

Optical Emission Spectroscopy of Low Temperature CVD Diamond

PATACSIL Crismar^{1,2}, MALAPIT Giovanni^{1,2} and RAMOS Henry²

¹ Department of Physical Sciences, College of Science, University of Philippines Baguio, Baguio City

² Plasma Physics Laboratory, National Institute of Physics, University of the Philippines, Diliman, Quezon City

(Received: 4 October 2004 / Accepted: 4 October 2005)

Abstract

The gas phase chemistry in low temperature ($< 300\text{ }^{\circ}\text{C}$) diamond and DLC chemical vapor deposition process was investigated using optical emission spectroscopy (OES) to determine the effects of the different deposition parameters such as methane concentration, substrate temperature, plasma current and gas pressure in relation to diamond growth on silicon substrates. The OES data were analyzed to determine the important factors favorable for diamond deposition such as the mean electron temperature, T_e , and the relative concentration levels of methane radicals (CH and CH^+). From the OES result, the optimum deposition parameters were determined for the low temperature diamond CVD system. Using these optimized parameters, film samples were attempted to be deposited at different substrate temperatures ($175\text{ }^{\circ}\text{C} - 300\text{ }^{\circ}\text{C}$). X-ray Diffraction (XRD), Raman Spectroscopy and Scanning Electron Microscopy (SEM) characterization of the deposited samples confirmed that diamond films were deposited at temperatures from $200\text{ }^{\circ}\text{C} - 300\text{ }^{\circ}\text{C}$.

Keywords:

optical emission spectroscopy, low temperature, diamond

1. Introduction

Previous researches at the Plasma Physics Laboratory, National Institute of Physics have shown that diamond and DLC thin films can be grown on silicon substrates with the Plasma Enhanced Chemical Vapor Deposition (PECVD) system via DC Glow discharge [1,2]. However, since the processes and mechanisms responsible for the diamond growth are still unclear [3,4], it was recommended that plasma diagnostics was needed to determine the optimum parameters such as plasma current, substrate temperature and chamber pressure to ensure successful and consistent deposition of good quality diamond and DLC films [5,6].

The Plasma Physics Laboratory acquired the Triax 320 Spectrometer to carry out such investigation by analyzing the optical emissions of the plasma. Optical Emission Spectroscopy (OES) is a non-invasive technique, which enables individually emitting plasma species to be monitored. In addition to identifying the chemical species present in the plasma, changes in the mean electron temperature, T_e , and relative concentration levels of the species can be monitored from the OES data. The electron temperature is an important plasma parameter since it is found to be directly proportional to the growth rate of diamond films [7]. This work reports the results of the electron temperature and concentration levels of CH and CH^+ radicals based on

the relative optical emission intensities of the plasma at different plasma deposition conditions.

2. Methodology

2.1 The experimental set-up

The experimental set-up is shown schematically in Fig. 1. It consists of the vacuum system, power source, plasma electrodes, diagnostic ports for probes, the heater, thermocouple and the vacuum gauge. Included in the diagram are the gases, mass flow controllers, multi gas controller, vacuum gauge controller and tem-

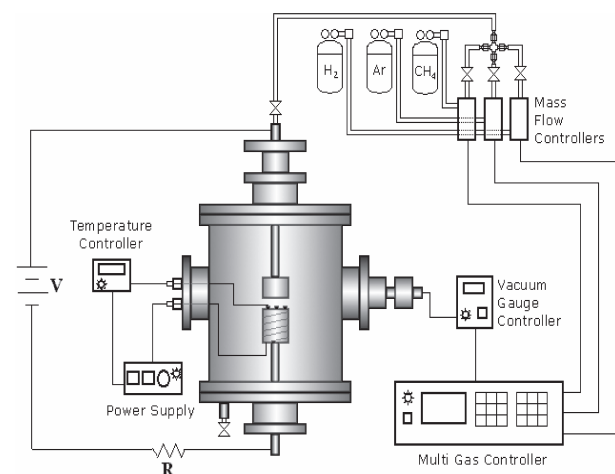


Fig. 1 Schematic Diagram of the PECVD system

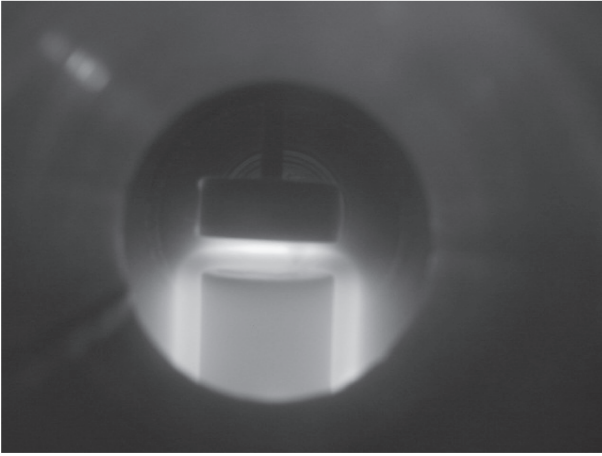


Fig. 2 Photograph of the plasma produced as seen from the viewport.

perature controller. The chamber has a view port for observing the plasma inside the chamber.

Figure 2 shows the DC glow discharge produced, cylindrical in shape (approx. 5.0 cm diameter). The dispersed plasma emission was collimated and focused on one end of a fiber optic and relayed into the spectrometer interfaced into a computer for data processing.

2.2 Theoretical background

2.2.1 CVD diamond and DLC films

Chemical vapor deposition process involves a gas phase chemical reaction that transforms gaseous molecules, which are called precursors, into a solid material in the form of thin film on the surface of a substrate. For the chemical vapor deposition of diamond films, hydrocarbon gas (*e.g.* methane) is used in excess of hydrogen. The molecules are excited, dissociated and ionized in the plasma principally by electron-impact bringing about excited species (atoms, molecules, radicals, atomic and molecular ions). Moreover, these species react with each other and are then transported to the surface of the substrate where nucleation and growth processes occur. The successful deposition of diamond film on the surface requires the following important conditions for the plasma: (1) high H concentration level to have a higher probability of hydrogen abstraction from the CH radicals leaving only carbon on the surface [9,10], (2) low CH radical concentration to prevent formation of graphitic carbon [11,12].

2.2.2 Optical emission spectroscopy

An electronically excited atom can undergo a spontaneous transition to a lower energy level and release a photon of light. This photon will have energy $E_{ji} = hc/\lambda_{ji}$ where i and j correspond to the lower and upper energy levels respectively. The emission intensity for

the transition $i \rightarrow j$ of the species x is given by:

$$I_x(i \rightarrow j) = C_x k_{xi} n_e N_x g(\lambda) \quad (1)$$

where C_x is a constant; k_{xi} is the rate constant for excitation of the species x to the state i by electron collisions; n_e is the concentration of electrons in the plasma; N_x is the concentration of the species x ; and $g(\lambda)$ is the probability that the photon of that wavelength will be collected and counted.

From equation (1), the emission intensity ratio of two lines, I_1/I_2 is given by:

$$I_1/I_2 \sim (k_1/k_2)(N_1/N_2) \quad (2)$$

For the same species, the intensity ratio of two lines, *e.g.* $I_{H\beta}/I_{H\alpha}$ is proportional to the rate constant of excitation of the species, which reflects an electron mean energy in the plasma, *i.e.* the electron temperature [8,13]. For different species existing in an excited environment, the intensity ratio reflects their relative concentrations [5,14].

3. Results and discussion

3.1 The effect of methane concentration

Previous papers on diamond deposition showed that the key parameter in diamond film depositions, where hydrogen and methane gases are used, is the methane concentration [11,12]. Figure 3 shows that the effect of methane concentration on the electron temperature as seen in the H_{β}/H_{α} plot is not significant. However, the same figure shows that higher methane concentration results in relatively high levels of CH and CH^+ confirming the results of other researches [5,13,14]. This means that lower methane concentration favors diamond deposition.

The SEM profiles of the deposited films using varying methane concentration are shown on Fig. 4.

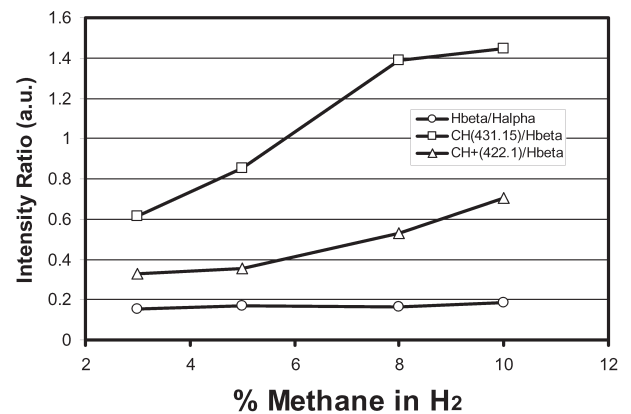


Fig. 3 Methane concentration vs. intensity ratio

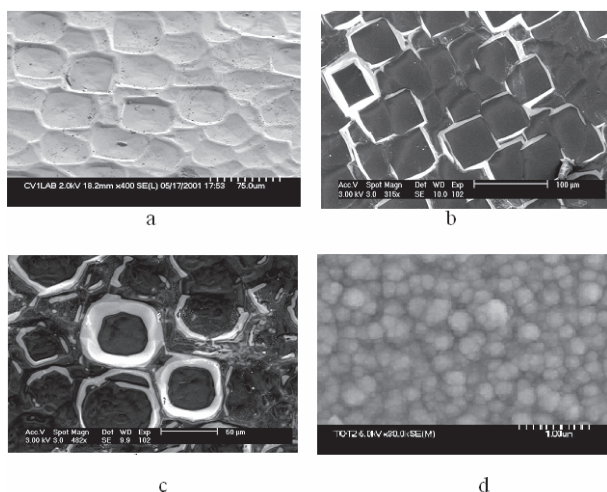


Fig. 4 SEM images of samples deposited at varying methane concentration (pressure=10 Torr; plasma current 50 mA): (a) Silicon substrate, (b) graphitic deposit on the silicon substrate (8% methane used), (c) DLC deposits on the silicon substrate (5% methane used), (d) Diamond deposited on the silicon substrate (1% methane used)

3.2 The effect of plasma current

The plasma current is controlled by the plasma voltage applied between the two electrodes. Figure 5 shows the relation of the relative intensity ratios as a function of plasma current. A very stable plasma is obtained at about 30 to 55 mA. The CVD facility was operated on these current ranges for the stable plasma (30 mA – 55 mA).

The graph indicates increasing electron temperature as the current increases from 30 mA to 55 mA. Figure 5 also shows an inverse relation between that the concentration levels of CH and CH⁺ and the plasma current. That is, the concentration levels of CH and CH⁺ decreases as plasma current increases. This therefore suggests that the higher the plasma current, the more favorable the diamond deposition.

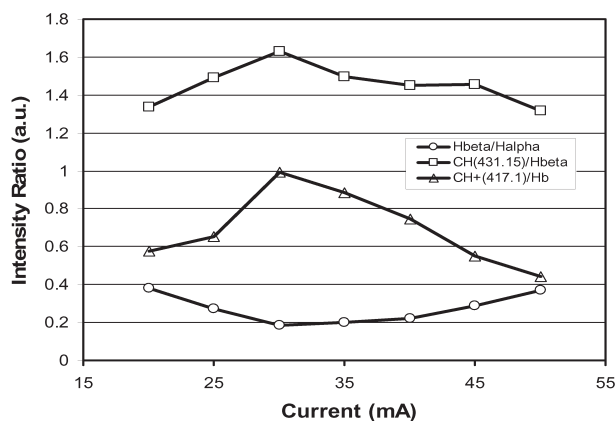


Fig. 5 Plasma current vs. intensity ratio

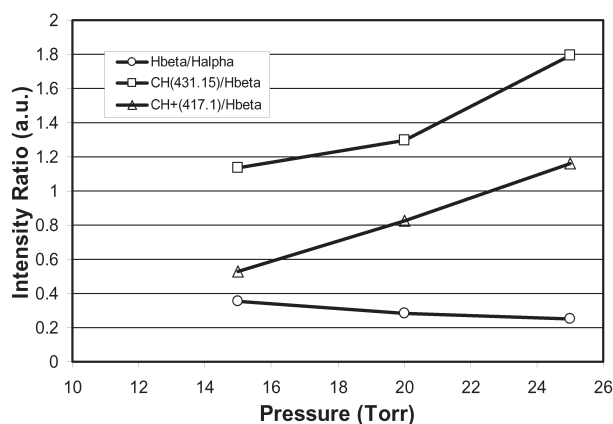


Fig. 6 Pressure vs. intensity ratio

3.3 The effect of pressure

The CVD chamber is evacuated to a base pressure of 10^{-6} Torr. Successively, hydrogen gas is introduced to the desired pressure, after which a potential difference between the electrodes ignited the plasma. For this research, stable plasma was attained only for pressure of 10 – 20 Torr because the power supply used has maximum output of about 600 V only. Figure 6 is seen to indicate that the electron temperature decreases as the pressure increases. Increasing levels of CH and CH⁺ concentrations were observed as the pressure increases. Both cases indicate that the lower the pressure, the more favorable the deposition of diamond.

3.4 The effect of substrate temperature

Figure 7 shows the relation of the intensity ratio as a function of the substrate temperature. It can be seen that the electron temperature does not vary much between temperatures 180 – 275 °C. However, the trend seems to indicate that the electron temperature increases significantly for substrate temperature above 250 °C.

Figure 7 also shows that as the substrate temperature is increased, the CH and CH⁺ concentration levels are

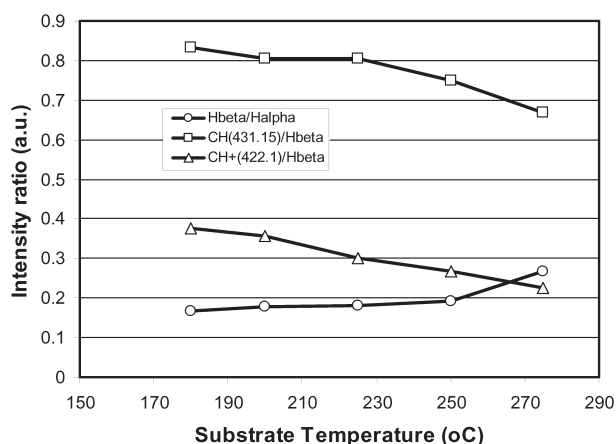
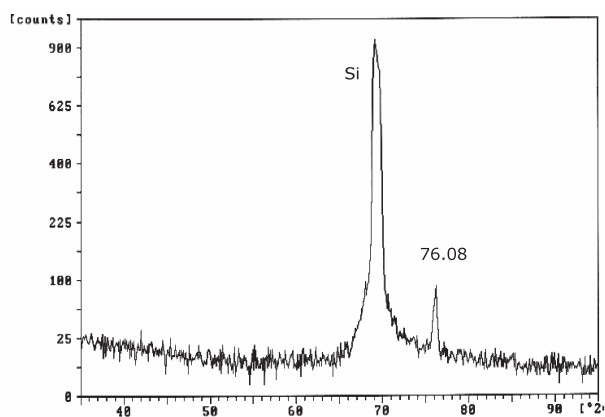
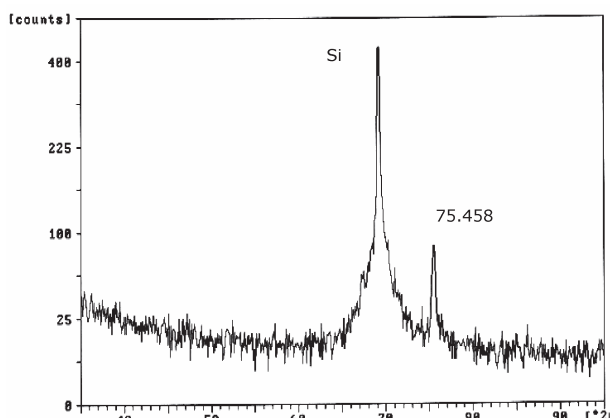


Fig. 7 Substrate temperature vs. intensity ratio



(a)



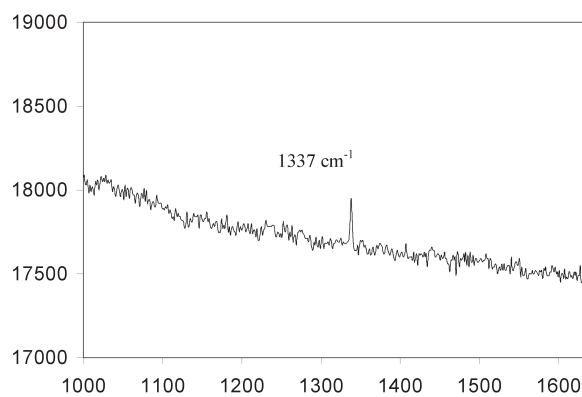
(b)

Fig. 8 XRD profiles of samples deposited at different substrate temperatures (1% CH₄ in H₂, pressure=20 Torr; plasma current 50 mA): , (a) 225 °C, showing diamond (220) peak at $2\theta=76.08$ and (b) 275 °C, showing diamond (220) peak at $2\theta=75.458$ °C.

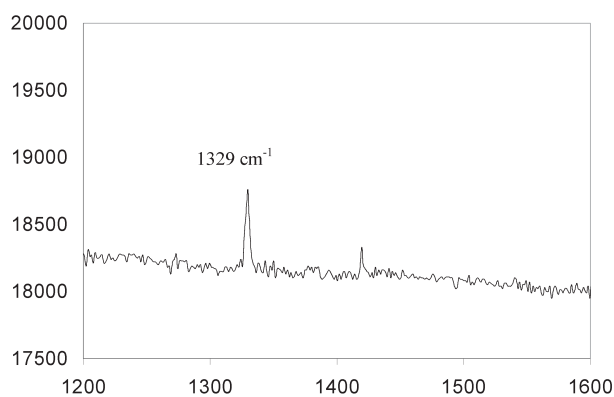
decreased. Although the results shows that higher substrate temperature favors diamond deposition, the researchers were able to deposit diamond at 200 °C using the optimum values of the previously discussed parameters. Figs. 8 and 9 respectively shows the XRD profile and Raman spectrograph of the sample deposited at different substrate temperatures with the diamond peak indicated.

Conclusion

Using the OES technique, the electron temperature and the concentration levels of methane radicals (CH and CH⁺) were inferred from the intensity ratios of spectral lines. Their values were plotted as functions of the different deposition parameters (plasma current, substrate temperature and pressure) and were analyzed to determine the optimum values of parameters for low temperature diamond deposition. Using these optimized values for methane concentration, plasma cur-



(a)



(b)

Fig. 9 Raman spectrograph of diamond samples deposited at different substrate temperatures showing diamond peaks (a) 200 °C and (b) 275 °C.

rent and pressure, diamond films were successfully deposited on silicon substrate at low temperature of 200 °C to 300 °C.

References

- [1] G. Malapit, "Low Temperature PECVD Diamond and DLC Thin Films", M.S. Thesis, 2001.
- [2] R. Nakan, "Diamond/DLC Deposition on Si using H₂/CH₄/O₂ Gas Mixture via DC Plasma CVD", B.S. Thesis, 2002.
- [3] J. Cui and R. Fang, *J. Appl. Phys.* **81**, (1997).
- [4] X. Jiang, M. Fryda, C.L. Jia, *Diamond and Related Materials*, **9**, (2000).
- [5] Y. Liao, C.H. Li, Z.Y. Ye, C. Chang, G.Z. Wang, R.C. Fang, *Diamond and Related Materials*, **9**, 1716 (2000).
- [6] F. Shahedipour, B.P. Conner, H.W. White, *J. Appl. Phys.*, **88**, No. 5, (2000).
- [7] S. Baldwin Jr., "Experimental Investigation of Atmospheric Plasma Chemistry for Plasma Assisted Chemical Vapor Deposition of Diamond Thin Films", High Temperature Gasdynamics Laboratory, Dept. of Mech. Eng'g, Stanford Uni-

- versity, (1996).
- [8] H. Griem, "Plasma Spectroscopy", McGraw-Hill, Inc., 269-291 (1964)..
- [9] C.G. Schwarzler, O. Schnabl, J. Laimer, Plasma chemistry and Plasma processing, Vol. **16**, No. 2, (1996).
- [10] J.C. Angus, C.C. Hayman, Science, **241**, 913 (1988).
- [11] A.M. Stoneham, I.J. Ford and P.R. Chalker, Mat. Resear. Soc., **23**, No. 9, (1998).
- [12] D.S. Dandy and M.E. Coltrin, "Diamond Thin Films Handbook", J. Asmussen and D. Reinhard (eds), Marcel Dekker, Inc (2002).
- [13] E.H. Wahl, T.G. Owano, C.H. Kruger, P. Zalicki, Y. Ma, R.N. Zare, Diamond and Related Materials **5**, 373 (1996).
- [14] S.J. Harris and A.M. Weiner, J. Appl. Phys., **67**, (1990).
- [15] H.C. Barshilia, B.R. Mehta, V.D. Vankar, J. Mater. Res., **11**, 2852 (1996).