Developing Non-Invasive Processing Methodology And Understanding the Properties Of Spin Coated Organic Semiconductors for Organic Thin Film Transistors with Polymeric Gate Dielectric

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ABSTRACT: Copper (II) 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. The present investigations comprise of the studies on the structural and topological characterizations of CuPc thin films. 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 40s and then cured for 30 min at 100 °C to form a uniform coating about 680 nm thick.The effect of thickness, substrate temperatures and air annealing on the electrical conductivity are studied. Activation energies are calculated. The measurements are performed in a subsidiary vacuum of 10^{-3} m. bar.

KEYWORDS: Thin film transistors, Dielectric, Spin Coating, Conductivity, Activation energy

I.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_2) acting as dielectric layer. However, the use of organic materials deposited at low temperatures as gate 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 field effect transistor.

Metal phthalocyanines are also used in the field of organic field effect transistor. 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]. 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 [8,9]. The electrical characteristics of our devices are also presented and correlated with the structural and optical properties of the CuPc films.

II. MATERIALS AND METHODS

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 spin coated. 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 40s and then cured for 30 min at 100 °C to form a uniform coating about 680 nm thick. PMMA has a high resistivity ($>2 \cdot 10^{15}$ Ω cm) and its dielectric constant is similar to that of silicon dioxide (e =2.6 at 1 MHz, e = 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 μm, respectively. The maximum process temperature was 100 °C, corresponding to the PMMA baking.

(a)
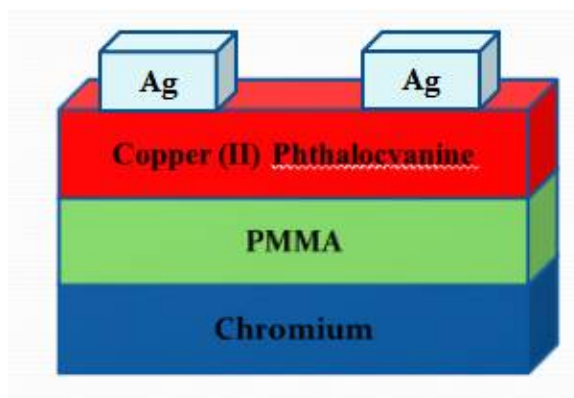
(b)

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 μm, the width 600 μm, and the thicknesses of the CuPc film and PMMA were 200–680 nm, respectively.

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.

Measurements on dark electrical conductivity are performed using a programmable Keithley electrometer (model No.617) in the constant current source mode. CuPc are mounted on the sample holder of the conductivity. Electrical contacts are made using copper strands of diameter 0.6mm and are fixed to the specimen with silver paste. To avoid contamination, measurements are performed in a subsidiary vacuum of 10^{-3} m.bar. Dark conductivity studies are done in the temperature range 320- 500K. The electrical conductivity measurements are done for CuPc thin films deposited in various thicknesses at room temperature, thin films of equal thickness deposited at various substrate temperatures and thin films of above materials in the same thickness deposited at room temperature were air annealed at different temperature and conductivity studies are made. The error bars of thickness measure measurements are $\pm$ 10A°. The activation energies are calculated within an accuracy of $\pm$ 0.01 eV in all measurements.

III. RESULTS AND DISCUSSION

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°, which corresponded to the (100) diffraction of the α-form crystal, which is the stable crystal form at substrate temperatures lower than 200 ℃ [13]. This diffraction peak resulted in a lattice spacing of 12.7 A °, 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 (12.6A°) [14].
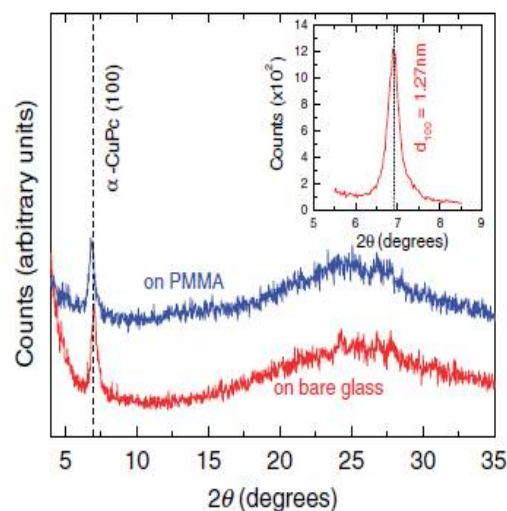
Fig. 2. XRD spectra of CuPc films deposited in the same run on bare and PMMA-coated glass substrates. The inset of the figure shows a detail of the XRD spectrum in the diffraction peak.

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
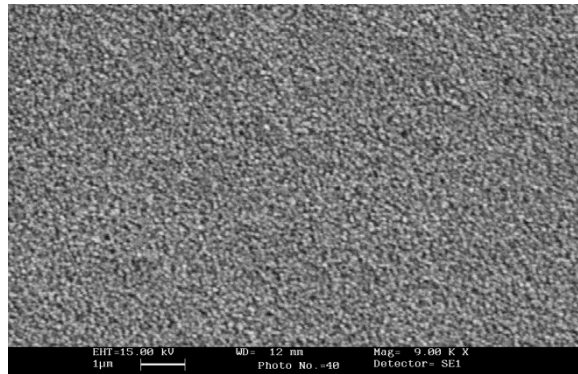
obtained were around 45–55 nm. A typical SEM planar view of the CuPc films deposited on crystalline silicon is given in Fig. 3.

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

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-π electron system and from the overlapping orbitals on the central copper atom.
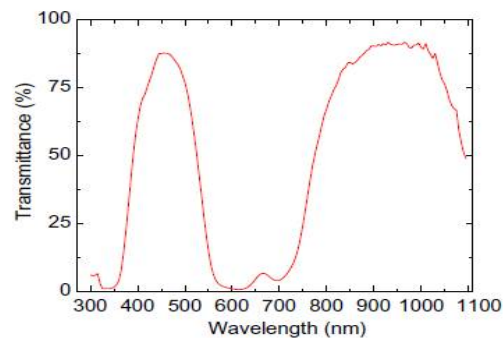
Fig. 4. Optical transmission spectrum of a 400 nm-thick CuPc layer deposited on glass.

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-π_* orbitals and is called the Soret band (B-band) [16, 17]. The Soret band is a characteristic of the metal phthalocyanines absorption spectrum . 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 615 nm. The high energy peak of this Q band has been assigned to the π–π_* transition on the phthalocyanine macrocycle, whereas the second peak at low energy has been assigned as a second π–π_* transition or due to the formation of excitons.

Dependence of film thickness

Resistances of CuPc thin films deposited at room temperature are measured using the programmable Keithley electrometer in the temperature range 320-500K at intervals of 5K. The corresponding electrical conductivity (σ) is estimated using the equation 1, knowing the length, breadth and thickness of the film. Plot of ln σ versus 1000/T yields

different linear regions. The thermal activation energies of these samples are calculated from the slopes of the linear portions of the graphs using the relation 2. Figures.5, 6 and 7 show the plots of ln σ versus 1000/T for CuPc thin films of thicknesses 150nm, 300nm and 470nm.

$$\sigma = A \exp(-E1/kBT) + B \exp(-E2/kBT) + C \exp(-E3/KBT) + ----- \quad [1]$$

where E1 is the pseudo intrinsic energy gap and E2, E3, the activation energy needed to excite the carriers from the corresponding trap levels to the conduction band. A, B, C are constants. The conductivity 'σ' of a film of resistance 'R', length 'l' breadth 'b' and thickness 't' is given by
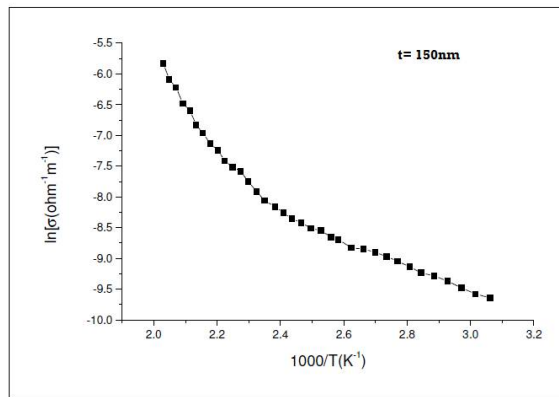
$$\sigma = l/Rbt ---- \quad [2]$$

Fig.5 ln σ versus 1000/T plot of CuPc thin film of thickness 150 nm

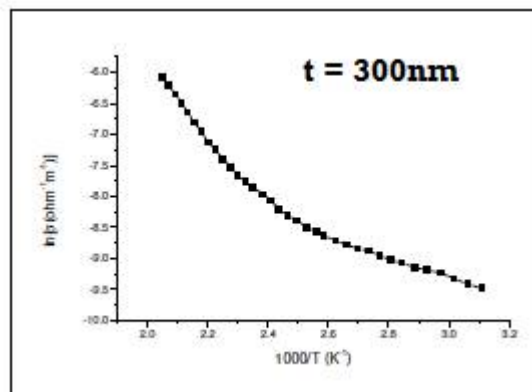**Fig.6** ln σ versus 1000/T plot of CuPc thin film of thickness 300 nm

VI.CONCLUSION

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 .No significant structural differences were seen from CuPc layers deposited on bare glass and those on PMMA.

Electrical conductivity measurements are performed using a programmable Keithley electrometer (model No.617) in the constant current source mode. The effect of film thickness on conductivity is studied in CuPc thin films with different thickness deposited on glass substrate at room temperature. Electrical conductivity studies are done in the temperature range 320 – 500K. The activation energies are calculated from the slopes of the linear portions of ln σ versus 1000/T plots. Tripple activation energies are observed for the three thin films CuPc. The activation energies are found reduced with increasing thickness. In another set of experiments, thin films of same thickness are deposited at

various substrate temperatures and their activation energies are calculated. The activation energies are found reduced in all the three sets of thin films deposited at higher substrate temperatures.

In the near future we will focus our investigation on low deposition rates (<1 nm/min) and moderate substrate temperature (>100 °C), expecting an improvement in the CuPc film properties and, consequently, in the field-effect mobility values. These organic semiconductors are expected to replace the present semiconductor devices soon. The area of very large scale integration and nanotechnology device fabrication using metal phthalocyanines will revolutionize the electronic industry in the next decade.

REFERENCES

[1] S.R. Forrest, Nature 428 (2004) 911.
[2]Z. Bao, A.J. Lovinger, A. Dodabalapur, Appl. Phys. Lett. 69 (1996)
 [3]S. Hoshino, T. Kamata, K. Yase, J. Appl. Phys. 92 (2002) 6028.
[4]K. Xiao, Y. Liu, G. Yu, D. Zhu, Synth. Met. 137 (2003) 991.
[5]K. Xiao, Y. Liu, G. Yu, D. Zhu, Appl. Phys. A 77 (2003) 367.
[6]H. Hoppe, N.S. Sariciftci, J. Mater. Res. 19 (2004) 1924.
[7]P. Peumans, A. Yakimov, S.R. Forrest, J. Appl. Phys. 93 (2003) 3693.
[8]F. Yang, M. Shtein, S.R. Forrest, Nat. Mater. 4 (2005) 37.
[9] J. Xue, B.P. Rand, S. Uchida, S.R. Forrest, Adv. Mater. 17 (2005) 66.
[10] S. Uchida, J. Xue, B.P. Rand, S.R. Forrest, Appl. Phys. Lett. 84 (2004) 4218.
[11] U. Haas, A. Haase, H. Maresch, B. Stadlober, G. Leising, 14th International Conference on Polymers and   Adhesives in Microelectronics and Photonics (POLYTRONICS 2014), 12–15 September 2004, Portland,USA.
[12] F. De Angelis, S. Cipolloni, L. Mariucci, G. Fortunato, Appl. Phys.Lett. 86 (2015) 203505.
[13] T. Nonaka, Y. Nakagawa, Y. Mori, M. Hirai, T. Matsunobe, M. Nakamura, T. Takahagi, A. Ishitani, Thin Solid Films 256 (2015) 262.
[14]M.K. Debe, R.J. Poirier, K.K. Kam, Thin Solid Films 197 (2016) 335.
[15]B.D. Cullity, Elements of X-ray Diffraction, Addison-Wesley, Boston, 1977.
[16] L. Edwards, M. Gouterman, J. Mol. Spectrosc. 33 (2013) 292.
[17] S. Ambily, C.S. Menon, Thin Solid Films 347 (2013) 284.
[18] A.T. Davidson, J. Chem. Phys. 77 (1982) 168.
[19]M. Fendrich, Wagner, and R. Möller, Phys. Rev., 73 (2015).