

## **Photoacoustic investigations of optical absorption, photoluminescence, and thermal diffusivity of Porous Diamond-Like-Carbon films**

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**Abstract.** Porous diamond-like-carbon (PDLC) has been investigated by photoacoustic spectroscopy (PAS) and photoluminescence (PL). From optical absorption data we have observed broad spectra distributions, spanning the wavelength interval, 350-850 nm, corresponding to phonon energies from 1.46 to 3.54 eV. For photoluminescence we have found a bright intensity around 360 nm. The complex energy transitions found have also been observed in porous silicon (PS) with much discussion. The amplitude and phase of the PA signals were measured at different frequencies of modulation in order to obtain the thermal diffusivity coefficient and has been obtained a value, which is about half of the crystalline silicon.

### **1. INTRODUCTION**

Surface porosity in different kinds of materials exhibits very interesting tribological, electrical and optical effect related to porous density and size, suggesting new technological application. More specifically Porous Diamond-LikeCarbon (PDLC) films have many attractive properties which can deal to potential applications [1]. Owing to the wide-ranging of possible technological applications in opto-electronic devices and biocompatible materials as well, the interest in characterizing PDLC has recently called our attention because of its similarity with porous silicon (PS) [2]. PS has been studied intensively since the discovery by Canham [3], that even at room temperature it can emit very bright photoluminescence (PL), in great contrast to crystalline silicon (c-Si).

### **2. EXPERIMENTAL PROCEDURE**

#### **2.1 Measures of PA absorption**

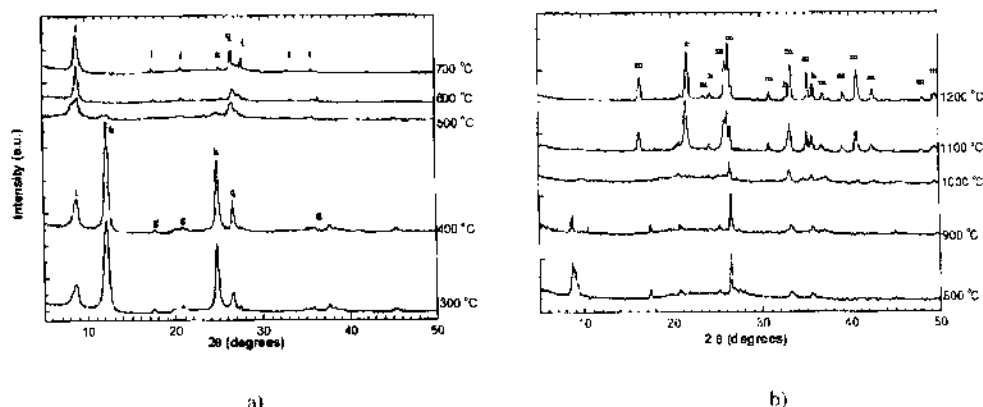
The PDLC thin films were obtained on (100) silicon substrate by DC low energy (150 W) magnetron sputtering and stored in atmosphere environment. The roughness (Rms) for PDLC is around 5 nm, and it does not change with the scanning area. Fig. 1 shows the Atomic Force Microscopy (AFM) image of the PDLC sample used in this work revealing similar roughness as observed in PS [2]. The photoluminescence (PL) measurements are done for two incident different wavelengths. The

This fine powder was extruded in order to obtain bricks with average dimensions of 100×20×10 mm. The bricks were dried at 110 °C during 24 h, thereafter submitted to a slow heating process, with a heating rate of 2 °C/min up to a set temperature level, then kept constant during 240 min. This procedure was used for samples fired at 300, 400, 500 and 600 °C. For 700, 800, 850, 900, 950, 1000, 1050, 1100, 1150 and 1200 °C the sample temperature was initially raised up to 600 °C and kept constant during 60 min, then increased to the final temperature level and kept during 180 min. This procedure allowed to avoid cracks due to a quartz phase transition at 575 °C. After firing, we determined the volumetric shrinkage, the water absorption, the open porosity, the apparent density and the bending rupture tension following standard procedures, as reported in a previous work [3].

X-ray diffraction data were measured at room temperature using Cu K $\alpha$  radiation at a conventional diffractometer, with a graphite diffracted beam monochromator. Diffraction data were measured in the range  $3^\circ \leq 2\theta \leq 75^\circ$  with step  $0.03^\circ$  and counting time 3 s. The crystalline volumetric fraction was calculated from each complete diffractogram using the ratio between the area under the crystalline peaks and the total area, which includes the amorphous background. For this purpose, the crystalline and amorphous contributions to the total intensity were deconvoluted using a suited software.

The thermal diffusivity was measured using the open photoacoustic cell. In this configuration, the external surface of a thermally thick and optically opaque sample is heated by a modulated radiation (He-Ne laser, operating at 93 mW), and the heat is transported through the sample to a closed air chamber, producing a pulsed acoustic signal. For the measurement of the photoacoustic signal, the soil samples were sieved (grain sizes lower than 75  $\mu\text{m}$ ) and pressed at 2 ton/min to make disks 500  $\mu\text{m}$  thick, which were submitted to the same firing procedures used for the bricks.

### 3. RESULTS



**Figure 1.** X rays diffraction patterns for ceramic samples treated at different temperatures ranging from 300 °C to 1200 °C. The curves are vertically displaced for better visualization. In order to show phases evolution some peaks are identified according to: k - kaolinite; g - gibbsite; i - illite/muscovite; q - quartz; a - anatase; h - hematite; c - cristobalite; m - mullite.

Figure 1 shows the evolution of the X rays diffraction patterns as a function of the firing temperature. For the natural powder soil and for samples treated up to 400 °C the diffractograms disclosed very similar mineralogical composition, with a large fraction of kaolinite (about 86 wt % [1]), and small fractions of illite / muscovite, gibbsite, anatase and quartz. Between 400 and 500 °C occurs the

transformation from kaolinite to a non-crystalline phase, metakaolin, while the other crystalline phases remain unchanged up to 900 °C. Treatments at 950 °C or higher cause the samples recrystallization, with the formation of mullite, cristobalite and hematite phases. It was previously reported [3] that between 900 and 1200 °C, the open porosity diminishes abruptly from 39.4 to 2.5 vol. %, while the volumetric shrinkage increases from 15.9 to 41.9 vol. % and the bending rupture tension presents a strong increase from 9.1 to 28.2 MPa. This behavior suggests that the recrystallization occurs accompanied by sintering process, leading to the improvement of the ceramic performance.

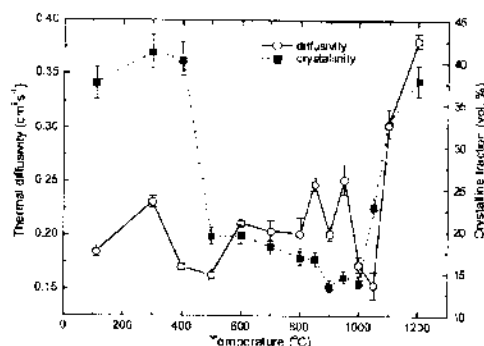


Figure 2. Thermal diffusivity and crystalline volumetric fraction for ceramic pieces fired at different temperatures.

From the diffraction data the crystalline volumetric fraction was determined, and the results (Figure 2) show the reduction in the crystalline fraction at 500 °C, due to kaolinite dehydroxilation, followed by the sintering and recrystallization of new phases above 1000 °C.

The thermal diffusivity results (Figure 2) confirm the correlation between microstructure and thermal transport in this material. For temperatures below 1000 °C the thermal diffusivity value is dominated by the air trapped in the porous system, thus showing an average value of 0.22 cm²/s. The thermal diffusivity presented a strong variation above 1000 °C, clearly associated to the reduction of porosity and to the increase in the crystalline fraction, in this temperature range. We conclude that this important thermal property can be used as a monitoring parameter of the quality of the final ceramic product.

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