Correlation between optical emission spectra and the process parameters of a 915 MHz microwave plasma CVD reactor used for depositing polycrystalline diamond coatings

AWADESH KUMAR MALLIK*, SANDIP BYSAKH,
SOMESWAR DUTTA and DEBABRATA BASU

CSIR - Central Glass and Ceramics Research Institute, Kolkata 700 032, India
e-mail: amallik@cgcricri.res.in

MS received 5 October 2012; revised 27 March 2014; accepted 28 March 2014

Abstract. In this paper, the hydrogen and hydrogen-methane mixed plasma have been generated inside a 33 cm diameter quartz bell jar with a low power (9 KW) and lower frequency 915 MHz microwave plasma chemical vapor deposition system. The reactor is being used for growing polycrystalline diamond (PCD) over large area (100 mm). The generated plasma is diagnosed by *in situ* optical emission spectroscopy method with wave length ranging from 200 to 900 nm. The effects of microwave power, chamber pressure and gas concentration on plasma characteristics have been studied in this work. Within the optical range, Balmer H_α , H_β , C_2 swan band and CH lines have been detected at the wavelengths of 655.95, 485.7, 515.82 and 430.17 nm, respectively. It has been observed that for hydrogen plasma, the amount of transition from hydrogen atom inner shell 3 to 2 (H_α) is almost constant with increasing microwave (MW) power (from 2000 to 2800 W) and pressure (from 15 to 30 Torr) initially, after that it increases with further increase of MW power and pressure, whereas, the transition from 4 to 2 (H_β) is slowly increased with increasing MW power and pressure. For hydrogen-methane plasma, intensities of C_2 swan band, i.e., the transitions from $D^3\Pi_g$ to $A^3\Pi_u$ energy levels, are also increased with the increasing microwave power and reactor pressure. It has been observed that the radicals present in the plasma are affected by variation of different reactor parameters like pressure, MW power, CH_4 concentration, etc.

Keywords. Optical emission spectroscopy; 915 MHz; microwave plasma CVD; polycrystalline diamond.

1. Introduction

Nowadays H_2 - CH_4 mixed plasmas are widely used for synthesis of diamond like carbon, amorphous carbon, diamond, carbon nanotube, grapheme, etc. using microwave and radio frequency

*For correspondence

plasma reactors (Okada *et al* 2003; Vazquez *et al* 2006; Lombardi *et al* 2004). Many researchers have studied H_2 and H_2 - CH_4 mixed plasma in different types of reactors such as hot filament chemical vapor deposition (HFCVD), Flame CVD, Microwave plasma chemical vapor deposition (MPCVD) (Larijani *et al* 2007; Dua *et al* 2004; Konjevic *et al* 2009; Li *et al* 2006; Ghajar and Bang 1993) and reactor of other types. Every deposition techniques has some advantages and disadvantages, but, good quality diamond can be deposited mainly using MPCVD reactor because it has no filament, cathode or anode inside the chamber, which thereby reduces the chances of contamination of the growing film. Growth of the good quality PCD inside a MPCVD reactor depends on the processing parameters. So an understanding of the reactor parameters and how does it influence the radicals present during PCD growth, will help to develop diamond coatings more efficiently for the intended applications. Langmuir probe, mass spectroscopy are the techniques available for *in situ* plasma diagnostics. But OES offers easier and non-contacting process for qualitatively and quantitatively diagnosing the plasma. It is an effective *in situ* plasma diagnostic tool for laboratory and industrial plasma, because it does not require any external light source for plasma investigation (Zuo *et al* 2008; Grotjohn *et al* 2005).

Microwave propagation depends on the geometry of the cavity. So there are many cavity parameters, like stage height, short length, probe length, diameters of the cavity, which determine the plasma formation at the correct location inside the cavity over the substrate. Moreover, other processing parameters such as microwave power, process gas flow, pressure, substrate temperature, etc. have important roles in controlling shape and size of the plasma over the substrate (Gicquel *et al* 2002; Lee & Chung 2005; Keys & Home 1926). Vazquez *et al* (2006) have studied the effect of plasma parameters such as power, pressure and Ar population density, of a H_2 - CH_4 -Ar rich plasma and another H_2 - C_2H_2 -Ar rich plasma, in a capacitive coupled radio frequency reactor. Lee & Chung (2005) diagnosed the hydrogen plasma characteristics using a radio frequency power source with *in situ* optical emission spectroscopy. Zuo *et al* (2008) showed that the substrate temperature profile and diamond film uniformity depends on pressure and microwave power for H_2 - CH_4 gas mixture inside a 2.45 GHz microwave plasma reactor. Tan & Grotjohn (1995) showed that the plasma volume decreases with increasing pressure, for a low pressure and low power plasma. Fu *et al* (1999) studied that, at the time of nucleation, the ratio of CH_4 and H_2 should be kept high, whereas, at the time of diamond growth, this ratio should be low for improving the quality. Okita *et al* (2007) showed that at a particular pressure, the density of CH_3 radical increases and the density of atomic hydrogen decreases, with decreasing $[H_2]/[CH_4+H_2]$ gas mixture ratio. Su & Chang (2008) observed that the intensities of C_2 , H_2 , H_α , H_β , CH plasma species depend on the substrate temperature, gas concentration and other processing parameters in the microwave plasma jet chemical vapor deposition (MPJCVD) system. Surface morphology and grain size were also influenced by plasma species in their study. Ma *et al* (2009) subdivided the plasma species into two groups according to their chemistry of generation. The production of species such as Ar, H_2 , and H atoms were attributed to the electron dominated chemistry, while the other species such as C_2 and CH exhibited the characteristic of thermally driven chemistry. They also showed quite different trends of these two families of species with variation in discharge parameters like power, pressure, CH_4 flow rate, etc. Lang *et al* (1996) reported that the intensities of the Balmer H_α , H_β , and H_λ lines are increased with increase in the CH_4 concentration up to 0.8% of the total gas mixture, and then the line intensities decreases with further increase in CH_4 concentration, in microwave-assisted plasma chemical vapor deposition system using CH_4 - H_2 -Ar gas mixture.

Literature survey reveals that the correlation between plasma species and reactor parameters is not so far reported for a 915 MHz frequency and low power (8–10 kW) microwave plasma chemical vapor deposition (MWPCVD) system, using optical emission spectroscopy (OES).

Using such microwave reactor authors have already reported optimization of the CVD processing parameters for growing diamond over large area (Mallik *et al* 2013). They have also studied in detail about the effect of microwave reactor parameters on thermal management of silicon substrate for uniform diamond deposition (Mallik *et al* 2012). In another paper, authors have described in detail about the property mapping of such diamond coatings over large area (Mallik *et al* 2014). In all of these previous publications the correlation between plasma reactor species and good quality coating has not been reported by the authors. To fill the gap in research of characterizing plasma species for growing good quality coating, here, H_2 and H_2-CH_4 mixed plasma have been ignited inside the same 915 MHz MWPCVD reactor (reported in the earlier papers) over 100 mm diameter Silicon wafer for deposition of polycrystalline diamond coating. The plasma formation characteristics have been diagnosed by OES with this type of MWPCVD reactor. Different plasma species and their concentrations were monitored by *in situ* OES while varying the reactor parameters.

2. Materials and methods

2.1 MPCVD reactor

H_2 and H_2-CH_4 mixed plasma were generated with a 915 MHz and 15 KW microwave power source (Lambda Technologies DT 1800) inside a 33 cm quartz fused bell jar with water cooled stage over a 100 mm silicon wafer (King *et al* 2008). The wafer was cleaned successively with de-ionized water, acetone and methanol in an ultrasonic bath. Then the substrate was seeded with detonation nano diamond (DND) slurry (ITC, USA) using the same ultrasonic bath for diamond nucleation enhancement (Shenderova *et al* 2010). The schematic of MWPCVD reactor with OES attachment is shown in figure 1. The Silicon substrate is heated by the microwave plasma and its temperature is maintained at around 1050°C. In order to maintain the structural integrity of the substrate holder, cold water at 25°C is flown through the inside of the holder, using a ball valve and a flow meter. The generated microwave energy from the magnetron (® Alter) propagates through the waveguide and is launched into the cavity through an antenna, called probe. Roughing pump (Edwards, model XDS 35i) and turbo pump (BOC Edwards) have been used for evacuating the chamber and its pressure is measured and controlled by suitable pressure gauges (MKS Baratron, Type 623) and valves (MKS type 153). The flow rates of precursor gases have accurately been maintained by mass flow controllers (MFC, MKS, type 1179A). Whereas, the substrate temperature is monitored using a double wavelength optical pyrometer (Williamsons, USA) and it is focused towards the middle of the substrate. By adjusting the probe, stage and short positions, the plasma is created inside the quartz bell jar using 99.9999% pure H_2 . Hydrogen gas is produced by electrolysis of de-ionized water in H_2 generators (Stirling Cryogenics, NMH₂ 600) whereas, 99.999% pure CH_4 (BOC India) is supplied from standard 47 liters cylinder for growing PCD.

2.2 Diamond recipe

A recipe has been adapted for deposition of diamond as per table 1. Initially, the MW power and pressure were increased simultaneously up to 5000 W power and 70 Torr pressure, over a certain period of time only under Hydrogen plasma. After that, CH_4 is added to the H_2 plasma and further, the power and pressure are simultaneously increased up to 8000 W and 110 Torr, respectively. H_2 plasma and H_2-CH_4 plasma, thus generated by this recipe, are diagnosed with the help of *in situ* optical emission spectroscopy (Ocean optics, USB 4000).

Figure 1. Schematics of microwave plasma chemical vapour deposition (MWPCVD) system.

Table 1. Process recipe program for diamond deposition inside the 915 MHz microwave plasma CVD reactor.

Rough down
Set short: 58.50 cm
Set Probe: 8.70 cm
Set stage: 0.5 cm
Set H ₂ flow: 500 sccm
Set pressure: 5 Torr
Set time: 00:00:30 HH:MM:SS
Strike plasma: 1500 Min Watts, 1800 Max Watts, 8 Max Secs
Ramp: 70 Target torr, 5000 Target Watts, 500 Target Secs, 600 Max Secs
Set time: 00:00:08 HH:MM:SS
Set H ₂ flow: 1000 sccm
Set CH ₄ flow: 10 sccm
Ramp: 110 Target torr, 8000 Target Watts, 300 Target Secs, 400 Max Secs
Set time: 00:00:05 HH:MM:SS
CH ₄ flow: 25 sccm
Set time: 30:00:00 HH:MM:SS
Auto shutdown: Executes the shutdown recipe

In this paper, H_2 plasma and H_2 - CH_4 plasma, at different chamber pressures, MW powers and methane concentrations, have been studied, while running the diamond growth recipe program in the 915 MHz reactor unit. Once the adapted recipe program is running under equilibrium condition to deposit polycrystalline diamond (PCD), variation of the process parameters are being done further, one by one, in order to assess the suitable plasma environment for high quality PCD growth.

2.3 Optical emission spectroscopy (OES)

Optical emission spectrometer consists of sub-components like optical fibre, slit, optical filter, optical bench, grating, focusing mirror, detector, etc. The block diagram of OES arrangement is given in the figure 2. One end of the Optical fibre is connected to the optical bench by one Sub Miniature version A (SMA) 905 connector and the other end is focused onto the plasma ball. The collected light from the plasma is entered through a rectangular aperture of about 5–200 micron. This light is then passed through a band pass and long pass filter, so that only 200–900 nm wavelength of radiations are allowed. The filtered light is then reflected off from the collimating mirror and onto the grating. Focusing mirror receives the diffracted light from the grating and further focuses them onto the detector which converts them into a digital signal. This digital signal is read by using a software application called ‘Overture’ in the connected computer (www.oceanoptics.com 2012).

2.4 Characterizations of diamond

Quality, thickness and surface morphology of the deposited PCD coatings have been evaluated using Raman spectroscopy (HR-800, HORIBA Jobin Yvon, Japan), and field emission scanning electron microscopy (Supra 35VP, Carl Zeiss, Germany), respectively.

3. Results and discussion

3.1 Hydrogen plasma

Microwave (MW) with maximum power capacity of 15 kW and of 915 MHz frequency, has been used in the present study for growing polycrystalline diamond coatings. Initially, H_2 plasma is

Figure 2. Block diagram of optical emission spectroscopy (OES) measurement technique.

ignited at 5 Torr pressure and 1500 W power, with 0.5 cm of stage height and 500 sccm of H_2 gas flow. Figure 3a shows the OES spectrum of the ignited plasma. Balmer H_α , H_β and Fulcher α H_2 lines have been identified at 655.95, 485.7 and 602.76 nm wavelengths, respectively. Now, the pressure and power are successively ramped up, as per the following program of the CVD recipe: a) 15 Torr, 2000 W; b) 30 Torr, 2800 W; c) 40 Torr, 3350 W; d) 50 Torr, 3900 W; e) 55 Torr, 4200 W; f) 60 Torr, 4450 W; g) 70 Torr, 5000 W, while the other reactor parameters were kept unchanged. Figure 4a shows the variations of the peak height intensities of the respective H_α and H_β lines, due to simultaneous change in MW power and reactor pressure. Figure 4a also shows that the H_α line intensity (I_{H_α}) is higher than the H_β line intensity (I_{H_β}). This is due to the fact that more electrons go to the energy level corresponds to $n = 3$ by absorbing small amount of energy, rather than going to the next higher energy level of $n = 4$. So the number of transitions from $n = 3$ to 2 is higher, than the transitions from $n = 4$ to 2. As a result, the H_α line is more intense.

3.1a Microwave power and pressure effect: From figure 4a it is observed that the peak height intensity (I_{max}) of Balmer H_α line remains nearly constant from 15 Torr to 30 Torr pressure and

Figure 3. Optical emission spectrum of (a) Hydrogen plasma at H_2 flow rate of 500 sccm with different MW powers (from 2000 to 5000 W) and different pressures (from 15 to 70 Torr); (b) H_2 - CH_4 plasma at different MW power levels, while pressure, H_2 flow rate and CH_4 flow rate are kept constant at 110 Torr, 1000 sccm and 10 sccm, respectively; (c) H_2 - CH_4 plasma at different reactor pressure levels, while MW power, H_2 flow rate and CH_4 flow rate are kept constant at 9000 W, 1000 and 25 sccm, respectively; (d) H_2 - CH_4 plasma at different CH_4 concentrations, while MW power, pressure and H_2 flow rate are kept constant at 9000 W, 110 Torr, 1000 sccm, respectively (for all the above variations a, b, c and d, stage height = 0.5 cm, probe height = 8.7 cm and, short length = 58.5 cm).

Figure 4. Peak height intensity plots of (a) H α , H β lines with corresponding variable power and pressure levels and other similar parameters as shown in figure 3a; (b) H α , H β , C $_2$, CH lines and the ratio of $I_{C_2}/I_{H\alpha}$ with corresponding variable MW power levels and other similar parameters as shown in figure 3b; (c) H α , H β , C $_2$, CH lines and the ratio of $I_{C_2}/I_{H\alpha}$ with corresponding variable reactor pressure levels and other similar parameters as shown in figure 3c; (d) H α , H β , C $_2$, CH lines and the ratio of $I_{C_2}/I_{H\alpha}$ with corresponding variable CH $_4$ flow rates and other similar parameters as shown in figure 3d (for all the above variations a, b, c and d, stage height = 0.5 cm, probe height = 8.7 cm and, short length = 58.5 cm).

from 2000 to 2800 W microwave power, and after that, the intensity of H α line is increasing with gradual increase of pressure (up to 70 Torr) and MW power (up to 5000 W). Whereas, the intensity of H β line is slowly increased with increasing of MW power and pressure. The reason behind such increment can be explained as the pressure increases then the mean free path of the gas molecules will decrease, so in effect, the collision probability among them will be increased. Also when MW power is increased, the electrons experience more energy inside the MW field and collide more vigorously with the gas molecules present in the plasma, which triggers greater number of electronic transitions from hydrogen inner shells, $n = 3$ to 2 and $n = 4$ to 2. As a result, the intensities of H α line are increased after a certain threshold value of pressure (30 Torr) and MW power (2800 W). So there is a combined effect of MW power and pressure, on the relative intensities of, both the H α and H β lines, at the beginning of the CVD diamond process recipe (table 1).

3.2 H $_2$ -CH $_4$ mixed plasma

According to the programmed recipe (table 1), 1% Methane in Hydrogen, was introduced into the H $_2$ plasma chamber, once the MW power and chamber pressure were ramped up to 5000 W

and 70 Torr, respectively. Further, the microwave power and pressure were again ramped up to 8000 W and 110, Torr respectively, within a time period of 400 s under H_2 – CH_4 mixed plasma. Finally, CH_4 was flown into the chamber, at 2.5% ratio to the hydrogen gas, as the final precursor recipe for polycrystalline diamond deposition. Thus, generated methane–hydrogen plasma, was probed by OES, and, its characteristics were recorded while successively varying MW power, reactor pressure and CH_4 concentration, but, only one parameter variation at a time. Table 2 (Lang *et al* 1996; Vandavelde *et al* 1999; Gorbachev *et al* 2007) shows the respective radical names and their corresponding transitions from the upper energy level to the lower energy level at certain wavelengths and corresponding reported literature values. H_α , H_β , CH lines have been detected at 655.95, 485.7 and 430.7 nm wavelengths, respectively. C_2 lines have been detected at three different frequency bands (from 553.59 to 562.9 nm, and from 512.4 to 515.82 nm and from 469.2 to 473.08 nm) for three different values of $\Delta\nu$ of -1, 0, and 1, respectively. Gorbachev *et al* (2007) numerically showed that the reaction time for generation of C_2 radicals from carbon containing species like CH_4 , CH_3 , CH_2 , CH, C, C_2H_6 , C_2H_5 , C_2H_4 , C_2H_3 , C_2H_2 , C_2H etc. is 0.1 ms, whereas, for the reverse reaction to occur, it takes 100 times longer duration of 10 ms. So it can be stated that since the life time of C_2 is higher than other carbon containing species inside the H_2 – CH_4 mixed plasma, C_2 radicals is detected but other carbon species, except CH, are not detected by OES. The variation of the peak height intensity ($I_{\max}$) values of C_2 ($\Delta\nu = 0$), CH, H_α and H_β lines with corresponding variations of MW power, pressure and CH_4 concentration, have been studied in this paper (figure 4).

3.2a Microwave (MW) power: Figure 3b shows the OES spectra of CH_4 – H_2 plasma when the MW power was varied from 7200 to 9500 W, while other parameters were not changed (110 Torr pressure, 1% CH_4). Plots of corresponding peak height intensity variations of H_α , H_β , C_2 , CH lines are shown in figure 4b with changing microwave power. The graphs are observed to move upwards with increase of MW power but with different slopes. This is due to the fact that the electrons absorb more energy from the increasing electromagnetic field and thereby collide more with the gases present in the plasma to generate more radicals corresponding to observed OES peaks.

It has been observed that although the peak height intensity of H_α line ($I_{\text{H}\alpha}$) increases (figure 4b) with increasing microwave power, but after 9000 W of MW power, the intensity of H_α line decreases, whereas, height of intensity for C_2 line (I_{C_2}) keep on increasing beyond 9000 W power. It is understood that for good quality of CVD diamond growth, the ratio of peak intensity heights $I_{\text{C}_2}/I_{\text{H}\alpha}$ should be kept as low as possible without compromising on the PCD

Table 2. Optical emission spectrum lines for H_2 – CH_4 mixed plasma.

Species	Observed wavelengths (nm)	*Reported literature values of wavelengths (nm)	Corresponding electronic transitions
H_α	655.95	656.3	Balmer $n = 3$ to 2
H_β	485.7	486.1	Balmer $n = 4$ to 2
H_2	602.76	602.1	$3p^3 \sum_u^+ \text{ to } 2s^3 \sum_g^+$
$\text{C}_2(\Delta\nu = +1)$	469.2–473.08	469.7, 471.5, 473.7	
$\text{C}_2(\Delta\nu = 0)$	512.4–515.82	512.9, 516.5	Swan $\text{D}^3\Pi_g \text{ to } \text{A}^3\Pi_u$
$\text{C}_2(\Delta\nu = -1)$	553.59–562.9	550.2, 554.0, 558.5, 563.5	
CH	430.79	431.4	$\text{A}^2\Delta \text{ to } \text{X}^2\Pi$

*Ma *et al* (2009), Vandavelde *et al* (1999), Gorbachev *et al* (2007)

growth rate. Since atomic hydrogen has an important role to etch out the non-diamond carbon, H_{α} value should be kept always higher. On the other hand, the concentration of CH_3 radicals is responsible for diamond phase formation, but as such there is no role of C_2 radicals for diamond CVD growth (Grotjohn & Asmussen 2002). Role of C_2 may be considered in the CVD growth of nanocrystalline diamond (NCD) (Rabeau *et al* 2004). It is the limitation of the OES plasma diagnostic method that it does not detect methyl radical, the main precursor for microcrystalline diamond CVD growth. But it is well-proven that the atomic hydrogen plays the most significant role in depositing high quality polycrystalline diamond (Piekarczyk & Prawer 1993; Johansson & Carlsson 1995; Dong *et al* 2002). So in this paper, it is attempted to search for an optimized process recipe, where, the $I_{C_2}/I_{H_{\alpha}}$ ratio is low/minimum at a given process parameter. Although the minimum value of $I_{C_2}/I_{H_{\alpha}}$ ratio is found to be 0.79 at 8800 W microwave power, but, 9000 W microwave power has been selected for optimum PCD processing, since the H_{α} value (5.274×10^4) is highest at such power level with an acceptable $I_{C_2}/I_{H_{\alpha}}$ ratio of 0.89 for good quality diamond deposition.

3.2b Reactor pressure: Figure 3c shows the OES spectra of CH_4 – H_2 plasma when the pressure was varied from 106 to 114 Torr, while other parameters were kept constant (MW power: 9000 W and CH_4 concentration: 2.5%). Since in the present case the methane percentage is kept at 2.5%, which is 2.5 times higher than the 1% CH_4 used in the previous section 3.2a for MW power variations, it is expected that the ratio of $I_{C_2}/I_{H_{\alpha}}$ will also get multiplied by 2.5 times. Figure 4c shows the plots of corresponding (figure 3c) peak height intensity variations of H_{α} , H_{β} , C_2 and CH lines with changing pressure. It is observed that the slope of the graph for C_2 is much steeper than the slope of the graph for H_{α} . This indicates that with the increase in pressure there is more and more formation of C_2 radicals compare to H atoms, which is well-reflected from the $I_{C_2}/I_{H_{\alpha}}$ ratio curve. The ratio of the peak height intensities for C_2 and H_{α} lines ($I_{C_2}/I_{H_{\alpha}}$) are significantly increased above 108 Torr (figure 4c). It is 2.57 (as expected in the tune of 2.5 times higher than the previous section 3.2a for microwave power variation) at 106 Torr but with increase in pressure from 108 to 114 Torr, the ratio rapidly increases from 2.63 to 3.08. This is due to the fact of rapid rise of the peak height intensities of C_2 (I_{C_2}) lines from 4.01×10^4 to 5.27×10^4 , whereas, the corresponding peak height intensity of H_{α} ($I_{H_{\alpha}}$) line increases very slowly from 1.56×10^4 to 1.71×10^4 , with increase in pressure. For good quality diamond growth, it is desired that the $I_{C_2}/I_{H_{\alpha}}$ ratio has to be kept as low/minimum as possible (Vandeveldel *et al* 1999), and as it is also essential to keep as much as atomic hydrogen in the reaction zone for high quality diamond growth. Though the ratio of $I_{C_2}/I_{H_{\alpha}}$ is least (2.57) at 106 Torr, 110 Torr reactor pressure has been chosen for the optimum recipe program, with $I_{C_2}/I_{H_{\alpha}}$ ratio of 2.79. This value is quite high when compared to the optimum condition ($I_{C_2}/I_{H_{\alpha}} = 0.89$) obtained in the previous section 3.2a, while varying only the microwave power. When the OES spectra were studied by changing only the MW power, the methane concentration was kept constant at 1%. But in the present case, while only varying the pressure, the methane concentration is kept constant at 2.5%. Figure 4d shows that the CH_4 percentage has been varied from 1 to 3% with step-wise increment of 0.5%. In the figure 4d, it can be observed that the $I_{C_2}/I_{H_{\alpha}}$ ratio is 1.3 at 2.5% methane percentage, when the MW power and pressure were kept constant at 9000 W and 110 Torr, respectively throughout such CH_4 % variations. So it is observed that, higher percentages of methane gas in the mixed plasma of CH_4 – H_2 , induces increased concentration of C_2 radicals, which is responsible for manifold increase of $I_{C_2}/I_{H_{\alpha}}$ ratio.

The reason behind choosing higher reactor pressure of 110 Torr over 106 Torr is to achieve higher substrate temperature of 1050°C for good quality diamond deposition. It has been found

that the substrate temperature remains below 1000°C at 106 Torr of pressure. Higher substrate temperature is necessary for good quality growth of CVD diamond.

3.2c CH₄ concentration: Figure 3d shows that the OES spectrum of H₂–CH₄ plasma at different concentrations of CH₄ gas, while the other parameters were kept constant (MW power: 9000 W and Pressure: 110 Torr). Plots of corresponding peak height intensity variations of H_α, H_β, C₂ and CH lines are shown in figure 4d, with changing methane percentages. From figure 4d, it is observed that the slope of the line corresponding to C₂ increases very fast, whereas, the similar plot for Balmer H_α line reveals slowly decreasing slope, with increasing percentages of CH₄ gas. The peak height intensity graphs for H_β and CH species remain parallel to the x-axis as shown in figure 4d. When the CH₄ concentration is 1.5%, the graphs of C₂ and H_α lines intersect with each other, i.e., the intensity ratio of I_{C₂}/I_{H_α} becomes 1. Since it is necessary to keep the C₂/H_α ratio below 1 for good quality diamond deposition, the 1% methane concentration in the present OES investigation has been chosen with I_{C₂}/I_{H_α} ratio of 0.725 (lowest) for deposition of good quality diamond in the final CVD recipe program for the 915 MHz reactor.

3.3 Diamond deposition and characterization

The CVD parameters have been selected according to OES observations of H₂–CH₄ plasma for growing good quality of diamond on a DND seeded 100 mm silicon wafer with lowest I_{C₂}/I_{H_α} ratio for obtaining maximum atomic hydrogen in the plasma. Methyl radical is the primary carbon species responsible for microcrystalline diamond growth (Mallik *et al* 2010), although not detectable under OES, whereas, C₂ radical have been reported to be the growth species, but for the smaller crystals of nanometer sizes. Excess presence of C₂ affects the microcrystalline diamond film quality negatively (responsible for cauliflower growth). So the optimum diamond growth environment is to keep methyl radical maximum in numbers with plenty of atomic hydrogen in the gas plasma. Atomic hydrogen is the most important chemical species in the growth of good quality diamond growth. It plays major role in etching non-diamond or graphitic depositions (which are due to the presence of other carbon-containing species inside the plasma). C₂ radicals being not the desired plasma species for polycrystalline diamond, the I_{C₂}/I_{H_α} ratio has to be kept at minimum value for good quality diamond growth, with the presence of maximum amount of nascent hydrogen species. Figure 5 shows the optical micrograph of such large area

Figure 5. Optical micrograph 100 mm diameter freestanding polycrystalline diamond wafer when viewed from, (a) nucleation side, (b) as-grown side.

Figure 6. OES spectrum of $\text{H}_2\text{-CH}_4$ plasma, for polycrystalline diamond deposition at the optimized processing conditions, with $I_{\text{C}_2}/I_{\text{H}\alpha}$ ratio of 0.89.

grown freestanding polycrystalline diamond wafer. The stand alone PCD coating is translucent (figure 5a) when viewed from the nucleation side but it is not transmitting light through the as-grown surface due to very high roughness of $4\ \mu\text{m}$ (figure 5b). Now, figure 5b also shows in the left hand top corner, an example of typical PCD coated 100 mm diameter Si wafer kept inside a plastic casing. 9000 W microwave power, 110 Torr reactor pressure, 1% CH_4 concentration has been used for such deposition. All the geometrical parameters (stage height, short length, probe length) were kept unchanged during such study (table 1). Figure 6 shows the typical optical emission spectra with C_2 , CH, $\text{H}\alpha$, $\text{H}\beta$ transition lines (table 2) at 515.82, 430.79, 655.95 and

Figure 7. (a) Raman spectroscopy and (b) FESEM image of the as-grown polycrystalline diamond coating.

485.70 nm, respectively, during the aforementioned CVD conditions. The value of the ratio for $I_{C2}/I_{H\alpha}$ is 0.89 under these conditions and the deposition was carried out for 30 h.

The diamond film quality is determined by Raman spectroscopy and surface morphology is observed under field emission scanning electron microscope. Figure 7a shows the Raman shift to occur at 1330.054 cm^{-1} with FWHM of 3.213 cm^{-1} . It is observed that there is only a narrow and sharp peak of sp^3 diamond phase with no other peak/hump corresponding to non-diamond content in this spectrum. Figure 7b shows well-polycrystalline microstructures with grain size ranging from 10 to $30\text{ }\mu\text{m}$. Cross sectional scanning electron microscopy image reveals typical columnar growth of polycrystalline diamond with 30 micron thickness (inset figure 7b). So it can be concluded that a growth rate of one micron per hour has been achieved under optimal processing condition of polycrystalline diamond. All these results indicate that using the optimum CVD process recipe, a good quality diamond coating has been grown by the 915 MHz and 9 kW microwave plasma CVD unit.

4. Conclusions

The H_2 and $\text{H}_2\text{--CH}_4$ gas plasma characteristics have been studied by varying MW power, reactor pressure and CH_4 concentration in a 915 MHz MWPCVD reactor. From the study of relative line intensities of hydrogen and carbon species, the optimum CVD process recipe is being achieved for good quality diamond growth on a 100 mm diameter silicon wafer. Reactor parameters like microwave power, pressure and methane concentration affect the presence of different plasma species and their corresponding line intensities. Rise in microwave power and reactor pressure produces more hydrogen in the hydrogen plasma. Similar trend is also observed for methane–hydrogen plasma. For optimum quality growth of polycrystalline diamond, the intensity ratio of $I_{C2}/I_{H\alpha}$ has to be kept to a minimum. It has been found that at 9000 W Microwave power, 110 Torr reactor pressure and 1% methane flow rate, the ratio between $I_{C2}/I_{H\alpha}$ is minimum at 0.89, which is conducive for growing good quality (intense Raman line at 1330.054 cm^{-1} with FWHM of 3.213 cm^{-1}) diamond inside the 915 MHz microwave plasma enhanced chemical vapor deposition reactor.

Acknowledgements

The authors thank the Council of Scientific and Industrial Research (CSIR), India for financial support from the network project title ‘Design and fabrication capabilities of very high power microwave tubes’ (CSIR Grant No. NWP 0024). Prof. D S Misra and Dr. R Bhattacharyya supported the present work as external advisors in this project. Authors also would like to acknowledge the continuous encouragements from the Directors of CSIR Central Glass and Ceramic Research Institute (CGCRI) and CSIR-CEERI Central Electronics Engineering Research Institute for the work in the diamond project.

References

- Dong L, Zhang Y, Ma B and Fu G 2002 Monte Carlo simulation of spatial distribution of atomic hydrogen in electron assisted CVD. *Diam. Relat. Mater.* 11: 1648–1652
- Dua A K, George V C, Friedrich M and Zahn D R T 2004 Effect of deposition parameters on different stages of diamond deposition in HFCVD technique. *Diam. Relat. Mater.* 13: 74–84

- Fu Y, Yan B, Loh N L, Sun C Q and Hing P 1999 Deposition of diamond coating on pure titanium using micro-wave plasma assisted chemical vapor deposition. *J. Mater. Sci.* 34: 2269–2283
- Ghajar A J and Bang K 1993 Parametric effect on the substrate temperature profile in Oxy-Acetylene Flames. *Heat. Transfer. Eng.* 14: 48–59
- Gicquel A, Hassouni K, Lombardi G, Duten X and Rousseau A 2002 New driving parameters for diamond deposition reactors: pulsed mode versus continuous mode. *Mater. Res.* 6(1): 25–37
- Gorbachev A M, Muchnikov A B, Vikharev A L, Radishchev D B and Koldanov V A 2007 Hydrocarbon plasma chemistry in a continuous microwave discharge, plasma. *Phys. Rep.* 33: 871–879
- Grotjohn T A and Asmussen J 2002 Chapter 7, Microwave Plasma-Assisted Diamond Film Deposition. *Diamond Films Handbook*, edited by Asmussen J and Reinhard D K, published by Marcel Dekker, Inc. p. 238–240
- Grotjohn T, Liske R, Hassouni K and Asmussen J 2005 Scaling behavior of microwave reactors and discharge size for diamond deposition. *Diam. Relat. Mater.* 14: 288–291
- Johansson E and Carlsson J O 1995 Effect of atomic hydrogen on the surface topography of chemically vapour deposited diamond films: An atomic force microscopy study. *Diam. Relat. Mater.* 4: 155–163
- Keys D A and Home M S 1926 A spectroscopic examination of the striated discharge in mixed gases. *Phys. Rev.* 27: 709–715
- King D, Yaran M K, Schuelke T, Grotjohn T A, Reinhard D K and Asmussen J 2008 Scaling the microwave plasma-assisted chemical vapor diamond deposition process to 150–200 mm substrates. *Diam. Relat. Mater.* 17: 520–524
- Konjevic N, Jovicevic S and Ivkovic M 2009 Optical emission spectroscopy for simultaneous measurement of plasma electron density and temperature in a low-pressure microwave induced plasma. *Phys. Plasmas* 16: 1–6
- Lang T, Stiegler J, Kaenel Y and Blank E 1996 Optical emission diagnostics and film growth during microwave-plasma-assisted diamond CVD. *Diam. Relat. Mater.* 5: 1171–1184
- Larijani M M, Normand F L and Cregut O 2007 An optical emission spectroscopy study of the plasma generated in the DC HF CVD nucleation of diamond. *Appl. Surface Sci.* 253: 4051–4059
- Lee S and Chung Y J 2005 Diagnostics of hydrogen plasma with in situ optical emission and silicon probes. *J. Appl. Phys.* 98: 1–8
- Li X, Perkins J, Collazo R, Nemanich R J and Sitar Z 2006 Investigating of the effect of the total pressure and methane concentration on the growth rate and quality of diamond thin films grown by MPCVD. *Diam. Relat. Mater.* 15: 1784–1788
- Lombardi G, Hassouni K, Benedic F, Mohasseb F, Ropcke J and Gicquel A 2004 Spectroscopic diagnostics and modeling of Ar/H₂/CH₄ microwave discharges used for nanocrystalline diamond deposition. *J. Appl. Phys.* 96: 6739–6751
- Ma J, Ashfold M N R and Mankelevich Y A 2009 Validating optical emission spectroscopy as a diagnostic of microwave activated CH₄/Ar/H₂ plasmas used for diamond chemical vapor deposition. *J. Appl. Phys.* 105: 1–12
- Mallik A K, Bysakh S, Pal K S, Dandapat N, Guha B K, Datta S and Basu D 2013 Large area deposition of polycrystalline diamond coatings by microwave plasma CVD. *Transactions of the indian ceramic society* 72(4): 225–232
- Mallik A K, Pal K S, Dandapat N, Guha B K, Datta S and Basu D 2012 Influence of the microwave plasma CVD reactor parameters on substrate thermal management for growing large area diamond coatings inside a 915 MHz and moderately low power unit. *Diam. Relat. Mater.* 30: 53–61
- Mallik A K, Bysakh S, Sreemany M, Roy S, Ghosh J, Roy S, Mendes J C, Gracio J and Datta S 2014 Property mapping of polycrystalline diamond coatings over large area. *J. Advanced Ceramics* 3(1): 56–70
- Mallik A K, Binu S R, Satapathy L N, Narayana C, Seikh M M, Shivashankar S A and Biswas S K 2010 Effect of substrate roughness on growth of diamond by hot filament CVD. *Bull. Mater. Sci.* 33: 251–255
- Okada K, Komatsu S and Matsumoto S 2003 Ion energy distributions and the density of CH₃ radicals in a low pressure inductively coupled CH₄/H₂ plasma used for nanocrystalline diamond deposition. *J. Vac. Sci. Technol. A* 21: 1988–1992

- Okita A, Suda Y, Oda A, Nakamura J, Ozeki A, Bhattacharyya K, Sugawara H and Sakai Y 2007 Effects of hydrogen on carbon nanotube formation in CH_4/H_2 plasmas. *Carbon* 45: 1518–1526
- Piekarczyk W and Prawer S 1993 Role of atomic hydrogen in preventing surface reconstruction and sp^2 bond formation during chemical vapour deposition of diamond. *Diam. Relat. Mater.* 2: 41–47
- Rabeau J R, John P, Wilson J I B and Fan Y 2004 The role of C_2 in nanocrystalline diamond growth. *J. Appl. Phys.* 96: 6724
- Shenderova O, Hens S and McGuire G 2010 Seeding slurries based on detonation nanodiamond in DMSO. *Diam. Relat. Mater.* 19: 260–267
- Su C-H and Chang C-Y 2008 Effect of CH/C_2 Species Density on Surface Morphology of Diamond Film Grown by Microwave Plasma Jet Chemical Vapor Deposition. *Mater. Trans.* 49: 1380–1384
- Tan W and Grotjohn T 1995 A Modelling the electromagnetic field and plasma discharge in a microwave plasma diamond deposition reactor. *Diam. Relat. Mater.* 4: 1145–1154
- Vandeveldt T, Wu T D, Quaeyslaegens C, Vlekken J, DOLieslaeger M and Stals L 1999 Correlation between the OES plasma composition and the diamond film properties during microwave PA-CVD with nitrogen addition. *Thin Solid Films* 340: 159–163
- Vazquez F J G, Camero M and Aleixandre C G 2006 Spectroscopic measurements of the electron temperature in low pressure radiofrequency $\text{Ar}/\text{H}_2/\text{C}_2\text{H}_2$ and $\text{Ar}/\text{H}_2/\text{CH}_4$ plasmas used for the synthesis of nanocarbon structures. *Plasma. Sources. Sci. T.* 15: 42–51
- www.oceanoptics.com, last accessed on 1st October, 2012
- Zuo S S, Yaran M K, Grotjohn T A, Reinhard D K and Asmussen J 2008 Investigation of diamond deposition uniformity and quality for freestanding film and substrate applications. *Diam. Relat. Mater.* 17: 300–305