MODELING AND THERMAL CHARACTERIZATION OF POLYMERIC THIN FILMS BY PHOTOACOUSTIC SPECTROSCOPY

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1. Introduction

Photothermal techniques are based on the conversion of absorbed optical energy into thermal energy.

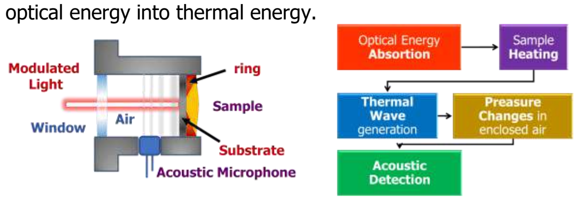


Figure 1. *Photoacoustic cell and Photoacoustic effect by Heat Diffusion*

A material's photothermal response depends on two parameters: thermal diffusivity (α) and thermal effusivity (e).

Heat Diffusion Equation:

$$(1)\quad \frac{\partial^2 T}{\partial x^2}+\frac{\dot{q}}{k}=\frac{1}{\alpha}\frac{\partial T}{\partial t}$$

$$(2)\quad T_i(x)=C_1 e^{\sigma_i x}+C_2 e^{-\sigma_i x}$$

2. Methodology

Evaporation Process Monitoring

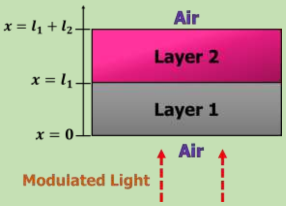


Figure 2. *Two-layer system*

The thickness and concentration of the second layer changes over time due to the evaporation process.

Normalized solution for temperature:

$$(3)\quad T_N(x=0)=\left(\frac{1+R'_{21}e^{-2\sigma_1 l_1}}{1-R_{g1}R'_{21}e^{-2\sigma_1 l_1}}\right)\left(\frac{1-R_{g1}^2 e^{-2\sigma_1 l_1}}{1+R_{g1}e^{-2\sigma_1 l_1}}\right)$$

$$R'_{21}=\frac{R_{21}+R_{g2}e^{-2\sigma_2 l_2}}{1+R_{21}R_{g2}e^{-2\sigma_2 l_2}},\quad \sigma_i=(1+j)\sqrt{\omega/2\alpha_i},\quad R_{mn}=\frac{1-\frac{e_m}{e_n}}{1+\frac{e_m}{e_n}}$$

Where $l_i, \alpha_i, e_i, R_{mn}$ are the thickness, diffusivity, effusivity and reflection coefficients of each layer.

Thickness variation of the sample considering the formation of a meniscus during the evaporation process:

$$(4)\quad h(t)\equiv l_2 =\frac{1}{\pi l^2}\left[\left(\frac{m(t)}{\rho_{solv}}+V_{solute}\right)+\frac{\pi}{3}(R-D)^2(2R+D)\right]$$

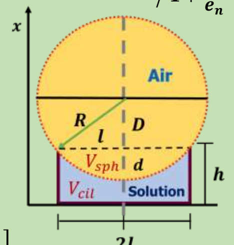


Figure 3. *Meniscus formation configuration during evaporation*

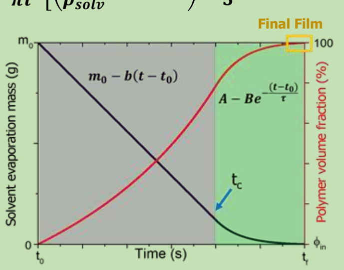


Figure 4. *Solvent mass and polymer fraction during evaporation process*

The effective properties of the System vary according to the evaporation rate and the change in polymer concentration, $\phi(t)$:

$$(5)\quad \phi(t)=\frac{\frac{m_{polymer}}{\rho_{polymer}}}{\frac{m_{polymer}}{\rho_{polymer}}+\frac{m(t)}{\rho_{solv}}}$$

PEDOT:PSS System Example

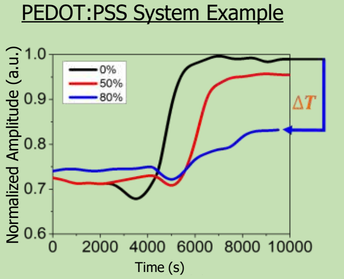


Figure 5. *Normalized amplitude for different concentrations, f=7Hz*

The system presents a three well defined zones.

An approximation of Eq. 3, relates the difference between the final amplitude with $(\rho C)_2$ y l_2, eq. 6:

$$(6)\quad \Delta T=4(1+j)\sqrt{\pi f}\,\frac{1}{e_1}*\frac{e^{-2\sigma_1 l_1}}{1-e^{-4\sigma_1 l_1}}(\rho C)_2 l_2$$

Thermal Resistance Model

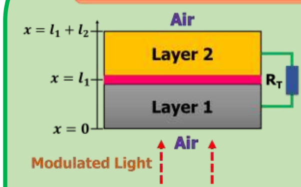


Figure 6. *Two-layer model separated by R_T*

Discontinuity condition:

$$(7)\quad T_2-T_1=-R_T k_1\frac{dT}{dx}$$

$$R_T=l/k$$

One dimensional solution approximation of eq. (1):

$$(8)\quad T(x=0)=\frac{Q}{\sigma_1 k_1}\left(\frac{1+R'_{21}e^{-2\sigma_1 l_1}}{1-R'_{21}e^{-2\sigma_1 l_1}}\right)*\left(1+\frac{R_T\sigma_1 k_1(1-R'_{21})(1+3e^{-2\sigma_1 l_1}-3R'_{21}e^{-2\sigma_1 l_1}-R'_{21}e^{-4\sigma_1 l_1})}{2(1-R'_{21}e^{-4\sigma_1 l_1})}\right)$$

$$R'_{21}=\frac{R_{21}+e^{-2\sigma_2 l_2}}{1+R_{21}e^{-2\sigma_2 l_2}}$$

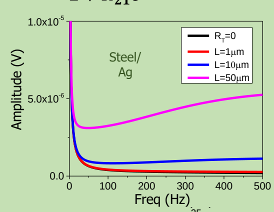
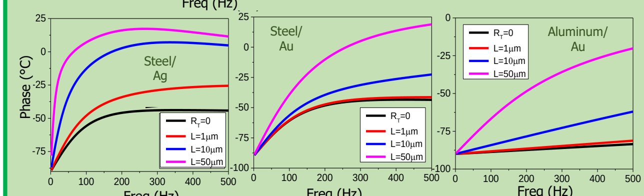
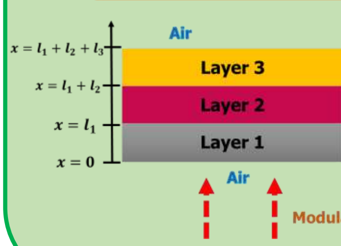


Table 1. *Comparison between the k of the materials used in the simulation*

Material	Conductivity (W/mK)
Polymer	0.2
Aluminum	~2x10[2]
Gold	~3x10[2]
Steel 316	~1x10
Colloidal Ag	~1x10



Three-layer system



$$(9)\quad T(0)=\frac{Q}{k_1\sigma_1}\frac{1+R'_{123}e^{-2\sigma_1 l_1}}{1-R'_{123}e^{-2\sigma_1 l_1}}$$

$$R'_{123}=\frac{R_{21}+R'_{32}e^{-2\sigma_2 l_2}}{1+R_{21}R'_{32}e^{-2\sigma_2 l_2}}\quad R'_{32}=\frac{R_{32}+e^{-2\sigma_3 l_3}}{1+R_{32}e^{-2\sigma_3 l_3}}\quad R_{32}=\frac{1-e_3/e_2}{1+e_3/e_2}$$

Figure 7. *Three-layer system model*

3. Conclusion

The graphs obtained show three well-defined stages. The signal starts almost constant, the second stage is characterized by a minimum, due to the interference of thermal waves, and finally, the amplitude increases to a stable value, corresponding to the formation of the film.

The volumetric heat capacity or thickness of the system can be calculated based on ΔT.

The conductivity, k, are obtained by solving the system considering a discontinuity in temperature, thermal resistance. The phase signal is highly sensitive to small changes in thickness of thin films, when the conductivities of the outer layers are of a similar order.

References

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