

Application of the photoacoustic technique to the determination of the thickness of multilayer films produced by magnetron sputtering

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Multilayer thin films consisting of alternate layers of metal and oxide have been prepared by magnetron sputtering. The films have been studied by optical and photoacoustic spectroscopy (PAS) and thicknesses determined from the interference patterns. The non-destructive PAS technique gives reliable results for dielectric layers thicker than about 100 nm.

1. Introduction

The study of the properties and applications of optical multilayer thin films is a fast growing field¹, which has attracted much interest for a number of years. Interference filters and high and low reflectivity coatings are some of the best known applications.

The optical quality of the films depends strongly on the preparation method. Final properties will also depend on the materials, refractive index, thickness, etc.

In this work, the preparation by magnetron sputtering of thin films with metal (copper) and dielectric (tin and zinc oxides) layers is reported. Film thicknesses have been determined by optical and photoacoustic spectroscopies, which can provide alternative interferometric methods of measurement. Multilayer semi-transparent films, have also been studied.

2. Experimental

The multilayer films were prepared by magnetron sputtering from metal targets, with the apparatus described elsewhere². The metal layers were deposited on optical glass slides in argon atmosphere while the deposition of the oxide layers was carried out in oxygen atmosphere. Different film thicknesses can be obtained by variation of the deposition times, the pressure or the distance between target and substrate.

Two types of films have been prepared (Figure 1). In type I

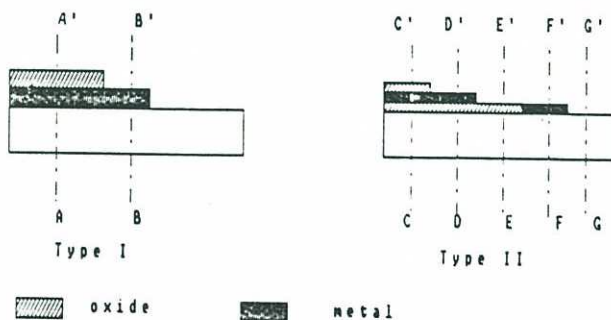


Figure 1. Schematic view of the two types of films produced. Measurements can be made in any of the directions shown.

films the first (metal) layer was optically opaque and the oxide layer was thicker than 100 nm. In type II films all layers were thinner than 100 nm and therefore the metal layer was semi-transparent. By appropriate masking, different numbers of layers could be deposited in different regions of the same substrate.

Transmittance and diffuse reflectance measurements were performed on type I and II films in the wavelength range 200–900 nm, using a double beam absorption spectrophotometer Shimadzu UV-260, provided with an integrating sphere attachment.

For the photoacoustic measurements of type I films, modulated light from a 150 W xenon lamp from PTI was used as an illumination source. Wavelength selection was accomplished with a Jarrel Ash 82410 monochromator. The samples were contained in a home-built small quartz cell and the acoustic signal detected by a Knowles 1753 miniature microphone. The magnitude and phase of the signal were measured with a lock-in amplifier controlled by a microcomputer. The spectra were corrected for the lamp-monochromator wavelength response using carbon black as a standard. Appropriate software was used for data acquisition and treatment.

The film structure was analysed by X-ray diffractometry.

3. Results and discussion

X-ray diffraction studies have shown that the zinc oxide and copper films are polycrystalline, while the tin oxide films are essentially amorphous. Comparing the diffractograms of the films and powder samples of the same substances, the first show a smaller number of peaks, which indicate preferential orientation of the microcrystals along some directions.

The main purpose of the optical studies in type I films was to compare thickness measurements by the two spectroscopic techniques mentioned previously. In photoacoustic spectroscopy (PAS) the absorption of modulated light by a material produces thermal waves which, upon reaching the sample surface, generate acoustic waves with the same frequency³. The photoacoustic spectrum of a single copper layer in the visible region has constant amplitude, corresponding to the optically opaque nature of the film. Tin oxide and zinc oxide films are transparent for $\lambda > 350$ nm and therefore they do not exhibit any photoacoustic signal.

Double layer films of type I show an interference pattern due to the superposition of the thermal waves generated in the absorbing (metal) layer by the light absorbed directly or after reflections at the air-oxide interface. For normal incidence, the phase difference between two waves depends on the wavelength, according to

$$\Phi = \frac{4\pi n_1 d}{\lambda} \quad (1)$$

where n_1 is the refractive index and d the thickness of the non-absorbing layer.

As the thermal waves are strongly damped, to obtain an acoustic signal the non-absorbing layer thickness must be less than the thermal diffusion length, μ_s , given by

$$\mu_s = \sqrt{\frac{2\alpha}{\omega}} \quad (2)$$

where α is the thermal diffusivity and ω is the modulation frequency of the exciting light⁴. Although the thermal diffusivity value of the oxide films was not known, it is possible to know whether $d < \mu_s$, by obtaining spectra at different frequencies, because in this case the signal amplitude should vary with ω^{-1} (ref 4).

The photoacoustic spectrum of a film of copper and tin oxide is shown in Figure 2. The thickness of the film can be calculated from the location of the maxima (or minima) of the spectrum by the equation

$$d = \frac{1}{2n_1(\lambda_2^{-1} - \lambda_1^{-1})} \quad (3)$$

where λ_1 and λ_2 are the wavelengths of two consecutive extrema and n_1 is the refractive index of the oxide. Equation (3) which is a special case of a more general expression derived by Mandelis et al⁵, assumes that the refractive indices do not change with wavelength. The value of n_1 was calculated by the procedure outlined below.

Thickness evaluation from interference effects in optical reflectance and transmittance spectra is a much better known method⁶. The expression used is identical to equation (3). The reflectance spectrum shown in Figure 3 refers to the same sample as the PAS

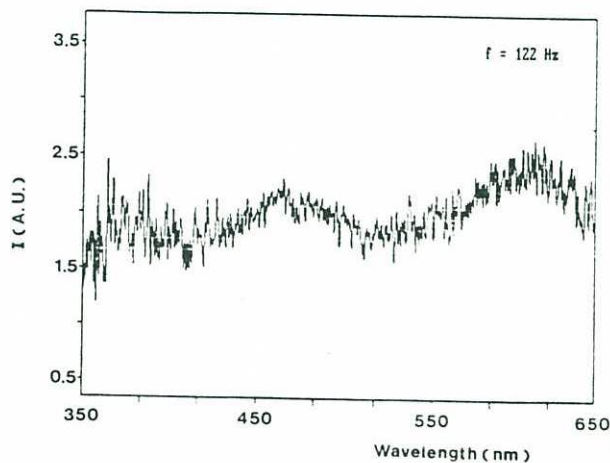


Figure 2. Photoacoustic spectrum of a double layer film of copper and tin oxide on glass.

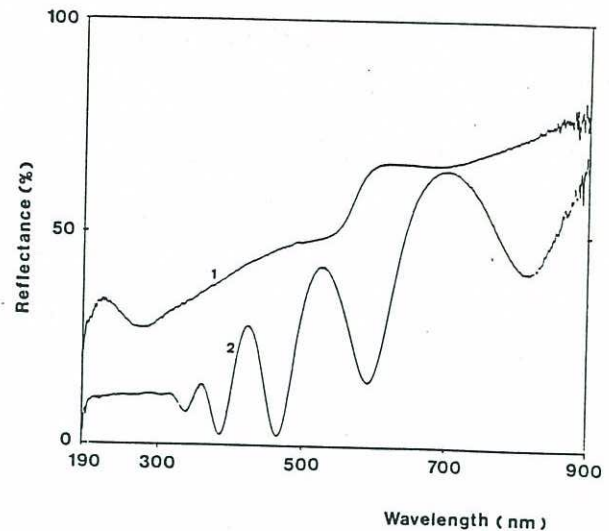


Figure 3. Reflectance spectra of type I films. (1) Copper on glass. (2) Copper and tin oxide on glass.

spectrum of Figure 2. It can be seen that the reflectance maxima correspond to the PAS minima and vice versa. Table 1 shows that values calculated by the two techniques are in good agreement. The values shown refer to the central region of the film, as the thickness tends to decrease near the edges.

The values of the refractive index used in equation (3) were determined from the interference extrema obtained in the transmittance spectra of a single oxide layer deposited on a similar glass slide by the same sputtering technique. We have used the following equations⁷:

$$T_{\max} = \frac{4n_3}{(n_3 + 1)^2} \quad (4)$$

and

$$T_{\min} = \frac{4n_1^2 n_3}{(n_1^2 + n_3)^2} \quad (5)$$

where T_{\max} and T_{\min} are the values of the transmittance in the maxima and minima and n_1 and n_3 are the refractive indices of the oxide and the glass, respectively. The values obtained for n_1 are shown in Table 1. It was found that the dependence of n_1 on the wavelength was negligible in this spectral region.

To measure the thickness by these interferometric techniques there should be at least two maxima (or minima) in the visible region. This restricts their application to layers thicker than about 100 nm.

The behaviour of the semi-transparent type II films has also

Table 1. Refractive index and thickness of oxide films measured by PAS and optical spectroscopy

Film	n_1	d (PAS)/nm	d (optical spectroscopy)/nm
Zinc oxide	2.3	400 ± 40	350 ± 25
Tin oxide	2.1	250 ± 40	273 ± 25

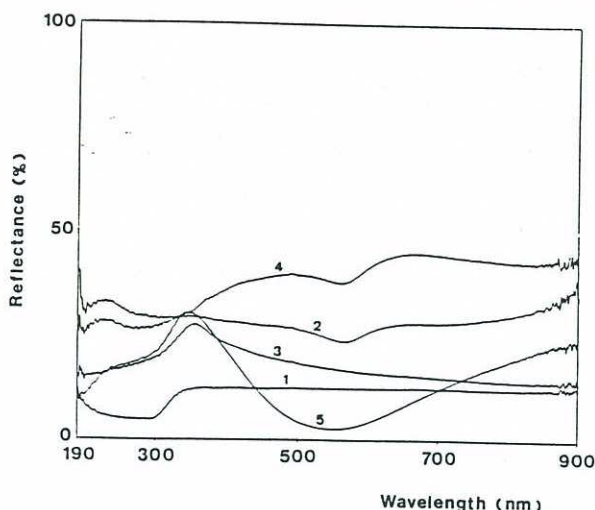


Figure 4. Reflectance spectrum of a type II film. (1) Substrate only. (2) Copper. (3) Zinc oxide. (4) Zinc oxide and copper (D-D' in Figure 1). (5) Zinc oxide, copper and zinc oxide (C-C' in Figure 1).

been investigated. Here the oxide layer thickness was estimated from the deposition times by extrapolation of type I film values, whereas the copper layer thickness was computed from the equation (see ref 8):

$$T = \frac{16n_3(n_2^2 + k_2^2)^2}{[(n_2 + n_3)^2 + k_2^2][(1 + n_2)^2 + k_2^2]} \exp\left(\frac{-4\pi k_2 d}{\lambda}\right) \quad (6)$$

where n_3 is the refractive index of the substrate, $n_2 + ik_2$ is the complex refractive index of copper, d is thickness and T is the transmittance of the sample. The values of n_2 and k_2 are from ref 9.

A reflectance spectrum of a type II film is shown in Figure 4. The presence of a zinc oxide layer beneath the copper layer increases the reflectance of the latter at wavelengths above 250 nm. The deposition of another oxide layer (Figure 1, C-C') causes a reduction of reflectivity in the green-yellow region and an increase in the blue and red regions. Changing the oxide layer thickness will result in changing the location of the reflectance maxima and minima. The system acts as an optical filter and the effect can be enhanced by deposition of more layers.

Photoacoustic spectroscopy of type II films is also possible. However, the signal is much weaker and therefore the observation of the interference effect becomes difficult. Further work is in progress in order to increase the sensitivity of our system and to develop the theoretical analysis in this more complex case of a metal layer which is not completely absorbing.

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