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Structural properties of polycrystalline diamond films prepared by Hot-filament Chemical Vapour Deposition technique

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Abstract

Polycrystalline diamond layers were deposited on silicon substrate using the hot filament chemical vapour deposition (HF-CVD) technique with a mixture of propane-butane/hydrogen as a working gas. The morphology and structural properties were observed using scanning electron microscopy (SEM), X-ray diffraction (XRD) and Raman spectroscopy, respectively. The SEM measurements have executed on films at different process duration. The films showed a pyramid shape with a preferential (111) morphology. The XRD patterns of films exhibited the whole spectra of diamond structure. At filament temperature of 2140°C and 2200°C followed with increasing the gas flow and deposition duration, the reflection peak at (111) is sharp and has a high intensity indicating good crystalline films. The crystalline size of films increased from 50nm to 255nm as process duration is decreased from 34h to 13h and the filament temperature is increased up to 2150°C.

On the other hand, an increase of filament temperature, gas flow rate and process duration to 2200°C, eight sccm, and 42h, respectively, the film showed the smallest crystalline size value of 29 nm among the other samples. The stress values of films were estimated using the Raman spectrum. The films have comparative stress generated during cooling down to room temperature.

Keywords: *diamond thin film, HF-CVD technique, X-ray diffraction, grain size*

1. Introduction

Diamond is an exciting material due to its unique properties that make it a highly desirable material for a passive and active electronic application. The properties of interest in this context include the wide gap (5.45 eV), exceptional thermal conductivity (5 times higher in comparison to

copper), high electrical resistivity (~ 10^{16} Ω·cm), and high elastic modulus (1050 GPa). Diamond based semiconductor devices will be able to operate at high temperatures, at high frequencies and high power. The diamonds low optical absorption over a wide spectral range and luminescence in the blue and green region are of interest for optoelectronic applications [1-3].

Among of many techniques to grow the diamond thin films from the gas, phase is the chemical evaporation method (CVB). It has been confirmed to be a very versatile apparatus [4]. Chow. L et al. [4] have prepared the nanocrystalline diamond thin films using the hot filament CVD technique with a mixture of CH4/H2/Ar as the reactant gas. They reported that the ratio of reactant gas is important to control the grain size of the diamonds and the growth of the nanocrystalline diamonds. Ong-On Topon et al. [5] have reported the X-ray diffraction studies on the grain size of nanocrystalline diamond and residual stress on silicon substrate prepared by hot filament CVD. They found that the maximum residual stress was recorded at 5.5 GPa, and it was nonuniform. S.A. Rahman et al. [6] have observed that the decrease in pressure and methane flow rate produced significant changes to the morphology of the grains formed of diamond thin films prepared by the hot filament CVD. In general, the quality of crystals is improved through these two factors [7,8].

This paper reported the morphology and structural properties of diamond film using scanning electron microscopy, X-ray diffraction and Raman spectroscopy. The samples were synthesized by the hot filament CVD technique (HF-CVD). This work could help in finding the optimal CVD process parameters in order to get better diamond films.

2. Experimental Approach

Polycrystalline diamond layers were deposited using the hot filament method using the apparatus whose scheme is presented in Figure 1. Its most important part is the settling chamber (1), where an appropriate reaction medium is made. The chamber walls are built of two layers, forcing in water between them, which cools off the whole thing and protects thermosensitive elements (hoses and gaskets) against overheating. In the chamber bases, two holes are made through the bottom one, the working mixture is let in (gas binding is executed in the supply conduit), and through the upper one, it is drawn outside. The measurement of gas pressure in the reactor is made using the diaphragm pressure gauge and its regulation through the proper setting of the suction valve of the rotary pump. The mixture entering the chamber first flows around the tungsten filament (2), then goes to the siliceous base (3) on the surface of which diamond is deposited. The filaments are heated with an alternating current of controllable intensity produced by a welding transformer. Filament's graphitoidal frame and the same table on which lies the holder with the base is cooled with flowing water. Along with the holder, additional tungsten wire is installed through which voltage (electron bombardment of the increased area) can be supplied to the silicon substrate. The substrate temperature can be regulated either by variation of current intensity or by variation of distance between the substrate and filament. In the experiment, the following constant parameters were taken into account:

a) The pressure in the reactor was stabilized at the level of 30 Torr.

b) The flow of hydrogen was 40 sccm.
c) The current going through filaments was set at 68A, and during the process (after half an hour), it was reduced to 58A and then kept at a constant level. The HF-CVD process parameters for the samples are arranged in Table 1.

3. The results and discussion

3.1 The SEM measurements

Figure 2 (a-d) shows the SEM measurements for the films at different process duration. The films show a pyramid shape with a preferential (111) morphology. The increasing filament temperature has associated with the increase of propane-butane flow rate up to 8 sccm, which led to appear the secondary nucleation (Figure 2d), and that causes the filling of surface irregularities on the film profile. The same results were reported by Hassan et al. for their diamond films deposited by pulsed bias enhanced hot filament CVD [9].

3.2 The XRD Analysis

Figure 3 shows the XRD pattern of the films prepared by the CVD method under variation of filament temperature value accompanied by variations in the propane flow and process duration. It can be seen that, at filament temperature of 2140°C for D1, the film shows full spectra of diamond structure which are concerned to the five reflexes, i.e. (111), (220), (311), (400) and (331). The reflection peak at (111) is sharp and has a high intensity indicating a good crystalline film. At filament temperature value of 2140°C with further increasing the gas flow and decreasing of process duration to 23h, D2 film exhibits few peaks with low intensities, these peaks related to reflexes (111), (220), (311) and (331). The same result has been observed for D3 film when the filament temperature value is increased to 2150°C followed by the decreasing of gas flow and process duration. The reflection peaks at (400) for both films D2 and D3 have low intensities. This is ascribed to the low value of the atomic form factor [10]. Also, the decrease in intensities for D2 and D3 films may be related to induce occurs due to lattice mismatch between the film and substrate [11]. The full pattern of diamond structure is observed of D4 sample at further increasing of filament temperature up to 2200°C, gas flow rate at 8 sccm, and process duration at 42h. Also, a clear shift in the position of the peak to the higher 2θ as filament temperature increases might be non-diamond is incorporated in the film structure [5,12].
The crystallite size of films was computed using a Sherrer's equation:

$$L = 0.9\lambda/\beta\cos\Theta \qquad (1)$$

where, β is the half-width of a particular reflex, λ is the wavelength of the X-ray and L is the crystalline size. The obtained results are shown in Figure 4. It can be seen that, the crystallite size of films is increased from 50nm to 255nm as process duration is decreased from 34h to 13h and

the filament temperature is also increased up to 2150°C. Further increase of filament temperature, gas flow rate and process duration to 2200°C, 8 sccm, and 42h, respectively, the D4 film showed the smallest crystalline size value of 29 nm among the other samples.

3.3 Raman Analysis

The Raman spectra were taken in the range of 1100-1800 cm^{-1}. For excitation, the green line (λ=514.5nm) from argon laser has been used. The fitting procedure was performed for each spectrum. It allowed deriving the half-width and position for the diamond Raman line 1332.5 cm^{-1} as shown in Figure 5.

The Raman spectrum analysis performed above allows estimating the amounts of stress in the diamond films using the following formula [13]:

$$\sigma_1 = E(1 - (\nu_0/\nu)^{1/2}) \qquad (2)$$

where E is the Young modulus,ν_0 is the diamond line position (ν_0=1332.5cm^{-1}), ν is the measured diamond line position, and σ_1 is the stress. The values of stress as a function of the deposition time have been calculated according to the harmonic oscillator approximation. However, the values of stress have also been calculated from the formula given for single diamond crystal [14]:

$$\nu = \nu_0 + \gamma\sigma_2 \qquad (3)$$

where σ_2 is the stress, and γ is the coefficient (3.2 $GPa^{-1}cm^{-1}$). The results are collected in Table 2. Generally, residual stress can be classified into three categories according to its origin. The first is thermal stress generated during cooling down to room temperature caused by differences in the coefficient of thermal expansion (CTE) between the diamond film and the Si substrate result of the comparative stress [15]. The second type of residual stress is lattice mismatch stress. However, in the case of the hot filament chemical vapour deposition (HF- CVD) method, epitaxial growth of diamond/Si cannot be expected. The third category is intrinsic stress, which varies with the amount of non-diamond carbon, grain size and defect in the films [16].

4. Conclusions

Polycrystalline diamond layers were deposited using the hot filament method. The films showed a pyramid shape with a preferential (111) morphology. The samples have peaks featured of the diamond. The long temperature and increasing the gas flow produced an excellent film structure with a small crystalline size. At filament temperature of 2140°C for D1sample, the film shows full spectra of diamond structure and with further increasing of filament temperature up to 2200°C, gas flow rate up to 8 sccm. Process duration up to 42h, the whole pattern was again observed of D4 sample. The Raman spectrum analysis utilized to estimate the amounts of stress in

the diamond films. The films have comparative stress due to the difference in the thermal expansion coefficient between the film and substrate.

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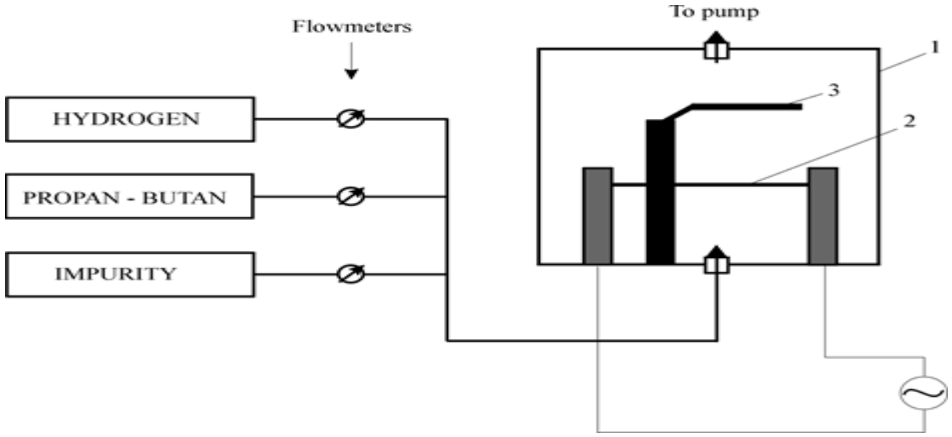

Fig 1. Schematic diagram of HF-CVD method, (1) Settling chamber. (2) Tungsten filament. (3) Siliceous base.

Table 1. The HF-CVD process parameters for the samples.

Sample	Propane-butane flow rate [sccm]	Filament temperature [°C]	Process duration [h]	Hf sample distance [mm]	Pressure [Torr]	Hydrogene flow rate [sccm]
D1	6	2140	34	9	30	40
D2	7	2140	23	9	30	40
D3	5	2150	13	9	30	40
D4	8	2200	42	9	30	40

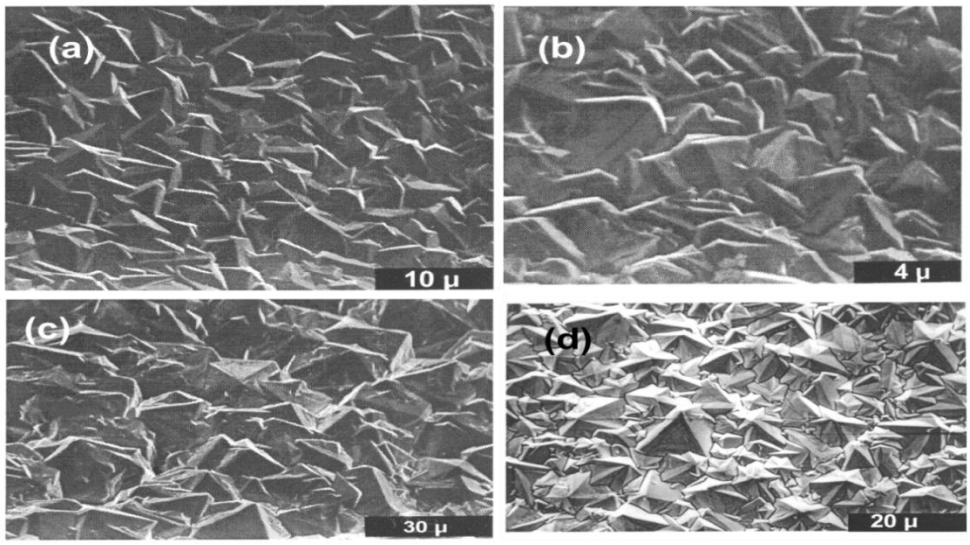

Fig.2. The SEM images of the films at different filament temperature, propane-butane flow rate, and process duration (a) D1 at 2140 °C, 6 sccm, and 34 h (b) D2 at 2140 °C, 7 sccm, and 23 h (c) D3 at 2150 °C, 5 sccm and 13 h (d) D4 at 2200 °C, 8 sccm, and 42 h.

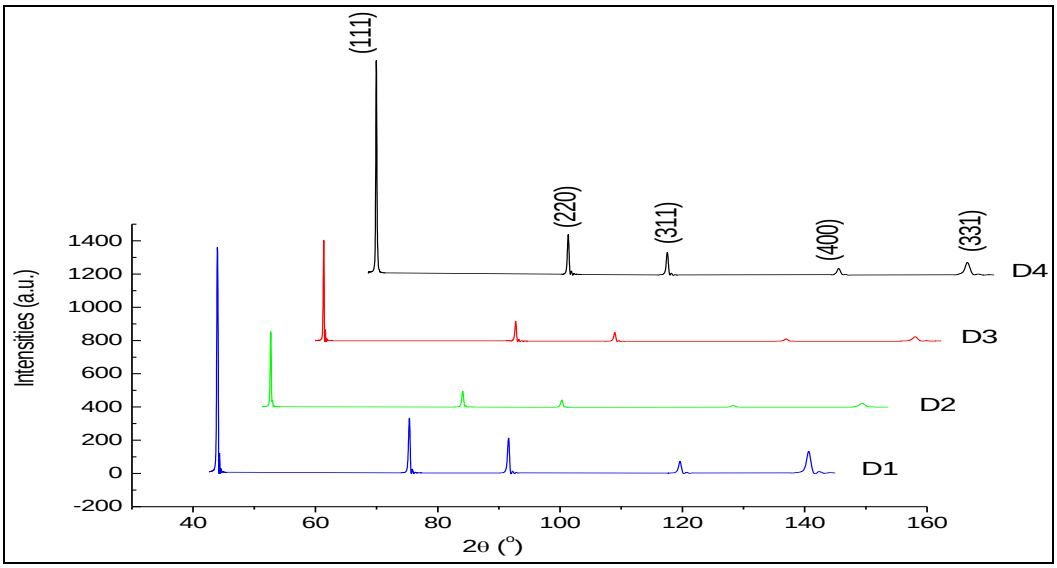

Fig. 3. The XRD patterns of the films. Full pattern of diamond structure is observed of D1 and D4 samples.

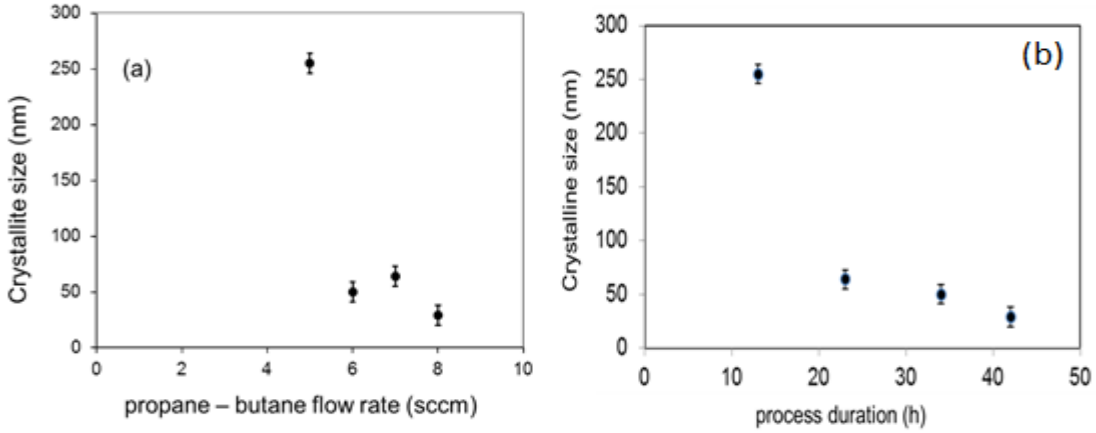

Fig.4. The variations of crystalline size verses (a) propane-butane flow rate and (b) process duration.

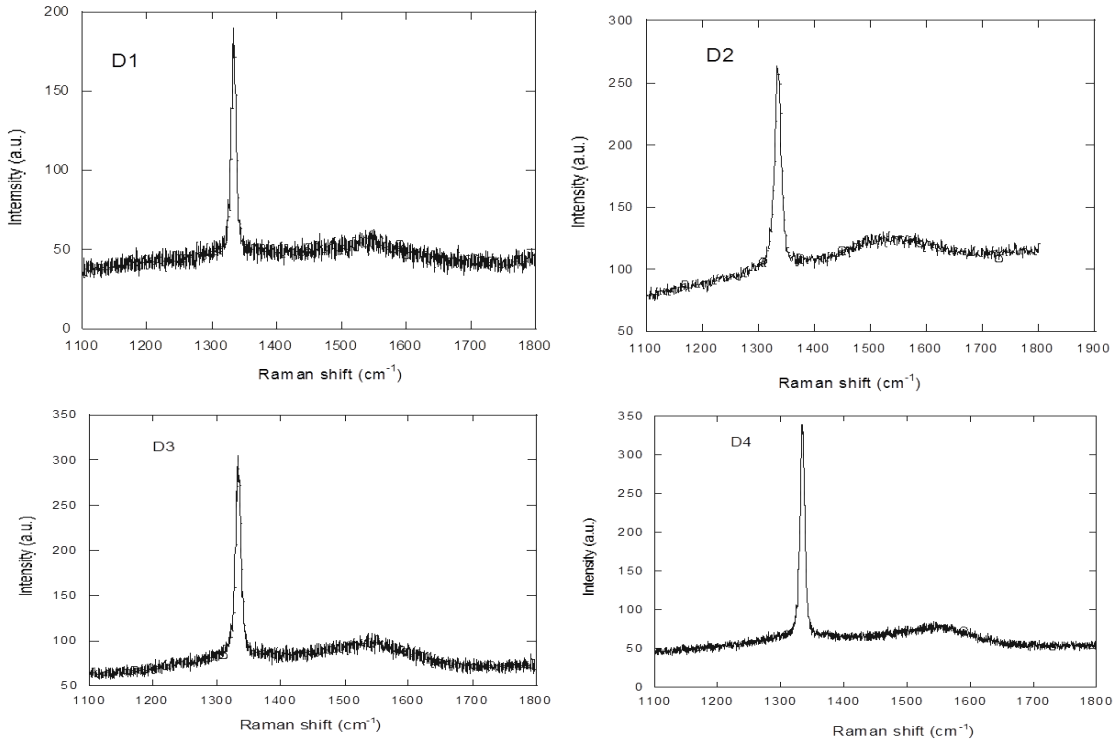

Fig.5. Raman spectra of the diamond films, the position for the diamond Raman line is observed at 1332.5 cm^{-1}.

Table 2. The values of stress estimated from the diamond Raman line position.

Sample	σ_1 [GPa]	σ_2 [GPa]
D1	0.43	0.34
D2	0.95	0.75
D3	0.24	0.19
D4	0.71	0.56