

Raman and Photoluminescence Spectroscopy of Nanocrystalline Diamond Films grown by Hot Filament CVD

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Abstract. Nanocrystalline diamond films were grown by hot filament chemical vapour deposition (HFCVD) in a mixture of methane and hydrogen gases. Three straight parallel wires filament configuration were used in the HFCVD system for the deposition of the films studied in this work. The deposition pressure for the growth of diamond films in this hot filament chemical vapour deposition (HFCVD) reactor have been optimized to be at 20 torr with the methane and hydrogen flow-rates fixed at 2 and 200 sccm respectively. The films studied in this work were grown at low deposition pressures of 2 and 5 torr using the same gas flow-rates used for the optimized diamond film growth including an additional film grown at pressure of 5 mbar with the methane flow-rate reduced to 1 sccm. The morphology showed the formation of closed packed diamond grains for the film grown at 5 torr with methane and hydrogen flow-rates fixed at 2 and 200 sccm. Decrease in pressure and methane flow-rate produced significant changes to the morphology of the diamond grains formed. X-ray diffraction showed that diamond phase phases were dominant in the films deposited at higher pressure. Raman and photoluminescence (PL) spectral analysis were performed using spectra acquired at 325 and 514 nm excitation energies. Raman analysis revealed that increase in deposition pressure from 2 to 5 Torr resulted in the transformation of the film structure from diamond-like-carbon to nanocrystalline diamond structure. UV excitation produced high PL emission intensity at 2.1 eV and the PL intensity was highest for the films deposited at the lowest pressure. Visible excitation on the other hand produced low intensity broad PL emission for all the films between 1.2 and 2.5 eV and the PL intensity was high for the films deposited at the highest deposition pressure.

Introduction

The exceptional set of physical properties such as extreme mechanical, excellent thermal conductivity and broad optical transparency from the deep ultraviolet to the far infrared of synthetic diamond films grown by chemical vapour deposition (CVD) method has made it a material of considerable scientific interest in last few decades [1,2]. However, the high surface roughness makes them unsuitable for conventional process technique of microelectronics [3]. The smoother surfaces and wide band gap of nanocrystalline diamond (NCD) makes them better candidates for advanced optical or electronic components [4]. Microwave and hot-filament CVD (MWCVD & HFCVD) have been used widely in the deposition of MCD films. MWCVD has the advantage of eliminating impurities from the filament material in the films but HFCVD is a much preferred technique because it is a very cost effective and simple method in the deposition of diamond films. Various ways have been adopted in producing NCD films by HFCVD method.

In this work, the effects of lowering deposition pressure and CH₄ to SiH₄ flow-rate ratio of standard polycrystalline diamond deposition parameters on formation of nanocrystalline diamond (NCD) films were investigated. X-ray diffraction was used to study the composition of the crystalline phase composition in the film structure. Raman scattering spectroscopy using ultra-violet and green

line excitation wavelength was used to determine the different phases of carbon (NCD, microcrystalline diamond and graphitic) present in the film structure. The influence the structural properties of the films on the photoluminescence properties of the films were also investigated.

Experimental Method

Diamond-like carbon films were deposited using a hot-filament chemical vapour deposition (HFCVD) using pure methane (CH_4) and hydrogen (H_2) as gas sources on c-Si (100) substrates. The substrates were pre-treated with mechanical diamond abrasion using diamond nanoparticles of size between 1 to 3 nm. Three sets of films were deposited at fixed CH_4 and H_2 flow-rates of 2 and 200 sccm respectively at pressures of 2, 3 and 5 torr (2T-2sccm, 3T-2sccm and 5T-2sccm) followed by another set deposited at a reduced CH_4 flow-rate of 1 sccm deposited at 5 torr (5T-1sccm). A newly designed filament configuration where the original coiled Ta filament configuration was replaced with three aligned Ta filaments configuration placed 3 mm above the substrates was used in the deposition of the films in this work. The substrate and filament temperature were maintained at 800 °C and 2400 °C, respectively. The deposition time was fixed to 4 h for all films. A structural investigation on the films was carried out with FESEM, XRD and Raman spectroscopy. Micro-Raman measurements were done with a Renishaw 2000 system operating at excitation wavelengths of 514 and 325 nm. The same system was used to obtain the photoluminescence (PL) spectra of the films at the same excitation wavelengths. A JEOL JSM 6330F scanning electron microscope was used to analyze the surface morphology of the films. XRD measurements were done using a Siemens D5000 XRD with Cu-K_α radiation ($\lambda_\alpha = 1.54056 \text{ \AA}$) and at grazing angle incidence of 2°.

Results and Discussion

Fig. 1 shows the SEM images and the corresponding XRD patterns of the films deposited by HFCVD from CH_4 and H_2 gases at different deposition pressures and gas flow-rate ratios. The film deposited at the lowest pressure of 2 torr produces cauli-flower-like morphology. The XRD pattern of the film showed the presence of sharp diffraction peaks at $2\theta \sim 35.7^\circ$, 60° and 75.4° corresponding to the (220), (111) and (222) orientation planes of the β -SiC phases, respectively. Weak XRD peaks observed at $2\theta \sim 74.06^\circ$ and 89.9° corresponds to the (220) and (311) orientation planes of diamond respectively [5]. A peak at $2\theta \sim 96.4^\circ$ was attributed to the (222) n-diamond orientation plane, a form of diamond structure in between rhombohedral graphite and diamond state [6]. The sharp SiC and the weak diamond peaks suggest that the cauli-flower-like morphology could be agglomerates of SiC microcrystals with diamond nanocrystallites covering the surface. Increase in the deposition pressure to 3 and 5 torr resulted in the formation of dense lattice of diamond crystals and larger diamond crystals are formed in the films deposited at 3 torr. However, decrease in the CH_4 flow-rate to 1 sccm shows formation of significantly smaller sized diamond crystals loosely scattered on the film surface. The XRD peaks corresponding to the SiC(100) and SiC(311) are totally suppressed in the films with diamond crystal formation suggesting that the SiC microcrystals with these preferred orientations are favourable nucleation sites for diamond crystals. The dominant presence of SiC crystals with preferred orientation in the (200) planes in the films with well formed diamond crystals suggests that this SiC plane was resistant to diamond growth. Increase in deposition pressure to 5 torr appeared to decrease the size of the diamond crystals as reflected by the FESEM images and the lower intensity of the diamond XRD peak. The higher pressure may increase the number of nucleation sites thus resulting in the formation of higher density of diamond crystals however reducing the crystallite size.

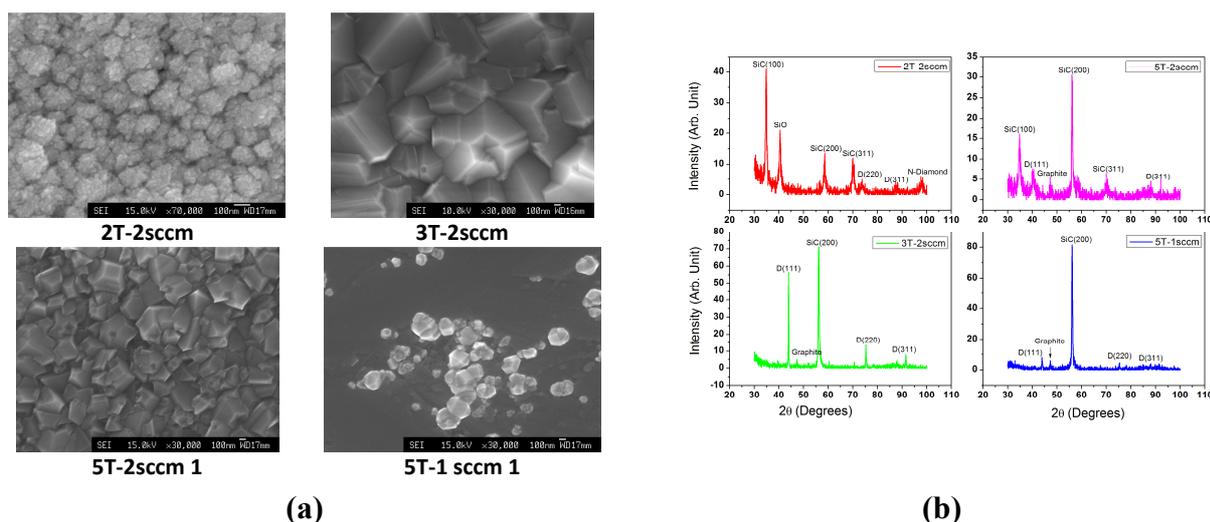


Figure 1(a). Morphologies and (b) XRD patterns of the DLC films showing the transformation of the film structure as result of change in the deposition pressure and CH_4 to H_2 flow-rate ratio.

Analysis using Raman spectra of CVD diamond films prepared using various CH_4 concentration in H_2 at different excitation wavelengths has been reported [7]. Figs. 2(a) and (b) present the Raman spectra of the diamond films samples studied in this work, excited with green and UV laser lights respectively. The Raman spectra excited by the green laser light for the films deposited at low deposition pressures of 2 and 3 torr reveal significant presence of nanocrystalline diamond phases as indicated by the shift of the relatively sharp diamond (D) band to ~ 1342 & 1353 cm^{-1} , respectively. The sharp graphite (G) bands at ~ 1542 & 1640 cm^{-1} respectively for these films also reveal that graphite phases are also present. Raman scattering produced by green light excitation is known to be about 50 times more sensitive to π -bonded amorphous carbon and graphite phases than to diamond [8] thus this explains the absence of Raman shift bands in the films deposited at 5 torr. This suggests that the presence of graphite phases is not significant in these films. The presence of small and sharp peaks at 1130 and 1430 cm^{-1} in the films deposited at 5 torr are attributed to the structure of nanocrystalline phase of diamond or disordered sp^3 phase [9] which maybe formed in between the diamond crystals or in the layer below the diamond crystals. The penetration depth for UV light is expected to be much lower than green light in all these films since absorption of UV light is very high in all these films as the energy clearly exceeds the bandgap energy of all these films. Significant presence of crystalline diamond phases in the films deposited at pressure of 3 torr and 5 torr is clearly shown by the UV Raman spectra for these films as reflected by the presence of sharp diamond peak at ~ 1335 nm. The significantly broadened G band seen in these spectra suggests that the graphite phases in these films are either amorphous or nanocrystalline in structure. The Raman spectra for the film deposited at 5 torr with CH_4 flow rate of 1 sccm are typical of nanocrystalline diamond films [10]. The UV Raman spectrum for the film deposited at 2 torr shows absolutely no signals particularly due to the fact that PL emission produced by this excitation is much higher than the Raman signals. Considering, the lower penetration depth for UV light compared to green light in these films, the presence of the strong diamond peak and broad G band in the UV Raman spectrum of film deposited at 3T, the Raman results indicate that upper and lower layers of this film have different phase composition. The upper layer is composed mainly of diamond crystalline phases surrounded with NCG or amorphous graphite and the lower layer as demonstrated earlier by the green Raman spectrum is composed of NCD and NCG phases.

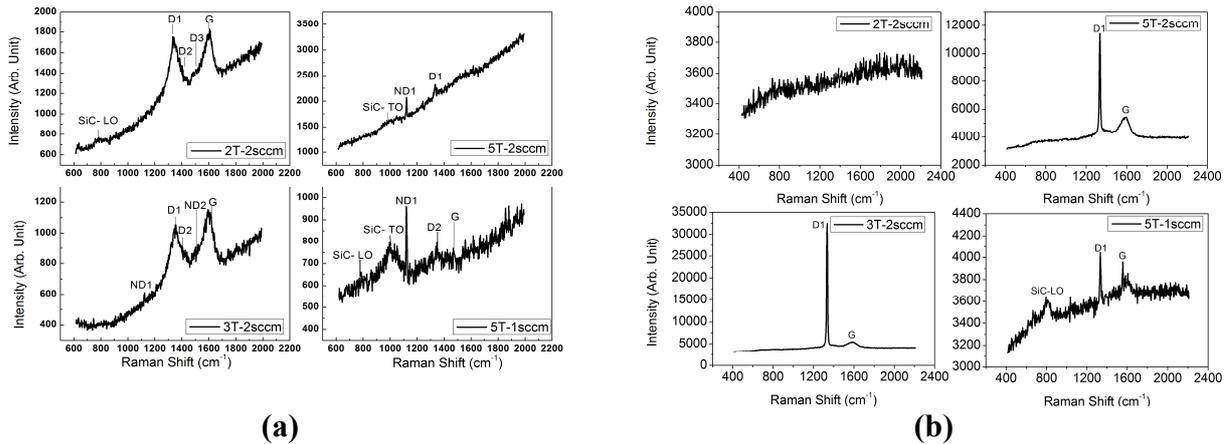


Figure 2(a). Raman spectra of the films excited with visible light at 514.5 nm wavelength and (b) Raman spectra of the films excited with ultra-violet light at 325 nm wavelength.

Fig. 3 shows the PL emission spectra of the films produced by green laser (right) light excitation. The PL band appears to be composed of a weak PL emission peak at ~ 650 nm (~ 2.1 eV) and a broad PL emission band produced by the overlapping of two PL emission bands with peaks at ~ 750 nm (~ 1.7 eV) and 900 nm (~ 1.4 eV). The characteristics of the PL emission spectra show dependence on the deposition pressure and CH_4 flow-rate. The PL emission peaks at 2.1 and 1.7 eV are present in all these films. The origin of this PL emission could be from the recombination of electron-hole pairs within the non-diamond phases in the film structure. The PL peak at the lowest energy is present only in the films deposited at 5 torr where the presence of graphite phases is less significant. The origin of this PL emission could be from the disordered sp^3 phases present in the film structure.

Fig. 4 shows the PL emission spectra of the films produced by UV light excitation. The UV PL spectrum of the film deposited at 2 torr shows a broad PL band with a peak at 600 nm (2.1 eV) wavelength. The film deposited at 3 torr produces similar PL emission band but the peak is blue-shifted to ~ 2.3 eV. The broad band UV PL emissions in these films may have its origin from transition of excited photo carriers from centres in the band gap introduced by disordered, graphite-like phases in the film structure [11]. K. Fabisiak et al [12] also related this PL emission band from their diamond film to this mechanism. This PL emission was significantly suppressed in the films deposited at 5 torr.

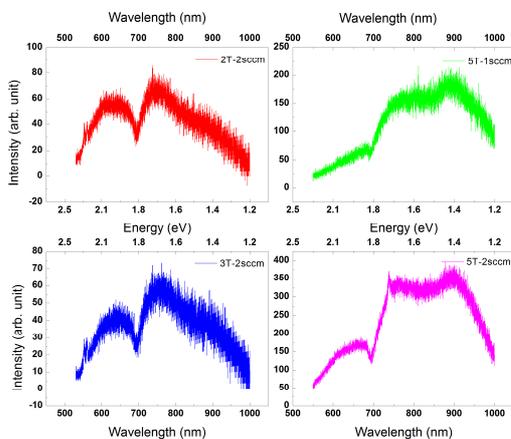


Figure 3. PL spectra of films excited with green light excitation at 514.5 nm wavelength.

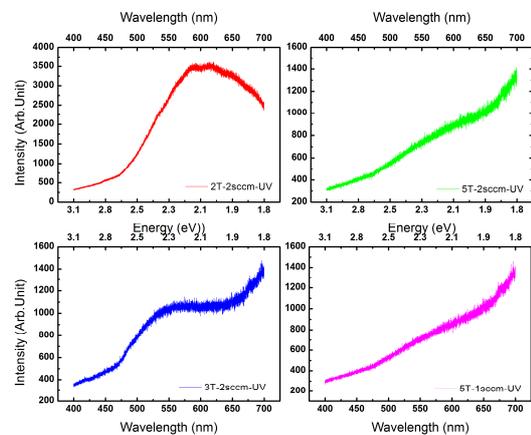


Figure 4. PL spectra of films excited with ultra-violet light (UV) excitation at 325 nm wavelength.

Conclusion

In this work, we have shown that the deposition pressure and the CH₄ to H₂ flow-rate ratio have strong influence on the transformation in the film structure from dominantly graphitic phase to dominant diamond and nanocrystalline diamond phases respectively. The morphology and structure of the film were strongly dependent on the deposition pressure and methane to hydrogen flow-rate ratio at low deposition pressures. Different phases present at different depths in the film structure can be determined through Raman spectra analysis excited at different wavelengths. Raman spectra excited by green light showed that graphitic phases are dominant in films deposited at low deposition pressure while Raman spectra excited by UV light showed diamond phases are predominant in films deposited at 5 Torr especially in the upper layers. The PL emission produced by green light excitation is mainly produced by the non diamond phases in the film structure. Strong visible PL emission is produced by films with predominant graphite phases when excited with UV light.

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