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Growth of nanocrystalline diamond films on quartz by hot-filament chemical vapor deposition

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In this study, a nanocrystalline diamond thin film is applied on a quartz substrate using hot filament chemical vapor deposition (HFCVD) with a mixture of methane and hydrogen gas. Taguchi's method with L_9 (3^4) orthogonal array is used to design the experimental parameters. Moreover, the effects of the CH_4/H_2 ratio, the chamber pressure, the substrate temperature, and total gas flow rate on the qualities of the nanocrystalline diamond film are discussed. Film growth rate, surface roughness and transmittance in the visible waveband are considered quality characteristics. With signal-to-noise ratio and the average value of the quality characteristics, optimal parameters can be found. In the analysis of variance and F test, an optimal quality characteristic can be predicted after eliminating factors with less influence. Before the diamond deposition, electrophoresis and Polyetherimide (PEI) adhesion methods as pretreatment on the quartz substrate are compared and discussed for their effects on nucleation density. The optimal parameters obtained in this study are 12% CH_4/H_2, the chamber pressure of 10 Torr, 600 °C substrate temperature, and total gas flow rate of 100 sccm. With these parameters, the transmittance in the visible waveband of a diamond film on quartz substrate can reach to 60%.

Key words: Taguchi's method, HFCVD, Nanocrystalline diamond.

Introduction

Due to the outmost characteristics of diamond, it can be applied in a lot of industries. It has the high potential for advanced material application in mechanical, medical, optical and electrical industries. Since the grain size of nanocrystalline diamond, with the similar characteristics of diamond, is about several tens of nanometer, lower surface roughness makes more applications come true. For example, diamond coated onto the nano-imprint template can be the protective film. Moreover, the hardness and the toughness of the template can also be improved together with its reliability and life. In addition, diamond can also be applied as the heat spreader or heat dissipation for electronic components [1], especially for high power devices. The nanocrystalline diamond film can be considered the optical protection film due to the high hardness and smoothness. With high quality of nanocrystalline diamond films of high optical transmittance, the nanocrystalline diamond film can be a protective film on the optical components.

The growth method of nanocrystalline diamond film can be divided into three categories. Taking CH_4/H_2 as reactants and increasing the proportion of methane can improve the nucleation density and the secondary nucleation to deposit nanocrystalline diamond film. This is a common deposition method of nanocrystalline diamond films [2-6]. The second is to apply a negative bias when depositing diamond in order to attract hydrocarbon ions (C^+ or CH^+) and hydrogen ion (H^+) impacting the substrate and to increase the secondary nucleation density and the deposition rate [7-9]. The third one is to change the reactant gas and use the inert gas instead of hydrogen to deposit nanocrystalline diamond thin film [10, 11].

In this study, Taguchi's method with L_9 (3^4) orthogonal array is used to design the experimental parameters. The effects of the CH_4/H_2 ratio, chamber pressure, substrate temperature, and total gas flow rate on the qualities of the nanocrystalline diamond film are discussed. Film growth rate, surface roughness and transmittance in the visible waveband are considered quality characteristics to obtain the optimal parameters.

Experimental

Experimental setup

The current study is divided into three parts: the deposition of nanocrystalline diamond film, the property measurement of diamond thin film, and the parameter analysis based on the Taguchi method. Hot filament chemical vapor deposition method is used by supplying the energy to the reactive gases (hydrogen and methane) at high filament temperature. With the mechanical pump, the pressure of the vacuum chamber is maintained to 10^{-3} Torr. As for the size of vacuum chamber of stainless steel, its diameter is 32 cm and the height is 45 cm. In addition to the inlet and outlet on

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Table 1. Taguchi L_9 (3^4) orthogonal array.

Exp.	A	B	C	D
L1	1	1	1	1
L2	1	2	2	2
L3	1	3	3	3
L4	2	1	2	3
L5	2	2	3	1
L6	2	3	1	2
L7	3	1	3	2
L8	3	2	1	3
L9	3	3	2	1

Table 2. Four factors and levels.

	Level 1	Level 2	Level 3
A (CH_4/H_2)	8%	12%	16%
B (Chamber pressure)	10 Torr	20 Torr	30 Torr
C (Substrate temperature)	600ºC	650ºC	700ºC
D (Total gas flow rate)	100 sccm	150 sccm	200 sccm

the wall and observation window, there are a number of cooling pipes in the internal wall to take the heat away and avoid the possible overheating in the chamber. Therefore, the substrate temperature remains between of 600 ºC ~ 700 ºC. The tungsten filament is of the purity of 99.95%. Three tungsten filaments of the diameter of 0.8 mm and the length of 140 mm are used. When the temperature is under control, the strength of the filament is maintained and the drooping effect can therefore be avoided due to the filament heating.

Experimental parameters

In order to deposit nanocrystalline diamond onto the heterogeneous substrate-quartz, two kinds of pretreatment methods in nano-diamond powder solution are selected: the electrophoresis and Polyetherimide (PEI) adhesion. After the pretreatment process, the concentration of carbon source, chamber pressure, substrate temperature and total gas flow rate are used as experimental parameters for further diamond deposition. Taguchi L_9 (3^4) orthogonal array, as shown in Table 1, is used in this study. Four factors with 3 levels of the process parameters are listed in Table 2. In order to have stable and accurate results, three experiments are progressed for each case to obtain the average data and the standard deviation.

Results and Discussion

Nucleation pretreatment

The pretreatment results by PEI adhesion with 0.01 wt%, 0.05 wt%, 0. wt%, and 0.5 wt% of diamond powder solution are shown in Fig. 1. The arrow points nano-diamond powders adhered on the quartz substrate. Diamond powder aggregation can be found on some parts of the surface. That is, the nano-diamond powders

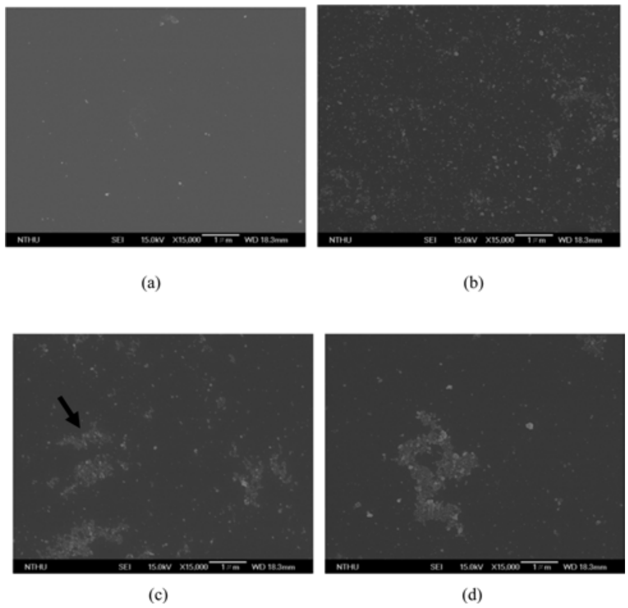


Fig. 1. SEM images of PEI pretreatment with diamond powder concentration of (a) 0.01 wt% (b) 0.05 wt% (c) 0.1 wt% (d) 0.5 wt%.

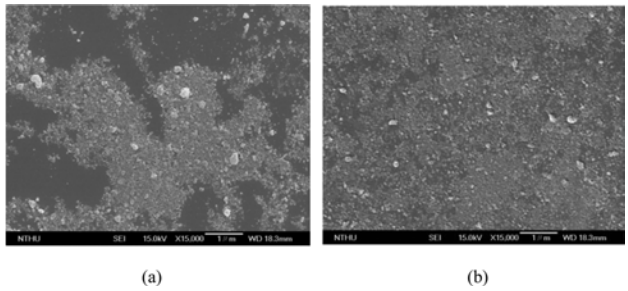


Fig. 2. SEM images of electrophoresis pretreatment with diamond powder concentration of (a) 0.01 wt% (b) 0.05 wt%.

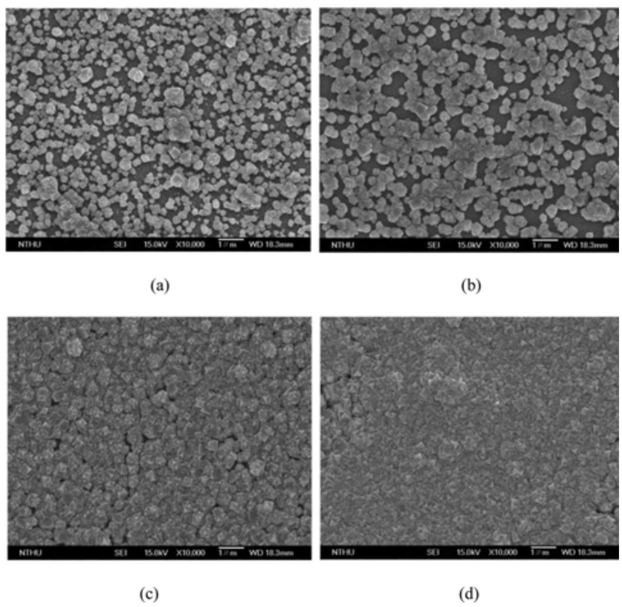
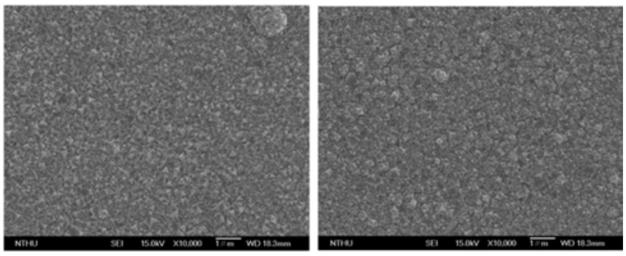


Fig. 3. Deposited nanocrystalline diamond after PEI pretreatment with diamond powder concentration of (a) 0.01 wt% (b) 0.05 wt% (c) 0.1 wt% (d) 0.5 wt%.



(a) (b)

Fig. 4. Deposited nanocrystalline diamond after electrophoresis pretreatment with diamond powder concentration of (a) 0.01 wt% (b) 0.05 wt%.

are not distributed evenly. Though the adhered amount of diamond particles is increased with the concentration of diamond powder solution, the adhesion density is still not high. Fig. 2 shows SEM images of 0.01 wt% and 0.05 wt% diamond powder solution by the electrophoresis pretreatment. From the result, the adhesion density of 0.01 wt% by electrophoresis is much higher than that by PEI pretreatment. While the concentration is increased to 0.05 wt%, the diamond powers uniformly and continuously adhere onto the quartz substrate. Therefore, the electrophoresis pretreatment is the best choice for diamond powder adhering onto the quartz substrate as the nucleation sites.

Fig. 3 shows the result of diamond deposition after the PEI pretreatment. From the figure, low adhesion density of diamond powder results in discontinuous diamond islands due to a few nucleation sites. While increasing the adhesion density, the deposited diamond is slightly improved by becoming more connected but is still not a completely continuous film. This implies that the PEI pretreatment method on the quartz substrate does not produce a satisfying result. Fig. 4 shows the diamond deposition result after electrophoresis pretreatment. Compared to the result after the PEI pretreatment, the deposited diamond proves to be a continuous film without any discontinuity even in the case of low adhesion density. In the current study, 0.05 wt% of diamond power solution by electrophoresis pretreatment is used for the following experiments.

Surface morphology and Raman spectroscopy analysis

Since it is not possible to identify the quality of diamond film from SEM images through Taguchi's method, some other quantitative data such as surface roughness and deposition rate are considered. In addition, diamond peak of 1332 cm^{-1} is detected by Raman spectroscopy to identify the diamond characteristics while the surface morphology and roughness are obtained

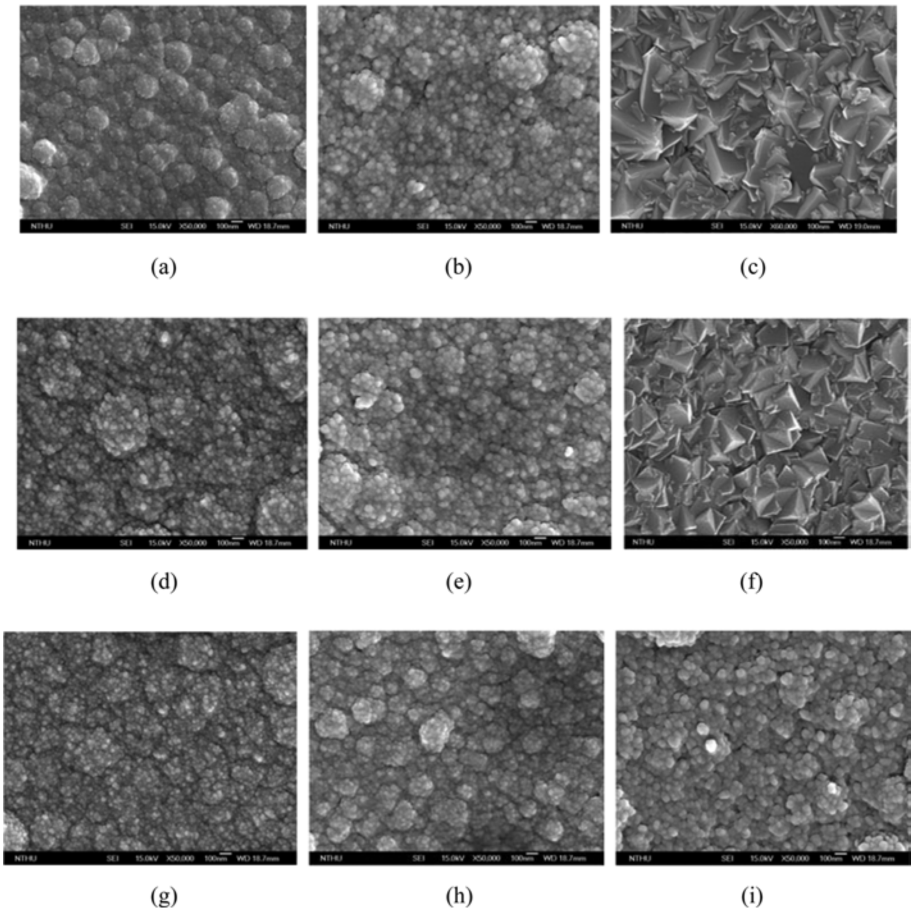
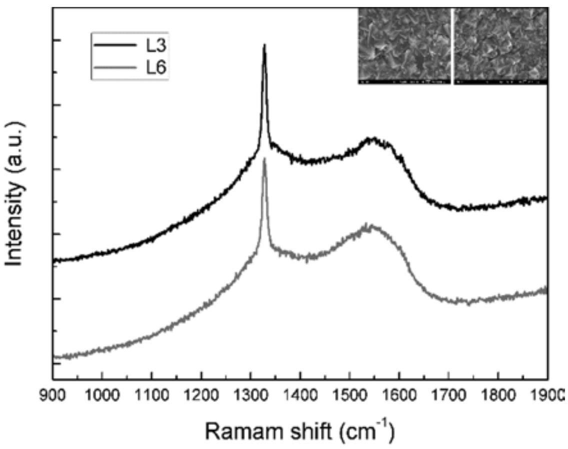
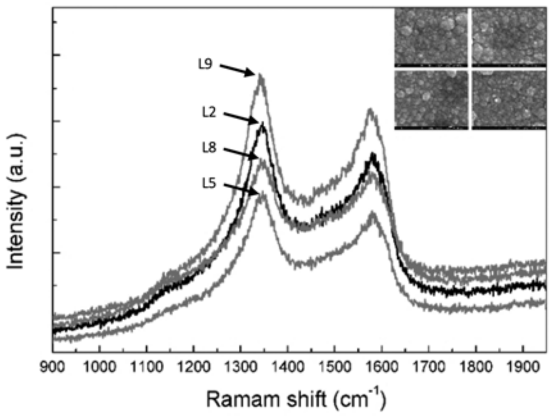


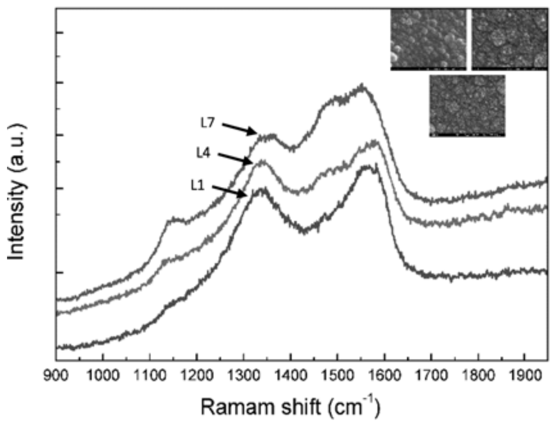
Fig. 5. SEM images from Taguchi experiments: (a) L1; (b) L2; (c) L3; (d) L4; (e) L5; (f) L6; (g) L7; (h) L8; (i) L9.



(a)



(b)



(c)

Fig. 6. Raman spectra from Taguchi experiments of (a) group one (L3 and L6); (b) group two (L2, L5, L8 and L9), and (c) group three (L1, L4 and L7).

by atomic force microscopy (AFM). Fig. 5 illustrates SEM images from the 9 experiments as shown in Table 1; while Fig. 6 illustrates the Raman spectra, in which three groups with similar profile are categorized.

The group one of L3 and L6 shows much sharper diamond peak than others and no obvious amorphous peak at 1580 cm^{-1} can be found. The diamond grain size is about 100 nm.

The group two of L2, L5, L8 and L9 shows slightly large FWHM of diamond peak and obvious amorphous phase at 1580 cm^{-1} compared to those of the group one. Though the chamber pressure for the L9 is 30 Torr, the high carbon concentration increases the high ratio of [C] to [H] on the surface of the substrate and therefore, increases both the secondary nucleation probability and the content of amorphous carbon. The grain sizes from the SEM image by L9 are smaller than those from the group one by the chamber pressure of 30 Torr.

For the group three of L1, L4 and L7, the chamber pressures are all 10 Torr. From the SEM images, there exists the smallest grain size of nanocrystalline diamond in the three groups. The high grain boundary makes the weak diamond peak by increasing the obvious amorphous phase. Since the secondary nucleation probably comes from the low chamber pressure, the grain size becomes smaller with more grain boundaries and thus more amorphous carbon.

Taguchi analysis on growth rate

The growth rate is calculated by dividing the thickness of diamond film obtained from the SEM image of the film cross-section according to the deposition time. All the growth rates from different experiments are listed in Table 3. Fig. 7 shows S/N ratios of growth rate (G), surface roughness (R) and transmittance (T) at the wavelength of 550 nm based on Taguchi orthogonal array.

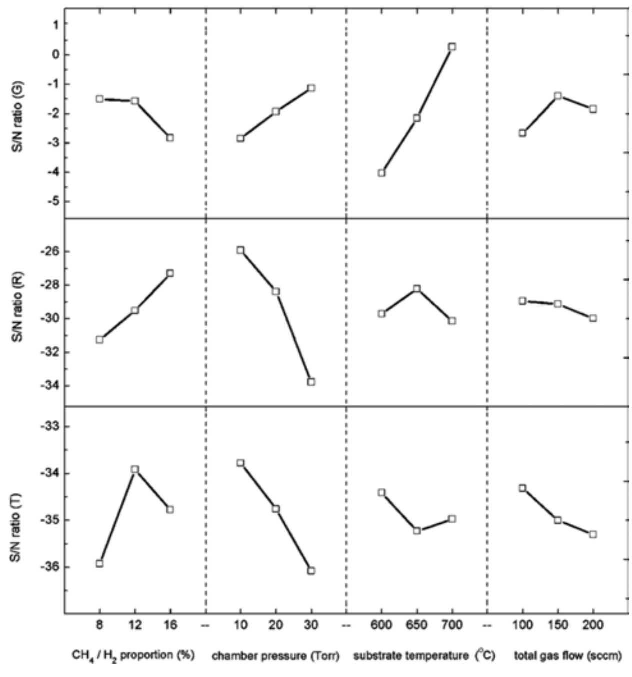


Fig. 7. S/N ratios of growth rate (G), surface roughness (R) and transmittance (T) at the wavelength of 550 nm based on Taguchi orthogonal array.

Table 3. Experimental results including growth rate (G), surface roughness (R) and transmittance (T) at the wavelength of 550 nm based on Taguchi orthogonal array.

Exp.	Growth rate (μm h^{-1})	S/N	Surface roughness (nm)	S/N	Transmission (%)	S/N
L1	0.560	−5.14	24.3	−27.77	48.0	−34.33
L2	0.883	−1.09	27.9	−28.92	31.8	−36.69
L3	1.231	1.69	71.2	−37.10	20.6	−38.00
L4	0.751	−2.51	18.9	−25.56	49.4	−34.13
L5	1.005	0.02	27.8	−28.94	50.9	−33.89
L6	0.798	−2.24	50.4	−34.07	42.3	−35.25
L7	0.906	−0.88	17.4	−24.86	47.8	−34.42
L8	0.591	−4.73	23.1	−27.31	43.4	−35.10
L9	0.721	−2.87	32.1	−30.17	35.6	−36.20
Average	0.827	−1.97	32.6	−29.41	41.4	−35.33

The average growth rate is 0.827 μm h^{-1} with the standard deviation of 0.069 μm h^{-1}. The growth rate can be the factor of the larger-the-better result based on the Taguchi's method. In addition, the average S/N ratio of the grow rate is −1.97 with the maximum of 1.69 at L3 experiment and the minimum of −5.14 at L1. That is, the highest growth rate of nanocrystalling diamond is obtained by adding 8% of CH_4/H_2. The growth rate decreases with increasing concentration of the carbon source from 8% to 16%. That the hydrogen content is lessening in the chamber results in less free radical on the diamond surface and hence the low growth rate.

In the current experiments, the growth rate reaches 1 ìm h^{-1} and the highest growth rate occurs at the substrate temperature of 700 °C. The higher the substrate temperature is, the higher the growth rate is as shown in Fig. 7. The reason may come from the high dissociation of gas at high temperature.

Analysis of variance is mainly conducted to evaluate the experimental error and the influence of each factor. In the current study, the confidence of each factor is set to above 95% to be considered a significant factor. With the experimental and calculated results based on the growth rate being a quality factor, the confidence of the CH_4/H_2 ratio, the chamber pressure, the substrate temperature and total gas flow rate is 98.0%, 99.0%, 100.0% and 96.5%, respectively. All the factors prove significant in the growth rate.

Taguchi analysis on surface roughness

The average surface roughness is obtained from atomic force microscopy. The surface roughness from different experiments is listed in Table 3. The average surface roughness is 32.6 nm with the standard deviation of 4.0 nm. The surface roughness can be the factor of the smaller-the-better result based on the Taguchi's method. The average S/N ratio is −29.41 with the maximum of −24.86 at L7 experiment and the minimum of −37.10 at L3.

The lowest surface roughness of the nanocrystalline diamond film occurs at the 16% ratio of CH_4/H_2. The change of methane concentration results in the concentration variation of active free radicals and hydrogen atoms on the substrate surface and the crystallization of diamond film. When the CH_4 concentration is 8%, low ratio of [C]/[H] on the substrate surface reduces the density of the secondary nucleation instead of nucleation and makes the diamond grow up. Therefore, the grain size of diamond becomes large and the surface roughness increases. In addition, the lowest surface roughness occurs at the chamber pressure of 30 Torr as shown in Fig. 7.

With the experimental and calculated results based on the surface roughness being a quality factor, the confidence of the CH_4/H_2 ratio, the chamber pressure, the substrate temperature and total gas flow rate is 99.9%, 100.0%, 97.1% and 93.5%, respectively. Only the total gas flow rate does not prove significant in the surface roughness and therefore can be ignored.

Taguchi analysis on transmittance in the visible waveband

The transmittance in the visible waveband (350 ~ 800 nm) is measured by spectrometer. The thickness of the thin film is controlled in the range of 1.0 ~ 1.5 μm. The transmittance at the wavelength of 550 nm is considered the quality factor. The transmittance from different experiments is listed in Table 3. The average transmittance is 41.1% with the standard deviation of 4.6%. The surface roughness can be the factor of the nominal-the-best result based on the Taguchi°Øs method though the highest transmittance is expected to be 100%. The average S/N ratio is −35.33 with the maximum of −33.89 at L5 experiment and the minimum of −38.00 at L3.

The highest transmittance occurs at the 12% ratio of CH_4/H_2. For the case of the 8% CH_4/H_2 ratio, the high average surface roughness of about 40 nm causes the scattering effect and therefore the transmittance is 33%. By increasing the CH_4/H_2 ratio to 12%, the surface roughness becomes smoother and raises the transmittance to about 50%. When the CH_4/H_2 ratio is increased to

16%, too much carbon source increases the amorphous content in the deposited film and the light absorption without transmittance.

With the experimental and calculated results based on the transmittance being a quality factor, the confidence of the CH_4/H_2 ratio, the chamber pressure, the substrate temperature and total gas flow rate is 99.9%, 100.0%, 96.5% and 97.7%, respectively. All the factors prove significant in the transmittance.

Optimized processes

Taking the growth rate, the surface roughness and the transmittance as the quality factors to design the optimal processing parameters is the following approach. According to results discussed in the sections from 3.3 to 3.5, the best predicted value within the confidence interval can be obtained when the growth rate, the average surface roughness and the transmittance are 1.24 ± 0.16 μm h^{-1}, 5.6 ± 7.7 nm and $62.0 \pm 9.3\%$, respectively.

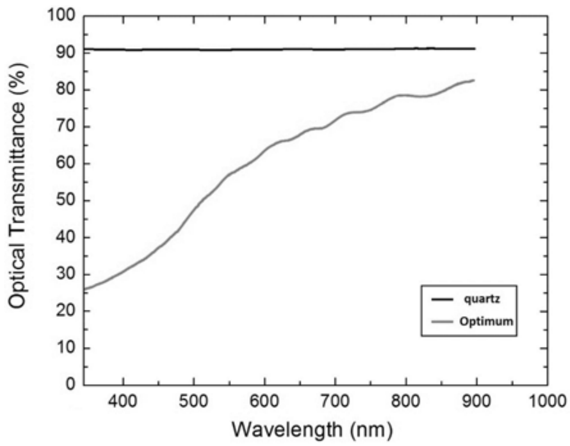


Fig. 8. Transmittance based on the optimal design parameters.

The optimal parameters obtained in this study are 12% CH_4/H_2, the chamber pressure of 10 Torr, 600 °C substrate temperature, and total gas flow rate of 100 sccm. Using the optimal parameters, the obtained nano-diamond films show the growth rate of 1.28 ± 0.12 μm h^{-1}, the average surface roughness of 14.7 ± 1.8 nm and the transmittance of $58.0 \pm 4.3\%$, respectively. Fig. 8 shows the best transmittance, while Fig. 9 illustrates the best surface roughness based on the optimal design parameters.

Conclusions

In this study, two kinds of pretreatment methods, PEI and electrophoresis, are studied. After pretreatment, Taguchi's method with L_9 (3^4) orthogonal array is used to design the experimental parameters. Moreover, the effects of the CH_4/H_2 ratio, the chamber pressure, the substrate temperature, and the total gas flow rate on the qualities of the nanocrystalline diamond film are discussed. The growth rate, the surface roughness and the transmittance in the visible waveband are considered as the quality characteristics. Major contributions are listed below.

(1) Diamond film is successfully deposited onto the heterogeneous quartz substrate.

(2) For the nucleation experiments, the diamond powders are distributed evenly on the quartz with the voltage of 300 V and 0.05 wt% of diamond powder to de-ionized water.

(3) The CH_4/H_2 ratio of 12% is relatively high in the current study while comparing with previous studies.

(4) The diamond grain size affects the transmittance in the visible waveband.

(5) The optimal experimental parameters are 12%

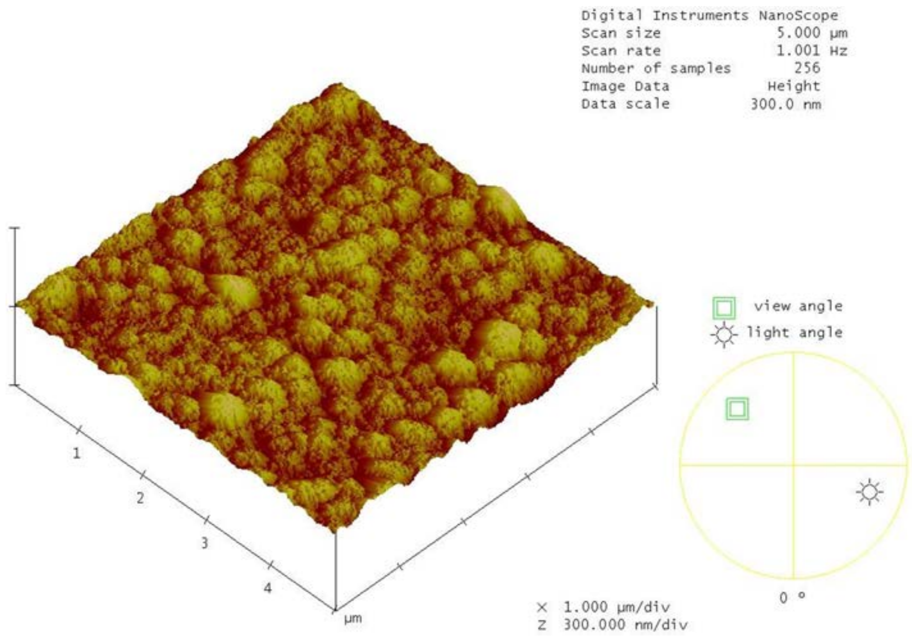


Fig. 9. Surface roughness based on the optimal design parameters.

CH_4/H_2, the chamber pressure of 10 Torr, 600 °C substrate temperature, and total gas flow rate of 100 sccm.

(6) The obtained nano-diamond films show the growth rate of 1.28 ± 0.12 μm h^{-1}, the surface roughness of 14.7 ± 1.8 nm and the transmittance of $58.0 \pm 4.3\%$, respectively.

Acknowledgments

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