

Nanocrystalline Diamond Films Deposited by the Hot Cathode Direct Current Plasma Chemical Vapor Deposition Method with Different Compositions of CH₄/Ar/H₂ Gas Mixture

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Nanocrystalline diamond films with different grain sizes were synthesized on Si substrate by the hot cathode direct current plasma chemical vapor deposition method with different compositions of CH₄/Ar/H₂ gas mixture. The morphology and microstructure of the obtained products were characterized by scanning electron microscopy, atomic force microscopy, high-resolution transmission electron microscopy, X-ray diffraction, and Raman spectroscopy. The results showed that the composition of the CH₄/Ar/H₂ gas mixture affected greatly the grain sizes, surface smoothness, and crystal quality of the nanocrystalline diamond films. With the increase of CH₄ concentration, the grain sizes got smaller and the surface of the films got smoother. However, the grain sizes got smaller and the crystal quality was weakened with the increase of Ar concentration. In the process of deposition, SiC was formed at the substrate before the growth of nanocrystalline diamond films, which increased the secondary nucleation of nanocrystalline diamonds. To obtain the nanocrystalline diamond films with uniform small grain sizes, good surface smoothness, and little non-diamond phase, the optimal composition of the CH₄/Ar/H₂ gas mixture is 6/70/30 and 7/70/30.

1. Introduction

Nanocrystalline diamond (NCD) has attracted considerable interest and attention because of its high surface smoothness, high fracture toughness, high hardness, wide band gap, low friction coefficient, high electron emission efficiency and light transmission, exceptional thermal conductivity and chemical inertness, and so on. These unique properties of NCD enhance the applications of diamonds in many fields, such as a protective coating for machining tools, as field electron emitters for cold cathode flat panel displays, as an optical window, as an X-ray radiation detector, and so on.^{1–5} Many researchers have tried to prepare high-quality NCD films by changing the synthesis conditions or by secondary treatment technology to satisfy the different applications of NCD films because the difference in grain sizes, surface smoothness, and crystal quality greatly affects the applications of NCD films in coatings, optical fields, and so on. However, it is preferred that the morphology and structure of NCD films could be controlled in the process of synthesis.

In previous reports, NCD films have typically been synthesized by microwave plasma chemical vapor deposition (CVD)

or the hot filament CVD method, and the gas mixture used was mainly CH₄–H₂, CH₄–Ar, CH₄–H₂–Ar (He or Ne), or CH₄–H₂–N₂.^{2,6–9} It was considered that C₂ radicals in noble-gas-rich plasmas were responsible for the deposition of NCD, and NCD films could be grown when the Ar/H₂ ratio was higher than 9.^{1,10–14} However, the nucleation mechanism of NCD has not been ascertained, and the composition of the gas mixture is not invariable in different synthesis methods. In addition, the high Ar concentration is unfavorable for the deposition of NCD films because the glow discharge is unstable due to Ar ionization and the non-diamond phase is increased in NCD grain boundaries. Therefore, the investigation of synthesis conditions (including deposition method, experimental parameters, etc.) is important for the fabrication and applications of NCD-based devices.

In this paper, we report the optimal synthesis of NCD films on Si substrate by the hot cathode direct current plasma CVD (DC-PCVD) method using a CH₄–Ar–H₂ gas mixture. We study the morphology and microstructure of NCD films by scanning electron microscopy (SEM), atomic force microscopy (AFM), high-resolution transmission electron microscopy (HR-TEM), X-ray diffraction (XRD), and Raman spectroscopy. Finally, we discuss the effect of gas composition on the grain sizes, surface smoothness, and crystal quality of NCD films.

2. Experimental Section

NCD films were prepared on Si (100) substrate by the hot cathode DC-PCVD method. The spacing between the tantalum (Ta) cathode and the copper anode was about 5 cm. A (100) Si

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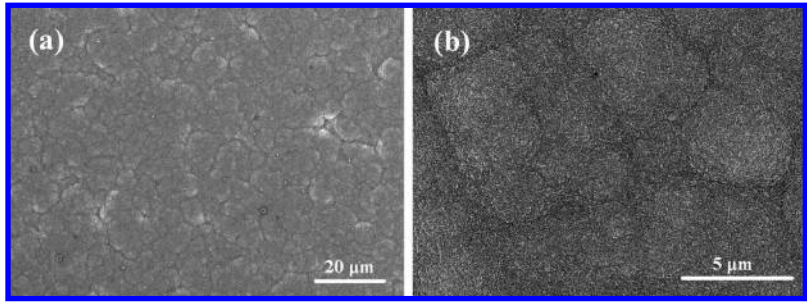


Figure 1. Low-resolution SEM images of NCD films. (a) For an area of $110 \times 80 \mu\text{m}^2$ and (b) for an area of $17.5 \times 13 \mu\text{m}^2$.

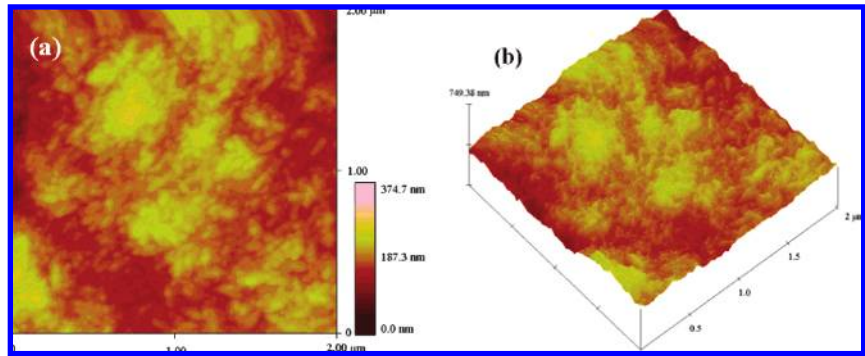


Figure 2. Tapping-mode AFM images of NCD films for an AFM window of $2 \times 2 \mu\text{m}^2$. (a) Two-dimensional pattern and (b) three-dimensional pattern.

TABLE 1: Experimental Parameters for the Growth of NCD Films

samples	a	b	c	d	e	f	g
flow ratio (sccm) $\text{CH}_4/\text{Ar}/\text{H}_2$	4:70:30	5:70:30	6:70:30	7:70:30	4:75:25	4:80:20	4:90:10
temperature (K)	1033	1013	1018	1023	1023	1013	1028
chamber pressure (kPa)	8.62	7.68	6.95	7.18	8.40	7.95	8.51
reaction time (h)	5	5	5	5	3	3	3

wafer with a diameter of 2 in. was placed onto the copper anode, on which the Mo wafers were used as the thermal conduct layers. Before the experiment, the Si wafer was ultrasonically scratched with 500 nm diamond powder for about 10 min and then were ultrasonically cleaned in deionized water for 10 min. The experimental parameters for the growth of NCD films were shown in Table 1. In the process of the experiment, the substrate temperature was controlled by gas composition, chamber pressure, DC voltage and current, and was measured by infrared temperature sensor. Before the introduction of gas, the chamber pressure was pumped out to below 6×10^{-2} Pa, then H_2 gas with a flow rate of 300 sccm was introduced into the chamber, and simultaneously DC voltage was increased to produce the glow discharge. When the plasma ball of H_2 was stable, the CH_4 and Ar gas mixture was introduced into the chamber. Then the composition of the $\text{CH}_4/\text{Ar}/\text{H}_2$ mixture and DC voltage were adjusted, by which the substrate temperature was achieved. The experimental conditions must be controlled carefully to obtain NCD films. After the deposition, the gas valves and power supply were shut off, and the chamber pressure was pumped out to below 6×10^{-2} Pa.

The morphology and smoothness of NCD films were characterized by a scanning electron microscope (Hitachi S-4800) operated with an accelerating voltage of 20 kV and atomic force microscope (Digital Instruments Nanoscope III) in tapping mode. The microstructure was characterized by a high-resolution transmission electron microscope (Tecnai F 30) operated with an accelerating voltage of 300 kV, an X-ray diffractometer (Rigaku D/MAX 2200VPC) with Cu $K\alpha$ radia-

tion, and a Raman spectrometer (Renishaw inVia) at the laser wavelength of 514.5 nm from an Ar^+ laser.

3. Results and Discussion

Figure 1 shows the typical low-resolution SEM images of NCD films. As seen in Figure 1a, the surface of NCD films consists of an island-like structure. In Figure 1b, it can be observed that the sizes of the island-like structure range from 3 to $5 \mu\text{m}$ and the region boundary of the islands is not obvious because the long growth time increases the nucleation sites of NCD. Figure 2 shows the two-dimensional and three-dimensional AFM patterns with tapping mode of NCD films. It can be noted that the surface roughness of the NCD films measured over an area of $2 \times 2 \mu\text{m}^2$ is below 300 nm, suggesting that the surface roughness of the NCD films is insensitive to the film thickness.

Figure 3-1 and Figure 3-2 show the high-resolution SEM images of NCD films prepared by different compositions of $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture. In the first experiment, the flow rates of Ar and H_2 are fixed at 70 and 30 sccm, respectively, and the flow rate of CH_4 increases from 4 to 7 sccm with 5 h deposition. As shown in Figure 3a, with the $\text{CH}_4/\text{Ar}/\text{H}_2$ ratio of 4/70/30, the NCD films have bad surface smoothness, and the average grain sizes are larger than 15 nm. With the increase of CH_4 concentration, the surface smoothness of NCD films gets better and better, and the grain sizes are smaller and smaller. As seen in Figure 3b–d, the average grain sizes of NCDs are about 13, 10, and 8 nm, corresponding to $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 5/70/30, 6/70/30, and 7/70/30, respectively. Furthermore, as observed

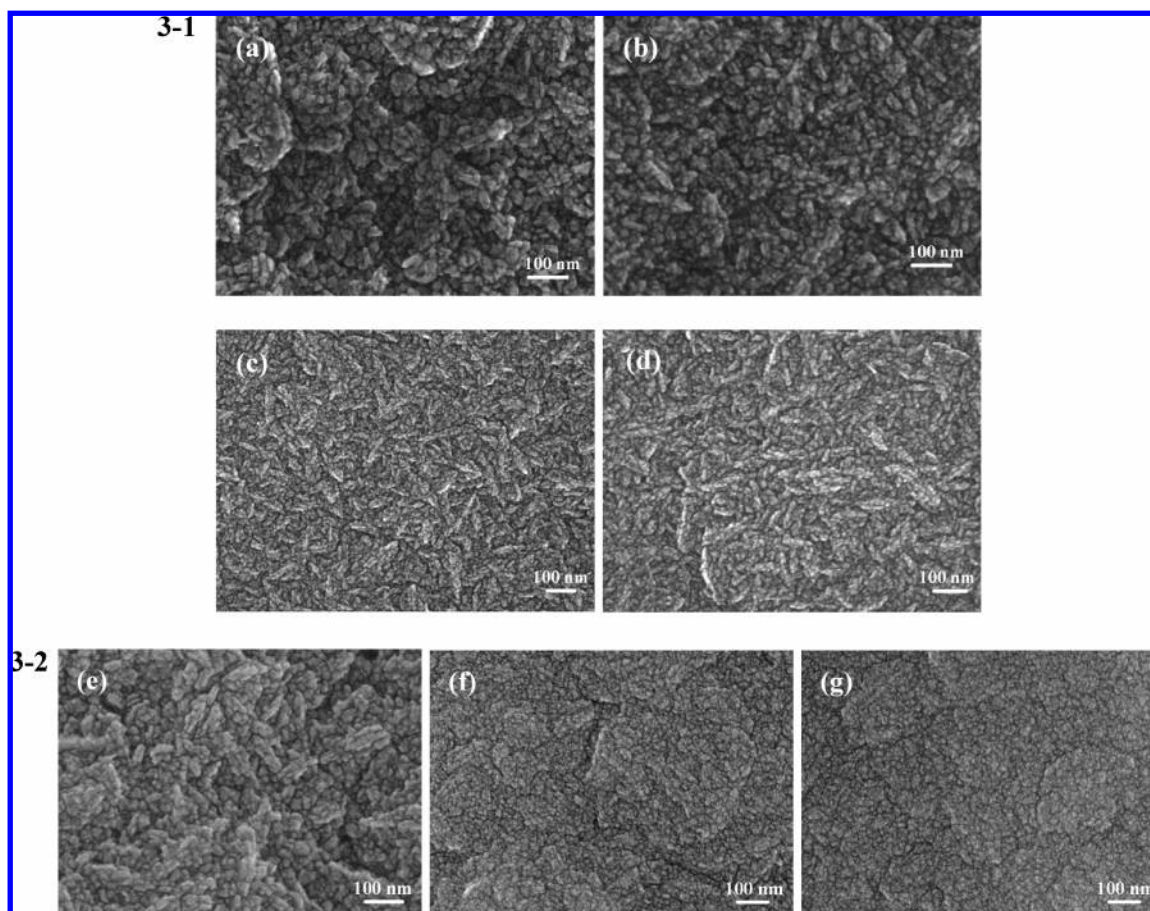


Figure 3. (3-1) High-resolution SEM images of NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/70/30 (a), 5/70/30 (b), 6/70/30 (c), and 7/70/30 (d). (3-2) High-resolution SEM images of NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/75/25 (e), 4/80/20 (f), and 4/90/10 (g).

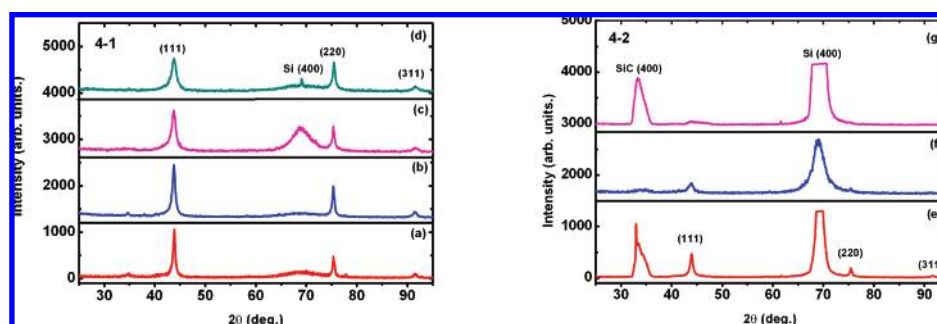


Figure 4. (4-1 and 4-2) XRD patterns of NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/70/30 (a), 5/70/30 (b), 6/70/30 (c), 7/70/30 (d), 4/75/25 (e), 4/80/20 (f), and 4/90/10 (g).

in Figure 3a–d, the growth of the NCD films is basically along columnar nucleation.

In the second experiment, the flow rate of CH_4 is fixed at 4 sccm, and the flow ratio of Ar/H_2 is 75/25, 80/20, and 90/10 with 3 h deposition, respectively. The SEM images are shown in Figure 3-2. As seen in Figure 3e, the morphology of the NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/75/25 is similar to that of the NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/70/30. With the increase of the flow ratios of Ar/H_2 to 80/20 and 90/10, respectively, the grain sizes of the NCDs distinctly decrease, and the surface smoothness of NCD films is better as shown in Figure 3f and g, respectively. Furthermore, the phenomenon of columnar nucleation of NCD disappears basically with the increase of the Ar concentration, which indicates that the high Ar concentration increases the self-nucleation of NCDs.

The XRD patterns of the NCD films with different compositions of $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture are shown in Figure 4-1 and

4-2. Curves a–d are the XRD patterns of the NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/70/30, 5/70/30, 6/70/30, and 7/70/30 for 5 h deposition, respectively. The diffraction peaks of (111), (220), and (311), corresponding to the diffraction pattern of diamond with a cubic structure can be observed. Furthermore, the broad peak of Si (400) is also observed, which comes from the Si substrate. In comparison with curves a–d, it can be found that the (111) peak of NCD broadens gradually from curve a to curve d, resulting from the decrease of grain sizes. On the basis of the Scherrer formula: $D = k\lambda/\beta \cos \theta$ (where $k = 0.89$ and $\lambda = 0.154056 \text{ nm}$), the average crystal sizes of the NCDs can be estimated to be about 15.70, 12.11, 8.15, and 7.18 nm, corresponding to curves a, b, c, and d, respectively. Curves e–g are the XRD patterns of the products with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/75/25, 4/80/20, and 4/90/10 for 3 h deposition, respectively. The (400) peak of the Si substrate is strongest in all, resulting from the short deposition time of the products. Different from

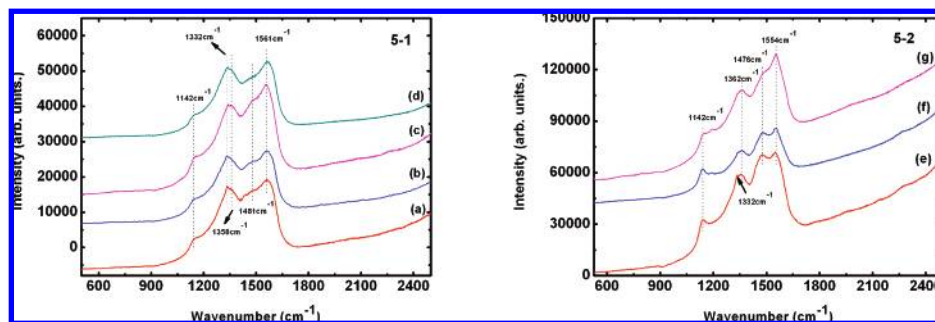


Figure 5. (5-1 and 5-2) Raman spectra of NCD films with $\text{CH}_4/\text{Ar}/\text{H}_2$ ratios of 4/70/30 (a), 5/70/30 (b), 6/70/30 (c), 7/70/30 (d), 4/75/25 (e), 4/80/20 (f), and 4/90/10 (g).

curves a–d, the strong peak of SiC (400) appears and the diamond peaks become weak, even disappearing in curve g. It can be concluded that SiC was formed between the Si substrate and NCD films at the initial stage of NCD growth. When the deposition time reached 5 h, the NCD films got sufficiently thick and the peak of SiC was almost not observed in the XRD patterns. Therefore, in the experiment, we considered that the NCDs can be formed on the Si substrate through an epitaxial SiC layer, which first nucleated at the beginning of deposition. With the increase of deposition time, the NCD films with uniform grain sizes were formed as a result of secondary nucleation. The nucleation phenomenon observed in the experiment is consistent with the published literature reported by Yan et al.¹⁵

The Raman spectra of the NCD films with different compositions of $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture are shown in Figure 5-1 and 5-2. In general, five peaks can be observed in the Raman spectra of NCD films. The characteristic peak of diamond is at about 1332 cm^{-1} , the graphite structure peak (G band) is at about 1560 cm^{-1} , the graphite disorder peak (D band) is at about 1360 cm^{-1} , and a pair of peaks of *trans*-polyacetylene is at about 1140 cm^{-1} and 1480 cm^{-1} , which is attributed to the structure of the NCD phase or disordered sp^3 carbon phase.^{16–20} The relative intensity of the G peak indicates the graphite content of the NCD grain boundary. As seen in Figure 5, the five peaks are present in the Raman spectra of the NCD films. In comparison with curves a–d, it was observed that the intensity of the G peak has a slight increase and the characteristic diamond peak at about 1332 cm^{-1} broadens gradually from curve a to curve d. It suggested that the graphite impurities of the products have a slight increase and the grain sizes decrease gradually with the increase of CH_4 concentration. In comparison with curves e–g, it can be found that the characteristic diamond peak at about 1332 cm^{-1} disappears other than that in curve e. The intensity of the G peak in curve g is distinctly enhanced, which indicates the high graphite impurities of products with the increase of Ar concentration. In addition, as shown in curves e–g, the peaks at about 1140 and 1480 cm^{-1} are narrower than those of curves a–d, resulting from the decrease of the grain sizes and the increase of the disordered sp^3 carbon phase in the NCD films. On the basis of the Raman spectra of the NCDs with different compositions of $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture, it can be concluded that the graphite impurities and disordered sp^3 carbon phase of the products increase with the increase of Ar concentration, but the increase of CH_4 concentration hardly has any effect on the quality of the NCD films other than the decrease of the grain sizes.

Figure 6 shows the HRTEM images of NCD. As seen in Figure 6a, the grain size is about 16.8 nm and the size of the cross section is about 11.4 nm , corresponding to the $\text{CH}_4/\text{Ar}/\text{H}_2$ ratio of 4/70/30. In the inset of Figure 6a, an interplanar

distance of 0.21 nm can be observed, which corresponds to the (111) plane of cubic diamond. As shown in Figure 6b, the grain size of the NCD is about 13.5 nm , in which the $\text{CH}_4/\text{Ar}/\text{H}_2$ ratio was increased to 5/70/30. The inset of Figure 6b shows the corresponding selected area electron diffraction (SAED) pattern. Three diffraction rings represent the (111), (220), and (311) planes of diamond with a cubic structure, which is also in accordance with the XRD analysis. Figure 6c shows the HRTEM image of NCD with a $\text{CH}_4/\text{Ar}/\text{H}_2$ ratio of 4/80/20. It can be found that the grain sizes of NCDs are smaller than 10 nm , even 3 nm which is the size of ultra-nanocrystalline diamond. In the edge of the NCD particles, some non-diamond structures are also present, which indicates the bad purity of the NCD films under the condition of a $\text{CH}_4/\text{Ar}/\text{H}_2$ ratio of 4/90/10. As seen in Figure 6d, the HRTEM lattice image shows clearly the lattice structure of diamond. The interplanar distance of (111) planes is measured to be 0.21 nm , which is consistent with the lattice parameters of diamond. In addition, the tetrahedral structure of diamond can also be observed clearly in the round of Figure 6d.

On the basis of the above results, it can be found that the composition of the $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture affects greatly the growth of NCD films. Therefore, it can be concluded that nucleation of NCD has a close correlation to the composition of the $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture. In previous reports, some authors considered that C_2 concentration was the key for the growth of NCD films, and the high Ar concentration was favorable for increasing the C_2 concentration.^{1,10} However, other authors considered that the C_2 did not play an important role,^{8,21} but C_1 was responsible for the formation of NCD films.²² Following the analysis in the experiment, on one hand, the high Ar concentration was favorable for the nucleation of grains. It can terminate the growth of grain sizes and improve the surface smoothness of NCD films. However, the high Ar concentration also decreased the crystal quality of NCD films, resulting from much more non-diamond phase at the boundary of grains. On the other hand, with the Ar flow rate of 70 sccm , the high CH_4 concentration can also decrease the grain sizes and improve the surface smoothness, but the crystal quality of NCD films was not decreased. In the experiment, with the Ar/H_2 ratio of 70/30 sccm, after the CH_4 flow rate was increased to 6 and 7 sccm, the obtained NCD films have uniform small grain sizes, good surface smoothness, and little non-diamond phase.

Compared with the results synthesized by microwave plasma CVD and the hot filament CVD method, the hot cathode DC-PCVD method is more favorable for improving the growth rates and crystalline quality of NCD films. In this experiment, NCD films can have uniform grain sizes with the Ar concentration about 70%, which is lower than above 90% in the microwave plasma or hot filament CVD methods.^{23,24} The low Ar concentration decreased the graphitic content of NCD films and

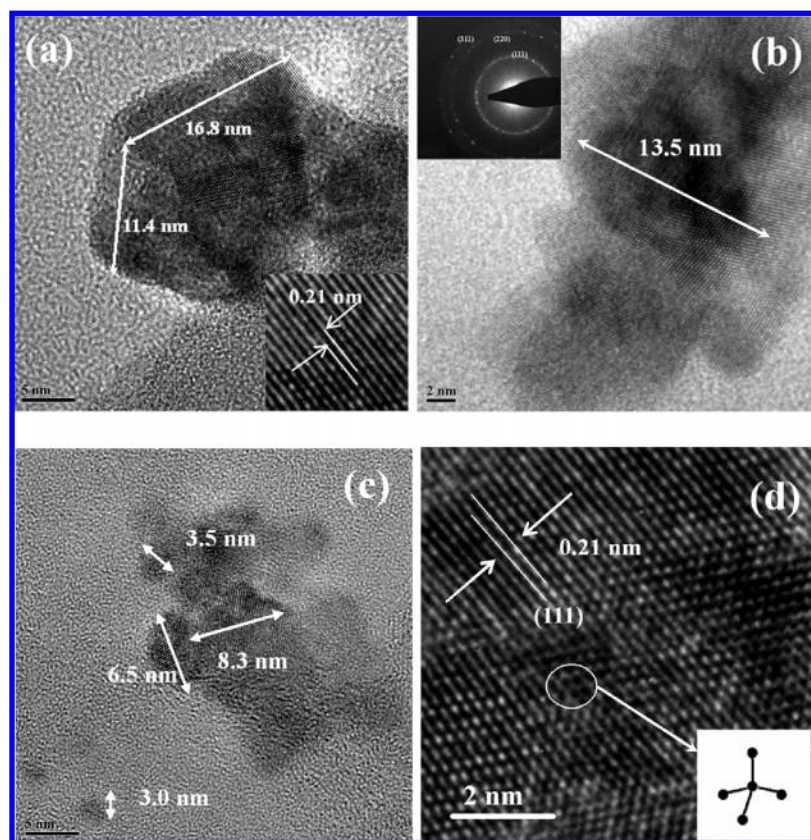


Figure 6. HRTEM images of NCD. (a) HRTEM image of NCD with large grain size, (b) HRTEM and SAED patterns of NCD with middle grain size, (c) HRTEM image of NCD with small grain size, and (d) HRTEM lattice image of NCD.

improved the stability of plasma glow discharge in the process of deposition. For the deposition of high-quality NCD films by the hot cathode DC-PCVD method, the CH_4 concentration is about 6–7%, which is higher than about 1–2% in the microwave plasma or hot filament CVD methods.^{24,25} The high CH_4 concentration increased the growth rates of NCD films but did not decrease the quality of NCD films. Furthermore, by controlling the experimental parameters in hot cathode DC-PCVD technology, the NCD films can be grown in large-area with uniform grain sizes, and the quality and smoothness of films were excellent, which is favorable for the fabrication and applications of NCD-based devices.

4. Conclusions

We report the synthesis of NCD films with different grain sizes on Si substrate by changing the composition of the $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture. The results showed that the high Ar concentration can decrease the grain sizes and improve the surface smoothness of NCD films, but the crystal quality was decreased resulting from much non-diamond phase at the boundary of grains. However, the NCD films had small grain sizes, good surface smoothness, and high crystal quality with the high CH_4 concentration. For the deposition of NCD films, the optimal composition of the $\text{CH}_4/\text{Ar}/\text{H}_2$ gas mixture was 6/70/30 and 7/70/30. Furthermore, the SiC structure was first formed at the interface between the Si substrate and the NCD films before the deposition of the NCD films, which accelerated the secondary nucleation of NCDs. These experimental findings are very interesting for further study on the properties of NCD films and will be valuable for broadening the applications of NCD films.

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