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# Laser-induced resonant excitation of ethylene molecules in $C_2H_4/C_2H_2/O_2$ reactions to enhance diamond deposition

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Vibrational resonant excitation of ethylene ( $C_2H_4$ ) molecules using a carbon dioxide laser was employed to promote reactions in precursors of ethylene, acetylene ( $C_2H_2$ ), and oxygen to enhance diamond deposition. One of the vibrational modes ( $CH_2$  wag mode,  $\nu_7$ ) of the  $C_2H_4$  molecules was selected to achieve the resonant excitation in the reactions. Optical emission spectroscopy was used to study the effects of laser resonant excitation on the reactions for diamond deposition. The optical emissions of CH and  $C_2$  species were enhanced with the laser excitation, indicating that there are more active species generated in the reactions. Thicknesses and grain sizes of the deposited films were increased correspondingly. Temperature calculations from the line set in the  $R$ -branch of CH emission spectra indicated that a nonthermal process is involved in the enhanced diamond deposition. © 2009 American Institute of Physics. [DOI: [10.1063/1.2986217](https://doi.org/10.1063/1.2986217)]

## I. INTRODUCTION

The unique properties of diamond, such as extreme hardness, high thermal conductivity, chemical inertness, wear resistance, transparency, and high electrical resistivity make it an important material in a wide range of applications. Many attempts have been performed to prepare diamond films mostly using low-pressure chemical-vapor deposition (CVD) in vacuum chambers.<sup>1,2</sup>  $C_2H_2/O_2$  combustion chemical reaction for diamond growth in open air was first reported by Hirose and Kondo,<sup>3</sup> which has attracted many efforts up to now.<sup>4–7</sup> Other techniques, such as pulsed laser deposition<sup>8</sup> and shock wave compression,<sup>9</sup> have also been developed.

Although diamond films have been deposited by the above-mentioned methods, deposition rate and film quality, which strongly depend on the reactions, are still to be improved. A variety of techniques have been used 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 which has been developed widely for high-quality diamond growth.<sup>10,11</sup> Plasma torch using radio frequency discharge or direct current discharge is used to deposit diamond films with high deposition rate.<sup>12</sup> Laser-assisted CVD was regarded as a promising way due to its unique means of fast heating<sup>13,14</sup> and selective optical pumping of the reactive species.<sup>15–17</sup> In addition, a number of substrate pretreatment methods, such as scratching and seeding,<sup>18,19</sup> have been studied to enhance the diamond nucleation.

In this study,  $CO_2$  laser resonant excitation of  $C_2H_4$  molecules in  $C_2H_4/C_2H_2/O_2$  combustion CVD of diamond films was investigated in open air to develop a new approach to promote diamond growth with laser resonant excitation of vibrational states of precursor molecules.  $C_2H_2$  and  $O_2$  have

been widely used as precursors for diamond growth in the combustion CVD method. Some other precursors, such as  $C_2H_4$ , were also used.<sup>20,21</sup> The selection of precursor molecules has been focused on the effects of atomic ratio of carbon, hydrogen, and oxygen in the reactions. In addition, laser pyrolysis and decomposition of precursors through control of vibrational states have been studied in this field and diamond powders were achieved.<sup>22</sup> However, significant enhancement of diamond film deposition by laser-induced resonant vibrational excitation of precursor molecules is rarely reported to date.

Other than the excitation of precursors, resonant electronic excitation of some radical species using a tunable laser has been used widely to study the species distribution in the reactions and the mechanism of diamond film depositions.<sup>23</sup> The average power of the probe laser used is very low. Different from these studies, the aim of resonant excitation of the precursor molecules using a high power laser in this study is to promote the reactions to significantly enhance diamond deposition.

One of the vibrational modes ( $CH_2$  wag mode,  $\nu_7$ ) of the  $C_2H_4$  molecules was selected to achieve the resonant excitation in the  $C_2H_4/C_2H_2/O_2$  reaction using a powerful  $CO_2$  laser in this study. Although both  $C_2H_2$  and  $O_2$  yield the best element ratio in combustion CVD of diamond, there is no powerful laser which has the specific wavelength to resonantly excite the  $C_2H_2$  or  $O_2$  molecules. Therefore,  $C_2H_4$  was added in order to couple the laser energy into the chemical reactions through resonant excitation. Optical emission spectroscopy (OES) was used to monitor reactive species in the reactions during diamond deposition. Flame temperatures were calculated through the rotational structure of CH emission spectra. A nonthermal process, which led to the enhancement of the diamond depositions, was proposed.

## II. EXPERIMENTAL SETUP

Figure 1 shows a schematic diagram of the diamond deposition system with  $CO_2$  laser resonant excitation and

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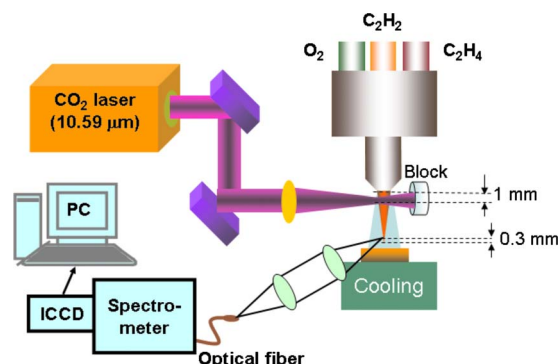


FIG. 1. (Color online) Experimental setup for laser-assisted  $C_2H_4/C_2H_2/O_2$  combustion-flame deposition of diamond films on WC-Co substrates with *in situ* OES.

OES diagnosis used in this study. A commercial welding torch was used to generate a  $C_2H_4/C_2H_2/O_2$  combustion flame that was directed to a tungsten carbide substrate perpendicularly. Different with our previous work,<sup>24</sup> a continuous-wave  $CO_2$  laser (PRC Co., 10.591  $\mu m$  wavelength) beam, in parallel with the substrate surface, was used to irradiate the flame so that laser heating of the substrate was avoided. The diameter of the laser beam was 14 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 (B7920 V, Spec-Air Gases & Technologies). The gas flow rates of  $C_2H_4$ ,  $C_2H_2$ , and  $O_2$  were adjusted to 0.7, 0.65, and 1.32 slpm, respectively.

The tungsten carbide (WC) substrate (BS-6S, Basic Carbide Corp.) with a dimension of  $25.4 \times 25.4 \times 1.6$  mm<sup>3</sup> and a cobalt composition of 6% was placed on a hollow brass block with water cooling. Surface roughness of the WC substrate was 400 nm. The substrates were cleaned in a supersonic bath of acetone for 15 min before film depositions. The distance between the substrate surface and the inner cone of the flame was about 1 mm in all experiments. The surface temperature of the substrate during deposition was monitored by a pyrometer (OS3752, Omega Engineering, Inc.). The readings of the pyrometer varied within  $\pm 10$  °C of the mean value in each measurement. The diamond deposition was carried out with a laser power of 600 W and a deposition time of 30 min. For a comparison, a diamond film was prepared without laser irradiation but with the same gas flow ratio and deposition time.

Optical emission spectra of the flames during film depositions were collected in a direction perpendicular to the flame. The flame emission was introduced into a spectrometer (Andor Shamrock SR-303i-A) coupled with an ICCD (Andor iStar DH-712) through two lenses and an optical fiber which were all made from UV-grade quartz. All the spectra were taken from 0.3 mm above the tip of the inner cone to compare the deposition conditions. The dimension ratio of the image and the flame was 1:1. The fiber, with a diameter of 50  $\mu m$ , was precisely positioned in the inner core of the

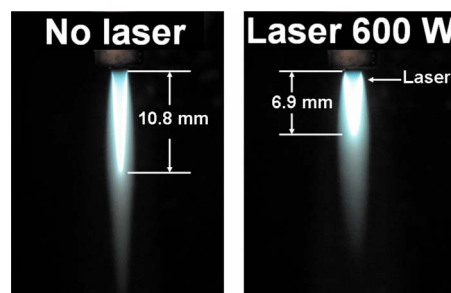


FIG. 2. (Color online) Optical images of the  $C_2H_4/C_2H_2/O_2$  flames with and without  $CO_2$  laser irradiation.

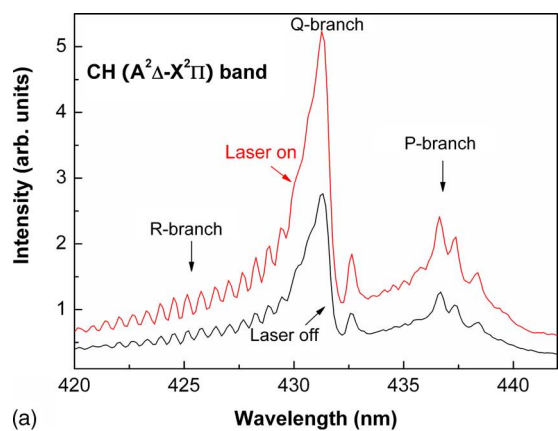
flame image. A background spectrum was taken before the collections of the emission spectra and subtracted in all results.

Surface morphologies of the deposited films were characterized by a scanning emission microscope (XL-30, Philips Electronics). A home-made 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 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).

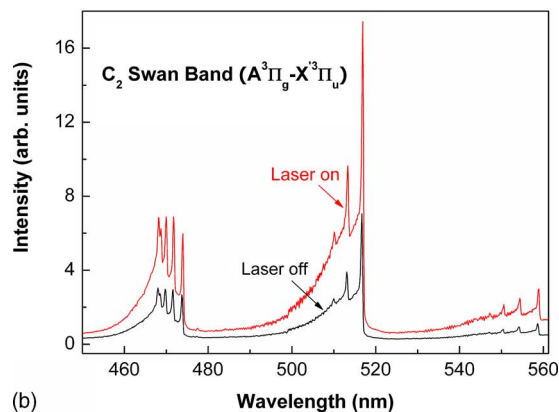
### III. RESULTS AND DISCUSSION

Figure 2 shows the optical images of the  $C_2H_4/C_2H_2/O_2$  flames used to deposit diamond films with and without the laser irradiation. The length of the flame inner cone was about 10.8 mm without the laser irradiation. When a laser beam with a power of 600 W irradiated the flame, the inner cone of the flame became brighter with a shorter length of 6.9 mm. The shorter inner cone is due to the enhanced reactions in the flame, which was induced by the laser excitation. The diameter of the flame inner core was increased about 25%. A power meter was used to monitor the laser power after flame absorption. Comparing the measured powers before and after the flame absorption, the absorbed laser power by the flame was about 4% under current experimental conditions. Without the  $C_2H_4$  precursor, a  $C_2H_2/O_2$  (1:1) flame had neither laser absorption nor visible change with the laser irradiation. This observation supported the resonance absorption of the  $C_2H_4$  molecules in the flame.

The  $CO_2$  laser used in this study has a wavelength of 10.591  $\mu m$  (equivalent to a wave number of 944  $cm^{-1}$ ). The infrared absorption band corresponding to the  $CH_2$ -wag vibration mode of the  $C_2H_4$  is centered at 949  $cm^{-1}$ , which is very close to the  $CO_2$  laser line. The rotational partition function will spread the  $C_2H_4$  population over a much wider range of levels under current experimental conditions. Therefore, the  $CO_2$  laser energy can be resonantly absorbed by the  $C_2H_4$  molecules through this vibrational mode due to the broadening of the absorption band. The laser energy absorbed by the  $C_2H_4$  molecules is coupled into the reactions by two mechanisms. First, the resonantly excited  $C_2H_4$  molecules participate in the reactions. Second, the laser energy can be transferred to other molecules through collisions with



(a)

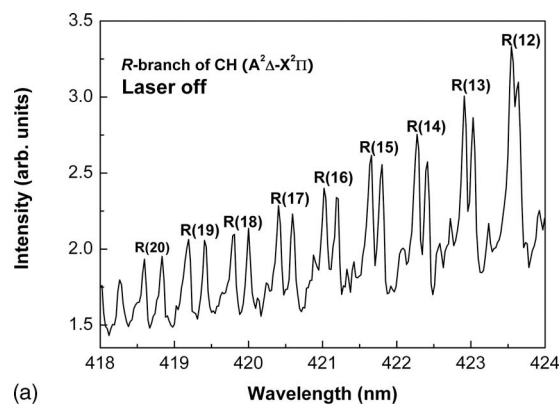


(b)

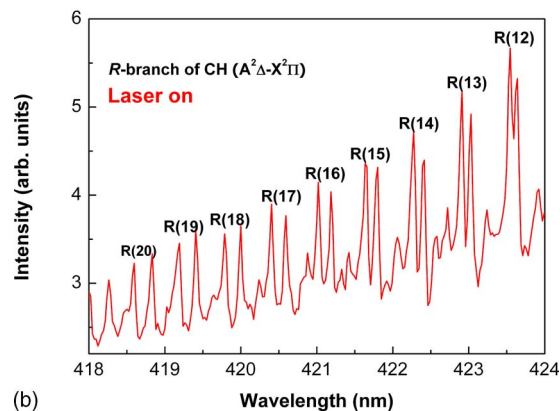
FIG. 3. (Color online) OES spectra of the CH and C<sub>2</sub> species with and without the CO<sub>2</sub> laser excitation of the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame. (a) CH A<sup>2</sup>Δ-X<sup>2</sup>Π (0,0) band and (b) C<sub>2</sub> swan band (A<sup>3</sup>Π<sub>g</sub>-X<sup>3</sup>Π<sub>u</sub>, Δ*v*=-1, 0, +1).

the excited C<sub>2</sub>H<sub>4</sub> molecules. The enhancement of the reactions by the laser excitation leads to a brighter emission from the inner cone. The reacting species in the inner cone are exhausted faster so that the inner cone is shortened.

OES study was performed to understand the process of the laser excitation in the reactions. It is reported that a number of chemical species in the reactions are related to diamond growths.<sup>21,23,25</sup> The resonant excitation using CO<sub>2</sub> laser can generate many possible species. CH and C<sub>2</sub> are two of the important species which are often detected in OES to study the mechanisms of diamond deposition.<sup>23,25,26</sup> The A<sup>2</sup>Δ-X<sup>2</sup>Π (0,0) band of the CH species emission was shown in Fig. 3(a). The overall emission intensities of all the three branches (*R*-, *Q*-, and *P*-branches) in the CH band were increased by 90% with the laser excitation. Similar to the CH species, the overall emission intensity of the C<sub>2</sub> Swan system (transition A<sup>3</sup>Π<sub>g</sub>-X<sup>3</sup>Π<sub>u</sub>, vibrant sequences Δ*v*=-1, 0, +1) in Fig. 3(b) was increased by 130% with the laser excitation. Each of the CH and C<sub>2</sub> spectra in Fig. 3 was accumulated for 100 times to reduce the random noises. The vibrational excitation of the precursor molecules can enhance the reactions to generate more radicals, which increased the concentrations of the species. Generally, in the combustion flame, the free electron concentration is too low to absorb the laser energy for exciting the species. To support this statement, a C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame with laser irradiation was observed for comparison. As expected, there was no enhancement in the optical emission from the active species. Therefore, the effect of



(a)



(b)

FIG. 4. (Color online) *R*-branches of the CH A<sup>2</sup>Δ-X<sup>2</sup>Π (0,0) band (a) without and (b) with the CO<sub>2</sub> laser excitation of the C<sub>2</sub>H<sub>4</sub>/C<sub>2</sub>H<sub>2</sub>/O<sub>2</sub> flame. The laser power was 600 W.

free electrons on the optical emission from the active species is weak in current experiments. Furthermore, the flame diameter was increased by 25%, which also led to a proportional increase in the measured emission intensity. Therefore, most of the enhanced optical emissions were induced by the generation of the species with the laser excitation of the reactants. In the research reported by Matsui *et al.*,<sup>27</sup> CH and C<sub>2</sub> species are considered to be important in diamond deposition because their ratio dependences are in good agreement with that of diamond growth rate. They also pointed out that CH concentrations had been found to be proportional to the diamond growth rates in the acetylene flame. Therefore, the increase in active CH and C<sub>2</sub> species in the enhanced reactions has positive effects on enhancing the growth rate of diamond films.

The line set in the *R*-branch is measured to estimate the flame temperature because the *R*-branch has the most widely spaced lines among the three branches in the CH band.<sup>21</sup> Figure 4 shows both spectra of the *R*-branches with and without the laser excitation. The emission lines are assigned as *R*(*N*''), where *N*'' is the rotational quantum number of the lower state to which the transition terminates. The radiometric response of the spectrum system was calibrated using a tungsten halogen light sources (LS-1, Ocean Optics Inc.) before acquiring the spectra. Both spectra in Fig. 4 were accumulated for 1000 times. The temperatures deduced from both spectra were the same, about 3300 K. The absorbed laser energy was much lower than the thermal energy generated by



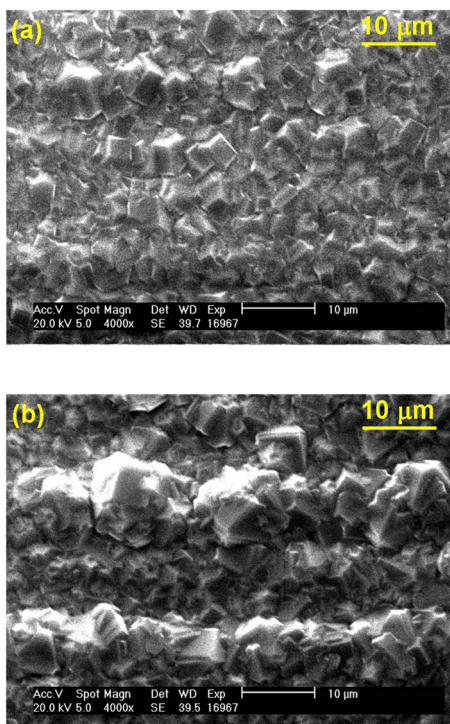


FIG. 5. (Color online) SEM images of the deposited diamond films: (a) without the laser excitation and (b) with a 600 W  $\text{CO}_2$  laser excitation.

the combustion reactions. Therefore, the flame temperature was not significantly affected by the laser excitation although more active species were generated.

Diamond films were deposited using the flames with and without laser excitation, respectively. The growth temperature was kept at 810 °C during both depositions. The representative SEM micrographs of the deposited films are shown in Fig. 5. It is observed that most of the diamond grains are around 3–5  $\mu\text{m}$  in the case without the laser excitation as shown in Fig. 5(a). In comparison, the film deposited with the laser excitation has grains larger than 10  $\mu\text{m}$  as shown in Fig. 5(b). The increase in grain size indicates the accelerated nucleation and higher growth rate with the laser excitation. The wider flame led to a larger deposition area. The thickness of the film was around 6  $\mu\text{m}$  without the laser excitation while the film thickness reached 9  $\mu\text{m}$  with the laser excitation, which suggests a 50% increase in deposition thickness.

The bonding structures of the deposited films were characterized by a home-made Raman system. The Raman scattering spectra of the deposited films in the wave number region from 1000 to 1800  $\text{cm}^{-1}$  are shown in Fig. 6. The spectrum (a) corresponds to the deposited film without the laser excitation. A peak at 1338  $\text{cm}^{-1}$  is a typical Raman signal of diamond. The shift of the diamond peak from 1332  $\text{cm}^{-1}$  is related to the stress in the films.<sup>28</sup> A weak broad band centered at 1568  $\text{cm}^{-1}$  ( $G$  band) in spectrum (a) is due to graphite-like carbon mixed with amorphous carbon. Considering the sensitivity in the Raman spectroscopy of the  $sp^2$  carbon phase is much stronger than that of the diamond phase, the films were predominantly diamond. The  $G$  band of graphitic and amorphous carbon is relatively increased in spectrum (b), but the center of the  $G$  band is positioned at

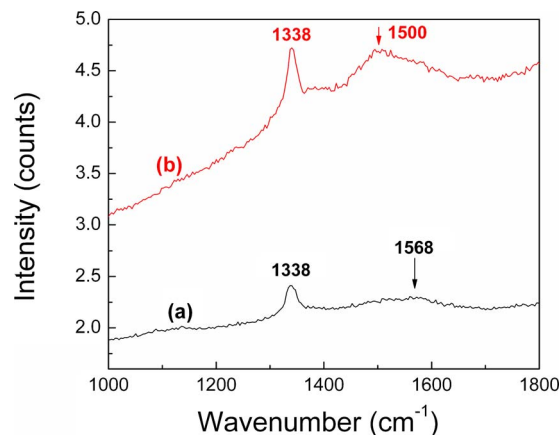


FIG. 6. (Color online) Raman spectra of the deposited films: (a) without the laser excitation and (b) with a 600 W  $\text{CO}_2$  laser excitation.

1500  $\text{cm}^{-1}$ . Compared with the  $G$  band position in spectrum (a), the redshift indicates the increase in the  $sp^3$  bonding in the film.<sup>29</sup> The intensity of spectrum (b), which was taken from the film deposited with the laser excitation, is approximately twice of spectrum (a). This is consistent with the increase in film thickness, since diamond crystals are transparent to the visible light. The probe Ar ion laser with a fixed power penetrates into the films. The Raman signal was collected not only from the film surfaces but also from inside of the films. Therefore, the higher intensity of spectrum (b) is related to the increased diamond thickness.

Considering the same flame and substrate temperatures during the film depositions, the enhancement of the diamond growth was not contributed by a thermal effect in this study. Resonant absorption of the  $\text{CO}_2$  laser energy by the  $\text{C}_2\text{H}_4$  molecules with vibrational excitation caused the promotion of the reactions, which is beneficial to produce more active species such as CH and  $\text{C}_2$ . The increase in active species could be responsible for the enhanced film deposition. For a comparison, a gas mixture of  $\text{C}_2\text{H}_2$  and  $\text{O}_2$  was also irradiated by the  $\text{CO}_2$  laser with the same power. There was no obvious change in the flame appearance, the emission spectra, and the diamond deposition rate.

#### IV. CONCLUSIONS

In summary, the reactions in  $\text{C}_2\text{H}_4/\text{C}_2\text{H}_2/\text{O}_2$  gas mixture for diamond deposition were enhanced using the  $\text{CO}_2$  laser resonant excitation of the  $\text{C}_2\text{H}_4$  molecules. The absorbed laser energy was coupled into the reactions which accelerated the consumption of the reactants. OES study shows that more active species, such as CH and  $\text{C}_2$ , were generated at the tip of the inner cone with the laser excitation. The enhancement of diamond deposition was related to the increase in the CH and  $\text{C}_2$  species. The diamond films deposited with laser excitation have larger grain size and faster growth rate than those without laser excitation. Independent of laser irradiation, both of the flames had the same temperature of 3300 K, as deduced from the emission spectra of the CH species. Therefore, a nonthermal process was introduced to promote the diamond nucleation and growth in

this study. The results indicate a promising method to enhance diamond deposition using laser resonant excitation of precursor vibrational states.

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<sup>1</sup>J. Wei, J. M. Chang, and Y. Tzen, *Thin Solid Films* **212**, 91 (1992).

<sup>2</sup>D. Michau, B. Tanguy, and G. Demazeau, *Mater. Lett.* **17**, 192 (1993).

<sup>3</sup>Y. Hirose and N. Kondo, *Program and Book of Abstracts*, Japan Applied Physics Spring Meeting, Tokyo, 1988 (unpublished).

<sup>4</sup>H. S. Shin and D. G. Goodwin, *Appl. Phys. Lett.* **66**, 2909 (1995).

<sup>5</sup>T. L. Huu, H. Zaidi, and D. Paulmier, *Thin Solid Films* **308-309**, 147 (1997).

<sup>6</sup>Y. Ando, S. Tobe, T. Saito, J. Sakurai, H. Tahara, and T. Yoshikawa, *Thin Solid Films* **457**, 217 (2004).

<sup>7</sup>B. Donnet, H. Oulanti, T. L. Huu, and M. Schmitt, *Carbon* **44**, 374 (2006).

<sup>8</sup>M. Novotny, M. Jelinek, J. Bulir, J. Lancok, V. Vorlicek, and J. Bonarski, *Appl. Phys. A: Mater. Sci. Process.* **79**, 1267 (2004).

<sup>9</sup>O. G. Epanchintsev, A. S. Zubchenko, A. E. Korneyev, and V. A. Simo-  
nov, *J. Phys. Chem. Solids* **58**, 1785 (1997).

<sup>10</sup>A. Gicquel, E. Anger, M. F. Ravet, D. Fabre, G. Scatena, and Z. Z. Wang, *Diamond Relat. Mater.* **2**, 417 (1993).

<sup>11</sup>D. Takeuchi, H. Watanabe, S. Yamanaka, H. Okushi, and K. Kajimura, *Phys. Status Solidi A* **174**, 101 (1999).

<sup>12</sup>J. Asmussen and D. K. Reinhard, *Diamond Films Handbook* (Dekker, New York, 2002), p. 141.

<sup>13</sup>J. Gaze, T. Obata, N. Oyanagi, H. Izawa, Y. Ikuhara, M. Kusunoki, and W. Zhou, *Nucl. Instrum. Methods Phys. Res. B* **121**, 427 (1997).

<sup>14</sup>Z. Tóth, Á. Mechler, and P. Heszler, *Appl. Surf. Sci.* **168**, 5 (2000).

<sup>15</sup>J. W. Rich and R. C. Bergman, *Chem. Phys.* **44**, 53 (1979).

<sup>16</sup>R. C. Bergman, G. F. Homicz, J. W. Rich, and G. L. Wolk, *Chem. Phys.* **78**, 1281 (1983).

<sup>17</sup>R. L. Deleon and J. W. Rich, *Chem. Phys.* **107**, 283 (1986).

<sup>18</sup>K. A. Snail, R. G. Vardiman, J. P. Estrera, J. W. Glesener, C. Merzbacher, C. J. Craigie, C. M. Marks, R. Glosser, and J. A. Freitas, *J. Appl. Phys.* **74**, 7561 (1993).

<sup>19</sup>D. B. Oakes, J. E. Butler, K. A. Snail, W. A. Carrington, and L. M. Hanssen, *J. Appl. Phys.* **69**, 2602 (1991).

<sup>20</sup>J. S. Kim and M. A. Cappelli, *Appl. Phys. Lett.* **65**, 2786 (1994).

<sup>21</sup>J. S. Kim and M. A. Cappelli, *J. Appl. Phys.* **84**, 4595 (1998).

<sup>22</sup>P. R. Buerki and S. Leutwyler, *J. Appl. Phys.* **69**, 3739 (1991).

<sup>23</sup>R. J. H. Klein-Douwel, J. J. L. Spaanjaars, and J. J. Meulen, *J. Appl. Phys.* **78**, 2086 (1995).

<sup>24</sup>H. Ling, Y. X. Han, M. Zhao, J. Sun, and Y. F. Lu, Proceedings of the Carbon Conference 2007, Seattle, 2007 (unpublished).

<sup>25</sup>F. G. Celii, *Annu. Rev. Phys. Chem.* **42**, 643 (1991).

<sup>26</sup>V. Mortet, Z. Hubicka, V. Vorlicek, K. Jurek, J. Rosa, and M. Vanecek, *Phys. Status Solidi A* **201**, 2425 (2004).

<sup>27</sup>Y. Matsui, A. Yuuki, M. Sahara, and Y. Hirose, *Jpn. J. Appl. Phys., Part 1* **28**, 1718 (1989).

<sup>28</sup>J. Asmussen and D. K. Reinhard, *Diamond Films Handbook* (Dekker, New York, 2002), p. 645.

<sup>29</sup>H. S. Myung, Y. S. Park, M. J. Jung, B. Hong, and J. G. Han, *Mater. Lett.* **58**, 1513 (2004).