

**RAMAN STUDY OF FREE-STANDING DIAMOND FILMS AND COATINGS
DEPOSITED ON TUNGSTEN CARBIDE TOOLS
PREPARED BY HOT-FILAMENT CVD METHOD***

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Hot-filament chemical vapor deposition (HFCVD) method is presented to prepare *i*) free-standing diamond films using Si (100) mirror-polished substrate and *ii*) diamond coatings deposited on WC/Co cutting plates. Both diamond films and coatings have been prepared with high quality as has been shown an analysis by micro-Raman spectroscopy. Raman spectra also have showed similar structure for both deposited films and coatings, respectively. We have found the almost same of position of a luminescence peak in the diamond coating as in the free-standing diamond film. A method is proposed for evaluation of relatively concentration of luminescence centers in the film. A discussion is considered about structure of such centers.

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1 Introduction

Research in the area of diamond thin film deposition has increased significantly in the last 15 years. The remarkable properties of diamond, including its extreme hardness, low coefficient of friction, chemical inertness, transparency and semi-conducting properties, make it attractive for a number of industry applications.

A common method for preparing diamond film is chemical vapor deposition (CVD) method. Among the multitude of diamond CVD processes which have been developed since about 15 years, the hot-filament CVD process together with the microwave-plasma CVD (MWPCVD) is one of the two first methods used in the diamond deposition.

It is believed, that the HFCVD is a good choice for many applications in which an ultra clean film is not mandatory. A major advantage of the hot-filament system is the ability to deposit a coating of very uniform thickness over a broad area. Unlike microwave reactors, the hot-filament system presents no potentially dangerous levels of microwave energy and no unintended hydrocarbon byproducts such as benzene or other potential carcinogens. From this point of view HFCVD should be in competition with MWPCVD for preparing the diamond films.

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In the present work we carried out an analysis by micro-Raman of the free-standing diamond film grown on a silicon substrate and of the diamond coating deposited on cutting plates, namely cemented carbides, by hot-filament CVD system. HFCVD reactor has some technological innovations to support better stability of a chemical vapor process. We have found the almost same luminescence peak in the diamond coating as in the free-standing thin film.

2 Experimental details

Diamond nucleation and growth were conducted in a HFCVD system [1]. A mirror-polished Si (100) substrate was held on a molybdenum holder, and three tungsten hot filaments were hung above the substrate. A plasma grid was placed over the heated filaments and a DC power so that plasma can be generated between this grid and the filaments. A substrate is placed on a rotating substrate holder to support a homogeneity of deposited films. The substrate holder is heated by an independent source with a special control unit.

The experimental parameters of the deposition process were as follows: gas flow H_2/CH_4 sccm (sccm denotes standard cubic centimeter per minute) was 300/3; total pressure was 3×10^3 Pa; filament temperature heated to ~ 2000 °C; substrate temperature held at ~ 600 °C as measured by a K-type thermocouple mounted on a molybdenum substrate holder, and ; the distance between wires and Si substrate was approx. 8 mm. Prior to deposition of diamond films the filaments were heated in a methane-hydrogen atmosphere to enhance the formation of the tungsten carbides layer covering the filament surface in order to reduce the tungsten evaporation during the deposition process. The silicon substrate was first ultrasonically cleaned in acetone, then immerse in NH_4OH and HF to remove the native oxide layer and to passivate the surface. After deposition of diamond film on the Si wafer the silicon substrate was removed by etching in a hot KOH solution. The initial step in preparing the plate surface for CVD coating was to etch of the surface cobalt using acid bath with $HCl:HNO_3$ (1:1) solution (15 min.). In the case of the cutting tools the diamond films were not removed from the substrate. The deposition process consisted of two stages: nucleation period and growth period. Nucleation was performed at negative substrate biasing of -170 V. The growth was achieved at positive substrate biasing of $+100$ V.

Micro-Raman spectra were carried out by means a Dilor system (Jobin Yvon /Spex /Dilor, Horiba Group) working with a He-Ne laser, which was focused on the sample to a spot size ~ 1 μm in diameter at the sample surface in the backscattering geometry. An ISA Labram equipment was used for Raman measurements. The excitation was carried out with He-Ne laser with a wavelength of 632.817 nm. All measurements were made by focusing a laser beam through $100 \times$ lens on the surface of the sample. For all measurements, a confocal hole diameter of 200 μm , a spectrograph entrance slit of 150 μm , and a 1800 grooves/mm diffraction grating were employed. The curve fitting of the Raman spectrum involved the use of a nine order polynomial function for baseline correction.

A first sample represents a free-standing ~ 0.03 mm thick diamond film grown on the Si wafer. From an optical microscope analysis an average grain size of 5-10 μm was estimated. The Raman spectra were performed in the center of the sample. The second sample was WC-Co plate with bulk cobalt of 6 % (10 mm \times 10 mm \times 4 mm) and the Raman spectra were obtained from diamond coating at the edge of the plate.

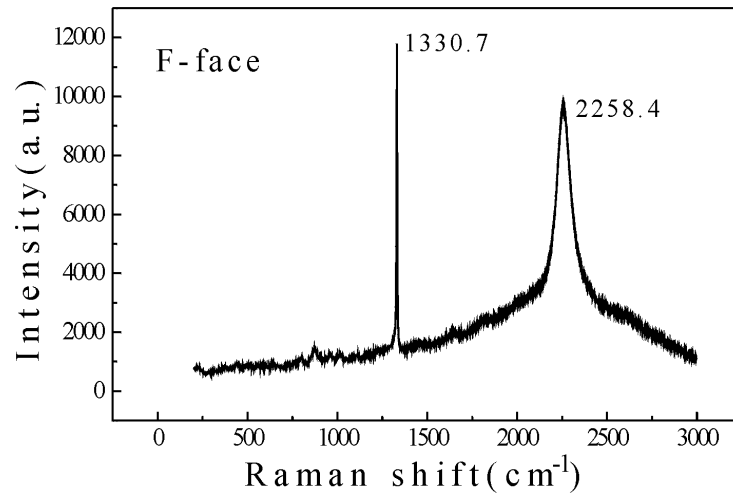


Fig. 1. Micro-Raman room temperature spectrum taken with He-Ne laser of the free-standing diamond film deposited on Si substrate from F-face.

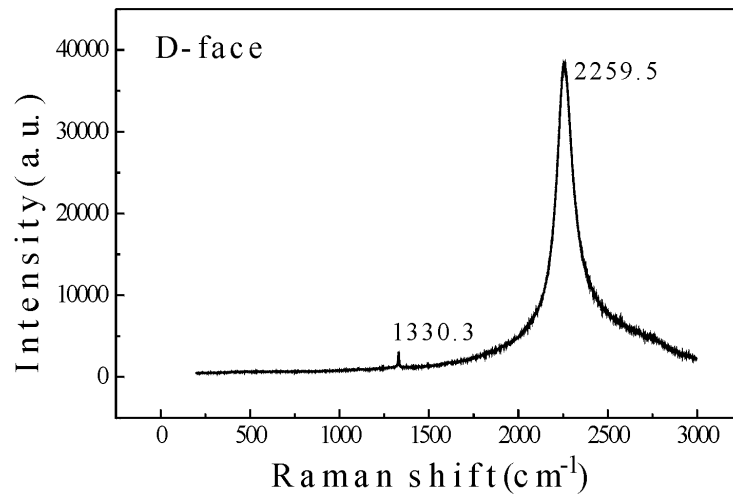


Fig. 2. Micro-Raman room temperature spectrum taken with He-Ne laser of the free-standing diamond film deposited on Si substrate from D-face.

3 Results and discussion

In Fig. 1 and Fig. 2 room temperature micro-Raman spectrum taken in different regions of slab, both in the front (F) and the back surface (D) are shown, respectively. Growth time of diamond film grown on the Si substrate was 97 hours and 30 minutes. Linear growth rates of roughly $0.3 \mu\text{m}$ were achieved under the conditions quoted above. The Raman spectrum of the material

deposited on Si substrate displays two main bands centered at $\sim 1331 \text{ cm}^{-1}$ and $\sim 2260 \text{ cm}^{-1}$. The sharp peak at 1331 cm^{-1} originates from the CVD diamond structure. It is known that natural diamond is characterized by its phonon at 1331 cm^{-1} with the full width at half maximum (FWHM) 1.8 cm^{-1} . For diamond different origins, the frequency varies from 1331 to 1336 cm^{-1} and FWHM from 1.8 to 3 cm^{-1} depending on the distortion from perfect cubic structure [2]. In Fig. 1 the F-face has the band at 1330.7 cm^{-1} and FWHM is 4.2 cm^{-1} . It means a relatively good quality of polycrystalline diamond films grown on the Si wafer at above deposition conditions. The wide band, centered at $\sim 2260 \text{ cm}^{-1}$ corresponds to an energy of 1.68 eV . Assignment of the line in Joules to the corresponding position in m^{-1} units determines the relation $E = hc(\lambda_{\text{laser}}^{-1} - \Delta\nu)$, where E is energy in Joules, c is the velocity of light, h is Planck constant ($h = 6.6262 \times 10^{-34} \text{ Js}$), λ_{laser} is the laser line 632.817 nm , $\Delta\nu$ is Raman shift in m^{-1} . It is widely accepted that a line at 1.68 eV in CVD diamond grown on Si is due to Si diffused from the substrate [3]. Symmetry of the center, experimentally determined in Ref. [4], suggests that this center consists of two or three point defects aligned to the $\langle 110 \rangle$ axis. The silicon-vacancy (Si-V) model was suggested for the 1.68 eV defect in Ref. [5]. The study of this emission in diamond films is more complex and different energy position, different phonon energies, and different de-excitation processes can be found in the literature [6]. The spectral fine structure close to 1.68 eV usually is not observed in polycrystalline CVD diamond. This is probably due, at least in part, to line-broadening effect caused by the internal stress and strain distribution which is commonly present in CVD diamond films. Figure 2 plots the distribution of the diamond Raman line and the non-Raman lines in the region of back surface. The diamond band is located at 1330.3 cm^{-1} and FWHM = 5.5 cm^{-1} - quality of the diamond film in the back side is lowered.

To study the Raman spectra quantitatively we use a ratio of diamond peak intensity to the defect luminescence peak intensity. R.E. Schroder *et al.* [7] have done analysis of the composite structure in diamond films using model where the ratio of the Raman scattering intensity of diamond to a graphite may be written as

$$\frac{I_D}{I_G} \propto \frac{A_D N_D V_D}{A_G N_G V_G}.$$

A is the angle- and polarization-averaged scattering efficiency per nearest-neighbor bond, N is atomic density of graphite or diamond, and V is the volume of material which is actually sampled by the Raman scattering. In our analysis we use the above model and instead of the graphite phase we take the luminescence centers in the deposited film. Consequently, the Raman scattering intensity is proportional to a concentration of defect centers in the film and the strength of the scattering also may be known. The cross-section could be calculated by quantum mechanics however, the theory lies outside the scope of the present work. According to the above facts it is suitable to use the ratio I_D/I_L for comparison of the results from the same samples prepared under different deposition conditions.

Table 1 shows our results obtained by HFCVD method with those published by M.R. Correia *et al.* [8]. Free-standing diamond film grown by MWPCVD had a thickness of 0.25 mm . The thickness of the film prepared by HFCVD was $\sim 0.03 \text{ mm}$. The results of calculations show that the ratio I_D/I_L for the sample grown by MWPCVD is higher than for that sample deposited at the HFCVD reactor. This could be explained mainly in difference of the thickness of diamond films prepared according to various methods. Many non-diamond carbon phases and defects usually occur at the beginning of diamond growth. The lower ratio I_D/I_L (see Table 1) for the

Method	ID/IL (F-face)	ID/IL (D-face)
HFCVD	1.6	0.1
MWPCVD [8]	2.9	0.2

Table 1. Comparison of different deposition methods of diamond films.

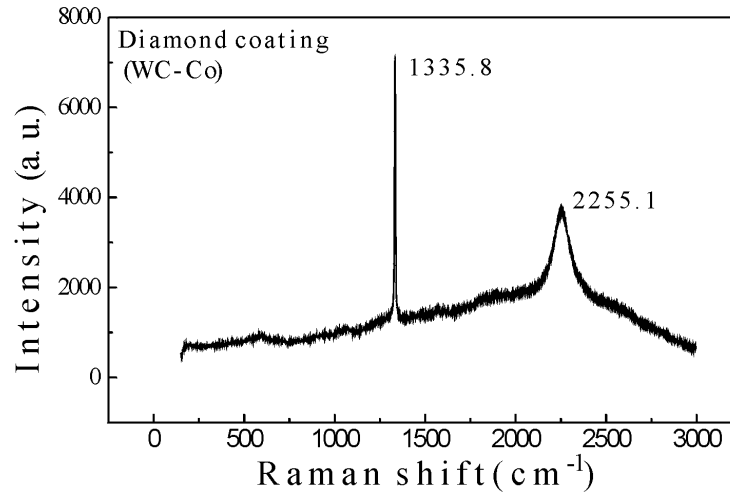


Fig. 3. The Raman spectra of diamond coating deposited on the WC-6 Co cutting plate.

backside spectrum confirms that there are relatively more defect centers at the back side than at the surface side. The Si impurity could be incorporated by diffusion along the grain boundaries. More thickness of free-standing films contain a relatively lower concentration of defects related to sp^3 bonds than those thinner layers.

An interesting result has been obtained for diamond coating deposited on the WC-Co plates. Figure 3 shows Raman spectrum of such a film. The diamond band is located at 1335.8 cm^{-1} with a FWHM of 8.0 cm^{-1} . This spectrum corresponds to the following deposition conditions: the nucleation stage-gas pressure 2 kPa, H_2 flow rate 300 sccm, CH_4 flow rate 3 sccm, the substrate temperature $600\text{ }^\circ\text{C}$, the filament temperature $\sim 2000\text{ }^\circ\text{C}$, the nucleation time 1 hour, the current density $\sim 0.5\text{ mA/cm}^2$. The growth stage consists of: gas pressure 3 kPa, H_2 flow rate 300 sccm, CH_4 flow rate 3 sccm, the substrate temperature $600\text{ }^\circ\text{C}$, the filament temperature $\sim 2000\text{ }^\circ\text{C}$, the growth time 8 hour, the distance between wires and substrate $\sim 4\text{ mm}$. The quality of coating is also very good. The Raman peak closely at 2260 cm^{-1} corresponds to the luminescence center in the diamond coating. Because the WC-Co phase has no Si atoms, probably we could not suggest that these centers consist of Si atoms. Preliminary results from the diamond films grown on molybdenum wafer also shown the luminescence band closely at 2260 cm^{-1} . Probably the center is related with the neutral vacancy in diamond, which also shows a spectral line close in this region of the spectrum [6,9]. Further analysis of this defect is under progress.

4 Conclusions

In this paper we have analysed the Raman spectra from polycrystalline diamond films grown on the Si wafer (free-standing film) and WC-Co cutting plates. The experimental results showed a sharp diamond peak and the luminescence band in the Raman spectra.

Both diamond films were successfully prepared by HFCVD method. The advantage of HFCVD over plasma CVD methods are the adaptability to product geometries and the moderate activation temperatures for deposition on temperature-sensitive substrates.

For active electronic device such as diamond transistors, the requirements on the material perfection are much higher. High-quality plasma-activated CVD should be the preferred deposition method for diamond in electronic applications. However, further technological development, as it has been shown in this work, make transfer the HFCVD-diamond technology to production of high-quality products on a large scale.

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