Plasma-deposited copper phthalocyanine: a single gas-sensing material with multiple responses

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INTRODUCTION

Metal phthalocyanines (MPcs) hold peculiar properties, which made these organic semiconductors very interesting for gas sensing applications based on the electrical conductivity changes induced by the adsorption of oxidizing or reducing gases such as NO_x and NH_3 [1]. High vacuum evaporation has become the most widely used method for the deposition of MPc films over the last decades, due to the low solubility of these compounds in organic solvents, which makes the chemical deposition methods difficult to be applied [1]. The solubility is usually enhanced by adding substituent groups to MPcs, which promote the film adhesion to the substrate as well [2]. Evaporated MPcs films revealed high sensitivity to NO_2 down to few tens of ppb [3]. However, MPc films exhibit slow response and recovery: for CuPc sensors, the total response and recovery times are in the order of several hours [4].

In this work copper phthalocyanine films have been deposited by means of a novel physical deposition technique named glow-discharge-induced sublimation (GDS), which produces very high porosity organic films. Electrical response to NO_2- and NO-containing atmospheres in the range 0.1-1.0 ppm and 10-100 ppm, respectively, has been measured by using a simplified method based on the change of the electrical current during the first tens of seconds after the gas mixture input. As a matter of fact, the change of the current against time, $\Delta I(t)$, can be linearly fitted and the slope of the fitting curve is related to the gas concentration. The NO_2 and NO concentration can be then derived after a period of less than 30 s. The application of this method to a final sensor device can be performed in a relatively easy way, because the measurement of the first derivative is done at a software level.

Optical response to ethanol vapours has been also tested by measuring the optical absorbance change at a fixed wavelength (λ=485 nm) upon ethanol exposure.

EXPERIMENTAL

The apparatus used for the deposition of CuPc films has been described in [5]. The electrical response to NO_x mixtures' was measured by means of a setup equipped with two mass flow controllers, to suitably dilute the gas mixture to the desired composition. A PC is connected to a ROD-2M control unit featuring two channels; each is connected in turn to a mass flow controller. After heating the samples up to 150°C under nitrogen flow, the electrical current at fixed voltage (1 V) was measured every 6 s. The gas mixtures in the bottles used for the measurements were N_2+NO_2 (0.98±0.05) ppm and N_2+NO (98±3) ppm.

Optical absorbance spectra were collected by a Spectrophotometer V-570 Jasco, after putting the sample in a test chamber, connected to two mass flow controllers.

RESULTS

Fig. 1 shows the electrical responses of the CuPc films to different NO_2 concentrations: after a starting period, during which the current is unchanged, the curve can be linearly fitted and the slope increases at increasing NO_2 concentration.

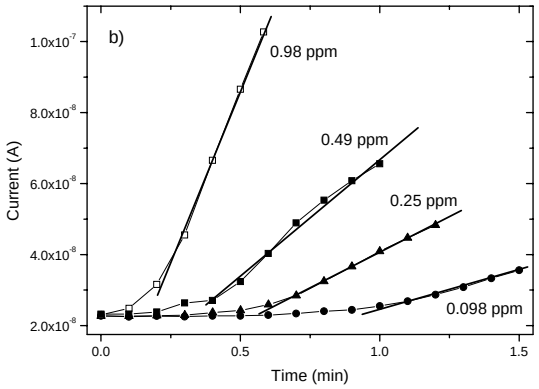

FIG. 1: *Electrical responses of a GDS CuPc film to all the tested NO_2–containing mixtures in the sub-ppm range.*

In Fig. 2 the slopes are reported against the NO_2 and NO concentration, respectively. The films exhibit a higher response to NO_2 than to NO, as could be expected. The response of CuPc films is linear in both cases, although at high NO_2 concentration a divergence from linearity is observed.

The effects of ethanol on the optical properties of CuPc films have been firstly studied by collecting the absorbance spectra in the range 200-800 nm before and during exposure to saturated vapours of ethanol (Fig. 3): clear

changes of both the Q and B bands appear due to vapour adsorption.

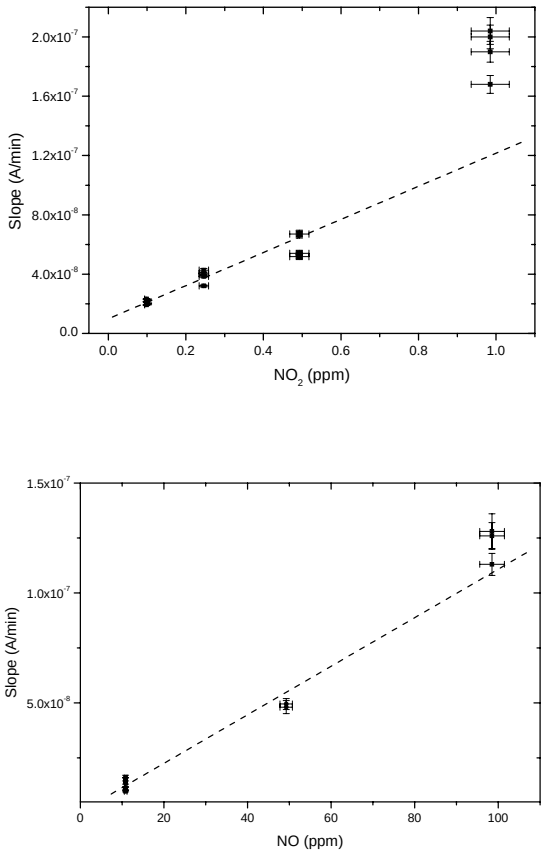

FIG. 2*: Slopes of the electrical responses of a GDS CuPc film as a function of NO_2 (upper) and NO (lower) concentrations.*

The kinetic test of the optical response of the GDS film to ethanol vapour has been then carried out. The absorbance change has been measured at a single wavelength, λ, with a line width Δλ=5 nm. The chosen wavelength (λ=485 nm) corresponds to the maximum reversible absorbance change found after the conditioning procedure. The ethanol concentration chosen was 1000 ppm. Fig. 4 shows the trend of the optical response to ethanol vapours (1000 ppm) as a function of the exposure time. In order to quantify the response and recovery speed of the CuPc sample, the parameter t_{50} has been measured: the t_{50} response time is defined as the time taken for the signal intensity to reach the 50% its final saturated value; the t_{50} recovery time is the time taken for the signal intensity to decrease to the 50% its saturated value in ethanol, during ethanol desorption. The response is characterized by a fast increase (t_{50}=18s) and a relatively fast recovery (t_{50}=58s) after mixture removal. It is noteworthy that evaporated CuPc films do not respond to the same mixture at all.

These first results show that plasma-deposited copper phthalocyanine is a promising material to be used in gas sensing devices by exploiting the changes of both its electrical and optical properties.

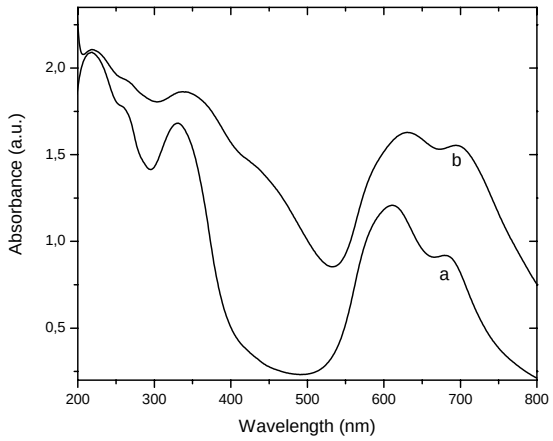

FIG. 3: *Absorbance spectra of a GDS CuPc film exposed to ethanol-vapour-containing atmosphere: a) before exposure (N_2 flow); b) during ethanol exposure (saturated vapour pressure).*

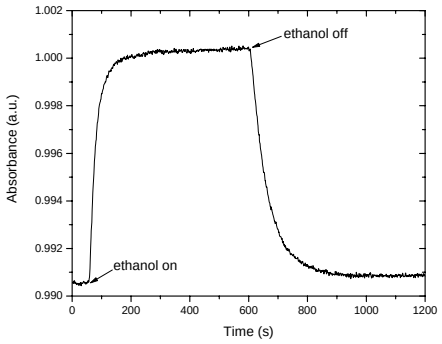

FIG. 4*: Absorbance change at a fixed wavelength (λ=485 nm) of a CuPc film exposed to 1000 ppm of ethanol vapour.*

ACKNOWLEDGEMENT

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