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W. McLean
B. E. Warner
M. A. Havstad
M. Balooch

Lawrence Livermore National Laboratory
Livermore, CA

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RAPID GROWTH OF DIAMOND-LIKE-CARBON FILMS BY COPPER VAPOR LASER ABLATION

W. MCLEAN, B. E. WARNER, M. A. HAVSTAD, M. BALOOCH
University of California, Lawrence Livermore National Laboratory, P.O. Box 808, L-460, Livermore, CA, 94550.

ABSTRACT

Visible light from a copper vapor laser (CVL) operating with 510 and 578 nm radiation (intensity ratio approximately 2:1), an average power of 100 W, a pulse duration of 50 ns, and a repetition frequency of 4.4 kHz has been shown to produce high quality diamond-like-carbon (DLC) films at fluences between $2x10^8$ and $5x10^{10}$ W/cm^2. Maximum deposition rates of 2000 µm•cm^2/h were obtained at $5x10^8$ W/cm^2. DLC films with hardness values of approximately 60 GPa were characterized by a variety of techniques to confirm DLC character, hydrogen content, and surface morphology. The presence of C_2 in the vapor plume was confirmed by the presence of the C_2 Swan bands in emission spectra obtained during the process. Economic implications of process scale-up to industrially meaningful component sizes are presented.

INTRODUCTION

PLD of DLC films has been demonstrated with both ultraviolet and infrared light from both excimer and Nd:YAG lasers[1-5] with irradiances on the ablation target of $2x10^8$ to over 10^{11} W/cm^2 respectively. One major impediment to commercialization of PLD processes for DLC (and other materials as well) is the rate at which material can be deposited on a substrate by these commercially available photon sources. This issue has been addressed by employing the visible light output of high power CVLs. By demonstrating peak deposition rates on the order of 1 µm/min, this work lays the foundation for follow-on development of PLD processes by less complex pulsed lasers operating in the visible wavelength regions at high pulse repetition frequencies (PRFs).

EXPERIMENTAL PROCEDURES

The characteristics of the CVLs employed in this work are summarized in Table I. Approximately 190 W (average power) of light from a single CVL oscillator and 500 W amplifier was directed through a fused SiO_2 window to a vacuum chamber on a rotating graphite target (POCO AXM-5Q, 5 µm average particle size) moving at a speed of 8 cm/s. Target texturing was minimized by exposing fresh tracks of graphite by indexing the target one beam diameter every revolution. Substrates were biased to - 500 V during the ablation process and to + 40 V between laser pulses.

Table I. CVL Operating Parameters

Wavelength	510, 578 nm (2:1 intensity ratio)
Pulse Width	50 ns (FWHM)
Pulse Energy	25mJ
Pulse Repetition Frequency	4400 Hz

A 500 mm focusing lens outside the vacuum chamber was used to set peak irradiances on the target by adjusting the beam diameter from 50 μm ($5x10^{10}$ W/cm^2) to 750 μm ($2x10^8$ W/cm^2). Target-to-substrate spacing was typically 7.6 cm. Film thickness and distribution data on Si(100) substrates were obtained by masking the substrates and measuring the step height from the bare Si to the coating surface with a standard laboratory profilometer. All depositions were performed at ambient temperature in a vacuum of $5x10^{-7}$ torr or better.

RESULTS AND DISCUSSION

Electron Energy Loss Spectra (EELS) were recorded for primary beam energies of 495 eV and analyzed with a single pass cylindrical mirror analyzer. A typical spectrum of DLC, in this case a 250 nm thick film grown at $6x10^8$ W/cm2 [Fig. 1(a)], show the absence of the $\pi \rightarrow \pi*$ loss feature 6 eV below the reflected primary beam. The absence of this feature is characteristic of sp^3 bonded material [Fig. 1(b)].[6,7] DLC coatings grown at fluences ranging from $2x10^8$ to $5x10^{10}$ W/cm^2 exhibited similar characteristics. Raman spectra from these specimens exhibited the asymmetric peak at 1550 cm^{-1} characteristic of DLC [Fig. 1(c)].[8]

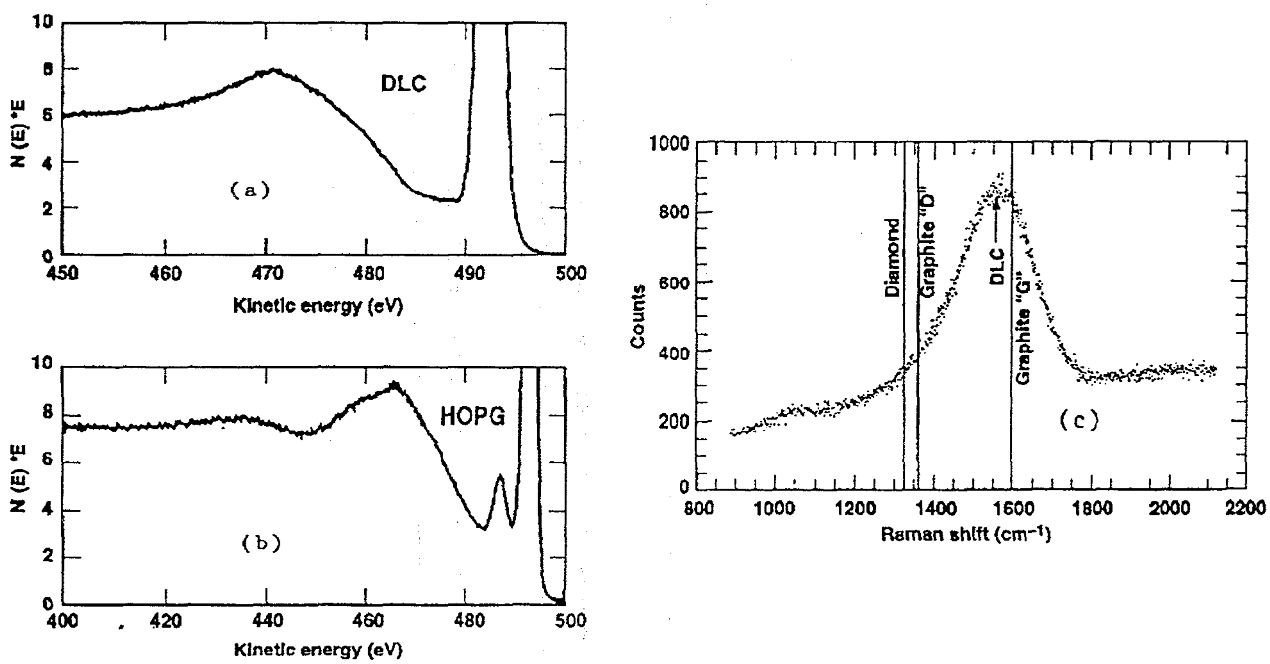

Figure 1. Characterization of DLC and graphite. (a) EELS of DLC grown at $5x10^8$ W/cm^2. (b) EELS of highly oriented pyrolytic graphite. (c) Raman spectrum of DLC from (a).

The deposition profiles on stationary substrates followed a $\cos^n(\phi)$ distribution where ϕ is the angle measured from the surface normal of the target and **n** is approximately equal to 10. A typical deposition profile resulting from 100,000 pulses (i. e., 23 s of laser-on time) at $5x10^8$ W/cm^2 is illustrated in Fig. 2(a). Integration of the volume defined by this curve yields a volume deposition rate of approximately 2000 μm•cm^2/h. The variation of peak deposition rate with fluence is illustrated in Fig. 2(b). The rate increases with fluence up to $5x10^8$W/cm^2. Beyond this level, it is believed that photon interaction with the ablation plume begins to mask the target and the effective coating rate decreases. No differences in the EELS or Raman spectra of material grown under the range of fluences investigated could be detected.

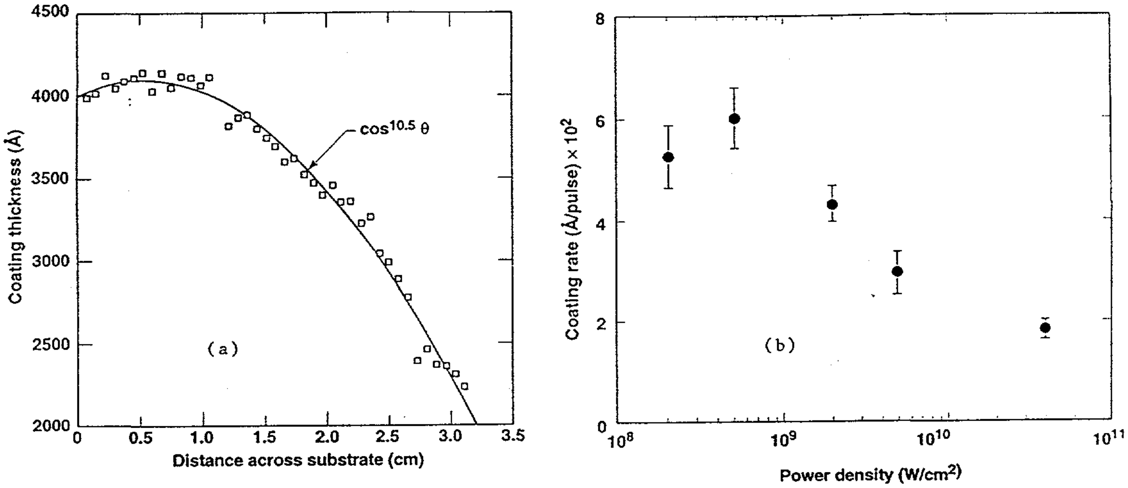

Figure 2. (a) Spatial distribution of DLC grown on a Si(100) substrate after 100,000 laser shots at 190 W average power and $5x10^8 W/cm^2$. (b) Variation of peak coating rate with fluence.

In agreement with other investigations at similar laser fluence (but shorter wavelength [248 nm] and higher pulse energy [250 mJ]),[9] the emission spectra obtained from the laser plume viewed parallel to the target surface were found to be dominated by the C_2 vibrational bands.[10] The $\Delta v = +1$ spectrum of the C_2 Swan bands at 473 nm is shown in Fig. 3. The intensity of the **1,0** line the was seen to roughly correlate with the coating rate measured at the substrate surface. Low and high resolution atomic force microscope images of typical DLC films are shown in Fig. 4. The characteristic grain size is on the order of 150 nm, and the rms surface roughness is less than 10 nm. Although large areas showing no macroscopic inclusions were found, typical 40 μm by 40 μm areas contained 2 - 8 macro particles with an average height of 200 ± 50 nm and width of 50 ± 10 nm.

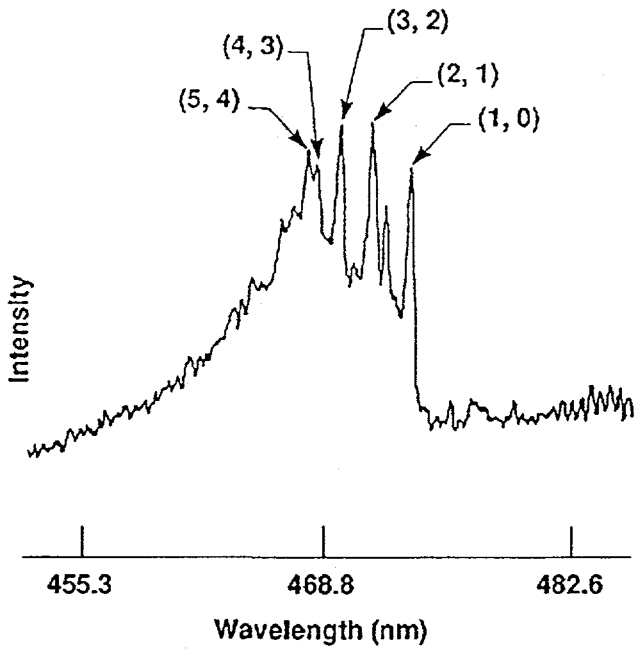

Figure 3. Optical Emission from the C_2 Swan bands during ablation at $5x10^8$ W/cm².

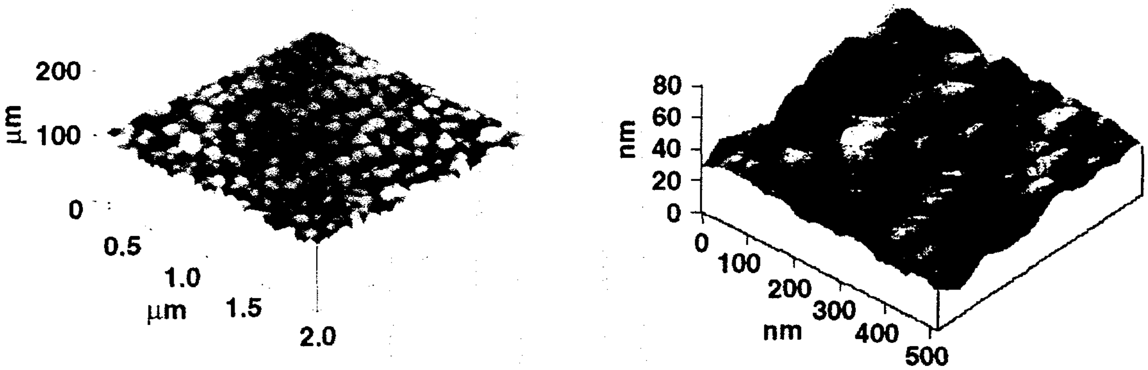

Figure 4. Surface morphology of DLC by AFM at low and high magnification.

A noteworthy companion to most violent PLD processes is the unwanted generation of large particles and their incorporation in the condensed films. It is believed that deep target penetration at the high powers typical of most PLD processes results in macroparticle generation by explosive removal of material around the periphery of the laser spot.[11] By employing relatively low energies per pulse (on the order of 25 mJ), roughly 0.1 μm/pulse (10^{15} atoms) depth was removed from the graphite target surface at maximum deposition rates. Approximately 1.5×10^{-6} coulombs were collected on the biased target per laser pulse, corresponding to a fraction ionized of 1 %. If the target speed is adjusted so that no more than 2 μm of graphite is removed from the target prior to exposing fresh material, the generation of large particles appears to be suppressed. This observation is based on the presence of large incandescent particles in the field of view parallel to the target surface at dwell times that allow drilling to greater depths, and, conversely, their absence at shorter dwell times. Inspections of target surfaces by AFM and optical microscopy provide additional support for this hypothesis.

Examination of DLC by forward recoil spectroscopy (FRS) of hydrogen by a 2.9 MeV He^+ beam revealed that the bulk of the material contained little, if any, hydrogen. Monolayer quantities of hydrogen (Fig. 5) were detected at the Si:DLC and DLC:vacuum interfaces. It has been suggested that the hardness of DLC films is inversely proportional to their hydrogen content.[12] Hardness of DLC from this study was characterized by a nanoindentation technique utilizing a diamond tipped AFM probe and found to be approximately 60 GPa. An AFM line trace through an indentation made with an applied force of 1.2×10^{-3} N is shown in Fig. 6.

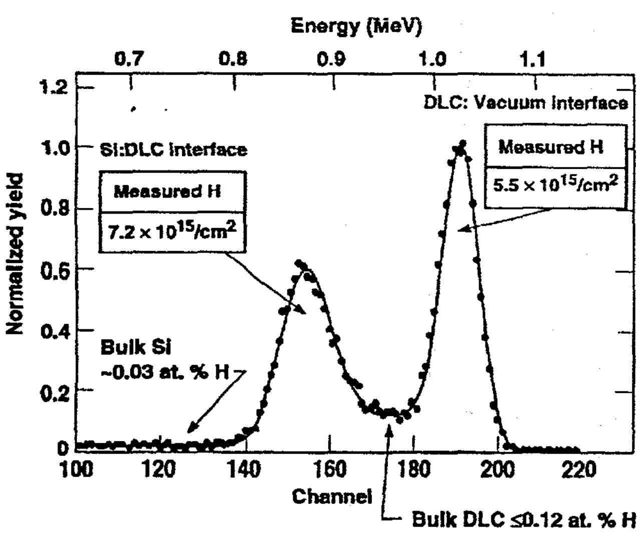

Figure 5. Forward recoil spectroscopy reveals presence of monolayers of H at DLC interfaces.

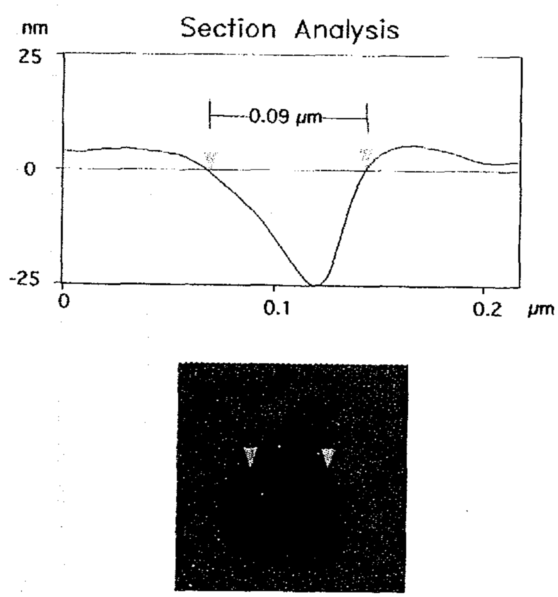

Figure 6. Nanoindentations in DLC show hardness to be 60 Gpa.

CONCLUSIONS

Deposition of DLC with visible light from high repetition rate copper vapor lasers has been demonstrated to be an efficient and effective method for coating specimens. DLC produced by this process at fluences of approximately $5x10^8$ W/cm^2 are smooth (10 nm rms roughness), hard (60 GPa) and economical to apply. Coating rates of 2000 μm•cm^2/h at 190 W average laser power set the stage for scaling this technology up to a practical industrial coating tool with the 500 W CVL sources developed at LLNL.

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