JMEPEG (2005) 14:666-670
DOI: 10.1361/105994905X64611

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1059-9495/$19.00

Surface Characterization of (111) and (100) Textured Diamond Coatings Deposited to Silicon

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(Submitted June 25, 2005; in revised form June 29, 2005)

The use of diamond for infrared (IR) transmitting applications is of paramount importance to the defense industries. Diamond-coated IR transmitting materials are used on smart weapons and aircraft that use substrate materials such as silicon and germanium. In this investigation, diamond sheets were deposited using chemical vapor deposition. The as-grown diamond sheets were characterized for hydrogen content using detailed IR analysis. The deconvolution of the spectra in a three-phonon region (2700–3150 cm^{-1}) showed a number of vibration modes corresponding to the $sp^m CH_n$ phase of carbon. The spectra representing (100) and (111) textured diamond sheets, grown under different conditions, were compared. The (100) textured sheets contained two dominant peaks centered at 2860 and 2930 cm^{-1}, which correspond to the symmetric and asymmetric stretch bands of the CH_2 group. However, the sheet with (111) texture displayed multiple CH, CH_2, and CH_3 peaks on the spectrum. Using a standard sample called polymethyl methacrylate with known concentration, the hydrogen content associated with various modes was evaluated in the diamond sheets. IR active hydrogen in the chemical vapor deposited diamond sheets was also calculated by evaluating the area of the IR band. A discrepancy of one order of magnitude was found in the calculated and measured value. Using these measurements we suggest that the oscillator strength of the different IR modes varies depending upon the structure and H content of CVD diamond sheets.

Keywords chemical vapor deposition, diamond, infrared transmitting materials, spectroscopy, surface engineering

1. Introduction

The ability to produce diamond thin films at subatmospheric pressure and low temperature in the laboratory using chemical vapor deposition (CVD) has stimulated enormous research interest (Ref 1-5), since the properties of these deposits appear to match those of natural diamond crystals. The interest in CVD diamond is mainly due to the enormous potential of this material for use in numerous application areas. For example, the transparency of diamond to a wide range of electromagnetic spectra makes it an ideal material for producing infrared (IR) windows and optical coatings. However, polycrystalline diamond films contain grain boundaries, which result in the presence of impurities. The impurities and defects in CVD diamond can induce a significant amount of absorption that renders less perfect diamond useless as IR windows. The elemental impurities include hydrogen, nitrogen, oxygen, etc. The source of hydrogen in the CVD diamond lattice comes mainly from the high concentration (≥99 vol%) of H_2 gas present in the gas mixture during the growth process. Such large concentrations of H_2 are required to generate high concentrations of atomic hydrogen (H) during growth, which is essential for the synthesis of diamond via CVD routes (Ref 6-10). The presence of H in the diamond lattice has serious repercussions for its characteristics. Despite this, there have been very few attempts to measure the concentration and the bonding of H in CVD diamond lattices (Ref 11-15). Fourier transform IR (FTIR) spectroscopy has proved to be a powerful and nondestructive technique for studying various optical centers in natural and CVD diamond.

In CVD diamond, hydrogen plays a major role in controlling various characteristics of the material. IR absorption in the C-H stretch region is important not only for identifying various modes of vibration, but also for the quantitative estimation of hydrogen bonded to the diamond lattice. As the absorption is due to the superposition of vibrations from different modes, where carbon is in different lattice configurations, the quantitative calculation of H content using a unique value of the oscillator strength often proves to be erroneous. Jacob and Unger (Ref 16) suggested that the constant proportional (A_n) to the oscillator strength does not have a unique value and depends upon the structure of the C:H films. A_n for polymer-like films with H/C ratio around 1 increases by a factor of 4 with a decreasing H/C ratio. Thus, for the determination of A_n, the exact concentration of H atoms bonded to carbon using an independent method is required.

In this study, we present results obtained from FTIR spectroscopy where the samples characterised were self-standing diamond sheets grown under different conditions. A simple and reliable method of the determination of the H content is proposed. The results are compared with the H content obtained using standard and integration methods on the same set of samples. The amount of hydrogen present in (111) and (100) textured films is also compared.

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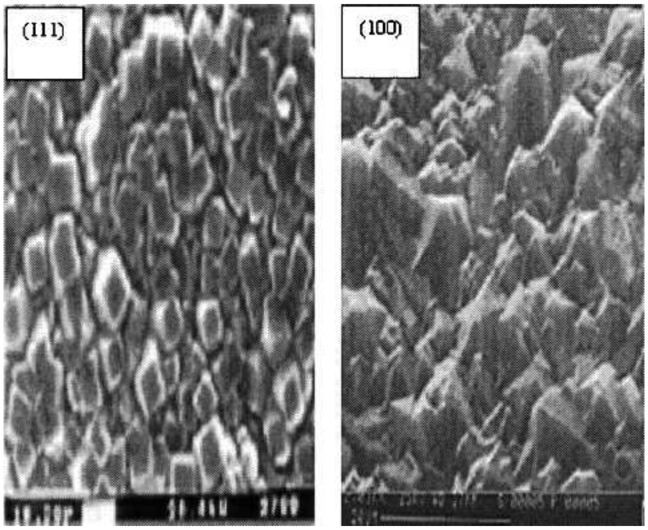

Fig. 1 SEM images of (111) and (100) textured diamond sheets

2. Experimental Method

Diamond sheets with thickness values in the range of 40-50 μm were deposited using a hot filament CVD (HFCVD) system, which has been described elsewhere (Ref 17). Silicon wafers with (100) orientation were used as substrates for the deposition of the diamond films. Methane (CH_4) and hydrogen (H_2) were used as process gases. The deposition pressure in the chamber was varied from 20 to 120 torr to grow samples with the desired quality. The temperature of the substrates (880 °C) was measured using a thermocouple and an optical pyrometer. (100) textured samples were obtained only by applying a gradient across the substrate during deposition. Chromium thin films (1 mm × 10 mm × 200 Å) were deposited to act as a heater by a thermal evaporation technique on the backside of the substrate to create a temperature gradient. The gradient was created across the sample by applying dc power to both ends of the heater using chromel wires. The gradient was measured by measuring the temperature at both ends of the sample using chromel-alumel thermocouples attached to the substrate holder. Further details about the temperature gradient method can be found elsewhere (Ref 18).

A window of diameter of 6-7 mm was cut in the center of the diamond sheets deposited on silicon substrates by using a chemical etching method. This facilitated the recording of the IR spectra on self-standing sheets that avoided unwanted interference from the substrates. Several sets of sheets were deposited and subjected to FTIR spectroscopy to check the reproducibility of the data and the methodology. The IR spectra were recorded in the range 400-4000 cm^{-1} on a Nicolet Fourier transform spectrometer (Thermo Electron Corporation, San Jose, CA) (www.thermo.com) in the transmission mode. The as-deposited diamond sheets were subjected for characterisation using scanning electron microscopy (SEM), x-ray diffraction (XRD), and Raman spectroscopy.

3. Experimental Results and Discussion

Figure 1 shows SEM micrographs of the typical (111) and (100) textured diamond films deposited in this study. XRD analysis (not shown) of these films showed (111) and (100) peak, respectively. Figure 2 shows the Raman spectra of (a) (111) film deposited at 20 torr, (b) (100) film deposited at 120 torr, and (c) (111) film deposited at 120 torr. The spectra showed characteristic sharp Raman lines at 1332 cm^{-1} indicating the presence of high quality sp^3 bonded carbon network in the sheets. However, the (111) film at 120 torr showed a higher percentage of nondiamond carbon. We have observed that the (111) samples grown at lower deposition pressure (20 torr) were translucent with white color that changed to a dark brown color as the deposition pressure in the chamber increased. In contrast, good quality (100) sheets were obtained at 120 torr. Figure 3 shows the FTIR spectra of (a) (111) diamond sheet and (b) (100) diamond sheet.

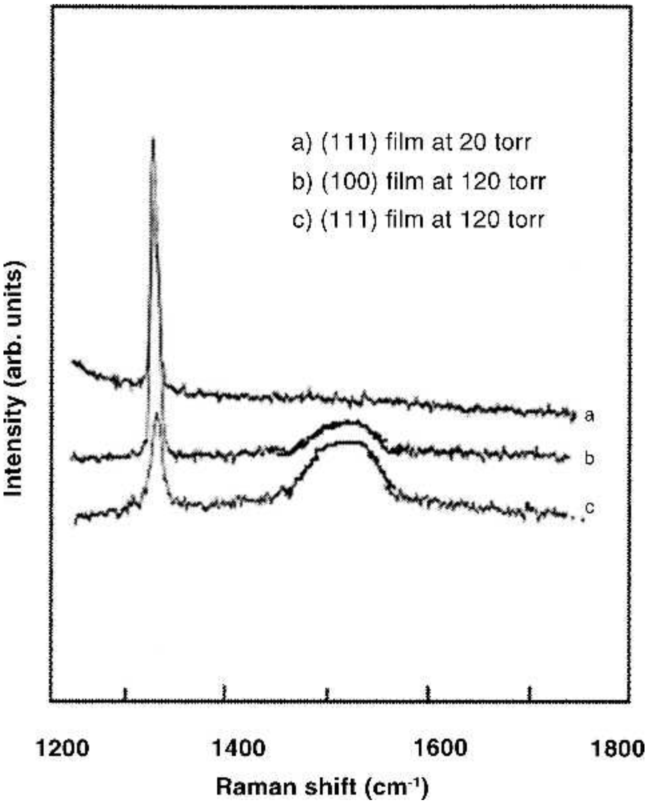

Fig. 2 Raman spectra

The spectra are corrected by using a suitable polynomial fit. As the absorption in the CH stretching region is significant, we studied the region 2700 to 3100 cm^{-1} in great detail. The spectrum in this region is a superposition of the CH vibrations from sp^m CH_n, where $m, n = 1, 2, 3$. Sharp absorption peaks in the CH region indicate strongly bonded hydrogen. The experimental spectrum was fitted using Gaussian peaks after background corrections. Analysis of the spectra was carried out on the basis of peak assignments available in the literature (Ref 19, 20). The half width and amplitude of the bands were taken as fitting parameters. The frequency of the vibration shifted slightly for C-H bonds in different local environments, allowing one to differentiate between various CH_n groups. Since each individual sp^m CH_n configuration is characterized by a specific IR absorption peak, one can use these spectral peaks to analyze the relative hybridisation of the carbon atoms. Deconvolution of the CH band showed mainly seven peaks in this region (Table 1).

Close examination of the CH stretch region showed that diamond sheets deposited at 120 torr and above also contained

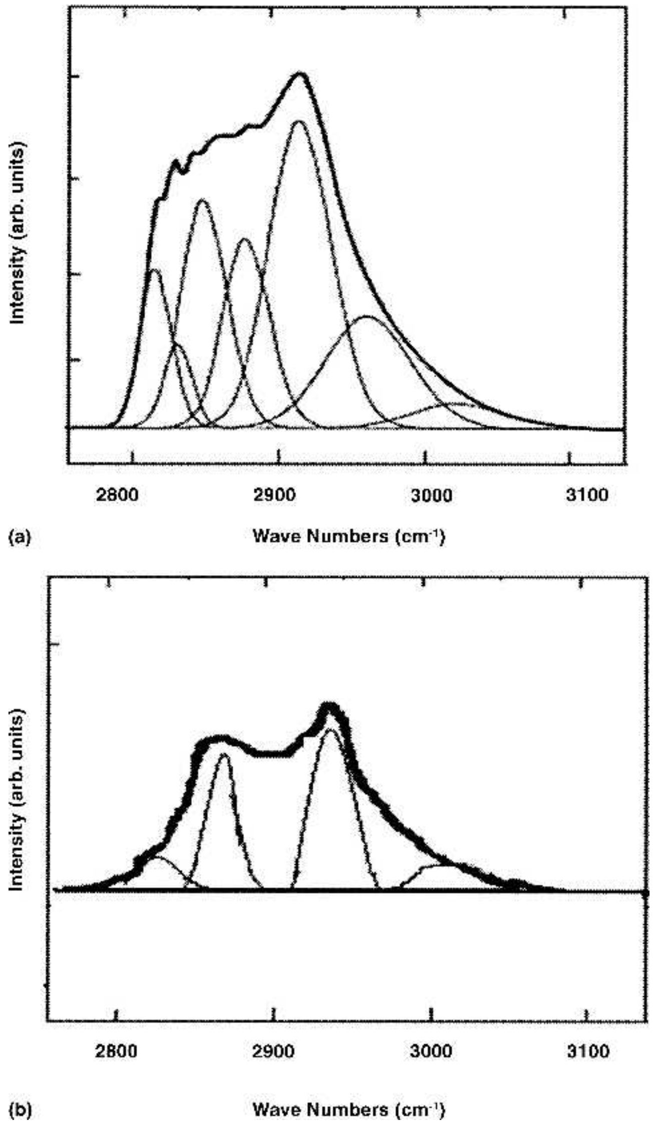

Fig. 3 FTIR spectra of diamond sheets of (a) (111) and (b) (100) film

hydrogen bonded to sp^2 carbon (3025 cm^{-1}). This is, however, considerably smaller than hydrogen bonded to sp^3 carbon. The dominant absorption peaks near 2850 and 2920 cm^{-1} are indicative of the symmetric and asymmetric stretch bands of sp^3 CH_2 group, respectively. The bands at 2880 and 2960 cm^{-1}, on the other hand, are due to symmetric and asymmetric stretch modes of sp^3 bonded CH_3 groups. The peaks at 2820 and 2832 cm^{-1} are related to N and O centers, respectively. They are the CH stretch vibrations of the carbon-hydrogen bond in N-CH_3 and O-CH_3 groups. These bands have also been assigned to H terminated diamond (111) surfaces (Ref 13). However, we find that the intensity of the band at 2820 cm^{-1} increased in the samples deposited with N_2 doping. Similarly, the intensity of the 2832 cm^{-1} band increased for diamond sheets that were treated with oxygen plasma. Unlike the spectra of (111) textured sheets, the (100) textured diamond sheets contained two dominant peaks centered at 2860 and 2930 cm^{-1}, which correspond to symmetric and asymmetric stretch bands of the CH_2 group. Therefore, it would appear that (100) growth mainly occurs via CH_2 species (Ref 18).

Table 1 Deconvolution of CH bands

Wave number, cm^{-1}	Mode of vibration
2820	N-CH_3
2832	O-CH_3
2850	Sym. sp^3CH_2
2880	Sym. sp^3CH_3
2920	Asym. sp^3CH_2
2960	Asym. sp^3CH_2
3025	Sp^2 CH

3.1 Concentration of Hydrogen: Quantitative Analysis

A range of techniques has been used to monitor the content of H in diamond films deposited using CVD. Some are direct techniques, such as elastic recoil detection analysis (ERDA), nuclear reaction analysis (NRA), etc., and others are indirect, such as nuclear magnetic resonance (NMR), IR absorption, etc. We have devised a simple and effective technique for measuring the H content in CVD diamond sheets. One to ten milligrams poly methyl methacrylate (PMMA) [-$CH_2C(CH_3)CO_2CH_3$-] in the powder form was mixed with 200 mg KBr and ground again to make pellets for IR transmission. The absorption spectra in these pellets were recorded in the sp^3 CH region (2700-3150 cm^{-1}) and fitted using Gaussian peaks after background correction (Fig. 4).

The total area under the curves was calculated. The concentration of PMMA was selected in such a way that the total integrated absorption under the CH stretch region of PMMA and the CVD diamond sheets was comparable. Also, the instrument's gain and other parameters were kept constant for recording the spectra on all samples and the standard. A large number of standard samples containing varying concentration of PMMA and H atoms were prepared and subjected to IR transmission to verify the reproducibility and consistency of the data. The area of the curve under CH stretch region was plotted as a function of H concentration for the standard sample. Slope and intercepts were obtained by fitting the data to a straight line. Taking these as the standard with a known total area in the CH stretch region of diamond samples, H contents were obtained.

3.2 Hydrogen Content by Integration Method

The integrated absorbance of each band can also be used to estimate the hydrogen concentration in a particular mode. As discussed by MacNamara et al. (Ref 13), the concentration of the oscillating species is proportional to the integrated intensity of the absorption band. The total hydrogen content (N_H) is given by the following relationship:

$$N_H = A_n \int \frac{\alpha(\omega)\, d\omega}{\omega} \qquad \text{(Eq 1)}$$

where A_n is the proportionality factor and $\alpha(\omega)$ is the absorption coefficient at frequency ω and A_n is proportional to the inverse of oscillator strength. We have chosen A_n to be 1×10^{20} and assumed it to be constant for all the modes and samples (Ref 16). $\alpha(\omega)$, the frequency dependent absorption coefficient, is assumed to be a Gaussian function.

Figure 5 shows the variation of the concentration of H atoms attached to individual modes in the diamond sheets deposited at different pressures. It can be seen that there is a significant inequality in absorption intensity in bonded H for

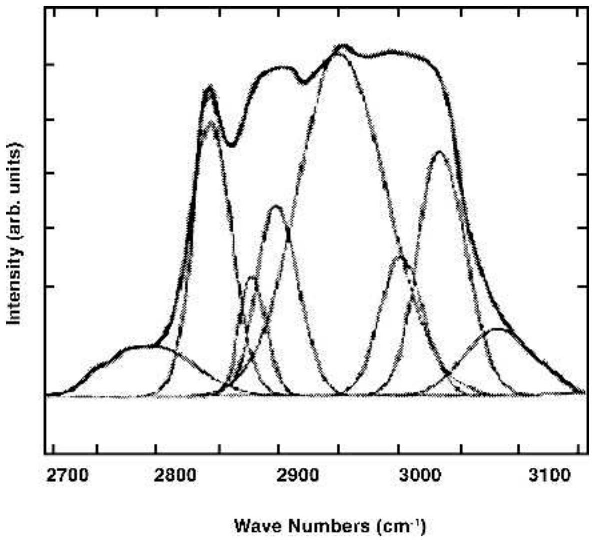

Fig. 4 Hydrogen content in different amounts of PMMA standard with the area under CH stretch region

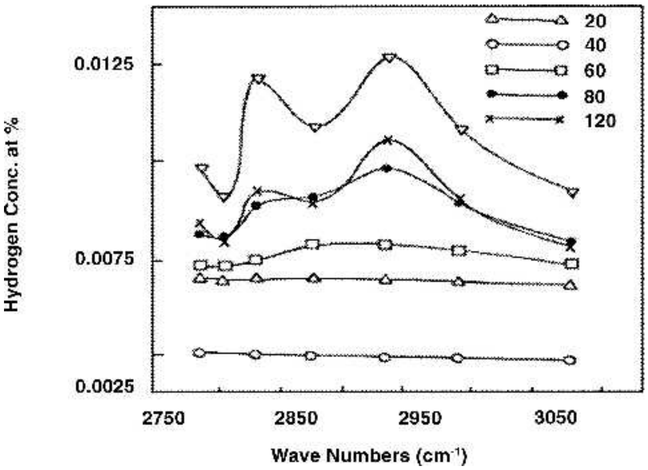

Fig. 5 H content associated with different vibrational modes of the sheets grown at different deposition pressures. H content was calculated using the comparison method.

Table 2 H content associated with each mode of vibration and the total H content in the sheets grown at different pressures. H content data obtained from both the integration and standard methods.

		Frequency, cm^{-1}								
		Hydrogen content, at.%								
Sample	Pressure, torr	2820	2832	2850	2880	2920	2960	3020	%H by integration	%H by standard
(111)	20	0.00728	0.00723	0.00726	0.00732	0.00734	0.00728	0.00725	0.051	0.048
(111)	40	0.00535	…	0.00533	0.00534	0.00532	0.00533	0.00531	0.032	0.039
(111)	60	0.00759	0.00756	0.00773	0.00816	0.0082	0.00808	0.00776	0.055	0.053
(111)	80	0.00841	0.00833	0.00917	0.00939	0.0102	0.00931	0.00837	0.056	0.049
(111)	120	0.00868	0.00955	0.009551	0.00929	0.01095	0.0094	0.00824	0.064	0.063
(100)	120	0.00582	…	0.00682	…	0.00721	…	0.00732	0.028	0.031

the symmetric and asymmetric bands of sp^3 bonded CH_2 and CH_3 groups in a diamond environment. This inequality, where the intensity of the asymmetric band is greater than the symmetric band, was observed dominantly in all the diamond sheets grown at higher deposition pressures. This may be due to the H content being high in these sheets. Even long chain hydrocarbon molecules show higher intensity for asymmetric peaks than symmetric peaks (Ref 21). The H content increased in the sheets deposited at higher pressure (Table 2). The calculations of the proportionality constant A_n for different modes of vibrations is almost impossible unless there is an independent technique that can calculate the exact number of H atoms bonded in different modes. Other workers have also emphasized this difficulty in growing CVD diamond (Ref 15, 16). Using the value of H content calculated for different modes using comparison method, we have estimated the value of A_n for various C-H modes in CVD diamond. These values are listed in Table 3. Similarly, the values of A_n are also calculated with the help of the total hydrogen concentration calculated from the comparison method. We found that A_n decreased with increasing H content in the sheets. Figure 6 shows the variation in A_n values for different sheets grown at different deposition pressures. The inset in Fig. 6 shows the change in intensity ratio of nondiamond (I_{nd}) and diamond (I_d) Raman bands with deposition pressure.

It can be seen that there is an order of magnitude difference in the value of A_n for the sheets with high and low values of I_{nd}/I_d . This implies that by knowing the quality of the diamond films, in terms of nondiamond/diamond intensity ratio from Raman spectra, one can select accordingly, a suitable A_n value for the calculation of bonded hydrogen in the diamond film. The variation in the values of A_n is not surprising considering that the environment surrounding each C-H mode varies significantly with deposition pressure and the structure of the sheets.

4. Conclusions

IR spectroscopy was used to investigate the hydrogen content in the diamond sheets grown under various conditions using the HFCVD process. The FTIR spectra showed the presence of bonded hydrogen in the films grown under different conditions. However, the amount varied according to the growth conditions. The quantitative analysis of hydrogen using standardization and integration methods was comparable, and it gave insight into various possible modes of vibration of the hydrogen atom. The results were comparable with the Raman results. The quantity of hydrogen was less in (100) textured sheets and the peaks were dominated by CH_2 species.

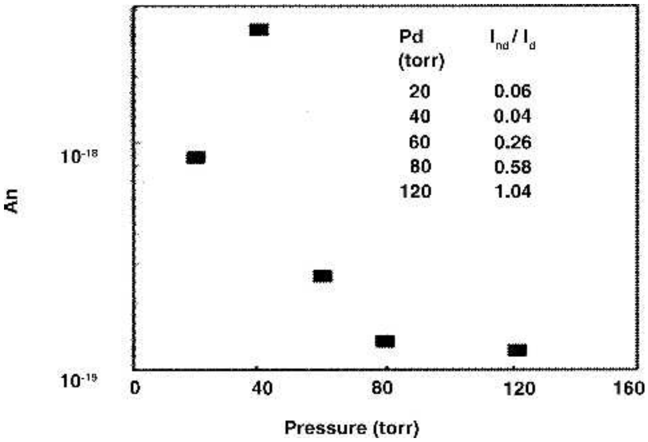

Fig. 6 Proportionality constant (A_n) for the sheets grown at different deposition pressures

Table 3 Variation of proportionality constant with different modes

Frequency, cm^{-1}	$A_n \times 10^{19}$
2820	2.045
2832	4.075
2850	1.085
2880	1.263
2920	6.899
2960	1.215
3020	4.645

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