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The effect of oxygen and nitrogen additives on the growth of nanocrystalline diamond films

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Abstract

Nanocrystalline diamond (NCD) films have been synthesized by using either nitrogen addition or oxygen addition to conventional CH₄/H₂ mixtures besides the most commonly used Ar/CH₄ with or without H₂ chemistry. However, the synthesis of NCD films using both nitrogen and oxygen addition simultaneously into CH₄/H₂ gases has not been reported thus far. In this work, we investigate the effect of simultaneous O₂ and N₂ addition to CH₄/H₂ plasma on the growth of nanocrystalline diamond (NCD) films, focusing particularly on the ratio between the amount of O₂ and N₂ additives into conventional CH₄/H₂ gas mixtures on the morphology, microstructure, texture, and crystalline quality of the NCD films. The NCD samples were produced by using a high microwave power (3 kW) in a microwave plasma-assisted chemical vapour deposition reactor with a maximum power of 5 kW on large silicon wafers, 2 inches in diameter, and characterized by high-resolution scanning electron microscopy, x-ray diffraction and micro-Raman spectroscopy. Our work demonstrates that, under the conditions investigated here, NCD films can be formed when the ratio of O₂/N₂ addition is increased from 0 through 1 up to 7/3 (at higher than 7/3, for example 4, a large-grained polycrystalline diamond film will form), and the crystalline quality is significantly enhanced with the increase of oxygen addition. The mechanism of O₂ and N₂ additives on the formation of NCD films is briefly studied.

1. Introduction

Nanocrystalline diamond (NCD) has received considerable attention recently; this is because NCD possesses high surface smoothness or low surface roughness, low friction coefficient, high hardness, high electron emission efficiency and exceptional chemical inertness due to the small grain size. These unique properties of NCD extraordinarily enhance the applications of diamond in many potential fields, such as use as a protective coating for machining tools for

mechanical applications and as a field electron emitter in cold-cathode flat panel electronic displays for electronic applications.

Inert gas Ar/CH₄ (with or without hydrogen) chemistries have been well developed by the Argonne National group to produce NCD and ultrananocrystalline diamond (UNCD) with fine diamond grains of 3–5 nm in size [1–6]. These are the most commonly used gas mixtures for the synthesis of NCD and UNCD both experimentally [7–12] and theoretically [13]. Alternatively, high CH₄ concentration in H₂ plasma, or CH₄/H₂ gases with a large amount of N₂ addition (more than 1%) using microwave power less than 1.5 kW [14–16], or from 4% to 42% CH₄ in H₂ plasma using 1 kW microwave power with constant 0.1% O₂ addition [17], or 2% CH₄ in H₂ plasma using 550 W microwave power with constant 1% O₂ addition under different substrate temperatures [18], or simply a large amount of N₂ (48 sccm) and a small amount of CH₄ (2 sccm) as reactant gases without additional H₂ [19], have been less explored as methods to fabricate NCD by a few research groups. In general, nitrogen addition tends to degrade the quality of chemical vapour deposition (CVD) diamond films, while oxygen addition may enhance the quality of CVD diamond films. Naturally the following questions arise. What will happen to the growth of CVD diamond films if both nitrogen and oxygen are added simultaneously into CH₄/H₂ mixtures? And how do they influence the gas-phase chemistry and substrate surface chemistry? It is well known that nitrogen and oxygen are readily available since they are the main ingredients of air. However, until recently, no investigations have been conducted on the synthesis of NCD films using both N₂ and O₂ addition to CH₄/H₂ gas mixtures.

In order to answer the above questions, we have tried and succeeded in the deposition of NCD films by using a small amount of N₂ and O₂ addition (their total concentration is kept constant at 0.24%) simultaneously into 4% CH₄/H₂ plasma operating at high power (3 kW) in a 5 kW type microwave plasma-assisted CVD (MPCVD) system. Here, we report this achievement and investigate the ratios between the amount of O₂ and N₂ additives for the formation of NCD films and their influences on the microstructure, grain size, and crystalline quality of the NCD films produced.

2. Experimental details

We produced the NCD films in a 5 kW ASTeX PDS-18 MPCVD reactor. Large (100) silicon wafers of 2 inches in diameter were used as substrates and they were pre-scratched with diamond powder of size 0–0.5 μm to facilitate diamond nucleation. Before each experimental run the vacuum system was pumped down to about 10⁻² Torr for at least several hours by a rotary pump. Then H₂ gas was introduced into the chamber first and it was kept running for about 10 min prior to the deposition process, in order to ensure that traces of residual air were removed from the vacuum chamber. The main controllable growth parameters were microwave power, 3000 W, pressure, 105 Torr, and H₂/CH₄ flow, 400/16 sccm (i.e. 4% CH₄/H₂). Under this set of conditions, the flows of oxygen and nitrogen (unit sccm, with the total flow of oxygen and nitrogen kept constant at 1 sccm, i.e. 0.24%) used for a series of seven samples in total are given in table 1. Among them, three are large-grained polycrystalline diamond (PCD) films, and the remaining four are NCD films. The flows used for O₂ and N₂ for the growth of the four NCD samples from N1 to N4 studied here in detail are 0.0/1.0, 0.2/0.8, 0.5/0.5 and 0.7/0.3, respectively, as listed in table 1. The thickness of the first three NCD samples is around 80 μm, and that of film N4 about 20 μm.

The morphologies, cross-sectional features and grain sizes of the nanocrystalline diamond films were characterized using a high-resolution Hitachi SU-70 scanning electron microscope (SEM) in the Ceramic Department of the University of Aveiro. The crystalline phase and texture of the nanocrystalline diamond films were studied by x-ray diffraction using a Philips

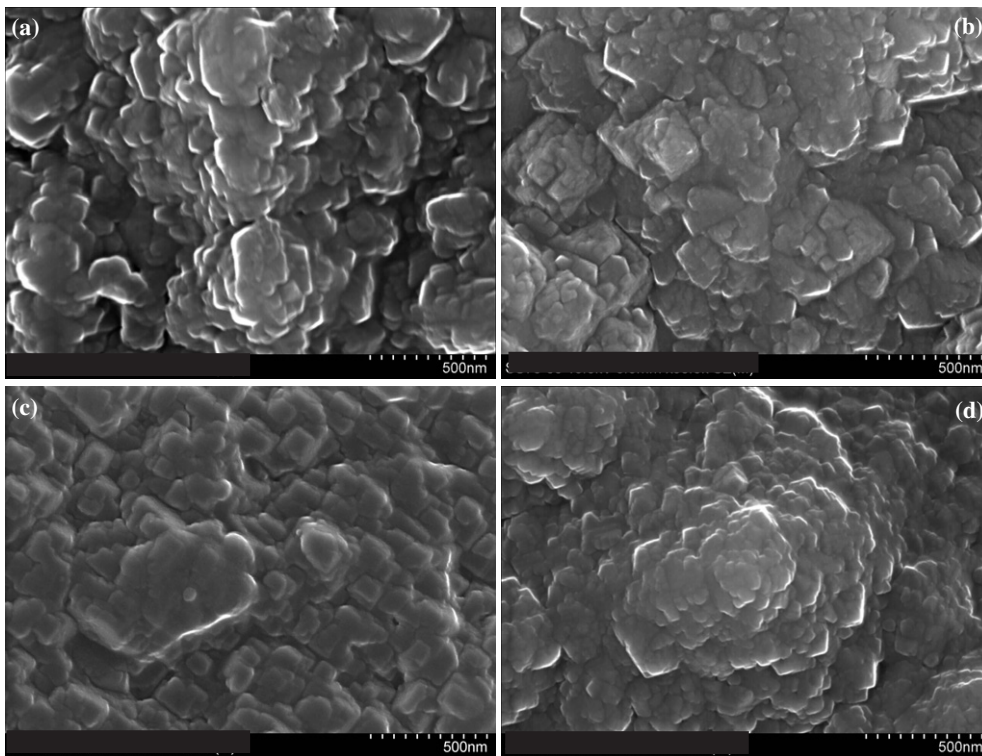


Figure 1. SEM images of the nanocrystalline diamond films: N1 (a), N2 (b), N3 (c), and N4 (d).

Table 1. The flows of oxygen and nitrogen (in sccm) used for the samples involved for this study, along with some characteristics of the samples.

Samples	N ₂	O ₂	Diamond type	FWHM (cm ⁻¹)	Texture
P1	0	0	PCD	6.0	⟨311⟩
P2	0	1.0	PCD	4.8	⟨211⟩ and ⟨311⟩
P3	0.2	0.8	PCD	6.1	⟨311⟩
N4	0.3	0.7	NCD	9.4	⟨110⟩
N3	0.5	0.5	NCD	7.5	⟨100⟩
N2	0.8	0.2	NCD	8.8	⟨110⟩
N1	1.0	0	NCD	13.1	⟨110⟩

X'Pert diffractometer with Cu K α radiation. Micro-Raman spectra of the samples were taken using a Jobin-Yvon Raman spectrometer with a 514.5 nm Ar⁺ laser and a 325 nm He-Cd ultraviolet laser, respectively.

3. Results and discussion

Figure 1 shows the high-resolution SEM micrographs of the four NCD samples N1–N4, which clearly demonstrate the different morphology and microstructure of the samples. These films are composed of large clusters of different irregular shapes. However, the large clusters consist of nanocrystalline grains smaller than 50 nm, commonly observed for all the samples, indicating the nanocrystalline nature of the samples.

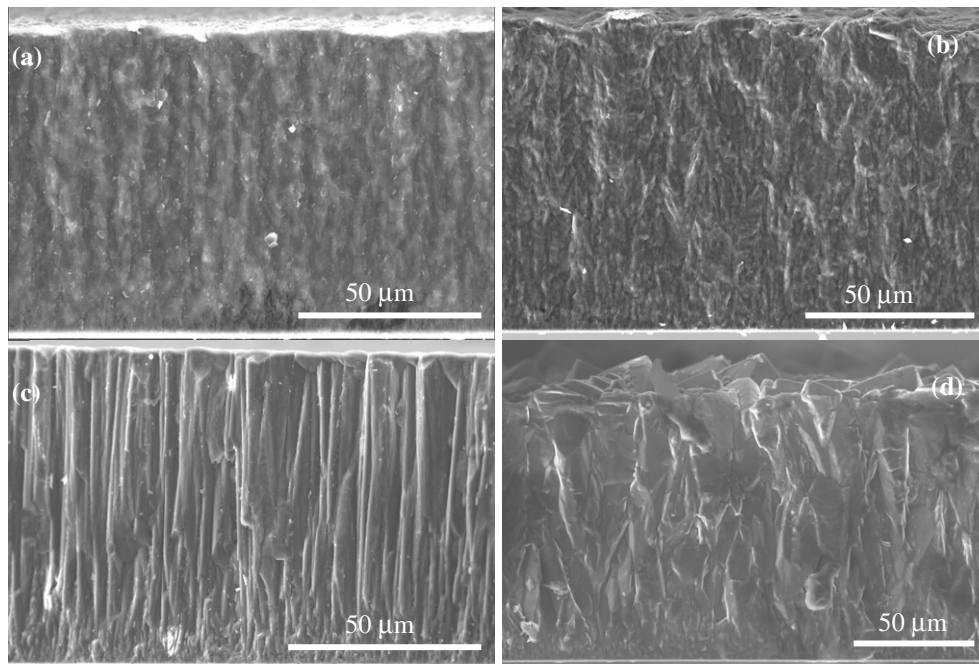


Figure 2. The cross-sectional SEM micrographs of the thick nanocrystalline diamond films: N1 (a), N2 (b), N3 (c), and one large-grained polycrystalline diamond film P3 (d) for comparison.

The cross-sectional SEM micrographs of the three thick nanocrystalline diamond films along with one large-grained polycrystalline diamond (PCD) film P3 for comparison are given in figure 2. We can see clearly that PCD film P3 of 116 μm thickness shows fibre-like near-columnar growth structure and that the grain size increases with film thickness; thus the top surface is rather rough. In stark contrast, NCD films N1 and N2 are still relatively smooth at the top surface, and there is no evidence of a columnar growth structure, although both films are quite thick, about 80 μm , and therefore providing evidence that their grain sizes do not increase with film thickness. It is very interesting to note that NCD film N3 shows a very clear columnar microstructure; however, its top surface is still quite smooth (even smoother than N1 and N2), although it is a very thick film of 76 μm , and the grain size does not increase with film thickness either, although the large clusters may slightly increase their size with thickness. Further study of this sample is under way.

The XRD patterns of the four NCD samples evidence their crystalline diamond nature by clearly showing the diamond diffraction peaks, mainly (111), (220), and (311), with (220) being the strongest in most cases. As an example, a typical XRD pattern of our NCD samples is shown in figure 3. Note that the huge diffraction peak at 69.7° together with the small one at 61.6° come from the (100) silicon substrate. The intensity ratio between the (220) and (111) diamond diffraction peaks is very close to 2, much higher than the value of 1/4 for randomly oriented diamond powder, indicating that a high $\langle 110 \rangle$ texture is formed in our NCD samples except for sample N3, which shows a $\langle 100 \rangle$ texture. The formation of $\langle 110 \rangle$ texture has also been confirmed even in very thin nanocrystalline diamond films of 3–4 μm thickness [20]. Note that $\langle 110 \rangle$ texture is very common in large-grained PCD films and it increases with film thickness due to columnar growth [21].

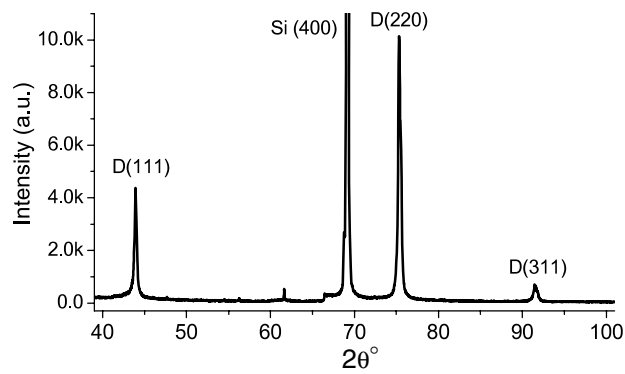


Figure 3. XRD pattern of the nanocrystalline diamond film N1, showing a typical (110) texture.

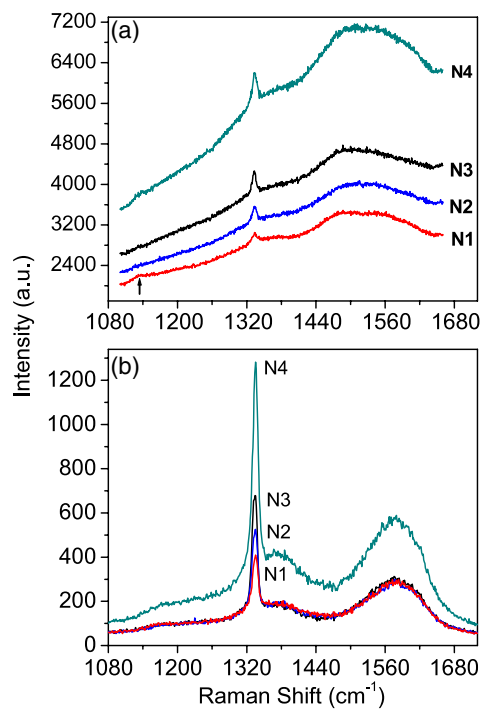


Figure 4. Raman spectra of the four nanocrystalline diamond films: (a) excited by 514.5 nm green Ar^+ laser, (b) excited by 325 nm ultraviolet He-Cd laser.

(This figure is in colour only in the electronic version)

Figure 4 shows the micro-Raman spectra of the NCD samples excited by both a 514.5 nm green Ar^+ laser and an ultraviolet (UV) 325 nm He-Cd laser for comparison of the crystalline quality of the samples. The occurrence of the first-order diamond line around 1333 cm^{-1} in all the Raman spectra apparently proves the diamond nature of these samples, as the XRD patterns do. One can see clearly in figure 4 that the diamond Raman peak gradually becomes stronger and narrower from sample N1 to N4 both in the visible and in the UV Raman spectra.

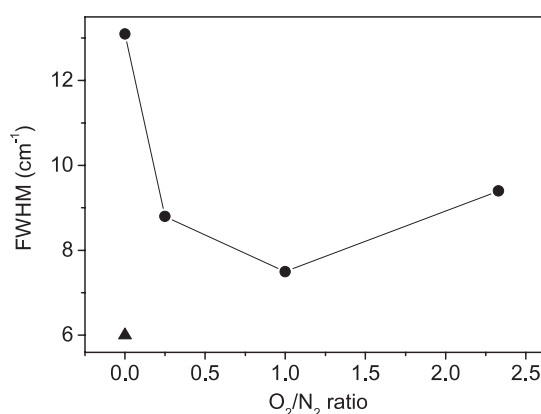


Figure 5. FWHM (cm⁻¹) of the diamond Raman peak in the visible Raman spectra of the nanocrystalline diamond films as a function of their O₂/N₂ ratios. The solid triangle represents the high-quality polycrystalline diamond film grown using CH₄/H₂ plasma only.

For the two NCD films N1 and N4, we observe a weak broad peak at about 1140 cm⁻¹ in the visible Raman spectra (figure 4(a)), which commonly appears in the Raman spectra of NCD and UNCD films deposited either using CH₄/H₂/N₂ gas mixtures [14], or using hydrogen-poor Ar/CH₄ chemistries [7]. So far, there is no consistent agreement on the origin of this peak. It was attributed either to trans-para-acetylene [22], or to trans-polyacetylene in the NCD films [23], or to carbon-hydrogen bonds at the grain boundaries of the UNCD films [24], or from vibration of the surface phonons of diamond [25]. In addition, a broad band centred around 1500 cm⁻¹ in the visible Raman spectra is observed in all the samples. The bands around 1330 and 1580 cm⁻¹ (about 1500 cm⁻¹ in the visible Raman spectra), which are more clearly seen in the UV Raman spectra of the samples (figure 4(b)), are assigned to the D and G band of graphite, respectively [26]. The increasing luminescence background from N1 to N4 in the visible Raman spectra (figure 4(a)) (but absent in the UV Raman spectra) may arise from nitrogen and oxygen impurities incorporated into the NCD films, due to the increase of O₂ addition to the gas phase. EDS (energy disperse spectroscopy) measurements did detect nitrogen and oxygen impurities in the NCD films.

The full width at half maximum (FWHM) of the diamond Raman peak in the visible Raman spectra of the NCD samples is plotted in figure 5 as a function of O₂/N₂ ratio. We can see that the FWHM of the diamond Raman peak decreases rapidly from 13.1 cm⁻¹ for N1 to 7.5 cm⁻¹ for N3, and then increases slightly to 9.4 cm⁻¹ for N4. Note that the FWHM of the diamond Raman peak for a IIa natural single diamond crystal measured under the same conditions is 4.0 cm⁻¹, and that for the PCD film P1 grown using CH₄/H₂ plasma only is 6.0 cm⁻¹. This result indicates that the crystalline quality of the NCD samples is greatly enhanced by increasing the amount of O₂ addition and diminishing the amount of N₂ addition, i.e., increasing the ratio of O₂/N₂ until 7/3, and it reaches the minimum FWHM or highest crystalline quality when the amount of O₂ and N₂ addition is equal. It is worth emphasizing that, beyond 7/3, further increasing the ratio of O₂/N₂ addition (for example, to 4 for sample P3) will result in the development of polycrystalline diamond.

In the following, we briefly analyse the role of nitrogen and oxygen addition on the formation of nanocrystalline diamond films.

First, we discuss this point in view of experimental work.

Our present results demonstrate that a small amount of oxygen addition (0–0.19%) improves the crystalline quality of nanocrystalline diamond films. This is consistent with the effect of oxygen addition on improving the crystalline quality of large-grained polycrystalline diamond films [27]. On increasing the amount of nitrogen addition (0.05%–0.24%), the crystalline quality of nanocrystalline diamond films degrades. Other experimental works have shown that the influence of nitrogen addition to CH₄/H₂ mixtures on diamond growth by CVD techniques strongly depends on the amount of nitrogen addition [28–32]. For example, a trace amount of nitrogen addition can facilitate the formation of {100} textured diamond (N₂ addition from 10 to 200 ppm) [29]; while on increasing the amount of nitrogen addition from several to 1000 ppm, a morphology transition and degradation of the crystalline quality of the polycrystalline diamond films occur [30–32]. In recent years, much higher N₂ concentration from several thousand ppm up to a few per cent has been used to deposit nanocrystalline diamond [14, 15].

Thus, when both oxygen and nitrogen are added into the growth chamber together, the beneficial effect of oxygen addition on diamond crystalline quality will effectively counteract the deleterious effect of nitrogen to some extent. Hence, a critical limit between oxygen and nitrogen additives for the formation of nanocrystalline diamond is encountered, which is the finding of this work: 7/3, under the condition investigated here.

Second, we propose the following growth mechanism of oxygen and nitrogen addition on the formation of NCD films from the point of view of gas-phase chemistry and diamond surface chemistry.

Lombardi *et al* have simulated microwave discharges of H₂ admixed with CH₄ for diamond deposition in a 6 kW MPCVD bell jar reactor with a 5 cm optimal diameter for the process or substrates up to 2 inches in diameter [33], which is comparable to our 5 kW MPCVD system from the point of view of the microwave coupling system. Their work has shown that under very high microwave power density, for example, 30 W cm⁻³ (i.e., 2000 W, 12 000 Pa), with a mixture of 5% CH₄ in H₂, and with the gas temperatures being above 3000 K, very near the substrate, H-atom and CH₃ radicals are the major species: the H-atom density is of the order of 10¹⁶ cm⁻³, the CH₃ density of the order of 10¹³ cm⁻³, and other species like CH₂, C and CH are within one order of magnitude lower than that of the CH₃ species [33]. Gas-phase thermodynamic models for the deposition of NCD by the MPCVD system have explained that the nitrogen-induced nanocrystallinity is caused by forming CN and HCN radicals in the gas phase [15]. Thus, the CH₃ radical, which adds to the diamond surface following hydrogen abstraction by H atoms, is considered as the main growth species in our MPCVD diamond system, regarding the high power and high pressure we used for this work, which is in accord with the general belief for standard diamond CVD. Meanwhile, competitive growth by other C1 (such as CH₂, CH and C) radical species that are present in the gas mixture close to the growing diamond surface, reacting with dangling bonds on the surface, should be considered too, as suggested by May *et al* [13]. Due to N₂ addition, CN and HCN radicals are formed in the gas phase. Because the N atom is close to the C atom in size, these radicals can easily attach to a surface radical site Cd* or a surface biradical site Cd*–Cd*, compared to CH₃ radicals, which have a larger barrier due to steric hindrance. Thus, CN and HCN radicals facilitate the growth of diamond by enhancing the competitive growth by C1 radicals. When the amount of N₂ addition is sufficiently high, secondary nucleation readily occurs: the diamond nuclei cannot grow large, and hence a NCD film is eventually formed.

On the other hand, due to O₂ addition, O₂ dissociates into O atoms and then can react with H atoms and form OH radicals, which can oxidize pyrolytic, non-diamond carbon [34], or may react with some C1 species like C or CH, and N atoms to form CO, NO or NO₂ and thus may reduce the mole fraction of hydrocarbon [35], C atoms and CN radicals to

some extent, or in other words, to cancel the degradation effect of nitrogen addition on the diamond crystalline quality to some extent. Therefore, the crystalline quality of the diamond film formed can be improved through O₂ addition. Further, when the amount of O₂ addition is above a certain value, the effect of O₂ addition will surpass the effect of N₂ addition, and eventually the nuclei will grow increasingly bigger to form a large-grained PCD film instead of a fine-grained nanocrystalline diamond film. For example, our experimental work shows that under the conditions explored here, the critical ratio between O₂ and N₂ for the formation of nanocrystalline diamond is 7/3.

For a deeper understanding of what really happens inside the plasma and on the surface of the substrate using CH₄/H₂/N₂/O₂ mixtures, there is much work which needs to be done by means of plasma diagnostics and plasma simulation.

4. Conclusion

In summary, in this work we developed a new gas composition, i.e., CH₄/H₂/O₂/N₂ gas mixtures, for the deposition of nanocrystalline diamond films. Our work demonstrates that by simply adjusting the small amount of pure O₂ and N₂ gases in a conventional CH₄/H₂ plasma, various large-area uniform nanocrystalline diamond films of different morphology, microstructure, grain size, crystalline quality and texture have been successfully synthesized by using a high power (3 kW) in a 5 kW type MPCVD reactor. Our results show that on increasing the ratio of O₂/N₂ addition from 0 to 1, the crystalline quality of the nanocrystalline diamond films is significantly improved. A critical limit ratio of O₂/N₂ addition (7/3) has been found for the formation of nanocrystalline diamond under the conditions explored here; beyond that a well-faceted diamond will grow. This new chemical path offers a simple way to tailor the growth of large-area uniform nanocrystalline diamond films with various morphology, microstructure, texture, and crystalline quality for different applications.

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