

OE spectra were obtained using an Oriel InstaSpec IV spectrophotometer. The emission from the plasma exiting through a viewport was focused onto a quartz

fibre-optic bundle. The focusing telescope and adjustable iris could be translated horizontally and vertically so as to sample light from different regions of the plasma ball with a spatial resolution of about 3 mm. The light was dispersed using a grating onto a CCD detector giving a resolution better than 0.3 nm. Emission spectra were obtained for a 300–800 nm window and peak intensities were corrected for the wavelength dependence of the grating reflectivity and the efficiency of the CCD.

Films were examined using scanning electron microscopy (SEM) to determine crystal morphology and film thickness, and by 514.5 nm (Ar^+) laser Raman spectroscopy (LRS) for film quality.

3. Results

3.1. Plasma emission observations

Fig. 1 shows the appearance of the plasma with differing CO_2 – CH_4 gas composition. In a CO_2 -rich mixture the plasma ball is uniform and bluish-white in colour. With increasing CH_4 addition the plasma colour takes on a slight yellow–blue tinge, especially towards the edges of the plasma. Above 60% CH_4 a distinct orange halo is observed surrounding the main plasma ball, becoming fainter and more diffuse further away from the centre (as seen in Ref. [5]). A bright violet/purple emission was observed from the region a few millimetres above the Si substrate surface.

3.2. Diamond deposition results

Also shown in Fig. 1 are examples of crystal morphologies grown using the different gas mixtures, with growth rates and Raman spectra presented in Fig. 2. Fig. 2a shows that no growth occurs below 44% CH_4 (in accord with the non-growth region of the Bachmann diagram [13]), but at higher $\text{CH}_4\%$ the growth rate rapidly increases. The films in this region exhibit well-faceted crystals (see Fig. 1), and give a relatively sharp 1332 cm^{-1} Raman line (see Fig. 2b), indicating good quality diamond. Above $\sim 50\%$ CH_4 content the growth rate increases more slowly, finally plateauing at $\sim 60\%$, and is accompanied by a broadening of the Raman line, indicating a decrease in diamond quality. Broad Raman features at 1120 – 1150 cm^{-1} indicate that deposition of nanophase diamond is also occurring at these gas compositions, along with disordered graphite (1460 – 1480 cm^{-1}) and ordered graphite (1550 cm^{-1}) [18]. The crystal size also decreases at higher $\text{CH}_4\%$, becoming more ‘ballas’-like. Optimal growth and quality occur at approximately the same composition — just under 50% CH_4 . These results agree with the sharp cut-off in the Bachmann diagram diamond domain, and with the results of Refs. [5,10]. Furthermore, by decreas-

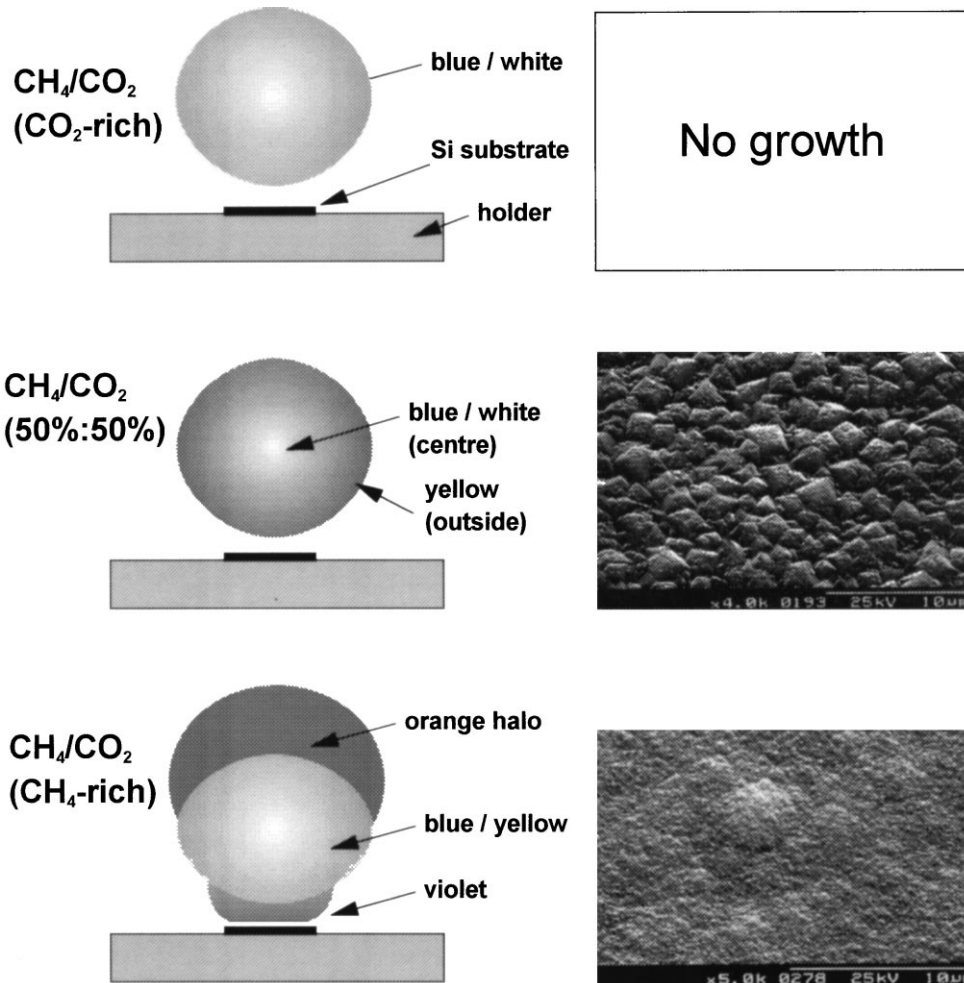


Fig. 1. Plasma appearance for different gas mixtures, along with electron micrographs illustrating the morphology of the diamond films grown under those conditions.

ing the microwave power, and with it the substrate temperature, we found it was possible to deposit good quality, (111)-faceted diamond films at reasonable rates ($0.5\text{--}1\ \mu\text{m h}^{-1}$) and at temperatures as low as 500°C .

3.3. Optical emission spectra — determination of plasma temperature

Evident in all spectra taken from plasmas containing $>30\%$ CH_4 is a rising baseline signal upon which various emission peaks are superimposed. An example is shown in Fig. 3 for a 50% $\text{CH}_4/50\%$ CO_2 plasma. This baseline is repeatable, and increases in intensity roughly in relation to the CH_4 content in the plasma, coincident with the yellowing in colour of the plasma ball and emergence of the orange halo. We propose that these features can all be explained by the creation of carbonaceous soot particles within the plasma, which then thermally diffuse to the cooler regions at the edge of the plasma and chamber walls. Evidence for this model is the fact that at the higher CH_4 content plasmas

soot was found to deposit on the walls of the chamber. Since the soot particles are macroscopic, they should attain approximate thermal equilibrium with species in the plasma bulk. Such particles should therefore radiate, and the characteristic colour of the emission could provide a measure of the plasma temperature. Thus, we attempt to model the rising background using a black-body Planck distribution [19] of the form:

$$B_\lambda = \frac{8\pi hc}{\lambda^5} \left[\exp\left(\frac{hc}{k_B \lambda T}\right) - 1 \right]^{-1}$$

where B_λ is the power density at wavelength λ , h is Planck's constant, c is the speed of light, k_B is the Boltzmann constant, and T the plasma temperature. To model the observed emission, we first convert the calculated power density into photon counts by dividing B_λ by the photon energy (hc/λ) at each wavelength λ . T was then used as a fitting parameter to match, with a pleasing degree of accuracy, the calculated curve to the experimental curve, as shown by the dashed line in

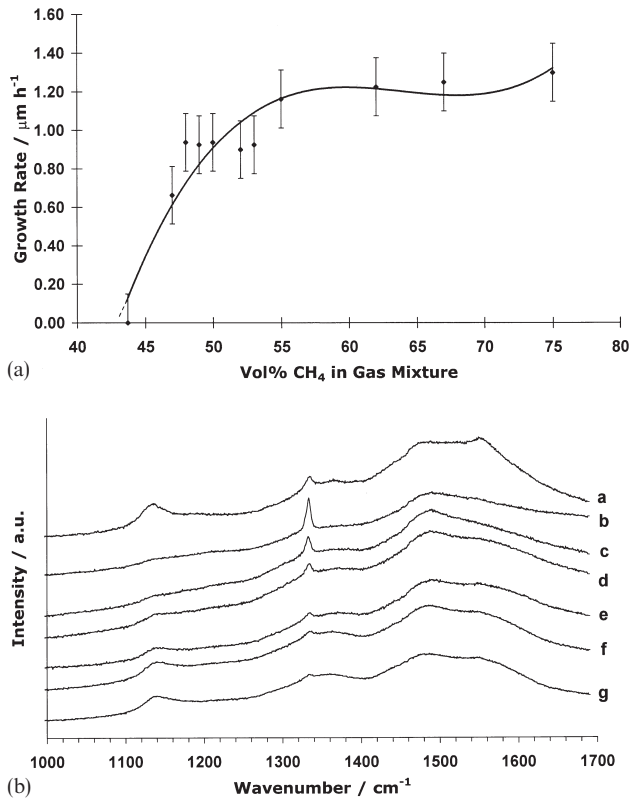


Fig. 2. (a) Film growth rate versus methane content in CH_4/CO_2 plasmas. Conditions: 1 kW microwave power, substrate temperature 650°C , total gas flow 100 sccm, pressure 45 Torr, growth time 8 h. Good quality diamond was only produced in the rising part of the curve between 45% and 55% CH_4 . In the plateau region (above 55%) the film became increasingly nanocrystalline with rising graphitic content [as shown in the Raman spectra in (b)]. (b) Raman spectra of films grown in CO_2/CH_4 mixtures with varying CH_4 content, other conditions as in (a). CH_4 content: a, 47%; b, 50%; c, 55%; d, 60%; e, 65%; f, 70%; g, 75%.

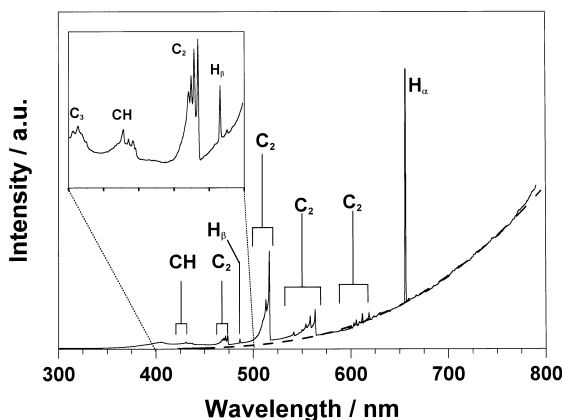


Fig. 3. An optical emission spectrum for 50% $\text{CH}_4/50\%$ CO_2 plasma, with peak assignments. Inset is an expanded region between 400 and 500 nm illustrating the structure within the weak CH and C_2 bands. Shown as a dashed line in the main figure is the calculated curve corresponding to emission from a blackbody having a temperature of 1925 K, highlighting the close match to the rising spectral background.

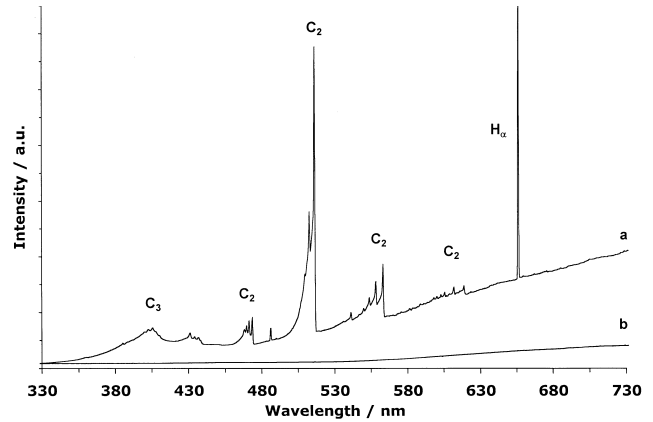


Fig. 4. Optical emission spectra from two different regions of a 100% CH_4 plasma: (a) the centre of the plasma; (b) the orange halo. Refer to Fig. 1 for an illustration of the different regions.

Fig. 3. This procedure yielded an average plasma temperature (in the regions containing the emitting carbonaceous particles) of ~ 1925 K. Note, however, that this value for an ‘average’ plasma temperature must be treated with some caution, since in reality there will be a smoothly varying temperature gradient along the sampling column. Nevertheless, it is reassuring to note that the temperature estimated by this method is consistent with values estimated by other methods in plasma systems of similar power and design [20].

Fig. 4 shows two example emission spectra taken from a 100% CH_4 plasma. The spectrum from the centre of plasma (a) is much brighter than that from the halo region (b), and we see the rising background with superimposed emission lines from H, C_2 and C_3 . The main difference between Fig. 4a and the previously seen 50% CO_2/CH_4 spectrum (Fig. 3) is that the C_3 band (~ 405 nm) is relatively more intense with respect to the C_2 bands, suggesting a greater tendency for the carbon radicals to aggregate into larger species in pure CH_4 plasmas. In contrast, the spectrum from the halo region (b) exhibits only the rising blackbody background with no discernible emission lines. This is probably because the electron energies at the extremities of the plasma ball are insufficient to cause the relevant molecular excitation processes. Spectra from the violet emission near the substrate (not shown) are very similar in appearance to that from the centre of the discharge, except that the intensities of the blue and violet C_2 emissions bands (450–475 nm and 500–515 nm) are relatively more intense.

3.4. Optical emission spectra — correlation of emission lines with diamond growth

As shown in Fig. 3, the spectra from CH_4/CO_2 mixtures are dominated by Swan band emission from C_2

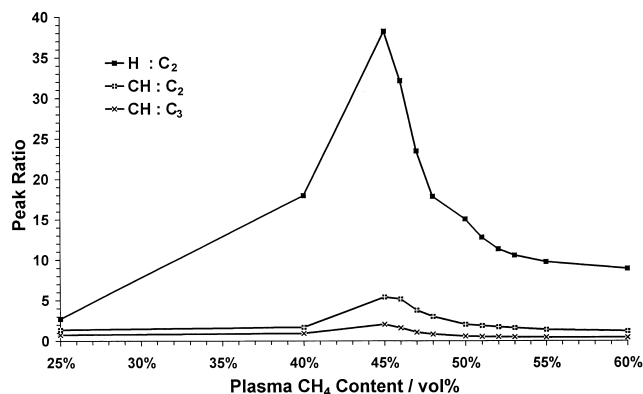


Fig. 5. The emission intensity ratios for CH (431.4 nm):H (656.1 nm), CH:C₂ (473.6 nm), CH:C₃ (405.4 nm) and C₂:C₃ as a function of CH₄ content in the gas mixture. Other conditions are given in the caption to Fig. 2a.

species, although sharp peaks are also seen for atomic H(α, β). Also present in some spectra were CH peaks at ~ 389 and 431 nm and the C₃ band seen at ~ 405 nm [21], the latter becoming more pronounced at higher CH₄ contents and in the violet region of the plasma near the substrate. The emission line intensity ratios for different pairs of species can be obtained by measuring the heights of the relevant peaks above the blackbody baseline mentioned earlier. We found a reasonable correlation between diamond growth rate and/or quality with the intensity ratios for H:C₂, CH:C₂ and CH:C₃, however, there is an offset of $\sim 5\%$. Fig. 5 shows that the three ratios have a maximum value at around 45% CH₄ content, whereas the observed diamond film quality [as determined from the full-width at half-maximum (FWHM) of the Raman lines seen in Fig. 2b] occurs at 50%. Clearly, such peak ratios can be used as an indicator of the process region close to optimal diamond growth conditions (as observed in Ref. [5]), but some degree of empirical process refinement must still be performed to determine the optimum process gas ratio for a particular deposition system.

We also found that the C₃ (405.4 nm):CH (431.4 nm) peak ratio increases slowly from a value of ~ 0.25 to ~ 1 as the CH₄ content increases from $\sim 25\%$ to 100% . This is consistent with there being a gradual increase in the size of carbon chains present in the plasma, from predominantly C₁ species (such as CH₃) favourable to diamond growth at low CH₄ content, to C₂ and then C₃ species at higher concentrations, finally leading to polymeric carbon or soot particles at still higher CH₄ concentrations.

3.5. Optical emission spectra from 100% CO₂, CO and CH₄ plasmas

Fig. 6 shows emission spectra taken for the two extremes of the gas mixture, 100% CO₂ and 100% CH₄,

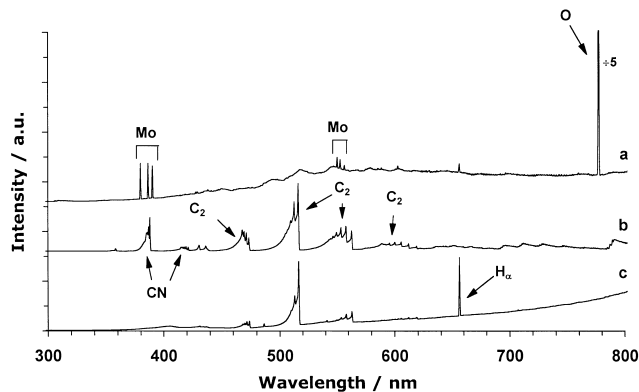


Fig. 6. Optical emission spectra from the centre of the plasma for varying composition: (a) 100% CO₂; (b) 100% CO; (c) 100% CH₄. The spectra have been displaced vertically for clarity. Note the atomic O line and Mo lines in (a) as well as possible CO bandheads at ~ 450 , 494 , 519 nm. Note also that the O line is in fact ~ 5 times larger and has been cut off for clarity.

as well as a spectrum from 100% CO for comparison. The spectrum for the pure CH₄ plasma (Fig. 6c) is not significantly different from those seen for CH₄/CO₂ mixtures (compare Fig. 3). However, the spectrum for pure CO₂ (Fig. 6a) shows notable differences from those from other compositions. First, there is no rising blackbody background, suggesting very few gas phase soot particles. Also evident is intense emission from atomic oxygen (777.1 nm) and possible CO bandheads (450 , 494 , 519 nm), as well as some very intense lines that can be assigned to atomic Mo. When the Mo substrate holder was covered in an alumina shield, the intensity of these lines was greatly reduced. Therefore, we conclude that these lines result from the etching of the Mo substrate holder. We observed that the Mo emission lines only appeared when the substrate holder temperature was above 500°C , and that if the holder was covered in a diamond coating from previous deposition experiments, there would be a delay of several minutes before the Mo lines appeared. We believe that this delay is due to the atomic O present in the plasma slowly etching away the diamond coating on the substrate holder to expose the Mo. A possible etching mechanism involves CO (created from the dissociation of CO₂ into CO and O) reacting with the hot Mo surface to form volatile Mo(CO)_x ($x=1-6$) compounds, which then desorb into the gas phase, and are there dissociated by electron impact to form CO and excited Mo*. The surface of the Mo holder was seen to turn yellow over a period of 20 min due to probable formation of MoO₃. Addition of even 0.5% CH₄ into a CO₂ plasma immediately caused the plasma to change colour from a bright white to light cyan, and all Mo peaks disappeared. This is probably because even small amounts of CH_x species reacted with and removed all the free O atoms, preventing the etching process.

Interestingly, a 100% CO plasma (Fig. 6b) behaves very differently from a 100% CO₂ plasma. There is still no blackbody background, but the CO spectra shows neither the Mo lines nor the atomic O line, and is dominated by C₂ emission. Comparing the C₂ bands in Fig. 6b and c, it is evident that the vibrational population distributions observed in the two spectra are very different. C₂* originating from a CO plasma is very highly vibrationally excited, suggesting either a much hotter plasma or, more probably, that the C₂* arises from exothermic chemical reactions involving metastable triplet CO species. We also found that CO plasmas did not etch the substrate holder. We believe that this is due to the fact that CO is very stable and does not readily dissociate to form O. Without atomic O to etch the diamond coating from the holder, the underlying Mo cannot be attacked and etched. Also seen in the CO spectrum are peaks due to the violet CN system at 387–388.4 and 421.6 nm. These result from N₂ impurities in the CO gas bottle, which were at a much higher value (0.5%) than in the other gases (0.005%).

4. Conclusions

CH₄/CO₂ plasmas show considerable promise for high quality, low temperature deposition processes. The OES results presented here and elsewhere have provided insight into some of the chemical processes responsible for diamond growth in these systems. However, we recognise that OES only provides information on the small range of species that emit in the wavelength range for which we have detection sensitivity. Future work will involve quantitative measurements of the concentrations of the ground state and other non-emitting species present within the plasma, both by absorption spectroscopy and by in situ molecular beam mass spectroscopy.

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