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Optical characterization of polyethylene and cobalt phthalocyanine ultrathin films by means of the ATR technique at surface plasmon resonance

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It is well known that the development and determination of optical properties of ultrathin films is an important issue in many technological areas. In this work organic polyethylene (PE) and cobalt phthalocyanines (CoPc) ultrathin films were deposited over metal films using the r.f. sputtering and thermal evaporation techniques, respectively. Attenuated total reflection (ATR) measurements for the system organic film/metal at the surface plasmon resonance (SPR) were used for determining the thicknesses and optical properties of the PE and CoPc thin films. Thicknesses of the order of some nanometers were found, fitting the theoretical multilayer ATR model, for p polarization monochromatic light, to the experimental reflection data. The dielectric function of CoPc ultrathin films was determined at a wavelength of 632.8 nm.

1 Introduction

The attenuated total reflection (ATR) is a technique commonly used to determine optical properties of thin-film samples. As mentioned in Ref. [1], instead of interacting with the sample through a collimated light beam as in the conventional methods like ellipsometry and reflectometry, in the ATR technique the incident light beam interacts with the sample through an evanescent wave. The electromagnetic field of the evanescent wave interacts with a material medium localized at the interface, for example a thin-film growth on the interfacial surface. Therefore, ATR is used in many applications like internal reflection spectroscopy [2] (IRS), gas detection [3] and surface plasmon resonance biosensors [4].

In the ATR scheme, if the interacting material is a metal like gold or silver, it can be possible to excite coherent and collective oscillations of free electrons known as surface plasmon waves (SPWs). When, furthermore, a dielectric thin film is coated over the metal film, the SPWs will interact with such a di-

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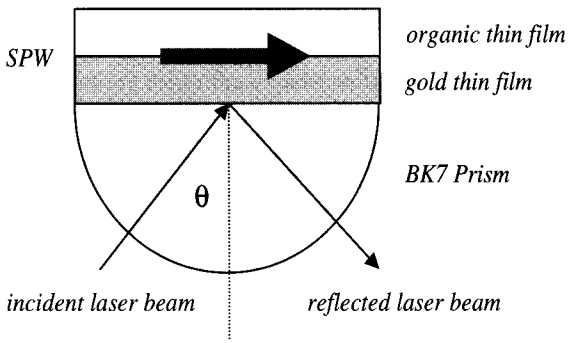

Fig. 1 (online colour at: www.pss-a.com) ATR configuration, not showing the substrate of the metal thin film.

electric film. This phenomenon is widely used for researching optical and structural properties [5, 6] of thin solid films, as for example, to determinate the thicknesses of organic ultrathin films like those deposited by the Langmuir–Blodgett method [1]. Because of the recent advances of thin-film development technology, we can now create thin metal films of some tens of nanometers that allow us to excite SPWs by means of monochromatic light [6]. The excitation/decay of surface plasmons is seen as an absorption/emission of light. The experimental configuration proposed by Kretschmann [7], shown in Fig. 1 for our multilayer system, couples the incident monochromatic light with nonradiative SPWs. As Krestchmann demonstrated, SPWs are excited on the metal/dielectric interface (see Fig. 1). When the component parallel to the surface of the metal of the wave vector of the incident light is equal to the wave vector of the surface plasmons; the energy of the light beam is totally transferred to the surface plasmons and consequently the reflected light is totally attenuated (ATR). This coupling between the wave vector of the incident light and the wave vector of surface plasmons reaches its maximum intensity at the resonance at a specific angle. This situation is known as surface plasmon resonance (SPR) and the specific angle is named the SPR angle. The resonance condition is influenced by the optical properties of the materials that surround the thin metal film. This means, if the dielectric function of some surrounding medium is changed then the SPR angle will also change. In this way, the spectrum reflectivity at SPR is used as a tool to measure the optical properties of the media that are surrounding the metallic thin film [7]. In this work, we are going to discuss the viability of the SPR technique to investigate the thickness and optical properties of organic ultrathin films. The thickness of PE and the dielectric function at a wavelength of 632.8 nm of CoPc thin films are studied. Regarding the researched materials, between many applications of PE, the fabrication of PE ultrathin films with known thickness has important applications, for example in long-chain hydrocarbon vapor sensors as reported in Ref. [8]. On the other hand, there are many applications of metal phthalocyanines and their derivatives as photoconductors, molecular organic semiconductors [9], agents for electrocatalysis, photovoltaic and photocatalysis, medicine, etc., [10], and especially as NO_2-sensing layers by means of the SPR transduction signal [11].

2 ATR theory model

The semiclassical calculus of the reflectivity for multilayer systems of nonradiative surface plasmons is based on the solution of Maxwell's equations for an incident light beam traveling through the system as shown in Ref. [12], and summarized in Ref. [13] for five layers. In the model, a light beam travels through a prism, with dielectric function ε_0, and impinges upon the metal film of dielectric function ε_1 and thickness d_1 where it is reflected. It may also be possible to grow different layer materials over the metal film with dielectric constants ε_2, ε_3, ... ε_n and whose sum of their thicknesses have to be less than the mid-wavelength of the incident light. So, solving the Maxwell equations for a monochromatic light with p-polarization, and satisfied by the boundary conditions for the normal and tangential components

of the electromagnetic field, the reflectivity for n number of layers is represented by:

$$R(\theta) = |r_{0,n}(\theta)|^2, \tag{1}$$

$$r_{i,n}(\theta) = \frac{r_{i,i+1}(\theta) + r_{i+1,n}(\theta)\exp(2jd_{i+1}k_{zi+1}(\theta))}{1 + r_{i,i+1}(\theta)\, r_{i+1,n}(\theta)\exp(2jd_{i+1}k_{zi+1}(\theta))}, \quad i = n-2,\ n-3,\ n-4 \ldots 0, \tag{2}$$

where

$$r_{i,i+1}(\theta) = \frac{\varsigma_{i+1}(\theta) - \varsigma_i(\theta)}{\varsigma_{i+1}(\theta) + \varsigma_i(\theta)}, \quad (i = 0, 1 \ldots, n-2), \tag{3}$$

and

$$\varsigma_i(\theta) = \frac{\varepsilon_i}{\kappa_{zi}(\theta)}, \quad (i = 0, 1, 2, \ldots, n), \tag{4}$$

$$k_{zi}(\theta) = \sqrt{\varepsilon_i\left(\frac{\omega}{c}\right)^2 - k_x^2}, \quad (i = 0, 1, 2, \ldots, n). \tag{5}$$

Here, θ is the angle of incidence as shown in Fig. 1, $r_{i,i+1}$ are the Fresnel coefficients at the interfaces, and κ_{zi} are the normal components of the wave vector of the transmitted light, better known as extinction coefficients of the electromagnetic wave.

3 Description of the experiments

Gold films of 52.4 nm and silver of 50 nm thicknesses were coated on 7059 glass corning substrates by the thermal evaporation method. The deposition pressure was of the order of 10^{-5} Torr. The commercial

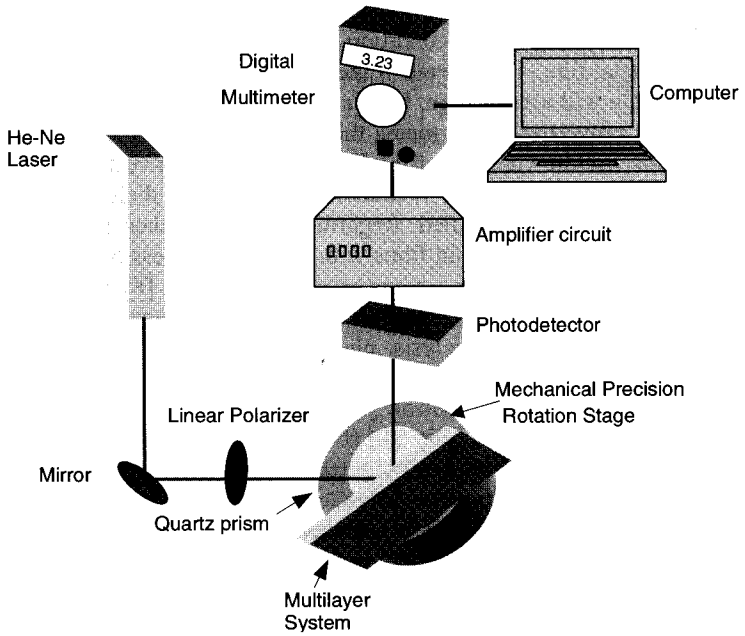

Fig. 2 (online colour at: www.pss-a.com) Experimental setup used for the SPR reflectivity measurements. It can be observed that a p-polarized He–Ne ($\lambda = 632.8$ nm) laser beam was focused onto the multilayer system. Measurements of the reflected light intensity were made from the photodetector voltage output readings, which were sent to a computer for processing.

monitor, MASTEK Inc., which uses a crystal resonator as sensor, was used to measure the thickness of the gold and silver films. Then, under normal environment conditions their reflectivity spectra were obtained by using the experimental setup shown in Fig. 2 and reported in Ref. [3]. The reflectivity measurements were obtained using a Newport controlled high-precision compact rotation stage with a resolution of 0.002 degrees and a silicon detector for capture of the reflected light (see Fig. 2). Soon after, transparent PE ultrathin films of different thicknesses by the r.f. sputtering method were deposited over the gold thin films. Argon gas was used to obtain the sputtering plasma. The r.f. sputtering initial pressure in the chamber was 1×10^{-6} Torr, and the final pressure of the argon plasma was about 10^{-3} Torr. Over the silver films, commercial CoPc powder (From Alfa Aesar Inc.) was thermally evaporated at a pressure of about 10^{-5} Torr to obtain ultrathin films with different thicknesses. Finally, the reflectivity measurements of the multilayer structure for both PE/gold and CoPc/silver systems were obtained under normal environmental conditions.

4 Results and discussion

When the PE thin films were sputtered, it was difficult to be sure if these were deposited because of their transparency. Then, atomic force microscopy images were made using a Digital Instruments Inc. multimode microscope (SPM Multimode). Figure 3 shows two topographic images of the gold thin films before and after the coating of the polyethylene ultrathin film was made. The coated organic material can be observed because of the differences in relief and roughness. While the gold image (Fig. 3a) shows important differences on the grains size and a considerable relative roughness, the image of PE/gold (Fig. 3b) shows in essence less roughness, which could mean the PE covers the spaces between grains and the grains in order to get a less roughness surface. The scales shown were $500 \times 500 \times 20$ nm and $500 \times 500 \times 17$ nm for Figs. 3a and 3b, respectively.

In Fig. 4 we can observe reflectivity measurements for two different PE/gold ultrathin films. Reflectivity measurements were obtained first for the gold and then for the PE/gold thin films. Experimental results are represented by the dots and the theoretical ones by the lines. An appreciable dispersion between the experimental data and the theoretical model can be observed; obviously, our gold films have surface roughness different from zero (see Fig. 4a) not involved in the theoretical model for the multilayer structure. Also, the alignment of the polarizer used in the experimental measurements involves an extra systematic error. These measurements show the critical angles equal to 43.6° (Fig. 4a) and 43.4° (Fig. 4b) for the gold thin films and 44.5° for both PE/gold films systems. In order to find the thicknesses and the optical properties of the films, a numerical fitting of the theoretical model, using only the value of the SPR angle position given by Eqs. (1)–(4), to the experimental data was made as follows. First, the reflectivity spectrum for the system prism–substrate(glass)–gold–air was obtained. In this system the

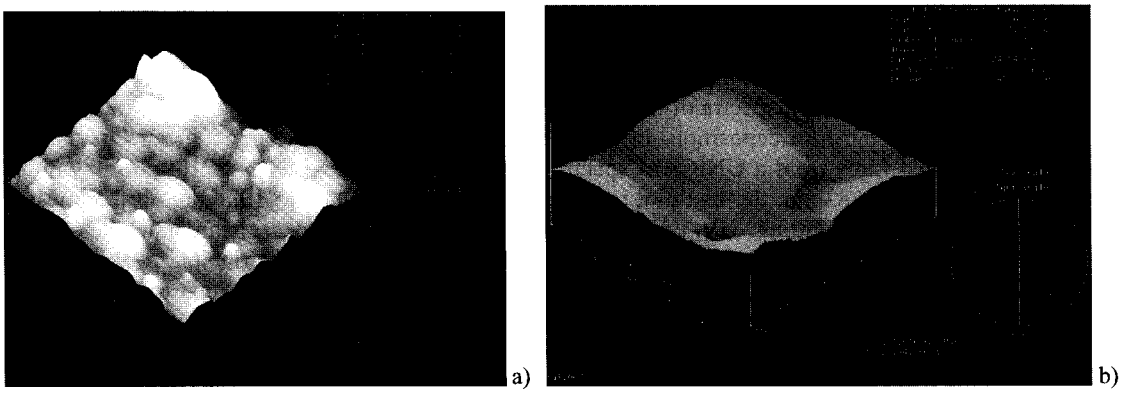

Fig. 3 (online colour at: www.pss-a.com) AFM images of a gold surface before a) and after b) the deposited thin film of polyethylene.

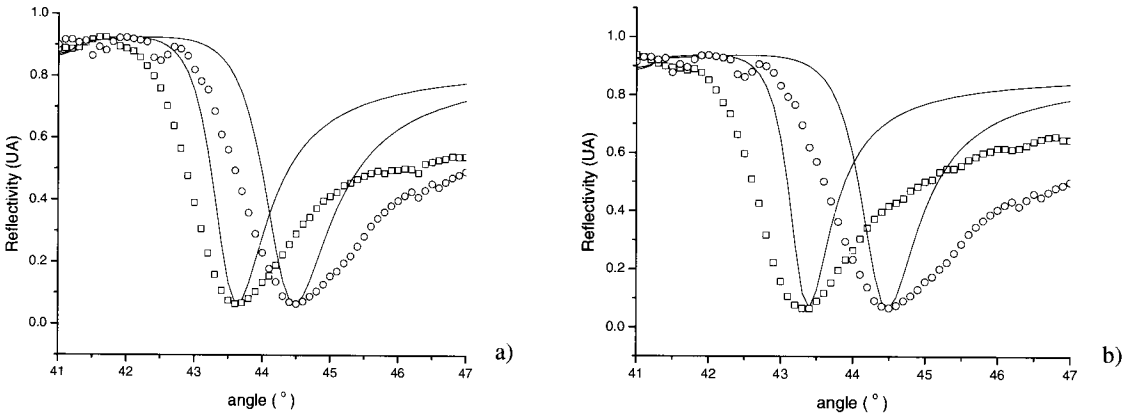

Fig. 4 Reflectivity measurements for two different PE/gold films systems a) and b). Before (graph at left in a) and b)) and after (graph at right in a) and b)) the polyethylene was deposited over the gold films. The obtained SPR angles before are 43.6° and 43.4° and after are 44.5° for both systems films. The position of the SPR angles correspond to 7.1 nm a) and 9.55 nm b) of thicknesses of the polyethylene film, respectively. The continuous lines are the corresponding theoretical fitting plots.

known data were: The dielectric function of the prism was equal to 1.51509^2, which is an interpolated value from experimental data provided by Newport Inc.; the values of the dielectric function and the thickness of the glass substrate were equal to 1.5176^2 (measured by spectroscopic ellipsometry) and 1 mm, respectively; the thickness of the gold films measured by a Maxtek monitor was equal to 52.4 nm; and the dielectric function of air is equal to 1. Adjusting the unknown dielectric function value of the gold films fitting to the experimental data we find $-12.32 + 1.5i$ for the film of Fig. 4a and $-13.59 + 1.36i$ for the film of Fig. 4b, which are values close to that reported in Table A.2 of Ref. [6]. Assuming both films have the same thickness, because these were placed at the same distance with respect to the source material in the evaporation system, the discrepancy of the fitted values in the dielectric function of the gold is because of the difference of their surface roughness attributed to differences on the flux vapor rate. For the estimation of the PE thin-films thickness, a model for the five-layer system considering the prism–substrate(glass)–gold–PE–air media was used. Using the parameters determined from the first system and the known value of the PE dielectric function, equal to 1.48^2 (obtained from the Palik's Handbook [1]), the thicknesses of the PE thin films was adjusted, resulting in 7.1 nm (Fig. 4a) and 9.55 nm (Fig. 4b) with ±0.17 nm of absolute uncertainty estimated from the data points, which were taken each 0.1 deg.

On the other hand, with respect to the fabrication of CoPc thin films, as mentioned above, commercial CoPc powder (from Alfa Aesar Inc.) was thermally evaporated over silver thin films at a vacuum pressure of about 10^{-5} Torr. In the same chamber, glass substrates were also positioned to obtain CoPc thin films with similar thicknesses to those obtained on the silver film substrates. Such samples were used to measure the UV-Vis absorbance spectra of the CoPc thin films. The aim of obtaining absorbance spectra is to be sure to obtain the film deposition. In Fig. 5 are shown UV–Vis absorption spectra of the obtained ultrathin CoPc films from a UNICAM spectrophotometer model FALCON 8710; cross symbols correspond to a film of 3.82 nm, the line plot to 6.5 nm and the dashed line to 10.8 nm, all thicknesses estimated by the ATR-SPR fitting. UV-Vis absorbance spectra of the Fig. 5 are similar to the spectra reported by Vukusic and Sambles [11]. On all UV-Vis absorption spectra three principal peaks close to 632.8, 680 and 780 nm can be seen, the last highly visible peak contrasts with those reported by Vukusik and Sambles [11] (at 632.8 and 680 nm). The additional 780 nm peak could be due to the different arrangement of the molecules in our samples compared with those of Vukusik and Sambles [11].

In Fig. 6, reflectivity measurements for a silver film of 50 nm measured thickness and for three different CoPc/silver systems are shown. Their corresponding theoretical plots from Eqs. (1)–(4) are shown by continuous lines. Similar to the treatment for polyethylen films, first, the SPR angle for the silver

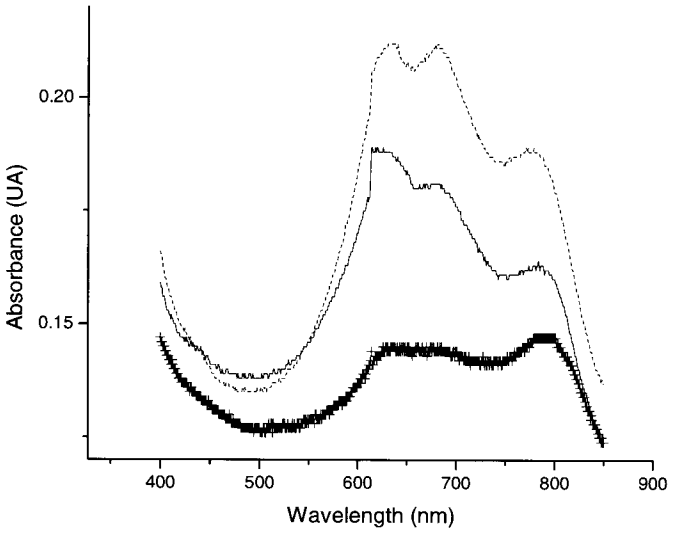

Fig. 5 UV–Vis absorbance spectra of three different CoPc thin films deposited on corning 7059 glass substrates. (+) correspond to a film of 3.82 nm, (–) to 6.5 nm and (– –) to 10.8 nm, thicknesses estimated by SPR fitting. A growing peak closel to 780 nm wavelength can be observed as the thickness increase.

thin film using the four-media system prism–silver–silver oxide–air was obtained. The use of silver oxide as another layer was considered because the silver films were exposed to the ambient conditions approximately one day before we deposited the CoPc films over them. In our model, one known parameter is the measured thickness of the two-layer silver–silver oxide system, equal to 50 nm. This means that we are considering that a percentage of the original thickness (50 nm) corresponds to silver oxide and the thicknesses needs to be re-adjusted with the fitting model. Another parameter that is known from averaged values reported in Ref. [14] is the real part of the dielectric function of the silver oxide film,

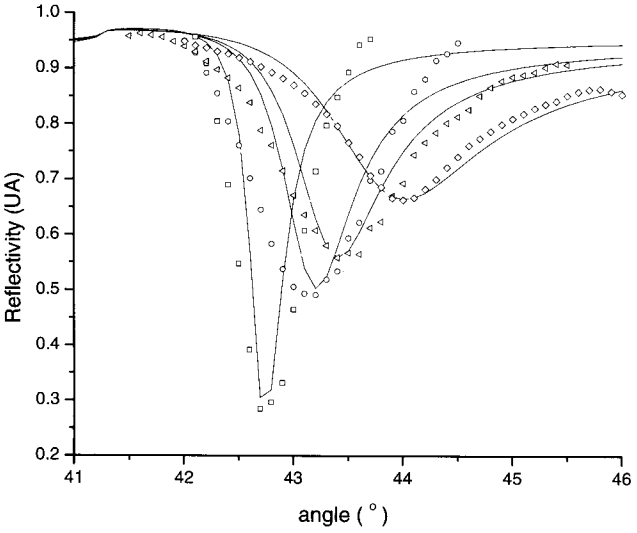

Fig. 6 SPR reflectivity for different CoPc/silver thin-film systems. Squares correspond to a subsystem of two layers: 48.8 nm of silver and 1.2 nm silver oxide, circles correspond to a CoPc film of 2.88 nm thickness deposited on the subssytems silver/silver oxide, triangles correspond to a film of 3.82 nm and diamonds to a CoPc thin film of 6.5 nm. The continuous lines are the corresponding theoretical fitting plots.

equal to 1.156[2]. Similar as for polyethylene films, we take the value of 1.51509[2] for the dielectric function of the prism. Fitting the model to the experimental squares curve of Fig. 6; the value of $-21 + 0.9045i$ is obtained for the dielectric function of the silver film with a thickness of 48.8 nm, and the value of the imaginary part of the dielectric function of the silver oxide film equal to 7 with a thickness of about 1.2 nm. After all parameters of the silver film were estimated, we now fit the circles, triangles and diamonds plots of Fig. 6 to obtain the CoPc films parameters. In this fitting we assume that the dielectric function of the CoPc films is constant, independent of the thickness and orientation of the molecules, such an assumption is not necessarily true, especially for organic ultrathin films, as demonstrated, for example, by Peisert et al. [15]. The obtained results are: dielectric function of CoPc thin films equal to $5.8 + 4.8i$ with thicknesses of 2.8, 3.82, 6.5 and 10.8 nm (plot not shown) with ± 0.98 nm of absolute error. The value of the dielectric function is of the order of that reported by Vukusic and Sambles [11].

5 Conclusions

Summarizing, PE and CoPc ultrathin films were well developed and optically characterized by means of the SPR technique. The thicknesses of the PE thin films were found to be equal to 7.1 and 9.55 nm. The dielectric function of the CoPc thin films, for light of 632.8 nm wavelength, was estimated as $5.8 + 4.8i$ and is in the range reported by other authors like Vukusic and Sambles [11]. It was also possible to obtain the thicknesses of the CoPc films resulting on 2.8, 3.82, 6.5 and 10.8 nm. Also, for the first time, an estimation of the imaginary part of the dielectric function of silver oxide films was obtained, equal to 7. It is very difficult to obtain the thickness of organic thin films using other methods like ellipsometry, therefore the ATR technique under SPR conditions is shown as a powerful tool for the determination of optical and structural parameters of organic thin solid films.

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