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Time-Modulated CVD Process Optimized Using the Taguchi Method

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The Taguchi method is used herein to optimize the time-modulated chemical vapor deposition (TMCVD) process. TMCVD can be used to deposit smooth, nanocrystalline diamond (NCD) coatings onto a range of substrate materials. The implementation of the Taguchi method to optimize the TMCVD process can save time, effort, and money. The Taguchi method significantly reduces the number of experiments required to optimize a fabrication process. In this study, the effect of five TMCVD process parameters is investigated with respect to five key factors of the as-grown samples. Each parameter was varied at four different values (experimental levels). The five key factors, taking into consideration the experimental levels, were optimized after performing only 16 experiments. The as-grown films were characterized for hardness, quality, surface roughness, and microstructure using scanning electron microscopy, Raman spectroscopy, surface profilometry, and Vickers hardness testing.

Keywords chemical vapor deposition (CVD) diamond, experimental design, process optimization, Taguchi

1. Introduction

Chemical vapor deposition (CVD) is a widely used technology for the deposition of polycrystalline diamond coatings onto a range of substrate materials for numerous industrial and consumer applications (Ref 1). Generally, CVD processes produce diamond films that display rough surfaces, which become pronounced with increasing film thickness. This limits their potential use in tribological, optical, and biomedical applications. It is highly desirable to be able to produce ultra-hard, smooth, nanocrystalline, and good-quality diamond films onto various materials. The most common and widely used technique for fabricating nanocrystalline diamond (NCD) films is by performing diamond-deposition at moderately high methane (CH_4) partial pressures (Ref 2). Diamond growth at high CH_4 concentrations favors NCD growth by inducing high nucleation rates and suppressing the growth of individual crystals. In addition to using CH_4 as the carbon-containing precursor, fullerenes can also be used to prepare NCD coatings (Ref 3-6). Gruen et al. (Ref 3) have successfully used fullerene molecules (C_{60}) and Ar-rich plasmas in a microwave CVD reactor to deposit nano-sized diamond films. NCD films can also be grown using gas dopants, such as N_2 (Ref 7-9) and Ar (Ref 10). Such gas dopants are used to dilute the CH_4 gas source during NCD deposition. The dilution approach alters the nucleation processes occurring during diamond CVD and favors NCD growth. In addition to the methods mentioned above, NCD films have also been reported to have been grown using a number of other techniques, including direct ion beam deposition (Ref 11), two-stage growth method (Ref 12, 13), microwave CVD (Ref 14-19), radio-frequency plasma CVD (Ref 20), bias-enhanced growth (Ref 21), and repetitive pulsed bias-enhanced nucleation (Ref 22). A new TMCVD process has recently been proposed for depositing smooth, NCD films onto a number of substrates, including Si, WC-Co, and pyrolytic carbon (PyC) (Ref 23-25). The flow rate of CH_4 into the vacuum reactor is a critical parameter in diamond CVD. Diamond deposition using CVD consists of two stages, namely, (a) the nucleation stage and (b) the film growth stage. It is known that diamond nucleation density increases with CH_4 concentration in the vacuum rector. However, diamond growth in CH_4-rich environments generally deteriorates the crystalline morphology and produces a much more disordered film (Ref 2). In developing the TMCVD process for diamond deposition, the above points were taken into consideration. The higher timed CH_4 modulation is used to ensure rapid diamond nucleation in forming the first monolayer of the film. The lower CH_4 pulse helps increase the quality of the depositing film and favors the columnar growth mode. The distinctive features of TMCVD, which differentiate this process from the rest for NCD deposition, are (a) utilizes timed CH_4 modulations, during film growth, whereas, in conventional diamond CVD process, CH_4 flow in the reactor is kept constant throughout the deposition process; and (b) uses only CH_4 and hydrogen as process gases as in a traditional CVD reactor. Although, the results obtained using TMCVD are promising, the process has not been optimized. The traditional approach to optimize a process involves changing one parameter at a time while keeping the remaining parameters constant. However, in CVD where numerous experimental parameters are involved, the use of the traditional optimization is difficult, because many experiments need to be performed before arriving at the optimum conditions. Furthermore, the results obtained from the traditional

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approach are only valid for fixed experimental conditions and their use under other conditions is uncertain. In the 1950s, Taguchi (Ref 26) developed a statistical tool for the design-of-experiments (DOE) to meet the above requirements. The Taguchi technique provides an efficient and systematic method to optimize designs for performance, quality, and cost (Ref 27). The DOE method has been successfully used in designing reliable, high-quality products at relatively low cost (Ref 28). The advantage of employing the Taguchi technique has been summarized by Weiser (Ref 29). Primarily, the method uses a limited number of experiments in the experimental design. Another important point is that many different variables can be examined simultaneously. This means that predominant parameters can be investigated whereas secondary parameters can be ignored. Therefore, time, energy, and resources can be saved. Finally, signal-to-noise (SN) in the Taguchi method can be used to optimize the process and to reduce the process variability. In this study, the Taguchi method has been used to optimize the TMCVD process. The following five key TMCVD process parameters are considered in the experimental design: (a) high CH_4 flow (HF), (b) low CH_4 flow (LF), (c) high-timed modulations (HTm), (d) low-timed modulation (LTm), and (e) substrate temperature (Temp). Details on the timed-CH_4 modulations in TMCVD can be found in an earlier communication (Ref 23). The optimized values for the deposition pressure and the filament power were obtained using the traditional approach (Ref 30). However, the principles of the TMCVD process have no connection to the deposition pressure, and thus, the pressure is kept constant throughout the time-modulated growth process. The effect of each of the five parameters, varied at four experimental levels, was investigated using surface roughness (Ra), average grain size, hardness, full width at half-maximum (FWHM), and quality (Q), in terms of the diamond-carbon phase purity. The as-grown films were characterized using micro-Raman spectroscopy, surface profilometry, Vickers hardness, and scanning electron microscopy (SEM).

2. Experimental Details

2.1 Depositions and Characterization

Diamond films were deposited onto (100) Si substrates (5 × 5 × 0.5 mm) using a hot-filament CVD system, which has been described elsewhere (Ref 23). The Si substrates were abraded with diamond powder (Lands Superabrasives, NY, Type LS600T, 2-4 μm) prior to film deposition to enhance the nucleation density. After abrading the substrates for 2 min using the diamond abrasive, the substrates were ultrasonically cleaned in acetone for 5 min to remove any loose abrasive particles. Also, prior to deposition, the Ta filaments were precarburized to prevent filament poisoning. Conditions used during filament precarburization together with the growth conditions used during the 16 experiments are shown in Table 1. A Hitachi 4100 scanning electron microscope (SEM) was used to characterize the as-grown films for morphology and to determine the average diamond-grain size. To measure the surface roughness of the film samples, a surface profiler (Hommelwerke, T1000) was used. In addition, a Renishaw 2000 micro-Raman system with a 514 nm He-Ne laser was used to characterize the deposited films for diamond-carbon phase quality and FWHM. At this laser wavelength, the nondiamond carbon phases scatter more effectively than diamond due to a resonance effect. The hardness of the coatings was measured using a Vickers hardness instrument (microhardness tester, Shimadzu HMV-2000). The load applied during the hardness testing was 5 N. The Q values were calculated from the Raman spectra. The quality, in terms of diamond phase purity (sp^3 to sp^2 bonding) was assessed. A semiquantitative measure of the quality of diamond films was calculated using the following equation (Ref 31):

Table 1 Experimental conditions employed during filament precarburization and diamond deposition using the TMCVD process

Parameter	Filament precarburization	Film deposition
Pressure, kPa	4	4
H_2 flow, sccm	15	150
CH_4 flow, sccm	4.5	0.9-9
Substrate temperature, °C	…	700-850
Filament power, W	280	168-272
Filament-substrate distance, mm	…	4
Deposition total time, min	30	60

$$Q = \frac{I_d}{(I_{glc} + I_d)} \quad \text{(Eq 1)}$$

where Q is the "quality factor" of the diamond film; I_d is the intensity of the diamond peak; and I_{glc} is the intensity of the graphite-like carbon peak. Note that pure diamond has a Q value of 1 (100%).

2.2 Design-of-Experiments (DOE)

Table 2 shows the key five TMCVD process parameters investigated at the four experimental levels. Because the distinctive feature of the TMCVD process is the timed CH_4 modulations, flow of CH_4 was metered into the vacuum chamber at high and low modulations. The values used for low CH_4 flows (LF) were 0.9, 1.5, 2.25, and 3 sccm, whereas the high CH_4 flows (HF) used were 4.5, 6, 7.5, and 9 sccm. The modulation times used for high CH_4 flow (HTm) were 2, 4, 6, and 8 min. Modulation times of 3, 6, 9, and 12 min were used for low CH_4 flows (LTm). The four substrate temperatures (Temp.) investigated were 700, 750, 800, and 850 °C. Table 3 shows the complete DOE used in this process optimization study. Only 16 experiments were designed. For each of the five parameters and for each experiment, the experimental levels 1-4 are shown in Table 3. Each level corresponds to a value, as shown in Table 2.

3. Results and Discussion

Table 4 shows the results of the 16 experiments performed. The average grain sizes were calculated from the SEM micrographs. Table 5 shows the calculated Taguchi results. The table shows a value for each parameter at each level and for the five factors considered. The information in Table 3 and 4 was used to calculate the data presented in Table 5. For example, the values shown in Table 5 for FWHM corresponding to HF at the four levels were calculated as follows:

Table 2 The five parameters considered and the four experimental levels investigated in this study

	Experimental level			
Parameter	**1**	**2**	**3**	**4**
HF, sccm	4.5	6	7.5	9
LF, sccm	0.9	1.5	2.25	3
HTm, min	2	4	6	8
LTm, min	3	6	9	12
Temperature, °C	700	750	800	850

Table 3 The design-of-experiments, DOE, by the Taguchi method for five parameters and four experimental levels

Experiment No.	HF, sccm	LF, sccm	HTm, min	LTm, min	*T*, °C	Total CH_4 flow, mL
1	1	2	3	2	3	180
2	3	4	1	2	2	252
3	2	4	3	3	4	252
4	4	2	1	3	1	412
5	1	3	1	4	4	158
6	3	1	3	4	1	212
7	2	1	1	1	3	176
8	4	3	3	1	2	418
9	1	1	4	3	2	169
10	3	3	2	3	3	240
11	2	3	4	2	1	255
12	4	1	2	2	4	248
13	1	4	4	1	1	248
14	3	2	2	1	4	306
15	2	2	2	4	2	162
16	4	4	4	4	3	324

Table 4 Experimental results

Experiment No.	FWHM, cm^{-1}	R_a, μm	Grain size, μm	Hardness, HV	*Q*, %	Total CH_4 flow, mL
1	9.9	0.28	0.48	1086	76	180
2	269.1	0.21	0.11	1282	61	252
3	243.9	0.26	0.22	1546	59	252
4	9	0.14	Am	1168	39	412
5	35.1	0.22	0.25	1479	64	158
6	13.05	0.17	0.64	1057	23	212
7	60.3	0.11	0.19	1466	57	176
8	∞	0.27	Am	1187	0	418
9	12.15	0.24	0.85	1185	67	169
10	70.2	0.22	0.11	1620	53	240
11	7.2	0.20	0.25	1199	40	255
12	71.1	0.17	0.15	905	51	248
13	∞	0.22	0.16	1428	0	248
14	27.45	0.14	Am	1773	49	306
15	9.9	0.13	0.49	1187	45	162
16	6.3	0.34	0.17	1178	25	324

Am, amorphous (=1); ∞ = 1000

Level 1: 9.9 + 35.1 + 12.15 + 1000 (∞) = 1057.15
Level 2: 243.9 + 60.3 + 7.2 + 9.9 = 321.3
Level 3: 269.1 + 13.05 + 70.2 + 27.45 = 379.80
Level 4: 9 + 1000 + 71.1 + 6.3 = 1086.4

Table 5 Calculated Taguchi results

	Level	HF, sccm	LF, sccm	HTm, min	LTm, min	*T*, °C
FWHM	1	1057.15	156.6	373.5	2087.75	1029.25
	2	321.3	56.25	178.65	357.3	1291.15
	3	379.8	1112.5	1266.85	335.25	146.7
	4	1086.4	1519.3	1025.65	64.35	377.55
Ra	1	0.96	0.69	0.68	0.74	0.73
	2	0.7	0.69	0.66	0.86	0.85
	3	0.74	0.91	0.98	0.86	0.95
	4	0.92	1.03	1	0.86	0.79
Grain size	1	1.74	1.83	1.55	2.35	2.05
	2	1.15	2.97	1.75	0.99	2.45
	3	1.86	1.61	2.34	2.18	0.95
	4	2.32	0.66	1.43	1.55	1.62
Hardness	1	5178	4613	5395	5854	4852
	2	5398	5214	5485	4472	4841
	3	5732	5485	4876	5519	5350
	4	4438	5434	4990	4901	5703
Q	1	207	198	221	106	102
	2	201	209	198	228	173
	3	186	157	158	218	211
	4	115	145	132	157	223

The remaining values shown in Table 5 have been calculated in the same manner as above. When making the calculations, it is important to refer to the information given in Table 3 in order to establish the correct levels in correspondence to the experiments. The effect of the five parameters, at the four levels, on the five factors is graphically shown in Fig. 1. It is evident that the parameters at all four levels have a profound effect on the five factors investigated. For a hard, smooth, good-quality diamond film, the FWHM, R_a, and average grain size values must be small and the hardness and *Q* values must be high. To select the optimum conditions, the two best values obtained for each parameter, at all four levels, were selected and have been shown on the graphs in Fig. 1 with a cross (+), appearing above the selected lines on all five graphs. The selected results have been tabulated and shown in Table 6. It can be seen that the optimum values for HF, LF, HTm, LTm, and Temp, are 6 sccm, 0.9-1.5 sccm, 2 min, 9 min, and 850 °C, respectively. Figure 2 displays the graph showing the optimized time-modulated CH_4 flows with deposition time. Primarily, CH_4 is introduced into the chamber at 6 sccm (HF) for 2 min (HTm), and then the CH_4 flow is reduced to 1.5 sccm (LF) and kept constant for 9 min (LTm). This modulated cycle is then repeated, and it is the repetition of such cycles that name the process ‘time-modulated CVD.” It is interesting to note that these optimum conditions have been obtained after performing only 16 experiments. If the traditional optimization method was used, a process having 5 parameters and 4 levels would require 4^5 (= 1024) experiments. Figure 3 shows SEM images of the surface morphologies of three film samples, prepared in experiments 2(a), 7(b), and 10(c). The apparent difference in the morphology and the microstructure of each film is evident. The variation in the film morphologies is due to use of different process conditions during the film growth process. Figure 4 shows the Raman spectra corresponding to the three SEM micrographs shown in Fig. 3. The Raman spectra, generally, show two types of peaks centered at around 1332 and 1600/cm. The generation of secondary diamond nucleation, which is also a key feature of the TMCVD process, is an important factor that is influenced by (a) deposition temperature, (b) CH_4 content, and (c) pressure. The deposition pressure was kept constant at 4 kPa in all 16 experiments. The rate of secondary nucleation is expected to increase with deposition temperature. Further-

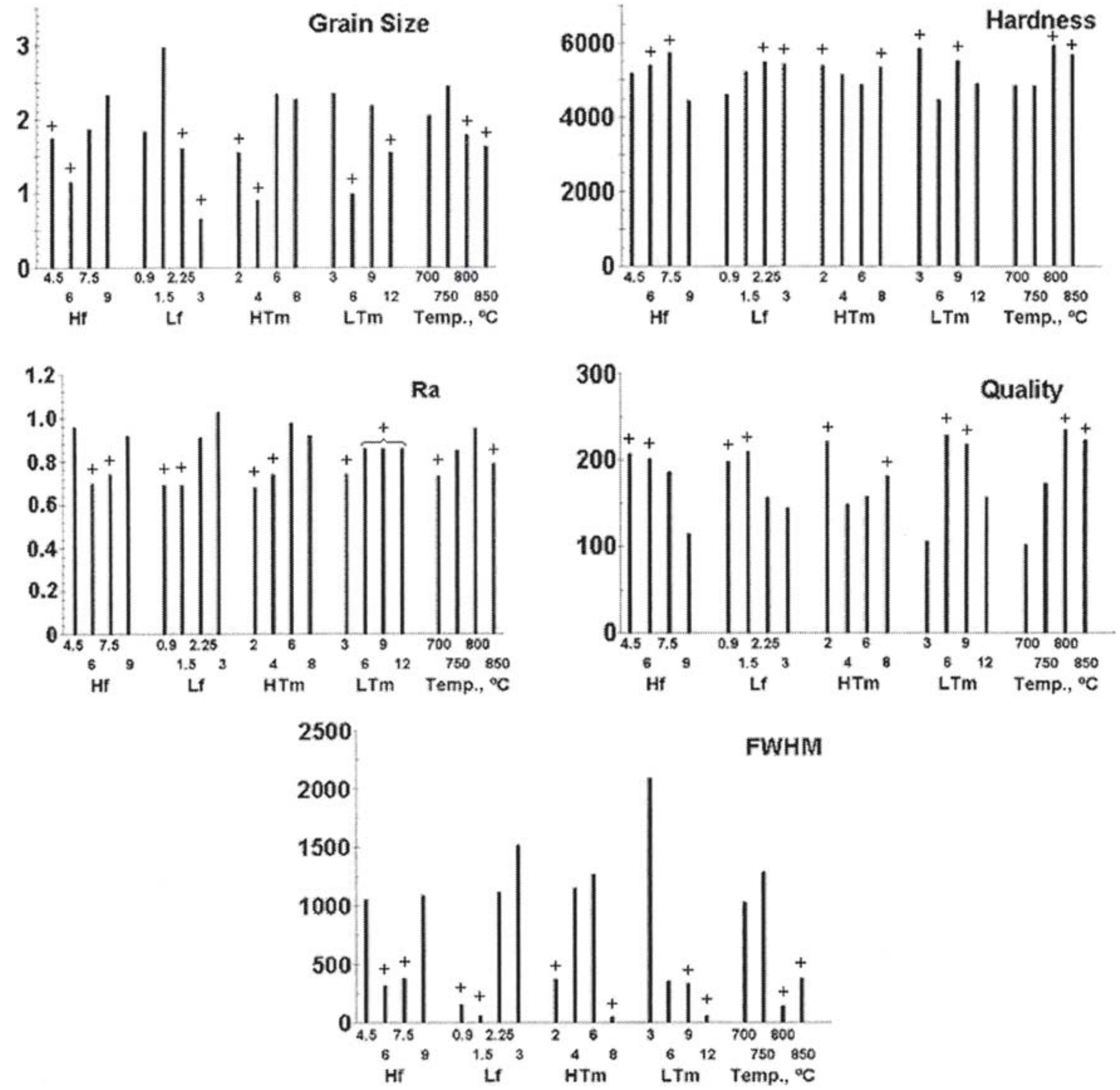

Fig. 1 Graphical representation of the data shown in Table 5. The (+) signs on top of the selected lines correspond to those values that were considered in determining the optimum conditions.

Table 6 Optimized results for the TMCVD process, as obtained from Taguchi analysis

Factor	HF, sccm	LF, sccm	HTm, min	LTm, min	*T*, °C
FWHM	6 7.5	0.9 1.5	2 8	9 12	800 850
R_a	6 7.5	0.9 1.5	2 4	3 6/9/12	700 850
Grain size	4.5 6	2.25 3	2 4	6 12	800 850
Hardness	6 7.5	2.25 3	2 8	3 9	800 850
Quality	4.5 6	0.9 1.5	2 8	6 9	800 850
Optimized value	6	0.9, 1.5	2	9	850

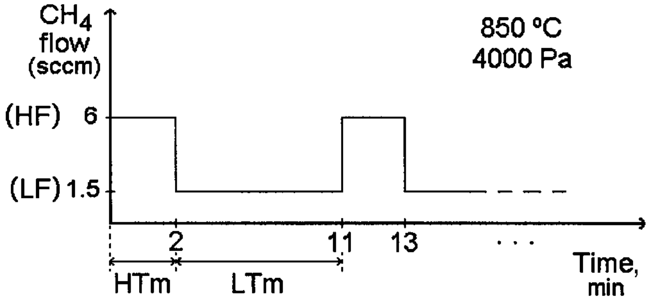

Fig. 2 Optimized, timed CH_4 flows (HF, LF) and modulation times (HTm, LTm) during the growth of diamond films using the TMCVD process

more, the secondary nucleation rate increases with CH_4 content, at suitable temperatures. The increase in secondary nucleation can result in the production of a smoother film surface profile by the effective filling of the surface irregularities during film growth. The generation of nano-sized diamond grains during TMCVD is responsible for improving the hardness of the coating samples. It was found that the films deposited in experiments 4, 8, and 14 were amorphous in nature. This can be attributed to the relatively higher total flow of CH_4 into the vacuum chamber during the complete growth process. The total flow of CH_4 into the deposition reactor for each of the 16 experiments is shown in Table 4.

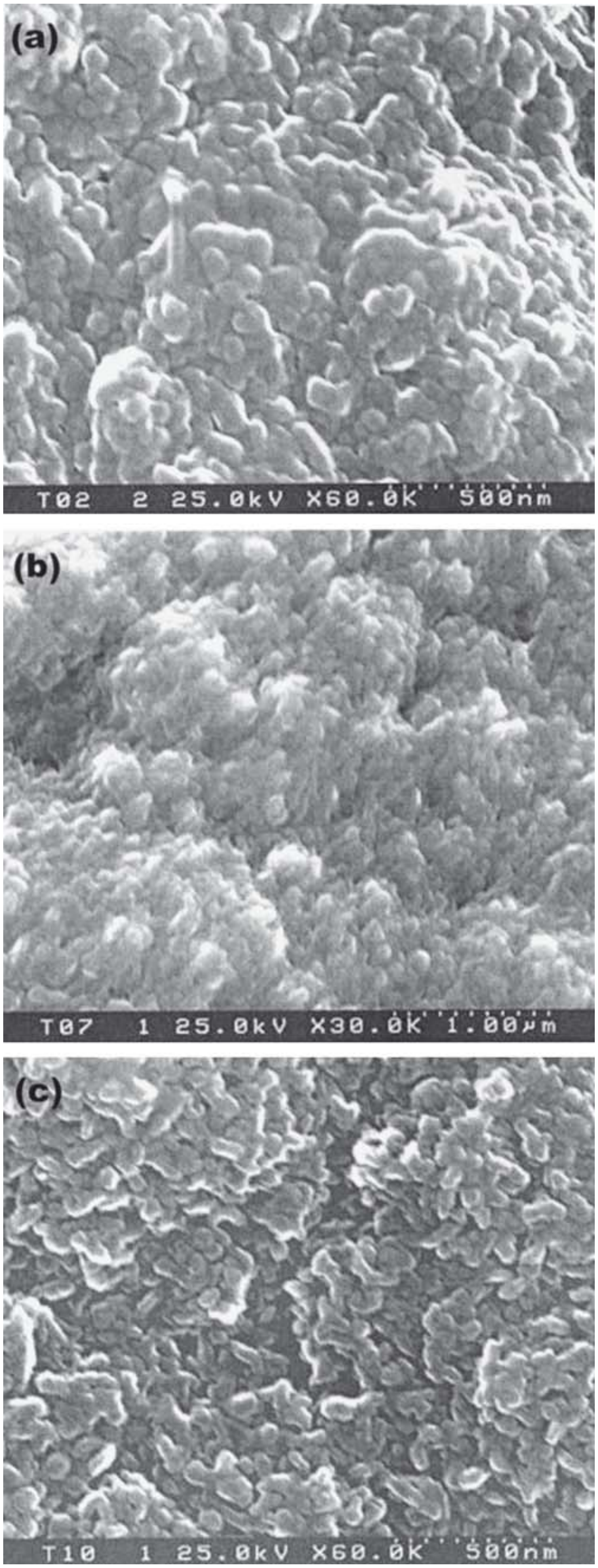

Fig. 3 SEM images of samples deposited in experiments 2(a), 7(b), and 10(c)

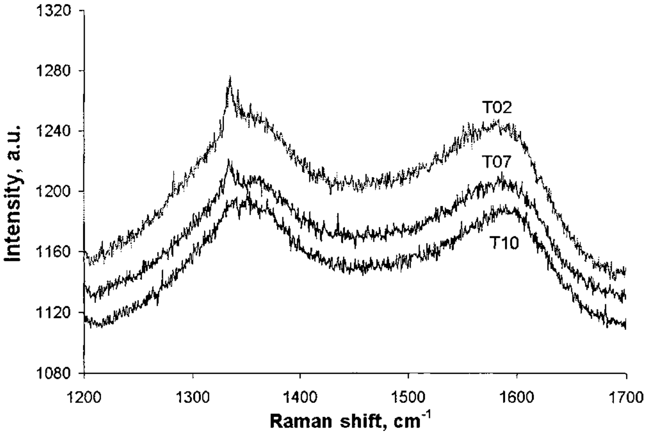

Fig. 4 Raman spectra of samples prepared in experiments 2 (TO2), 7 (TO7), and 10 (T10)

4. Conclusions

In this paper, it was reported that the optimization of the time-modulated CVD process has been optimized to produce NCD coatings using the DOE approach by Taguchi. The as-grown films were characterized using Raman spectroscopy, surface profilometry, Vickers hardness tests, and SEM. Five factors, five parameters, and four experimental levels were considered in this investigation. Optimum conditions were obtained after performing only 16 experiments.

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