University of Nebraska - Lincoln
DigitalCommons@University of Nebraska - Lincoln

Faculty Publications from the Department of Electrical Engineering

Electrical Engineering, Department of

11-26-2006

KrF excimer laser-assisted combustion-flame deposition of diamond films

Y. X. Han

Hao Ling
University of Nebraska - Lincoln, hling4@unl.edu

Yongfeng Lu
University of Nebraska - Lincoln, ylu2@unl.edu

Follow this and additional works at: http://digitalcommons.unl.edu/electricalengineeringfacpub

Part of the Electrical and Computer Engineering Commons

Han, Y. X.; Ling, Hao; and Lu, Yongfeng, "KrF excimer laser-assisted combustion-flame deposition of diamond films" (2006). *Faculty Publications from the Department of Electrical Engineering.* Paper 89.
http://digitalcommons.unl.edu/electricalengineeringfacpub/89

This Article is brought to you for free and open access by the Electrical Engineering, Department of at DigitalCommons@University of Nebraska - Lincoln. It has been accepted for inclusion in Faculty Publications from the Department of Electrical Engineering by an authorized administrator of DigitalCommons@University of Nebraska - Lincoln.

KrF excimer laser-assisted combustion-flame deposition of diamond films

Y. X. Han, H. Ling, and Y. F. Lu[a)]
Department of Electrical Engineering, University of Nebraska-Lincoln, Lincoln, Nebraska 68588-0511

(Received 2 July 2006; accepted 18 October 2006; published online 26 December 2006)

Cobalt (Co) composition has detrimental effects on the deposition of diamond films on cemented tungsten carbide (WC-Co) substrates. It decreases adhesion of the deposited films to the substrates and causes a transformation of sp^3-bonded diamond to sp^2-bonded graphite. In this study, a KrF excimer laser with a wavelength of 248 nm, a pulse width of 23 ns, and a pulse energy range of 84–450 mJ was used in the combustion-flame method to improve the quality of the deposited diamond films. Scanning electron microscopy, energy dispersive x-ray analysis, and Raman spectroscopy of the deposited films showed that a laser irradiation during combustion-flame deposition of diamond decreased the cobalt composition drastically. Based on the experimental results, the influence of the laser irradiation on the deposition process was analyzed. © *2006 American Institute of Physics*. [DOI: 10.1063/1.2402977]

I. INTRODUCTION

Diamond coatings are of great interest to industrial applications and scientific research due to their unique properties such as high hardness, high thermal conductivity, chemical inertness, wear resistance, transparency, and high electrical resistivity.[1] Many techniques, including chemical vapor deposition (CVD),[2,3] pulsed laser deposition (PLD),[4] and shock wave compression technique[5,6] have been developed to deposit diamond films on various substrates. However, most of the deposition techniques require high temperature and high pressure, or are based on the reaction of special gases (e.g., CH_4, H_2, etc.) in a vacuum chamber, which limit their potential for a large-scale production. Up to now, the only published technique that can obtain diamond films in open atmosphere is the combustion-flame method,[7–10] which uses the flame of C_2H_2 (or other hydrocarbon gases) and O_2 gases to create a reaction zone for diamond growth. QQC Inc., a Michigan-based company, applied patents[11,12] for their unique technique using three lasers with CO_2 and N_2 gases in open atmosphere to obtain high-quality diamond films. But the data in their patents are very limited and few groups could repeat their experimental results in the past years.

Since the invention of the combustion-flame method by Hirose and Komaki in 1988,[13] many researchers have made tremendous efforts to improve the technique to obtain high-quality and uniform diamond films. The most significant parameters in this technique are the gas ratio, the total flow rate, the growth temperature, and the distance between the substrate surface and the inner cone of the flame.[7] It is generally agreed that diamond growth can be achieved by a gas ratio (C_2H_2/O_2) of 0.9–1.2[14] and a temperature range of 400–1200 °C.[7] Abe *et al.*[15] obtained highly uniform and dense diamond microcrystalline thin films using a combustion flame surrounded by an inert gas flow. Thorpe *et al.*[16] used a growth-etch cycling method to achieve high-quality diamond. By placing the flame in an enclosed chamber, Takeuchi and Murakawa[17] reduced the effect of N_2 composition in open air. Donnet *et al.*[18] treated WC-Co substrates in a boiling solution of 17% HCl to minimize the Co content and increase the roughness on substrate surfaces for better deposition. All these research efforts improved the technique in certain aspects.

In this study, a KrF excimer laser was used with a combustion flame to deposit diamond coatings on WC-Co substrates. The objectives of this work were to obtain an understanding of the interactions and effects of pulsed laser irradiation on the diamond growth, and to explore the conditions that could achieve better diamond film quality.

II. EXPERIMENTAL SETUP

Figure 1 shows a schematic diagram of the experimental setup used in this study, which contains a KrF excimer laser (COMPexPro 205, Lambda Physik), optics for directing the laser beam, a commercial C_2H_2/O_2 combustion-flame welding torch, a gas supply, and a water-cooling system. The welding torch had an orifice with a diameter of 1.5 mm. The gas ratio of C_2H_2/O_2 was controlled to be 0.90 by flow meters (B7920V, Spec-Air Gases & Technologies) and the total gas flow was settled at 2.38 slm (standard liters per minute). WC-Co substrates were placed on the surface of a hollow brass block with water coming in from one side and going out from the other side. The distance between the sub-

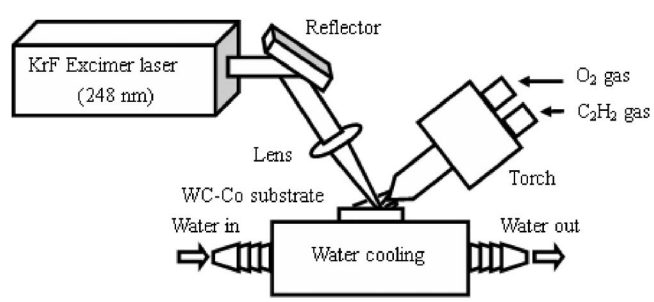

FIG. 1. Schematic experimental setup for laser-assisted combustion-flame deposition of diamond films on WC-Co substrates.

[a)]Author to whom correspondence should be addressed; electronic mail: ylu2@unl.edu

 © 2006 American Institute of Physics

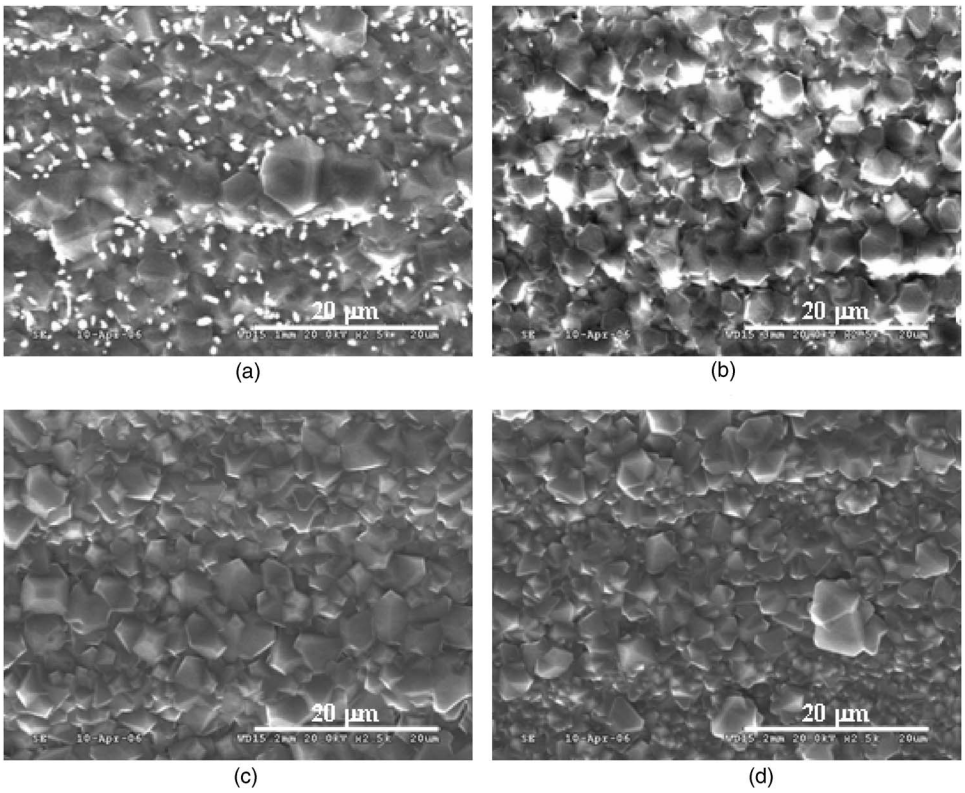

FIG. 2. SEM images of the center of diamond films after 15 min deposition: (a) no laser irradiation, and with a pulsed KrF excimer laser irradiation at 1 Hz with fluences of (b) 142, (c) 247, and (d) 361 mJ/cm^2.

strate surfaces to the inner cone of the flame was 1 mm. A KrF excimer laser beam with a wavelength of 248 nm, a pulse width of 23 ns, and a pulse energy range of 84–450 mJ was directed by mirrors and focused by a convex lens with a focusing length of 150 mm to the substrate surfaces right under the flame. The incident angle of the laser beam was fixed at 35° to the normal of the substrate surfaces. The flowing direction of the flame was kept at 55° to the normal of the substrate surfaces. The laser beam covered the whole deposition area. Deposition time was 15 min. The WC-Co substrates (BS-6S, Basic Carbide Corp.) with a dimension of $25.4\times25.4\times1.6$ mm^3, a Co composition of 6%, and a surface roughness of 0.40 μm were ultrasonically cleaned in an acetone liquid for 30 min before deposition. The surface temperature of the substrates was monitored during deposition by a pyrometer (OS3752, Omega Engineering, Inc.) and was controlled to be 750 °C by varying the contact condition between the substrates and the water-cooling brass block. The repetition rate of the laser pulse was set to be 1 Hz and the incident laser fluence on the substrate surfaces was varied. After each experiment, an Ar gas flow was used to replace the flame immediately to protect the substrate surfaces from being oxidized.

A scanning electron microscope (SEM) (Hitachi S-3000N) was used to characterize the morphologies of the deposited films. The SEM has an Oxford Inca energy dispersive x-ray (EDX) analysis system with a light element x-ray detector [15 mm working distance; distance between focal plane and detector (WD)] and has a spectrum imaging software which allows spectra to be collected corresponding to the SEM images. The thickness of the deposited films was characterized by a stylus profilometer (XP-2, Ambios Technology). A homemade Raman system,[19] consisting of a 514.5 nm Ar ion laser (Innova 300, Coherent, Inc.), a triple-grating dispersive imaging spectrograph (SP-2300i, Princeton Instrument) equipped with a charge-coupled device (CCD) camera (PIXIS 400B, Princeton Instrument), and optics, was used to examine the bonding structures in the films. The Ar ion laser power used was between 20 and 30 mW, which produced efficient Raman excitation while maintaining no damage to the examined area. The laser beam was focused to a spot diameter of approximately 2 μm. Prior to and after Raman characterization of the deposited films, the Raman system was calibrated and rechecked using a Si substrate and a pure graphite plate. Three spectra at different positions of each film were recorded and averaged to minimize the random effects.

III. RESULTS AND DISCUSSION

A. Film morphology

Diamond films were obtained after 15 min deposition under all conditions with and without laser irradiation. The morphologies of deposited films were studied with a SEM. The images at the center of the films are shown in Fig. 2. In all cases, deposited films consist of polycrystalline grains. It is observed that in the case without laser irradiation, as shown in Fig. 2(a), the film was interspersed by impurities (tiny white spots) with a diameter of around 1 μm. When a KrF excimer laser beam with a repetition rate of 1 Hz and a fluence of 142 mJ/cm^2 was introduced during the deposition process, there were fewer impurities in the obtained film, as shown in Fig. 2(b). If the laser fluence was increased to 247 mJ/cm^2, almost no impurities could be observed, as in

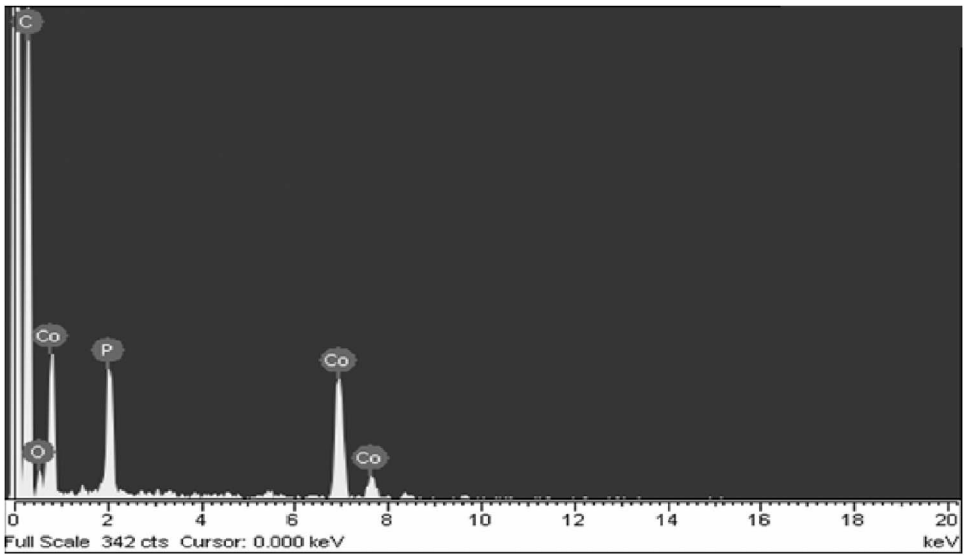

FIG. 3. An EDX spectrum of the impurities (white spots) dispersed on the deposited diamond films.

the case of Fig. 2(c). With a higher laser fluence, 361 mJ/cm^2, a similar result was obtained, and the SEM image is shown in Fig. 2(d).

From the SEM images shown in Fig. 2, it is also noticed that the average diamond crystal size became smaller when a laser irradiation was introduced. Under current experimental parameters, the higher the laser fluence was, the smaller the diamond crystals were. The film thickness was examined by a stylus profiler to be about 5 μm in the center of the films in all cases, which meant similar diamond growth rates. The change in crystal size could be explained by the fact that higher laser energy introduced more crystal defects during deposition, and each defect could serve as a new site for a secondary nucleation. Since the flow rate and the gas ratio were fixed, the C source was unchanged. Under a fixed deposition time, the incoming C atoms were distributed to the newly introduced nuclei, and thus led to smaller crystal sizes.

B. Film composition

An EDX analysis associated with SEM was used to characterize the composition of deposited films. Figure 3 shows an EDX spectrum of the impurities presented in Figs. 2(a) and 2(b). It can be seen that there was high content of Co and O in the impurities. Donnet *et al.*[18] explained the diffusion of Co in diamond films synthesized by a combustion flame as a thermally induced process. At high substrate temperatures, ball-shaped Co particles were formed on the substrate surfaces at initial deposition times. The Co atoms interacted with C atoms and were transformed to C-saturated Co. The growth of diamond crystals developed a displacement of Co, and the particles were reassembled and increased in size. The defects around Co particles provided sites for a secondary diamond nucleation, which, in turn, could displace the Co particles. With the increase in deposition time, diamond crystals could grow over some Co particles, but a large number of Co containing particles attached on the diamond facets were moved to the top surface and eventually fell together.

Table I shows a quantitative EDX analysis of the composition in the deposited films according to the SEM images in Figs. 2(a)–2(d). From Table I, it could be observed that the main composition in all films was C, which was in agreement with the diamond crystals observed in Fig. 2. It is also noticed that there were O and Co compositions in all films. The O composition was introduced either by flame reaction during the deposition or by the intermittent retraction of the flame and replacement of the Ar gas. The Co composition was from the WC-Co substrates. From Table I, it was observed that with the increase in laser fluence, the C composition increased and the Co composition decreased correspondingly.

The absence of Co particles in Figs. 2(c) and 2(d) could possibly be explained by the laser cleaning effect.[20,21] During the deposition process, diamond crystals were formed on substrate surfaces while Co composition came out of the substrates and formed Co particles due to high temperature.[18] The adhesion force between the Co particles and the substrate surfaces was mainly van der Waals force. Under a laser pulse, the Co particles absorbed the laser energy, causing an abrupt thermal expansion which occurred within a very short period of time, resulting in a large acceleration sufficient to eject the Co particles from the substrate surfaces. Since diamond has a poor absorption of the laser light, the cleaning efficiency for the synthesized diamond crystals was much lower. Most of the diamond crystals remained on the substrate surfaces and served as nuclei for further growth.

C. Film structures

The atomic bonding structures in the deposited films were characterized by a homemade Raman system.[19] Figure 4 shows a series of Raman spectra corresponding to the de-

TABLE I. Composition of diamond films (at. %) after 15 min deposition: (a) no laser irradiation, and with KrF excimer laser irradiation at 1 Hz with fluences of (b) 142, (c) 247, and (d) 361 mJ/cm^2.

Element	Film a	Film b	Film c	Film d
C	94.31	97.57	97.82	97.89
O	4.12	1.51	2.09	1.95
Co	1.20	0.68	0.09	0.08

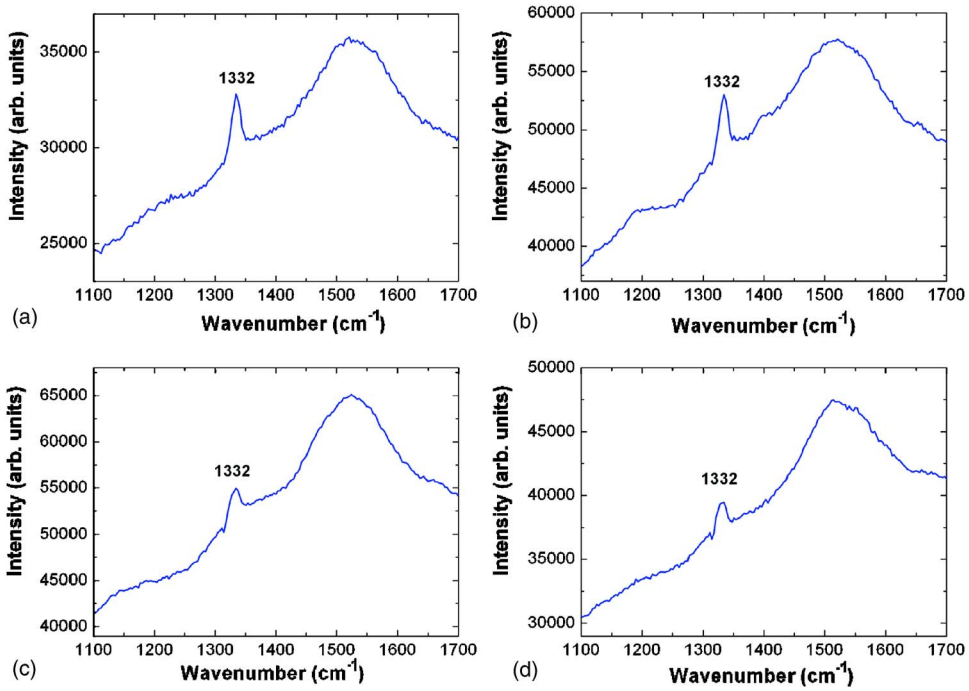

FIG. 4. (Color online) Raman spectra of the center of diamond films after 15 min deposition: (a) no laser irradiation, and with a pulsed KrF excimer laser irradiation at 1 Hz with fluences of (b) 142, (c) 247, and (d) 361 mJ/cm^2.

posited films shown in Figs. 2(a)–2(d), respectively. The sharp peaks due to diamond were detected at 1332 cm^{-1}, which correspond to low stressed diamond films. The broad peaks centered at ~1520 cm^{-1} stand for amorphous (nanocrystalline) carbon. This means that the films consisted of diamond crystals in a matrix of amorphous carbon. However, from literature[22] the sensitivity of the Raman spectroscopy to the sp^2 carbon hybridization-bond phase is about 50 times greater than that of the sp^3 diamond hybridization-bond phase. Thus the films were predominantly composed of diamond crystals. Under current experimental conditions, no crystalline (1580 cm^{-1}) or microcrystalline (1350 cm^{-1}) graphite phonons[23] were observed in the Raman spectra.

The quality of the deposited diamond films was characterized by the ratio of diamond to amorphous carbon (1332 cm^{-1}/1520 cm^{-1}) peak heights,[23] R_{dc}, in the Raman spectra and was plotted versus laser fluence, as shown in Fig. 5. The highest-quality diamond, as determined by the ratio,

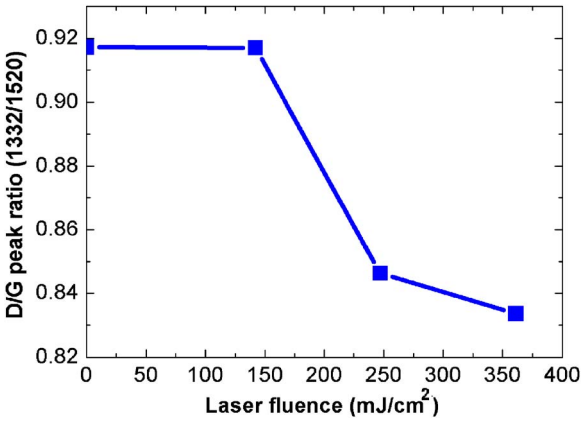

FIG. 5. (Color online) Ratio of the diamond Raman peak intensity (1332 cm^{-1}) to the amorphous carbon peak intensity (1520 cm^{-1}) as a function of the laser fluence.

was obtained when there was no laser involved. When a laser beam was introduced in the process, the diamond quality decreased. Higher laser fluences produced diamond with lower quality. However, it is noticed from Fig. 5 that a low-fluence laser beam (142 mJ/cm^2) did produce similar diamond quality as the case without laser irradiation. Referring to the SEM images presented in Fig. 2 and EDX analysis in Table I, it could be concluded that the deposition process with a laser fluence of 142 mJ/cm^2 was optimal, with low Co impurities in the film and high diamond quality.

It is well known that diamond is a metastable form of carbon at low temperatures. At high temperatures or with external actions such as ultrashort laser pulses or high-energy electron/ion beam irradiation, it tends to transform to its stable form of graphite.[24] The increased composition of sp^2-bonded composition (amorphous carbon and graphite) with higher laser fluences in this study was due to laser-induced graphitization of diamond.[24–26] Higher laser fluences produced more photons, which were absorbed by the surface carbon atoms and assisted their transition from a diamond state (sp^3 bonding) to a graphite or amorphous state (sp^2 bonding). Laser energy might have other functions which potentially affect the diamond deposition process. More investigations are being carried out.

The Raman spectroscopy of a single diamond grain was performed with a commercial micro-Raman system (Renishaw inVia Raman Microscope). The Raman spectrum is shown in Fig. 6. The Raman system consists of a 488 nm Ar ion laser and an integrated confocal microscope. Prior to the characterization, the system was calibrated using a Si substrate, and a Raman shift at 520 cm^{-1} was detected. From Fig. 6, both a sharp diamond peak at 1337 cm^{-1} and a low-intensity broad peak at 1550 cm^{-1} indicate that the diamond crystal is of high quality.

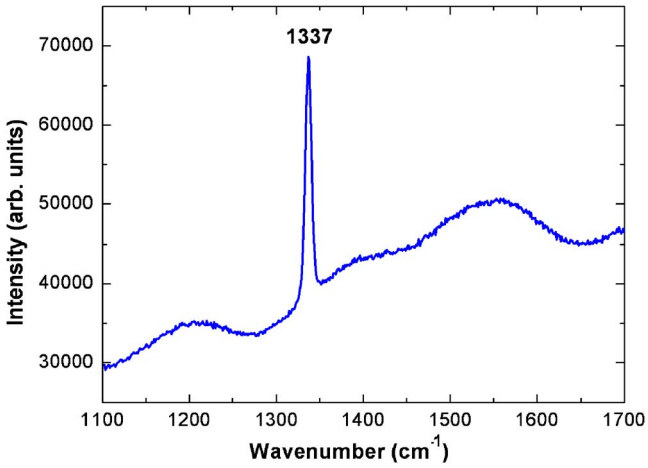

FIG. 6. (Color online) A Raman spectrum of a diamond grain at the film center after 15 min deposition without laser irradiation.

IV. CONCLUSIONS

Diamond films were obtained on WC-Co substrates in open atmosphere using a C_2H_2/O_2 combustion flame combined with a KrF excimer laser irradiation. SEM images showed that after 15 min deposition the films consisted of C-saturated Co particles. The laser irradiation was found to reduce the Co impurities, while it decreased the crystal size of the synthesized diamond. The removal of Co impurities was possibly due to the laser cleaning effect, while the decrease in crystal size was explained by the fact that the laser-induced crystal defects provided more nuclei for a secondary diamond nucleation. Raman spectra of the deposited films showed that the introduction of a high-fluence laser irradiation decreased the diamond quality. It was found that under current experimental conditions, a laser fluence of 142 mJ/cm^2 was optimal to produce high-quality diamond films with low Co impurities.

ACKNOWLEDGMENTS

The authors would like to thank Dr. D. Doerr and Dr. D. Alexander of the Department of Electrical Engineering at the University of Nebraska-Lincoln (UNL) for providing convenient access to their SEM, Dr. N. Ianno for offering access of his stylus profilometer, Dr. Y. Zhou of the Beadle Center at UNL for help on SEM and EDX, and Dr. S. W. Martin and his students of the Department of Materials Science and Engineering at the Iowa State University for their help on the micro-Raman system. The homemade Raman system was built by K. J. Yi, who the authors would like to thank for great efforts. This work was financially supported by the U.S. Office of Naval Research (ONR) through the Multidisciplinary University Research Initiative (MURI) Program.

[1]Y. F. Lu, S. M. Huang, X. B. Wang, and Z. X. Shen, Appl. Phys. A: Mater. Sci. Process. **66**, 543 (1998).
[2]J. Wei, J. M. Chang, and Y. Tzen, Thin Solid Films **212**, 91 (1992).
[3]D. Michau, B. Tanguy, and G. Demazeau, Mater. Lett. **17**, 192 (1993).
[4]M. Novotny, M. Jelinek, J. Bulir, J. Lancok, V. Vorlicek, and J. Bonarski, Appl. Phys. A: Mater. Sci. Process. **79**, 1267 (2004).
[5]O. G. Epanchintsev, A. S. Zubchenko, A. E. Korneyev, and V. A. Simonov, J. Phys. Chem. Solids **58**, 1785 (1997).
[6]D. J. Erskine and W. J. Nellis, Nature (London) **349**, 317 (1991).
[7]T. L. Huu, H. Zaidi, and D. Paulmier, Thin Solid Films **308**, 147 (1997).
[8]J. B. Donnet, H. Oulanti, T. L. Huu, and M. Schmitt, Carbon **44**, 374 (2006).
[9]Y. Ando, S. Tobe, T. Saito, J. Sakurai, H. Tahara, and T. Yoshikawa, Thin Solid Films **457**, 217 (2004).
[10]H. S. Shin and D. G. Goodwin, Appl. Phys. Lett. **66**, 2909 (1995).
[11]M. C. Turchan and P. Mistry, U.S. Patent No. 5,554,415 (10 September 1996).
[12]P. Mistry and M. C. Turchan, U.S. Patent No. 5,731,046 (24 March 1998).
[13]H. Hirose and K. Komaki, European Patent Publication No. EP0324538 (19 July 1988).
[14]D. W. Zhang, Z. J. Liu, Y. Z. Wan, and J. T. Wang, Appl. Phys. A: Mater. Sci. Process. **66**, 49 (1998).
[15]T. Abe, M. Suemitsu, and N. Miyamoto, J. Appl. Phys. **74**, 3531 (1993).
[16]T. P. Thorpe, R. A. Weimer, and J. A. Freitas, Appl. Phys. Lett. **65**, 2490 (1994).
[17]S. Takeuchi and M. Murakawa, Thin Solid Films **377**, 290 (2000).
[18]J. B. Donnet, D. Paulmier, H. Oulanti, and T. L. Huu, Carbon **42**, 2215 (2004).
[19]K. J. Yi, Y. F. Lu, and H. Ling, Proc. SPIE **6107**, 610700 (2006).
[20]Y. W. Zheng, B. S. Luk, Y. F. Lu, W. D. Song, and Z. H. Mai, J. Appl. Phys. **90**, 2135 (2001).
[21]D. R. Halfpenny and D. M. Kane, J. Appl. Phys. **86**, 6641 (1999).
[22]D. Paulmier, T. L. Huu, and H. Zaidi, Surf. Sci. **377**, 866 (1997).
[23]D. B. Oakes, J. E. Butler, K. A. Snail, W. A. Carrington, and L. M. Hanssen, J. Appl. Phys. **69**, 2602 (1991).
[24]V. N. Strekalov, V. I. Konov, V. V. Kononenko, and S. M. Pimenov, Appl. Phys. A: Mater. Sci. Process. **76**, 603 (2003).
[25]C. Z. Wang, K. M. Ho, M. D. Shirk, and P. A. Molian, Phys. Rev. Lett. **85**, 4092 (2000).
[26]S. Preuss and M. Stuke, Appl. Phys. Lett. **67**, 338 (1995).