Effects of laser photolysis of hydrocarbons at 193 and 248 nm on chemical vapor deposition of diamond films

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Abstract: In this work, the influence of ultraviolet (UV) laser photolysis of hydrocarbons on combustion chemical vapor deposition of diamond films was investigated at 193 and 248 nm. Although the output fluence of the 193 nm laser was one order of magnitude lower than that of the 248 nm laser, UV laser irradiations at 193 and 248 nm led to similar enhancement of diamond growth: a twofold increase in the diamond deposition rate and a 3% increase in diamond quality compared to those obtained without laser irradiation. *In situ* thermionic measurement of emission currents revealed that the diamond nucleation time was reduced from 9.5 min without laser irradiation to 4.2 and 7.0 min, respectively, with UV laser irradiations at 193 and 248 nm. These results suggest the advantages of using UV laser photolysis in diamond deposition achieved by suppressing nondiamond carbon accumulation. Spectroscopic investigation of the flame chemistry showed that UV laser irradiations of the diamond-forming combustion flames led to photo-

generated reactive species, OH, CH, and C₂, which play critical roles in diamond growth. The more pronounced flame chemistry change and diamond growth enhancement with UV laser irradiation at 193 nm than 248 nm is attributed to a higher photon energy, 6.4 eV, which is above the energetic dissociation threshold of most hydrocarbons for more efficient photodissociation.

Introduction

Diamond has been referred as “the ultimate engineering material” for a wide range of applications which is attributed to its exceptional thermal, optical, mechanical, and electronic properties.¹ Chemical vapor deposition (CVD) of diamonds at low pressure has been extensively studied over the past decades due to its numerous advantages, including low cost, high growth rate, and high diamond quality.^{2,3} All CVD methods, including plasma, hot-filament, and combustion-flame CVD, involve a number of chemical reactions of hydrocarbon precursors near thermal equilibrium,⁴⁻⁷ where a lack of selectivity among different reaction channels take place, towards products or desired products.

With the significant advances in laser technology, lasers provide a unique means for efficient dissociation of precursors or radicals by exciting specific transitions (electronic, vibrational, rotational) in reactant molecules, enabling reaction control to some extent.⁸⁻¹⁰ Laser chemistry has long been explored as a means of seeking chemical control of molecular reactions.¹¹⁻¹⁵ Zare and co-workers demonstrated vibration control of an isotopic variant of water, HOD, to influence outcome through selective bond cleavage with wavelength-matched infrared (IR) laser irradiation.¹⁶ Ding and co-workers showed that ultraviolet (UV) photolysis of glyoxal, (CHO)₂, proceeded through different pathways depending on the photolysis wavelength, subsequently leading to different products.¹⁷ Laser assisted CVD (LCVD) opens up new possibilities in thin-film deposition and enables one to study new reaction pathways, which has been employed to fabricate different types of microstructure and to grow various thin films, including metal (W, Al, Cu, etc.)¹⁸⁻²⁰ semiconductor (Si, Ge, GaAs, etc.),²¹⁻²³ and insulator (Al₂O₃, SiO₂, etc.).²⁴

In previous works, the potential of laser chemistry was extended from the study of molecular reactions to practical material synthesis and significant enhancement in diamond growth by

introducing infrared (IR) and UV laser irradiations in combustion diamond CVD was achieved.^{25–}

²⁹ In particular, we found that UV photolysis of hydrocarbons effectively suppressed the nondiamond carbon formation in diamond growth.³⁰ The photodissociation channels and quantum yields are known to be wavelength dependent. Understanding how UV laser photolysis at different wavelengths affects diamond growth not only advances the knowledge of the roles of photodissociation in material synthesis but also expands the process compatibility to a broad range of materials.

In this work, a comparative study of diamond growth using combustion CVD assisted by UV laser irradiations at two laser wavelengths, 193 and 248 nm, was performed. A more pronounced influence on the diamond growth process and the flame chemistry was found with UV laser irradiation at the shorter laser wavelength of 193 nm. With one order lower laser fluence at 193 nm than 248 nm, UV laser irradiations at both wavelengths resulted in similar increments in the deposition rate and improvement in diamond quality, suggesting the effectiveness of a short wavelength. The *in situ* study of the nucleation process demonstrated that the nucleation time was shorter with UV laser irradiation at 193 nm, indicating a more significant suppression of nondiamond carbon formation. Optical emission spectroscopy (OES) was used to reveal how UV laser irradiations at different wavelengths affect the flame chemistry. It was found that UV laser irradiations altered the flame chemistry to produce key radicals, leading to the enhancement in diamond growth. Possible light-molecule interaction mechanisms and photodissociation pathways were considered for UV laser irradiations at 193 and 248 nm.

Experimental Section

A schematic diagram of the UV-laser-assisted combustion CVD setup is shown in **Figure 1**. The combustion flame was generated from a mixture of ethylene (C₂H₄), acetylene (C₂H₂), and oxygen

(O₂). Tungsten carbide (WC) plates with dimensions of 12.5×12.5×1.6 mm³ and 6 wt. % cobalt were used as substrates. The substrates with water cooling were placed on a three dimensional (3D) moving stage. The temperature of the substrate was monitored to be around 1053 K and measured with a noncontact pyrometer (OS3752, OMEGA Engineering, Inc.). The distance between the inert cone and the substrate was fixed at 0.8 mm. A krypton fluoride (KrF) excimer laser (Lambda Physik[®], COMPex[®] 205, 248 nm, 20 ns) and an argon fluoride (ArF) excimer laser (Lambda Physik[®], COMPex[®] 205, 193 nm, 15 ns) were used separately as the UV irradiation source to study how the laser wavelength affects diamond growth. A UV convex lens with a focal length of 25 cm was used to focus the laser beam from 24 × 10 mm² to 7 × 4 mm² to cover the whole combustion flame. The ArF excimer laser beam was enclosed in a nitrogen (N₂)-filled path to reduce its air absorption before it reached the combustion flame. Laser powers were measured using a power meter. The laser frequency was 35 Hz. The laser fluence was calculated by dividing the laser power by the laser spot area. The laser fluence was tuned from 600 to 900 mJ/cm² and from 10 to 25 mJ/cm² for the 248 and 193 nm lasers, respectively. The low laser fluence output of the 193 nm laser was due to a significant absorption of the laser energy by air, although most of the beam was enclosed in the N₂-filled path to avoid the air absorption.

Optical emission spectroscopy of the combustion flame was performed using an optical spectrometer (Andor Technology, 3 gratings: 150, 600, and 2400 l/mm; range: 190-800 nm). A detailed illustration of the OES setup is shown in **Figure S1**. The spectrometer was equipped with an intensified charge-coupled device (ICDD). The laser and the spectrometer were synchronized through a digital delay generator (Stanford Research Systems DG 535, 5 ps delay resolution). Data acquisition parameters were fixed for all experiments with a gate delay of 0 μs, gate width of 10 μs, gratings of 250 lines/mm, and a laser frequency of 35 Hz. Spectra and optical images were

taken with a horizontal slit width of 50 μm and 2500 μm , respectively. All optical images and spectra consisted of the accumulation of 500 laser pulses. A background spectrum was subtracted from all spectra. The high-resolution spectra for rotational temperature measurements were collected with a horizontal slit width of 5 μm centered at the primary flame using a grating of 2400 lines/mm.

Figure 1. Schematic illustration of the UV-laser-assisted combustion CVD setup and light-molecule interaction mechanisms of UV laser irradiations at different wavelengths.

The nucleation process was studied by *in situ* measuring the field-enhanced thermionic emission current from the diamond nuclei during diamond growth. The bias voltage on the substrate was -5 V with respect to the flame torch. The current between the substrate and the torch was measured by a nanoampere meter. Scanning electron microscopy (SEM; XL-30, Philips Electronics) was used to characterize the surface morphologies and cross-sectional microstructures of the diamond

films. The diamond film thickness was measured using a 3D optical profiler (ZYGO NewView™ 8300). The deposition rate was calculated by dividing the film thickness by the deposition time. A micro-Raman spectrometer (inVia™, Renishaw) was used to evaluate the diamond quality. An Ar⁺ion laser was used as an excitation source with a wavelength of 514.5 nm and a power of 50 mW. The beam was focused to a spot of approximately 5 μm using a 20× objective lens.

Results and Discussion

To identify how UV laser irradiations at different wavelengths affect diamond growth, diamond films were prepared under UV laser irradiations at 193 and 248 nm, respectively. **Figure 2(a)** shows the SEM micrographs of the surface morphologies of the diamond films after 1 hr of deposition. The diamond film deposited without laser irradiation consisted of randomly oriented diamond crystals with an average size of 2.5 μm. It was noticed that UV laser irradiations did not change the diamond grain shape but resulted in an obvious increase in the grain size. The average diamond grain size increased with respect to the laser fluence at both wavelengths, 193 nm and 248 nm, reaching 5 μm at a laser fluence of 25 mJ/cm² for the 193 nm laser and 3.5 μm at a laser fluence of 900 mJ/cm² for the 248 nm laser, respectively.

The surface profiles of the diamond films are shown in **Figure S2**, and the deposition rate was plotted as a function of the laser fluence in **Figure 2(b)**. The diamond film prepared without UV laser irradiation had a deposition rate of 5 μm/h. With UV laser irradiations, the deposition rates increased to 11 μm/h at a laser fluence of 25 mJ/cm² for the 193 nm laser and 10.3 μm/h at a laser fluence of 900 mJ/cm² for the 248 nm laser. In addition, the diamond film quality was evaluated by Raman spectroscopy. All Raman spectra were constituted with a diamond peak at 1332 cm⁻¹ and two bands at 1370 (D-band) and 1500 cm⁻¹ (G-band), which represent graphitic carbon, as shown in **Figure S3**. The diamond quality was evaluated from the Raman spectra by calculating

the quality factor using the equation, $Q_i = I_{\text{diamond}} / (I_{\text{diamond}} + I_{\text{a-carbon}} / 233)$, where, I_{diamond} and $I_{\text{a-carbon}}$ are the integrated intensities of the diamond peak and the sum of the integrated intensities of the nondiamond carbon bands, respectively.³¹ **Figure 2(c)** shows the quality factors plotted as a function of the laser fluence for the 193 nm and the 248 nm lasers. The diamond quality factor increased with respect to the laser fluence. The quality factor was 93.2% without laser irradiation and reached 96.5% and 95.5% with UV laser irradiations at a laser fluence of 25 mJ/cm² for the 193 nm laser and at a laser fluence of 900 mJ/cm² for the 248 nm laser, respectively.

Figure 2. (a) SEM micrographs of surface morphologies of the diamond films prepared for 1 hr deposition under 193 or 248 nm laser irradiation at different laser fluences; (b) growth rates and

(c) quality factors of the diamond films plotted as functions of the laser fluence: black solid squares and red solid triangles are for the 193 nm and 248 nm lasers, respectively.

It is worthy to note that the laser fluence had a linear influence on the growth rate and the quality factor at 248 nm, but a super-linear influence at 193 nm. A larger grain size, a higher deposition rate, and a higher diamond quality factor were obtained with UV laser irradiation at 193 nm than those obtained at 248 nm, although the laser fluence of the 193 nm laser was one order of magnitude lower than that of the 248 nm laser. The results suggest the advantage of a short laser wavelength from the irradiating laser source in promoting the diamond growth.

During the CVD process, diamond films grow with a columnar microstructure where the lateral grain size increases as the films become thicker.³² To further understand the effects of UV laser wavelength on the lateral grain evolution, the cross-sectional microstructures of the diamond films were studied using SEM as shown in **Figure S4**. Diamond films prepared with UV laser irradiations exhibited faster lateral grain size evolution than those without laser irradiations. However, the effect of the UV wavelength on the lateral grain size evolution was not obvious. The fast lateral grain size evolution indicates that the UV laser irradiation effectively suppressed secondary nucleation, which is known to impede the expanded growth of diamond grains. Secondary nucleation occurs when nondiamond carbon accumulates as the diamond nuclei grow. The original crystal growth direction is then altered, or even stopped; and a new nucleation site starts on the original nuclei.³³ The fast lateral grain size evolution observed in the diamond films prepared with UV lasers irradiations indicate that nondiamond carbon formation was suppressed efficiently during diamond growth.

Figure 3. (a) Thermionic current curves *in situ* measured during the diamond growth without and with 193 nm or 248 nm laser irradiation at different laser fluences, (b) the nucleation time plotted as a function of the laser fluence under 193 nm or 248 nm laser irradiations, (c) SEM images of surface morphologies of the 10-min diamond films prepared without and with 193 nm or 248 nm UV laser irradiations at different laser fluences.

Suppression of nondiamond carbon formation by UV laser irradiation is indicated based on the study of lateral grain size evolution through diamond film thickness. Nucleation is sensitive to nondiamond carbon formation because the initial diamond nucleus is believed to nucleate from an amorphous carbon layer which forms during the incubation stage. To further confirm the suppression effects of nondiamond carbon formation by UV laser irradiation, the diamond nucleation was monitored by *in situ* measurement of the field-enhanced thermionic current during diamond growth under UV laser irradiations at 193 nm and 248 nm. The setup for the thermionic emission current measurement is described in **Figure S5**. Three distinct regions were identified as the incubation, nucleation, and growth stages from the thermionic emission current curves, as shown in **Figure 3(a)**. The nucleation time was retrieved and plotted as a function of the laser fluence for the 193 nm and 248 nm laser irradiations in **Figure 3(b)**. Compared with a long nucleation time of 9.5 min without laser irradiation, UV laser irradiations reduced the nucleation time to 4.2 and 7.0 min for the 193 nm and 248 nm lasers, respectively, as shown in **Figure 3(b)**. Similar to the variation trend of growth rate and diamond quality, the nucleation time decreased linearly with respect to the laser fluence at 248 nm, but exhibited a super-linear relation with the laser fluence at 193 nm, which suggests that laser with a shorter wavelength influenced the diamond growth more efficiently.

A much shorter nucleation time with 193 nm laser irradiation compared to 248 nm laser irradiation suggests that the 193 nm laser irradiation affected the diamond growth in the initial nucleation in a more efficient way, suppressing nondiamond carbon formation. To confirm the suppressing effects of UV laser irradiation on amorphous graphitic carbon accumulation, the diamond nucleation process was further investigated by preparing diamond films for a short time, i.e., 10 min. The surface morphologies of the 10-min diamond films prepared at 193 nm and 248 nm are

shown in **Figure 3(c)**. Nanocrystalline diamond films were obtained without laser irradiation while UV laser irradiation transformed the nanodiamond feature to a larger faceted microcrystal structure. The influence was more significantly observed in the diamond films prepared at 193 nm.

An increase in the deposition rate, improvement in diamond quality, fast lateral grain size evolution, and significantly reduced nucleation time with the UV laser irradiation of the diamond-forming combustion flame have been identified in the diamond growth process. Irradiation at the short wavelength of 193 nm was found to affect the diamond growth process in a more pronounced way. Material synthesis by CVD is highly sensitive to the gas phase chemistry change.^{9,15} To reveal the effects of UV laser irradiation on diamond growth, the flame chemistry was studied under laser irradiations at 193 nm and 248 nm using OES. As shown in **Figure 4(a)**, the ICCD gate time of the spectrometer and the laser pulses were synchronized to acquire OES signals at the beginning of each laser pulse with a 0 μ s gate delay for a gate width of 10 μ s.

Figure 4. (a) Time relationship between the synchronized ICCD gate of the spectrometer and the laser pulses for the OES measurements, (b) flame images with and without the filters under laser irradiation, (c) flame temperature (K) vs. 193 nm laser fluence (mJ/cm²) and 248 nm laser fluence (mJ/cm²).

different laser irradiation conditions, and (c) plots of the flame temperatures as functions of the laser fluence.

Three species were identified in the OES spectra (**Figure S6**): diatomic carbon (C_2), methylidyne radical (CH), and hydroxyl radical (OH).⁵ It was found that the emission intensities of all species increased with respect to the laser fluence. To visualize the two-dimensional (2D) distribution of the excited species within the flame, images were collected with and without the UV laser irradiations at 193 and 248 nm, as shown in **Figure 4(b)**. False colors were used to indicate the emission intensities and scaled under the same scale range, representing the excited species abundance. The flame under the UV laser irradiation was much brighter than the flame without laser irradiation; and the brightness increased as the laser fluence increased, suggesting that more species were generated with the laser excitation. Three band-pass filters were placed in the optical path to distinguish the emission bands of the following individual excited species: C_2 , CH, and OH. More enhanced emission intensities were identified with the 193 nm laser irradiation than were identified with the 248 nm irradiation, suggesting an increase in the amounts of all observed emissive species. It is worth mentioning that the laser fluence of the 193 nm laser is about 40 times lower than that of the 248 nm laser. The larger the laser fluence is, the higher the photo flux is, which means that the UV-laser-induced yield of the excited species per photon was much higher with the 193 nm laser irradiation than it was with the 248 nm laser irradiation.

Optical images show an increase of OH, CH, and C_2 abundance with UV laser irradiations. All three species were reported to positively influence the diamond growth. The OH radical functions as carbon etchant by etching the surface-bond hydrogen and stabilizing the sp^3 hybridized surface carbon bonds.³⁴ The CH radical was believed to be helpful in diamond growth.³⁵ The addition of a C_2 to a hydrogen-terminated diamond (110) surface is energetically favorable and makes the

growth of the existing crystal proceeds readily.^{36,37} The increments of all three radicals explain why both growth rate and crystal quality were improved in the UV-laser-assisted combustion deposition of diamond films. To determine how the species were generated by UV laser irradiations, the flame temperatures were estimated for both laser wavelengths at different fluences. Due to a strong coupling between the translational and rotational energy states of the molecules, the flame temperature was approximated by the rotational temperature derived from high-resolution rotational line emission intensities of CH using the Boltzmann plot.³⁸ The detailed measurement and deduction procedure is illustrated in **Figure S7**. The flame temperatures with the UV laser irradiations at 193 nm (black square curve) and 248 nm (red triangle curve) were plotted as functions of the laser fluence, respectively, as shown in **Figure 4(c)**. The flame temperatures fluctuated around 2450 K with an error of ± 40 K, showing weak dependence upon the laser fluence and wavelength. The fact that UV laser irradiation does not elevate the flame temperature suggests that the UV-laser-induced generation of the excited species is nonthermal.

The 2D flame images provide a general overview of species distribution and their abundance. To qualitatively compare the effects of the UV laser irradiations at 193 and 248 nm on the change in species abundance, emission peak intensities assigned to each species were integrated and plotted as functions of the laser fluence in **Figures 5 (a)-(c)**. Although accompanied by large error bars due to the low peak intensity of OH, increases of OH with respect to the laser fluence at both 193 and 248 nm were observed. Interestingly, it was found that the increasing curves of CH and C₂, with respect to the laser fluence at 248 nm, were well fitted linearly, while they were exponentially fitted in the case of laser fluence at 193 nm. This well matches the relations of growth rate, quality factor, nucleation time with respect to the laser fluence. Different fitting strategies imply different mechanisms governing the photo-induced generation of these species at 193 and 248 nm. As

mentioned previously, the laser fluence of the 193 nm laser was 40 times less than that of the 248 nm laser. By retrieving the slopes of the integrated intensity curves with respect to laser fluence, it was found that 193 nm laser irradiation led to approximately a two orders of magnitude higher increment rate of integrated peak intensity for all species, as shown in **Figure 5(d)**, confirming that the 193 nm laser is much more efficient in changing the flame chemistry than the 248 nm laser.

Figure 5. Integrated intensities of emission peaks assigned to species, (a) OH, (b) CH, and (c) C₂, plotted as functions of the laser fluence at 193 and 248 nm, respectively, (d) slopes retrieved from the peak integration curves for the 193 nm and 248 nm lasers.

Chemical changes occur when the molecules are raised to an excited state possessing more than sufficient energy to break the weakest bond in the molecules. Electronic excitations or direct photolysis of simple molecules occur by absorbing photons in the UV regions, in which the primary products are generally in either electronically excited molecules or their dissociation products, i.e., reactive species. The photochemical process can be very specific, depending on the region of absorption. The advantages of a short laser wavelength, 193 nm, in modifying the flame chemistry over a wavelength of 248 nm were identified, indicating that high photon energy was more efficient in photodissociations of hydrocarbons in the combustion flames. To determine the photodissociation pathways of the two hydrocarbon precursors, C₂H₂ and C₂H₄, upon absorbing photons with different photon energies, their energies and photochemical behaviors were carefully examined. The C-H bonding energy of C₂H₂ and C₂H₄ was 5.38 and 4.81 eV, respectively. The 193 nm photodissociation of C₂H₂ and C₂H₄ was extensively studied.^{39–41} The 193 nm photodissociation of C₂H₂ proceeded through two steps, as illustrated in **Figure 6(a)**. By absorbing one 193 nm photon, a C₂H₂ molecule was excited to the ¹A_u *trans-bent* excited state following by the primary dissociation process:⁴¹

The early emission studies by McDonald, Baronavski, and Donnelly showed that at high laser intensities,⁴² two-photon photodissociation channels open up and proceed via sequential elimination of H atoms:

Figure 6. Possible photolysis mechanisms of hydrocarbon precursors: (a) C_2H_2 and (b) C_2H_4 .

Emissions from both C_2 (swan band) and CH (A-X) were detected in their experiments.⁴⁴ These studies well support the observation of UV-laser-induced generation of a large quantity of C_2 and CH in our OES study.^{40,41,44,45} The 193 nm photodissociation of C_2H_4 has also been well characterized.⁴⁶ Ethylene molecules can be electronically excited by absorbing a 193 nm photon. The decay of excited $C_2H_4^*$ decomposes the molecule into acetylene and either hydrogen or dihydrogen atoms, as illustrated in **Figure 6(b)**.⁴⁶ Apparently, the 193 nm photons possess sufficient energy leading to direct photodissociation of C_2H_2 and C_2H_4 via either one-photon or two-photon processes. Photolysis rate, the number of times a photodissociation occurs per photon absorbed, is highly wavelength dependent. The lower the wavelength of the radiation is, the higher photolysis rate is. Although C_2H_4 has a C-H bond energy which is around 0.2 eV below the 248 nm photon energy, the photolysis rate is much lower than that at 193 nm because the 193 nm photo energy is around 1.5 eV higher than the C-H bond energy. Compared with 193

nm laser irradiation, direct photodissociation of either C_2H_2 or C_2H_4 by absorbing the 248 nm photon is difficult and has to proceed through a two-photon process, which requires high laser intensity. This explains why, although the output fluence of the 193 nm laser was one order of magnitude lower than that of the 248 nm laser, the 193 nm laser irradiation of the combustion flame led to a more pronounced enhancement in diamond growth and a more significant increase in the generation of key radicals.

Conclusion

In this paper, the effects on diamond growth of UV laser irradiation of the diamond-forming combustion flame at different laser wavelengths were reported. The 193 nm laser irradiation was found to be more efficient in enhancing diamond growth and modifying the flame chemistry than the 248 nm laser irradiation. Investigation of the lateral grain size evolution and the diamond nucleation process suggested that the secondary nucleation was significantly suppressed by the UV irradiation to the flame at 193 nm. A higher increment rate of reactive species under the 193 nm laser irradiation was identified by analyzing the flame chemistry using OES. The more pronounced effects of the 193 nm irradiation can be attributed to the high photon energy which leads to the direct photodissociation of hydrocarbon precursors.

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References

- (1) J. E. Field (Ed.). The Properties of Natural and Synthetic Diamond. Academic Press, London 1992. £ 90.00. ISBN 0-12-255352-7. *Cryst. Res. Technol.* **1993**, 28 (5), 602–602.
- (2) Ravi, K. V. *Diamond and Related Materials* **1995**, 4 (4), 243–249.
- (3) Alers, P.; Hänni, W.; Hintermann, H. E. *Diamond and Related Materials* **1993**, 2 (2), 393–396.
- (4) Haubner, R.; Lux, B. *Diamond and Related Materials* **1993**, 2 (9), 1277–1294.
- (5) Yalamanchi, R. S.; Harshavardhan, K. S. *Journal of Applied Physics* **1990**, 68 (11), 5941–5943.
- (6) Asmussen, J.; Grotjohn, T. A.; Schuelke, T.; Becker, M. F.; Yaran, M. K.; King, D. J.; Wicklein, S.; Reinhard, D. K. *Applied Physics Lettrs* **2008**, 93 (3).
- (7) Donnet, J. B.; Oulanti, H.; Huu, T. L.; Schmitt, M. *Carbon* **2006**, 44 (2), 374–380.
- (8) Okabe, H. *Photochemistry of Small Molecules*; John Wiley & Sons Inc: New York, 1978.
- (9) Crim, F. F. *Science* **2007**, 316 (5832), 1707–1708.
- (10) Knox, B. E.; Palmer, H. B. *Chem. Rev.* **1961**, 61 (3), 247–255.
- (11) Kitahama, K.; Hirata, K.; Nakamatsu, H.; Kawai, S.; Fujimori, N.; Imai, T.; Yoshino, H.; Doi, A. *Appl. Phys. Lett.* **1986**, 49 (11), 634–635.
- (12) Goto, Y.; Yag, T.; Nagai, H. *MRS Online Proceedings Library Archive* **1988**, 129.
- (13) Kitahama, K. *Appl. Phys. Lett.* **1988**, 53 (19), 1812–1814.
- (14) Tyndall, G. W.; Hacker, N. P. *MRS Online Proceedings Library Archive* **1989**, 162.
- (15) Zare, R. N. *Science* **1998**, 279 (5358), 1875–1879.
- (16) Bronikowski, M. J.; Simpson, W. R.; Zare, R. N. *J. Phys. Chem.* **1993**, 97 (10), 2194–2203.
- (17) Zhu, L.; Kellis, D.; Ding, C.-F. *Chemical Physics Letters* **1996**, 257 (5), 487–491.

- (18) Zama, H.; Miyake, T.; Hattori, T.; Oda, S. *Jpn. J. Appl. Phys.* **1992**, *31* (5A), L588.
- (19) Heszler, P.; Landström, L.; Lindstam, M.; Carlsson, J. O. *Journal of Applied Physics* **2001**, *89* (7), 3967–3970.
- (20) Han, J.; Jensen, K. F.; Senzaki, Y.; Gladfelter, W. L. *Appl. Phys. Lett.* **1994**, *64* (4), 425–427.
- (21) Karam, N. H.; Liu, H.; Yoshida, I.; Jiang, B.-L.; Bedair, S. M. *Journal of Crystal Growth* **1988**, *93* (1), 254–258.
- (22) Bilenchi, R.; Gianinoni, I.; Musci, M.; Murri, R.; Tacchetti, S. *Appl. Phys. Lett.* **1985**, *47* (3), 279–281.
- (23) Skouby, D. C.; Jensen, K. F. *Journal of Applied Physics* **1988**, *63* (1), 198–206.
- (24) Demiryont, H.; Thompson, L. R.; Collins, G. J. *Appl. Opt., AO* **1986**, *25* (8), 1311–1318.
- (25) Xie, Z. Q.; Bai, J.; Zhou, Y. S.; Gao, Y.; Park, J.; Guillemet, T.; Jiang, L.; Zeng, X. C.; Lu, Y. F. *Scientific Reports* **2014**, *4*, srep04581.
- (26) Fan, L. S.; Xie, Z. Q.; Park, J. B.; He, X. N.; Zhou, Y. S.; Jiang, L.; Lu, Y. F. *J. Laser Appl.* **2012**, *24*, 022001.
- (27) Zhou, Y. S.; Fan, L. S.; Xie, Z. Q.; Jiang, L.; Silvain, J.-F.; Lu, Y. F. *Current Opinion in Solid State and Materials Science* **2015**, *19* (2), 107–114.
- (28) Fan, L. S.; Zhou, Y. S.; Wang, M. X.; Gao, Y.; Liu, L.; Silvain, J. F.; Lu, Y. F. *Laser Phys. Lett.* **2014**, *11* (7), 076002.
- (29) Fan, L. S.; Xie, Z. Q.; Park, J. B.; He, X. N.; Zhou, Y. S.; Jiang, L.; Lu, Y. F. *J. Laser Appl.* **2012**, *24*, 022001.
- (30) Fan, L.; Constantin, L.; Li, D.; Liu, L.; Keramatnejad, K.; Huang, X.; Rabiee Golgir, H.; Lu, Y.; Ahmadi, Z.; Wang, F.; et al. *Nature : Light Sci. Appl* **2018**, *In press*.
- (31) Bąk, G. W.; Fabisiak, K.; Klimek, L.; Kozanecki, M.; Staryga, E. *Optical Materials* **30** (5), 770–773.
- (32) Asmussen, J.; Reinhard, D. *Diamond Films Handbook*; CRC Press, 2002.
- (33) Liu, H.; Dandy, D. S. *Diamond Chemical Vapor Deposition: Nucleation and Early Growth Stages*; Elsevier, 1996.
- (34) Komaki, K.; Yanagisawa, M.; Yamamoto, I.; Hirose, Y. *Jpn. J. Appl. Phys.* **1993**, *32* (4R), 1814.
- (35) Miller, J. A.; Melius, C. F. *Combustion and Flame* **1992**, *91* (1), 21–39.
- (36) Redfern, P. C.; Horner, D. A.; Curtiss, L. A.; Gruen, D. M. *J. Phys. Chem.* **1996**, *100* (28), 11654–11663.
- (37) Gruen, D. M.; Redfern, P. C.; Horner, D. A.; Zapol, P.; Curtiss, L. A. *J. Phys. Chem. B* **1999**, *103* (26), 5459–5467.
- (38) Kim, J. S.; Cappelli, M. A. *Journal of Applied Physics* **1998**, *84* (8), 4595–4602.
- (39) Kovács, T.; Blitz, M. A.; Seakins, P. W. *J. Phys. Chem. A* **2010**, *114* (14), 4735–4741.
- (40) Irion, M. P.; Kompa, K. L. *Appl. Phys. B* **1982**, *27* (4), 183–186.
- (41) Balko, B. A.; Zhang, J.; Lee, Y. T. *The Journal of Chemical Physics* **1991**, *94* (12), 7958–7966.
- (42) Donnelly, V. M.; Baronavski, A. P.; McDonald, J. R. *Chemical Physics* **1979**, *43* (2), 271–281.
- (43) Pasternack, L.; McDonald, J. R. *Chemical Physics* **1979**, *43* (2), 173–182.
- (44) Sorkhabi, O.; Blunt, V. M.; Lin, H.; Xu, D.; Wrobel, J.; Price, R.; Jackson, W. M. *The Journal of Chemical Physics* **1997**, *107* (23), 9842–9851.
- (45) Nakayama, T.; Watanabe, K. *The Journal of Chemical Physics* **1964**, *40* (2), 558–561.

- (46) Cromwell, E. F.; Stolow, A.; Vrakking, M. J. J.; Lee, Y. T. *The Journal of Chemical Physics* **1992**, 97 (6), 4029–4040.

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A comparative study of diamond growth using combustion CVD assisted by UV laser irradiations at two laser wavelengths, 193 and 248 nm, was performed. A more pronounced influence on the diamond growth process and the flame chemistry was found with UV laser irradiation at the shorter laser wavelength of 193 nm.