CHAPTER IV

RESULTS AND DISCUSSION

The main purpose of this research is to investigate and characterize the effect of CVD diamond growth conditions deposited on alumina substrates including methane concentration, deposition pressure, and deposition time, which were used for the MW-PECVD system during the films formation on the films morphology, films quality, surface roughness, as well as films hardness.

4.1 Effect of methane concentration on the DLC films formation

The DLC films were deposited under various CH_4 concentrations namely 0.5%, 1%, 2%, 3%, and 5%. These samples were grown at microwave power of 700 W, deposition pressure of 30 torr, deposition time of 30 hr, and substrate temperature of 300-350 °C for all depositions in this section. The surface morphology, surface roughness, films quality and films hardness are presented below.

4.1.1 Film surface morphology and roughness

The investigations of surface morphology were observed with SEM and surface roughness was obtained with AFM. The SEM and AFM images deposited at different CH_4 concentrations in the range of 0.5-5% are shown in Fig. 4.1 - 4.5.

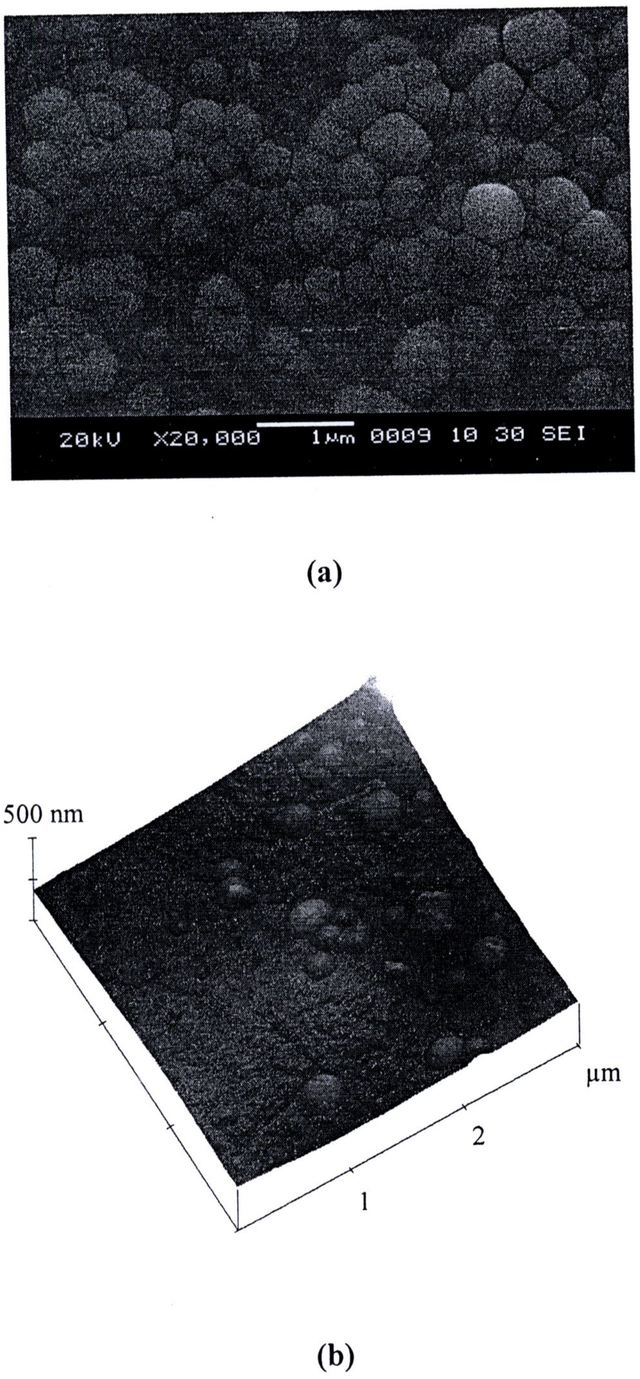
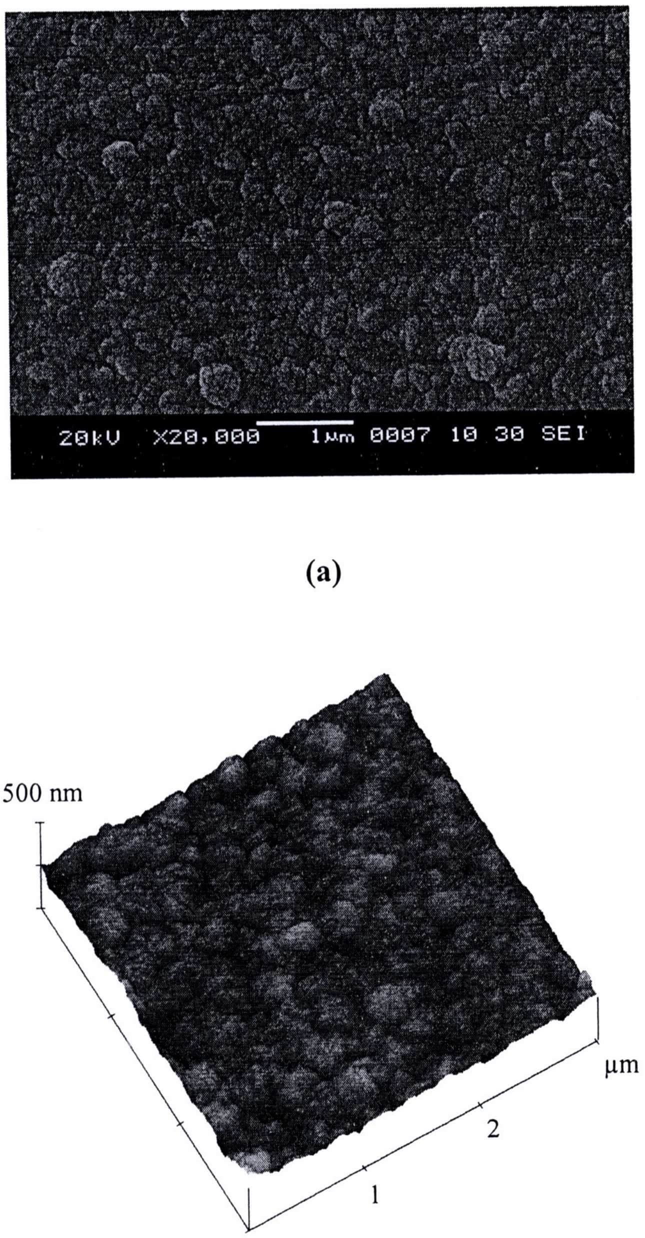


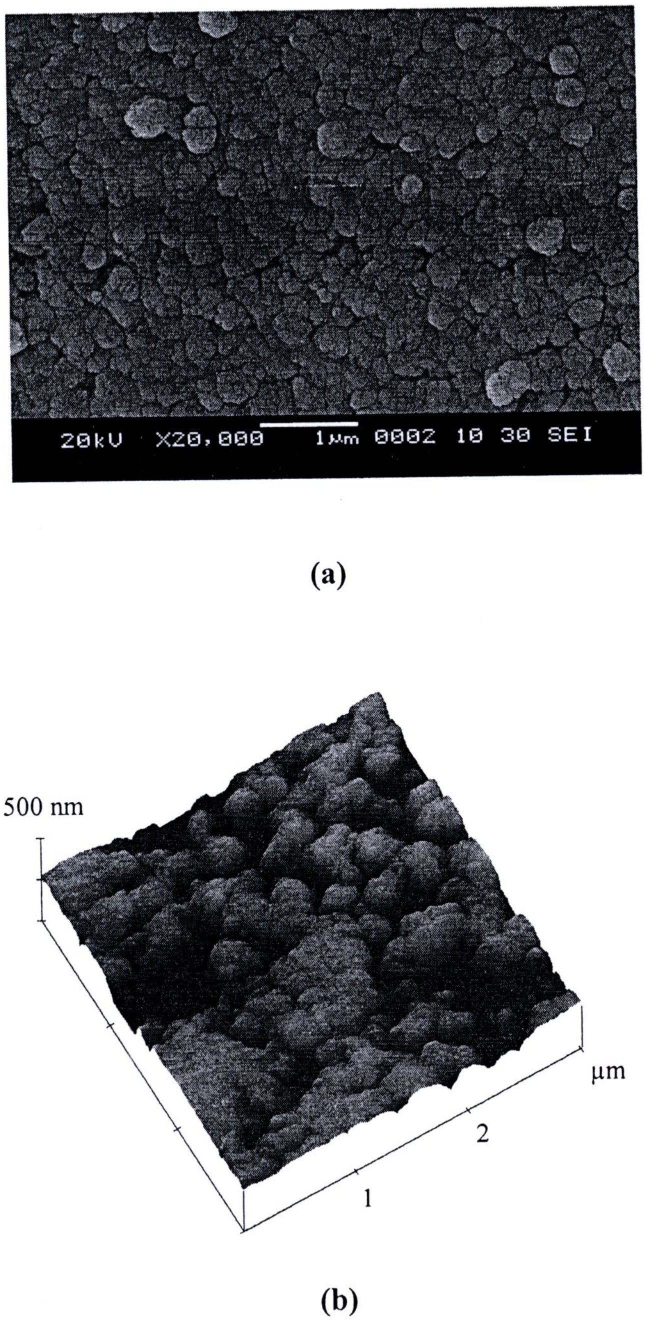
Figure 4.1 (a) SEM photograph, and (b) 2D AFM image of the film grown under CH_4 concentration of 0.5% and deposition pressure of 30 Torr.



(a)

(b)

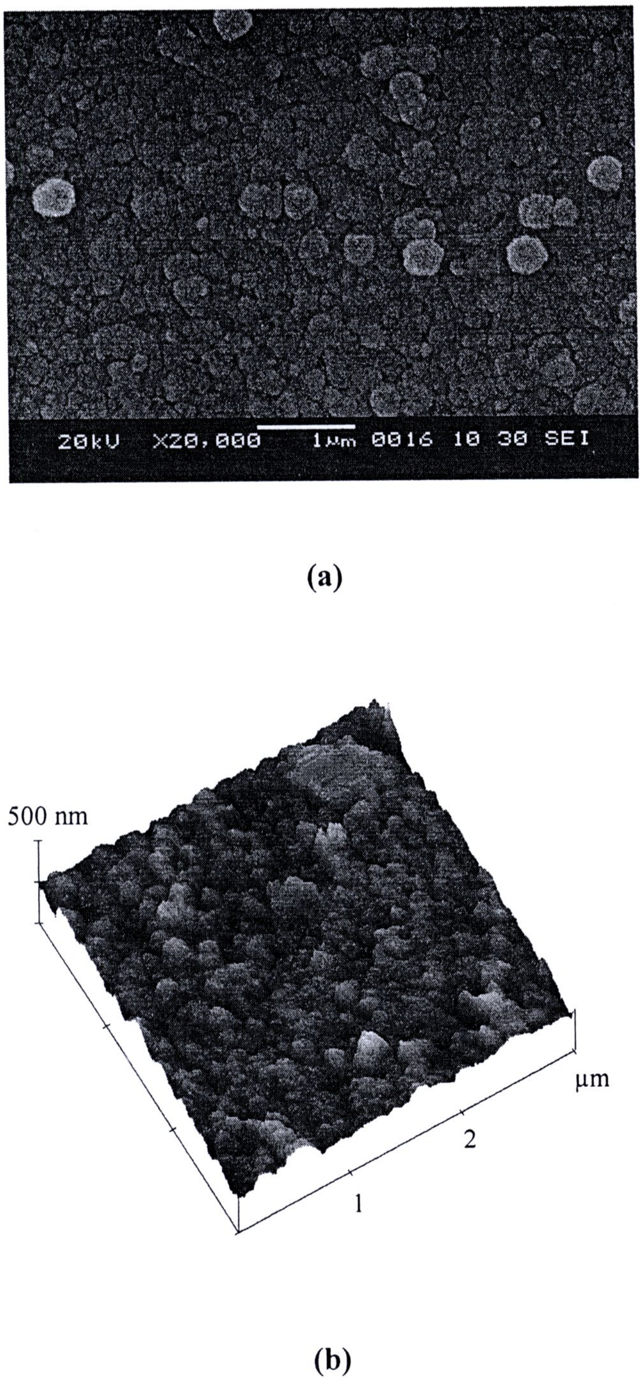
Figure 4.2 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 concentration of 1% and deposition pressure of 30 Torr.



(a)

(b)

Figure 4.3 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 concentration of 2% and deposition pressure of 30 Torr.



(a)

(b)

Figure 4.4 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 concentration of 3% and deposition pressure of 30 Torr.

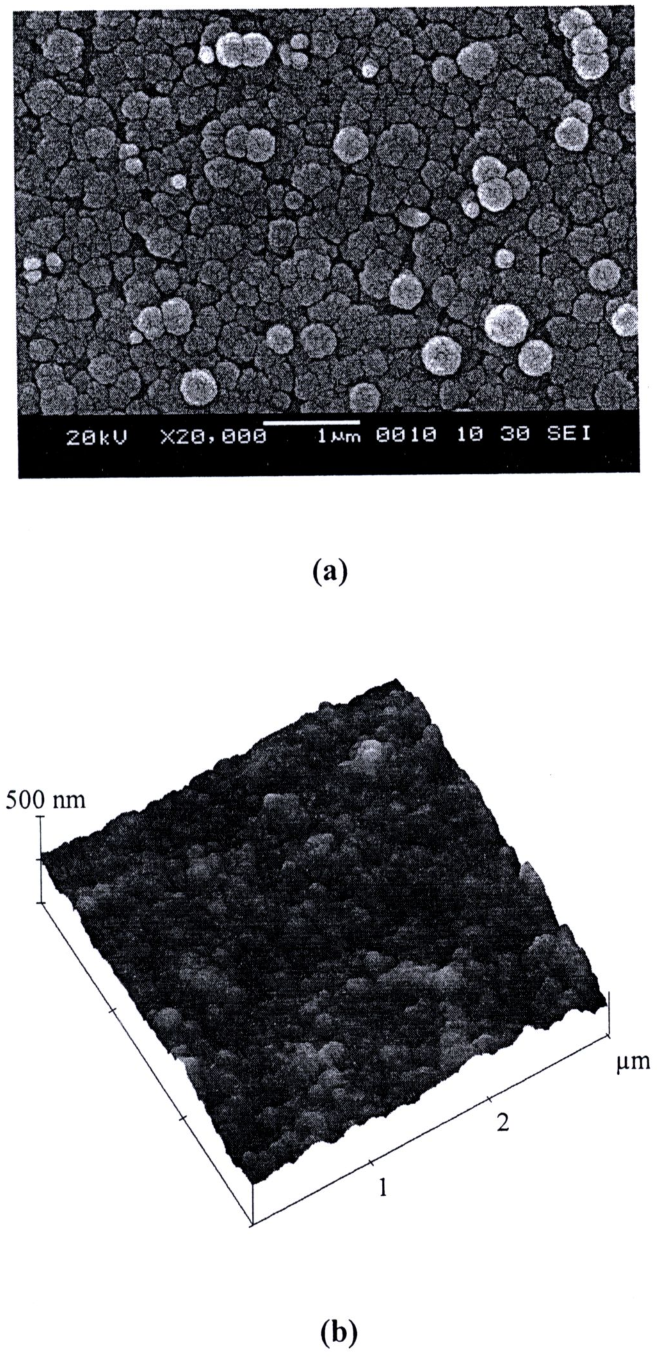


Figure 4.5 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 concentration of 5% and deposition pressure of 30 Torr.

The SEM image of the film in Fig. 4.1 shows the growth of DLC film at 0.5% CH_4 concentration was a ballas-like morphology and the average grain size determined by the AFM analysis was approximately about 357.1 nm. However, the surface morphology of the film investigated in this condition revealed that a continuous film was not observed on the substrate. It may cause the results from a very low flow rate of CH_4 (0.5 sccm) during the deposition process.

With increasing CH_4 concentration, a fine cauliflower-like morphology surface and continuous film of which the smaller grain size in the range of 53.6-107.1 nm was observed, as shown in Fig. 4.1-4.5. The smaller grains were formed as a consequence of the enhanced secondary nucleation effect during the deposition process. Furthermore, the surface roughness of the films decreased when the grain size reduced as shown in Fig. 4.6. The RMS surface roughness of the films was found to be decreased from 33.0 nm to 29.6 nm (shown in Table 4.1) when CH_4 concentration increased from 1% to 5%. For these experiments, it was concluded that nano-sized particles were found on the surface of the DLC films. It could also be observed that nucleation density increased with increasing CH_4 concentration, leading an indication that CH_4 concentration had a significant effect on nucleation density and grain size.

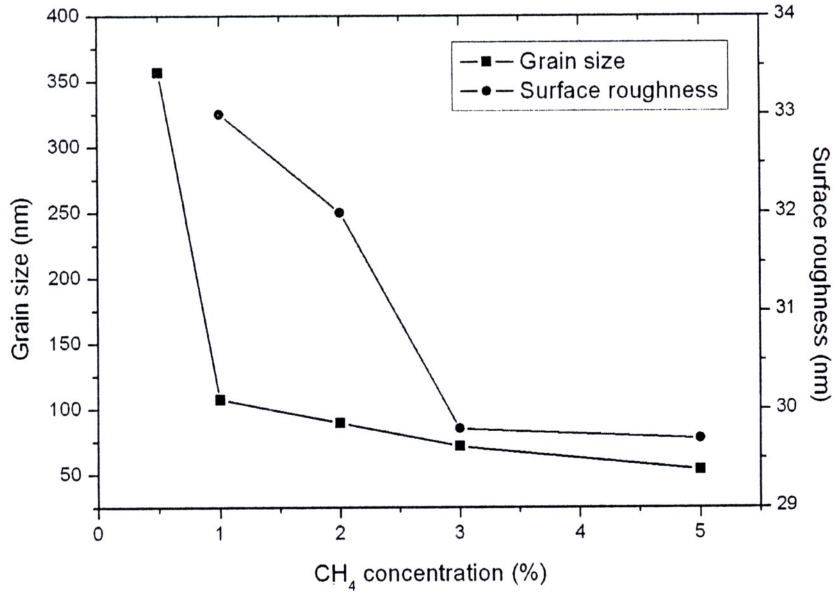


Figure 4.6 The grain size and surface roughness of the DLC films versus CH_4 concentration (%).

There are numbers of researchers who studied the influence of CH_4 concentration on the film morphology [11, 19, 43, 46]. Based on Malika *et al.* [60] research, their research demonstrated that with increasing CH_4 concentration, the grain size tended to decrease with gradual loss in quality. At 2% CH_4 concentration, the surface morphology of the diamond films on silicon nitride (Si_3N_4) was a cauliflower-type growth. They described that an increase in CH_4 concentration in the gas phase could lead to an increase in the secondary nucleation on the diamond films. This could prevent the available crystals from growing completely, leading to a decreasing of grain size. This also indicated that CH_4 concentration in the gas phase may dominate the deposition process by increasing the nucleation density

Askari *et al.* [46] described that an increase in CH_4 concentration could lead to more secondary nucleation effect. This could repress the individual crystal growth, resulting in a decreasing of grain size and surface roughness. It means that the carbon radical concentration in the gas phase may play a dominant the deposition process by increasing the nucleation density as well as reducing grain size.

4.1.2 Film quality

All Raman in this research were measured by Raman spectroscopy at a laser wavelength of 514.5 nm. The Raman spectra of diamond gives only on sharp peak, which indicate the characteristic of diamond peak located around 1332 cm^{-1} (Fig. 4.7). Fig. 4.8 shows the Raman spectra of the films at various CH_4 concentrations from 1% to 5%. The Raman spectra of these films indicated the characteristic diamond peak at 1332 cm^{-1} and the broad hump peak around 1550 cm^{-1}, corresponding to graphite or amorphous carbon phase. The difference between all of these spectra could be seen from the peak positions and intensities, which were also upon to the deposition condition.

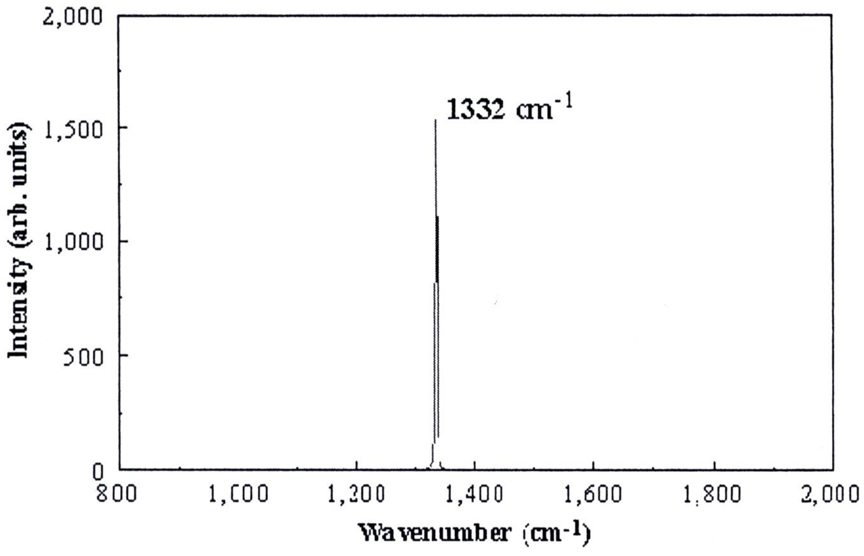


Figure 4.7 Raman spectrum of natural diamond showing the characteristic sharp peak at 1332 cm^{-1} [61].

Raman spectroscopy could be used to evaluate the film quality. For diamond films, the broad hump peak around 1550 cm^{-1} on the Raman spectra was caused by amorphous carbon and quite a sharp peak around 1332 cm^{-1} was caused by diamond phase.

The Raman spectra of the films at different CH_4 concentrations are illustrated in Fig. 4.8. The Raman peak was compared with the respect to the diamond and amorphous carbon phase. For the film grown at CH_4 concentration of 0.5% (Fig. A-1), the broad hump peak around 1550 cm^{-1} could be observed. It could also be found that the diamond peak around 1332 cm^{-1} with a full width at half maximum height (FWHM) approximately 76.5 cm^{-1}. The FWHM of the film deposited at CH_4 concentration of 0.5% was higher than the others spectra, which indicated that this films had relatively low purity.

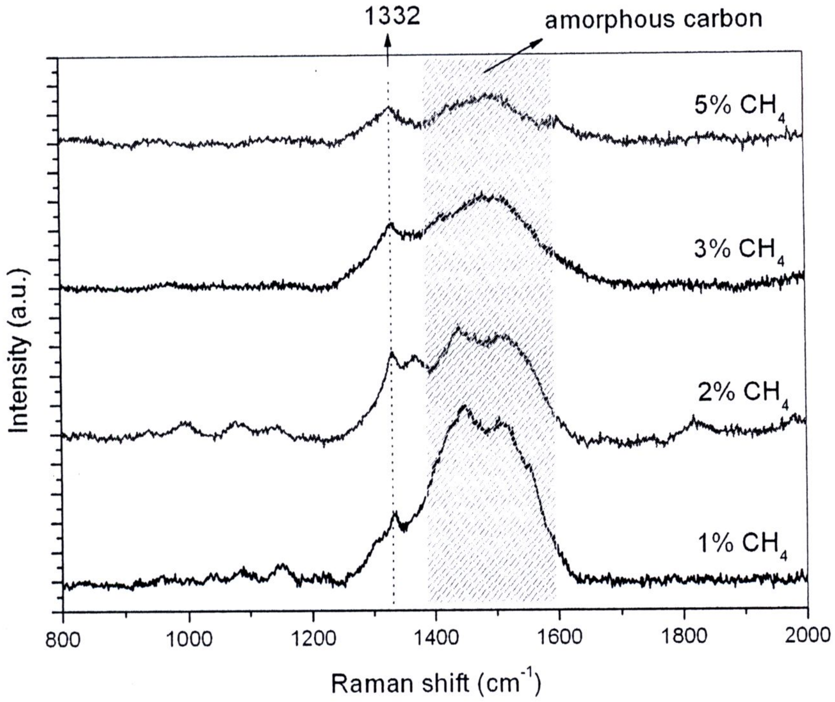


Figure 4.8 Raman spectra of the DLC films grown at deposition pressure of 30 torr under various CH_4 concentrations.

The diamond band around 1332 cm^{-1} was significant broaden that by increasing CH_4 concentration from 1% to 5%, a full width at half maximum height (FWHM) around 1332 cm^{-1} increased from 61.2 cm^{-1} to 74.8 cm^{-1} respectively. The FWHM in this section are shown in Table 4.1. The broad band around 1500-1600 cm^{-1} represented sp^2-bonded carbon or amorphous carbon phase. It indicated that the films had a lower sp^3-bonded carbon and higher sp^2-bonded carbon with increasing CH_4 concentration, which means that the films have low diamond phase purity [51]. The FWHM normally reflected the amount of defect assembled in the films. Thus, an increase in the FWHM of 1332 cm^{-1} with increasing CH_4 concentration was significant. An increase in the FWHM could be attributed to an increase in the defects and the non-diamond contents with increasing CH_4 concentration as described by Mallika et al. [60]. The results are in good agreement with the variation of hardness shown in Fig. 4.11.

In the characterization, all the Raman spectra of the DLC films were fitted using Gaussian peak with variable parameters for peak width at half maximum and position. In order to obtain a good fit, different numbers of peaks were used for different samples, which reflect the change in the films, depending on the deposition conditions. After the curve fitting, the Raman spectra were found that two main peaks occur (Fig. 4.9), quite a broad diamond peak around 1332 cm^{-1} and broad hump peak around 1550 cm^{-1}, corresponding to graphite-like sp^2 structure. However, some Raman spectra were fitted with three Gaussian line shape peak. The third peak in Fig. 4.10 was found at around 1470 cm^{-1}, which was speculatively due to carbon-hydrogen bonds in the grain boundaries [17]. Some researchers attributed this band to the diamond nanocrystals [62], others assigned this band to trans-polyacetylene situated at the grain boundaries of the diamond nanocrystallites [63]. An example curves fit of the DLC films Raman spectra are shown in Fig.4.9-4.10. For the others Raman spectra are shown in Appendix A.

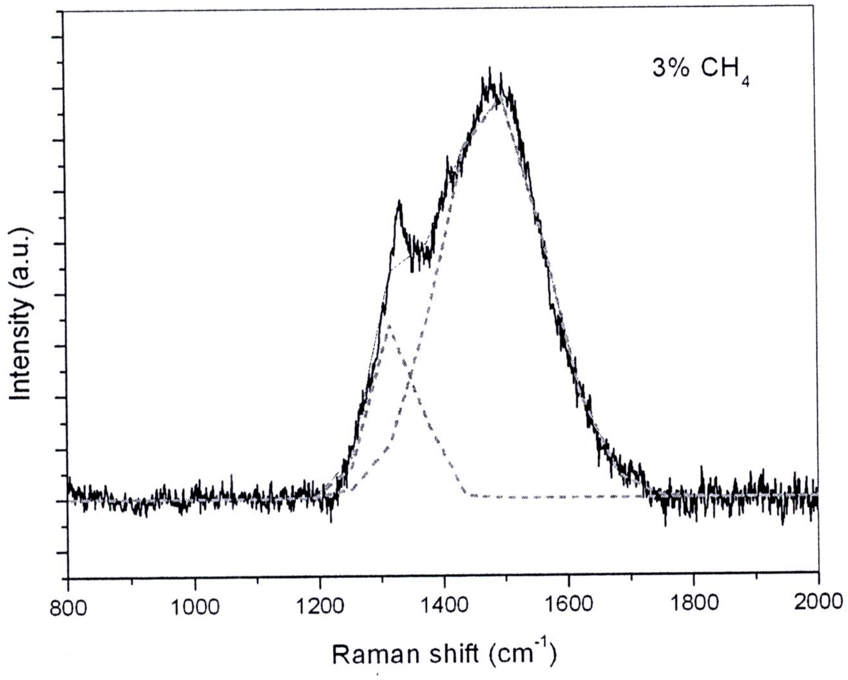


Figure 4.9 Example of Raman spectra of DLC film with two Gaussians peak.

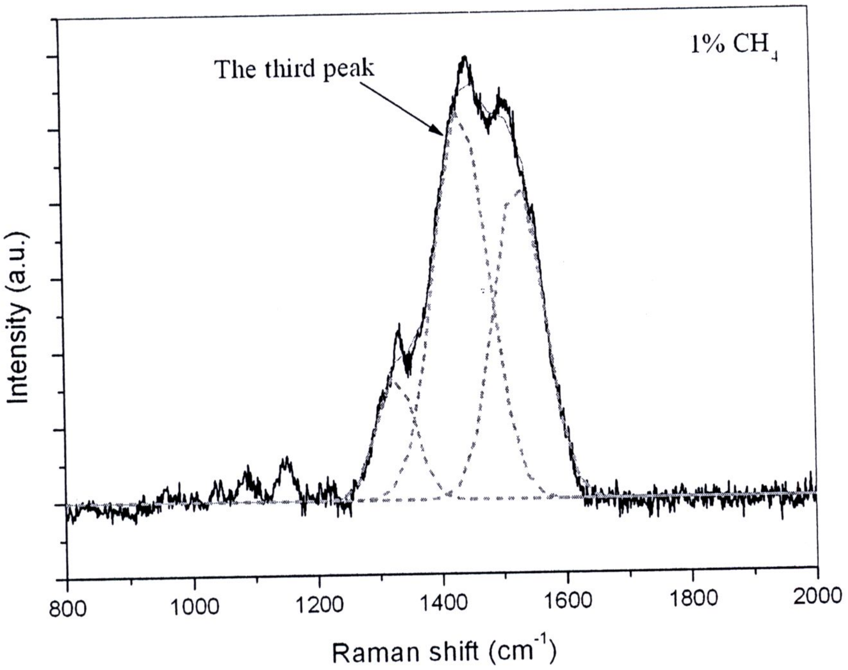


Figure 4.10 Example of Raman spectra of DLC film with three Gaussians peak.

4.1.3 Film hardness

The hardness of the DLC films was evaluated by the Nano-indentation test. The composition of DLC films (hydrogen, sp^3, and sp^{2}contents) determined the hardness values of the films. Hardness values of uncoated alumina and after coated with the DLC films as a function of CH$_4$ concentration are plotted in Fig. 4.11. The hardness of alumina found to increase from 7.3±2.0 GPa in uncoated to 39.4±10.0 – 52.2±2.1 GPa after coated with DLC. It was found that the film hardness increase with increasing CH$_4$ concentrations reached at maximum at a CH$_4$ concentration of 1% and then started decreasing with an increasing in CH$_4$ concentration of 2%. As a result, the maximum value hardness was 52.2±2.1 GPa at CH$_4$ concentration of 1%. The hardness values were even higher when the films were grown under optimized parameters, in which the structure will be mostly sp^3-bonded carbon with a trace amount of sp^2 fractions [64]. The surface roughness, FWHM values, and hardness of the films at different CH$_4$ concentration are summarized in Table 4.1.

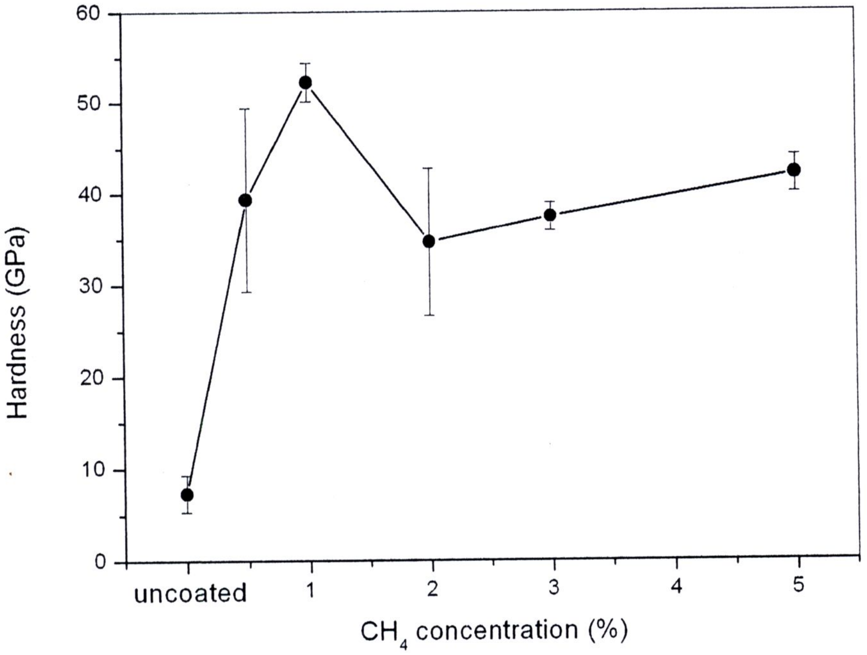


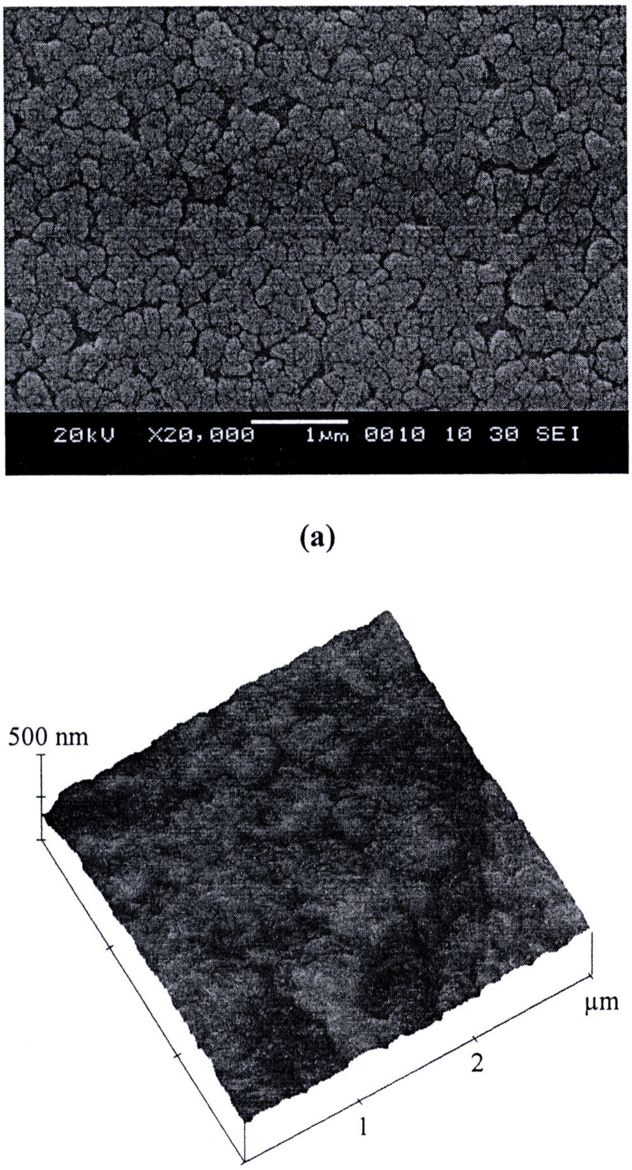
Figure 4.11 Hardness of DLC films deposited at deposition pressure 30 torr under various CH_4 concentrations.

Table 4.1 The grain size, surface roughness, FWHM (1332 cm^{-1}) and hardness of the DLC films at different CH_4 concentration.

CH_4 concentration (%)	**Grain size (nm)**	**Surface roughness (nm)**	**FWHM (cm^{-1})**	**Hardness (GPa)**
0.5	357.1	32.4	87.6	39.4±10.0
1	107.1	33.0	42.9	52.2±2.1
2	89.3	32.0	53.0	34.6±8.1
3	71.4	29.8	60.7	37.4±1.5
5	53.6	29.7	61.1	42.1±2.1

4.2 Effect of deposition pressure on the DLC films formation

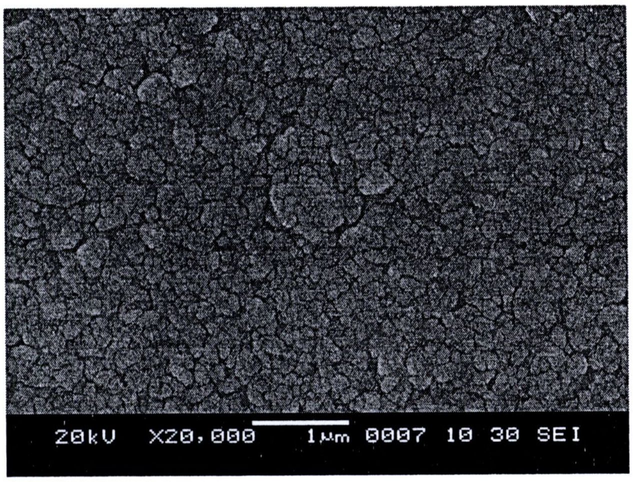
The DLC films were deposited at different deposition pressure of 10 torr, 20 torr, 30 torr, and 50 torr. These samples were grown at microwave power of 700 W, CH_4 concentration of 1%, deposition time of 30 hr, and substrate temperature of 300-350 °C for all depositions in this section. Details of the films characteristics *e.g.* surface morphology, surface roughness, films quality, and films hardness were described in the following sections.



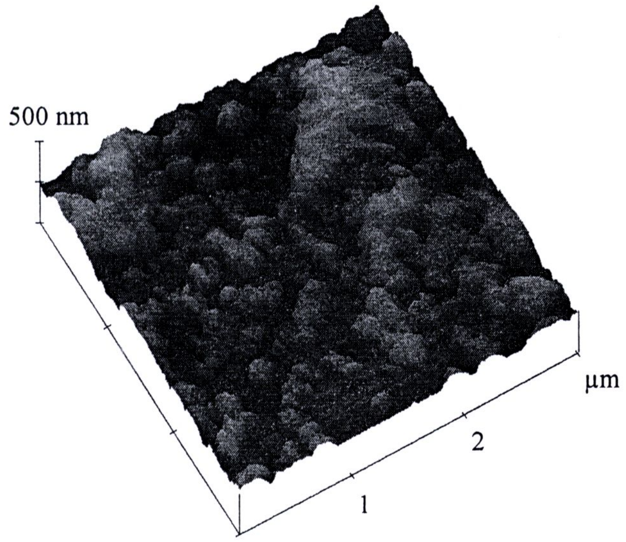
(a)

(b)

Figure 4.12 (a) SEM photograph, and (b) 3D AFM image of the film grown under the CH_4 concentration of 1% and deposition pressure of 10 Torr.

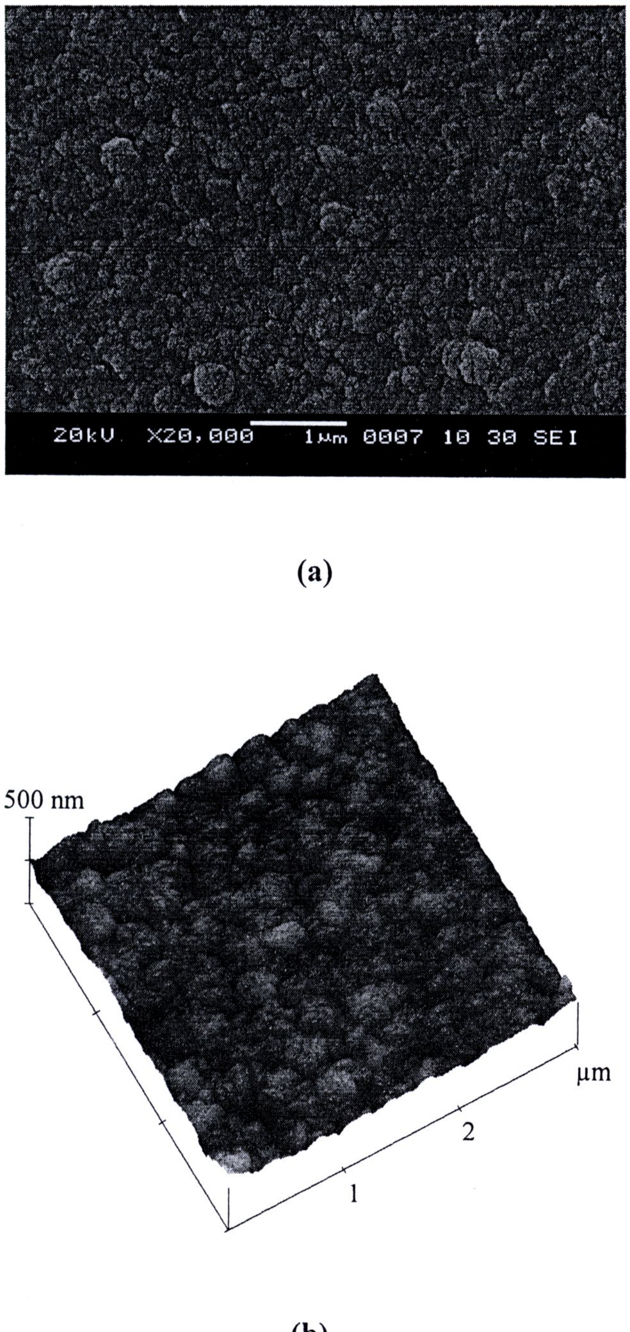


(a)



(b)

Figure 4.13 (a) SEM photograph, and (b) 3D AFM image of the film grown under the CH_4 concentration of 1% and deposition pressure of 20 Torr.



(a)

(b)

Figure 4.14 (a) SEM photograph, and (b) 3D AFM image of the film grown under the CH_4 concentration of 1% and deposition pressure of 30 Torr.

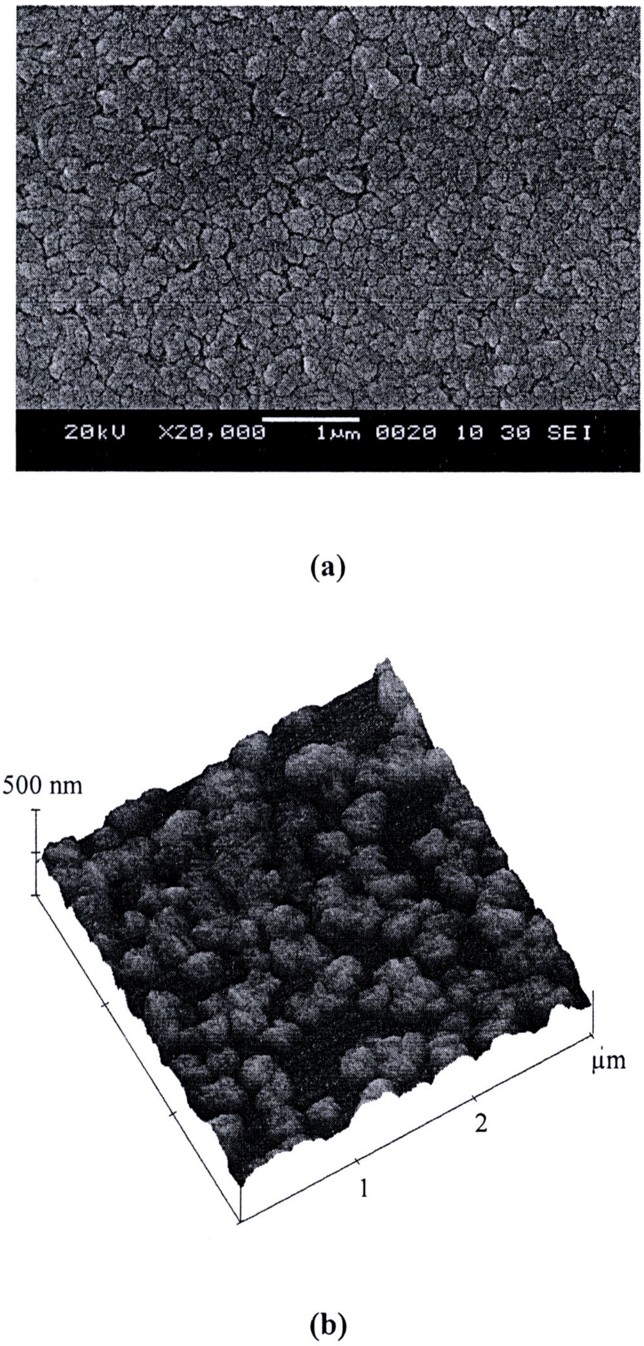


Figure 4.15 (a) SEM photograph, and (b) 3D AFM image of the film grown under the CH_4 concentration of 1% and deposition pressure of 50 Torr.

4.2.1 Film morphology and roughness

The investigations of surface morphology were observed with SEM and surface roughness was obtained using AFM. Fig. 4.12-4.15 show SEM and AFM images of the deposited DLC films under various deposition pressures in the range of 10-50 torr.

As seen in Fig. 4.12, SEM image shows a cauliflower-like morphology and continuous film on alumina substrate. When the deposition pressure increased from 10 to 50 torr, the grain sizes increased gradually from 53.6 to 125 nm, and the dense continuous film could be observed. The diamond crystals started to grow uniformly with increasing deposition pressure, as shown in Fig. 4.13-4.15. This indicates an extremely high nucleation density and growth rate. The smaller grains were formed at low deposition pressure, which were considered as the result of enhanced secondary nucleation.

A comparison of the surface roughness of the films grown at various pressures was carried out by AFM. The surface roughness of the films at 10 torr (Fig. 4.12) was about 23.1 nm, which was lower than that of the others. From AFM images in Fig. 4.13-4.14, the surface roughness evaluated at 33.0 nm and 42.0 nm for the films grown at deposition pressure of 20 and 30 torr respectively. At higher deposition pressure of up to 50 torr (Fig. 4.15), the surface roughness of the film was about 45.0 nm, indicating the amount of secondary nucleation decreased. This showed that the surface roughness of the films increased significantly with increasing deposition pressure. The variations of grain size and surface roughness of the DLC films as a function of deposition pressure are plotted in Fig. 4.16.

These results correspond to the earlier observation by Liang *et al.* [14]. They investigated the influence of deposition pressure on the diamond films from CH_4/H_2 gas mixture in the HF-CVD system. They reported that with reducing deposition pressure, the diamond grain sizes decreasing gradually to nanometer scale. Furthermore, the surface roughness of the films decreased with the reduction of grain sizes. They described that according to kinetic theory of gaseous, the mean free path between electrons and molecules increases with decreasing pressure and leads to an increase in the amount of H atoms etching onto the substrate. Thus, there are few or no collisions of H atom on the substrate, so the kinetic energy remains high. The high kinetic energy caused enhanced surface mobility of these active species, which leads to high rate of secondary nucleation.

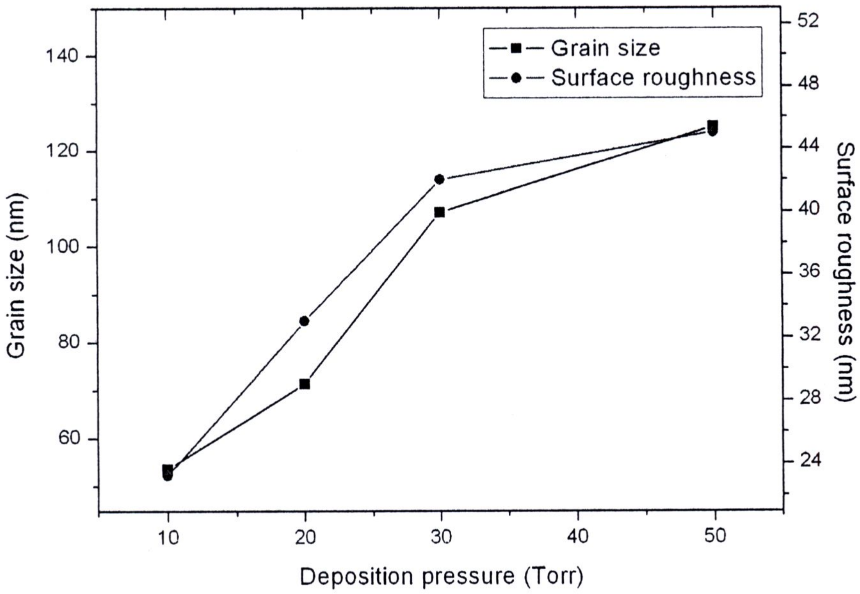


Figure 4.16 The grain size and surface roughness of the DLC films versus deposition pressure (Torr).

4.2.2 Film quality

As seen in Fig. 4.17, at a fixed CH_4 concentration of 1%, the DLC films quality increased with increasing deposition pressure, as indicated by FWHM values of the diamond peak at around 1332 cm^{-1} in Raman spectra. According to the spectra, a Raman peak around 1332 cm^{-1}, indicated the occurrence of diamond phase. The broad hump peak around 1550 cm^{-1} corresponds with the graphite-like sp^2 bonded structure. The FWHM of the 1332 cm^{-1} absorption characteristic of diamond was quite broad. With increasing deposition pressure from 10 torr to 30 torr, the FWHM of the diamond peak decreased from 79.4 cm^{-1} to 56.9 cm^{-1}, resulting in higher purity of the diamond phase. Johnson et al. [65] reported that the broadening effect can be caused by the large mismatch in thermal expansion coefficients between alumina and diamond, which could introduce residual stress on the films.

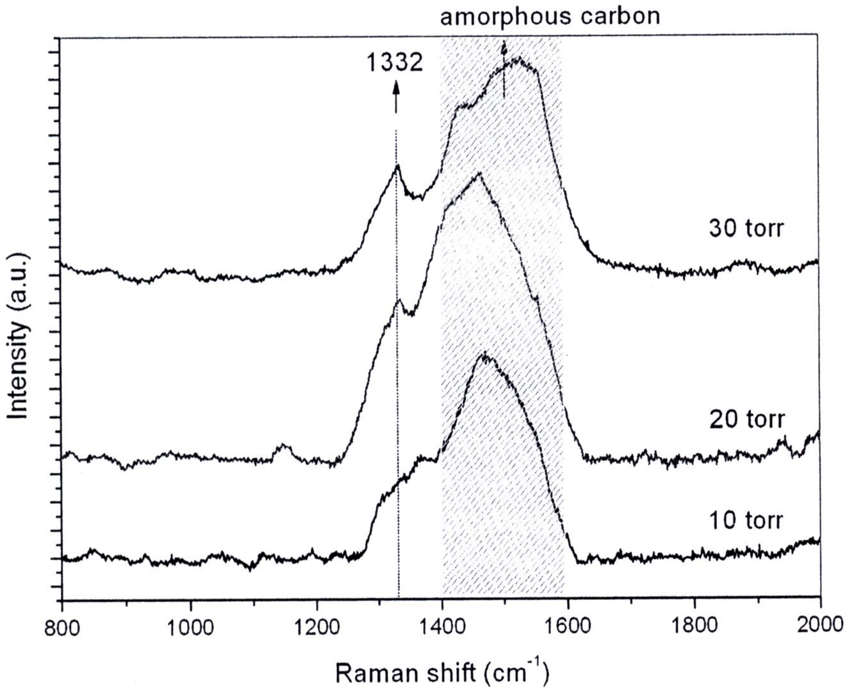


Figure 4.17 Raman spectra of the DLC films deposited at 1% CH_4 concentration under different deposition pressure.

Liang *et al.* [14] reported that the FWHM of the diamond peak increased when deposition pressure decreased. The FWHM of the diamond peak was quite broad. They believed that the FWHM broadening was primarily due to crystallite size effect. In addition, it may be caused by the average crystallite size decreased as deposition pressure decreased.

4.2.3 Film hardness

The variations of hardness values of uncoated alumina and after coating with the DLC films as a function of deposition pressure are plotted in Fig. 4.18. The hardness of alumina found to increase from 7.3±2.0 GPa in uncoated to 13.9±1.3 – 52.2±2.1 GPa after coated with DLC. The hardness value of the film grown at deposition pressure of 10 torr was 13.9±1.3 GPa. With increasing deposition pressure, the films hardness increased first, reaching a maximum at 52.2±2.1 GPa, then decreased to a lower value at 40.8±8.8 GPa. The results were corresponding with the results from FWHM values. The summaries of surface roughness, FWHM values, and hardness of the films under various deposition pressures are showed in Table 4.2.

Generally, the hardness of CVD diamond is known to be varied over a wide range of sp^3 and sp^2 bonding ratios, depending on the kinetic energy of the active species and amount of H atom [66]. The hardness of DLC films increased dramatically with decreasing amount of H content. However, such increase increased more than to offset the decreased in hardness due to decreasing sp^3 content, could explain the substantial increase in the hardness of the film as described by Ravi *et al.* [67]. Basically, diamond structure formed by sp^3-bonded carbon or small non-diamond carbon gives high hardness.

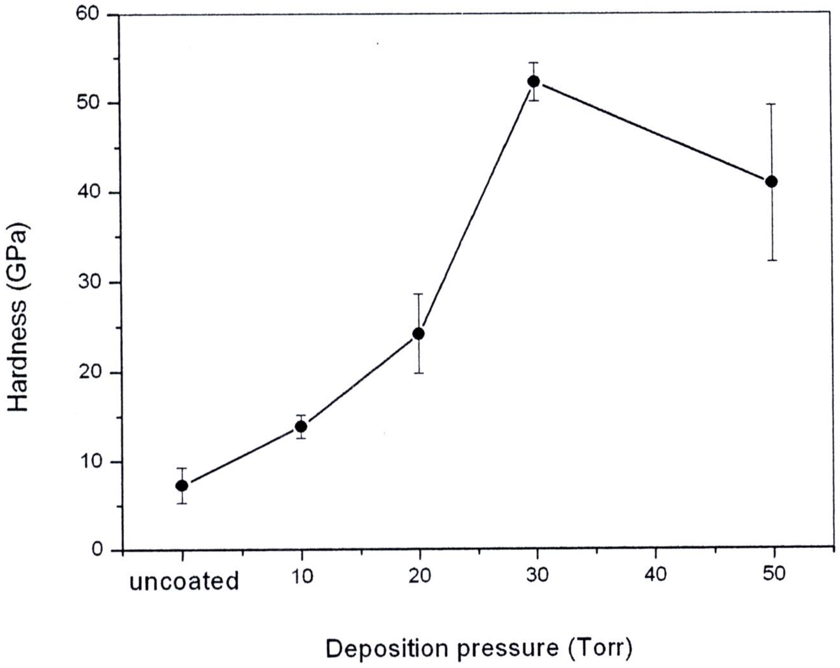


Figure 4.18 Hardness of uncoated alumina and after coated with DLC film deposited at 1% CH_4 concentration under various deposition pressures.

Table 4.2 The grain size, surface roughness, FWHM (1332 cm^{-1}) and hardness of the DLC films under various deposition pressures.

Deposition pressure (Torr)	Grain size (nm)	Surface roughness (nm)	FWHM (cm^{-1})	Hardness (GPa)
10	53.6	23.2	79.4	13.9±1.3
20	71.4	33.0	59.7	24.2±4.4
30	107.1	42.0	56.9	52.2±2.1
50	125.0	45.0	70.6	40.8±8.8

4.3 Effect of deposition time on the DLC films formation

The DLC films were deposited at various deposition times, namely 5 hr, 10 hr, 20 hr, and 30 hr. These samples were grown at microwave power of 700 W and substrate temperature of 300-350 °C. Deposition pressure was kept at 30 torr and CH_4 concentration was held constant of 1%. The various contributions of the surface morphology, surface roughness, quality, and hardness within these films were discussed as below.

4.3.1 Film surface morphology and roughness

The SEM images of the DLC films are prepared at different deposition time in the range of 5-30 hr, as shown in Fig. 4.20-4.22. Obviously, it could be found that the nucleation density was a function of deposition time. For the film deposited at deposition time of 5 hr (Fig. 4.20), the film contained very small individual diamond nuclei. With increasing deposition time to 10 and 20 hr, the grain sizes of individual diamond nuclei increased, as shown in Fig. 4.21 and 4.22 respectively. When deposition time reached at 30 hr (Fig. 4.23), the film became a dense continuous DLC coating all over the alumina substrate. Furthermore, a minimum surface roughness of the films after 5 hr was obtained at about 8.2 nm. With increasing deposition time from 10 hr to 30 hr, not only grain size increased from 87.7 to 107.1 nm but also surface roughness increased from 22.9 nm to 33.0 nm, respectively. Surface roughness and grain size of the DLC films as a function of deposition time are plotted in Fig. 4.19. The variation of the DLC films formation with deposition time was similar to the observations of earlier researchers [13, 68].

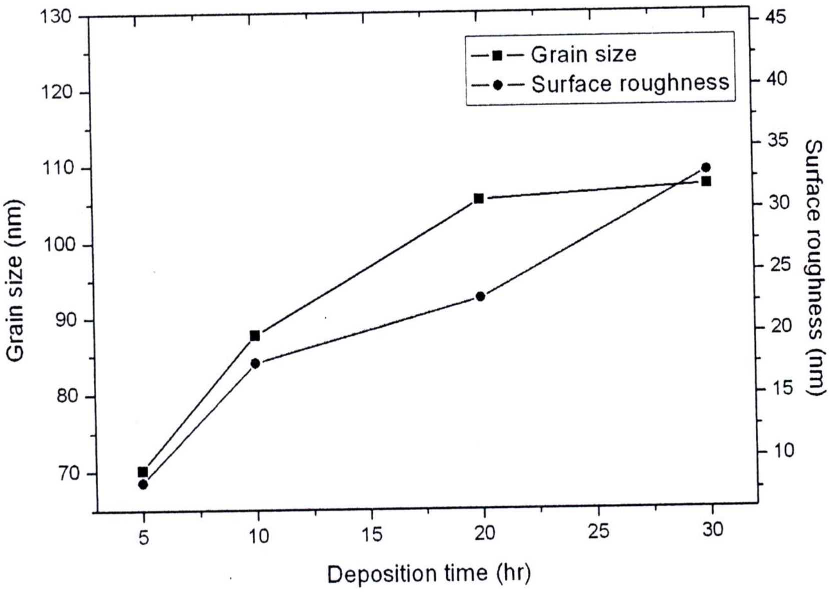
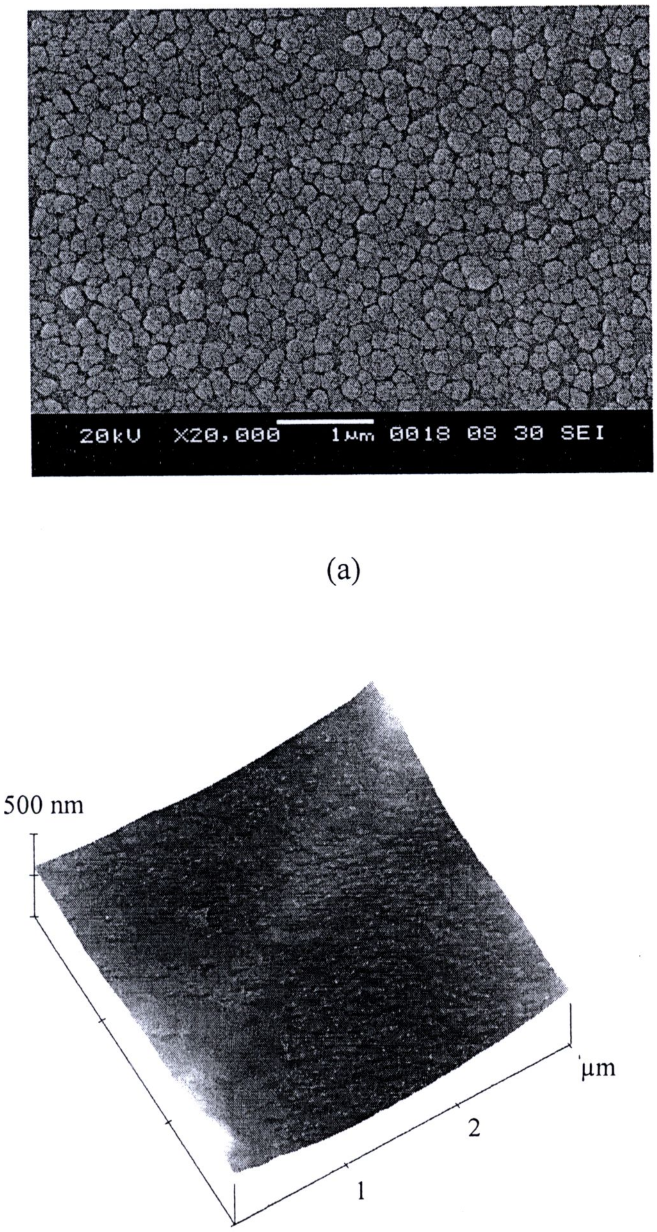


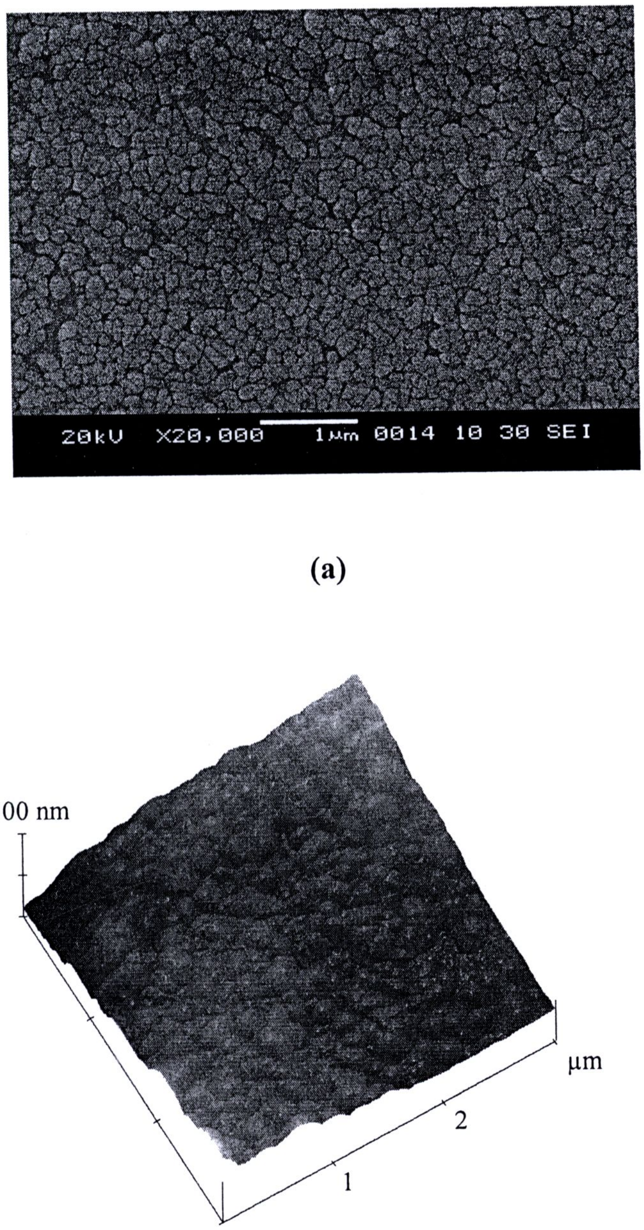
Figure 4.19 The grain size and surface roughness of the DLC films as a function of deposition time (hr).



(a)

(b)

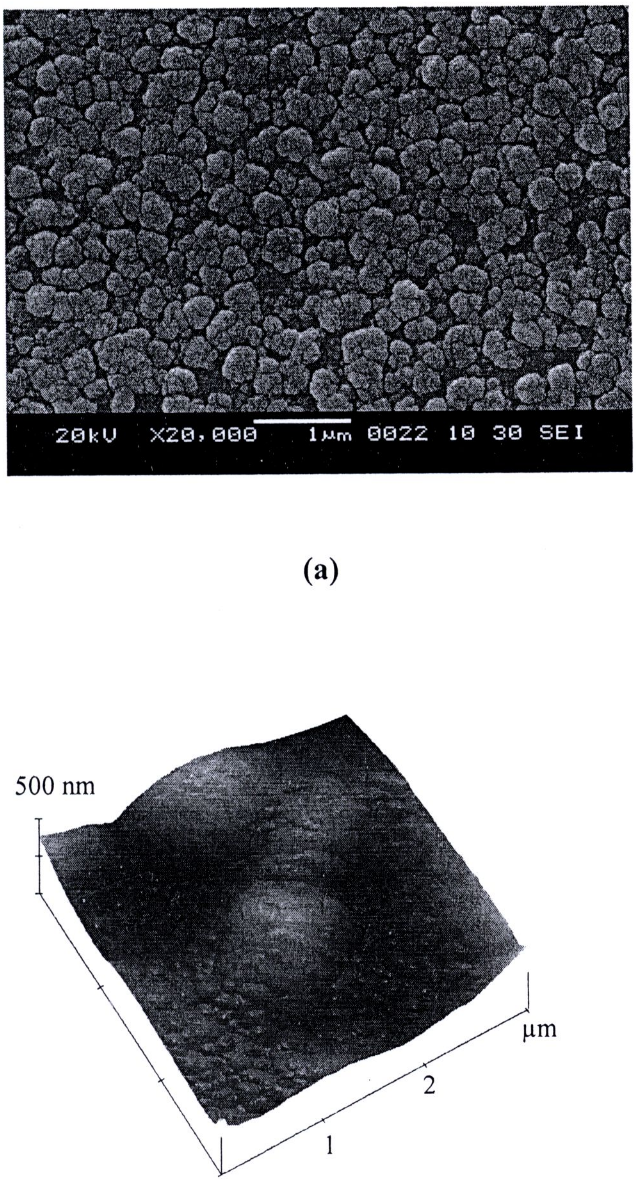
Figure 4.20 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 of 1% and deposition pressure of 30 Torr at deposition time of 5 hr.



(a)

(b)

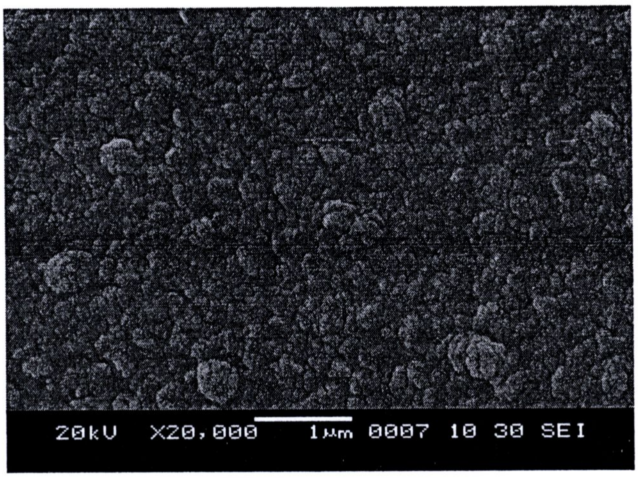
Figure 4.21 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 of 1% and deposition pressure of 30 Torr at deposition time of 10 hr.



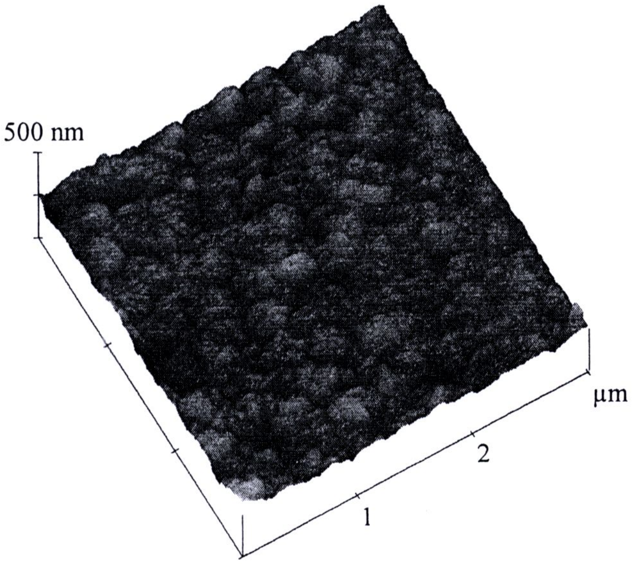
(a)

(b)

Figure 4.22 (a) SEM photograph and (b) 2D AFM image of the film grown under the CH_4 of 1% and deposition pressure of 30 Torr at deposition time of 20 hr.



(a)

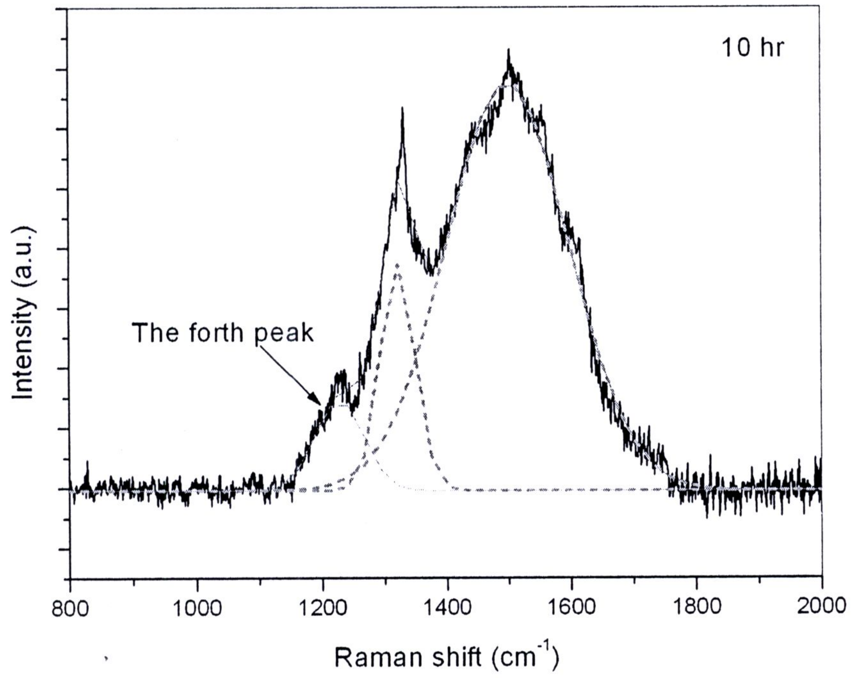


(b)

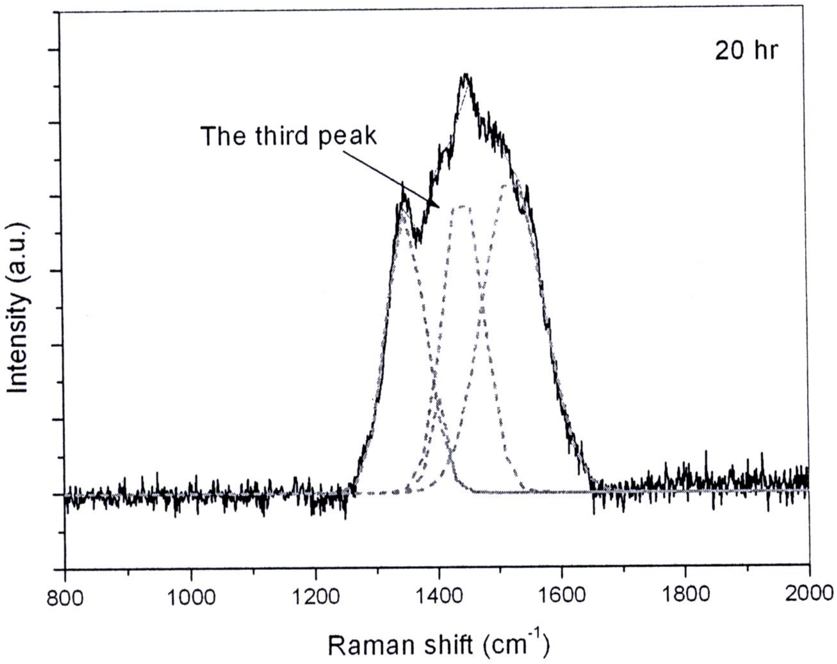
Figure 4.23 (a) SEM photograph, and (b) 2D AFM image of the film grown under the CH_4 of 1% and deposition pressure of 30 Torr at deposition time of 30 hr.

4.3.2 Film quality

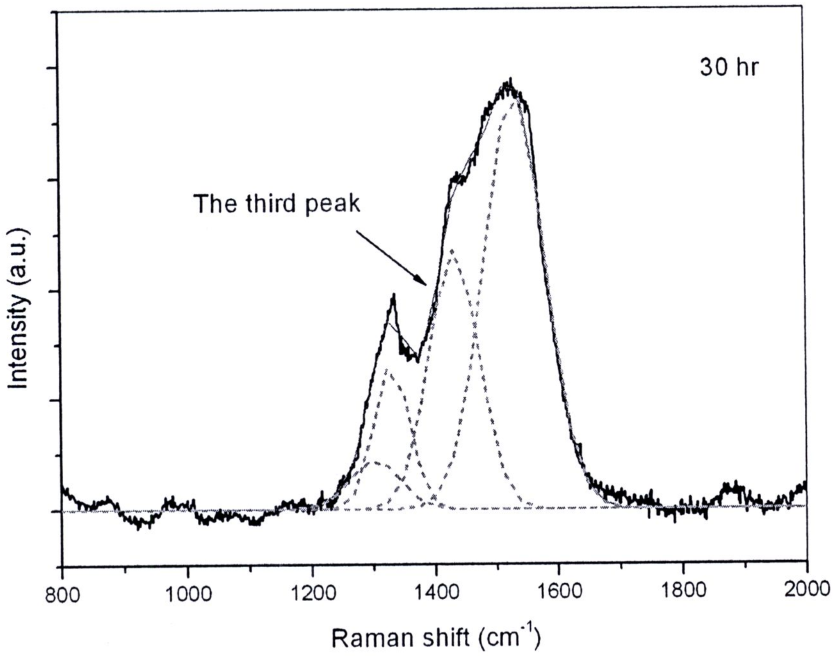
The Raman spectra of the DLC films grown at various deposition times from 10 hr to 30 hr were measured by employing the 514.5 nm excitation. The deconvolutions of the Raman spectra with three and four Gaussians in these films are shown in Fig. 4.24. Two of which are situated around 1332 and 1550 cm^{-1}, could be assigned to the typical Raman spectrum of diamond and graphite-like sp^2 bonded structure, respectively. The Raman spectra in Fig. 4.24(b) and (c) were fitted with four peaks. The forth peak in Fig. 4.24(a) was situated at around 1230 cm^{-1}, which attributed to the polycrystalline structure of diamond [43]. While the third peak in Fig. 4.24(b) and (c) were found at around 1470 cm^{-1}, which was speculatively due to carbon-hydrogen bonds in the grain boundaries [17] or the diamond nanocrystals [62-63]. The FWHM of the diamond peak decreased from 64.2 cm^{-1} to 56.9 cm^{-1} with increasing deposition time from 20 hr to 30 hr. It indicated that higher purity of the diamond phase was significant. Besides, the Raman shift from the standard diamond peak to 1335-1345 cm^{-1} resulting from residual stress, due to the large mismatch in thermal expansion coefficient between the alumina substrate and diamond films with increasing thickness of the films, as described by Ye *et al.* [68].



(a)



(b)



(c)

Figure 4.24 Deconvolution of the Raman spectrum with two and three Gaussians in the DLC film grown under various deposition times, (a) 10 hr, (b) 20 hr, and (c) 30 hr.

4.3.3 Film hardness

Hardness values of uncoated alumina and after coating with the DLC films as a function of deposition time are plotted in Fig. 4.25. The hardness of alumina was found to be increased from 7.3±2.0 GPa in uncoated to 15.8±4.5 – 52.2±2.1 GPa after coated with DLC. At a deposition time of 5 hr, the film hardness value was 15.8±4.5 GPa. With increasing deposition time from 10 hr to 20 and 30 hr, the films hardness values increased from 30.7±3.2 GPa to 37.3±1.0 and 52.2±2.1 GPa, respectively. This result indicates that higher hardness values of the films with increasing deposition time were significant, corresponds with the FWHM values of the Raman spectra in these films under the same conditions. The summaries of surface roughness, FWHM values, and hardness of the films at different deposition time are showed in Table 4.3.

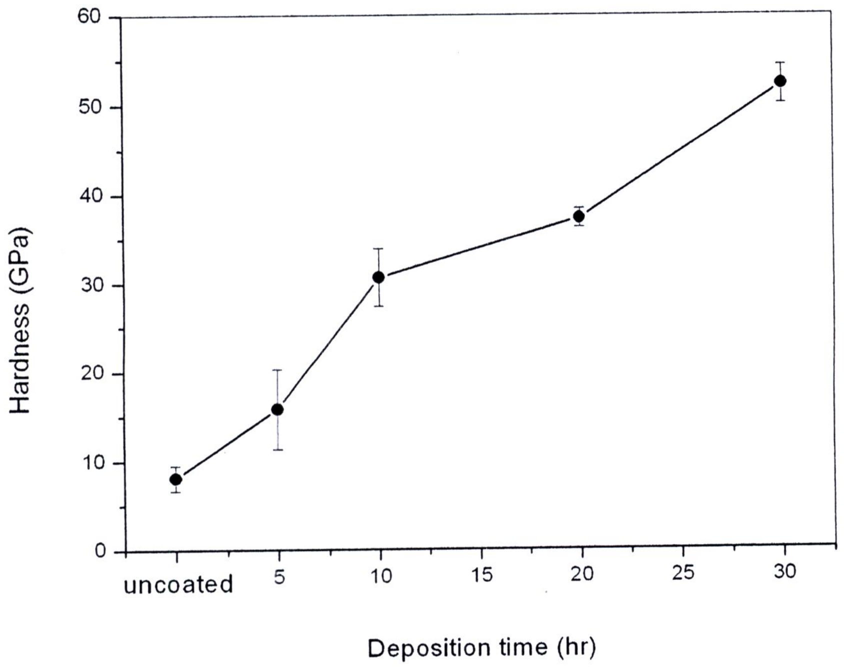


Figure 4.25 Hardness of uncoated alumina and after coated with DLC film grown at 1% CH_4 concentration and deposition of 30 torr under various deposition times.

Table 4.3 The grain size, surface roughness, FWHM (1332 cm^{-1}) and hardness of the DLC films under various deposition times.

Deposition time (hr)	**Grain size (nm)**	**Surface roughness (nm)**	**FWHM (cm^{-1})**	**Hardness (GPa)**
5	70.2	8.2	-	15.8±4.5
10	87.7	17.7	55.7	30.7±3.2
20	105.3	22.9	64.2	37.3±1.1
30	107.1	33.0	56.9	52.2±2.1