PULSED LASER DEPOSITION OF DIAMOND-LIKE CARBON THIN FILMS: ABLATION DYNAMICS AND GROWTH

PEIDONG YANG, Z. JOHN ZHANG, JIANGTAO HU, CHARLES M. LIEBER
Department of Chemistry and Chemical Biology and Division of Engineering and Applied Sciences, Harvard University, Cambridge, MA 02138

ABSTRACT

Thin films of diamond-like carbon have been grown by pulsed laser deposition using a Nd:YAG laser at 532 nm. Time-of-flight mass spectroscopy was used to investigate the effects of laser power density and background gas pressure on the plume characteristics including the species in the plume and the kinetic energy distribution of each species. We found that with increasing laser power density (1) the relative amount of C^+ ions increases, (2) the kinetic energy distributions of C^+ get broader and can be deconvoluted into fast and slow components, and (3) the kinetic energy of the fast component of C^+ ions increases from several to 40 eV. The resistivity and the local carbon bonding in films grown under these same conditions were also characterized. It was found that there is direct correlation between the characteristics of fast part of C^+ ions in the plume and the diamond-like properties of the thin films. Under optimal growth conditions diamond-like carbon films with a large fraction of sp^3 bonding can be prepared, although the maximum fraction appears to saturate at 70%. The implications of these results are discussed.

INTRODUCTION

The growth of hydrogen-free, diamond-like carbon (DLC) films has attracted much interest due to their potential applications in microelectronics, optics, and tribology [1]. In general, DLC films are amorphous in structure and display a high degree of sp^3 bonding. A number of approaches, including cathodic arc, ion beam, ion beam sputtering and laser deposition, have been employed to prepare DLC films [1]. A feature common to these techniques is that the deposition is energetic; that is, the carbon species arrive at the substrate with kinetic energies significantly greater than that corresponding to the substrate temperature.

In pulsed laser deposition (PLD), which has been used by several groups to prepare DLC films [2-5], the laser-generated plasma creates energetic species [6,7]. In general, it is known that the energies of these species depend on the ablation conditions. However, there is limited information about the kinetic energy distributions of carbon species generated under conditions employed for film deposition, and furthermore, little data exists correlating plasma dynamics with deposited film properties [8]. This information is, however, critical to understanding the growth mechanism of DLC films. Herein, we report detailed studies of laser-generated carbon plasmas produced under a range of conditions used for thin film deposition. The carbon ion species and their kinetic

Mat. Res. Soc. Symp. Proc. Vol. 438 © 1997 Materials Research Society

energy distributions were characterized by time-of-flight mass spectroscopy (TOF-MS) and the fraction of tetrahedral, sp^3-bonded carbon in corresponding films was determined by electron energy loss spectroscopy (EELS). Implications of these results to the growth of carbon-based films with controlled local bonding are discussed.

EXPERIMENT

The laser deposition system has been described elsewhere [9]. Briefly, the beam from a Nd:YAG laser (SHG, 532 nm) was focused on a rotating highly-oriented pyrolytic graphite (HOPG) target at an incident angle of 45°. The power density was varied from 1×10^8 to 1×10^{11} W/cm^2. During film deposition, the substrate-target distance was fixed at 4 cm and the substrate was cooled with LN_2. Plume characterization was carried out using TOF-MS (Fig. 1). The chamber pressure during TOF and film growth experiments was varied from 1×10^{-8} to 1×10^{-4} torr. All mass spectra were obtained by averaging 100 laser pulses. The procedure for mapping the mass and kinetic energy distribution of laser-generated ions was as follows. The positive ions generated by ablation reach the repeller region where these ions are pushed into the acceleration region after a delay time (t_{delay}). The ions are accelerated into the drift region, detected by a microchannel plate assembly and the resulting signal is digitized. Each TOF spectrum records ions that arrive at the repeller region during time interval between t_{delay} and

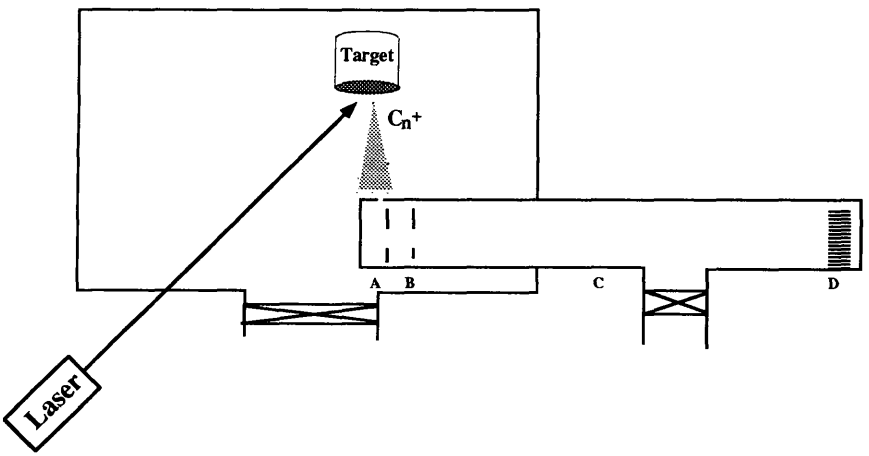

Fig 1. Time-of-flight mass spectroscopy experimental set-up: A, Repeller region; B, Acceleration region; C, Drift region; D, Microchannel plate detector.

$t_{delay} + t_{width}$ (repeller pulse width). Mass and kinetic energy distributions were obtained by integrating the ion peak intensities for spectrum obtained at each delay time ranging from 0 to 20 μs with 500 ns steps.

A number of techniques were utilized for film characterization. Temperature dependent resistivities were determined using four and two probe techniques on films deposited onto quartz substrates. C(1s) K-edge EELS was used to determine the local carbon bonding in the films [10]. Using the approximation that the ratio of the integrated areas within 284-290 eV (1s to π^* transition) and above 290 eV (1s to σ^* transition) are proportional to the ratio of π and σ orbitals, the sp^3 fraction in the films can be estimated within accuracy of ± 5 %.

RESULTS AND DISCUSSION

Figures 2a-2c show typical ion cluster abundance distributions for laser plumes generated using power densities from 2×10^8 to 9×10^8 W/cm^2. These data show several important features. First, the major carbon ion species in the plume changes from C_3^+ to C^+ with increasing power density; C^+ ions are the dominant species for power

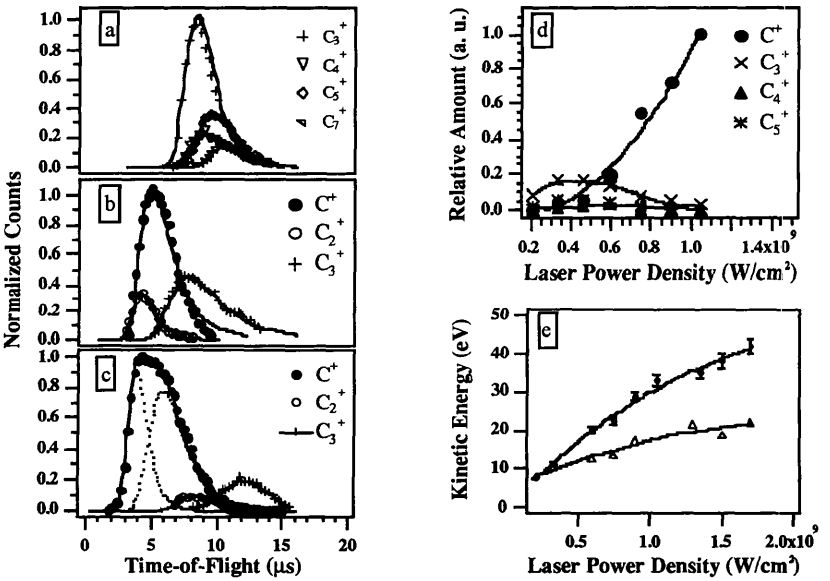

Fig. 2. The cluster abundance and kinetic energy distributions for laser generated plumes in vacuum at (a) 2.1×10^8 W/cm^2, (b) 6×10^8 W/cm^2, and (c) 9×10^8 W/cm^2. The data are fit with center-of-mass Maxwell-Boltzmann distributions. (d) Carbon ion relative fractions vs. laser power densities. (e) The kinetic energies of the fast C^+ component (●) and the average kinetic energy of C^+ ions (△) vs. laser power densities. The kinetic energy of the fast component were obtained from the most probable time-of-flight in the distributions.

densities greater than 5×10^8 W/cm^2. The changes in carbon ion abundance are summarized in Figure 2d for power densities from 2×10^8 to 2×10^9 W/cm^2. These results show directly that the C^+ ion fraction increases over this range of power densities, while the fraction of C_n^+ (n=2,3...) clusters first increases and then decreases for power densities $\geq5\times10^8$ W/cm^2. The decrease in cluster ion concentration above this point is believed to be due to increasing fragmentation within the plume [11]. These results show clearly that the ablation power density can be used to investigate how C_n^+ cluster size affects film growth and properties.

Second, the kinetic energies of the ion clusters change with the laser power density. We compare the kinetic energies determined from the most probable values in the TOF distributions (Fig. 2). For C_n^+ (n=2,3...), the kinetic energies first increase but then decrease at the point where these clusters begin to fragment. For C^+, the kinetic energy distributions get broader with increasing laser power density. This broadening may be due in part to a space charge effect [12]. C^+ ions that originate from the dissociation of clusters (C_n^+, n=2,3...) may also contribute to the observed broadening. In addition, these broadened C^+ distributions must be fit with at least two components; we have termed these "fast" and "slow" components (Fig. 2c). The kinetic energy of the fast component increases from several to 40 eV over our experimental power density range (Fig. 2e) while the average kinetic energy of the C^+ ions seems saturate when the laser power density is over 1×10^9 W/cm^2.

Systematic film growth studies have also been carried out under the same conditions used for the TOF investigations to elucidate correlations between laser plume and film properties. We find that carbon films grown using laser power densities less than 6×10^8 W/cm^2 are black and conducting. Furthermore, EELS analyses indicate that the films contain large fractions (>75%) of sp^2-bonded carbon. To obtain high-quality, DLC films, the laser power density must exceed 6×10^8 W/cm^2. This value of the power density corresponds to the point where C^+ becomes dominant and where the energy of the fast component exceeds 20 eV (Figs. 2d,e). It is interesting to compare this value to the critical value for obtaining DLC by ablation at 1064 nm, 5×10^{10} W/cm^2 [2], and that at 248 nm, 3×10^8 W/cm^2 [3]. This comparison suggests that the photon energy plays an important role in determining the energy of the species in the plume, and hence the formation of high-quality DLC films. TOF studies that elucidate the kinetic energy distributions produced at these different wavelengths are, however, needed to confirm this suggestion. The importance of ion kinetic energy has also been reported previously on the basis of ion beam deposition studies [13,14].

Our best DLC films were obtained under conditions that produced C^+ ions with most probable kinetic energies (fast component) of 20 to 40 eV (Fig. 3). Figure 3a suggests that higher kinetic energy C^+ species lead to higher sp^3 fractions in deposited films. The importance of kinetic energy is further confirmed by growing films using the same laser power density in different background gas pressures. These experiments show that the percentage of sp^3 carbon in films decreases with increasing pressure as expected since the background gas thermalizes the plume species. Because the fraction of sp^3

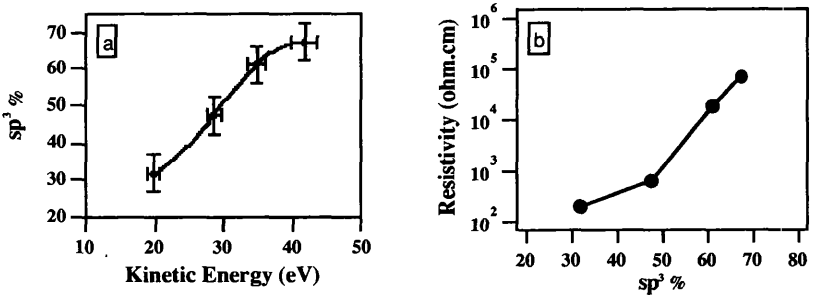

Fig 3. (a) Fraction of sp^3-bonded carbon in films as a function of the kinetic energy of the fast C^+ component. (b) Correlation of the electrical resistivity at room temperature with fraction of sp^3 carbon in films.

carbon determines film properties such as resistivity (Fig. 3b), these results demonstrate that an understanding of plume dynamics is important to controlling film properties.

The broad kinetic energy distributions observed in our studies are common for laser ablation [12], and could have important consequences for film growth and properties. For example, it is interesting to ask whether the limiting value in $\%sp^3$ bonded carbon originates from co-deposition of fast and slow component ions. To investigate this issue we have compared the relative amount of C^+ ions with kinetic energies higher than a preset critical value and the $\%sp^3$ bonded versus laser power density (Fig. 4). This shows

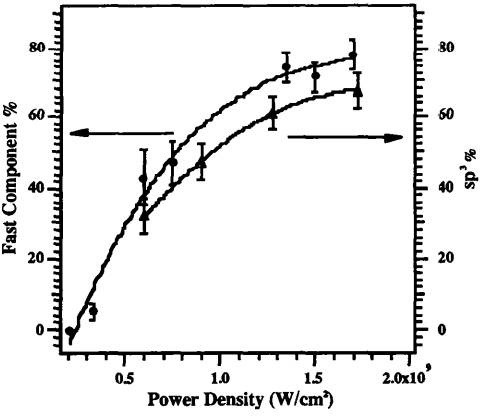

Fig 4. The relative amount of C^+ fast component (●) determined using a cut-off energy of 16 eV compared with the sp^3 percentage (△) in the films at different laser power densities. The relative fraction of C^+ was determined by integrating the area under the kinetic energy distribution for energies greater than the cut-off.

that there is a reasonable correlation when we use 16 eV as the critical kinetic energy value. It is especially worth noting that both the maximum $\%sp^3$ bonded carbon in the films and fraction of fast C^+ ions saturate at higher laser power density. We believe that

this is due to the intrinsic broadening of the TOF distributions that leads to the deposition of a finite fraction of relatively low energy C^+ species.

CONCLUSIONS

The plasma generated by 532 nm laser ablation of graphite under a broad range of power densities has been characterized using TOF-MS. These studies have shown that (1) the major plume species changes from C_3^+ to C^+, (2) the fraction of energetic ions increases, and (3) the ion kinetic energy distributions become bimodal with increasing power density. We have also shown that diamond-like structural and physical properties of thin films correlates well with the fraction of the fast component in the C^+ TOF distributions. The bimodal C^+ TOF distributions leads, however, to a saturation in the fraction of energetic ions and consequently a limiting percentage (~70%) of sp^3 bonded carbon in the films. In addition, the understanding of carbon film growth obtained from these studies of ablation plume dynamics is expected to guide the growth of other metastable phases such as carbon nitride materials [9,10].

ACKNOWLEDGMENTS

This work was supported primarily by the MRSEC Program of the National Science Foundation under Award Number DMR-9400396.

REFERENCES

1. J. Robertson, Prog. Solid St. Chem. **21**, 139 (1991).
2. C. L. Marquardt, R. T. Williams, D. J. Nagel, Mat. Res. Soc. Symp. Proc. **38**, 325 (1985).
3. D. L. Pappas, J. J. Cuomo, K. L. Saenger, J. Bruley, W. Krakow, T. Gu, R. w. collins, J. App. Phys. **71**, 5675 (1992).
4. F. Davanloo, E. M. Juengerman, T. J. Lee, C. B. Collins, J. Mat. Res. **5**, 2398 (1990).
5. F. Xiong, R. P. H. Chang , Mat. Res. Soc. Symp. Proc. **270**, 451 (1992).
6. P. T. Marray, D. T. Peeler, D. V. Dempsey, Mat. Res. Soc. Symp. Proc. **235**, 825 (1992).
7. D. J. Krajnovich, J. Chem. Phys. **102**, 726 (1995).
8. J. J. Cuomo, D. L. Pappas, J. Bruley, J. P. Doyle, K. L. Saenger, J. Appl Phys. **70**, 1706 (1991).
9. Z. J. Zhang, P. Yang, C. M. Lieber, Mat. Res. Soc. Symp. Proc. **388**, 271 (1995).
10. Z. J. Zhang, S. Fan, J. Huang, C. M. Lieber, Appl. Phys. Lett. **68**, 2639 (1996).
11. G. Seifert, S. Becker, H. J. Dietze, Int. J. Mass Spectrom. Ion Processes, **84**, 121 (1988).
12. L. Wiedeman, H. S. Kim, H. Helvajian. Mat. Res. Soc. Symp. Proc. **201**, 575 (1991).
13. Y. Lifshitz, G. D. Lempert, E. Grossman, Phys. Rev. Lett. **72**, 2753 (1994).
14. S. Fahy, S. G. Louis, M. L. Cohen, Phys. Rev. B **34**, 1191 (1986).