

Laser deposition of diamondlike carbon films at high intensities

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Unhydrogenated diamondlike carbon (DLC) thin films have been deposited by laser ablation of graphite, using a high power Ti: sapphire solid state laser system. DLC films were deposited onto silicon substrates at room temperature with subpicosecond laser pulses, at peak intensities in the 4×10^{14} – 5×10^{15} W/cm² range. A variety of techniques, including scanning and transmission electron microscopy (SEM and TEM), Raman spectroscopy, spectroscopic ellipsometry (SE), and electron energy loss spectroscopy (EELS) have been used to analyze the film quality. Smooth, partially transparent films were produced, distinct from the graphite target. sp^3 volume fractions were found to be in the 50%–60% range, with Tauc band gaps ranging from 0.6 to 1.2 eV, depending on laser intensity. Kinetic energies carried by the carbon ions in the laser induced plasma were measured through time-of-flight (TOF) spectroscopy. Their most probable kinetic energies were found to be in the 700–1000 eV range, increasing with laser intensity. © 1995 American Institute of Physics.

The growth of hydrogen-free diamondlike carbon (DLC) films has attracted much interest due to the fact that these films possess properties close or similar to that of diamond. These properties include transparency in the infrared (IR) and near-infrared range, high microhardness, high electrical resistivity, as well as excellent chemical inertness. A variety of applications are anticipated for these films, primarily in the microelectronics, optics, and tribology industries.^{1–6}

Recently, high quality DLC films with sp^3 volume fraction higher than 70%, and “amorphous diamond” films with microhardness comparable to natural diamond, have been produced through pulsed laser depositions (PLD).^{7,8} It is suggested that, as a kinetic condensation process, pulsed laser deposited DLC film quality is closely related to its deposition parameters, among which the kinetic energies of the carbon particles, as well as their charge states in the plasma, are two of the most consequential factors.^{9,10}

Most successful PLD depositions of DLC thin films conducted so far, employed either UV excimer (KrF, ArF, XeCl) or Nd:YAG lasers, all with pulse durations in the nanosecond range. Depending on laser energy and spot size focused onto the target, power densities in the 10^8 – 10^{11} W/cm² range were delivered. Previous experiments have shown that, for a certain laser system, the higher the laser intensity, the more diamondlike (i.e., higher sp^3 fraction) are these films.^{11,12} Until now, the highest intensity used to deposit DLC films was 5×10^{11} W/cm² carried out by Collins *et al.*, with a Nd:YAG laser.¹³ They suggested that this high laser intensity will give rise to a more highly ionized plasma, the plasma being expected to contain charged carbon particles with high kinetic energies, and consequently leads to a higher volume fraction of sp^3 bonded carbon atoms.

It therefore would be interesting to study the effects of

even higher laser intensity on the DLC film properties. However, intensities higher than 10^{12} W/cm² are often not achievable for nanosecond lasers, because substantially higher laser energy is of limited availability while submicron beam spots suffer from diffraction limitations. Instead of nanosecond lasers, we used a high power solid-state Ti: sapphire laser system, capable of producing laser pulses in the picosecond and femtosecond range. With this laser system we are able to induce laser intensities in the 10^9 – 10^{16} W/cm² range.

The depositions were carried out with a chirped-pulse amplified (CPA) Ti:sapphire laser system developed at the Center for Ultrafast Optical Science, University of Michigan. This system enables the generation of variable length laser pulses going as short as 70 fs (FWHM). The laser beam is near-Gaussian shaped and centers at 780 nm wavelength. Details concerning the laser system are discussed elsewhere.¹⁴

The deposition station consists of a high vacuum chamber maintained by a cold-trapped oil diffusion pump. A rotating graphite target is placed at an angle of $\sim 45^\circ$ to the incident laser beam. The separation between the target and substrate is 4 cm. The compressed laser pulse was measured as 250 fs (FWHM), it was then delivered across ~ 5 m of air and through a 1 cm SiO₂ window into the vacuum chamber. A plano-convex lens was then used to focus the beam onto the target. The nonlinear refractive index contributions from the atmosphere and glass components were estimated to have increased the pulse duration by a factor of about 2 when the beam reaches the target. Typical experimental conditions used in this study are listed in Table I.

The DLC films deposited on silicon substrates at room temperature are visually smooth and uniform with golden bluish tint. They are virtually featureless under a scanning electron microscope (SEM), similar to the DLC films produced by nanosecond KrF laser pulses (248 nm). Significant

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TABLE I. Deposition conditions for DLC films.

Laser source	Ti:sapphire (780 nm)
Repetition rate	10 Hz
Pulse duration	~500 fs (FWHM)
Laser energy	15–45 mJ
Spot size	50–100 μm
Peak power density	4×10^{14} – 5×10^{15} W/cm ²
Substrate	Si, NaCl
Substrate temperature	Room temperature
Film thickness	2500–3000 Å

increase of surface particle density as a result of longer wavelength (780 nm), a common feature of PLD techniques,¹⁵ is not observed. Transmission electron microscopy (TEM) indicated the films to be amorphous.

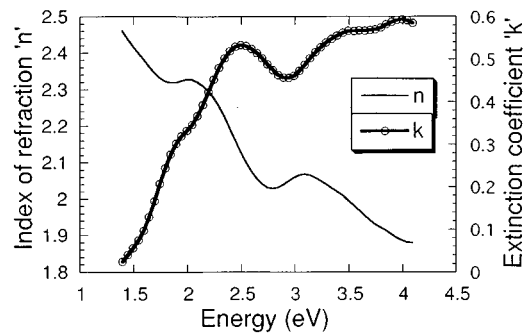
Sensitive to longitudinal and translational symmetry of materials, Raman spectroscopy is widely used in thin-film characterization. Raman spectra of the films deposited at different density levels showed similar features: a predominant “G” peak centered at about 1540 cm⁻¹ along with a broad “D” peak at a lower wavenumber, typical of room-temperature deposited DLC films. The probe power on the specimen was 100 mW with an Ar ion excitation wavelength of 514 nm. Best fits are obtained using two damped harmonic oscillator functions. Parametric values used in the fitting procedure are summarized in Table II. The “D” peak centers were found to decrease, while their full width at half-maximum (FWHM) increased at higher laser intensities, indicative of possible increasing bond-angle disorder in the films.¹⁶ Different intensities showed no obvious effects on the “G” peaks.

The refractive indices (n) and extinction coefficients (k) of the DLC films were measured with a variable angle spectroscopic ellipsometer (VASE), in the 1.5–4.5 eV range. Figure 1 shows n and k of sample A as a function of photon energy. The refractive indices n decrease as a function of increasing photon energy, and its extinction coefficients k showed a steep increase in the energy range at ~2.5 eV (500 nm) and start to level off at higher energies, suggesting the films are partially transparent in IR and near-IR range, and become absorbing at higher energies. Samples deposited at different intensity levels showed similar trends. The effective optical band gaps of the DLC films are obtained from the Tauc relationship by extrapolating a plot of $(\alpha E)^{0.5}$ (α is the absorption coefficient) as a function of photon energy E . For samples A, B, and C, deposited at successively higher intensities, optical band gaps were found to be 1.2, 0.8, and 0.6 eV, respectively.

Electron energy loss spectroscopy (EELS) was em-

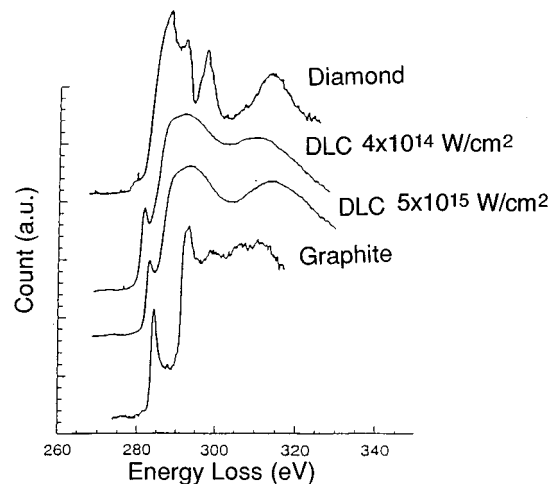
TABLE II. Raman fitting parameters of DLCs deposited at different densities.

Power density (W/cm ²)	G (cm ⁻¹)		D (cm ⁻¹)		I_D/I_G
	Center	FWHM	Center	FWHM	
4×10^{14} (sample A)	1539	171	1369	351	0.82
8×10^{14} (sample B)	1538	179	1364	362	0.97
5×10^{15} (sample C)	1537	175	1363	376	0.95


 FIG. 1. Refractive index n and extinction coefficient k of DLC deposited at 4×10^{14} W/cm².

ployed to quantify the sp^3 volume fraction in the deposited DLC films. Films were first deposited onto NaCl substrates at room temperature, with thickness of about 400 Å, and later removed to make EELS samples. Shown in Figure 2 are the K -shell edge EELS spectra of DLC samples deposited at 4×10^{14} (sample A) and 5×10^{15} W/cm² (sample C), along with that of a reference graphite film (assumed to contain 100% sp^2 bonding) and CVD diamond (100% sp^3). Notice the strong absorption peak at ~285 eV from the graphite sample, caused by $\pi \rightarrow \pi^*$ transitions, characteristic of sp^2 bonding structure. On the other hand, spectra from the two DLC samples are dominated by the $\sigma \rightarrow \sigma^*$ peaks at around 289 eV, with only a small π^* peak being present for each of these samples. However, the distinct features found in CVD diamond at above 290 eV are not observed in these DLC films. The sp^3/sp^2 ratio was extracted by normalizing the area of the π^* and σ^* peaks in the 280–320 eV range and comparing this ratio to the value of graphite.¹⁷ The sp^3 fractions for samples A and C are determined to be 60% and 50%, respectively.

To better understand the mechanism of DLC film formation under high laser intensities, a multigrad TOF drift tube coupled with a Faraday cup was used to measure the kinetic energies of ablated carbon ions. The experimental setup is similar to that introduced by Demtröder and Jantz.¹⁸ Assum-


 FIG. 2. K -shell edge EELS of DLC, CVD diamond, and graphite.

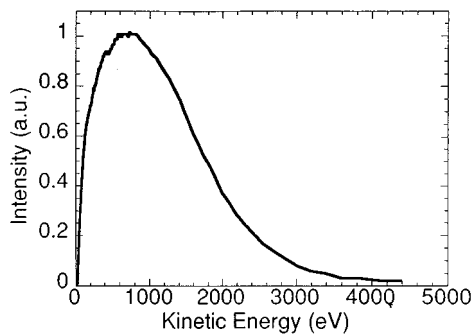


FIG. 3. Kinetic energy distribution of carbon ions at 4×10^{14} W/cm².

ing the ablated carbon particles are atomic ions under these high intensities, their median kinetic energies were found to be in the 700–1000 eV range, increasing with laser intensity. These numbers are at least 10–20 times higher than what have been observed with nanosecond laser pulses.¹⁹ Figure 3 shows the particle kinetic energy distribution at 4×10^{14} W/cm². In this relatively high energy regime, subsurface penetration and ion implantation will occur, resulting in possible film structure rearrangement and disruption, which may also explain why the DLC films have somewhat lower sp^3 content as well as lower band gaps at higher intensities.

In conclusion, we have deposited diamondlike carbon thin films with subpicosecond laser pulses, to study the effects of high laser intensities on DLC film properties. The films are smooth with few particles. They are amorphous, partially transparent, with optical band gaps varying from 0.6 to 1.2 eV. The sp^3 volume fraction was estimated to be in the 50%–60% range. It appeared that laser intensity of 4×10^{14} W/cm² result in films with higher Sp^3 bond percentage and higher band gaps, while films made at intensities in the 10^{15} W/cm² range are relatively more graphitic. We attribute this to possible ion implantation damage introduced by the carbon particles, resulting from a more energetic hydrodynamic plasma expansion under higher laser intensities.

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