Substrate influence on the morphological and conductive properties of modified iron-phthalocyanine thin films

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Abstract In this work, molecular thin films prepared with the cyano(phthalocyaninate)iron(III) [PcFeCN]$_n$ macrocycle axially modified with the 1,8-dihydroxyanthraquinone ligand were studied. The films were formed by using electrodeposition and evaporation techniques onto Si(001) and 7059 Corning glass substrates in order to investigate the influence of the substrate and the preparation method on the morphological and conductive properties of the films. In this study, Fourier transform infrared spectroscopy, scanning electron microscopy, energy-dispersive spectroscopy and atomic force microscopy (AFM) techniques were employed. From AFM measurements, it was found that the evaporated films exhibited a more regular distribution with low roughness values in contrast with the electrodeposited films. The electrical conductivity results for the evaporated films exhibited semiconductor behaviours with conductivity values at room-temperature of 10^{-6} Ω^{-1}cm^{-1}. Better conductivity results were obtained for films onto glass substrates.

1 Introduction

Over the last years, there has been an increasing interest on molecular materials because of their intrinsic electric, magnetic and/or optical properties, which may lead to electronic device applications [1, 2]. Nowadays, recent research work has been directed to the formation of molecular thin layers since it is well known that a regular stacking of molecules allows the formation of semiconducting or conducting thin films [3]. Although, UHV methods have been commonly employed in the formation of homogeneous thin films, more simple techniques such as chemical vapour deposition and electrosynthesis have successfully produced molecular conductors of tetrathiofulvalene-tetracyanoquinodimethane (TTF-TCNQ), among others [4–6]. In addition, molecular semiconductor films of tetrabenzo (b,f,j,n) {1,5,9,13} tetraazacyclohexadecine copper(II) and nickel(II) bisanthraflavates have been prepared by using low vacuum thermal evaporation [7]. Nowadays, other molecular conductors such as metallophthalocyanines are been extensively studied due to their interesting electrical properties and their ability to form good-quality thin films which are of particular interest in the study of low-dimensional metals and semiconductors. Although the conduction path in these systems has been described as originated from the π–π overlapped of the stacked molecules, it has been notice that the conductivity can be modified or enhanced by adding organic

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bridging ligands which allow electron migration from one metal atom to the other [8]. In particular, by using linear bidentate axial ligands coordinated to the metallophthalocyanine nuclei, low-dimensional electronic conduction within polymeric films has been achieved [9]. Furthermore, it has been noticed that organic ligands such as dihydroxyanthraquinone derivativies, have influenced the sensitivity and the stability of the organic conducting film response during the electrochemical polymerization of conductive polymers [10].

On the other hand, although chemical vapour deposition has been extensively used to produce molecular films onto conductive substrates typically employed in technological applications such as corning glass and silicon wafers [11, 12], the formation of thin films by using electrosynthesis directly onto conductive substrates has been scarcely investigated [13]. Since there is a great interest in the characterization of hybrid organic–inorganic structures to produce low-cost semiconductor thin films, in this work we studied the influence of the preparation technique, the type of substrate employed and the addition of a bidante ligand on the morphological and conductive properties of [PcFeCN]$_n$ thin films. The film characterization was performed by using Fourier transform infrared spectroscopy (FTIR), scanning electron microscopy (SEM), energy-dispersive spectroscopy(EDS) and Atomic force microscopy (AFM) techniques. Finally, the electrical behavior of the films was evaluated by means of the four-probe technique.

2 Experimental section

Compound 1,8-dihydroxyanthraquinone was obtained from commercial suppliers and used without further purification. The complex (μ-cyano)(phthalocyaninate) Fe(III) or [PcFeCN]$_n$ was synthesized from iron(III) phthalocyanine chloride as reported elsewhere [14, 15].

The electrochemical reaction was carried out according to the method described by Tuck [16]. The synthesis took place in a two-compartment electrochemical cell separated by a porous bridge. Solutions of (μ-cyano)(phthalocyaninate) Fe(III) (0.17 g) and 1,8-dihydroxyanthraquinone (0.18 g) in acetonitrile (40 mL) were introduced into the cathode and anode compartments, respectively. Finally a, Galvanostatic electrolysis was conducted at a constant current density of 5 μA cm^{-2} and 298 K. The final product was obtained in the anode compartment after 5–7 days when a blue thin film appeared on the electrode surface.

The thin film deposition was carried out by low pressure vacuum thermal evaporation onto Corning 7059 glass slices and Silicon (001), 200 Ω cm wafers. The substrate temperature was kept at 298 K during deposition. The Corning 7059 substrates were ultrasonically decreased in warm ethanol and dried in a nitrogen atmosphere. The single-crystalline silicon substrates underwent chemical etching with a p solution (10 mL HF, 15 mL HNO$_3$, and 300 mL H$_2$O) in order to remove the native oxide from the Si(001) surface. To prevent the condensation of powder products onto the substrates surface, the evaporation source was a molybdenum boat with two grids. It must be noted that the synthesized compounds sublimate, although the sublimation was negligible in comparison with the evaporation process. The temperature through the molybdenum boat was slowly increased until it reached 453 K, below the first significant signal change observed in the thermogravimetric analysis thermogram in order to prevent thermal decomposition of the compound. Finally, the boat temperature was kept at 453 K during the evaporation process while it was monitored with a chromel–alumel thermocouple.

Fourier transform infrared spectroscopy (FTIR) measurements of the thin films were made with a Perkin Elmer 282-B spectrophotometer. Scanning electron microscopy (SEM) was carried out in a Jeol JSM 5200 CX microscope were a 5 kV potential was used for all samples. An atomic force microscope (AFM) JEOL JSPM 4210 was used in the tapping mode in order to investigate the surface morphology of the films. The electrical conductivity of the films was studied by means of a four-probe method. The current–temperature dependence of the films was measured with a Keithley 230 voltage source and a Keithley 485 pico-amperimeter coupled to a PC-controlled HP3421 data acquisition system.

3 Results and discussion

The electrosynthesis of (PcFe)L$_2$ on the different substrates was found to be very reproducible. The electrodeposits did not spontaneously peel off from the electrode surface in any case. The use of large-surface anodes was effective in terms of quantity production, that is, approximately 35 mg of product was obtained in each experiment. This was only valid when the reactant's concentration, the current supplied to the electrosynthesis cells and the working temperature values were the same. So, under the same experimental conditions, the electrosynthesis process between the macrocycle and the ligand was independent of the kind of substrate employed. Finally, the longer the reaction time the larger the amount of electrodeposited material. In this case, the thickness of the film onto 7089 Corning glass was 383 nm while the thickness of the film onto Si(001) was 388 nm by using the evaporation technique. On the other hand, the thickness of the films by using electrodeposition methods were 302 nm for the glass and 325 nm the silicon substrates, respectively.

Table 1 IR (cm^{-1}) characteristic bands for all the thin films

Compound	IR (CN$^-$)	IR (C=O) cm^{-1}	IR (C–O) cm^{-1}
Electrodeposited thin film on 7059 Corning glass	–	1,612	1,080
Electrodeposited thin film on (001)-oriented silicon	–	1,612	1,082
Evaporated thin film onto 7059 Corning Glass	–	1,610	1,084
Evaporated thin film on (001)-oriented silicon	–	1,610	1,082

IR spectroscopy results of the materials formed by electrodeposition onto Si(001) are shown in Table 1. From these results, one can notice that the (PcFe)L$_2$, L = 1,8-dihydroxyanthraquinone species exhibits C=O and C–O functional groups with wavelengths around 1,612 cm^{-1} and 1,082 cm^{-1}, respectively. On the other hand, the absence of the 2,158 cm^{-1} wavelength corresponding to the cyano group of the [PcFeCN]$_n$, supports the idea that the cyano group has been substituted by the 1,8-dihydroxyanthraquinone species in the fifth and sixth positions of the coordination sphere of the iron atom [14]. Similar results were obtained after analysing the evaporated films onto Si(001). This modification allows the formation of long symmetric chains to obtain axially modified molecular materials and introduces anisotropy to the system.

In Fig. 1, SEM images of the films formed onto 7089 Corning glass are shown. Figure 1a corresponds to the evaporated film while Fig. 1b corresponds to the electrodeposited film. From these figures, it is clear that the evaporated process produced a more homogeneous surface in comparison with the electrodeposited method. EDS analysis on these films shows the presence of iron and oxygen as expected from the [PcFeCN]$_n$ molecule and the 1,8-dihydroxyanthraquinone species, respectively. Similar results were obtained for the evaporated and electrodeposited films onto Si(001) (images not shown here).

Atomic force microscopy has been independently used to assess the surface quality of the thin films. Figure 2 shows the AFM images obtained from thin films onto Corning 7059 glass slices by 2a) evaporation and 2b) electrodeposition processes. Figure 2a shows an irregular granular aspect onto the glass surface with grain diameters from 200 to 500 nm. The RMS roughness value of this surface is 27 nm which suggest a semi-planar film. On the other hand, Fig. 2b shows a highly corrugated surface where large deposition areas are observed. This film contains aggregates and flat terraces at different levels. The RMS roughness value of this surface is 243 nm, which suggest a more corrugated surface in comparison with the evaporated film.
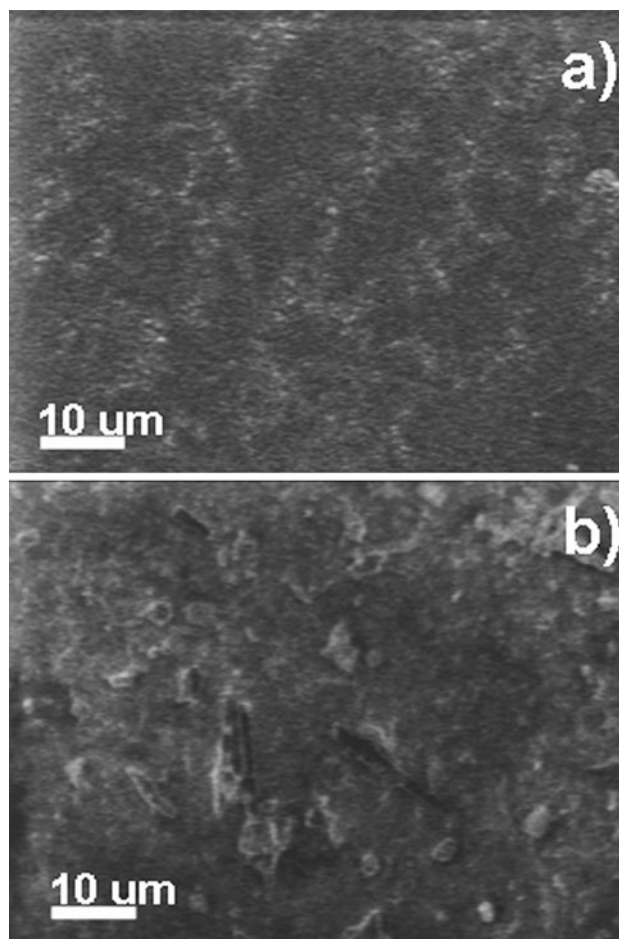
Fig. 1 SEM images of the molecular films onto 7089 Corning glass slices by using **a** evaporated and **b** electrodeposited methods

In Fig. 3, the films obtained onto Si(001) are shown. Figure 3a corresponds to the evaporated, while Fig. 3b corresponds to the electrodeposited film. As in the previous case, and in agreement with the SEM images, the evaporated film looks more regular in comparison with the electrodeposited one, although both films have similar RMS roughness values (15 nm). From these results, the films of molecular materials onto Si(001) exhibited in general a better aspect in comparison with the ones obtained onto glass possible due to the substrate crystalline properties.

The temperature-dependent resistance of the thin films was evaluated with the four-probe method. This is one of the most popular techniques for conductivity measurements in the semiconductor industry and is performed along a line over the material surface having equal spaces between the test points. This technique uses low electric currents to avoid sample heating. The voltmeter must have high input impedance and measurements must be made for enough contacts so that any injected minority charge carrier recombines. The electrical current variation with
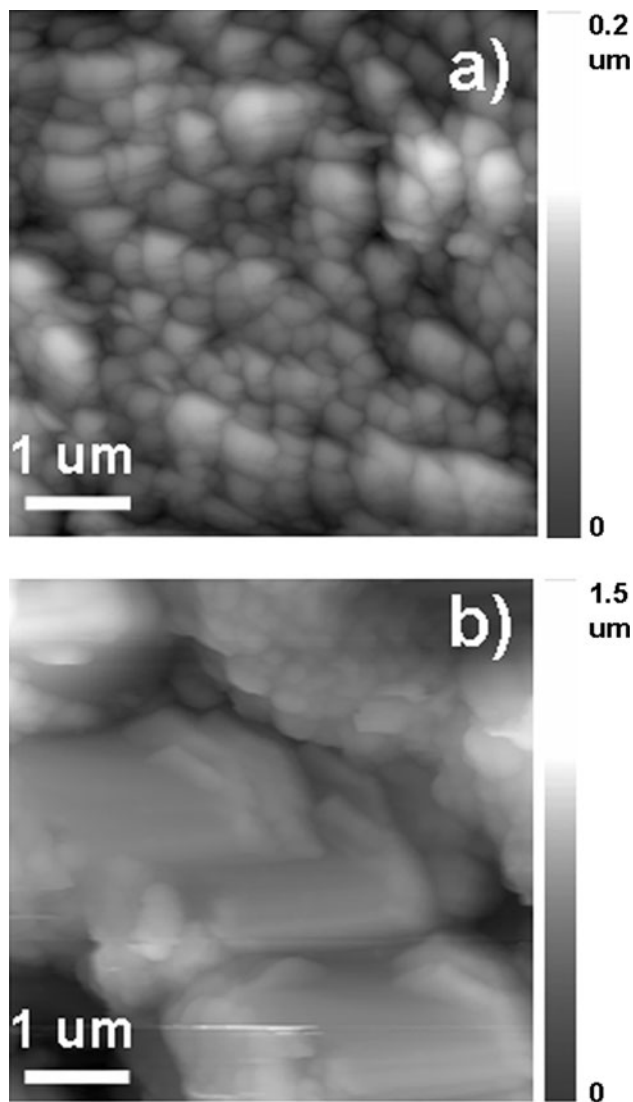
Fig. 2 AFM images showing the surface morphology of the thin films deposited onto Corning 7059 glass slices by using **a** evaporated and **b** electrodeposited methods. Images are 5 × 5 μm

Fig. 3 AFM images showing the surface morphology of the thin films deposited onto (001)-oriented silicon wafers by using **a** evaporated and **b** electrodeposited methods. Images are 5 × 5 μm

temperature was evaluated by applying a voltage ramp from 0 to 1000 V. Figure 4 shows the electric current variation through the films for each of the synthesized molecular material films at different temperatures at a constant applied voltage in the ohmic regime. The plots for these molecular materials thin films showed semiconductor behaviours. In all cases, the current decreases as temperature decreases. From this graph, it is observed that films grew onto corning glass exhibited the largest current variation for the analysed temperature range. From these two plots, it is clear that the evaporated film showed the highest electrical current at high temperatures but the lowest current at low temperatures in comparison with the electrodeposited film. On the other hand, the lowest current variation was found on the films onto Si surfaces. From
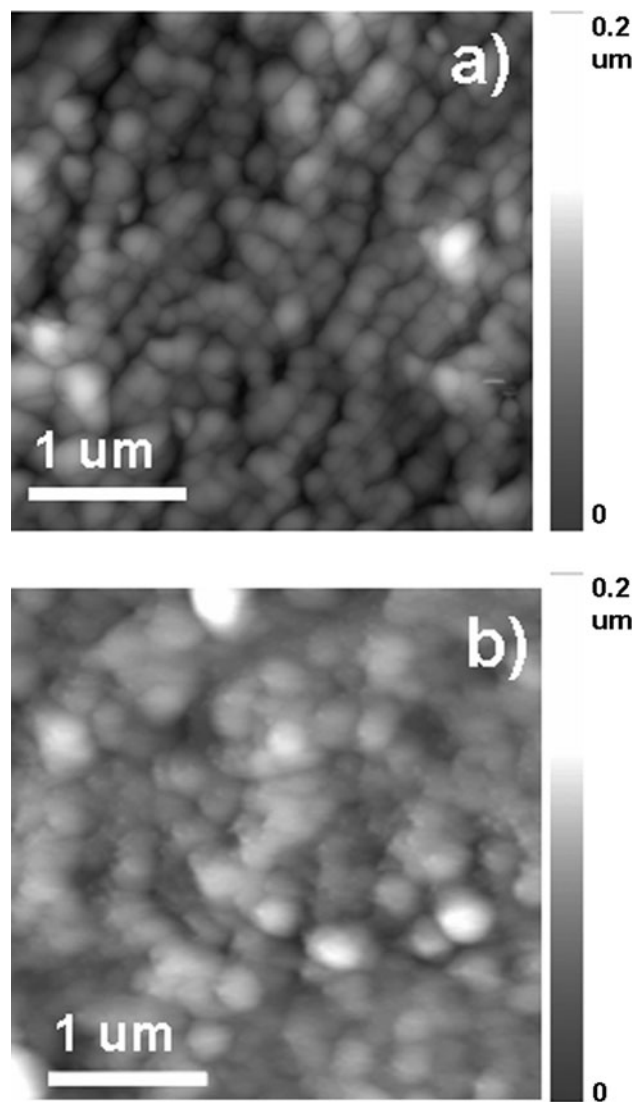
these two curves, the evaporated film exhibited higher current at high temperatures but lower current at low temperatures in comparison with the electrodeposited film. Finally, at low temperatures, the electrodeposited film onto Si substrates exhibited the higher current, meanwhile, at high temperatures, the evaporated film onto the Glass substrate showed the higher current.

The electrical conductivity of each material was also evaluated at 25 °C for the films onto Corning 7059 glass slices. The conductivity values found by the evaporation method were $1.6 \times 10^{-5} \ \Omega^{-1}cm^{-1}$, meanwhile, $1.43 \times 10^{-6} \ \Omega^{-1}cm^{-1}$ was obtained for the electrodeposited one. As we can see, these conductivity values are lower than those obtained for $[PcFeCN]_n$ pure systems ($6 \times 10^{-3} \ \Omega^{-1}cm^{-1}$) [8]. Nevertheless, the electrical
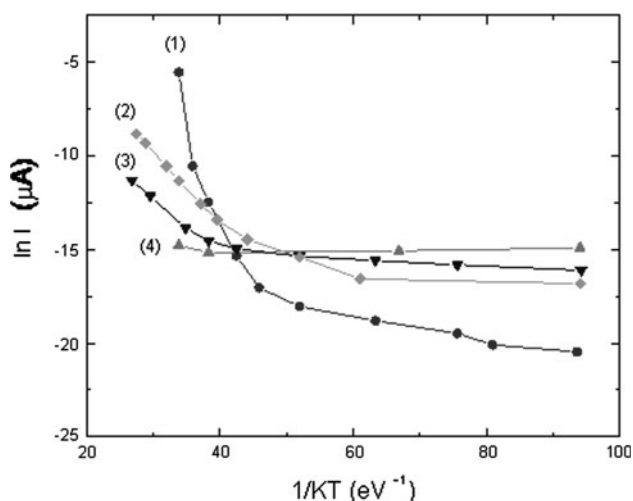
Fig. 4 Electric current as a function of temperature for (*1*) evaporated on Corning 7059 glass, (*2*) electrodeposited on Corning 7059 glass, (*3*) evaporated on (001)-oriented silicon wafers and (*4*) electrodeposited on (001)-oriented silicon wafer thin films

conductivity value for the electrodeposited film was higher than those previously reported for pure PcFe compounds [17] and similar modified iron phthalocyanines molecules onto glass substrates by using evaporation techniques [18].

4 Conclusions

In this work, we reported the growth of (PcFe)L$_2$, L = 1,8-dihydroxianthraquinone thin films onto silicon and 7059 Corning glass as a preliminary step towards the use of such molecular materials in future electronic applications. The (PcFe)L$_2$ thin films exhibited a semiconductor behaviour. These thin films were easily produced and showed good adhesion. The Corning glass substrate was the one that exhibited the best conductivity, homogeneity and adherence results. At low temperatures, the films onto Si exhibited the highest conductivity, while at higher temperatures, the highest conductivity was found on the films onto the glass substrate. In this work, it was observed that although both preparation processes produced films with similar physical properties, the electrodeposition technique involved one single step while the evaporation technique required two separated procedures (synthesis and evaporation) for the film formation. Finally, although the preparation of molecular materials for future electronic applications remains a challenge, these results may provide different information to produce molecular-materials thin films in a more practical and efficient way.

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