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Study of porous carbon thin films produced by pulsed laser deposition

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Abstract

Amorphous carbon is an interesting material and its properties can be varied by tuning its diamond-like (sp^3) fractions. The diamond-like fractions in an amorphous carbon films depends on the kinetic energy of the deposited carbon ions. Porous amorphous carbon thin films were deposited onto silicon substrates at room temperature in a vacuum chamber by Glancing Angle Pulsed Laser Deposition (GAPLD). Krypton fluoride (248 nm) laser pulses with duration of 15 ns and intensities of 1–20 GW/cm^2 were used. In GAPLD, the angles between the substrate normal and the trajectory of the incident deposition flux are set to be almost 90°. Porous thin films consisting of carbon nanowires with diameters less than 100 nm were formed due to a self-shadowing effect. The kinetic energies of the deposited ions, the deposition rate of the films and the size of the nanowires were investigated. The sp^3 fraction of the porous carbon films produced at intensity around 20 GW/cm^2 were estimated from their Raman spectra.

Keywords: Porous thin films; Nanowires; Glancing Angle Pulsed Laser Deposition (GAPLD); Diamond-like Carbon (DLC); Amorphous carbone

1. Introduction

Diamond-like carbon (DLC) is a form of amorphous carbon which contains sp^3 hybridized bonds normally found in diamond. DLC films have a number of interesting properties, including high mechanical hardness, optical transparency, chemical stability and high thermal conductivity. Potential applications of DLC films include, protective coatings [1] and high temperature capacitors [2].

It is well known that pulsed laser deposition (PLD) can be used to produce DLC thin films with large sp^3 fraction. While the understanding of the physical processes involved in the generation of DLC films via PLD is far from complete, it is clear that the ion energy plays an important role [1–8]. In addition, it was reported the ion charge state can also play an important role [1]. Of course, the ion energy and ion charge state vary with the laser intensity on target, so that the sp^3 fraction of the DLC film can be tuned by adjusting the laser intensity, which resulting in variation of film properties, such as conductivity, hardness, index of refraction, etc.

Thin films with controlled nanostructures can be produced by glancing angle deposition (GLAD) due to a self-shadowing effect. GLAD films are highly porous, and this porosity is dependent on the deposition angle θ. The films consist of a large number of columnar microstructures, which assume a variety of forms depending on the deposition conditions; helical columns, staircase structures and posts have been reported [9–12]. Many potential applications rely on the enhanced surface area provided by the structure of these films. For example, it has been suggested that porous carbon films can be used as supercapacitors or as energy storage devices [13].

Previously, the production of porous carbon films by pulsed laser deposition has been reported [11]. In this paper, the preceding study is extended by characterizing the energy of the ion emission and the angular distribution of the ion energy. Additionally, the laser intensity on target is varied, and the resulting variations in the ion energy and the film properties are investigated. Clearly, characterization and control of the ion emission from laser-produced plasmas is important in predicting and improving the quality of deposited films. In addition, the monitoring of the ion emission characteristics would provide a useful method of ensuring the reproducibility of the plasma conditions under which films are deposited.

2. Experiment

A schematic of the experimental setup is given in Fig. 1. For the experiments, a Lumonics Excimer-500 KrF 248 nm laser

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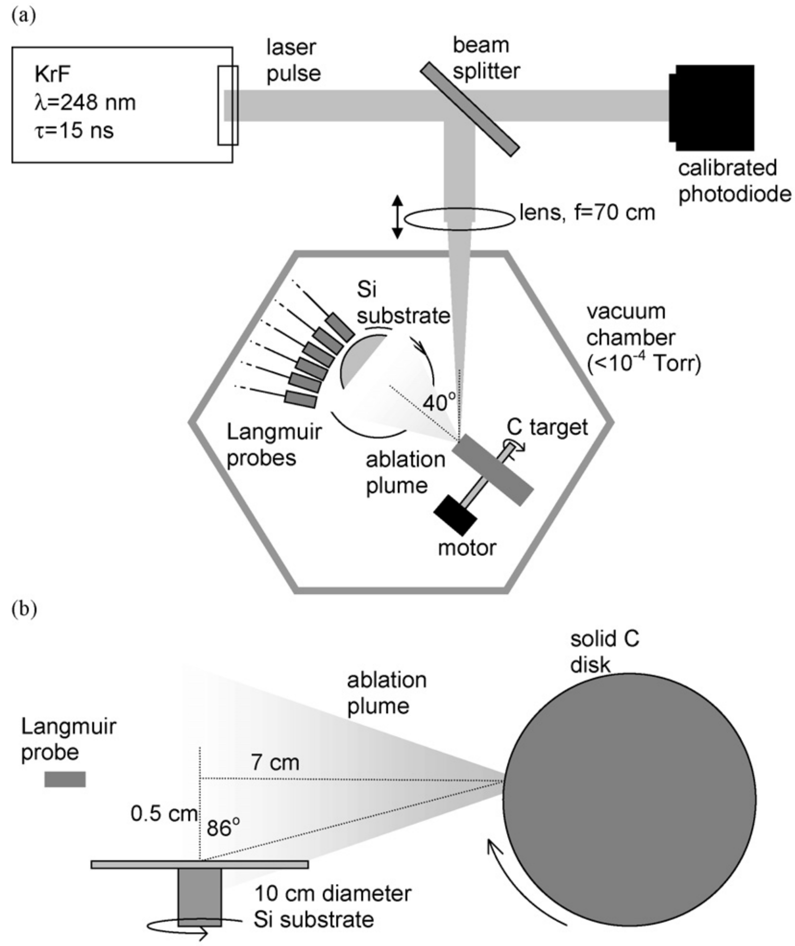

Fig. 1. A schematic of the experimental setup used for PLD and ion measurements: (a) top view and (b) side view.

was employed. This laser provided ~40–130 mJ pulses on target, with 15 ns duration.

The laser was operating in the unstable resonator configuration, producing a multimode rectangular beam. The laser pulses were focused onto the target using a planoconvex lens with a 70 cm focal length, located 3 m away from the laser output. The longitudinal position of the lens was variable, and this provided a means to control the laser spot size (and thus, the laser intensity) on target. In a separate measurement, the laser spot size on target was determined, using a filtered CCD camera (COHU 6612D), with image capturing software (Spiricon LBA-400PC). The measurement indicated that the focal spot was asymmetric, with the horizontal dimension larger than the vertical dimension. The asymmetry worsens for larger focal spots (at smaller lens-to-target distances). This is largely due to the multimode quality of the laser beam itself.

Assuming the digitized pixel values from the camera are proportional to the energy of the laser beam incident on a pixel, the area which contains 90% of the laser energy was calculated. The photodiode, positioned before the lens as in Fig. 1, was calibrated using a calorimeter (painted pyroelectric crystal) with a sensitivity of 2.67 V/J. The laser intensity was calculated using 90% of the laser energy within the 90% contour area.

For the depositions, the laser was operated at a repetition rate of 30 Hz; for the 60 min deposition times used in this experiment, this corresponds to 1.1×10^5 laser pulses. The silicon substrate (10 cm diameter) was positioned such that the GLAD deposition angle was 86°. In the vertical plane, the substrate captured ions emitted at angles ranging from 2° to 14° (measured with respect to the target normal). In the horizontal plane, the substrate captured ions emitted at angles ranging from 0° to 36°. The substrate was rotated at ~0.5 rotations/min.

The target was a solid molded graphite disk. The target was rotated using a DC motor in order to provide a fresh target area for each laser pulse. The angle of incidence of the laser pulses on target was approximately 40° (with respect to the target normal).

The vacuum chamber pressure was typically around 1×10^{-5} Torr (as measured with an Edwards Active Magnetron Gauge, AIM-S-NW25), which is sufficiently low to ensure that the target particle flux reaches the substrates and ion detectors.

The Langmuir probes used to detect the ion component of the ablation plume were located at distances of 17–18 cm from the carbon target, in the horizontal plane, at angles ranging from 6° to 60° (measured with respect to target normal). The probes were typically biased at voltages between −40 and −90 V. The