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Thin-film deposition by a new laser ablation and plasma hybrid technique

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We have developed a new laser ablation and plasma hybrid technique for depositing thin diamond-like carbon (DLC) films on Si⟨100⟩ substrates at room temperature and at 110 °C with improved optical and mechanical properties. The technique involves coupling of laser energy ($\lambda = 0.308\,\mu$m, pulse duration = 40 ns, and power 125 MW/cm^2) to a graphite target and superimposing capacitively stored energy (2–3 J at 3 kV) to the laser ablated spot. The laser- and plasma-deposited diamond-like carbon films were analyzed by spectroscopic ellipsometry and microhardness measurements. These films showed considerable improvements in both uniformity and homogeneity. Optical properties and hardness of the films deposited by this technique closely match the DLC films. We discuss possible causes of improvements in the above properties of these films.

The laser ablation and deposition technique has been used to produce a variety of films: high quality, high transition temperature superconducting oxide films[1,2]; hard, hydrogen-free diamond-like carbon films[3,4]; amorphous Si films[5]; and epitaxial TiN films from TiN targets,[6] Ge, SiO_2, GeO_2, Au, Cu, etc. The primary advantage of the laser deposition technique lies in its simple implementation, near stoichiometric deposition from multicomponent targets on substrates at low temperatures, and control of microstructure. The laser deposition process manifests nonequilibrium features during deposition such as atomically and electronically excited (as well as ionized) species and fast quenching, which lead to the formation of films in metastable states with unique physical and mechanical properties. The physical evaporation of carbon atoms from a graphite target using nanosecond excimer laser irradiation has been shown to result in the deposition of hard diamond-like films.[4] In this letter, we report that further nonequilibrium features can be incorporated into laser ablated plasma by coupling capacitively stored energy to the laser ablated spot in synchronism with the laser pulse. Uniform depositions over a significantly large area are characteristic of this deposition method, and the amorphous hard carbon films deposited by this method show improved optical properties as well as increased hardness as compared to films deposited by the conventional laser ablation method. The technique is quite general and can be applied to a variety of materials. Properties of high T_c superconducting films, TiN and TiO_xN_y films, and Ge oxide films deposited by this new technique will be reported in the near future. However, it may be noted that recently Wagal *et al.* have reported optical quality carbon film deposition by accelerating the ions produced in the laser produced plasma plume[7] and by flowing a plasma current in the laser plume.[8]

The conventional setup for producing thin films of materials by laser ablation is schematically shown in Fig. 1(a). The vacuum chamber ($< 10^{-7}$ Torr) contains the substrate on a heated substrate holder separated from a graphite target by ~25 mm. The laser beam from a 40 ns full width at half maximum (FWHM) XeCl excimer laser is focused by a lens onto the target at a power density of $\sim 1.25 \times 10^8$ W/cm^2. Under these conditions the visible extent of the plasma plume (without filters) is less than 5 mm. The films deposited on Si and MgO substrates were found to be hard, highly adherent, and amorphous with diamond-like refractive in-

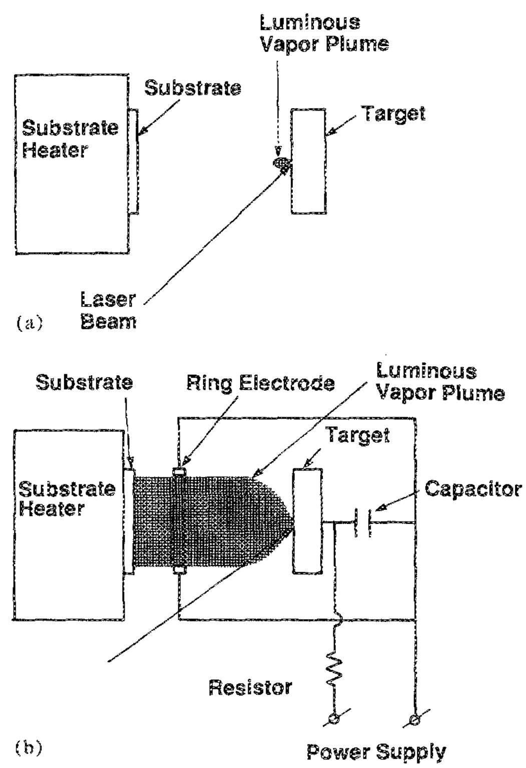

FIG. 1. (a) Schematic diagram illustrating the conventional laser ablation technique. The tiny plasma plume (<5 mm) at the target surface is representative of a plume from a graphite target produced by an ablating laser energy density of ~5 J/cm^2. (b) Schematic diagram illustrating the laser ablation and plasma hybrid technique. The capacitively stored energy is fed synchronously into the laser ablated spot producing a large area, large volume plume at the same laser energy density as in (a). Notice the plume extending from the target to the substrate (~26 mm).

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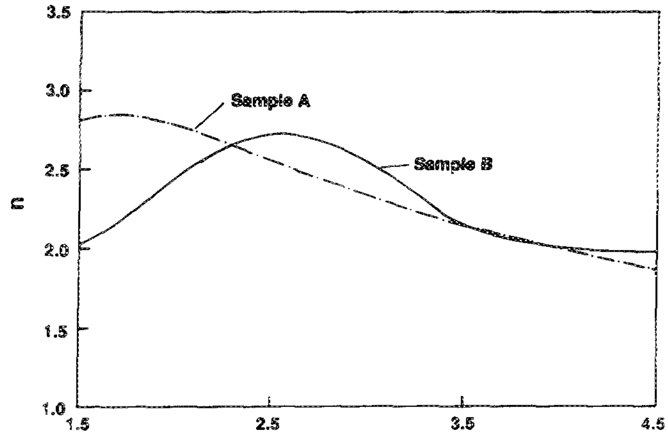
dex (for low-temperature deposition).[3,4] A schematic diagram of the new laser ablation/plasma hybrid technique is schematically shown in Fig. 1(b). A 0.5 μF capacitor, placed outside the vacuum chamber is connected by feedthroughs between a 20-mm-diam graphite ring electrode (0.65 cm from the target) and the graphite target. The capacitor is charged to 3 kV by a stabilized dc source. Synchronously with the impingement of the laser pulse on the target, the capacitor is automatically discharged and a large discharge plume which extends from the ablated spot to the ring and beyond upto the substrate is formed even at low chamber pressure. The inductance of the capacitor-ring-target circuit was not very critical to discharge the capacitor. It may be mentioned that in this preliminary study neither the value of the capacitance nor the charging voltage of the capacitor was optimized.

In order to monitor the effect of such a plasma on the deposited film properties, samples A and B were deposited under otherwise identical conditions except that the thin film on sample B was deposited with the 0.5 μF capacitor synchronously feeding its charge to the laser produced plasma. The films were deposited at an incident laser energy density of 5 ± 0.3 J/cm^2, at substrate temperatures of 25 °C ($\sim$3000 pulses) and 110 °C ($\sim$4800 pulses) with the vacuum chamber pressure between 5 and 8×10^{-7} Torr. The capacitor discharge markedly alters the vapor plume by extending it from the ablated spot to the substrate. Deposition on sample B was found to be more uniform and over a larger area as compared to that on sample A. Sample A film showed the "domed" profile in thickness as recently reported,[8] but sample B film was more uniform. The deposited film thicknesses of both films were in the range of $\sim$150 nm with sample B film $\sim$40% thicker than sample A film (on the film deposited at 110 °C) as measured with a stylus type instrument. Deposited films were analyzed by spectroscopic ellipsometry and microhardness measurements.

Spectroscopic ellipsometry measurements were carried out on the deposited films using apparatus and methods described previously.[9-11] The n (real) and k (imaginary) components of the complex refractive index of the deposited film are found by matching the pseudo-optical properties of the substrate-film composite to that generated by a computer for a substrate-film-ambient three-phase model. Using the known properties of the ambient and the substrate, the film properties of the model are adjusted until an exact match with the measured optical properties is obtained. Figures 2(a) and 2(b) show the real (n) and imaginary (k) parts of the refractive index for the two samples, A and B, between 1.5 eV (0.8267 μm) and 4.5 eV (0.2756 μm), respectively. Tauc[12] plots were drawn using the measured extinction coefficient versus photon energy curves, and the optical band gap was found by extrapolating the Tauc plots. The optical band gap of sample A was $\sim$0.47 eV and that for sample B was $\sim$1.27 eV for the 25 °C deposition and $\sim$0.3 eV (sample A) and $\sim$0.7 eV (sample B) for the 110 °C deposition. This trend of decrease in optical band gap with substrate temperature is similar to that reported earlier by the authors.[4] The capacitive discharge technique leads to the deposition of films with higher band gap although adhering to the same



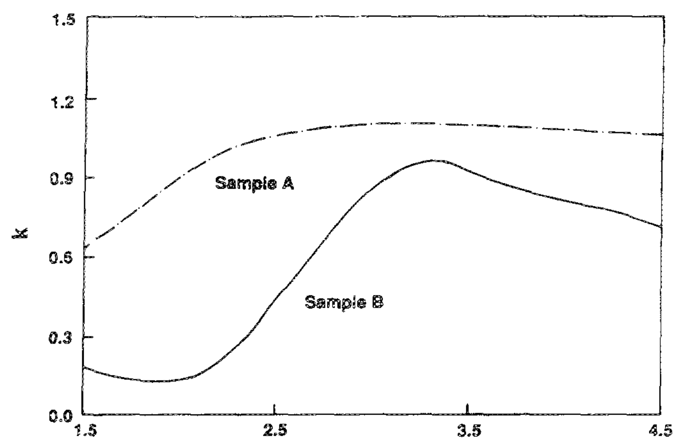


FIG. 2.(a) Real part and (b) imaginary part of the complex refractive index of film deposited at 25 °C in vacuum ($\sim 10^{-7}$ Torr) at an incident laser energy density of $\sim$5 J/cm^2 obtained by spectroscopic ellipsometry.

trend with respect to substrate temperature. The real and imaginary parts of the complex refractive index of the film deposited by the capacitive discharge technique are similar to diamond-like values of the ion beam deposited films at the lowest power.[13]

Microhardness measurements were carried out on a Nanoindenter®[14] at the Oak Ridge National Laboratory. The diamond indenter tip of the Nanoindenter® was slowly pushed into the surface of the specimen at a constant rate of less than 10 nm/s until the desired load was reached. The indenter tip was then retracted at the same rate. Load versus position was measured with a resolution of 1.8 mN in the 0–120 mN load range and with a resolution of 0.4 nm in position. The results of hardness measurements of the films deposited under the two conditions pertinent to samples A and B at two different temperatures averaged over several indenter locations across the sample surface are shown in Table I. Lower substrate temperatures are conducive to the deposition of harder films. The hardness of films deposited at 25 °C without the capacitive discharge technique was similar to Si_3N_4 ($\sim$16 GPa) and that at 110 °C without discharge was similar to Si ($\sim$10 GPa). This trend is similar to what has been reported earlier.[5] The hardness of films depos-

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TABLE I. Hardness at 25 and 100 nm from surface of DLC films deposited by the new technique as compared to the conventional laser ablation technique.

Deposition temperature (°C)	Pressure during deposition (Torr)	Hardness (GPa) With discharge Sample B 25nm	100 nm	Without discharge Sample A 25 nm	100 nm	No. of Pulses
25	10^{-7}	$18.1 \pm 10\%$	$19 \pm 10\%$	$13.6 \pm 20\%$	$15.5 \pm 10\%$	3000
110	10^{-7}	$22.0 \pm 10\%$	$27.0 \pm 5\%$	$9.5 \pm 10\%$	$10.6 \pm 10\%$	4800

ited by the new technique produces films with greater hardness lying in the same range as those of SiC (~ 22 GPa) and Al_2O_3 (~ 24 GPa). These extremely hard films are similar to ion beam deposited films at the lowest power level with $\sim 70\%$ diamond-like component.[13]

The other effects observed by the new deposition technique were that thicker and more uniform films were produced as compared to the conventional laser ablation technique. The uniformity of the film was not measured, but compared to the more localized depositions (bull's eye or "domed") of the conventional technique, the films deposited by the new technique were more uniform. This is due to the spreading of the plasma plume as shown schematically in Fig. 1(b).

Both space and time-resolved spectroscopic actinometric and mass spectroscopic studies will be needed to explain the properties of films obtained by the new technique. However, we envisage that several other excited species are produced in addition to the ones produced by the laser alone. Also, the energy distributions of particles are different from the ones produced by conventional laser ablation which are responsible for the altered properties. It is anticipated that by reducing the inductance of the capacitor-ring-target circuit, further modifications may be obtained due to enhanced nonequilibrium processes and appearance of particle beam components[15] that accompany the rapid current rise.

In summary, a new laser ablation and plasma hybrid deposition technique is described. Hard amorphous carbon films deposited by this technique were found to be superior to those produced by the conventional technique with regard to their optical properties, hardness, and uniformity. The substrate temperature remains close to ambient during deposition, thus paving the way for coatings on heat-sensitive substrates. The present technique is more versatile than the conventional laser ablation technique for producing diamond-like coatings on a variety of substrates.

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