Thermal characterization of polymeric thin films by photoacoustic spectroscopy

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The determination of the thermal properties is an important and well stablished application of Photoacoustic techniques. These methodologies are non-destructive methods based on the generation of thermal waves using a modulated light source [1,2]. However, the study of thin films is limited due to the restrictions established by the thermal diffusion length. In this work, we show a methodology which allows to perform a complete thermal characterization of thin films as a two-step characterization process in the same photoacoustic cell.

The heat diffusion equation for a modulated flux, was solved considering a flat two-layer system, surrounded by air. Two configurations were considered, the first one with a perfect match between the layers and the second with a thermal interface resistance between both the layers (e.g., Fig. 1).

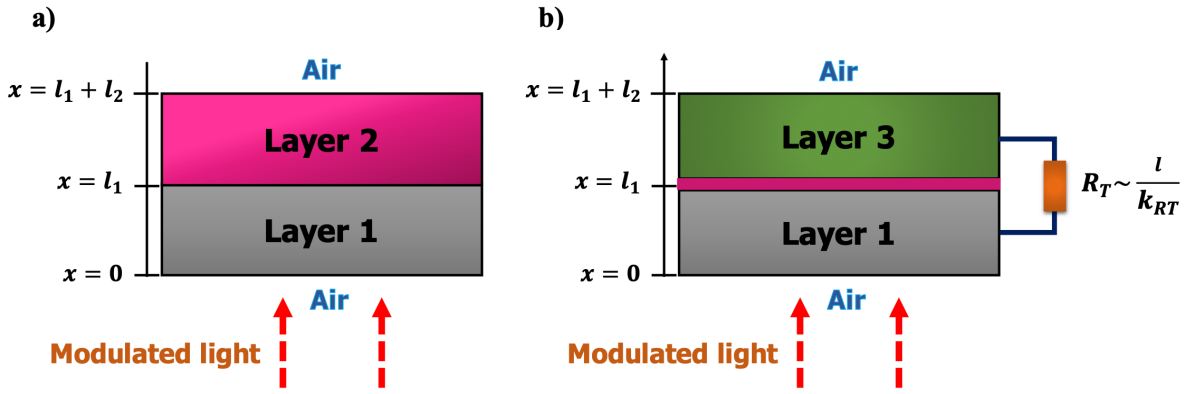

Fig. 1. Two-layer system diagram **a)** with temperature continuity between layers, and **b)** with thermal interface resistance

The first step of the experiment consists in depositing a layer of variable thickness (layer 2) on a substrate (layer 1). If the thickness of layer 1 is made very thin, the normalized temperature at the front face can be expressed as

$$\Delta T = 4\frac{1}{e_1} * \frac{e^{-2\sigma_1 l_1}}{1-e^{-4\sigma_1 l_1}} (\rho C)_2 \left[\sqrt{2\pi f}\, l_2 - \frac{2\pi f}{\sqrt{\alpha_2}} {l_2}^2\right] \quad \text{Eqn. 1}$$

$$\text{with} \quad \sigma_1 = (1+i)\sqrt{\frac{\pi f}{\alpha_1}}$$

Where ΔT is the gap between the beginning and the final of the signal, f is the frequency, e_1 and α_1 are the thermal effusivity and diffusivity of layer 1, respectively. Indicating a simple dependence on the volumetric heat capacity $(\rho C)_2$, the thermal diffusivity α_2, final thickness l_2 of layer 2.

For the second step system a third layer is deposited on top of layer 2. Considering a temperature discontinuity between both layer as a thermal resistance, R_T, which is related to the thermal conductivity [3], the temperature at the front face is given by

$$T(x=0) = \frac{Q}{\sigma_1 k_1}\left(\frac{1+R'_{31}e^{-2\sigma_1 l_1}}{1-R'_{31}e^{-2\sigma_1 l_1}}\right) + QR_T\left[\frac{(1-R'_{31})}{1-R'_{31}e^{-2\sigma_1 l_1}}\right]^2 e^{-2\sigma_1 l_1} \qquad \text{Eqn. 2}$$

$$\text{with } R'_{31} = \frac{R_{31}+e^{-2\sigma_3 l_3}}{1+R_{31}e^{-2\sigma_3 l_3}}, \quad R_{31} = \frac{1-e_3/e_1}{1+e_3/e_1}, \quad \sigma_j = (1+i)\sqrt{\frac{\pi f}{\alpha_j}}$$

Where Q is the power of the laser, k , l , e and α are de thermal conductivity, thickness, thermal *jjjj*

effusivity and diffusivity of each layer (j = 1, 3), respectively. The subscripts 1 and 3, refer to the layers 1 and 3 (e.g., Fig. 1b).

This expression allows to determine the thermal conductivity of the inner layer. Both equations 1 and 2 allow to perform the complete thermal characterization of the film.

The experiments were performed using a closed photoacoustic cell and 304- stainless steel as a substrate. Polymeric solution of starch biopolymers and PEDOT: PSS were dropped on the substrate and the amplitude signal was recorded on time. At the end of the evaporation process a film is formed and the amplitude of the photoacoustic signal becomes stable. Applying Eqn. 1, the volumetric heat capacity and thermal diffusivity of the sample were obtained, in agreement with reported parameters [1,4].

On the top of the film formed a thick drop of colloidal graphite is deposited, and the phase signal is recorded as a function of the frequency. The data are fitted using Eqn. 2, and changes in the signals are related to the thermal conductivity and thickness of the polymeric film enclosed.

The conditions under our methodology can provide reliable results for films of a few micros are presented and discussed.

References

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