CO₂ LASER-ASSISTED LOCAL DEPOSITION OF DIAMOND FILMS BY COMBUSTION-FLAME METHOD

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Abstract

Diamond films were synthesized on WC-Co substrates in open air by CO₂ laser-assisted C₂H₂/O₂ combustion-flame deposition. A CO₂ laser was used to irradiate the growth area to create a locally heated zone while the bulk of the substrate was kept at a lower temperature by efficient water cooling. Diamond grains grew with various orientations such as (100) and (111) in laser-induced craters. A sharp diamond peak was observed in Raman spectroscopy indicating high quality of the diamond crystals. Surface morphologies of the deposited films were characterized by scanning electron microscopy (SEM) with energy dispersive X-ray (EDX) analysis so that element distribution on the WC surfaces after deposition was measured simultaneously. Some diamond grains were embedded into the WC-Co substrate surfaces, which was promising to increase adhesion between the deposited films and the substrates. A two-stage approach was developed to deposit dense films without peeling off.

Keywords: diamond, combustion-flame deposition, CO₂ laser irradiation, scanning electron microscopy

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 (Asmussen, 2002). A variety of techniques of diamond film growth have been accomplished in the last 50 years since the 1950s. Methods of diamond film growth under conditions of pressures less than one atmosphere and substrates temperatures less than 1100 °C, such as chemical vapor deposition (CVD) (Wei, 1992; Michau, 1993) and microwave plasma deposition, (Itoh, 1998) have been developed besides the high-pressure and high-temperature (HPHT) technique. C₂H₂/O₂ combustion-flame method for diamond film growth in open air was first reported by Hirose and Kondo in 1988 (Hirose, 1988), which promoted the applications of diamond films.

Although high quality diamond films have been prepared by these abovementioned methods, there are still some remaining issues in diamond growth. The growth temperature around 800 °C still prevents diamond films from growing on some substrates that cannot endure such high temperatures for a long time. Adhesion between the diamond films and the substrates is not as good as expected after such a thermal process. Therefore, local heating is a promising method to deposit diamond films in a desired area on a substrate, without heating the whole substrate entirely. Furthermore, the local high temperature can induce a surface melting with a depth of several micrometers in growth area, which could lead to an embedded growth of diamond grains.

Laser heating and melting have been widely used in scientific research and industry. Silicon substrate illumined by a CO₂ laser in hot-filament CVD was reported to keep the substrate temperature at 800 °C (Gaze, 1997). Local laser-assisted hot filament CVD of diamond films using precursors of CH₄/H₂ in a chamber was carried out by Toth et al. (Toth, 2000). A continuous-wave Nd:YAG laser with a power of tens of milliwatts was used in their experiments to achieve a local growth. However, most of the reports are related to laser-assisted CVD in a chamber that restricts the applications in industry.

In this study, laser-assisted combustion-flame deposition of diamond films in open air was investigated. A high-power CO₂ laser was used to heat the growth area while the whole substrate was sufficiently cooled. The deposition time was around 10 min. Diamond films were deposited at the desired area. Some diamond grains were embedded into the WC-Co substrate surfaces, promising to increase the adhesion between the deposited films and the substrates. To prevent the films from peeling off, a high laser power was used to promote the seeding in the initial 1 min and then a low laser power was used to maintain the growth temperature for 10 min.

Experimental setup

Figure 1 shows a schematic diagram of the experimental system used for CO₂ laser-assisted combustion-flame deposition in this study. A tungsten carbide substrate (BS-6S, Basic Carbide Corp.) with a cobalt composition of 6% (WC-Co) was placed on a hollow brass block with efficient water cooling. A commercial welding torch was used to generate a C₂H₂/O₂ combustion flame that was directed to the WC-Co substrate with an incident angle of 45°. The welding torch had an orifice with a diameter of 1.5 mm. The gas ratio of C₂H₂/O₂ was controlled to be 0.90 by two flow meters (B7920V, Spec-Air Gases & Technologies). The total gas flow was fixed at 2.38 standard liters per minute (slm). The distance between the substrate surface and the inner cone of the flame was about 1 mm. Purities of the C₂H₂ and O₂ gases were 99.6% and 99.996%,

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respectively. Dimensions of the substrates were 25.4×25.4×1.6 mm³ with a surface average roughness of about 400 nm. The substrates were cleaned in a supersonic bath of acetone for 30 min before film deposition. A continuous-wave CO₂ laser (PRC Company) beam with 10.6 μm wavelength was focused to the substrate surface perpendicularly by a ZnSe convex lens. The focal length of the ZnSe lens was 190 mm. The laser power was 400 or 50 W in current experiments. The surface temperature of each substrate during deposition was monitored by a pyrometer (OS3752, Omega Engineering, Inc.).

Surface morphologies of the diamond films were studied by an SEM including an EDX system (Hitachi S-3000N). Raman spectroscopy was performed using a Renishaw Invisa Micro-Raman system consisting of a 488 nm Ar⁺ laser to characterize the structures of the films. The micro-Raman is capable of measuring selected areas about several square micrometers, which was used to characterize the bonding vibration frequency of the embedded grains in substrates.

**Results and discussion**

A diamond film was obtained after a 10 min flame deposition with a 400 W laser irradiation. The surface temperature of the substrate in the aimed area by the pyrometer was about 750 °C during the deposition. When there was no laser irradiation, the surface temperature was below 600 °C because of the efficient cooling, which led to slow deposition of the film. The temperature reading from the pyrometer was an average temperature of the aimed area detected through the pyrometer. The temperature gradient caused by the laser beam (Toth, 2000) in this aimed area could not be determined by the pyrometer. The detected area, depending on the distance between the pyrometer and the sample, was usually larger than the growth area in current experiments.

Figure 2 shows SEM images of a diamond film prepared with a CO₂ laser power of 400 W during the 10 min deposition.
It was clear that diamond grains with (111) facet grew on the substrate surface densely in the center of the laser-induced crater. The grain sizes were several micrometers while the deposition rate was about 1 μm/min. The Raman spectrum of the diamond film was shown in Fig.3. The sharp peak at the wavenumber of 1335 cm⁻¹ is the typical Raman signal of diamond. A broad band centered at 1550 cm⁻¹ corresponds to graphite-like carbon (G peak), which was at 1580 cm⁻¹ for graphite crystal. The red shift of G peak indicates the increase in sp³ bonding in the film, which is in agreement with the growth of diamond. It is noticed that the position of the diamond peak is higher than the normal wavenumber of the single crystal diamond at 1332 cm⁻¹ (Donato1, 2001 and Brescia1, 2003). The shift may be due to the stress in the film caused by the quenching process when the laser and the flame were shut down.

Peeling off of the deposited film was observed in most of the crater area was possibly due to the quenching as well. In Fig. 2, the area densely covered by diamond grains is only about a quarter of the crater area. Figure 4 shows the surface

![Figure 3. Raman spectrum of diamond film deposited with 400 W CO₂ laser irradiation for 10 min.](image)

![Figure 4. SEM images of different areas in a crater irradiated by 400 W CO₂ laser irradiation for 10 min.](image)
features in detail at different positions in the crater. The boundary between the densely and sparsely covered areas is clear while some diamond grains can be observed in the sparsely covered area. The diamond grains near the boundary show square facets, indicating that the (100) orientation was dominant (Ferrari, 2000). The growth orientation near the boundary is different from that in the crater center, which is related to the temperature gradient (Titus, 2002).

It is observed that some diamond grains can be embedded into the substrate surface in the sparsely covered area in the crater. EDX analysis associated with SEM was used to characterize the composition of the embedded grains. For a comparison, Figure 5 shows an EDX spectrum taken from an untreated WC-Co substrate. The composition of carbon is about 42% in the untreated substrate. Figure 6 shows an SEM image taken from a sparsely covered area in the crater. Some crystal grains with several micrometers in size were embedded into the WC-Co surface. EDX analysis of a randomly selected grain reveals the composition in the grain has carbon over 96%. The surrounding area, however, has a carbon composition about 44%, which is close to the carbon composition in the untreated substrate. Micro-Raman spectrum was also taken with a

![Figure 5. EDX spectrum of an untreated WC-Co substrate.](image1)

![Figure 6. EDX and Raman spectra of the embedded grain.](image2)
randomly selected grain. The spectrum shows a diamond peak at the wavenumber of 1334 cm\(^{-1}\). G band in the spectrum indicates that the sp\(^2\) bonds were formed simultaneously. The sp\(^2\) carbon is possibly the impurities in the diamond grain. Since the sensitivity of Raman spectroscopy to the sp\(^2\) carbon hybridization-bond phase is much higher than that of the sp\(^3\) hybridization-bond phase (Paulmier, 1997), the composition of the sp\(^2\) carbon is very low. Another possibility is that the sp\(^2\) carbon exists outside of the diamond grain. Because the diamond grain is transparent to the 488 nm Ar\(^+\) laser, the Raman signal of graphitic carbon under the diamond grain can still be detected.

Holes and gaps besides the embedded grains can be observed in the SEM image. When the laser beam was focused onto the substrate surface, the surface melting occurred with a depth of several micrometers without affecting the bulk of the substrate (Duitsch, 2004). The nucleation of diamond occurred with some surface defects that could be induced by laser irradiation. Some seeds were sunk into the melting layer and grew larger. As a result, some diamond grains were embedded into the substrate surface, which is promising to increase the adhesion between the film and the substrate.

Since the film peeling off occurred when using the 400 W laser irradiation, a lower laser power of 50 W was used to assist the flame deposition. However, there were few diamond grains on the substrate after 10 min deposition. An approach using two-stage laser heating with different powers was designed to improve the diamond film growth without peeling off. In the first stage, a laser power of 400 W was used for 1 min at the beginning of deposition. After 1 min, the laser power was adjusted to 50 W to maintain the growth temperature around 700 °C in the second stage for 10 min.

Figure 7 shows the SEM images of a deposited film by the two-stage laser heating. The crater in Fig. 7 is not as clear as that in Fig. 2, which indicates the low damage of substrate surface. Diamond grains covered all over the crater densely after deposition although some gaps with dimensions of several micrometers could be found at some locations. In the gap shown in Fig. 7, it is found that the film is not a single layer. The grain size in Fig. 7 is smaller than that in Fig. 2, implying that the growth rate is lower than the case with 400 W laser irradiation for 10 min. The Raman spectrum of the deposited film is shown in Fig. 8. A sharp diamond peak at 1334 cm\(^{-1}\) and a broad G band in the spectrum are ascribed to the high quality diamond grains mixed with sp\(^2\)-bonded carbons.

Surface reflection of the WC-Co substrate results in a low efficiency of laser absorption. When the 50 W laser power was introduced to the untreated WC-Co surface, the absorption of the laser energy was not effective to heat the growth area. Therefore, the temperature was insufficient to promote the diamond nucleation that depends on the surface temperature.

**Figure 7.** SEM images of the diamond film deposited with CO\(_2\) laser power (400 W 1 min plus 50 W 10 min).
intensively (Asmussen, 2002). As a result, little nucleation led to the few deposited grains. When a laser power of 400 W was used, the energy absorbed by the WC-Co surface was sufficient to increase the temperature in the growth area. The laser heating not only supported the temperature for the nucleation, but also enhanced the nucleation by making some defects on the WC-Co surface (Asmussen, 2002). Furthermore, the diamond nucleation on the WC-Co surface improved the absorption of the laser energy due to the modification of the surface morphology that decreases the surface reflection. Thus a laser power of 50 W was sufficient for deposition during the second stage of 10 min deposition.

**Conclusions**

Diamond films were synthesized on the WC-Co substrates in open air by the CO$_2$ laser-assisted C$_2$H$_2$/O$_2$ combustion-flame deposition with strong water cooling. Raman spectra with the sharp diamond peak proved the high quality of the deposited diamond grains in the films while some graphitic carbons were also detected. Orientations were dominantly (100) and (111) in different areas in the crater due to the temperature gradient. A high laser power of 400 W could lead to growth of embedded diamond grains while film peeling off occurred possibly because of the quenching process. The two-stage laser heating to obtain diamond films without peeling off was realized. A laser power of 400 W was efficient to enhance the nucleation of diamond at the beginning of 1 min. A laser power of 50 W was better to maintain the growth temperature without excessive heating during the later 10 min. Based on the experimental results, CO$_2$ laser-assisted combustion-flame deposition is a promising method for local heating during diamond film growth although the temperature control remains a challenge.

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**References**


