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Diamond-like carbon thin films produced by femtosecond pulsed laser deposition of fullerite

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ABSTRACT

Diamond-like carbon films have been deposited from a fullerite target by ultra-short pulsed laser deposition technique. The results indicate that the films morphology and structure, determined by scanning electron microscopy, atomic force microscopy and energy dispersive X-ray diffraction, depend strongly on the substrate temperature. X-ray photoelectron, X-ray Auger electron, Raman and surface enhanced Raman scattering spectra indicate that the fs-DLC films composition involves a mixed sp, sp^2 and sp^3 carbon network consisting of aromatic rings and sp^3 diamond-like structures linked by chains of different lengths and composition. The films deposited at room temperature, presenting the higher content of sp^3 carbon (48%), also contain C_{60} crystalline phase and show a very high hardness of 49 GPa.

1. Introduction

Diamond-like carbon (DLC) films are extensively used in a large number of industrial applications including razor blades, magnetic hard discs, engine parts, mechanical face seals, scratch-resistant glasses. In fact, they exhibit a number of very interesting properties, such as high density and electrical resistivity, chemical inertness, IR transparency, high elastic modulus and elevated hardness [1,2]. In particular, their wear-resistance, low friction coefficient and biocompatibility make DLC coatings suitable for use in biomedical applications [3–5].

During the last years, DLC thin films have been deposited by several different CVD and PVD methods [1]. Among these methods, Pulsed Laser Deposition (PLD) plays an important role due to its simple experimental apparatus and to its versatility that, in general, make of this technique one of the most useful methods to deposit a large range of films of materials with technological interest [6]. PLD has been widely used to deposit DLC thin films, using both short [7–10] and ultra-short [11,12] pulse lasers as ablation sources. By the use of both sources, coatings consisting of carbon materials with structures and properties, varying from graphite-like to diamond-like, depending on laser output parameters, background environment and substrate temperature, have been obtained.

In general, the ablation targets used in the PLD of DLC films are graphite or polymers, but other carbon-based materials can also be utilized. In a previous work [13], we have studied the films deposited by ablating a C_{60} target (fullerite) by a frequency doubled Nd:YAG laser, and in the present paper we present the results about ultra-short PLD applied to the same type of target. In this case, the ablation laser is a Nd:glass laser with a pulse duration of 250 fs. The deposited films have been analyzed by scanning electron microscopy (SEM), atomic force microscopy (AFM), Raman and surface enhanced Raman spectroscopy (SERS), X-ray photoelectron (XPS) and Auger spectroscopy (XAES), energy dispersive X-ray diffraction (EDXRD). Finally, the micro-hardness of the deposited films has been tested by a Vickers pyramidal indenter.

2. Experimental

The ablation and deposition experiments were performed by an apparatus already described [14]. It consisted of a stainless steel vacuum chamber, evacuated down to a pressure of 1.5×10^{-4} Pa, equipped with a rotating target holder, to minimize target craterization, and with a heatable substrate support. The ablation source was a frequency doubled Nd:glass laser ($\lambda = 527$ nm, $\tau = 250$ fs, repetition rate = 10 Hz), and the laser beam was oriented with an inclination angle of 45° with respect to the target. The fullerite target was prepared by cold pressing of C_{60} powder (99.98%, Therm-USA) into pellets. The films were deposited on Si(111) substrates at different substrate temperatures (25, 300, and 500 °C), and the substrate–target distance was kept at 2 cm. The laser fluence was kept at 10.0 J/cm^2 and the deposition time was 2 h.

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Raman and SERS spectra were recorded in backscattered configuration using a Jobin-Yvon LABRAM HR 800 micro-Raman spectrometer, equipped with two gratings (600 g/mm and 1800 g/mm) and with an Olympus microscope supplied with 10×, 50× and 100× objectives. The spectrometer was connected to a liquid N_2 cooled CCD detector. Excitations were performed by 632.8 nm radiation from a He–Ne laser source. The laser power was maintained at 20 mW. The spectra were acquired using the 600 g/mm grating and the 100× objective. In these conditions, the estimated resolution was around 4 cm^{-1}.

To obtain SERS spectra, a thin nanostructured silver film was deposited on the surface of the DLC films using femtosecond laser ablation of a pure Ag target. Optimal condition for SERS analysis were obtained using a fluence of 12 J/cm^2 and a target-substrate distance of 2 cm. The deposition time was 10 minutes and the silver film thickness was about 60 nm.

XPS and XAES spectra were acquired by a LH Leybold X1 spectrometer using non-monochromatized MgKα radiation operating at a constant power of 260 W. Wide and detailed spectra were collected in Fixed Analyzer Transmission (FAT) mode with a pass energy of 50 eV and channel widths of 1.0 and 0.1 eV, respectively. The acquired XPS spectra were analyzed using a curve-fitting program, Googly, described in [15], which allows the simultaneous fitting of photo-peaks in the form of a Voigt function and their associated background in a wide energy range. Derivative XAES spectra were obtained using a 23-point Savitzky–Golay convolution array. A second-order polynomial was used in the Savitzky–Golay analysis.

EDXRD experimental apparatus consisted of a non-commercial diffractometer [16] making use of a non-monochromatized primary beam. After the interaction with the sample, the X-ray beam was analyzed by a solid-state detector, capable of performing the energy scan of the diffracted photons. The set-up is characterized by a very simple geometry, since neither monochromator nor goniometer are required in the Energy Dispersive mode, no movement being needed during the measurements. The Bremmsstrahlung used as a probe is produced by a 3 kW power, tungsten anode X-ray tube. An EG&G high purity germanium solid-state detector, whose energy resolution is about 1.5–2% in the 20–50 keV energy range, accomplishes the energy scan.

A Rocking Curve analysis was carried out by recording for each film the intensity of the diffracted radiation as a function of an asymmetry parameter $\alpha = (\vartheta_i - \vartheta_f)/2$, where α_i and α_f are the initial (incidence) and final (deflection) angles, and $\vartheta_i + \vartheta_f = 2\vartheta$ is kept constant. EDXRD experiments were performed adopting the reflection geometry and working at E = 55 KeV, scattering angle $2\vartheta = 6.00°$, collimation slits aperture 300 μm*300 μm.

SEM (LEO 1450 Variable Pressure apparatus), working in secondary and backscattered electron modes, was used for morphological studies of the deposited films. The resolution of the apparatus in vacuum conditions was about 4 nm. Both plane and cross section view images of the film samples were obtained, the latter being necessary for thickness measurements. Since the images of the film cross sections were obtained by tilting the samples at 45°, the measured thickness values were multiplied by $\sqrt{2}/2$. The film thickness measurements were carried out in the backscattered electron mode by means of the 4 quadrants detector.

AFM measurements were performed in tapping mode using a Park XE 120 microscope. The topographic images were collected from representative portions of the films in order to evaluate the surface texture and roughness.

Micro-hardness measurements were performed by means of a Leica VMHT apparatus, equipped with a standard Vickers pyramidal indenter (square-based diamond pyramid of 136° face angle). The loading and unloading speed were 5×10^{-6} m/s, and the time under the peak load was 15 s. The hardness of the Si(111) substrate and of the deposited films was measured according to the procedure described in detail in our previous works [17,18]. For hardness measurements on the film/Si(111) substrate system, indentations were made applying 4 loads ranging from 0.147 up to 0.981 N. For each sample, approximately 10 random indentations were made at each load.

3. Results and discussion

3.1. Films morphology

The SEM micrographs of thin films deposited at different substrate temperatures show the typical morphology of films obtained by fs-PLD [19]. In fact, these films seem to be formed by the coalescence of a large number of particles with nanometric size (Fig. 1), even if the presence of a compact matrix cannot be excluded. The presence of particles is clearer in the films deposited at room temperature (RT), but also at higher temperatures, where the matrix is more evident, the matrix itself is composed by smaller particles as shown by AFM images reported in Fig. 2. This picture is confirmed by films roughness, expressed in terms of root mean square roughness (R_q), which was 12 nm at 25 °C, 5 nm at 300 °C and 2 nm at 500 °C. The thickness of

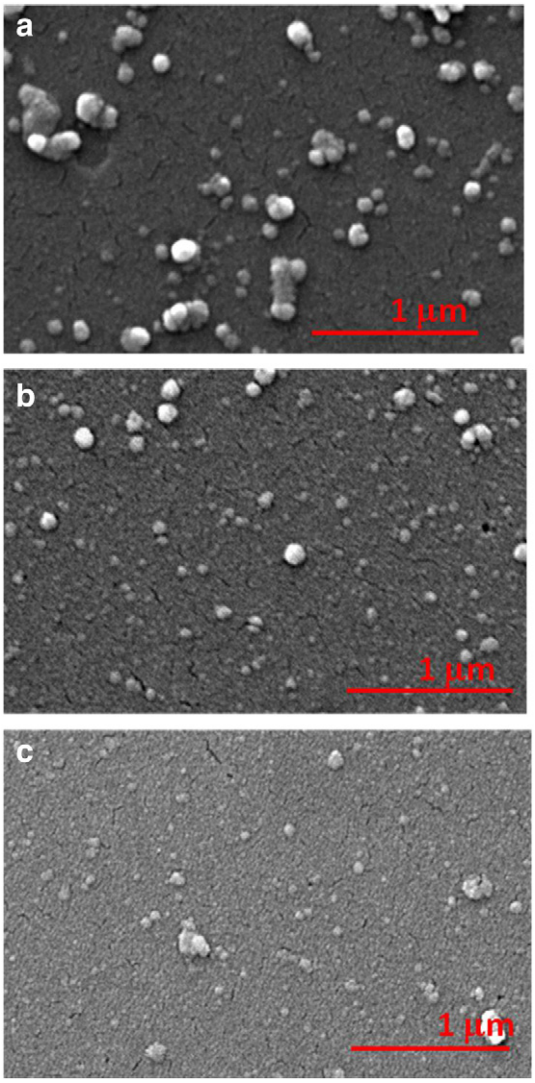

Fig. 1. SEM micrographs of the surface of films obtained by ablation of a C_{60} target: (a) film deposited at room temperature, (b) film deposited at 300 °C, (c) film deposited at 500 °C.