Microscopy Studies of Metallophthalocyanine Thin-Film Morphology

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Semiconductor thin film deposition of MPcs (M = Al, Ga, Si, Pb) was carried out by vacuum thermal evaporation onto Corning 7059 glass slices, quartz and (100) single-crystalline silicon (c-Si), 200Ω-cm wafers. Nanocrystals of α and β phases, which have also been found in relatively thick (>100 nm diameter) wires. The difference between these two phases is the angle formed between the symmetry axis and the stacking direction. Alpha crystals have angles strongly depend on the degree of molecular organization. Phthalocyanine thin films are frequently made by a vacuum evaporation technique that produces highly pure films without decomposition [4]. MPc thin films frequently have a crystalline or amorphous structure that depends mainly on the molecular self-stacking capability of the derivative, but also on the thin-film fabrication process [5].

1. Introduction

The use of polymers and small organic molecules in the fabrication of organic light emitting devices (OLEDs) has generated considerable interest in the electroluminescence and photoluminescence properties of these materials and their films [1]. Of particular relevance is the interplay between optical properties, electronic structure, and morphology of OLED materials [1]. A typical OLED comprises a sandwich of an electron transport layer and a hole transport layer between two electrodes. Metallophthalocyanines (MPcs) are a prominent class of organic molecules with many optical and optoelectronic applications which can be taken advantage of in the production of inexpensive, high-quality organoelectronic devices, such as OLEDs [2].

MPcs and their complexes absorb light on either side of the blue-green region in the visible spectrum [3]. In recent years, there has been an increased interest in extending the absorption band of MPcs into the near-infrared region of the spectrum [4]. The UV-VIS spectra from MPcs originate from the molecular orbital within the aromatic 18-π electron system overlapping on central metallic ions. The most essential characteristic of the MPcs is the double chain and two-band structure: a metal d-chain and 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 [5]. MPcs exhibit high chemical and thermal stability, are highly polarizable and can be easily sublimated to get pure thin films without decomposition [4]. MPc thin films frequently have a crystalline or amorphous structure that depends mainly on the molecular self-stacking capability of the derivative, but also on the thin-film fabrication process [6]. The control of the film structure is of great importance in thin-film technology because the main optoelectronic properties, including the photogeneration of charge carriers, strongly depend on the degree of molecular organization [6]. Phthalocyanine thin films are frequently made by a vacuum evaporation technique that produces highly pure films without decomposition [7]. Typical thin films exist as either α- or β-phases, which have also been found in relatively thick (>100 nm diameter) wires. The difference between these two phases is the angle formed between the symmetry axis and the stacking direction. Alpha crystals have angles of 26.5°, while beta crystals involve angles of 45.8° (see Figure 1 for CuPc). In thin-film crystals, there are significant molecular interactions leading to dramatic changes in their optical properties and complicating their study [2]. The stabilities of these films are strongly influenced by the growth parameters and post-deposition treatments, such as annealing [8]. Material deposited at room temperature crystallizes in the α-phase, but this can be converted into one of the other forms by post-annealing or by depositing at a higher substrate temperature [9]. Deposition at high substrate temperatures usually causes the formation of the more stable β-phase material [7,9]. The absorption spectra of different polymorphs of some phthalocyanine compounds show significant differences among each other [7]. Hence, it is worthwhile to examine the effect of annealing treatment on the structural, electrical and optical properties of these thin films.
A simple method has been developed to synthesize molecular semiconductors from the chemical reaction of MPc followed by thermal evaporation. New thin films have been produced by thermal evaporation. Film characterization was performed through Fourier-transform infrared (FT-IR) spectroscopy, scanning electron microscopy (SEM), transmission electron microscopy (HRTEM) and atomic force microscopy (AFM). All the samples were annealed at a temperature 473 K for two hours in air. In this communication, we report the determination of important optical parameters related to the principal optical transitions in the UV-Vis region. Optical band gap calculations are presented as well.

2. Experimental

All the reagents employed were acquired from commercial sources. The reagents were used without previous purification. Thin film deposition of compounds was carried out by vacuum thermal evaporation (Figure 2) onto Corning 7059 glass slices, quartz and (100) monocrystalline silicon (c-Si) 200 Ω-cm wafers. In order to achieve a high purity for these thin films, a vacuum chamber was used with a diffusion pump and a special tantalum crucible with a double-grid cover. Quartz fiber was added inside the crucible to avoid the ejection of grains towards the substrate at a temperature of 298 K. The Corning 7059 glass slices and quartz substrates were ultrasonically degreased in warm methanol and dried under a nitrogen atmosphere. The silicon substrates were chemically etched with a p-etch solution (10 ml HF, 15 ml HNO₃ and 300 ml H₂O) in order to remove the native oxide from the c-Si surface. The evaporation temperature in the boat was 453 K, which is lower than the decomposition temperature of the materials synthesized for this study. This value was measured by means of a chromel-alumel K-type thermocouple. The pressure in the vacuum chamber before the film deposition (1x10⁻⁶ Torr) and the evaporation rate (70 Å/s) were the same in all cases. The thicknesses were monitored throughout the deposition processes using a quartz crystal monitor. In spite of these similarities, significant differences in the thicknesses of the deposited films were detected, which may be related to differences in the sublimation rates of the compounds employed. All the samples were annealed at a temperature 473 K.
for two hours in air. FT-IR measurements were obtained with a Nicolet iS5-FT spectrophotometer using silicon flakes as substrate for the thin films. For SEM, a Leica Cambridge scanning electron microscope (model Stereoscan 440) was coupled to a microanalysis system and operated at a voltage of 20 kV and a focal distance of 25 mm. HRTEM was performed at 200kV with a JEOL-2010FEG TEM, fitted with an energy-dispersive, X-ray spectrometer (Noran, Voyager 4.2.3). Topography and roughness of surfaces were analyzed by atomic force microscopy (AFM), using an Autoprobe CP Thermomicroscopes model in Tapping mode. For the SEM and AFM characterization of the films, quartz and Corning glass substrates were used, respectively. Ultraviolet-visible spectroscopy was carried out in a Unicam spectrophotometer, model UV300, with a quartz substrate.

3. Results and Discussion

FTIR spectroscopic measurements on thin films were made to determine if there were significant changes in the raw materials after thermal evaporation. Table 1 shows the IR band spectra for the newly synthesized compounds in their different forms (powder and film). The IR spectra show that thin films have the same absorption bands as the powder used for evaporation. The slight shifts observed may be due to internal stress produced by the evaporation process. These results suggest that thermal evaporation is a molecular process that does not change the relative chemical composition of the synthesized compounds. The deposited films are formed by the same macro-ions as those of the original synthesized powder. Table 1 shows the signals corresponding to macrocycle [10]: two bands appearing at about 3048 and 2854 cm\(^{-1}\) are assigned to CH (symmetric stretching vibrations in the ring and asymmetric stretching vibrations in the alkyl). From the IR spectra, all the highly-relevant bonds, the vibrations of C=C and C=N bonds, and the aromatic C-H bonds, could be located for the MPcs (M= Al, Ga, Si, Pb). The band appearing around 1610 cm\(^{-1}\) was assigned to the C-C stretching vibration for pyrrole. The peaks responsible for carbon/nitrogen stretching and bending occur at 1588 and 1339 cm\(^{-1}\). The peaks located at 1165 and 1114 cm\(^{-1}\) result from the interaction of carbon with the peripheral-ring hydrogen atoms [11]. The peaks in the 800-700 cm\(^{-1}\) interval very likely arise from vibrations in the benzene ring interacting with the pyrrole ring. The spectral pattern in this region depends strongly upon the molecular structure of the complexes and its chemical structure for the central metal with D\(_{4h}\) molecular symmetry [10]. The main spectral features distinguishing the different crystalline forms of MPc were found to lie in the region 800-700 cm\(^{-1}\). These spectral differences are attributed to the different crystalline packings of the MPc molecules, especially those around 731 and 777 cm\(^{-1}\) for the \(\beta\)-form and those around 720 cm\(^{-1}\) for the \(\alpha\)-form [7]. It should be stressed that the signal at approximately 750 cm\(^{-1}\), found between the other two phase signals, is related to the non-planar C-H bond vibrations [11, 12]. From these studies, we are able to determine the phase and any significant chemical changes which may occur in these materials during the thermal evaporation and after annealing at 473 K for two hours. The spectra display a signature around 720 cm\(^{-1}\) which indicates the presence of the \(\alpha\)-form, which is the predominant phase for the powdered form of these MPc compounds. When this material is deposited over the substrate at 298 K and annealed at 473 K, a transition from \(\alpha\) form to \(\beta\)-form takes place. A nucleation towards the crystalline form seems to occur and, after the cooling-down, the spectrum shows bands at approximately 731 and 779 cm\(^{-1}\), which indicates continuous transformation towards the \(\beta\)-form.
Table 1  Characteristic FT-IR bands for powders and thin films (cm\(^{-1}\))

<table>
<thead>
<tr>
<th>MPc</th>
<th>(\nu) (C-H) cm(^{-1})</th>
<th>(\nu) (C-C) cm(^{-1})</th>
<th>(\nu) (C=N) cm(^{-1})</th>
<th>(\alpha)-form cm(^{-1})</th>
<th>(\beta)-form cm(^{-1})</th>
</tr>
</thead>
<tbody>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Si Thin Film</td>
<td>3050, 2852, 1630, 1612, 756</td>
<td>1612</td>
<td>1584, 1340</td>
<td>775, 734</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Si KBr pellet</td>
<td>3052, 2855, 1632, 1613, 755</td>
<td>1611</td>
<td>1585, 1339</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Pb Thin Film</td>
<td>3049, 2855, 1622, 1617, 752</td>
<td>1603</td>
<td>1587, 1336</td>
<td>778, 733</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Pb KBr pellet</td>
<td>3050, 2853, 1624, 1618, 752</td>
<td>1608</td>
<td>1584, 1339</td>
<td>721</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Ga Thin Film</td>
<td>3065, 2862, 1165, 1114, 750</td>
<td>1610</td>
<td>1588, 1339</td>
<td>777, 731</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Ga KBr pellet</td>
<td>3064, 2863, 1167, 1117, 750</td>
<td>1611</td>
<td>1584, 1338</td>
<td>720</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Al Thin Film</td>
<td>3060, 2843, 1169, 1120, 752</td>
<td>1609</td>
<td>1582, 1329</td>
<td>776, 730</td>
<td></td>
</tr>
<tr>
<td>C(<em>{32})H(</em>{16})N(_{8})Al KBr pellet</td>
<td>3061, 2843, 1168, 1120, 754</td>
<td>1608</td>
<td>584, 1331</td>
<td>726</td>
<td></td>
</tr>
</tbody>
</table>

The morphologies and roughness of the thin films were examined by atomic force microscopy in order to provide a large surface inspection of the micro-structural arrays. Topographical structures, porosities and film qualities are summarized in Figure 3 for MPc (M= Al, Ga, Si, Pb) films. 3D topography and phase images at 5 µm x 5µm reveal thin films spreading where the presence of granular aggregates is observed. The size and distribution of the grains, as well as the roughness, change for each MPc, although all of them show compact deposits. The GaPc and PbPc films shows a homogenous coverage with small aggregates and the calculated rms roughness values are 66 and 50 Å, respectively. On the other hand, AlPc exhibits the largest grain irregularities distributed throughout the film and its rms roughness is 116 Å. Finally, the rms roughness for SiPc is 43 Å; this material produced what seems a rather semi-planar film. The difference in the roughness values may be related to the different metal in each MPc. Although the same deposition and annealing processes were used in the preparation of all the MPc films, the metallic ion in the macrocycle center has a considerable effect on film morphology. Those materials with Si and Pb produced flatter films with lower roughness values.

Fig. 3  AFM three-dimensional images of films deposited onto Corning 7059 glass from a) AlPc, b) GaPc, c) SiPc and d) PbPc.
SEM micrographs for PbPc (Figure 4) show conglomerates of irregular shapes and sizes between 10μm and 1 μm. From the aggregates’ texture and color, a homogeneous composition is clear in both cases. At 1700x (Figure 4a), some elongated shapes can be observed within a matrix of rounded particles which become clearly visible at 7000x and 13000x (Figure 4b/c). Figure 4c shows that the material is formed by rounded grains of different sizes. Some of these particles suggest preferential orientations, but their arrangement is not periodic and some of them have rather capricious forms. Grain superposition and preferred orientations are also to be found in a few zones, implying some sort of short-range arrangement. All MPc SEM micrographs provided the same results and showed an amorphous appearance with no periodicity.

![SEM micrographs of PbPc thin film at (a) 1700x, (b) 7000x and (c) 13000x.](image)

A complementary study of the nanometric PbPcs crystals was performed with the use of transmission electron microscopy (TEM). In Figure 5, bright field images of the PbPc are shown. Figure 5a shows a dendritic appearance that can be contrasted with those in figures 5b-d. It seems that the annealing process a slow crystal nucleation occurred along preferential directions, leading to the dendritic-growth pattern. The low substrate temperature (298 K) -which contrasted with the high MPc deposition temperature (larger than 473 K)- generated a considerable thermal gradient, permitting the nucleation of a few Pc crystals at a relatively high growth rate along the dendritic pattern. Figures 5a/d show high resolution images of particles, ranging in size between 0.2 and 2 nm. The shape of the particles is irregular, although some quasi-spherical forms can be seen. A heterogeneous dispersion of the nanoparticles can be also observed. From these images, it was difficult to determine the crystalline arrangement. On the other hand, a structure is found in Figure 5c which is consistent with the SEM observation. In this figure, a conglomerate of rounded particles making one of the inter-dendritic branches can be seen. On the other hand, it is difficult to discern crystalline planes in this image, suggesting that it may belong to an amorphous structure. An EDS analysis was performed to determine the chemical composition of the MPcs. The chemical composition remained the same in all cases, in agreement with previous work made with IR spectroscopy (Table 1), so it may be concluded that, during thin-film formation, no changes in MPc composition occur. MPcs thermal stability thus permits their processing through the evaporation technique.

![HRTEM micrographs of PbPc nanoparticles.](image)
The UV-Vis optical transmission spectra results were analyzed in the strong absorption-edge region (Figure 6). Differences in the transmittance of the films under examination can be attributed to differences in film thickness and their aggregation state as observed in the AFM-micrographs (see Figure 3). Furthermore, it was observed that the positions of the transmittance bands were weakly influenced by the metallic atom of the compounds. Phthalocyanines show two typical absorption bands, namely the Q band in the visible region (600-800 nm) and the B band or Soret band in the violet or near-ultraviolet region (300-480 nm) [9]. The Q band can be attributed to the allowed highest occupied molecular orbital (HOMO)-lowest unoccupied molecular orbital (LUMO) (π-π*) transitions [13]. MPcs (M = Al, Ga, Si, Pb) have the strongest absorption peaks, occurring around the 680 nm region; the exact position of these bands depends on the particular structure and metal complexation. Metal incorporation induces a decrease in the extinction coefficient for the Q band. For peripherally substituted MPcs, the degenerate Q band shows some splitting due to the reduction in symmetry [13]. Since the ligands may increase the interfacial distance between MPc rings, the direct π-π overlap of the macrocycles does not occur and the Q-band is maintained. The presence of this absorption band may be interpreted as an overlap of π-orbitals through the ligand, where the electrons are able to transfer energy throughout the structure [14, 15]. The Soret band appears in the region between 340 and 480 nm for the thin films. The Soret band is due to electronic transitions between molecules of an intermediate ionic degree that characterize the synthesized molecular materials. The broad absorption band in the UV region is preceded by the ultraviolet absorption band edge of the phthalocyanine moiety [7]. MPc thin films absorb light on either side of the blue-green region and may be used as photoconductors.

![Fig. 6](image)

**Fig. 6** The spectral distribution of transmittance for MPc thin-films.

The absorption coefficient is defined by the Beer-Lambert law and can be calculated from the optical transmittance. Equation (1) was used to obtain the absorption coefficient (α) for each wavelength the materials were irradiated with in terms of the transmittance T and thickness τ of the sample.

\[
α = -\frac{1}{d} \ln(T) \quad (1)
\]

On the other hand, equation (2) was used to calculate the photon energy (hν) for each wavelength.

\[
E_{\text{photon}} = \frac{hc}{λ} \quad (2)
\]

In order to evaluate the nature of the transition (direct or indirect), equation (3), deduced for the domain of the fundamental absorption edge [16], was used:

\[
αhν = A(hν − E_g)^n \quad (3)
\]

In this relation, α denotes the absorption coefficient, hν the photon energy, \(E_g\) the band gap energy, \(n\) is a number characterizing the transition process and \(A\) is a characteristic parameter for respective transitions that can be assumed to
be constant within the optical frequency range [7]. For allowed direct transitions, \( n = \frac{1}{2} \), and for allowed indirect transitions, \( n = 2 \). Thus, the optical gaps for both transitions could be determined by the extrapolation to zero of the linear regions of the \((\alpha h \nu)^2 = f(h \nu)\) and \((\alpha h \nu)^{1/2} = f(h \nu)\) plots, i.e., \(E_{gD}\) and \(E_{gi}\), respectively [17]. To obtain information about direct or indirect interband transitions, the fundamental absorption edge data are analyzed within the framework of the one-electron theory of Bardeen et al. [18]. This theory has been used to analyze the absorption edge data of molecular solids, such as phthalocyanine [19]. The absorption \((\alpha \geq 10^4 \text{ cm}^{-1})\) is related to direct band transitions [20]. In amorphous semiconductors, the optical transitions are dominated, to a first approximation, by the so-called indirect transitions. [7,12,15]. Although \(\alpha\)- and \(\beta\)-phase crystals can be found in the thin films, the SEM and HRTEM results indicate a general amorphous structure. Figure 7 shows the Tauc plots [21] for indirect transitions from which the optical band gaps for each MPc are obtained. AlPc has an optical activation energy of 1.7 eV, whereas SiPc, PbPc and GaPc have optical gaps of 1.6, 1.5 and 1.3 eV, respectively. The optical energy gaps do not show any remarkable differences from the values in the as-deposited films. This may be attributed to the two polymorphs that have the same system and differ only in the tilt angle of the molecules within the columns and the mutual arrangement of the columns [7, 22-23].

4. Conclusions

Thin films of MPcs (M=Al, Ga, Si, Pb) have been prepared using the vacuum deposition technique. According to their FT-IR spectra, they are formed by the same chemical units as those of the corresponding synthesized powders. Thus, the thermal evaporation process can be, in general, considered as a molecular process. The effect of post-deposition annealing upon the optical properties has been investigated. After annealing at 473 K for two hours, no remarkable changes were observed in the parameters for the annealed samples, in comparison to the as-deposited ones. A preliminary TEM study revealed that MPc (M = Al, Ga, Si, Pb) crystals have irregular shapes and exhibit dimensions between 0.2 and 2.0 nm. The optical properties of the thin films have been characterized from spectrophotometric measurements of transmittance in the 200-1200 nm spectral range. Two absorption regions were identified as the Q and B bands. The peaks which appeared in the visible and the near-ultraviolet regions are related to the \(\pi-\pi^*\) transitions. The optical band gap \((E_g)\) of the thin films was determined from the \((\alpha h \nu)^{1/2}\) vs. \(h \nu\) plots for indirect allowed transitions. The energy gaps were estimated to be between 1.3 and 1.7 eV for the as-deposited films. On the basis of the optical band-gap values and the feasibility of preparing these compounds as thin films, it can be concluded that these materials may have a potential use in electronic device fabrication.

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References


