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# Stoichiometry of the diamond/silicon interface and its influence on the silicon content of diamond films

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Thin films of diamond were grown by microwave plasma chemical vapor deposition at growth pressures of 10, 20, 40, and 60 Torr keeping the substrate temperature constant at 975 °C. Increase in the growth pressure reduced the size of the plasma ball resulting in an increase in the microwave power density (MPD). The films were characterized by scanning electron microscopy, micro-Raman, and photoluminescence (PL) spectroscopy. A systematic variation was observed in surface morphology and quality of the films. The intensity of the peak at 1.68 eV in the PL spectra of the films, which is assigned to Si impurities was also observed to increase consistently with the MPD. The stoichiometry of the diamond/silicon interface was studied by x-ray photoelectron spectroscopy (XPS) and found to be a sensitive function of the MPD. XPS results showed the formation of nonstoichiometric SiC along with other carbon phases in the initial stages of the growth. A correlation was observed between the composition of the interface and the intensity of the 1.68 eV peak. The above results are explained in terms of the increase in the impingement flux density of atomic hydrogen with the MPD. © 1998 American Institute of Physics. [S0021-8979(98)05002-6]

## I. INTRODUCTION

The properties of diamond make it an interesting material for the scientist as well as the technologist.<sup>1</sup> It can be used as a hard coating on cutting tools on one hand<sup>2</sup> and as a heat sink for laser diodes on the other.<sup>3</sup> The development of diamond growth from the vapor phase<sup>4</sup> at subatmospheric pressure and low substrate temperature ( $T_s$ ) was a major breakthrough responsible for the recent upsurge in diamond related research. Microwave plasma chemical vapor deposition (MPCVD) is one of the techniques that has been used extensively to grow the films.<sup>1,5</sup> The high density and energy of the electrons in a microwave plasma dissociate  $H_2$  molecules to provide the high concentration of atomic hydrogen (H),<sup>6</sup> which not only preferentially etches  $sp^2$  carbon but also enhances the density of  $sp^3$  carbon species.<sup>7</sup> However, owing to the nature of the plasma processes, various growth parameters such as  $T_s$ , growth pressure, and microwave power become dependent upon each other making it difficult to identify the parameters affecting the growth significantly. Moreover, the mechanism of nucleation and growth of diamond on Si substrates is still not well understood.

It was observed that in the initial stages of growth an interfacial layer of silicon carbide (SiC) is formed and the carbon-rich regions of the SiC layer may act as nucleation centers for diamond.<sup>8</sup> Alternatively, a thin nondiamond carbon layer on top of the SiC may also be responsible for the

nucleation of diamond.<sup>9</sup> Clearly, the diamond/Si interface plays a dominant role in the growth and nucleation of the diamond. In the present work, we report the influence of the microwave power density (MPD) on the crystalline quality and impurity content in the diamond films. We also present detailed x-ray photoelectron spectroscopy (XPS) investigations of the diamond/silicon interface. The study indicates that the stoichiometry of the interface depends sensitively on the MPD. Further, an interesting correlation is deduced between the Si content in the diamond films, observed by the intensity of the 1.68 eV Si photoluminescence (PL) peak<sup>10-15</sup> as a function of the MPD, and the stoichiometry of the interface.

## II. EXPERIMENT

Polycrystalline diamond films were grown in a quartz reaction chamber using MPCVD.<sup>16</sup> One-side polished single crystals of silicon were used as substrates, mounted on a graphite holder, and were heated in the microwave plasma without using any external heater. The  $T_s$  was measured using a chromel–alumel thermocouple, and it was kept constant at 975 °C for all the samples. The flow of the precursor gases ( $CH_4$  and  $H_2$ ) was controlled and measured using electronic mass flow controllers. Two sets of the films were grown for 0.5 and 3 h at 10, 20, 40, and 60 Torr. The variation of growth pressure changes the volume of the glow discharge region (plasma ball), which in turn significantly changes  $T_s$ . Therefore, the MPD defined as the ratio

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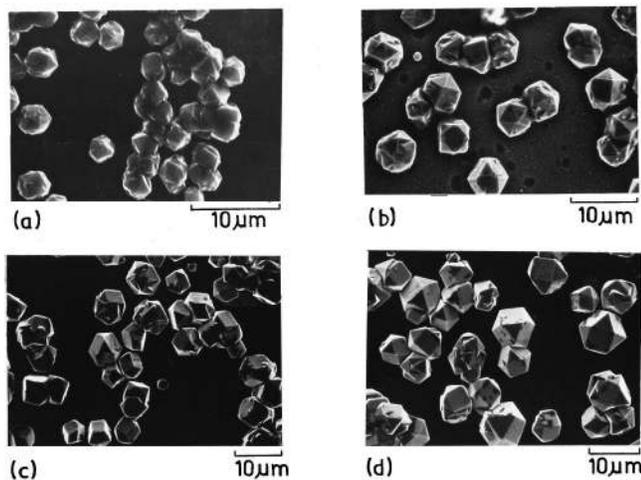


FIG. 1. SEM of diamond films grown at (a)  $3 \text{ W/cm}^3$ , (b)  $4 \text{ W/cm}^3$ , (c)  $20 \text{ W/cm}^3$ , and (d)  $75 \text{ W/cm}^3$  showing a consistent increase in grain size and in sharpness of the crystallites.

of the microwave power to the volume of the plasma ball (measured by visual inspection) is the variable parameter. The values of the MPD corresponding to the above growth pressures were estimated to be 3, 4, 20, and  $75 \text{ W/cm}^3$ , respectively. It should be noted that the absolute values may be different due to the error introduced in measuring the volume of the plasma ball visually, but the increasing trend in the values of the MPD with pressure will remain the same.

All the films were systematically characterized by various techniques. Scanning electron microscopy (SEM), micro-Raman, and PL studies were done on the samples deposited for 3 h. The micro-Raman and PL spectra were obtained using an  $\text{Ar}^+$  laser ( $\lambda = 488$  and  $514.5 \text{ nm}$ ) as an excitation source and detected by a photomultiplier tube as described elsewhere.<sup>17</sup> XPS studies were carried out on the samples deposited under the same conditions for 0.5 h. For the depth profile studies, the films were sputtered by an  $\text{Ar}^+$  beam inside the analysis chamber at different time intervals. XPS measurements were carried out using a Shimadzu 850 spectrometer with a base pressure of about  $5 \times 10^{-8} \text{ Pa}$ .  $\text{Mg } K_{\alpha}$  radiation was used as the excitation source and the spectrometer was calibrated with  $\text{Au } (4f_{1/2})$  at  $83.8 \text{ eV}$ .

### III. RESULTS

#### A. SEM

Figure 1 shows the SEM pictures of the diamond films grown for 3 h. It can be seen from Fig. 1 that the morphology and the grain size of the crystallites are sensitive to the MPD. For example, the films grown at  $3 \text{ W/cm}^3$  have smaller crystallites with poor surface morphology while the films grown at  $75 \text{ W/cm}^3$  show clear, sharp crystal facets and enlarged crystallites. The facets are not sharp in the former case, owing probably to the presence of nondiamond carbon at the grain boundaries. However, in the latter case as the MPD increases, the morphology of the crystallites improves greatly and the grain size increases to a moderate extent.

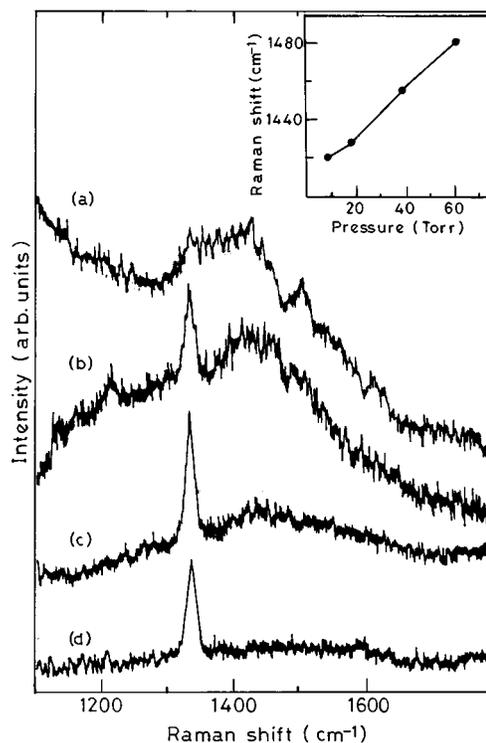


FIG. 2. Raman spectra of the films deposited at (a)  $3 \text{ W/cm}^3$ , (b)  $4 \text{ W/cm}^3$ , (c)  $20 \text{ W/cm}^3$ , and (d)  $75 \text{ W/cm}^3$ . All the samples were excited by a  $514.5 \text{ nm}$   $\text{Ar}^+$  laser. The inset shows the shift of the nondiamond Raman band with growth pressure.

#### B. Micro-Raman and PL

The micro-Raman spectra of the films grown for 3 h are given in Fig. 2. With the exception of Fig. 2(a), the spectra indicate the presence of a peak at  $\sim 1332 \text{ cm}^{-1}$ , an unambiguous signature of crystalline diamond.<sup>18</sup> The spectra also show a broadband ( $\sim 1400\text{--}1600 \text{ cm}^{-1}$ ) in all the samples, which is assigned to nondiamond carbon phases present at the interfacial layer and the grain boundaries. There is a marked decrease in the overall relative intensity of the nondiamond to the crystalline diamond peak with the MPD indicating a reduction in the nondiamond carbon phase in the films. For example, the films grown at  $75 \text{ W/cm}^3$  contain almost none or very little nondiamond carbon [Fig. 2(d)]. This is further supported by the observation of very clear and sharp crystal facets in the films grown at higher MPD (see Fig. 1).

To verify the broadband as a Raman band, the samples grown at  $4 \text{ W/cm}^3$  were excited by laser wavelengths of  $514.5$  and  $488 \text{ nm}$ , respectively [Figs. 3(a) and 3(b)]. Though there is a shift of a  $10\text{--}12 \text{ cm}^{-1}$  wave number in the position of the broadband as we change the wavelength of the excitation source from  $514.5$  to  $488 \text{ nm}$ , this is very small in comparison to the expected shift of  $1056 \text{ cm}^{-1}$  (the difference of the excitation wavelengths) for a PL band. It can, therefore, be concluded that the broadband is a Raman band. Also, the fact that the broadband is a contribution from the nondiamond carbon from different regions (interface and grain boundaries) is evident from Fig. 3(b) in which the broadband has separated into two bands. For example, the

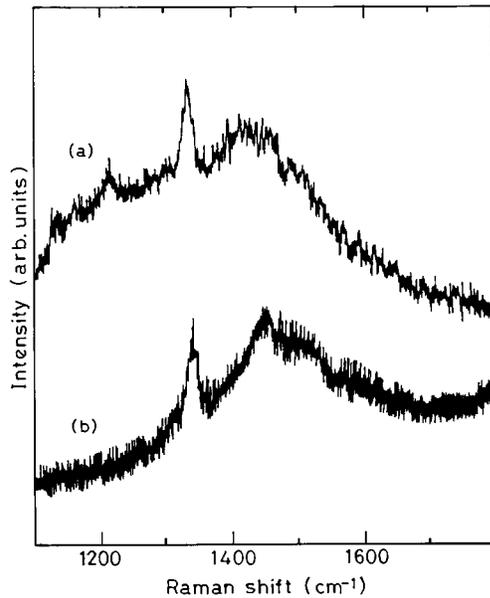


FIG. 3. Raman spectra of the films deposited at  $4 \text{ W/cm}^3$  (a) excited with a  $514.5 \text{ nm Ar}^+$  laser, and (b) excited with a  $488 \text{ nm Ar}^+$  laser.

band in the range  $1400\text{--}1500 \text{ cm}^{-1}$  may correspond to carbon-rich SiC:H alloys present at the interface as confirmed by several studies in SiC and CVD diamond.<sup>10,19–22</sup> A shift in the position of this band is also observed (see the inset in Fig. 2). The other band in the region  $1500\text{--}1550 \text{ cm}^{-1}$  corresponds to amorphous hydrogenated carbon, a-C:H.<sup>10,19,23,24</sup>

The PL spectra of the diamond films are shown in Fig. 4. A sharp peak at  $1.68 \text{ eV}$  on the broad background, typical of

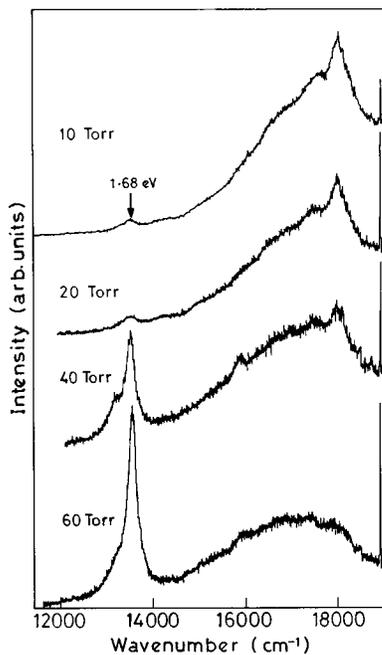


FIG. 4. PL spectra of the diamond films deposited at various pressures (or MPD). Sharp Raman features of diamond are also present along with the silicon ( $1.68 \text{ eV}$ ) PL peak. The spectra show an increase in the intensity of the silicon peak with pressure.

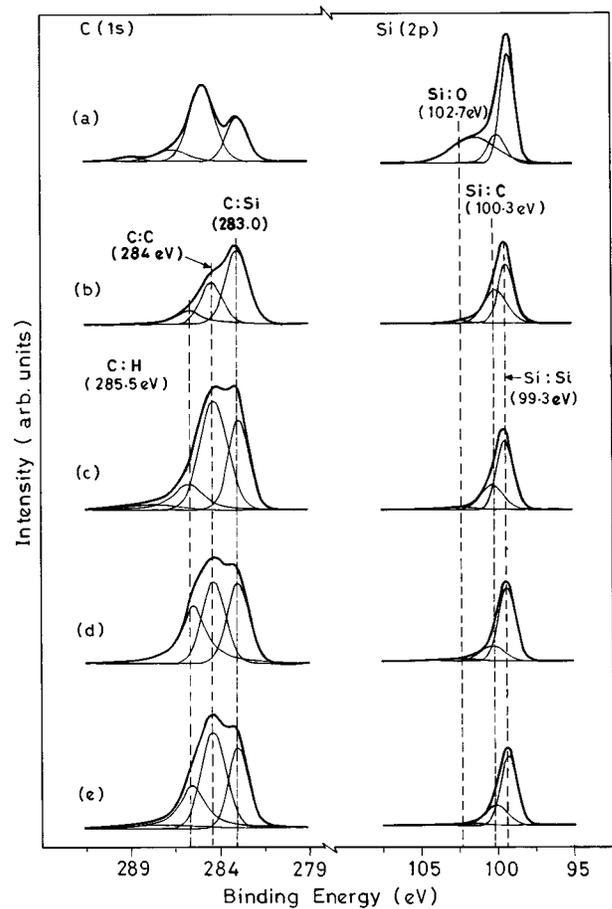


FIG. 5. XPS spectra of  $0.5 \text{ h}$  films grown at various MPD. (a)  $3 \text{ W/cm}^3$ , (b)  $3 \text{ W/cm}^3$ , (c)  $4 \text{ W/cm}^3$ , (d)  $20 \text{ W/cm}^3$ , and (e)  $75 \text{ W/cm}^3$ . All the spectra were recorded after  $\text{Ar}^+$  sputtering for  $30 \text{ min}$  except (a), which was done in the as-received condition.

CVD diamond, can be seen. It is interesting to note that the intensity of the peak increases significantly with the MPD. This peak is attributed to a defect level created by the incorporation of Si impurities in diamond lattice<sup>10–15</sup> and indicates that Si inclusion increases with the MPD.

### C. XPS

Figure 5 shows the XPS results of the films deposited on scratched Si(100) substrates for  $0.5 \text{ h}$  as a function of the MPD. To study the interface, we chose  $0.5 \text{ h}$  for the deposition time, as the nucleation period of diamond for low-pressure CVD methods is  $30\text{--}45 \text{ min}$ . The spectra in the C(1s) region for all the films show a broad peak with shoulders. Deconvolution of the spectra using a standard fitting program gave three distinct peaks at  $283.0$ ,  $284.4$ , and  $285.5 \text{ eV}$ . These are assigned to carbidic (SiC), pure carbon (diamond, nondiamond, graphite) and hydrogenated/hydrogen terminated carbon (diamond, nondiamond), respectively.<sup>25–27</sup> It is, however, not possible to distinguish between the different carbons such as diamond, nondiamond, and graphitic by XPS because of the very similar binding energies ( $\sim 284.5 \text{ eV}$ ). The presence of SiC was further confirmed by scanning in the Si(2p) region. Two transitions corresponding to Si and SiC were observed at  $99.3$  and  $100.3 \text{ eV}$ ,

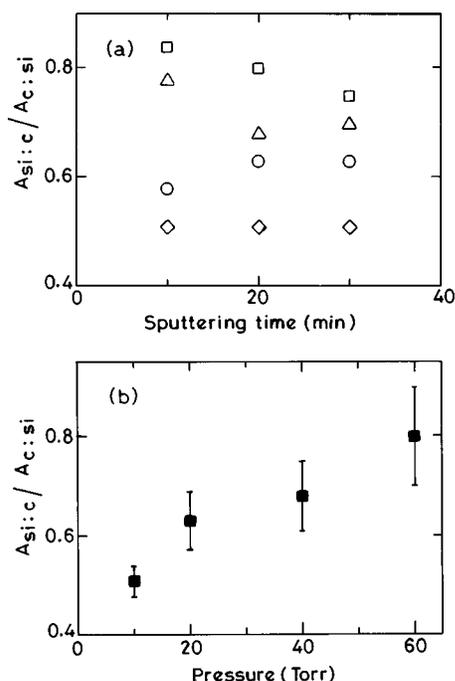


FIG. 6. Ratios of the areas under the carbide curves in the Si ( $2p$ ) and C ( $1s$ ) regions as a function of MPD: (a) Si/C ratio as a function of sputtering time;  $\diamond$ , 3 W/cm<sup>3</sup>;  $\circ$ , 4 W/cm<sup>3</sup>;  $\triangle$ , 20 W/cm<sup>3</sup>; and  $\square$ , 75 W/cm<sup>3</sup>. (b) Si/C ratio, after 30 min sputtering, as a function of growth pressure.

respectively.<sup>8,9</sup> Table I summarizes the peak positions and full width at half maximum values of the carbide peaks in the C( $1s$ ) and Si( $2p$ ) regions. The high intensity of the Si peak at 99.3 eV may be arising from the bare Si covered by the oxide layer. It is expected that the oxide layer will be etched by atomic hydrogen during CVD. However, the oxide layer may grow again before the XPS analysis. The peak at 102.7 eV observed in the as-deposited sample corresponding to the SiO<sub>2</sub> phase supports our conjecture.

An interesting point to note here is that the composition of SiC changes as a function of the MPD. To illustrate this, the ratio of the area under the individual peaks ( $A_{Si:C}/A_{C:Si}$ ) of SiC in the Si( $2p$ ) and C( $1s$ ) regions, respectively, are plotted in Fig. 6. The ratio will be qualitatively proportional to the Si to C ratio in the SiC layer. Figure 6(a) shows the variation in  $A_{Si:C}/A_{C:Si}$  in the films grown at various MPD, obtained after Ar<sup>+</sup> sputtering for different times. A nearly constant value of the ratio with respect to the sputtering time indicates that the interface SiC composition is not changing with the depth in the individual samples. This was further confirmed from Auger depth profile analyses in our

TABLE I. Carbide peak positions and FWHM values.

Pressure (Torr)	MPD (W/cm <sup>3</sup> )	Si:C (Si $2p$ ) Position/FWHM (eV)	C:Si (C $1s$ ) Position/FWHM (eV)
10	3	100/1.8	283/1.5
20	4	100.2/1.8	282.9/1.4
40	20	100.3/1.8	283/1.5
60	75	100.1/1.6	282.9/1.3

samples.<sup>28</sup> The ratio  $A_{Si:C}/A_{C:Si}$  is plotted as a function of the MPD in Fig. 6(b). Although the scatter in the data is large (estimated error  $\approx 10\%$ ), the ratio increases in the films with the MPD. On the basis of this experimental evidence, we can conclude that the interface of the films grown at higher pressure (MPD) is silicon rich prior to diamond nucleation.

#### IV. DISCUSSION

The above results are very interesting and indicate a systematic variation in the interface composition and film characteristics as a function of the MPD. The features of SEM and micro-Raman spectra can be explained by taking account of the increase in the impingement flux density of H atoms (IFDH) on the growing surface as the MPD increases. It has been shown previously that the dissociation rate of molecular hydrogen increases with the increase in the MPD.<sup>6</sup> This is in spite of the increased recombination at higher pressure because of the considerable reduction in the size of the plasma ball. In agreement with Loh and Capelli,<sup>29</sup> we also observe that as the size of the plume decreases the temperature of the plasma (plasma ball) as well as the atomic H content increases. The increase in atomic H at higher MPD results in higher IFDH. This explains the improvement in the surface morphology, viz., the sharpness of the crystal facets of CVD diamond and the decrease in the nondiamond carbon as observed in the films grown at higher MPD (Figs. 1 and 2, respectively).

To understand the XPS results and increased Si content in the films with the MPD, we look at the initial phase of growth. Initially, the exposure of Si substrates to the hydrogen plasma at high temperature (975 °C) converts the top few layers to hydrogenated silicon alloy (Si:H). Subsequently, upon the introduction of methane, the incoming flux of carbon atoms interacts with the modified substrate and may form SiC:H. From the XPS results reported above, the composition of the interfacial layer is dependent upon the MPD and becomes Si rich with the increasing MPD. At the same time, the intensity of the 1.68 eV PL peak in the film grown for 3 h under the same conditions increases with the MPD. This implies that a Si-rich interface results in a higher concentration of Si in the films. Our results indicate that the incorporation of Si in the diamond lattice may be taking place *via* the formation of volatile Si-H complexes due to the interaction between the atomic hydrogen and SiC:H layer. A continuous depletion of the Si from the interface will result in an alteration of its composition. This may be responsible for the observed shift in the position of the non-diamond Raman band from 1420 to 1480 cm<sup>-1</sup> with the MPD (see the inset of Fig. 2) in 3 h deposited films.

The explanation of the Si incorporation from the interface would not be applicable if the Si impurities in the diamond films were coming from the walls of the quartz deposition chamber.<sup>10</sup> However, as the growth pressure increases, the microwave plasma moves away from the wall and is confined in the center of the quartz tube. This would result in a decrease in the PL intensity with the growth pressure, in contrast to the observed PL results, which therefore, eliminate the quartz tube as a possible source of silicon impurity.

## V. CONCLUSION

The following conclusions have been drawn from the present study:

- (1) The various characteristics such as morphology and non-diamond carbon content of the diamond films, grown by MPCVD, are a sensitive function of the MPD.
- (2) The stoichiometry of the interfacial SiC layer changes consistently with the MPD prior to diamond nucleation.
- (3) Si concentration in the diamond films increases with the MPD and correlates with the change in the composition of the interface.
- (4) The effect of the MPD on the growth of diamond is explained in terms of the increase in atomic H in the gas phase as a function of the MPD. This results in higher IFDH on the growing surface.

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