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Hao Ling

University of Nebraska - Lincoln, hling4@unl.edu

Q. Xie

University of Nebraska at Lincoln

T. Gebre

University of Nebraska - Lincoln

X. K. Shen

University of Nebraska - Lincoln

Yongfeng Lu

University of Nebraska - Lincoln, ylu2@unl.edu

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Enhanced chemical vapor deposition of diamond by wavelength-matched vibrational excitations of ethylene molecules using tunable CO₂ laser irradiation

H. Ling, Z. Q. Xie, Y. Gao, T. Gebre, X. K. Shen, and Y. F. Lu^{a)}
 Department of Electrical Engineering, University of Nebraska–Lincoln, Lincoln,
 Nebraska 68588-0511, USA

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Wavelength-matched vibrational excitations of ethylene (C₂H₄) molecules using a tunable carbon dioxide (CO₂) laser were employed to significantly enhance the chemical vapor deposition (CVD) of diamond in open air using a precursor gas mixture of C₂H₄, acetylene (C₂H₂), and oxygen (O₂). The CH₂-wag vibration mode (ν_7) of the C₂H₄ molecules was selected to achieve the resonant excitation in the CVD process. Both laser wavelengths of 10.591 and 10.532 μm were applied to the CVD processes to compare the C₂H₄ excitations and diamond depositions. Compared with 10.591 μm produced by common CO₂ lasers, the laser wavelength of 10.532 μm is much more effective to excite the C₂H₄ molecules through the CH₂-wag mode. Under the laser irradiation with a power of 800 W and a wavelength of 10.532 μm , the grain size in the deposited diamond films was increased by 400% and the film thickness was increased by 300%. The quality of the diamond crystals was also significantly enhanced. © 2009 American Institute of Physics.
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I. INTRODUCTION

Vibrational excitations of molecules using photons of specific energy are widely studied in photodesorption, photodissociation, and photoionization.^{1–3} Photons are directed to a selected chemical bond in a molecule to achieve a high-efficiency energy coupling into a physical or chemical process. The purpose of the resonant excitation is to realize selective bond breaking and control reaction pathways. Although IR multiphoton absorption in a chemical reaction has been studied for many years⁴ and made great progress, it is still difficult to reach precise reaction control. Most vibrational frequencies of organic molecules are in the wavelength ranges from midinfrared to terahertz. The narrow ranges of light sources limited the further development of the research. Fast energy redistribution at the vibrational states is also a key issue. Recently, breakthroughs have been achieved in some researches. For example, Liu *et al.*² achieved selective desorption of H from Si(111) by resonant excitation of the Si-H vibrational stretch mode using a free-electron laser. Bond-selective control of a heterogeneously catalyzed reaction has been achieved by Killelea *et al.*⁵ However, applications of vibrational excitations in material growth are in their infant stage.

Lasers are ideal energy sources for vibrational resonant excitations. Laser-assisted chemical reaction control was investigated during the past years.⁶ CO₂ laser is a typical energy source widely used in laser chemistry due to its high energy efficiency and high output power. However, common commercial CO₂ lasers only produce a fixed wavelength of 10.591 μm , which cannot match the wavelengths required

for effective vibrational resonant excitations. In our previous study, a common CO₂ laser at 10.591 μm was used to achieve the vibrational resonant excitation of C₂H₄ molecules through the broadening of the absorption band.⁷ In this study, a tunable CO₂ laser with a high power output up to 1000 W was used to replace the common CO₂ laser. The CO₂ laser wavelength can be precisely tuned to match the CH₂-wag mode (ν_7) of C₂H₄ molecules to achieve the optimal resonant excitation to significantly improve the diamond deposition in the chemical vapor deposition (CVD) processes using the C₂H₄/C₂H₂/O₂ gas mixture. Instead of the commonly used 10.591 μm , the CO₂ laser wavelength was tuned to 10.532 μm to perfectly match the vibrational frequency of the CH₂-wag mode.

Diamond has many unique properties such as extreme hardness, high thermal conductivity, chemical inertness, and high electrical resistivity, which make it an important material in a wide range of applications. Diamond films are typically deposited using CVD in vacuum chambers.^{8,9} C₂H₂/O₂ combustion chemical reaction for diamond growth in open air was first reported by Hirose and Kondo,¹⁰ which has attracted many efforts until now.^{11–14} Other techniques, such as pulsed laser deposition¹⁵ and shock wave compression,¹⁶ have also been developed. However, improvements on deposition rate and film quality, which strongly depend on the reaction processes, are highly desired. A variety of techniques have been developed to promote the deposition rate and improve the film quality by activation of the precursor gases to stimulate the chemical reactions during film depositions. Microwave-plasma-enhanced CVD is a representative method for high-quality diamond growth.^{17,18} Plasma torch is used to deposit diamond films with high deposition rate.¹⁹

^{a)}Corresponding author: Tel.: 402-472-8323; FAX: 402-472-4732; Electronic mail: ylu2@unl.edu.

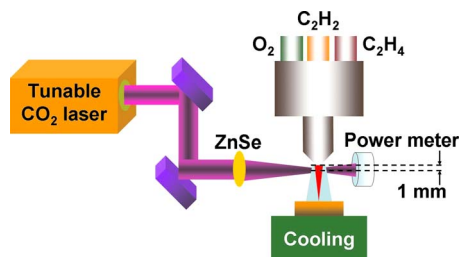


FIG. 1. (Color online) Experimental setup for vibrational excitation of C_2H_4 molecules using a tunable CO_2 laser in diamond deposition.

Other methods, such as fast heating,^{20,21} optical pumping,^{22–24} and substrate pretreatment,^{25,26} have also been studied.

In this study, vibrational resonant excitation of C_2H_4 molecules by perfect wavelength match using a tunable CO_2 laser in $C_2H_4/C_2H_2/O_2$ combustion CVD of diamond films was investigated in open air. Although both C_2H_2 and O_2 yield an ideal element ratio in combustion CVD of diamond, there is no powerful laser which has required wavelengths to resonantly excite the C_2H_2 or O_2 molecules. Therefore, C_2H_4 , which is also a suitable precursor for diamond growth,^{27,28} was added in the combustion flame to couple the laser energy into the chemical reactions through the resonant excitation. Laser pyrolysis and decomposition of C_2H_4 molecules through vibrational excitations have been studied and used to produce diamond powders,²⁹ but not diamond films. However, vibrational resonant excitation of precursor molecules using a tunable CO_2 laser has rarely been reported to date. Through the perfect wavelength matching, high-efficient energy coupling into the CVD reactions, and significant enhancement of diamond growth using the tunable CO_2 laser resonant excitation were investigated in this study.

II. EXPERIMENTAL SETUP

Figure 1 shows a schematic of the experimental setup used for investigating vibrational excitation of C_2H_4 molecules using a tunable CO_2 laser in diamond deposition. A commercial welding torch was used to generate a $C_2H_4/C_2H_2/O_2$ combustion flame, which was perpendicularly directed to a tungsten carbide substrate. Different from our previous work,⁷ a continue-wave tunable CO_2 laser (PRC Company) was used in this study. The laser beam, in parallel with the substrate surface, was used to irradiate the flame so that no laser energy was absorbed by the substrate. The wavelength of the CO_2 laser can be tuned from 9.2 to 10.9 μm using different emission lines. Both wavelengths of 10.532 (perfect match with the CH_2 -wag vibration mode of C_2H_4 , ν_7) and 10.591 μm (generated by common CO_2 lasers) were used in this study to compare the excitation effects. The original diameter of the CO_2 laser beam was 13 mm. A ZnSe convex lens with a focal length of 190 mm was used to focus the laser beam to 1 mm diameter in the flame. The interaction zone of the laser beam and the flame was about 1 mm below the torch nozzle. The C_2H_4 (99.999%), C_2H_2 (99.6%), and O_2 (99.996%) gases were mixed in the torch through three gas flow meters (B7920V, Spec-Air

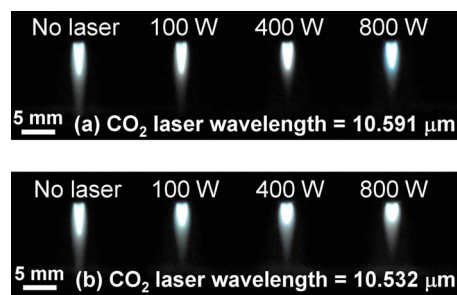


FIG. 2. (Color online) Optical images of the $C_2H_4/C_2H_2/O_2$ flames with laser irradiations at (a) 10.591 μm and (b) 10.532 μm .

Gases & Technologies). The gas flow rates of C_2H_4 , C_2H_2 , and O_2 were 0.62, 0.62, and 1.20 slpm, respectively.

A tungsten carbide (WC) substrate (BS-6S, Basic Carbide Corp., containing 6% cobalt) with a dimension of $25.4 \times 25.4 \times 1.6$ mm³ was placed on a hollow brass plate, which was cooled by a water flow. The surface roughness of the WC substrate was 400 nm. The substrate was cleaned in a supersonic bath of acetone for 15 min before diamond deposition. The distance between the substrate surface and the inner cone of the flame was about 1 mm in all experiments. The temperature of the substrate surface during deposition was monitored by a noncontact pyrometer (OS3752, Omega Engineering, Inc.). The readings of the pyrometer varied within ± 10 °C of the mean value in each measurement. The pyrometer was aimed to a circle area at the center of the substrate below the tip of the flame. The diameter of the circle area was about 4 mm. The measured temperature was an average value over this area. The diamond deposition was carried out with different laser powers of 100, 400, and 800 W for each wavelength. The deposition time was 15 min in all experiments. For a comparison, a diamond film was prepared without laser irradiation but with the same gas flow ratio and deposition time.

Surface morphologies of the deposited diamond films were characterized by a scanning electron microscope (XL-30, Philips Electronics). A home-made micro-Raman system with an Ar ion laser (514.5 nm, Innova 300, Coherent, Inc.) as the excitation source was used to examine the bonding structures in the deposited films. Prior to and after Raman characterization of the deposited films, the Raman system was calibrated using a single crystal silicon (100) sample and commercial diamond powders. The thickness of the deposited films was characterized by a stylus profiler (XP-2, Ambios Technology).

III. RESULTS AND DISCUSSION

Figure 2 shows the optical images of the $C_2H_4/C_2H_2/O_2$ flames under irradiations of the tunable CO_2 laser with 10.591 and 10.532 μm , respectively. The length of the flame inner cone was about 6 mm without the laser irradiation. When a CO_2 laser beam of 10.591 μm irradiated the flame, the inner cone of the flame became brighter and shorter as shown in Fig. 2(a). When the laser power was increased from 100 to 800 W, the length of the flame inner cone was shortened to 4.8 mm with a 20% increase in the diameter. This is similar to the results obtained in our previous study.⁷ Figure

2(b) shows the optical images of the flame under laser irradiations with the wavelength of 10.532 μm , which is a perfect match with the CH_2 -wag vibration mode of C_2H_4 (ν_7). At this wavelength, the flame inner cone under the irradiation of 100 W was as short as that under the irradiation of 800 W at 10.591 μm . When the laser power was increased to 800 W, the length of the flame inner cone was reduced to 3.6 mm with an 80% increase in the diameter. The shorter inner cone is due to the enhanced reactions in the flame induced by the laser resonant excitation. The chemical reaction becomes stronger and faster and hence expanded horizontally. A power meter was used to monitor the absorption of the laser powers by comparing the measured powers with and without the flame absorption. When the laser power was around 800 W, 3.4% of the incident laser power was absorbed by the flame at 10.591 μm , whereas 6.7% of the incident laser power was absorbed for at 10.532 μm under the same experimental condition. Without the C_2H_4 gas, a $\text{C}_2\text{H}_2/\text{O}_2$ (1:1) flame had neither laser absorption nor visible change in the flame.

The CH_2 -wag vibrational mode of C_2H_4 molecule shows a vibrational wavenumber at 949.3 cm^{-1} . For most common commercial CO_2 lasers, the wavelength is 10.591 μm (equivalent to a wavenumber of 944.2 cm^{-1}), which is close to the infrared absorption band corresponding to the CH_2 -wag vibration mode of the C_2H_4 . The rotational partition function spreads the C_2H_4 population over a much wider range under current experimental conditions. Therefore, the CO_2 laser energy can almost be resonantly absorbed by the C_2H_4 molecules through this vibrational mode due to the broadening of the absorption band. However, the efficiency of the resonant absorption under this wavelength is relatively low. The absorption coefficient of gaseous C_2H_4 is about 1.77 atm/cm at room temperature. When the CO_2 laser wavelength is tuned to 10.532 μm (equivalent to a wavenumber of 949.5 cm^{-1}), the absorption coefficient of gaseous C_2H_4 increases to about 29 atm/cm at room temperature. Although the environment condition in pure C_2H_4 gas at room temperature is different with that in a flame, the difference between the absorption coefficients can indicate the high efficiency of the resonant absorption of the laser energy when the CO_2 laser wavelength is tuned to 10.532 μm . The experimental results supported a high efficiency of vibrational resonant excitation at wavelength of 10.532 μm .

The energy redistribution at vibrational states is usually on a picosecond time scale or even faster under the current experimental conditions. Therefore, it is not clear whether the absorbed laser energy is only used to break the C–H bonds in the C_2H_4 molecules, although the resonant excitation was applied to the CH_2 -wag mode. Since the C–H and C=C bond energies of the C_2H_4 molecules are about -113.6 and -171.6 kcal/mol, respectively, the C–H bond is easier to be broken than the C=C bond. Considering the energy absorption through the CH_2 -wag mode, the probability of C–H bond breaking in current experiments is higher than the C=C bond breaking in the C_2H_4 molecules. Most absorbed energy could be directed to the C–H bonds in the experiments which was beneficial to generate hydrogen atoms in the reactions. The absorbed laser energy could also be trans-

ferred to other molecules through collisions with the excited C_2H_4 molecules. The excitation of the reaction species led to a faster reaction in the CVD of diamond films.

Diamond films were deposited using the flames with the vibrational excitations of the C_2H_4 molecules. Both laser wavelengths of 10.591 and 10.532 μm were used for the excitations. The temperature of the WC substrates was kept at 780 $^\circ\text{C}$ during all depositions. Figure 3 shows the scanning electron microscope (SEM) images of the deposited films without laser excitation and with 100, 400, and 800 W laser excitations at 10.591 μm . It is observed that most of the diamond grains are around 2 μm in the case without the laser excitation as shown in Fig. 3(a). The grain sizes in Figs. 3(b)–3(d) increase with increasing laser power. In Fig. 3(d), most of the grain sizes are about 5 μm which was deposited with the laser excitation of 800 W. When the excitation wavelength was tuned to 10.532 μm , the grain sizes of the deposited films showed a significant increase. Figure 4 shows the SEM images of the deposited films without laser excitation and with 100, 400, and 800 W laser excitation at 10.532 μm . In Fig 4(c), most of grain sizes are larger than 5 μm . When the laser power of 800 W was applied, the grain size of the film increased to about 10 μm which was four times larger than the film without laser excitation and twice of the film deposited with the laser excitation of 800 W at 10.591 μm . The increase in grain size indicates the accelerated nucleation and higher growth rate with the laser excitation at a wavelength perfectly matching the vibrational mode.

Figure 5 shows the profiles of the deposited films. Without the laser excitation, the film thickness is about 4 μm as shown in Fig. 5(a). When the C_2H_4 molecules were excited at 10.591 μm , the film thicknesses in Figs. 5(b)–5(d) increased to 5, 6.5, and 8 μm with the irradiation powers of 100, 400, and 800 W, respectively. Using the common CO_2 laser wavelength, the growth rate increased by 100% with 800 W excitation. In our previous study, the film thickness was increased by 50% with a laser excitation of 600 W at this wavelength using different gas ratio.⁷ Figures 5(e)–5(g) show the profiles of the films with perfect matching excitations at 10.532 μm . The film thickness is about 14 μm in Fig. 5(f) with 400 W excitation and 16 μm in Fig. 5(g) with 800 W excitation. Compared with the Fig. 5(a), the growth rate was increased by 300% with 800 W laser power at 10.532 μm .

To compare the quality of the diamond films deposited with different laser wavelengths and powers, the bonding structures in the diamond films were characterized by Raman spectroscopy. The Raman spectra of the deposited diamond films in the wavenumber region from 1000 to 2000 cm^{-1} are shown in Fig. 6. Spectrum (a) corresponds to the diamond film deposited without laser excitation. A peak at 1335 cm^{-1} is a typical Raman signal of diamond. The shift from the typical diamond peak at 1332 cm^{-1} is related to the stress in the films.³⁰ A broad band centered at 1500 cm^{-1} (*G* band) in spectrum (a) is due to graphitelike carbon mixed with amorphous carbon. There is a step from 1340 to 1400 cm^{-1} on the

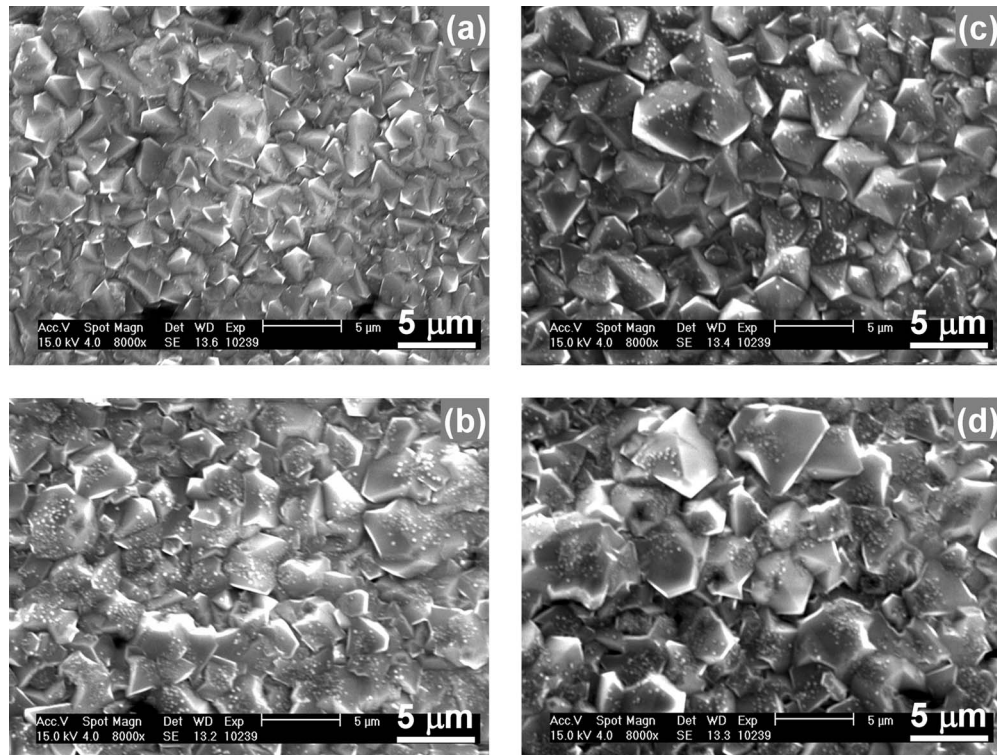


FIG. 3. SEM images of the deposited diamond films with the CO₂ laser excitations at 10.591 μm : with (a) no laser excitation, (b) 100 W, (c) 400 W, and (d) 800 W laser excitations.

right side of the diamond peak, indicating that the diamond peak is overlapping with a weak *D* band reflecting disordered carbon in the film.

Raman spectra of the diamond films deposited using the

10.591 μm excitation with different laser powers of 100, 400, and 800 W are shown in spectra (b), (c), and (d), respectively. It is clear that the *D* band in spectrum (a) decreased gradually from spectra (b) to (d) with the increasing

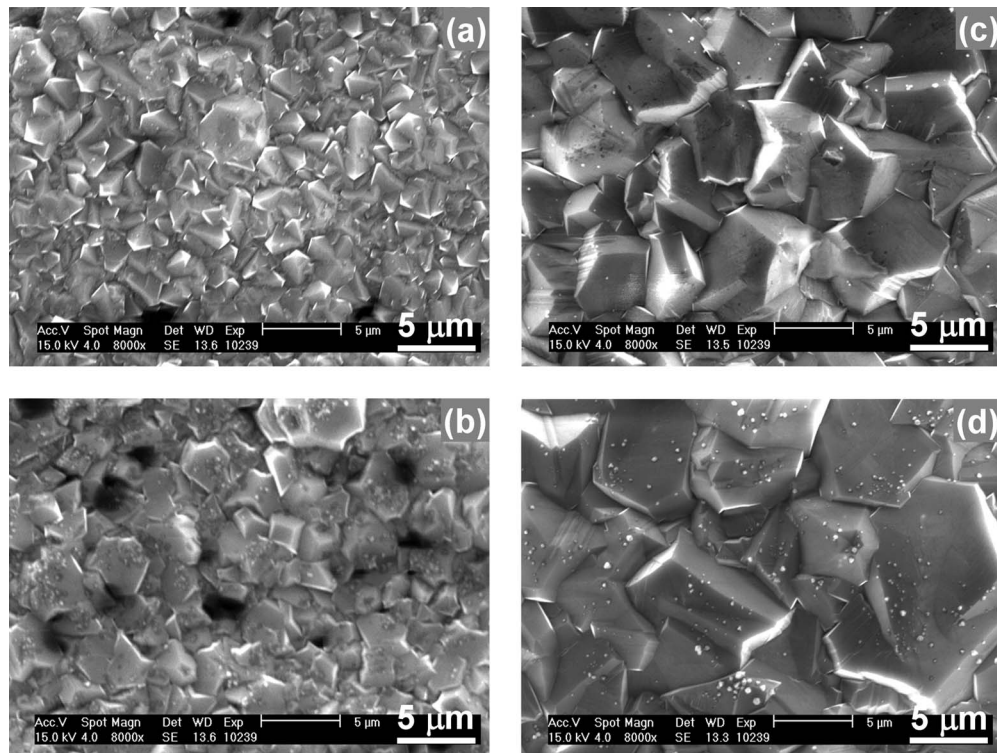


FIG. 4. SEM images of the deposited diamond films with the CO₂ laser excitations at 10.532 μm : with (a) no laser excitation, (b) 100 W, (c) 400 W, and (d) 800 W laser excitations.

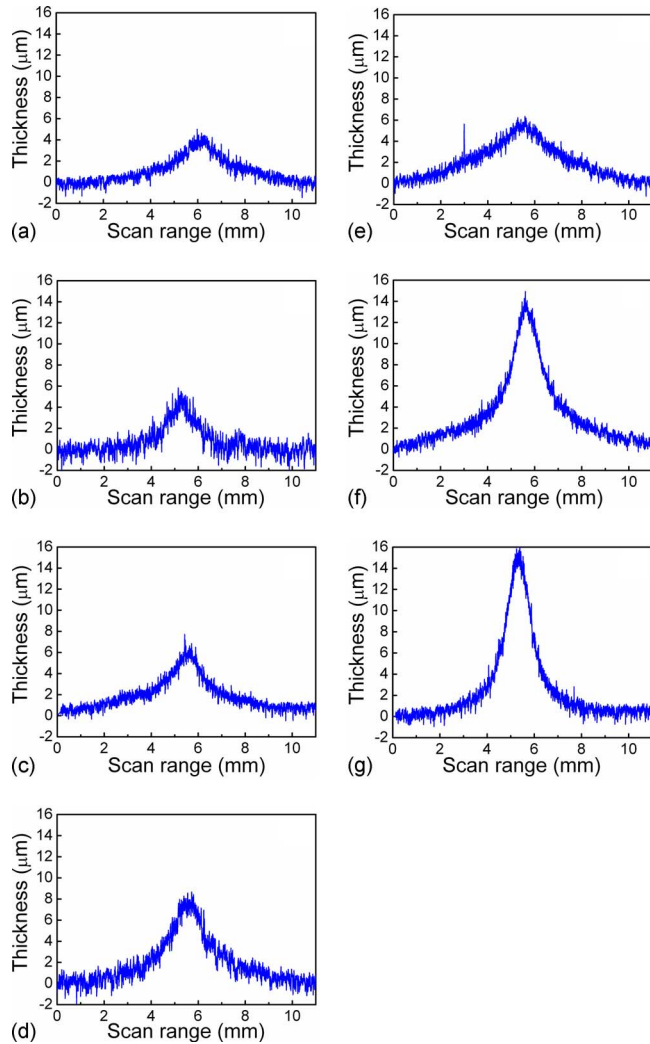


FIG. 5. (Color online) Profiles of diamond films deposited under the conditions: with (a) no laser excitation, (b) 100 W, (c) 400 W, and (d) 800 W laser excitations at $10.591 \mu\text{m}$; with (e) 100 W, (f) 400 W, and (g) 800 W laser excitations at $10.532 \mu\text{m}$.

laser power. The disappearing of the *D* band indicates the improved crystallization and reduced disordered carbon in the films with the laser excitations. However, the intensity ratio of the diamond peak versus the *G* band has no obvious

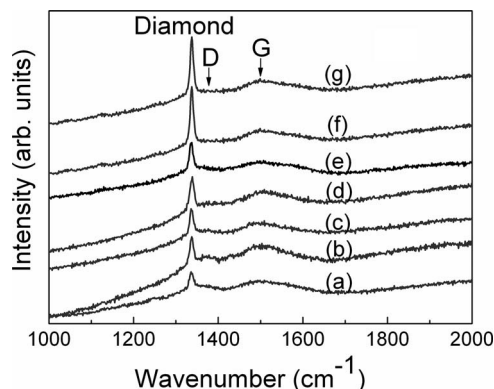


FIG. 6. Raman spectra of diamond films deposited under the conditions: with (a) no laser excitation, (b) 100 W, (c) 400 W, and (d) 800 W laser excitations at $10.591 \mu\text{m}$; with (e) 100 W, (f) 400 W, and (g) 800 W laser excitations at $10.532 \mu\text{m}$.

change. When the laser wavelength was tuned to $10.532 \mu\text{m}$ for perfect wavelength matching with the C_2H_4 vibration mode, the diamond peak in spectrum (e) shows an obvious increase with 100 W laser excitation. Spectra (f) and (g) show the Raman signals of the films deposited with 400 and 800 W laser excitations. The diamond peaks in both Raman spectra are much sharper and stronger than those in other spectra associated with the weakening *G* band. Therefore, the diamond films not only increased in the thickness, but also improved in the crystallinity. These results indicate the high quality of the diamond films and fast growth rate using $10.532 \mu\text{m}$ excitation with high laser powers.

In our previous study, it was demonstrated that the vibrational excitation of the C_2H_4 molecules in the flame is a nonthermal process during the diamond depositions.⁷ Under current experimental conditions, it is still difficult to achieve a real bond-selective chemistry through the vibrational resonant excitation. However, the continuous vibrational excitation of the C_2H_4 molecules in open-air reactions was beneficial to promote the diamond growth. As discussed above, the C–H bonds of C_2H_4 molecules are easier to break than the C=C bonds, which could improve the generation of hydrogen atoms. The hydrogen atoms are the radicals beneficial to diamond deposition. The excited reactants could also accelerate the desired reactions for the diamond growth. For a comparison, a gas mixture of C_2H_2 and O_2 was also irradiated by the tunable CO_2 laser with the same laser power. There was no obvious change in the flame appearance and the diamond deposition rate.

IV. CONCLUSIONS

Vibrational resonant excitation of the C_2H_4 precursor molecules was achieved using a tunable CO_2 laser in open-air CVD of diamond films. The CVD processes were accelerated due to the stronger laser energy coupling with the C_2H_4 molecules. Compared with the common CO_2 laser at $10.591 \mu\text{m}$, the laser wavelength of $10.532 \mu\text{m}$ is much more effective to excite the C_2H_4 molecules through the CH_2 -wag vibration mode. The diamond films deposited with the tunable laser excitation have larger grain size, better crystallinity, and faster growth rate than those without laser excitation. Under the laser irradiation of 800 W at the wavelength of $10.532 \mu\text{m}$, the diamond grain size and film thickness increased by 400% and 300%, respectively. Besides the increases in grain size and the film thickness, the crystallization of diamond structure was also enhanced in the film. The results indicate a promising approach to use vibrational resonant excitations of precursor molecules to enhance diamond deposition in open air.

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