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Photoacoustic spectroscopy and thermal diffusivity measurement on hydrogenated amorphous carbon thin films deposited by plasma-enhanced chemical vapor deposition

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ABSTRACT

In this work, the photoacoustic spectroscopy and the open photoacoustic cell method are employed in the thermo-optical characterization of hydrogenated amorphous carbon thin films. The samples were fabricated in a modified plasma-enhanced chemical vapor deposition system with varying deposition time from 2 to 30 min. The optical absorption spectrum was determined for wavelengths of 300 to 2200 nm. The optical transmission spectrum was also recorded from photoacoustic spectroscopy. The energy gap was determined from the optical absorption spectra. The thermal diffusivity was found using open photoacoustic cell technique. The thickness of the films was confirmed to be an important parameter for the optimization of the fabrication process and the improvement of thermo-optical performances of the thin films. Spectroscopic results showed lower absorption and UV transparency for the thinner film. In the infrared region the −OH band decreased with increasing film thickness. On the other hand, the thermal diffusivity measurement presented an increase of this variable with decreasing film thickness.

1. Introduction

Diamond-like-carbon (DLC) films are widely used in biotechnology and material science. DLC is an amorphous carbon film that got its name because it has very similar properties to diamond, such as high hardness, high wear resistance, low friction, high chemical inertness and high electrical resistance [1]. Their versatility allows them to be used in a wide range of commercial and industrial applications such as aerospace protective coatings, automotive, auto racing, cosmetics, bearings, electronics, industrial wear parts, infrared optics, medical implants (such as hip and knee), medical/dental instruments, dry lubrication, antireflective and wear-resistant coatings for infrared (IR) and ultraviolet (UV) optics, protecting anticorrosion chemical for all types of steel, metal working, military, textiles and tools/dies/molds.

DLC thin-film deposition techniques and conditions [1,2] strongly influence DLC quality, its thermal and optical properties [3–7] as well as the adherence degree to the surfaces and its wear resistance [8–12]. Very smooth surfaces are required when DLC films are used as protective coatings for magnetic media, biological implants and microelectronic applications [9]. With the miniaturization of moving or sliding components in many technological devices, such as thermal microelectromechanical systems (MEMS) and the magnetic hard disk drives, surface forces like friction and adhesion are very important [10]. In particular, for the magnetic recording industry is crucial to develop very thin (~2 nm) and smooth protective coatings with a very low coefficient of friction and extremely good wear resistance, for the hard disk drives generation [9–11].

DLC can be classified into several categories according to the ratio of sp^3 to sp^2-hybridized carbon atoms and hydrogen (H) content in the film [1]. Typically, those containing up to about 50 at.% H and sp^3 fractions smaller than 50% are called hydrogenated amorphous carbon (a-C:H). The properties of a-C:H thin film fabricated by plasma-enhanced chemical vapor deposition (PECVD) are sensitive to deposition parameters. Many efforts to prepare high-quality DLC thin films with lower defect density and higher structural stability have been made. However, further investigation in the effect of deposition time on the thermo-optical properties of a-C:H thin films has not been done yet. Furthermore the thermal and optical properties of thin films of DLC can be associated with their applications. In the present study, we evaluate the thermo-optical characterization of a-C:H thin films deposited in a PECVD system with varying deposition time.

The photoacoustic (PA) techniques [13–17] are non-destructive tools for determining the optical thermal and transport properties of materials. PA techniques are versatile because the signal produced depends on both the amount of heat generated in the sample and how this heat diffuses. This technique offers two possibilities as a technique for monitoring. One of them would be as a spectroscopic technique

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[18,19] to monitor the spectra photoacoustic evolution during sample processing. The other one [13,16] would be as a tool to study changes in thermal diffusion by a particular treatment. The first option provides important elements in the study of energy bands [20,21] of a given element by measuring the optical transitions involved. On the other hand, the second possibility can measure thermal diffusivity [22–26] for the study of parameters such as defects, crystallinity degree, impurities and microstructure effects. Photoacoustic spectroscopy is thus able to monitor the transmission and absorption spectra of a-C:H thin films, as well as the behavior of its thermal diffusivity as a function of the film thickness.

2. Experimental

In this work, two photoacoustic techniques were applied for the films characterization: photoacoustic spectroscopy (PAS) [18–21] and open photoacoustic cell (OPC) [15,23,26,27].

2.1. Photoacoustic spectrometer

The PAS was used in spectroscopic measurements to quantify the optical absorption bands of the samples in the ultraviolet–visible (UV–VIS) region (330 to 760 nm) and the near (NIR) and mid (MIR) infrared (900 to 2200 nm) regions. In these measurements, the sample was placed inside a conventional photoacoustic cell. The lighting was produced by a xenon lamp (Xe) and diffracted in a narrow band wavelength by a grating monochromator, which permits the scanning of a region from 330 to 2200 nm. The acoustic signal comes from the heat generated by the sample after absorbing the monochromatic light modulated by a mechanical chopper at frequency ω. The heat is transferred to the gas at the same frequency ω producing the periodic pressure fluctuation inside the chamber. A sensitive microphone coupled in the cell detects this effect resulting in the PA signal, which depends on the absorption spectrum of the sample under investigation. Transmission spectra were also measured. In photoacoustic transmission measurements, the thin film was positioned at the focus of modulated light, but outside the photoacoustic cell. Inside the cell, a black carbon was used to absorb all the light transmitted through the thin film. Therefore, the photoacoustic signal measured was the transmission spectrum of the thin film. A photoacoustic spectrum is a power spectrum and the PA spectra are normalized to a black carbon spectrum conveniently obtained from the reference channel.

2.2. Open photoacoustic cell technique

The OPC technique is another way to detect the photoacoustic signal and was used to measure the thermal diffusivity. In this technique, the sample was placed directly on the front air chamber of a commercial electret microphone. The sample therefore closed the PA chamber microphone. The resulting pressure fluctuation in the photoacoustic gas chamber can be calculated using the Rosencwaig and Gersho (RG) thermal diffusion model [17]. For an opaque sample, pressure variation $P(\omega)$ on the electrets foil is given by [23]:

$$P(\omega) = \frac{\gamma P_0 I_0 \left(\alpha_g \alpha_s\right)^{1/2}}{\ell_g T_0 k_s \omega} \times \frac{\exp\left[j\left(\omega t - \frac{\pi}{2}\right)\right]}{\sinh(\sigma_s \ell_s)}. \tag{1}$$

$P(\omega)$ is a function of modulation of light amplitude with $\omega = 2\pi f$, where f is the modulation frequency. In Eq. (1), $\gamma = c_p/c_v$ is the specific heat ratio; P_0 and T_0 are the ambient pressure and temperature; I_0 is the flux of the incident monochromatic light; ℓ_i, k_i and α_i are the thickness, thermal conductivity and diffusivity, respectively; and $\sigma_i = (1 + j)a_i$ is the complex diffusion coefficient, which is frequency dependent and with a_i being the thermal diffusion coefficient. The subscript i can be "g" or "s" to indicate the gas or the sample, respectively. Depending on the linear thermal expansion coefficient and thickness of the sample, a thermoelastic contribution may appear in thermally thick regime ($\ell_s a_s \gg 1$) [23]. However, this contribution is only relevant at frequencies above those used in our experiment, so it may be theoretically ignored. Then the OPC amplitude, Eq. (1), is simplified substantially in the thermally thick regime [27]. The resulting expression is

$$P = \left(\frac{A}{f}\right) \times \exp\left(-b\sqrt{f}\right). \tag{2}$$

The coefficient A contains the instrumental transfer function and is independent of the samples thickness. So the thermal diffusivity can be calculated from the exponential dependence of the sample's frequency scan that allows one to fit the parameter $b = \sqrt{\pi \ell^2/\alpha_s}$ where the thickness ℓ is known.

The experimental OPC system for performing the frequency scans consisted of white light bulb tungsten, which is mechanically chopped (SR540, Stanford Research System) and uniformly focused directly on the sample. A lock-in amplifier (SR530, Stanford Research System) was used to measure the amplitude of the microphone signal. The electret microphone has a non-flat frequency response from 4–150 Hz. Its frequency response was obtained by running a frequency scan of a 102-μm-thick aluminum sample. This sample is thermally thin ($\ell_s a_s \ll 1$) up to 10 kHz, and one would expect the dependence of the PA signal on the modulation frequency to be $f^{-1.5}$ [23]. Therefore, the frequency scan allows getting the microphone response function (χ) [27].

2.3. Materials

The a-C:H thin films were deposited on a glass substrate (microscope cover slip). The substrate was cleaned in soapy water in ultrasonic bath for 5 min, rinsed in water and again put in an ultrasonic bath for 2 min. Subsequently, the substrate was cleaned with acetone p.a. in ultrasonic bath for 2 min. Then placed in the reactor discharge modified pulsed DC plasma-enhanced chemical vapor deposition (PECVD) system, in a stainless steel chamber with mechanical and diffusion pumps, with a residual vacuum of 10^{-6} Torr. The pre-cleaning of the substrate surface was performed with discharge argon at a pressure of 10^{-1} Torr for 5 min. Finally, the DLC deposition was conducted in an atmosphere of methane, at a pressure of 10^{-1} Torr, with temperatures at about 80 °C and deposition rate of 1 μm/h. The hardness achieved is about 25 GPa. The a-C:H films were grown with different deposition times: 2, 5, 10, 20 and 30 min. Film characteristics are summarized in Table 1, where "zero" represents the uncoated glass (substrate). Deposition rates showed small variation from 3.0 to 4.0 ± 0.3 nm min^{-1}, and the increase in the deposition time results in a slower rate. The samples showed a transparent optical appearance presenting a yellowish aspect with the increasing thickness and deposition time.

To perform the PA measurements, the samples were cut without a defined geometric shape, but with a length of approximately 10 mm. The thickness of the entire sample was 150 μm. The implicit condition for optical opaqueness required for Eq. (1) was met by using a circular aluminum foil (20 μm thick and 2 mm in diameter) and attached to the front side of the sample using a thin layer of oil. The thermal thickness of the foil was thus negligible compared to the samples thicknesses [28] since $\ell_{\text{aluminum}} \ll \ell_s$. Thus, we measured the effective thermal diffusivity of the system 20-μm-thick Al-thin film substrate. Certainly, the main conclusions made extended to the thin film itself are not contradictions, since it represents only a systematic error. Furthermore, as described before the aluminum foil is thermally thin for modulation frequencies up to some few kHz ($\alpha_{\text{aluminum}} = 0.92$ cm^2.s^{-1}), so that it introduces neither significant attenuation in the PA signal amplitude nor significant delay in its phase [29].