

Crystallinity evolution in ceramic materials monitored by thermal diffusivity

R. Toledo¹, D.R. dos Santos¹, R.T. Faria Jr.¹, L.C.M. Miranda², L.T. Auler¹ and H. Vargas¹

¹*Universidade Estadual do Norte Fluminense Darcy Ribeiro – UENF, Av. Alberto Lamego, CEP: 28013-602, 2000 Campos dos Goytacazes, RJ, Brazil*

²*Instituto Nacional de Pesquisas Espaciais – INPE, Av. dos Astronautas, CEP: 12227-010, 1758 São José dos Campos, SP, Brazil*

Abstract. In this work, we present a detailed analysis of the thermal and crystalline evolution in ceramic samples produced from natural soil and heated at different temperatures, ranging from 300 to 1200°C. The crystalline and amorphous volumetric fractions, as well as the crystalline phases evolution as a function of the applied temperature were determined from X-ray diffraction data. The structural modifications are responsible for drastic changes in the properties related to the ceramic performance. The thermal diffusivity results were correlated to the structural properties of the ceramic pieces, showing that this important thermal property can be used as a monitoring parameter of the quality of the final product.

1. INTRODUCTION

Large clay deposit areas situated in the Rio de Janeiro State, Brazil, supply raw material for the ceramic industry, an important economical activity in this region. A series of studies has been carried out in order to completely characterize the soil from this sedimentary basin, which has kaolinite, illite, quartz, goethite, anatase and gibbsite as the main crystalline phases [1,2]. We have also been concerned with the environmental impact of the gases released during firing of clay materials. Emissions of CO, CO₂, NO, N₂O and CH₄ have been detected, while NH₃ and SO₂ have not been observed within our detection limit [3]. In a previous work the soil clay fraction was isolated and its thermal properties were determined, showing that thermal diffusivity, heat capacity and thermal conductivity are very sensitive to the amorphous-crystalline phase transition that occurs when the clay fraction is heated above 950°C, which is a typical temperature applied in the manufacturing process to obtain ceramic materials with desirable performance [4]. In this work, we present a detailed analysis of the thermal diffusivity and crystalline evolution in ceramic pieces produced from the previously characterized raw material, and fired at different temperatures. The thermal diffusivity results were correlated to the structural and rheological properties of the ceramic pieces, showing that this important thermal property can be used as a monitoring parameter of the quality of the final ceramic product.

2. EXPERIMENTAL PROCEDURES

Small pieces were produced from natural soil following procedures similar to the industrial processes used for production of bricks and roof tiles. Soil samples were selected from a mining site at different depths below the surface. These samples showed a high plasticity, a large clay fraction (about 50 % in mass of particles with grain sizes lower than 2 µm) and about 95 % of particles below 50 µm in size.

experimental PA spectroscopy apparatus consisting of a high-pressure 1000W xenon arc lamp (Osram), a chopper (HMS Elektronik, model 220A) and a monochromator (Sciencetech, model 9010) [4,5]. From optical absorption (Fig. 2) and PL (Fig.3) data we have observed broad spectra distributions, spanning the wavelength interval, 350 - 850 nm, corresponding to phonon energies from 3.54 to 1.46 eV and for PL just in the 280 nm- 440 nm range corresponding to 4.42 to 2.82 eV. Several spectral features are seen, revealing the complex energy band system originated from the surface roughness as shown in Figs. 2 and 3 for PDLC. Evidently, these absorption as well as PL spectra reveal complex structures in contrast to those obtainable from ordinary semiconductor materials with one fundamental band-gap which a well-defined absorption edge is observed. Fig.2 also shows a band around 760 nm when the PDLC film face is exposed to the light at the modulation frequency of 100 Hz. That band does not appear when the substrate face is illuminated at low frequency (20 Hz). This fact reveals that the effect is on the surface and it is originated in the PDLC film.

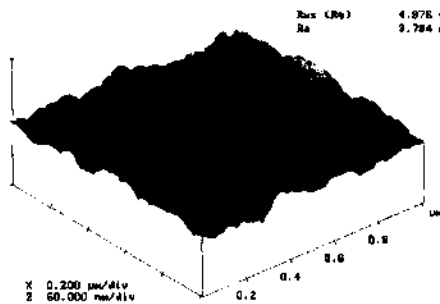


Figure 1. AFM of PDLC.

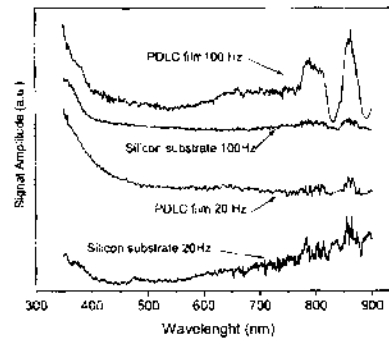


Figure 2. Absorption spectrum of DLC sample.

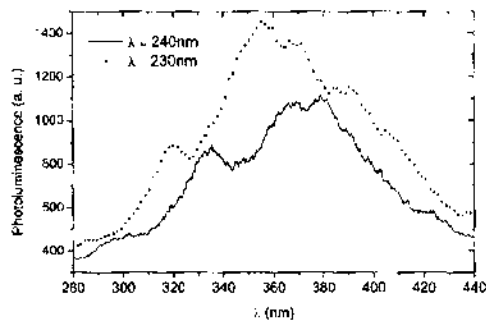


Figure 3. Photoluminescence of PDLC.

2.2 Measures of thermal diffusivity

To determine the coefficient of thermal diffusion of sample DLC, a 300 mW Melles Griot argon laser was used as light source. The monochromatic light beam was modulated with a chopper; model SR540 of Stanford Research Systems (SRS). The cell used is fully described in reference [6] and it allows front and rear illumination. The signal produced in the cell was detected with a Sennheiser microphone, amplified with the Lock-in of the SRS, recorded and interpreted by a computer program. The amplitude and phase of the PA signals of the diamond-like-carbon were measured at different frequencies of modulation. These measurements were carried out with rear illumination, first with the

PDLC film face receiving the light and afterwards with the substrate face illuminated. In both cases the thermal diffusion coefficient found was almost the same. Moreover due to a very low roughness and thickness of the PDLC thin film compared to silicon substrate we treat the thermal diffusivity as an effective mean value. This has been done for porous silicon with very good results [5].

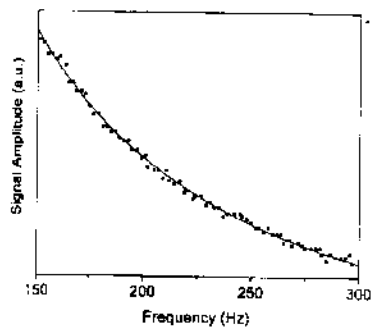


Figure 4. PA signal amplitude measurement as function of the modulation frequency of a DLC sample.

As the sample is thermally thick in that frequency range and the signal amplitude is proportional to $S \propto \frac{1}{f} \exp\left(-a_s f^{1/2}\right)$,

the predominant mechanism in the generation of the photoacoustic signal is the thermal diffusion [7].

Fig 4 shows the fitting of the experimental curve with the above expression. From this adjustment and the following mathematical expression, it was possible to get the diffusion coefficient.

$$\alpha = \pi \left(\frac{l_s}{a_s} \right)^2$$

where $l_s = 0,042$ cm is the thickness of the sample.

Therefore, the value obtained for the thermal diffusion coefficient of diamond-like-carbon is $\alpha = 0,48$ cm²/s.

3. CONCLUSIONS

In this work we have obtained through the photoacoustic technique the absorption and thermal diffusivity, from PL a bright intensity and through the AFM the complex structure of the band-gap energies of the PDLC, which exhibit several energy onsets. This is by itself an usual richness in structures in comparison to the cases where semiconductor materials with ordinary band structures have been studied, and it shows similarities with PS suggesting that PDLC also has a potential for applications in optic-electronic device structures. The effective thermal diffusivity result is $\alpha = 0.48$ cm²/s, a value, which is about half of the crystalline silicon.

Acknowledgements

This work was financially supported in part by the Brazilian National Research Council (CNPq), CNPq/NanoSemiMat under grant no. 550.015/01-9, CT-FVA/CNPQ 01/2003-REMAN and FAPESB-Bahia.

References

- [1] Santos L.V., Trava-Airoldi V.J. Iha K., Corat E.J., and Salvadori M.C., *Diamond and Rel. Mater.*, **10** (2001), 1049.
- [2] Ferreira da Silva A., Rosa R.R., Roman L.S., Veje E., and Pepe I., *Solid State Commun.*, **113** (2000), 703.
- [3] Canham L. T., *Appl. Phys. Lett.*, **57** (1990), 1046.
- [4] Zelaya-Angel O., Alvarado-Gil J.J., Montes R.L., Vargas H., and Ferreira da Silva A., *Appl. Phys. Lett.*, **64** (1994), 291.
- [5] Ferreira da Silva A., Silva T.S., Nakamura O., Aguiar Neto M.M.F., Pepe I., Roman L.S., and Veje E. *Mater. Research*, **4** (2001), 23.
- [6] Silva T.S, Alves A.S., Pepe I., Tsuzuki H., Nakamura O., Ferreira da Silva A., Veissid N., An C.Y., *J. Appl. Phys.*, **83** (1998), 6193.
- [7] Vargas H., Miranda L.C.M., *Physics Reports (Review Section of Physics Letters)*, **161** (1988), 101.