
M. E. Sánchez-Vergara¹, C. Álvarez-Toledano², A. Garduño², J. R. Alvarez-Bada¹

¹Facultad de Ingeniería, Universidad Anahuac del Norte. Avenida Universidad Anahuac 46, Col. Lomas Anáhuac, 52786, Huixquilucan, Estado de México. México. E-mail: elena.sanchez@anahuac.mx
²Instituto de Química, Universidad Nacional Autónoma de México, Circuito Exterior, Ciudad Universitaria, 04510 México, D.F., México

Considerable research work has been devoted to the formation and characterization of molecular-material thin films, due to their potential application in photonic, optoelectronic or electronic devices. This work reports the preparation and deposition of anisotropic, semiconducting thin-films of metal phthalocyanines and δ-lactones using two methods: low-pressure evaporation and electrodeposition in the electrochemical module of the atomic force microscope (AFM). This last approach permits the observation and monitoring of material deposition during film growth. Low-pressure evaporation is the conventional technique for thin-film preparation and involves the sublimation of molecular material, followed by its deposition on different types of substrates. Thin-film preparation on the electrochemical module of the AFM, on the other hand, has the advantage of permitting the analysis of conducting as well as insulating films. In terms of material characterization, the AFM is also compared favourably with the scanning electron microscope (SEM) because of its good topographic contrast with direct height measurements and surface imaging with similar or better lateral resolution.

Keywords: Atomic Force Microscopy; Scanning Electron Microscopy; Thin Films; Electrical Properties

1. Introduction

Research on new materials for electronics and optoelectronics applications has recently surged after a long period of inorganic-material predominance. Materials of organometallic or organic nature with electronic characteristics have ever more applications and are of great importance nowadays, due to their growing use in electronic devices. These materials show an anisotropic behavior, with electrons moving along the planes but not between them, or moving along chains of atoms. Their microstructures are of special interest because they are usually formed by regular molecular patterns that can generate preferential paths for electrical conduction, which is why they are sometimes called quasi-one-dimensional solids or low-dimensional linear chains. Their highly anisotropic conductivity almost reaches metallic values along a preferred direction defined by their structural configuration. This arises from a great number of long and parallel chains or molecular stacks along which conduction seems to occur. These materials are also known as low-dimensional solids, and a good example is tetrathiafulvalene-tetracyanoquinodimethane (TTF-TCNQ), which has an electric conductivity of up to 100 S·m⁻¹ at room temperature; as soon as temperature decreases, its conductivity increases up to 80 KS·m⁻¹. The columns of every type of molecule in TTF-TCNQ interact to form delocalized orbitals. Some electrons in the highest filled energy band of TTF move crosswise to partially fill a TCNQ band, so both types of columns have partially occupied bands [1-3]. Examples of organometallic compounds with electronic properties of potential interest are the metallophthalocyanines (MPc): a kind of molecular semiconductors which forms stacks parallel to the counter-ions. When phthalocyanines partially oxidize, the crystals of these compounds have very high electric conductivities in the direction of the stacks. The most essential feature of the charge-transfer salts of phthalocyanine is their double chain and two-band structure where a metal d-chain and a macrocycle π-chain coexist within the same molecular column and a narrow 3d-band is located near the Fermi level of a wide π-band [4]. Research has been made showing that several organic anisotropic compounds have optical properties of potential use in optoelectronics. Lactones are another example of compounds used in the synthesis of anisotropic materials with special electronic properties.

One-dimensional materials represent a major development in the field, because they show new mechanical, chemical, magnetic, optical and electrical properties, among others. Thus, these materials have become a very important subject of study, especially when dealing with electronic conduction. Recent research work has been oriented to the formation and characterization of molecular thin films [5]. The use of chemical vapor deposition to grow thin films of molecular conductors, such as TTF-TCNQ, has been reported [6, 7]. A regular stacking of molecules, such as is found in molecular materials, may lead to the formation of semiconducting, conducting, or superconducting thin films. The production of thin films from organic materials for device applications is relevant in this context, given the potential design simplicity, low fabrication costs, and ease of characterization in the optical and electrical domains [8, 9]. This work concerns the preparation and deposition of anisotropic, semiconducting thin-films of metallic phthalocyanines (MPc) and δ-lactones (C₁₀H₁₀F₆N₂O₆S₂) using two methods: low-pressure evaporation and
electrodeposition in the electrochemical module of the atomic force microscope (AFM). This last approach permits the observation and monitoring of material deposition during film growth. Low-pressure evaporation is the conventional technique for thin-film preparation and involves the sublimation of molecular material, followed by its deposition on different types of substrates. Thin-film preparation on the electrochemical module of the AFM, on the other hand, has the advantage of permitting the analysis of conducting as well as insulating films. In terms of material’s characterization, the AFM also compares favourably with the scanning electron microscope (SEM) because of its good topographic contrast with direct height measurements and surface imaging with similar or better lateral resolution. The material characterization was performed by using infrared (IR) and mass-spectroscopy techniques. The electrical conductivity was measured at different temperatures in order to evaluate the conductivity behavior of these compounds. After the synthesis and characterization, a comparative study was made between these materials and their relation in terms of the highly-ordered structure and marked anisotropy that generates a preferential direction for the transport of electric charges.

2. Experimental Procedure

High-purity raw materials were obtained from commercial suppliers with no further purification. The synthesis of lactone C$_{10}$H$_{10}$F$_{2}$N$_{2}$O$_{6}$S$_{2}$ via trifluoromethanesulfonic anhydride in pyridine and the crude purification by column chromatography were followed according to Garduno-Alva et al [10]. Vibrational spectra were obtained with a Perkin Elmer IR spectrophotometer, model 282-B. Scanning electron microscopy (SEM) was carried out in a Leica Cambridge, Stereoscan 440 model with a coupled microanalysis system including X-ray energy-dispersive spectrometry (EDS).

2.1. Synthesis of C$_{38}$H$_{20}$F$_{2}$N$_{8}$O$_{2}$S$_{2}$Fe, C$_{26}$H$_{12}$N$_{10}$OSGa and C$_{26}$H$_{12}$N$_{10}$OSNi

Add 0.03 g (0.05 mmol) of iron phthalocyanine chloride to 0.03 g (0.069 mmol) of δ-lactone or 0.09 g (0.2 mmol) of nickel phthalocyanine to 0.06 g (0.10 mmol) of gallium phthalocyanine to 0.06 g (0.14 mmol) of δ-lactone and dissolve in 20 ml of ethanol. Keep in reflux for 72 hours. The solid was filtered off, washed with absolute ethanol and vacuum dried. The product was recrystallized in a 1:1 ethanol-water solution. $C_{38}H_{20}F_{2}N_{8}O_{2}S_{2}Fe$ (Compound 1). Yield reaction 56%. IR (ν, cm$^{-1}$) $\nu_{\text{max}}$: 2963, 2874 (=CH); 1295 (C-N); 1770 (CO); mp 310°C.

Add 0.03 g (0.05 mmol) of gallium phthalocyanine or 0.06 g (0.10 mmol) of gallium phthalocyanine to 0.06 g (0.10 mmol) of gallium phthalocyanine to 0.06 g (0.14 mmol) of δ-lactone and dissolve in 20 ml of ethanol. Keep in reflux for 72 hours. The solid was filtered off, washed with absolute ethanol and vacuum dried. $C_{26}H_{12}N_{10}OSGa$ (Compound 2). Yield reaction 55%. Calculated analysis for C$_{26}$H$_{12}$N$_{10}$OSGa: IR (ν, cm$^{-1}$) $\nu_{\text{max}}$: 2963, 2872 (=CH); 1297 (C-N); 1779 (CO); mp 370°C.

Add 0.03 g (0.05 mmol) of iron phthalocyanine or 0.06 g (0.10 mmol) of gallium phthalocyanine to 0.06 g (0.10 mmol) of gallium phthalocyanine to 0.06 g (0.14 mmol) of δ-lactone and dissolve in 20 ml of ethanol. Keep in reflux for 72 hours. The solid was filtered off, washed with absolute ethanol and vacuum dried. $C_{26}H_{12}N_{10}OSNi$ (Compound 3). Yield reaction 55%. Calculated analysis for C$_{26}$H$_{12}$N$_{10}$OSNi: IR (ν, cm$^{-1}$) $\nu_{\text{max}}$: 2966, 2877 (=CH); 1299 (C-N); 1772 (CO); mp 340°C.

2.2. Thin film electrodeposition

The initial stages of electrochemical deposition by cyclic voltammetry and the AFM surface characterization were carried out in situ in the electrochemical (EC) fluid cell of the Nanoscope IIIa Digital Instrument atomic force microscope (Figure 1a). Here, highly oriented pyrolytic graphite (HOPG) was used as a working electrode, with platinum wire as a counter electrode and silver wire as a reference electrode. The AFM works by scanning a high-resolution tip over the surface, which in this case is the material deposited in situ over a graphite disk. The tip has a pyramidal shape and lays below a cantilever a few hundred micrometers long. As the tip is attracted or repelled by the surface due to interaction forces, the cantilever is deflected. The deflection magnitude can be detected by an optical system in which a laser beam reflected from the cantilever is detected by a photodiode and generates electrical signals dependent on the deflection amplitude. These signals are provided to a computer in order to generate an image of the molecular-material surface. Thus, as the tip scans the surface, the force field acting on the cantilever and the surface remains constant in such a way that the vertical motion of the tip provides topographic information about the specimen. The output signal from the photodiode controls the force field acting on the tip to keep it constant.

The AFM morphological characterization of the electrodeposited thin films was performed in situ in the contact mode using low scanning forces (0.3 Nm$^{-1}$) in the open circuit mode. For this study, 0.1 M tetrabutylammonium tetrafluoroborate was used as support electrolyte. The AFM characterization of the thin films was performed in the presence of an aqueous electrolyte (50 μl). In order to compare the electrode surface modifications before and after deposition, the HOPG was imaged before the electrochemical reactions and after different potential scan cycles (PSC). The use of AFM for the electrodeposition of thin films permits the study of the reduction-oxidation electrochemical processes occurring in the cell, with the aid of an electrochemical module (potentiostat/galvanostat). The main parts of the AFM electrolysysthesis module used in the electrodeposition were:
Fluid cell: It is made of a device containing small quantities of the solution (in the order of microliters to milliliters), with internal canals where the electrodes are located.

Substrate: It consists of a cylindrical-shaped tablet where the material to be studied with the AFM is deposited. For electrodeposition, the substrate provides the location where material will accumulate as current flows. It is usually made of highly oriented graphite, as flat, uniform surfaces are required to obtain thin films as uniform as possible. Since graphite is a conducting material, it can work as an electrode (counter electrode), which is necessary for the electrodeposition of a material from the solution.

Electrodes: They are two wires that are in contact with the fluid. One is the working electrode (platinum wire) and the other is the reference electrode (silver wire). Electric current flows through them and polarizes the fluid.

Variable voltage source: It is a device capable of generating voltages with various waveforms, depending on the desired type of signal. For this work, the source generated saw tooth waveforms.

![Electrosynthesis cell for AFM electrodeposition and chamber for low-pressure evaporation](image)

**Figure 1.** (a) Electrosynthesis cell for AFM electrodeposition and (b) chamber for low-pressure evaporation

### 2.3. Thin film deposition

For the evaporation process, the solid material undergoes a heating process leading to evaporation within a vacuum chamber as shown in Figure 1b. As temperature increases, the material melt, evaporates, and is then deposited over different substrate types. For the evaporation of thin films, a vacuum chamber was used with a diffusion pump and a special molybdenum crucible with a double-grid cover (Figure 1b). A quartz fiber was put inside the crucible to avoid the ejection of grains towards the substrate at a temperature of 563 K. The material was deposited on Corning 7059 glass substrates, which were ultrasonically degreased in warm methanol and dried in nitrogen, and on single-crystalline c-Si wafers, which were chemically etched 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 c-Si surface. The base pressure used in the evaporation process was $10^{-5}$ torr at room temperature.

### 2.4 Electrical measurements

Electrical measurements were made in a line on the film having equal spaces between the test points. The use of films is a trustworthy way of evaluating the electrical conductivity. Care was taken to ensure that the current involved was low enough to prevent sample heating and the voltmeter had high input impedance. The electrical conductivities at room temperature for the electrodeposited and the evaporated thin films were calculated.

### 3. Results and Discussion

IR spectroscopy was performed to determine the presence of functional groups, and most importantly, the presence of representative bonds of the various synthesized compounds to determine chemical changes during the electrodeposition process (see Experimental Procedure). The deposited films were formed from the same macro-ions as those of the original synthesized powder, as found by comparison with the position of the absorption bands in the spectra of the synthesized powders and those of the deposited films (evaporated and electrodeposited thin films). All compounds show stretching vibrations at the C=C (cm$^{-1}$) 1643-1630 and C=N (cm$^{-1}$) 1537-1552 bonds, as is usual for this kind of compounds formed from a metallic phthalocyanine and the lactone. The vibrations C-N (cm$^{-1}$) around 1290 and the
vibrations of the CO (cm\(^{-1}\)) bond around 1775 suggest the presence of \(\delta\)-lactone that is bound to the phthalocyanine macrocycle. This had already been reported [11-13] for similar compounds.

Table 1. IR data for the reported compounds, obtained by electrochemical deposition and low-pressure evaporation. All units cm\(^{-1}\).

<table>
<thead>
<tr>
<th>Compound</th>
<th>(\nu) (=CH) (cm(^{-1}))</th>
<th>(\nu) (CO) (cm(^{-1}))</th>
<th>(\nu) (C-N) (cm(^{-1}))</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (electrodeposited thin film)</td>
<td>2962, 2872</td>
<td>1777</td>
<td>1294</td>
</tr>
<tr>
<td>1 (evaporated thin film)</td>
<td>2960, 2870</td>
<td>1774</td>
<td>1290</td>
</tr>
<tr>
<td>2 (electrodeposited thin film)</td>
<td>2966, 2877</td>
<td>1775</td>
<td>1295</td>
</tr>
<tr>
<td>2 (evaporated thin film)</td>
<td>2963, 2875</td>
<td>1776</td>
<td>1294</td>
</tr>
<tr>
<td>3 (electrodeposited thin film)</td>
<td>2966, 2877</td>
<td>1775</td>
<td>1295</td>
</tr>
<tr>
<td>3 (evaporated thin film)</td>
<td>2964, 2778</td>
<td>1777</td>
<td>1295</td>
</tr>
</tbody>
</table>

Figure 2 shows the AFM images of the electrodeposited thin films. From these images, it is clear that the film surface changed dramatically as a function of the starting material, although we tried to keep a constant deposition parameter. The variation in the films’ surface may be due to the change of the metallic ion in the macrocycle. Similar results have been obtained for thin films of phthalocyanine and its complexes (magnesium, manganese, iron, cobalt, zinc and lead phthalocyanine) [4]. The root mean square (r.m.s.) roughness evaluated from the AFM measurements of the thin films is 13.11, 5.3 and 34.4, for Compound 1, Compound 2 and Compound 3, respectively. The roughness differences may be related to the different metallic ions in each molecular material. The materials showing the smallest r.m.s. roughness were those belonging to the d electronic group; such compounds were synthesized from iron (1) and nickel (2). The material with the largest roughness was synthesized from gallium phthalocyanine (34.41 nm). This is the material from which the smallest conductivity was expected, as it belonged to the p group. The Ni phthalocyanine-based material, on the other hand, was expected to have the largest electrical conductivity, due to its low roughness and its d-group character.

![Figure 2](image)

Figure 2. AFM images of the substrate surface at early stages of film growth (a) Compound 1, (b) Compound 2 and (c) Compound 3. All images are 10x10 \(\mu\)m. The vertical scale is 100 nm in all cases.

Meanwhile, an appreciable change in the electrodeposited material was found in the low-pressure evaporation case. Figure 3 shows the image of the Ni-based synthesized material (compound 2); the evaporated film’s morphology is completely homogeneous. On the other hand, its r.m.s. roughness is 64, much higher than that obtained in electrodeposited films, so a significant reduction in the transported electrical current is to be expected. Similar results were obtained for the iron and gallium films.
The morphology observed for all materials in the SEM micrographs showed an amorphous appearance with no periodicity. Figure 4 shows the micrograph at 1500x corresponding to thin film electrodeposited (4a) and deposited by evaporation (4b). In the case of those materials deposited in the AFM module, larger particles are to be found than in the evaporation-deposition case. In both cases, one can discern smooth grains of a usually rounded shape, although some of them have rather more capricious shapes.

Energy dispersive spectroscopy (EDS) analysis was made for molecular materials synthesized as powder and electrodeposited as thin films. The results for iron materials may be observed in Figure 5. C_{38}H_{20}F_{2}N_{8}O_{2}S_{2}Fe (Compound 1) was synthesized from the organic compound lactone C_{10}H_{10}F_{6}N_{2}O_{6}S_{2}, and from the inorganic compound iron (III) (μ-cyano) phthalocyaninate C_{32}H_{16}N_{9}Fe. In Figures 5, one observes the presence of O, S, F, which belong to the cationic part of material, as well as the presence of Fe, which belongs to the anionic part. Similar results were obtained for materials synthesized from nickel and gallium. These results confirm the fact that, during the electroplating process, no chemical change occurred in the materials.
This use of the AFM is proposed as a more efficient way to generate molecular materials, as it permits thin-film synthesis to be monitored and manipulated before characterization. The proposed method has several advantages when compared with the traditional, low-pressure evaporation method.

A faster deposition is an advantage of using the AFM module, as this method requires only about one hour for this process, while the traditional method requires about three hours for preparing the substrates and evaporating the compound. Another advantage is that the AFM-generated materials are directly deposited in thin-film form, while those materials obtained from the traditional method are synthesized previously and require an additional evaporation process to produce a thin film. The use of AFM permits the analysis of samples made from conducting, insulating and semiconducting materials and provides good topographic contrast and lateral resolution when imaging surfaces [3].

The electric current transported, as well as the resistance and the conductivity of each material, were evaluated at 25°C. The results are presented in Table 2. The conductivity values at room temperature for both materials are in the range of the electrical conductivities for semiconducting molecular materials (from $10^{-2}$ to $10^{-6}$ S/m) [14]. This is important because a molecular semiconductor is generally defined in terms of its conductivity at room temperature, besides its structure, stacking form and orbital overlap. The material with nickel presents the largest conductivity at room temperature. Both Ni and Fe belong to the 3b period; in this case, symmetry allows d orbitals from different metallic atoms to overlap. As the first series of transition metals in the periodic table is traversed, a contraction of the size of the 3d orbitals occurs; so, the 3d orbital overlap decreases, and the 3d band becomes narrower for the Ni case, as compared to the Fe case. In a narrow band, the electrons are more strongly bound to the nuclei and inter-electronic rejections become considerably larger, including rejections between electrons of the same atom.

### Table 2. Electrical conductivity for thin films electrodeposited and evaporated

<table>
<thead>
<tr>
<th>Compound</th>
<th>Conductivity at 295 K (S·cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1 (electrodeposited thin film)</td>
<td>1.7 x 10¹</td>
</tr>
<tr>
<td>1 (evaporated thin film)</td>
<td>3.5 x 10⁻³</td>
</tr>
<tr>
<td>2 (electrodeposited thin film)</td>
<td>2.6 x 10¹</td>
</tr>
<tr>
<td>2 (evaporated thin film)</td>
<td>4.5 x 10⁻³</td>
</tr>
<tr>
<td>3 (electrodeposited thin film)</td>
<td>1.4 x 10¹</td>
</tr>
<tr>
<td>3 (evaporated thin film)</td>
<td>3.1 x 10⁻³</td>
</tr>
</tbody>
</table>

In amorphous materials, the absence of long-range order leads to the apparition of tails in the energy bands [15]. These tail bands are formed by localized electronic states; they are separated from extended states in the bands by a mobility edge. The electrical activation energy is related to the energy necessary to delocalize charge carriers through
electronic transitions from localized states towards extended states. The activation of the intrinsic electrical conductivity in semiconductor-like materials may be also explained by thermal excitation from valence band to conduction band. In our case, the difference in conductivity between the thin films may be attributed to the character of the metallic ions employed. Furthermore, these compounds show an important orbital overlap, probably due to the spatial extension of the transition-metal orbitals as suggested by Simon and Tournillac [16]. On the other hand, Jircitano and Timken [17] reported that charge transfer for molecular materials along particular directions can be related to highly ordered structures.

4. Conclusions

Semiconductor materials from iron, gallium and nickel phthalocyanines and δ-lactone were synthesized. The films were formed by electrodeposition and evaporation techniques on highly oriented pyrolytic graphite, 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. From AFM measurements, it was found that the evaporated films exhibited a more regular distribution with higher roughness values than the electrodeposited films. Although the deposited material is amorphous in nature, it is formed by the same chemical units as the synthesized powder: neither the low-pressure evaporation process nor the electrodeposition process lead to chemical decomposition of the synthesized material. The morphology of the deposited films is further investigated by X-ray energy-dispersive (EDS) analysis of these films, which shows the presence of metallic and other characteristic atoms of the phthalocyanine thin films. All the films are in the range of electrical conductivity values typical for molecular semiconductors (10⁻⁶ – 10¹ S cm⁻¹). From the electric current values, it is found that all the molecular thin films show a semiconductor-like behavior. The results obtained indicate that the metal at the macrocycle is the factor determining the electrical conductivity of a material; the order of the conductivity depends on the capability of the metallic macrocycle to allow the flux of electric current through itself. The thin film with greatest roughness was the one made of C₂₆H₁₂N₁₀OSGa, which also showed less electric conductivity than the others, while the thin film of C₂₆H₁₂N₁₀OSNi was the one that had the highest electric conductivity and lowest roughness. The type of deposited material and its roughness is very important for electrical conduction; the best results were obtained with electrodeposited thin films, where conductivity was larger by various magnitude orders.

These new molecular materials represent a new class of organometallic materials for diverse applications. New concepts for photoactive and electroactive molecular materials have recently been developed, which include conducting, photochromatic and amorphous molecular materials for their use in electronics, optoelectronics and photonic devices. Amorphous materials have found use in OLED applications. Furthermore, photochromatic molecular materials have a potential use in image formation and molecular memories. Molecular amorphous resistances may be promising candidates for future nanolithography, as they are featured by the absence of grain boundaries in amorphous materials, leading to a uniform contact between the metal/organic electrode and the organic layers.

Acknowledgements. The authors wish to thank the technical assistance of Abel Moreno (IQ-UNAM). One of the authors (M.E. Sánchez-Vergara) gratefully acknowledges the financial support of the SEP-CONACYT-México, under project number 153751.

References


