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Manufacturing Diamond Films Using Copper Vapour Lasers

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Abstract
Fifty nanosecond pulses of visible light have been used to produce hard, hydrogen-free diamond-like-carbon (DLC) films at irradiances between $5 \times 10^8$ and $5 \times 10^{10}$ W/cm$^2$. The films were characterized by a number of techniques including: Raman spectroscopy, Electron Energy Loss Spectroscopy (EELS), atomic force microscopy, and spectroscopic ellipsometry. The cost for manufacturing DLC with high average power, high-pulse repetition frequency, visible light is low enough to compete with other diamond thin film production methods.

Introduction
The production of thin film coatings by the pulsed laser deposition (PLD) process has been demonstrated for over 100 compounds. It is interesting to note that the majority of these experiments have been performed with excimer lasers and that very few reports of PLD with visible light have been published. This is in spite of the fact that visible light is well established as a means for laser cutting of a number of industrially important materials such as stainless steels, SiC, Al$_2$O$_3$, etc. In this report we discuss the use of the visible light (510 and 578 nm) generated by high average power, high pulse repetition frequency (PRF) copper vapour lasers (CVLs) to form diamond-like-carbon (DLC) films. The use of such lasers makes the mass production of DLC films at competitive prices possible.

DLC is an interesting material from many points of view. It possesses a high degree of hardness, a low coefficient of friction, a low electronic work function, and is chemically inert to strong acids and bases as well as bio-compatible. DLC is finding increasing use in wear coatings on machine tools, bearing surfaces for machinery and prosthetic joints, protective coatings on magnetic information storage media and farinfrared detectors, and, in an intriguing application, as a cold cathode emitter for advanced electronic components such as flat panel displays. DLC produced by the PLD process is distinguished from that produced by standard chemical vapor deposition (CVD) techniques in that it is hydrogen free and because PLD is a room temperature process. Because it is a low temperature process it is possible to deposit high quality DLC films on materials, such as plastics, with low melting points. DLC produced by PLD is also different from the hydrogen free materials made by cathodic arc techniques in that it is extremely smooth and particulate free.
Experimental

The laser system used in this work consisted of a 30-W CVL oscillator whose output beam was directed into one or more 300-W CVL amplifiers in series as shown in Fig. 1. The laser beam was directed into a stainless steel vacuum chamber through a fused SiO$_2$ window with anti-reflective coatings. A thin (0.25 μm) Mylar film was advanced past the interior surface of the window to prevent the build-up of ablation products. A reel-to-reel Mylar roller system held sufficient material to protect the window for several hours of continuous coating. The output characteristics of the CVL chain were as follows:

- Wavelength: 510 nm + 578 nm (at a roughly 2:1 ratio)
- Pulse width: 50 ns (FWHM)
- PRF: 4.4 kHz
- Pulse power: 20–70 mJ

Fluence at the target surface was adjusted by means of a 1500-mm focal length dichroic lens to levels of 25–1000 J/cm$^2$.

The target itself consisted of a 150-mm diameter disk of graphite (POCO AXM-5Q grade) that had been formed by standard machine shop practices with a surface finish of

![Figure 1. Pulsed laser ablation system.](image-url)
±0.8 μm. The disks were repetitively cleaned in an ultrasonic cleaner filled with deionized water until fresh batches of water remained clear for a period of two minutes or more. In order to provide an ample supply of virgin target material for long duration coating experiments, up to 25 of the target disks could be stacked on a rotary/linear vacuum feedthrough. The target stacking and changing mechanism is illustrated in Fig. 2. During the PLD process the target disk was rotated by a variable speed motor such that, at any disk radius, the linear velocity was approximately 8 cm/s. Fresh “tracks” of target material could be exposed by translating the disk beneath the fixed laser beam. The disk could be translated a linear distance of 50 mm such that 85% of the target surface could be accessed by the laser. When the target was consumed, it was picked up by a simple shuttle mechanism and moved to a second position where it was stacked on similar spent targets. At this point the new target was translated vertically to the focal plane of the laser. By limiting the targets to 1 pass through the laser impact zone at a velocity of 8 cm/s, we were able to suppress the formation of large particles in the ablation plume. We believe that by limiting the depth of the crater produced by the laser that we minimize the opportunities for surface roughening that often results in particle removal.

Figure 2. Target stacking and changing system.
Substrates consisted of 150-mm Si(100) disks that had been cleaned in 10% solutions of HF and H₂O shortly before insertion into the vacuum chamber. The substrates were mounted on a long throw (750 mm) linear/rotary vacuum feedthrough in an ante chamber (or load lock) at the top of the vacuum system. The substrate holder was provided with sliding electrical contacts that allowed heating and/or biasing while the disks were rotated. The coating thickness distribution on the substrate could be tailored by translating the rotating substrate back and forth over the laser impact zone. Film thickness distributions were determined *ex situ* by diamond stylus profilometry of steps created by masking portions of the substrate with strips of adhesive mylar tape prior to coating and subsequently removing the strips. Thicknesses could also be measured *in situ* by translating the substrate vertically until it could be accessed by a spectroscopic ellipsometer mounted to the vacuum chamber. An additional diagnostic consisted of an emission spectrometer mounted to view the vapor plume above the target.

**Results**

An atomic force microscope (AFM) image of the surface of a typical DLC film is illustrated in Fig. 3. At high magnifications, small nodules with a diameter of 0.25 μm and a surface roughness of ±10 nm are seen. At lower magnifications, the absence of large particles is notable but typical of the films grown with this system. Macroscopic views of cross sections of thick films are of little interest. The absence of features such as voids, cracks, nodules, or grains illustrates the dense, amorphous nature of the films. The variation of thickness across a 150-mm substrate (that was not rotated) is illustrated in Fig. 4 and follows the characteristic $\cos^m\phi$ distribution where $\phi$ is the angle measured from the target normal and $m$, in this case is 6.5. The distribution in Fig. 4 was produced by 88 k laser shots (or 20 seconds of laser time) at a substrate to target spacing of 150 mm and an irradiance of $5 \times 10^8$ W/cm² with an average power of 300 W. The integrated volume of the distribution gives a coating rate of 8,000 μm cm⁻²/h at this power level. It should be noted in passing that the integrated volume at fixed irradiance scales linearly with the average power of the laser.

There have been suggestions in the literature that the formation of DLC by PLD is wavelength dependent; that one should, in fact, not make high quality DLC with visible light [1]. For this reason, we endeavored to physically characterize the material produced with CVLs as carefully as possible. The most reliable measurement of diamond-like character is Raman spectroscopy. The Raman spectrum of a DLC film grown at $5 \times 10^8$ W/cm² is shown in Fig. 5. A single asymmetric peak centered at 1580 wavenumbers was observed. Such peaks are characteristic of DLCs and are distinctly different from other forms of carbon such as the graphite spectrum inset on the upper right of Fig. 5 and the diamond spectrum inset on the upper left [2]. The shape and position of the Raman peak did not change significantly as a function of irradiance.

Another estimate of diamond-like character can be made with electron energy loss spectroscopy (EELS). We performed EELS with a standard Auger spectrometer by decreasing the primary electron beam energy to approximately 495 eV and examining the loss peaks in the N(E) vs. E operating mode. The resulting spectrum is shown in Fig. 6. First note the absence of any vestiges of the $\pi$-to-$\pi^*$ transition characteristic of sp² (or graphitic) carbon bonds that generally appears at a loss of about 6.5 eV. Absence of this feature is strongly indicative of the absence of
long range order in any graphitic phases and suggests the presence of sp³ bonding in the sample. The degree of sp³ bonding can be estimated from the position of the wide plasmon peak seen at a higher loss energy of 26.4 eV. Correlations of plasmon loss energy with sp³ content suggest that these specimens contain approximately 40% sp³ bonding [3].

The spectral ellipsometer was used to determine the optical constants of PLD DLC films at several positions across the width of a 150-mm disk. The optical constants (n, k) were typical of diamond; between 400 and 800 nm n increased from 2.4 to 2.9 while k decreased.
Figure 4. The variation of thickness across a 150-mm substrate.

Figure 5. Raman spectrum of DLC film.
monotonically from 0.9 to 0.65. These values did not vary appreciably with location on the specimen. In addition, the thickness predicted for the coating agreed well with physical measurements of this quantity. It was also reassuring that the surface roughness predicted by the ellipsometry software agreed closely with that measured with the AFM. Emission spectra from the vapor plume above the laser impact zone indicated both C₂ vibration bands and ionic species. Ion currents detected at the substrate suggest that approximately 1–2% of the material arriving at the substrate was ionized.

One of the characteristics of diamond films grown by CVD and ion beam assisted deposition (IBAD) processes is a high degree of hydrogen content in the films. The hardness of DLC films is a strong function of hydrogen content, decreasing by a factor of up to 2 as hydrogen content increases. Because PLD films are created in a vacuum, there is little reason to suspect hydrogen incorporation in the deposits. This was confirmed by examining the forward recoil spectrum (FRS) of He⁺ ions on our specimens. A typical FRS is illustrated in Fig. 7 and clearly shows a layer of hydrogen at the Si:DLC interface (probably due to hydrogen termination of the

Figure 6. EELS spectra of DLC and HOPG.
Figure 7. Forward recoil spectroscopy at DLC surfaces.

Si after HF cleaning) and a layer of hydrogen on the DLC surface (probably from adsorbed moisture) but no detectable hydrogen in the bulk.

The hardness of a 0.5-μm-thick film grown at $5 \times 10^8$ W/cm² was estimated by inserting a diamond stylus equipped AFM into the surface and dividing the applied force by the projected area as measured by the AFM. The resulting hardness of 60 GPa is midway between natural diamond (100 GPa) and SiC (35 GPa). As an interesting sidelight, we coated the standard Si tip of an AFM probe with approximately 200 Angstroms of DLC and determined that the lifetime of the tips could be increased by an as yet undetermined amount. This is illustrated in Fig. 8 where we compare the appearance of an uncoated tip after tracing across a SiC surface until it was unable to correctly reproduce surface features with that of a DLC coated tip operated under identical conditions for an identical time period. The DLC coated tip looks unchanged while the uncoated tip is clearly unserviceable.

Discussion

Although PLD has the unique ability to stoichiometrically transfer material from targets to substrates and has been demonstrated on large numbers of industrially significant compounds, it has not found its way into the mainstream of coating technologies. The majority of sales for PLD systems has been to university and government laboratories. Part of the reluctance of
Figure 8. DLC overlayers on a Se AFM tip microscope tips.

industry to adopt this unique coating method is probably based on the perceived cost of producing coatings at useful rates coupled with the high cost of photons. The cost per watt of various laser systems is summarized in Table I. At this time it is clear that CVLS remain competitive in this area. When compared to the lamp-pumped, Q-switched YAG systems, CVLS still look attractive based on their reliability and beam quality. Future developments in diode-pumped solid-state lasers may bring them into the PLD market as well.

We have demonstrated that, in the case of DLC, coatings can be made with visible light from CVLs at respectable rates. For example, the coating rates quoted for CVD and cathodic arc technologies are on the order of $\mu$m/h. The peak coating rates for DLC by PLD with high PRF CVLs are dependent on the size of the illuminated spot on the target surface and the target-to-substrate spacing, but are generally in the 0.5–1 $\mu$m/min range. When we scale the volume coating rate at 300 W (8000 $\mu$m cm$^2$/h) to a 1500 W copper vapour laser chain operating at 85% availability around-the-clock and divide the capital and operating costs of the laser and coater systems by the resulting coating volume, we find that DLC can be produced at a cost of $0.01–0.02 per $\mu$m cm$^2$.

Table I: Laser Type vs. Photon Cost (based on 1500 W average power)

<table>
<thead>
<tr>
<th>Laser Type</th>
<th>Photon Cost ($)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Copper Vapour</td>
<td>$667/W</td>
</tr>
<tr>
<td>YAG</td>
<td>$600/W</td>
</tr>
<tr>
<td>Excimer</td>
<td>$2800/W</td>
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</table>
We, and other authors, have also demonstrated the efficacy of PLD with visible light for other materials as well. Materials of slightly more complexity include ZnO2 (phosphors) [4], and HfO2 (antireflective coatings) [5]. Because visible light is less expensive to generate, easier and less expensive to transport and control (fused SiO2 optics, fiber optic delivery systems, etc.), and allows the user the simple option of protecting his optical surfaces with inexpensive mylar films, we believe that their use represents the most economical industrialization path for PLD. High-average-power CVLS have been commercially developed to act as pump lasers for the Atomic Vapor Laser Isotope Separation (AVLIS) process and are increasingly available to the manufacturing public.

Summary

High volumes of DLC have been produced with the visible light output of industrial CVLs. The high production rates, approaching 1 cm³ per hour, are possible because of both the high average power and high PRFs of these systems. The DLC contains roughly 40% sp³ bonds, and is both hard and smooth. These attributes were demonstrated by coating a Si AFM tip with DLC prior to imaging a rough SiC surface.

References


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