ACS APPLIED NANO MATERIALS

Atmospheric-Pressure Flame Vapor Deposition of Nanocrystalline Diamonds: Implications for Scalable and Cost-Effective Coatings

Adrian Manjarrez, Kai Zhou, Changqiang Chen, Yan-Kai Tzeng, and Lili Cai*

Cite This: ACS Appl. Nano Mater. 2022, 5, 10715–10723



ACCESS	III Metrics & More	E Article Recommendations	s Supporting Information

ABSTRACT: Nanocrystalline diamonds (NCDs) are one of the many carbon allotropes that have attracted great attention for the advancement of many technologies owing to their superior mechanical, thermal, and optical properties. Yet, their synthesis must be improved for availability at low costs and their widespread application. Here, we report the atmospheric-pressure flame vapor deposition (FVD) synthesis of NCD particles and thin films over an area of more than 27 cm² using methane—hydrogen—air flat flames. Synthesis at atmospheric pressure is beneficial as it can lower costs and be more time-efficient when compared to the batch-by-batch synthesis of low-pressure and high-pressure processes. Also, the abundance of methane gas available can further lower costs and improve scalability, while generating lower



flame temperatures to mitigate the need of extensive cooling. Notably, the FVD method unlocks conditions for diamond growth beyond the previously considered diamond-growth region of the C-H-O phase diagram. By modeling the flame radical species as a guidance, we experimentally demonstrate that the FVD growth of NCDs can be facilely controlled by tuning the reactant gas composition, substrate material, and seeding density. Moreover, we show that the addition of an external electric bias was influential in controlling the porosity and thickness of the NCD films. Overall, with the low cost and simplicity for operation without the need of vacuum, this atmospheric-pressure FVD approach will offer opportunities to facilitate the scaling-up of NCD synthesis for applications in optical, tribological, thermal, and biomedical coatings.

KEYWORDS: nanocrystalline diamond, combustion synthesis, flat flame, atmospheric pressure, chemical vapor deposition, methane

1. INTRODUCTION

Nanocrystalline diamond (NCD) particles and films have received widespread interest because they exhibit many exceptional properties at the nanoscale including high hardness, high thermal conductivity, broad optical transparency, high refractive index, chemical inertness, good biocompatibility, versatile surface chemistry, and so forth.^{1–4} Furthermore, NCDs offer several superior properties compared to their bulk and microcrystalline counterparts, such as exhibiting a lower surface roughness which is essential for tribological, optical, and biomedical applications.^{5–7} In addition, it was reported that NCDs show higher mechanical strength for use in protective coatings and microelectrome-chanical systems.^{8–10} Besides, NCD particles and films have large surface areas, which can lead to better performance for electrochemical devices and drug delivery applications.^{11,12}

To fully exploit the promising properties of NCDs for applications in optical, tribological, thermal, and biomedical coatings, it requires scalable and low-cost fabrication processes that can produce them with good control and high quality. To date, the most commonly used techniques for synthesizing NCD particles and films include detonation, high-pressure and high-temperature (HPHT) method, and chemical vapor deposition (CVD).¹³⁻¹⁸ However, these methods involve either high-pressure or low-pressure operations, which impedes the large-scale production of NCDs. Among the synthesis methods, the combustion flame synthesis process has the unparalleled capability to synthesize diamond at atmospheric pressure with high growth rates, lower costs, and simpler operation due to the absence of complex and expensive reactor vessels.

Initial studies of combustion diamond synthesis began in the late 1980s with Hirose first demonstrating diamond growth in oxygen–acetylene flames using a welding torch at atmospheric conditions.¹⁹ This method obtained high growth rates between 100 and 170 μ m/h but had drawbacks including small and non-uniform growth areas and significant amounts of non-

 Received:
 May 10, 2022

 Accepted:
 July 8, 2022

 Published:
 July 21, 2022





diamond carbons. Subsequent attempts implemented flat flame configurations, which significantly improved the uniformity and allowed for growth over larger areas.^{20–22} However, previous work mostly focused on acetylene as the hydrocarbon fuel, which is relatively expensive and has the disadvantage of high flame temperatures (around 3000 °C). The high cost of acetylene represents a substantial fraction of the overall production cost for the combustion synthesis of diamond, which makes it not economically viable for scaling up. The high flame temperature limits the potential substrate materials, and substantial substrate cooling is typically required. To address these issues, more research on alternative hydrocarbon fuels is needed for the combustion flame synthesis of NCDs.

In this work, we report the atmospheric-pressure flame vapor deposition (FVD) of NCDs over large areas of more than 27 cm² using a flat flame burner operating with premixed gases of methane, hydrogen, and air $(CH_4/H_2/air)$. The operation at atmospheric pressure allows for continuous production, which is more time-efficient and cost-effective compared to the batchby-batch synthesis of low-pressure or high-pressure processes. Also, utilizing methane as the hydrocarbon fuel offers the opportunity to lower costs and improve scalability, as methane is inexpensive, abundant, and generates a lower flame temperature. We model the profiles of radical species in $CH_4/H_2/air$ flames to identify the optimal growth conditions. The effects of varying the reactant gas compositions, substrates, and external electric fields are also investigated to control the NCD growth behavior. Significantly, this growth approach allows us to extend diamond synthesis into the previously thought "no growth region" of the C-H-O phase diagram. Our results demonstrate the promise of using atmospheric-pressure CH₄/H₂/air flat flames to fabricate high-quality NCDs in a scalable and cost-effective manner for diverse coating applications.

2. EXPERIMENTAL SECTION

2.1. Substrate Seeding. The substrates were first cleaned by sonication in acetone and methanol, which were then rinsed with deionized water and air dried. After cleaning, the substrates were plasma treated in the Harrick Plasma High Power Expanded Plasma Cleaner for 1 min at medium power to produce a negative surface potential for promoting the adhesion and dispersion of the diamond seed solution on the substrate surface, as the seed solution exhibits a positive zeta potential. Prior to seed coating, the seed solution (0.5 wt % in DSMO, Adámas Nanotechnologies) was cleaned in concentrated H₂SO₄–HNO₃ (9:1, vol/vol) solution at 75 °C for 3 days, followed by separation with centrifugation and extensive rinse with deionized water.²³ The seeding step was conducted by coating the substrates with the seed solution containing 5–10 nm diamond nanoparticles, followed by air drying.

2.2. Nanocrystalline Diamond Synthesis. The growth of NCDs was performed using a McKenna burner operating on premixed gases of CH4, H2, and air, which generated a flat flame at atmospheric pressure in air. Mass flow controllers regulated the gas transport to obtain steady flow rates. The seeded substrate was held horizontally at 2 mm above the burner surface. The growth duration was controlled at 1 h. The gas compositions used for three different growth cases are $CH_4/H_2/air = 0.3:4:6$, $CH_4/H_2/air = 0.75:2.2:6$, and $CH_4/H_2/air = 0.9:1.6:6$, where the ratios correspond to the individual flow rate of each gas in standard liters per minute (SLPM). The corresponding gas flow velocities at the burner surface were calculated to be 6.1, 5.3, and 5 cm/s, respectively. Due to their small magnitudes and close values, the effects of the differing gas velocities on diamond growth were assumed to be negligible when comparing the three conditions. The flame temperatures for $CH_4/H_2/air = 0.3:4:6$, $CH_4/$ $H_2/air = 0.75:2.2:6$, and $CH_4/H_2/air = 0.9:1.6:6$ conditions were

around 800, 760, and 680 $^{\circ}$ C, respectively, as measured by a K-type thermocouple (Omega Engineering) that was placed in the flame at the growth height until the temperature reading stabilized. For samples with an applied external electric field, electrodes were attached to the substrate holder and burner to provide positive or negative biases of 36 and 72 V at the substrate with respect to the burner. A relatively low voltage was used to apply the electric field due to the substrate's close proximity to the burner. All sample parameters can be seen in Table 1.

Table 1. Synthesis Parameters for FVD Nanocrystalline Diamond Growth a

	CH Aave	U flow	Ain florer		
Sample	rate (SLPM)	rate (SLPM)	rate (SLPM)	Substrate material	Substrate bias
Α	0.30	4	6	Si	none
В	0.75	2.2	6	Si	none
С	0.90	1.6	6	Si	none
D	0.75	2.2	6	stainless steel	none
Е	0.75	2.2	6	Si	+36
F	0.75	2.2	6	Si	-36
G	0.75	2.2	6	Si	+72
Н	0.75	2.2	6	Si	-72
^{<i>a</i>} All dian	nond synthes	is experimen	ts were carr	ied out for 1	h.

2.3. Flame Simulation. To determine the optimal flame conditions for diamond growth, Cantera was utilized to model the flame chemistry of a burner-stabilized flat flame at atmospheric pressure with the GRI-Mech 3.0 reaction mechanism and the multi-component transport model. For the simulation, the flow rate of air was kept at a constant value of 6 SLPM, and the H₂ and CH₄ flow rates were varied to obtain the mole fraction values of the principal radicals that are considered to influence the diamond growth, primarily H, O, OH, and C₁ species. The obtained mole fraction values were then plotted on a contour plot.

2.4. Material Characterization. Raman spectroscopy was performed with a 532 nm excitation wavelength on a Horiba LabRAM HR 3D-capable Raman spectroscopy imaging system to confirm the presence of sp^2 - and sp^3 -bonded carbon. Additionally, scanning electron micrographs were taken with a Hitachi S-4800 High Resolution scanning electron microscope (SEM) to determine the size of the diamond particles and study the morphology of the particles and films at the varying CH₄ and H₂ gas ratios. Atomic force microscopy (AFM) was performed with the Asylum Research Cypher to determine the surface roughness and estimate the film thicknesses. Transmission electron microscopy and electron energy loss spectroscopy (EELS) were performed on an FEI Themis Z Advanced Probe Aberration Corrected Analytical TEM/STEM, and Grazing incidence X-ray diffraction (GIXRD) was performed on the Bruker D8 Advance to determine the crystallinity and purity of the diamond samples.

3. RESULTS AND DISCUSSION

The FVD method utilizes high-temperature combustion reactions between fuel and oxidizer to generate various reactive radical species for the deposition of diamonds (Figure 1a,b). In our work, a 6 cm-diameter McKenna premixed flat flame burner shown in Figure 1a,c is employed, which can generate flat flames with radial uniformity for large-area diamond growth. In previous studies, flame synthesis of diamond using methane as the fuel gas was only reported at low pressures, since atmospheric-pressure flat flames are less stable.^{24,25} Here, we demonstrate that the premixed CH₄/H₂/ air flat flame configuration with the addition of H₂ to CH₄ as the fuel and air as the oxidizer could improve the flame stability at atmospheric pressure. Atmospheric operation also provides



Figure 1. (a) Schematic of the flame vapor deposition setup for the NCD synthesis. (b) Schematic of the diamond growth process involving flame radical species at the substrate interface. (c) Photograph of the premixed $CH_4/H_2/air$ flat flame generated by the McKenna burner.

the advantage of higher growth rates and system simplicity without the need for a vacuum chamber. $^{26}\,$

In the diamond growth process, it is widely regarded that carbon-containing radicals are key participants for the formation of sp²- and sp³-bonded carbon, with CH_3 considered to be the dominant species that induces higher diamond growth rates.²⁷⁻³⁰ Moreover, the presence of H, O, and OH radicals are vital in diamond growth as they contribute to the etching of graphitic carbon configurations and assist in stabilizing sp³ bonds.²⁹ On the (100) diamond surface, carbon dimers are made accessible through the abstraction and absorption of atomic hydrogen. Oxygen radicals can assist in the abstraction of absorbed hydrogen atoms and generate active sites on the (100) diamond surface.³¹ The addition of oxygen can also lead to an increase in H and OH species for the removal of non-diamond carbon and reduce the amount of pyrolytic carbon species.³² Therefore, controlling the concentrations of these radical species will have a significant influence on diamond growth.

To determine suitable conditions for diamond growth in premixed $CH_4/H_2/air$ flat flames at atmospheric pressure, we simulated their radical species profiles using chemical kinetics modeling. Figure 2 computes the concentrations of selected

radical species at the height of 2 mm above the burner with different CH₄ and H₂ gas flow rates, while the air flow rate is fixed at 6 standard liter per minute (SLPM). The CH₄ gas flow rate was varied in the range of 0-1 SLPM, and the H₂ gas flow rate was varied between 0 and 10 SLPM. It is seen that the concentrations of CH₃, CH₂, CH₂ and C radicals increase as the CH_4 flow rate increases and the H₂ flow rate decreases. CH₃ has the highest concentration among all the C1 radical species, which reaches its peak concentration with the CH₄ flow rate around 0.75 SLPM and the H₂ flow rate around 1 SLPM. Considerable amounts of H radical are generated at elevated H₂ flow rate. Besides, H, O, and OH radicals obtain their peak concentrations when CH₄ and H₂ are held at flow rates below 0.5 and 2 SLPM, respectively. The modeling of atmospheric-pressure CH₄/H₂/air flat flames suggests that the profiles of radical species can be effectively controlled by varying the reactant gas composition, which could be an important factor that influences diamond growth.

Under the guidance of the modeling results, we attempted FVD diamond growth at three different conditions of CH₄/ H_2/air flat flames to determine the effects of varying the reactant gas composition. The reactant gas flow rates (SLPM) were chosen at $CH_4/H_2/air = 0.3:4:6$, 0.75:2.2:6, and 0.9:1.6:6, and the equivalence ratio was maintained at approximately $\phi = 2$ for each case. With a low seeding density on Si substrates, the formation of diamond nanoparticles was observed for all three flame conditions (Figure 3). Figure 3a shows the representative scanning electron microscopy (SEM) image of a well-faceted, rectangular-shaped particle obtained at the reactant gas composition of $CH_4/H_2/air = 0.3:4:6$. Raman spectrum of the particle in Figure 3b displays a narrow peak centered at the Raman shift of 1332 cm⁻¹ with a full width at half maximum (FWHM) of 5.37 cm^{-1} , matching well with the characteristic Raman peak of sp³-bonded carbon.^{33,34} No peaks near 1345 and 1605 cm⁻¹, corresponding to the D and G bands of sp²-bonded graphitic carbon, respectively, were detected on the measured diamond particles. These characterization results confirmed the high quality of diamond nanoparticle growth that can be achieved using CH₄/H₂/air flat flames.



Figure 2. Simulation of the mole fraction values for carbon-containing (C1) species, H, O, and OH radicals in the $CH_4/H_2/air$ flat flame as a function of varying flow rates of H_2 and CH_4 . The air flow rate was fixed at 6 SLPM.



Figure 3. (a) SEM micrograph of a representative well-faceted diamond particle grown by the FVD method. (b) Raman spectra of the particle growth at different gas ratios. (c-h) SEM micrographs showing the density, size, and morphology for the NCD particle growth at different gas ratios.

As the CH₄ flow rate increased and the H₂ flow rate decreased, it was observed that the average particle size decreased, and the morphology of the particles became more irregular, as shown in Figure 3c-h. The average particle size using the reactant gas ratios of $CH_4/H_2/air = 0.3:4:6$, 0.75:2.2:6, and 0.9:1.6:6 were measured to be 303, 176, and 139 nm, respectively (Table S1). Additionally, the particle density on the substrate was found to increase with the increasing CH₄ flow rate and decreasing H₂ flow rate. This occurrence may be explained by the different radical concentrations at different conditions. The $CH_4/H_2/air =$ 0.3:4:6 case has a higher concentration of atomic hydrogen and lower concentration of carbon-containing radicals. We speculate that the higher concentration of atomic H radical rapidly etches away the diamond seeds, leaving a lower density of nucleation sites for growth to occur. With the lower nucleation density, more carbon-containing radicals like CH₃ can readily react with each available nucleation site, leading to larger particles.

The diamond particle quality at the different growth conditions were evaluated using Raman spectroscopy. For the cases, $CH_4/H_2/air = 0.75:2.2:6$ and 0.9:1.6:6, all of the diamond particles showed a narrow peak centered around 1332 cm⁻¹ with FWHMs of 5.17 and 5.30 cm⁻¹, respectively. No apparent D and G bands, similar to that of the $CH_4/H_2/air = 0.3:4:6$ case, were observed in the Raman spectra of the

diamond particles. However, additional small amounts of nondiamond carbon with Raman peaks centered around 1345 and 1605 cm⁻¹, corresponding to the D and G bands in sp²-bonded graphitic carbon, respectively, were detected in very small regions on the substrate, especially near the areas where the substrate was held (Figure S1).³⁵ The occurrence of sp² carbon particles was slightly higher for the growth utilizing the reactant gas flow rate ratio of $CH_4/H_2/air = 0.9:1.6:6$. In the other two growth cases of $CH_4/H_2/air = 0.3:4:6$ and 0.75:2.2:6, the graphitic carbon particle growth was found to be more sporadic and minimal. This is likely owed to the increased concentration of atomic H radicals, which greatly contributes to the removal of graphitic carbon deposits.

It should be pointed out that Bachmann et al. previously introduced the C–H–O phase diagram to generalize and determine a trend of suitable gas reactant compositions for the major diamond synthesis methods based on experimental results over the years, as the synthesis methods had the commonality of using gas phase ratios composed of carbon, hydrogen, and oxygen.³⁶ By graphing the C, H, and O atom fractions of the gas phase compositions from the experimental works, it was discovered that most diamond growth occurs within a narrow wedge shape along the CO line in the diagram. Growth above the upper boundary was limited to the nondiamond carbon growth, and no carbon growth was typically seen below the lower boundary. Notably, our results reveal new C-H-O compositions, shown in Figure 4, that extends the diamond growth region into the previously thought no-



Figure 4. New C–H–O phase diagram depicting the extended growth region in this work.

carbon-growth region of the C-H-O phase diagram. The C-H–O phase diagram depicts that our diamond synthesis is very oxygen-rich. Bachman et al. also found that diamond growth that occurred closer to the boundary of the no growth region had slower growth rates but higher phase purity, with narrower widths of the sp³ Raman peaks and decreased intensities of the sp² carbon bands due to the larger amounts of O radicals that would more quickly etch away the non-diamond carbons.³⁶ It is likely that this is the reason that our NCD growth reveals sharp diamond Raman lines with narrow widths and negligible graphitic carbon bands. Overall, this demonstrates that the FVD method using atmospheric-pressure CH₄/H₂/air flat flames unlocks new possibilities for high quality diamond synthesis beyond conventional methods. Furthermore, it should be noted that this diagram is simplistic as it only considers the atomic ratios of C, H, and O. Other common growth parameters such as the pressure, temperature, and diluent gasses were not taken into account. More experimentation would be required to determine the impact of these parameters on the phase diagram.

Additionally, FVD growth of NCD thin films was achieved with a higher seeding density on Si substrates. As shown in Figure 5a–c, the film growth was very porous and discrete at $CH_4/H_2/air = 0.3:4:6$. When the CH_4 and H_2 flow rates were increased and decreased, respectively, the surface became less porous and more continuous at $CH_4/H_2/air = 0.75:2.2:6$ and 0.9:1.6:6. The Raman spectra in Figure 5g exhibit sharp peaks at 1332 cm⁻¹ with no apparent sp² carbon peaks. Contrary to the Raman measurements of the particles in Figure 3b, the $CH_4/H_2/air = 0.9:1.6:6$ condition, followed by the $CH_4/H_2/air = 0.75:2.2:6$ condition, showed higher relative intensities than the $CH_4/H_2/air = 0.3:4:6$ condition. Overall, the latter synthesis condition generated films containing more pores, and thus, the sp³ carbon peak intensity was likely smaller due to the smaller volume fraction of sp³ carbon molecules (the same

laser power and integration times were used in all measurements). The film of the $CH_4/H_2/air = 0.9:1.6:6$ growth condition appeared to have the densest grains, resulting in a higher Raman intensity. Meanwhile, the thickness of the films may have also had some contribution to the differing Raman intensity profiles. Raman mapping acquisitions of the films in Figure 5d-f also showed relatively good uniformity of the FWHM of the 1332 cm⁻¹ peak over the scanned area (50 μ m) \times 50 μ m), confirming the growth of high-quality and uniform NCD films. The corresponding sample maps plotted as a function of the peak intensity also show good uniformity (Figure S2). Furthermore, it was observed that the overall FWHM of the $CH_4/H_2/air = 0.9:1.6:6$ condition is slightly higher, compared to the other two conditions, indicating the influence of the gas ratios on the quality of the as-deposited NCD films. Atomic force microscopy (AFM) characterization of the representative NCD thin film grown on the Si substrate at $CH_4/H_2/air = 0.75:2.2:6$ revealed a thickness of approximately 423 nm (Figure S3).

Grazing incidence X-ray diffraction (GIXRD), transmission electron microscopy (TEM), and electron energy loss spectroscopy (EELS) were also performed to determine the crystallinity and purity of the FVD-grown diamond samples for the case involving the gas flow rate ratio of $CH_4/H_2/air =$ 0.3:4:6. The GIXRD scan detected a peak at 43.9° (Figure S4), which corresponds to diamond (111) planes, confirming the crystallinity of FVD-grown diamond thin films.³⁷ The EELS spectrum of the carbon K edge in Figure 5h shows a major σ^* peak centered around 291 eV, which is a characteristic diamond peak arising from the transition of 1s core level electrons to the unoccupied anti-bonding σ^* states for sp³-bonded carbon $(1s \rightarrow \sigma^* \text{ transition})$.^{38–41} The shape of the carbon K-edge fine structure extended beyond 290 eV also resembles the distinct near-edge features of 1s $\rightarrow \sigma^*$ transitions for diamond. Besides, no π^* peak at 285 eV for sp^2 carbon (1s $\rightarrow \pi^*$ transition) was detected, suggesting that the graphitic carbon phase was not present in the sample. Additionally, EELS measurements showed no peak centered near 400 eV from the N-K edge, indicative of negligible N impurities in the sample.^{42,43} Furthermore, from the TEM image in Figure 5i, it is evident that the diamond sample has nanocrystalline structures, consisting of crystallites in the size range of 10-20 nm. The high-resolution TEM images in Figure 5j show clear lattice fringes with the spacing of approximately 0.206 nm, consistent with that of the diamond (111) lattice planes.⁴⁴ The electron diffraction pattern of the NCD lattice by Fast Fourier Transform (FFT) in Figure 5k shows well-defined rings and spots that agree with the (111) and (220) planes of diamond, which confirms the good crystallinity and high purity of the FVD-grown NCD sample.

Next, we investigated the effect of different substrate materials on the growth of NCDs by the FVD process. Synthesis of NCD films was carried out on stainless steel substrates, prepared in the same manner as the Si substrates and using the condition of $CH_4/H_2/air = 0.75:2.2:6$, to compare with that of the Si substrate. Raman spectroscopy characterization of the sample in Figure S5a showed a sharp peak at 1332 cm⁻¹ with a large FWHM of 9.42 cm⁻¹, confirming the successful growth of NCDs. For the growth on Si substrates, the average grain size and roughness (R_a) of NCD films were measured to be 40 and 2.1 nm, respectively (Figure S5b,c). In comparison, the resulting NCD thin films on the stainless steel substrate were found to have sharp-edge



Figure 5. (a-c) SEM micrographs of the NCD films obtained at different gas ratios. (d-f) Raman maps of the NCD films showing the FWHM uniformity of the 1332 cm⁻¹ Raman line. (g) Raman spectra of the NCD films grown at different gas flow rate ratios. (h) EELS spectrum of the carbon-K edge for the FVD-grown NCD sample. (i) TEM image depicting the polycrystalline structure. (j) High-resolution TEM showing the lattice spacing of diamond (111) planes. (k) Corresponding FFT image displaying the electron diffraction pattern of the sample.

grains with a larger grain size of 152 nm and an increased roughness (R_a) of 8.6 nm, as seen in Figure S5d,e. It should be noted that the low roughness values achieved can be applied to create smoother interfaces for optical, tribological, thermal, and biomedical applications. The morphology differences between the growth on Si and stainless steel substrates can be due to the increased surface roughness of the stainless steel

substrate.^{45,46} It was found that increasing the substrate roughness leads to a more faceted growth, whereas smoother substrates produced a rounder, cauliflower-like morphology.

Finally, we demonstrate that the FVD system allows for facile addition of external electric fields to further control the growth of NCD films. It is known that ions are widely present in flames, which are produced by chemi-ionization and a series

Article



Figure 6. Cross-sectional SEM micrographs of the NCD films grown at a gas flow ratio of $CH_4/H_2/air = 0.75:2.2:6$ with applied substrate biases of (a) 0, (b) +36, and (c) -36 V. (d) Corresponding Raman spectra.

of other ion-molecule reactions.^{47,48} In fuel-rich flames, these include positive ions, such as H_3O^+ and $C_nH_x^+$ ($n \ge 1$, $x \ge 0$) and negative ions, such as OH⁻ and $C_n H_x^{-}$ $(n \ge 2, x = 0 -$ 3).^{49,50} Because of the presence of various ion-radical interactions in flames, it is anticipated that an external electric field could influence the diamond growth behavior. As shown in Figure 6a, the unbiased sample grown on the Si substrate had a very porous structure. In contrast, the porous structure of the film was substantially decreased in the growth with a positive bias added to the substrate (Figure 6b) and no pores were evident in the growth performed with a negative substrate bias (Figure 6c). Additionally, it was observed that both biasing cases led to better substrate coverage of the diamond film and there were no significant differences between the grain sizes of the films grown with and without substrate biasing. From the Raman spectra in Figure 6d, it can be seen that the biased and unbiased cases all showed sharp, narrow peaks at 1332 cm⁻¹ signifying their high quality. We speculate that the smoother and denser films achieved with the biased cases can be ascribed to better homogeneity of the flame radicals under the applied electric field that directs the flame radicals to reach the substrate surface with the same incidence. Additional samples with the same gas flow rate ratio were synthesized with larger substrate biases of +72 and -72 V, with respect to the burner, to determine the influence of the substrate bias magnitude. Similar results were seen with no evident pores found in the films, even with the positive substrate bias (Figure S6). Besides, the larger bias also contributed to thicker films than the 0, +32, and -32 V samples. We speculate that the increased electric field between the burner and substrate also provided more energy to increase the rate at which the radicals arrive to the nucleation sites on the substrate, leading to increased growth rates. Nevertheless, more experimentation will be needed in future studies to fully understand the mechanisms governing the diamond growth behavior under electric field-assisted flame conditions.

4. CONCLUSIONS

In summary, we have demonstrated the synthesis of highquality NCD particles and films on Si and stainless-steel substrates in premixed $CH_4/H_2/air$ flat flames at atmospheric

pressure. We have shown that faceted NCD particles with a low seeding density and porous NCD thin films with a high seeding density were achieved at $CH_4/H_2/air = 0.3:4:6$. Increasing the CH₄ flow rate and decreasing the H₂ flow rate were found to not only increase the density and decrease the size for particle growth but also reduce the porosity and enhance the coverage density for the thin film growth. The large concentration of H₂ and O₂ gases contributes to significant removal of sp²-bonded carbon and high-quality growth of NCDs. Notably, the growth conditions applied by the FVD method also provide new points on the C-H-O phase diagram beyond conventional methods to enable diamond growth. Additionally, the lower flame temperature generated by the combustion of methane-hydrogen-air flames can allow for diamond growth on different substrate materials. The substrate material strongly influenced the morphology of the NCD film growth, with stainless steel substrates leading to sharper faceted grains, larger grain sizes, and smooth films but with increased roughness compared to that of the Si substrate. Furthermore, substrate biasing proved beneficial in the FVD growth of smoother, denser, non-porous NCD thin films. Given its simplicity, versatility, and low cost, we believe the atmospheric-pressure FVD approach can open a new pathway for scaling up the production of nanocrystalline diamond particles and thin films for important applications in optical, tribological, thermal, and biomedical coatings.

ASSOCIATED CONTENT

Supporting Information

The Supporting Information is available free of charge at https://pubs.acs.org/doi/10.1021/acsanm.2c02059.

Particle size data table, Raman spectrum of sp² hybridized carbon, AFM height measurements of NCD film growth on Si, Raman spectrum of NCD film growth on stainless steel, SEM and AFM roughness measurements comparing the NCD film growth on Si and stainless steel substrates, and GIXRD pattern of NCD film (PDF)

Corresponding Author

Lili Cai – Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; orcid.org/0000-0003-1222-248X; Email: lilicai@illinois.edu

Authors

- Adrian Manjarrez Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; O orcid.org/0000-0003-4064-2924
- Kai Zhou Department of Mechanical Science and Engineering, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States; o orcid.org/0000-0003-4653-6436
- Changqiang Chen Materials Research Laboratory, University of Illinois at Urbana-Champaign, Urbana, Illinois 61801, United States
- Yan-Kai Tzeng Department of Physics, Stanford University, Stanford, California 94305, United States;
 orcid.org/ 0000-0003-3603-1661

Complete contact information is available at: https://pubs.acs.org/10.1021/acsanm.2c02059

Author Contributions

L.C. conceived and supervised the project. A.M. and K.Z. contributed to experimentation and the synthesis of nanodiamond samples. A.M. performed Raman spectroscopy, AFM and SEM measurements, and corresponding analysis, as well as computational studies for the flame species. K.Z. performed XRD measurements and analysis. C.Q.C. contributed to the TEM/EELS measurements. Y.K.T. prepared the seed solutions. L.C. and A.M. wrote the manuscript. All authors reviewed and commented on the paper.

Funding

This research was financially supported by the startup funds of University of Illinois. L.C. and A.M. gratefully acknowledge support from the National Science Foundation (NSF) through award #1720701.

Notes

The authors declare no competing financial interest.

ACKNOWLEDGMENTS

Scanning electron microscopy, transmission electron microscopy, X-ray diffraction, and atomic force microscopy were carried out in the Materials Research Laboratory Central Research Facilities, University of Illinois.

REFERENCES

(1) Gibson, N.; Shenderova, O.; Luo, T. J. M.; Moseenkov, S.; Bondar, V.; Puzyr, A.; Purtov, K.; Fitzgerald, Z.; Brenner, D. W. Colloidal stability of modified nanodiamond particles. Diamond Relat. Mater. 2009, 18, 620-626.

(2) Amanda, M., Schrand, J. J., Dai, L., Hussain, S. M., John, J., Schlager, L. Z., Yiling, H., Osawa, E. Cytotoxicity and Genotoxicity of Carbon Nanomaterials; Springer, 2008; pp 159-187.

(3) Mochalin, V. N.; Shenderova, O.; Ho, D.; Gogotsi, Y. The properties and applications of nanodiamonds. Nat. Nanotechnol. 2012, 7, 11-23.

(4) Li, L.; Davidson, J.; Lukehart, C. Surface functionalization of nanodiamond particles via atom transfer radical polymerization. Carbon 2006, 44, 2308-2315.

(5) Johnstone, G. E.; Cairns, G. S.; Patton, B. R. Nanodiamonds Enable Adaptive-Optics Enhanced, Super-Resolution, Two-Photon Excitation Microscopy; Royal Society Open Science, 2019; Vol. 6, p 190589.

www.acsanm.org

(6) Hsieh, F. J.; Sotoma, S.; Lin, H. H.; Cheng, C. Y.; Yu, T. Y.; Hsieh, C. L.; Lin, C. H.; Chang, H. C. Bioorthogonal Fluorescent Nanodiamonds for Continuous Long-Term Imaging and Tracking of Membrane Proteins. ACS Appl. Mater. Interfaces 2019, 11, 19774-19781.

(7) Marko, M.; Kyle, J.; Branson, B.; Terrell, E. Tribological Improvements of Dispersed Nanodiamond Additives in Lubricating Mineral Oil. J. Tribol. 2015, 137, 011802.

(8) Liu, S.; Ulugun, B.; DeFlorio, W.; Arcot, Y.; Yegin, Y.; Salazar, K. S.; Castillo, A.; Taylor, T. M.; Cisneros-Zevallos, L.; Akbulut, M. Development of durable and superhydrophobic nanodiamond coating on aluminum surfaces for improved hygiene of food contact surfaces. J. Food Eng. 2021, 298, 110487.

(9) Fu, Y.; Chen, X.; Zhang, B.; Gong, Y.; Zhang, H.; Li, H. Fabrication of nanodiamond reinforced aluminum composite coatings by flame spraying for marine applications. Mater. Today Commun. 2018, 17, 46-52.

(10) Guillén, F. J. H.; Janischowsky, K.; Kusterer, J.; Ebert, W.; Kohn, E. Mechanical characterization and stress engineering of nanocrystalline diamonds films for MEMS applications. Diamond Relat. Mater. 2005, 14, 411-415.

(11) Nagata, A.; Oku, T.; Kikuchi, K.; Suzuki, A.; Yamasaki, Y.; Osawa, E. Fabrication, nanostructures and electronic properties of nanodiamond-based solar cells. Prog. Nat. Sci.: Mater. Int. 2010, 20, 38 - 43

(12) Cheng, X. B.; Zhao, M. Q.; Chen, C.; Pentecost, A.; Maleski, K.; Mathis, T.; Zhang, X. Q.; Zhang, Q.; Jiang, J.; Gogotsi, Y. Nanodiamonds suppress the growth of lithium dendrites. Nat. Commun. 2017, 8, 336.

(13) Haubner, R.; Lindlbauer, A.; Lux, B. Diamond deposition on chromium, cobalt and nickel substrates by microwave plasma chemical vapour deposition. Diamond Relat. Mater. 1993, 2, 1505-1515.

(14) Carrington, W. A.; Hanssen, L. M.; Snail, K. A.; Oakes, D. B.; Butler, J. E. Diamond growth in O2 + C2H4 and O2 + C2H2 flames. Metall. Trans. A 1989, 20, 1282-1284.

(15) Wang, T.; Xin, H. W.; Zhang, Z. M.; Dai, Y. B.; Shen, H. S. The fabrication of nanocrystalline diamond films using hot filament CVD. Diamond Relat. Mater. 2004, 13, 6-13.

(16) Ekimov, E.; Kondrina, K.; Mordvinova, N. E.; Lebedev, O.; Pasternak, D.; Vlasov, I. I. High-Pressure, High-Temperature Synthesis of Nanodiamond from Adamantane. Inorg. Mater. 2019, 55, 437.

(17) Amans, D.; Chenus, A.-C.; Ledoux, G.; Dujardin, C.; Reynaud, C.; Sublemontier, O.; Masenelli-Varlot, K.; Guillois, O. Nanodiamond synthesis by pulsed laser ablation in liquids. Diamond Relat. Mater. 2009, 18, 177-180.

(18) Danilenko, V. V. On the history of the discovery of nanodiamond synthesis. Phys. Solid State 2004, 46, 595-599.

(19) Hirose, Y. Synthesis of Diamond Using a Combustino Flame in the Atmosphere. Science and Technology of New Diamond; Cambridge International Science Publishing, 1990; pp 51-54.

(20) Glumac, N. G.; Goodwin, D. G. Diamond synthesis in a lowpressure flat flame. Thin Solid Films 1992, 212, 122-126.

(21) Murayama, M.; Uchida, K. Synthesis of uniform diamond films by flat flame combustion of acetylene/hydrogen/oxygen mixtures. Combust. Flame 1992, 91, 239-245.

(22) Cooper, J. A., Jr; Yarbrough, W. A. Diamond Optics III; SPIE, 1990; pp 41-54.

(23) Fu, C.-C.; Lee, H.-Y.; Chen, K.; Lim, T.-S.; Wu, H.-Y.; Lin, P.-K.; Wei, P.-K.; Tsao, P.-H.; Chang, H.-C.; Fann, W. Characterization and application of single fluorescent nanodiamonds as cellular biomarkers. Proc. Natl. Acad. Sci. 2007, 104, 727-732.

Article

(24) Kim, J. S.; Cappelli, M. A. Diamond film synthesis in lowpressure premixed methane-oxygen flames. *Appl. Phys. Lett.* **1995**, *67*, 1081–1083.

(25) Glumac, N. G.; Goodwin, D. G. Diamond growth in a novel low pressure flame. *Appl. Phys. Lett.* **1992**, *60*, 2695–2696.

(26) Wolden, C. A.; Davis, R. F.; Sitar, Z.; Prater, J. T. Flat-flame diamond CVD: The effect of pressure and operating conditions for specific applications. *Diamond Relat. Mater.* **1998**, *7*, 133–138.

(27) Harris, S. J. Mechanism for diamond growth from methyl radicals. *Appl. Phys. Lett.* **1990**, *56*, 2298–2300.

(28) May, P. W.; Harvey, J. N.; Smith, J. A.; Mankelevich, Y. A. Reevaluation of the mechanism for ultrananocrystalline diamond deposition from Ar/CH4/H2 gas mixtures. *J. Appl. Phys.* **2006**, *99*, 104907.

(29) Lee, S. S.; Minsek, D. W.; Vestyck, D. J.; Chen, P. Growth of Diamond from Atomic Hydrogen and a Supersonic Free Jet of Methyl Radicals. *Science* **1994**, *263*, 1596–1598.

(30) Meeks, E.; Kee, R. J.; Dandy, D. S.; Coltrin, M. E. Computational simulation of diamond chemical vapor deposition in premixed C2H2/O2/H2 and CH4O2-strained flames. *Combust. Flame* **1993**, *92*, 144–160.

(31) Sun, B.; Zhang, X.; Zhang, Q.; Lin, Z. Effect of atomic hydrogen and oxygen on diamond growth. J. Appl. Phys. **1993**, 73, 4614–4617.

(32) Harris, S. J.; Weiner, A. M. Effects of oxygen on diamond growth. *Appl. Phys. Lett.* **1989**, 55, 2179–2181.

(33) Yoshikawa, M.; Mori, Y.; Maegawa, M.; Katagiri, G.; Ishida, H.; Ishitani, A. Raman scattering from diamond particles. *Appl. Phys. Lett.* **1993**, *62*, 3114–3116.

(34) Solin, S. A.; Ramdas, A. K. Raman Spectrum of Diamond. *Phys. Rev. B* 1970, *1*, 1687–1698.

(35) Ferrari, A. C.; Basko, D. M. Raman spectroscopy as a versatile tool for studying the properties of graphene. *Nat. Nanotechnol.* **2013**, *8*, 235–246.

(36) Bachmann, P. K.; Leers, D.; Lydtin, H. Towards a general concept of diamond chemical vapour deposition. *Diamond Relat. Mater.* **1991**, *1*, 1–12.

(37) Tu, R.; Xu, T.; Li, D.; Zhang, S.; Yang, M.; Li, Q.; Zhang, L.; Shimada, T.; Goto, T.; Shi, J. Morphology and mechanical behavior of diamond films fabricated by IH-MPCVD. *RSC Adv.* **2018**, *8*, 16061–16068.

(38) Hamon, A.-L.; Verbeeck, J.; Schryvers, D.; Benedikt, J.; Sanden, M. C. M. ELNES study of carbon K-edge spectra of plasma deposited carbon films. *J. Mater. Chem.* **2004**, *14*, 2030–2035.

(39) Roddatis, V. V.; Kuznetsov, V. L.; Butenko, Y. V.; Su, D. S.; Schlögl, R. Transformation of diamond nanoparticles into carbon onions under electron irradiation. *Phys. Chem. Chem. Phys.* **2002**, *4*, 1964–1967.

(40) Qian, F.; Singh, R. K.; Dutta, S.; Pronko, P. P.; Weber, W. H. Femtosecond Laser Deposition of Diamond-Like Carbon Films. *MRS Proc.* **1995**, 397, 297.

(41) Feng, Z.; Lin, Y.; Tian, C.; Hu, H.; Su, D. Combined study of the ground and excited states in the transformation of nanodiamonds into carbon onions by electron energy-loss spectroscopy. *Sci. Rep.* **2019**, *9*, 3784.

(42) Pichot, V.; Stephan, O.; Comet, M.; Fousson, E.; Mory, J.; March, K.; Spitzer, D. High Nitrogen Doping of Detonation Nanodiamonds. J. Phys. Chem. C **2010**, 114, 10082–10087.

(43) Vlasov, I. I.; Shenderova, O.; Turner, S.; Lebedev, O. I.; Basov, A. A.; Sildos, I.; Rähn, M.; Shiryaev, A. A.; Van Tendeloo, G. Nitrogen and luminescent nitrogen-vacancy defects in detonation nanodiamond. *Small* **2010**, *6*, 687–694.

(44) Tzeng, Y.-K.; Zhang, J. L.; Lu, H.; Ishiwata, H.; Dahl, J.; Carlson, R. M. K.; Yan, H.; Schreiner, P. R.; Vučković, J.; Shen, Z.-X.; Melosh, N.; Chu, S. Vertical-Substrate MPCVD Epitaxial Nanodiamond Growth. *Nano Lett.* **2017**, *17*, 1489–1495.

(45) Ellis, P. J.; Buhaenko, D. S.; Stoner, B. R. Some effects of silicon substrate roughness on the growth of highly oriented $\langle 100 \rangle$ diamond films. *Diamond Relat. Mater.* **1995**, *4*, 406–409.

(46) Mallik, A.; Binu, S. R.; Satapathy, L.; Narayana, C.; Seikh, M.; Shivashankar, S.; Biswas, S. K. Effect of substrate roughness on growth of diamond by hot filament CVD. *Bull. Mater. Sci.* **2010**, *33*, 251.

(47) Chen, B.; Wang, H.; Wang, Z.; Han, J.; Alquaity, A. B. S.; Wang, H.; Hansen, N.; Sarathy, S. M. Ion chemistry in premixed rich methane flames. *Combust. Flame* **2019**, *202*, 208–218.

(48) Axford, S. D. T.; Hayhurst, A. N. Mass spectrometric sampling of negative ions from flames of hydrogen and oxygen: the kinetics of electron attachment and detachment in hot mixtures of H_2O , O_2 , OH and HO_2 . *Proc. R. Soc. London, Ser. A* **1996**, 452, 1007–1033.

(49) Goodings, J. M.; Bohme, D. K.; Ng, C.-W. Detailed ion chemistry in methane—oxygen flames. II. Negative ions. *Combust. Flame* **1979**, *36*, 45–62.

(50) Goodings, J. M.; Bohme, D. K.; Ng, C.-W. Detailed ion chemistry in methane—oxygen flames. I. Positive ions. *Combust. Flame* **1979**, *36*, 27–43.

Recommended by ACS

Mesoporous Carbon Nitride with π -Electron-Rich Domains and Polarizable Hydroxyls Fabricated via Solution Thermal Shock for Visible-Light Photocatalysis

Zhimin Zhai, Hongbin Lu, et al. NOVEMBER 30, 2022 ACS NANO

READ 🗹

Nanoporous TiCN with High Specific Surface Area for Enhanced Hydrogen Evolution Reaction

Harpreet Singh Gujral, Ajayan Vinu, *et al.* APRIL 12, 2022 ACS APPLIED NANO MATERIALS

	F A		
к	FF	AL J	-
	- '	~	_

Chemical Cutting of Network Nodes in Polymeric Carbon Nitride for Enhanced Visible-Light Photocatalytic Hydrogen Generation

Xin Bai, Yongping Zhang, et al. DECEMBER 29, 2021 ACS APPLIED NANO MATERIALS

READ 🗹

RFAD

Porous and Few-Layer Carbon Nitride Nanosheets via Surface Steam Etching for Enhanced Photodegradation Activity

Baihua Long, Sugang Meng, *et al.* MAY 24, 2022 ACS APPLIED NANO MATERIALS

Get More Suggestions >