

# Copper phthalocyanine thin-film transistors with polymeric gate dielectric

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## Abstract

Copper phthalocyanine (CuPc) thin-film transistors have been fabricated using polymethyl methacrylate (PMMA) as gate dielectric. A bottom gate, staggered structure was selected to study the device performance. CuPc thin-films were deposited by thermal evaporation in a high vacuum system. The maximum process temperature achieved was 100 °C, corresponding to the baking of the PMMA. The devices showed satisfactory p-type electrical characteristics with field-effect mobility and threshold voltage values around  $0.2 \times 10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$  and 6 V, respectively. The device electrical characteristics were correlated with the structural and morphological properties of the CuPc thin-films.

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## 1. Introduction

Organic semiconductors have lately attracted much attention due to their successful application in optical and electronic devices with encouraging performances [1]. These devices include organic photovoltaic solar cells (OSC), thin-film transistors (OTFT) and light-emitting diodes (OLED). Among the wide range of organic semiconductors considered, metal phthalocyanines (Pc) are one of the most promising candidates to be used in the fabrication of such organic devices [2]. Phthalocyanines are small organic molecules characterized by their high symmetry, planarity and electron delocalization. Besides, Pcs can be easily sublimed in high vacuum systems resulting in high-purity thin films with excellent growth properties

and chemical stability, taking into account that the use of the sublimation technique allows the deposition of thin films with controlled thickness and structural properties.

Among the devices previously cited, thin-film transistors are usually considered for their use in display technology, although the simplicity of their structure also makes them a good tool to evaluate the electronic properties of the active semiconductor acting as channel in the device. Therefore, OTFTs enable to evaluate the field-effect mobility of a given semiconductor avoiding the influence of the electrodes, subsequently such information can be used in other devices like organic solar cells.

There are several papers devoted to the fabrication of copper phthalocyanine (CuPc) based OTFTs [2–5]. In general, these transistors are fabricated using crystalline silicon substrates covered with thermally grown silicon dioxide (SiO<sub>2</sub>) acting as dielectric layer. However, the use of organic materials deposited at low temperatures as gate

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dielectric in OTFTs is more challenging. The use of such dielectrics would allow the fabrication of OTFTs on plastic substrates, opening up the possibility to fabricate flexible devices. Besides, the study of the CuPc thin-film properties deposited on top of organic materials can also provide useful results regarding its morphological and structural properties, which consists also of valuable information for the fabrication of organic solar cells.

Metal phthalocyanines are also used in the field of organic solar cells. In these devices, different deposition techniques and device structures are under investigation. One of the most successful approaches is the deposition at high vacuum of different small molecules [6,7]. To date, the best thin film organic solar cells have been reported by Forrest group at Princeton. This group uses CuPc as donor material and fullerene ( $C_{60}$ ) or 3,4,9,10-perylenetetracarboxylic *bis*-benzimidazole (PTCBI) as acceptor. Depending on the solar cell structure (bilayer or mixed configuration) efficiencies achieved range between 3.5% and 5% [8–10]. In all cases, the CuPc film morphology plays an important role in the final electrical performance of the solar cell [8].

In this paper we present a comprehensive study regarding the structural and optical characterization of CuPc films, with the frame of mind of future use in solar cells. Optimized CuPc films have been used to fabricate OTFTs using polymethyl methacrylate (PMMA) as gate dielectric. PMMA has already been used as gate dielectric in the fabrication of pentacene OTFTs with acceptable electrical performances [11,12]. The electrical characteristics of our devices are also presented and correlated with the structural and optical properties of the CuPc films.

## 2. Experimental

The chemical structure of CuPc is shown in Fig. 1(a). The material used was commercially available from Aldrich chemical (98% purity) and no further purification process was performed. CuPc thin films were thermally evaporated in a high-vacuum system with a base pressure of  $10^{-6}$  mbar. The layers were grown at room temperature and at moderate deposition rates ( $\sim 5 \text{ \AA s}^{-1}$ ). Both bare and PMMA spin-coated glass substrates (Corning 7059)

were used to study the optical and structural properties of the CuPc films. PMMA was spun at 4000 rpm for 40 s and then cured for 30 min at  $100^\circ\text{C}$  to form a uniform coating about 680 nm thick. PMMA has a high resistivity ( $>2 \times 10^{15} \Omega \text{ cm}$ ) and its dielectric constant is similar to that of silicon dioxide ( $\epsilon = 2.6$  at 1 MHz,  $\epsilon = 3.9$  at 60 Hz).

In addition, CuPc OTFTs were fabricated using PMMA as gate dielectric. An inverted staggered configuration was used, as can be seen in Fig. 1(b). The bottom gate was a chromium layer thermally evaporated on crystalline silicon. To define and isolate the devices, CuPc was evaporated through a shadow mask. Finally, gold was also evaporated through a shadow mask to form the drain and source electrodes. The CuPc and gold thicknesses were 200 and 60 nm, respectively. The OTFTs had a channel length ( $L$ ) and width ( $W$ ) of 120 and 600  $\mu\text{m}$ , respectively. The maximum process temperature was  $100^\circ\text{C}$ , corresponding to the PMMA baking.

The film structure and surface morphology were investigated by X-ray diffraction (XRD) and scanning electron microscopy (SEM), whereas the optical properties of CuPc films were studied by optical transmission. Finally, the electrical characterization of the OTFTs was done in air at room temperature by means of a HP5156 parameter analyzer.

## 3. Results and discussion

### 3.1. Material characterization

The XRD spectra of two CuPc films deposited in the same run on bare and on PMMA-coated Corning glass are shown in Fig. 2. The thickness of both samples was of approximately 400 nm. The spectra revealed the existence of a diffraction peak at  $6.90^\circ$ , which corresponded to the (100) diffraction of the  $\alpha$ -form crystal, which is the stable crystal form at substrate temperatures lower than  $200^\circ\text{C}$  [13]. This diffraction peak resulted in a lattice

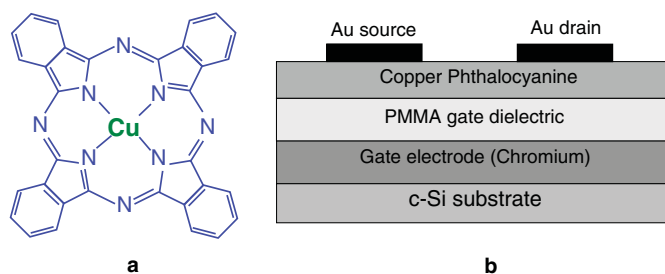


Fig. 1. (a) Molecular structure of CuPc. (b) Schematic cross-section of the CuPc OTFT inverted staggered configuration used. The length of the channel was 120  $\mu\text{m}$ , the width 600  $\mu\text{m}$ , and the thicknesses of the CuPc film and PMMA were 200–680 nm, respectively.

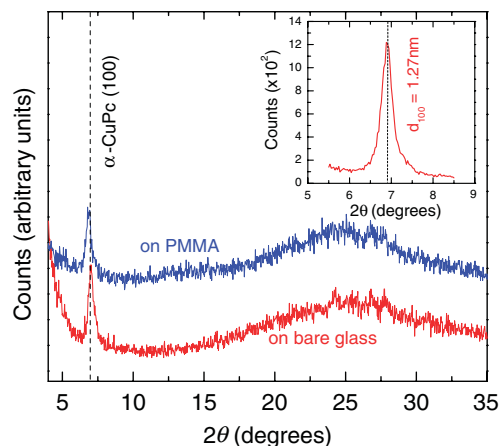


Fig. 2. XRD spectra of CuPc films deposited in the same run on bare and PMMA-coated glass substrates. The inset of the figure shows a detail of the XRD spectrum in the diffraction peak.

spacing of 12.7 Å, which corresponds to the distance between the plane of the copper atoms in one layer and the ones in the next layer, and was in good agreement with the reference value found in literature (12.6 Å) [14]. The strong background of the XRD scans is visible due to the scattering from the amorphous glass substrate and from air at low diffraction angles. No differences were observed between samples deposited on bare glass and those deposited on PMMA coated glass.

The domain size of the crystalline grains can be calculated from the full width at half maximum of the diffraction peak by using the Scherrer formula [15]. In our samples the crystallite sizes obtained were around 45–55 nm.

A typical SEM planar view of the CuPc films deposited on crystalline silicon is given in Fig. 3. There it can be seen that the film was made of homogeneous small crystal grains with an average diameter of 40–50 nm. This value was in good agreement with the crystallite sizes calculated from the XRD measurements. Since charge mobility is higher in crystalline materials than in amorphous ones, the existence of dense small crystalline grains would favour the fabrication of TFTs with higher field-effect mobility.

Regarding the optical properties of the studied layers, the optical absorption spectrum of a CuPc thin film is shown in Fig. 4. Different absorption peaks were observed in the UV–visible region. These peaks are originated from the molecular orbitals within the aromatic 18- $\pi$  electron system and from the overlapping orbitals on the central copper atom.

Two absorption bands were observed in the 300–450 nm and in the 600–750 nm regions. The intense band at 300–450 nm, which gives the absorption edge, is related to direct electronic transition from d- $\pi^*$  orbitals and is called the Soret band (B-band) [16,17]. The Soret band is a characteristic of the metal phthalocyanines absorption spectrum [18]. On the other hand, strong absorption band in the red region of the spectrum (600–750 nm) is also common in metal phthalocyanine films, and accounts for the blue colour of these materials. This absorption band, called the Q band, yields two trapping levels around 690 and

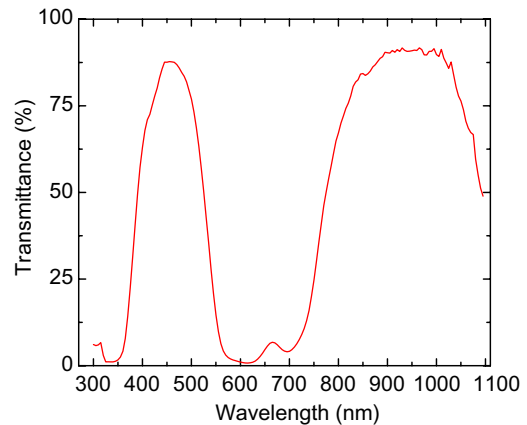


Fig. 4. Optical transmission spectrum of a 400 nm-thick CuPc layer deposited on glass.

615 nm. The high energy peak of this Q band has been assigned to the  $\pi$ - $\pi^*$  transition on the phthalocyanine macrocycle, whereas the second peak at low energy has been assigned as a second  $\pi$ - $\pi^*$  transition or due to the formation of excitons [18].

### 3.2. Device characterization

Several CuPc-based OTFTs were deposited using PMMA as gate dielectric and characterized. In Fig. 5, the output characteristics of one of the CuPc OTFTs fabricated, i.e., the drain current ( $I_D$ ) as a function of the drain-source voltage ( $V_{DS}$ ) for different gate-source voltages ( $V_{GS}$ ), can be seen. All devices exhibited the operating characteristics of a p-channel field-effect transistor. Neither current crowding for low  $V_{DS}$  nor kink effect for higher  $V_{DS}$  values was observed, this indicating low contact resistance at the drain and source electrodes with a low carrier injection.

Fig. 6 shows the  $I_{DS}$  plotted on a log scale as a function of  $V_{GS}$  for a  $V_{DS}$  of  $-10$  V (transfer characteristic). The on-off current ratio measured was about  $10^2$ . Besides, hys-

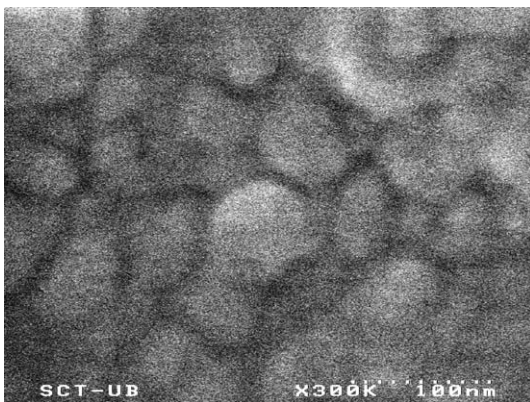


Fig. 3. Scanning electron microscopy image of a CuPc layer deposited on glass.

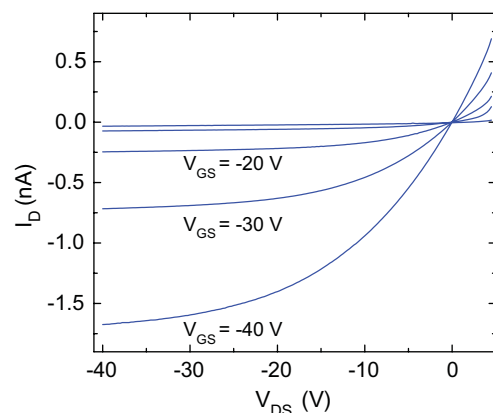


Fig. 5. Output characteristics of a CuPc OTFT studied.

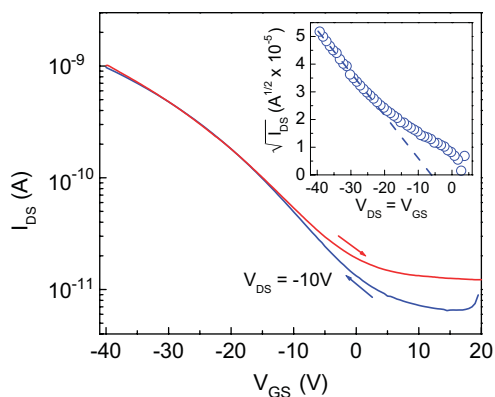


Fig. 6. Transfer characteristics of a CuPc OTFT. The inset shows the saturation regime, from which the mobility and the threshold voltage can be deduced.

teresis in the  $I_{DS}$ – $V_{GS}$  curve was quite apparent. This effect is known to be caused by the impurities and trapped charges at the semiconductor–dielectric interface and/or those in the bulk of the dielectric. This gate dielectric hysteresis leads to an uncertainty in the threshold voltage depending on the direction of the sweep of the  $V_{GS}$  voltage. It has been reported that the use of a bilayer insulator would reduce this undesirable effect [19].

The inset in Fig. 6 shows  $|I_{DS}|^{1/2}$  versus  $V_{GS}$  in the saturation regime, i.e., measured with  $V_{DS} = V_{GS}$ . The field-effect mobility ( $\mu$ ) and the threshold voltage ( $V_T$ ) can be obtained from the saturation characteristics by applying the following equation:

$$I_D \sim (\mu WC_0/2L)(V_{GS} - V_T)^2,$$

where  $W$  and  $L$  are the channel width and length of the TFT and  $C_0$  is the capacitance of the insulator per area unit.  $\mu$  was estimated to be around  $0.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ , whereas a positive value of 6.0 V was obtained for the threshold voltage. The measured  $\mu$  and  $V_T$  values were consistent with results reported for CuPc-based OTFTs measured in ambient conditions and deposited on a  $\text{SiO}_2$  dielectric layer [2–5].

It has been reported that field-effect mobility in CuPc TFTs strongly depends on the CuPc thickness [3]. Hoshimo et al. have shown that for CuPc based TFTs on  $\text{SiO}_2$  dielectric the mobility is higher for thicknesses around 80 nm and that  $\mu$  decreases as the CuPc layer becomes both thinner or thicker. In our case, having used CuPc film thicknesses around 200 nm,  $\mu$  values obtained were in good agreement with the above-mentioned results.

The CuPc active layer of the transistors studied was grown on PMMA. Several papers indicate that the use of PMMA influences the growth properties of organic semiconductors deposited on top. In particular, pentacene molecules tend to grow more vertically on a PMMA surface. Although the inherent mechanism is not yet well understood, it seems that PMMA reduces the interaction between a  $\pi$ -conjugated system and the metal or dielectric

substrate, allowing the deposition of more polycrystalline films, in the same way that a self-assembled monolayer (SAM) does [12,20,21]. Actually, PMMA has the same methyl ending groups ( $-\text{CH}_3$ ) as octadecyltrichlorosilane (OTS), which is one of the most widely studied SAMs.

Although CuPc is a conjugated molecule characterized by two dimensional  $\pi$ -electrons delocalized, our experimental results (as can be seen in the XRD spectra in Fig. 2) seemed to indicate that structural and morphological properties of CuPc films deposited on bare glass and on a PMMA coated surface were very similar. Conversely, Xiao et al. have recently reported that the use of OTS greatly improves the performance of CuPc-based OTFTs [22]. Their results indicate that field-effect mobility on the OTS-treated substrates is one to two orders of magnitude larger than on an untreated substrate.

#### 4. Conclusions

Copper phthalocyanine OTFTs were fabricated at low temperature using PMMA as gate dielectric. This organic insulator with low baking temperature can be spin cast on inexpensive substrates. The devices, in spite of the absence of any purification step of the CuPc material and of the structure used, presented satisfactory electrical performance, resulting in mobility values around  $0.2 \times 10^{-4} \text{ cm}^2/\text{Vs}$ . Good agreement was found between the properties of the CuPc thin films and the values measured for the transistors. No significant structural differences were seen from CuPc layers deposited on bare glass and those on PMMA.

In the near future we will focus our investigation on low deposition rates ( $<1 \text{ nm}/\text{min}$ ) and moderate substrate temperature ( $>100 \text{ }^\circ\text{C}$ ), expecting an improvement in the CuPc film properties and, consequently, in the field-effect mobility values.

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