# STUDY OF METALLIC-PHTHALOCYANINES BY TRANSMISSION ELECTRON MICROSCOPY AND ATOMIC FORCE MICROSCOPY

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## Abstract

In the present work, powder and thin films of Metallic-Phthalocyanines (FePc, CoPc, and PbPc) have been characterized by transmission electron microscopy (TEM), X-ray diffraction (XRD), and atomic force microscopy (AFM). XRD and selected area electron diffraction (SAED) patterns were used to determine the crystalline structures of the phases in powder samples. The crystalline phases in the metallic-phthalocyanines correspond to β-monoclinic type. The samples have been obtained in powders by organic syntheses and subsequently, the powders have been deposited onto silicon (100) substrates by thermal evaporation in a vacuum chamber to obtain the thin films. The surface topography of the films has been characterized by AFM. Needle-like and granular features randomly oriented in the films are visible.

## Resumen

En este trabajo se han caracterizado ftalocianinas metálicas (FePc, CoPc, and PbPc) obtenidas en polvo y películas delgadas. Tal caracterización se ha llevado a cabo por microscopía electrónica de transmisión (TEM), difracción de rayos X (XRD) y microscopía de fuerza atómica (AFM). Además de la XRD, se ha empleado difracción de área selecta (SAED) para determinar las fases cristalinas presentes en las muestras en polvos. Las fases cristalinas de las ftalocianinas metálicas corresponden al politipo β-monoclínico. Las muestras se han obtenido en polvo por una síntesis orgánica y posteriormente estos polvos han sido evaporados térmicamente en una cámara de vacío y depositados en películas delgadas sobre sustratos de silicio (100). La topografía de las películas depositadas se ha estudiado por medio de AFM. Dicha topología muestra una superficie de agujas y granulares orientadas de forma aleatoria.

**Keywords**: Organic Semiconductors, Electron Diffraction, X ray Diffraction, Atomic Force Microscopy

## Introduction

Metallophthalocyanines (MPcs) are a kind of organic conducting polymers based on macrocyclic metal complexes, which have attracted wide attention due to their multitude of applications in material science. More than 70 elements have been used as the central metal atom in the phtalocyanine that controls the oxidation potential, which lead to very different electrical and optical properties. The high chemical and thermal stability as well as the interesting optical properties of phthalocyanines and their derivates give rise to various applications in the field of electronic and optical devices [1].

It is known that most of the MPcs macrocyclic rings are practically planar. The centrosymmetric planar molecule and the central metal atom of the MPcs produce a crystalline series of macrocyclic organic with an extraordinary stability. The low symmetry of MPcs is the principal cause of pronounced anisotropy of the lattice, which is a characteristic feature of many organic crystals [2]. This lattice's anisotropy is one of the most important reasons for the changes in optical, electrical, magnetic, mechanical and other physical properties of the crystal. MPcs commonly exist in at least two different crystalline phases, α and β forms [3-4]. It was reported that the β-form is a monoclinic crystal belonging to the p21/a space group and that there are two MPcs molecules per unit cell [5].

In order to determine the crystalline structures of MPcs electron, X-ray, and neutron diffractions have been applied [6-8]. Moreover, direct methods were used to electron diffraction data in order to examine the atomic structure and bonding of metastable α-Cu phthalocyanine crystals [9]. The first test of direct methods to n-beam dynamical electron diffraction data was published [10].

Polymorphism is a common phenomenon in molecular crystals and the existence of polymorphs of MPcs has been investigated [11]. The growth of thin films of MPcs is a difficult process. Generally the metastable polymorphs can be obtained in thin films under rapid growth conditions where the product consists of very small crystals. Thermal evaporation is the most optimized technique in order to obtain MPcs in thin films [12-13].

The aim of this work has been the structural characterization in powder Iron, Cobalt and Lead phthalocyanines by XRD and TEM techniques, and their subsequent study by AFM of the topography of these powder MPcs deposited onto silicon substrates by thermal evaporation.

## Experimental procedure

The phthalocyanine molecule and the Iron, Cobalt and Lead metals are the precursors in the synthesis of the MPcs. This MPcs have been obtained in powder form. More details about the syntheses and thermal evaporation, as well as their electrical and optical properties are reported in a previous work [13]. Subsequently, thin films depositions have been prepared by conventional thermal evaporation technique, deposited onto Si (100) substrates.

The phase identification of the powder samples has been carried out using XRD and SAED techniques. The XRD results have been obtained in a diffractometer of Brucker AXS D8. The XRD patterns were obtained with a step scan of 0.02º 2θ and 3 seconds per step, between 5º and 100º 2θ, at 35 kV and 30 mA, using CuKα radiation, 1.54056 Å. The experimental XRD patterns have been indexed using the international JCPDF (the Joint Committee for Powder Diffraction Files) database, searchable by the position of the X-ray diffraction peaks.

Moreover, the powder samples have been studied by in electron diffraction in TEM. The sample was crushed and deposited on a cooper grid for the analysis in a JEOL 1200 EX transmission electron microscope operated at 120 kV. The SAED patterns were obtained in a rotation-double-tilt holder and registered on standard photographic films. The electron diffraction patterns images were digitalized and calibrated for the indexing, using the electron microscopy image simulation software package (EMS) considering the MPcs crystalline phases reported by other authors [6-8]. The SAED patterns have been indexed using the EMS software package [14].

AFM was used to study the topography of the thin films deposited onto silicon substrates. For AFM measurements a Scanning Probe Microscope JEOL, JSPM–4210 has been utilized. The microscope was operated under ambient pressure conditions, in tapping mode, with a resonant frequency in the range 120 – 190 kHz and ultra–sharp silicon cantilevers NSC 12. Additionally, XRD has been used in the thin films in order to study crystalline phases and their possible transformations in the evaporation process of the powder samples.

## Results and discussion

The XRD results show a good agreement with the β crystalline phases of MPcs; the positions of the X-ray diffraction peaks are indexed with the international JCPDF database. The experimental XRD results for powder MPcs samples are shown in Fig. 1.

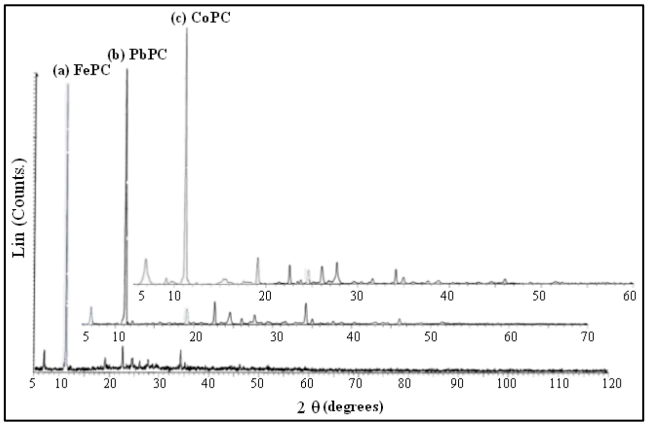

Fig.1. X-ray diffraction patterns of powder MPcs:
(a) FePc, (b) PbPc, and (f) CoPc.

In the powder samples, SAED patterns have been obtained in different zone axes. The α and β crystalline phases were introduced to EMS software. The lattice parameters and space group of these crystalline phases introduced to EMS software have been the same of the database used in XRD analysis; the atomic positions were generated with the RPS code.

The solutions for the indexed SAED patterns in all samples correspond to β crystalline phases. The experimental SAED patterns for β-FePc, β-PbPc, and β-CoPc are shown in Fig. 2a, 2b and 2c, respectively, as well as their corresponding $g_1$ and $g_2$ reflections. Both, XRD and SAED patterns are in agreement with the crystalline structures used in the simulation for their determination.

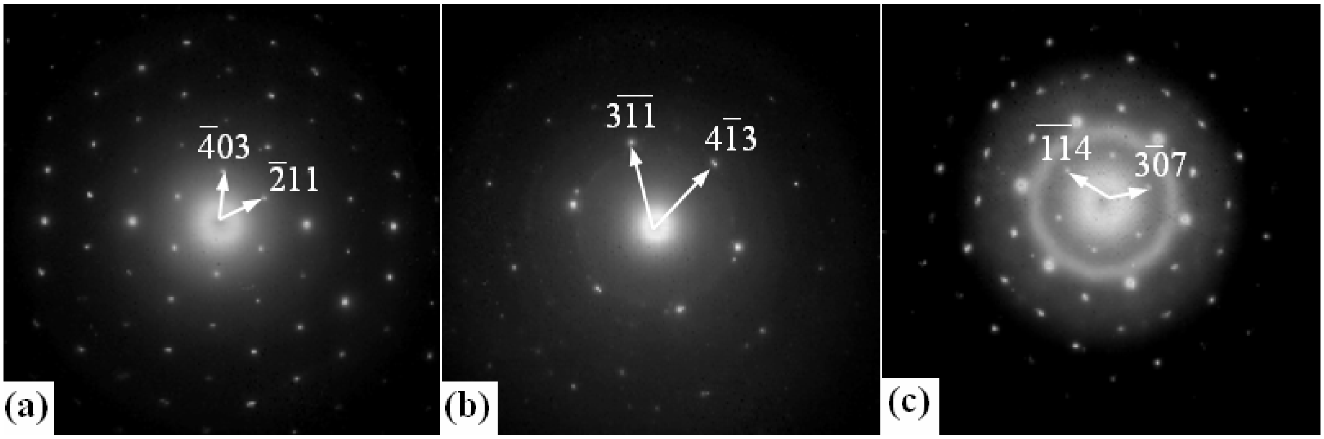

Fig. 2. Selected area electron diffraction patterns of (a) β-FePc, (b) β-PbPc, and (c) β-CoPc.

The study of the topography by AFM in the thin films shows elongated and small structures. The huge feature size difference corresponds to nucleation sites. The range of the surface roughness oscillates between 145 and 580 nm all in a 2.5 x 2.5 µm area. 3D-AFM images of the thin films grown on silicon substrates are shown in the Fig. 3. At higher resolution, the surface topography of the FePc (Fig. 3a) is characterized by needle-like features randomly oriented in the film plane, with a length of up to several 100 nm.

Granular features for the PbPc and CoPc thin film samples are observed (Fig. 3b and 3c). Needle-like and granular features are related to the inherently strong anisotropy of the MPcs crystallites in structure and shape [2].

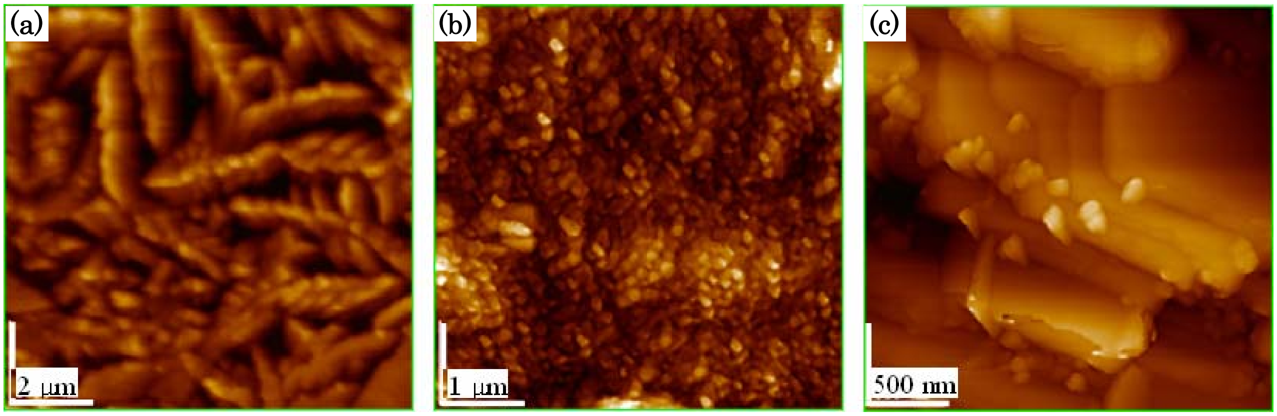

Fig. 3. AFM micrographs for thin film samples deposited onto silicon substrates: (a) FePc/Si, (b) PbPc/Si, and (c) CoPc/Si.

## Conclusion

Electron and X- ray diffraction patterns obtained for powder and thin films of thermally evaporated Fe, Pb, and Co – phthalocyanines show that the stable monoclinic β-phases exist in all specimens.

Electron diffraction shows a good agreement with the X-ray diffraction patterns for powder specimens. The topography of the surface for thin samples is characterized by AFM. Needle-like and granular features randomly oriented in the film plane are visible.

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