ELLIPSOMETRIC AND SURFACE PLASMON RESONANCE EFFECTS ON LB FILMS OF ORGANIC MATERIALS IN CONTROLLED ATMOSPHERE.

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ABSTRACT: Langmuir-Blodgett (LB) films of Cu(II) tetrakis-(3,3-dimethyl-1-butoxicarbonyl)phthalocyanine have been studied as regard their optical property. In particular electronic spectra in the UV-VIS spectral range and the optical constant of the LB multilayers have been carried out. In order to use these LB films as optical gas sensors, ellipsometric and surface plasmon resonance (SPR) measurements were carried out in controlled atmosphere. SPR measurements were conducted by using a system based on the Kretschmann configuration. LB monolayers of Cu(dmbc)Pc deposited as selective layer on a metal surface show changes of the reflectance on exposure to nitrogen dioxide mixed with dry air in low concentration. Moreover, ellipsometric measurements carried out on LB multilayers of Cu(dmbc)Pc deposited onto silicon substrates, have shown variation at a fixed wavelength in the thickness and complex refractive index when are exposed to different concentrations of toluene and tetrachloroethene.

Keywords: Lamgmuir-Blodgett; Optical properties, Chemo-Optical Sensors.

INTRODUCTION

In the last years, considerable attention has been paid to the deposition of very thin films of various organic materials like phthalocyanine macromolecules owing to their different optical and electrical properties which depend on the Pc molecular ring orientation into the films [1]. The main goal has been their possible applications in technology and in particular in the field of gas-sensors [2]. In the latter case, the change of the optical properties of the active layer during the interaction with toxic gases can be used to detect their presence. In this work we report on the preparation of Langmuir-Blodgett films of Cu(II) tetrakis-(3,3-dimethyl-1-butoxicarbonyl)phthalocyanine deposited onto different substrates. Ellipsometric measurements in controlled atmosphere performed onto (LB layer)/Silicon structure give us information about their use as optical sensors towards toluene and tetrachloroethene. Moreover, SPR measurements in controlled atmosphere are reported for the Cu(dmbc)Pc LB monolayers interacting with nitrogen dioxide in the low concentration range.

EXPERIMENTAL AND DISCUSSION

The Cu(dmbc)compound was obtained in our laboratory and the details of the synthetic procedures have already been described [3]. LB films of such derivatised copper phthalocyanine were deposited by a KSV5000 System 3 LB apparatus (850 cm^2). The phthalocyanine was dissolved in ethyl acetate ($2x10^{-4}$ M) and 200 ?l of the spreading solution was spread onto ultrapure water. After the solvent evaporated, the floating film was compressed to the constant pressure of 15 mN/m and the films deposited onto different substrates, depending on the subsequent physical characterisation, at a speed of 5 mm/min. The surface pressure ? vs area per molecule isotherm of a monolayer formed from a spread solution of Cu(dmbc)Pc in ethyl acetate is shown in Fig. 1.

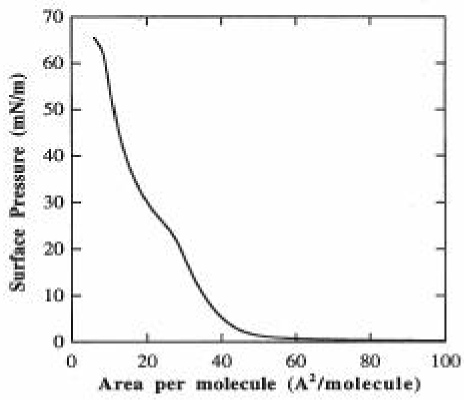

Figure 1: Surface-Pressure isotherm of Cu(dmbc)Pc

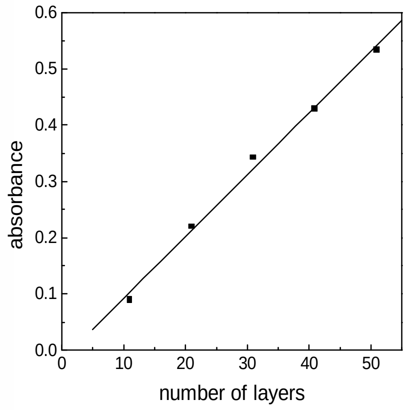

Figure 2: Thickness dependence on the number of Cu(dmbc)Pc LB layers

The condensed phase region observed for this monolayer gives a limiting molecular area of about 0.43 nm^2. Reproducibility in the deposition process was assessed by recording the variation of the intensity of the **Q**-band with the number of deposited layers. In Fig. 2 are reported the thickness of the corresponding LB multilayers. As one can see, the results indicate that the LB transfer was reasonably reproducible. Spectroscopic ellipsometry measurements was used for the calculus of thickness and complex refractive index N=n+ik of the Cu(dmbc)Pc LB film in dry-air and toxic gaseous ambient respectively by using a test chamber realised in laboratory. Fig. 3 shows the normalised refractive index of the sensing layer in the presence of different concentration of toluene and tetrachloroethene.

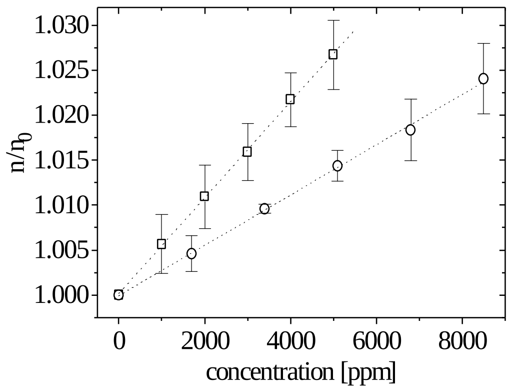

Figure 3: Normalised refractive index at a ?= 570 nm and dependence of the concentration of toluene (O) and tetrachloroethene

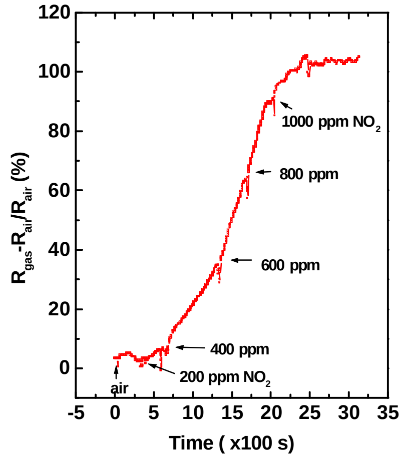

Figure 4: Response in the presence of different NO_2 concentration in the mixture with dry air

As regarding the SPR measurements carried out onto our Cu(dmbc)Pc LB films we have realised a structure consisting of 60 nm thick silver deposited onto corning glass substrates.

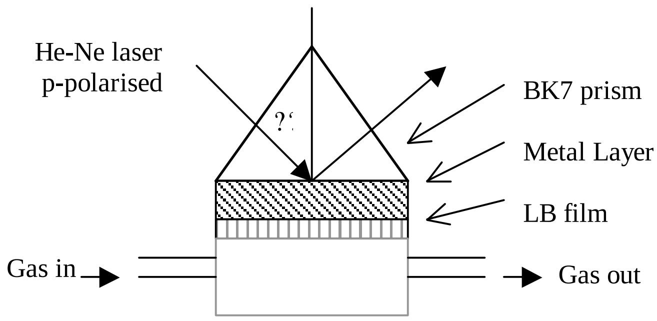

Figure 5: Schematic diagram of the SPR measurement system

Such substrates was used for the LB deposition of 2 monolayers of Cu(dmbc)Pc. The reflectivity of the LB monolayers at 633 nm was monitored as a function of the time at an external incidence angle of about 42.6° near the minimum reflectance SPR angle (43°). The measurements were first made in air and then repeated with the chamber filled with a mixture of NO_2 gas and dry-air (Fig. 4-5). As one can see, in both cases the preliminary measurements have shown that LB films of the novel Cu(dmbc)Pc compound are potentially suitable as chemo-optical gas sensor material.

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