White-Light Photothermal Mirror Spectrophotometer

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Abstract: We describe an arc-lamp based pump-probe photothermal mirror spectrophotometer to measure the spectrum of the thermal quantum yield of the surface of solid samples. We discuss advantages of the method to characterize solid nontransparent materials.

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1. Introduction

This work introduces a new kind of spectrophotometer based on the photothermal mirror (PTM) effect aimed to study the spectral photothermal response of the surface of solid samples. The focusing of a beam of light onto the sample's surface generates a nanometric bump of thermal origin due to the thermoelastic effect [1-2]. The bump acts as a mirror affecting the diffraction pattern of the reflected beam at the far field. The effect is similar to the well-known thermal lens phenomenon, but instead of analyzing the transmitted beam, it investigates the diffraction pattern distortion of the reflected beam. In a pump-probe configuration, we use a probe beam of relatively low power to test the generated photothermal mirror. Using a tunable excitation light source makes possible to measure a PTM spectrum. As a tunable light source, we use a Xenon lamp and a set of interference filters to produce quasi-monochromatic light in the spectral region 370 nm to 800 nm. We show that the method provides the thermal quantum yield spectrum, which measures the ability of the surface to produce heat upon absorption of light as a function of the wavelength. The presence of effects like surface luminescence, generation of electrical carriers, sound, and other processes of non-thermal origin affect the shape of the spectrum. Determination of thermal diffusivity, thermoelastic coefficient, and other photothermal properties is also possible. The technique is useful to characterize transparent and non-transparent samples, including thin films. As examples of applications of the method, we measure the PTM spectra of a highly absorbing glass plate, and a nontransparent film of silver nanoparticles deposited on a glass substrate. The technique represents a new way of characterization of the surface of a solid sample different from regular reflectivity and transmission methods.

The concurrent resolution of the thermal diffusivity and thermo-elasticity equations provides a theoretical model for the determination of the PTM surface deformation [3-9]. Further, a Fresnel diffraction approximation yields the diffraction pattern of the probe field at the far field. The model shows that the thermal quantum yield is

$$\psi(\lambda) = K \cdot \frac{S(t,\lambda)}{P_e(\lambda)} \quad , \qquad (1)$$

where $P_e(\lambda)$ is the power of the light of wavelength λ, $S(t,\lambda)=(T(t,\lambda)-T_o)/T_o$, $T(t,\lambda)$ is the transmission of the probe light through an aperture located at the far field for the pump light of wavelength λ, T_o is the probe beam transmission through the same aperture in the absence of pump light, and K is a proportionality coefficient which does not depend on the wavelength values λ.

2. Method

Figure 1a shows a simplified schematic of the PTM spectrophotometer. The light from a Xenon arc-lamp is modulated at low frequency (2 Hz) using the optical chopper Ch. A small glass plate redirects part of this light to a detector D_1 used for reference purposes. Lens L_1 (15 cm focal length) collimates the pump light before passing through an interference filter. We use 44 interference filters to produce quasi-monochromatic light in the spectral region 370-800 nm with a spectral resolution of 5 nm. Lens L_2 (10 cm focal-length) focuses the filtered pump light onto the sample with a resulting beam spot radius of 0.5 mm. A 2 mW CW He-Laser (632 nm) provides the probe light. The telescope Co collimates the probe beam extending its radius up to two mm. Mirror M_1 redirected the collimated probe beam toward the sample covering the spot of the focused pump beam. This way the spot dimension of the probe at the sample's plane is more than ten times larger than the spot dimensions of the pump beam. Mirror M_2 collects the reflected probe beam of light and redirects it toward the aperture. The aperture is at the center of the beam. A semiconductor diode records the probe light transmitted through the aperture. A current preamplifier amplifies the signal before sending it to a digital oscilloscope for averaging. The oscilloscope yields $S(t,\lambda)$. A calibrated power sensor measures the power $P(\lambda)$ at the sample position. The method requires an optical-quality reflecting surface of the samples under study.

3. Results and Analysis

Figures 1b and 1c show the PTM spectra of a glass plate of high absorbance in the visible (OD>5) and a nontransparent film of silver nanoparticles deposited over a glass substrate. The standard deviation corresponds to an average of five experiments. The observed peaks correspond to the plasmonic response of the samples. The secondary peaks in the silver sample correspond to the effect of nanoparticles agglomeration. The peaks show the spectral areas where the sample generates heat with the highest efficiency upon absorption of light photons.

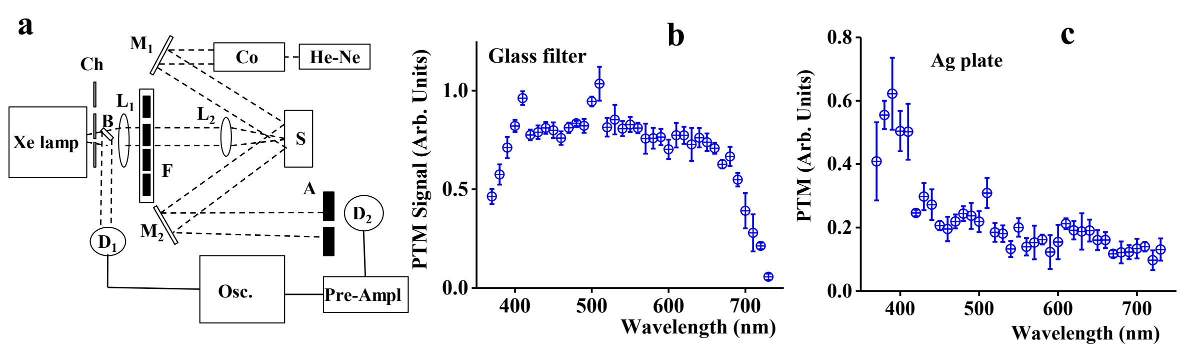

Figure 1. a) PTM spectrophotometer scheme; b) PTM spectrum of a glass filter; c) PTM spectra of a film of silver nanoparticles.

4. Conclusions

This work shows the feasibility of the PTM spectrophotometers as a new instrument for characterization of the ability of the first atomic layers of the sample's surface to generate heat. The method is particularly useful for the study of non-transparent samples where transmission spectroscopy cannot work.

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6. References

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