Structure characterizations of nanoparticles tin phthalocyanine dichloride thin films

M. M. EL-NAHASS, A. M. FARID, H. H. AMER[a], K. F. ABDEL-RAHMAN, H. A. M. ALI[*]
Faculty of Education, Ain Shams University, Roxy 11757,Cairo, Egypt
[a]National Centre for Radiation Research & Technology, Nasr City, Cairo, Egypt

Thin films of tin phthalocyanine dichloride, $SnPcCl_2$, of different thicknesses were prepared by thermal evaporation technique in a high vacuum system. The molecular structure of $SnPcCl_2$ thin films was confirmed by the analysis of (FTIR) spectra. The crystal structure of $SnPcCl_2$ was determined. Careful evaluation of X-ray data for the powder of $SnPcCl_2$ demonstrated a monoclinic unit cell with a = 20.816 Å, b = 9.487 Å, c = 14.142 Å and β = 97.9°. The film morphology was characterized by TEM and SEM. The effect of heat-treatment on the morphological characterization for $SnPcCl_2$ thin films was studied.

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1. Introduction

Phthalocyanines, Pc's, are organic molecules characterized by high symmetry, planarity and electron delocalization. Besides, Pc's can be easily sublimated in high vacuum system 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 [1]. Phthalocyanines are one of the promising compounds due to the possibility of application in electro-optic devices, photoconducting agents, photovoltaic cell elements, non-linear optics, electro-catalysis and other photoelectronic devices [2].

The structure, morphology, electronic and optical properties of the films are crucial for their technological applications. Molecular orientation of Pc's on various substrates such as conducting polymer, glass, quartz glass, silicon, gold, etc. has been studied for the thin films deposited under various experimental conditions. Such studies have indicated that the orientation of the film grains depends on the substrate, the deposition technique, heat-treatment temperature and the conditions of substrates during film depiction [3]. Recently, a variety of techniques with high sensitivity have been used for the characterization of organic thin films.

In the present paper, the structure and the surface morphology of tin phthalocyanine dichloride, $SnPcCl_2$, thin films were investigated by using X-ray diffraction, XRD, and scanning electron microscope, SEM the crystallographic structure of $SnPcCl_2$ thin films were studied by means of transmission electron microscope, TEM, and electron diffraction. Fourier transformation infrared, FTIR, measurements were used to check the chemical and thermal stabilities of the material under study. The effect of heat-treatment on the morphological characterization for $SnPcCl_2$ was also studied.

2. Experimental

The chemical structure of $SnPcCl_2$ is shown in Fig. 1. Its molecular formula is $C_{32}H_{16}N_8SnCl_2$. The molecular structure of $SnPcCl_2$ has a centrosymmetric molecule stantially "crumpled" apparently owing to an oversize tin atom.

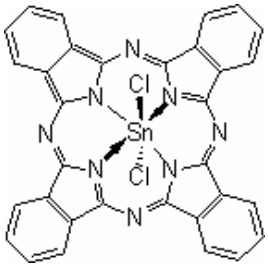


Fig. 1. Molecular structure for $SnPcCl_2$.

Their model shows that the molecule is curled like two half saucers centrosymmetrically related [4]. The material used was obtained from ACROS organic company, USA, with purity of 98.85% and no further purification process was performed. Slide glass was used as a substrate. After cleaning each substrate with distilled water and isopropyl alcohol, substrates were dried in a flow of dry nitrogen gas. $SnPcCl_2$ thin films were thermally evaporated using a high vacuum coating unit (Edward, E306 A). The evaporation was carried out by sublimation of the $SnPcCl_2$ powder from a quartz crucible source heated by a tungsten coil in a vacuum of 10^{-4} Pa. The deposition rate was controlled at 2.5 nms^{-1}, using a quartz crystal thickness monitor (FTM4, Edwards). The film thickness was determined using the same thickness monitor and also measured interferomtry after deposition

by Tolansky's technique [5]. Infrared spectroscopy of $SnPcCl_2$was performed using Bruker, Vector 22 infrared spectrophotometer in the range from 400 to 2000 cm^{-1}. For this study, 1 mg of $SnPcCl_2$ powder was mixed with vacuum dried IR-grad KBr and then deposited onto KBr optically flat substrate kept at room temperature. X-ray diffraction patterns of $SnPcCl_2$ thin films were detected in 2θ° angle range from 4° to 60° using Philips X-ray diffractometer (model X′ pert). With monochromatic CuK_α radiation of wavelength λ = 0.154056 nm, operated at 40 kV and 25 mA. The internal microstructure of $SnPcCl_2$ thin films was studied with a transmission electron microscope, type JEOL JEM-1230. Diffraction patterns of $SnPcCl_2$ thin films were obtained by the same apparatus. For morphology characteristics, a scanning microscope, type JEOL JXA-840 electron probe micro-analyzer was used for recording the scanning electron micrograph images of the $SnPcCl_2$ thin films. In order to study the effect of heat-treatment on the structure characterization of $SnPcCl_2$ thin films, some samples of $SnPcCl_2$ thin films were heated at 523 K for 2h and others were heated at 623 K for 2h.

3. Results and discussion

3.1 Infrared spectroscopy

Fourier transformation infrared (FTIR) absorption spectroscopy is used for providing information on absorbed species and for the assignment of vibrational wave numbers in the large molecular systems as metal phthalocyanines [6,7]. Fig. 2 shows the IR spectra of the powder, the as-deposited film and the annealed film of $SnPcCl_2$ at 623 K. It is clear from the figure that the $SnPcCl_2$ compound has thermal and chemical stability by either thermal evaporation or by annealing process. A summary of the main absorption frequencies for the powder, as-deposited film and annealed film of $SnPcCl_2$ is given in Table 1.

The 700 – 800 cm^{-1} region is particularly sensitive for differentiating between the polymorphs of phthalocyanines. The C-H wagging band, which appeared at 721.247 cm^{-1} in the powder of $SnPcCl_2$ and at 719.318 cm^{-1} in the as-deposited thin film of $SnPcCl_2$, is shifted to 723.175 cm^{-1} in the annealed film. This result indicates that the powder and thin film of $SnPcCl_2$ have α-polymorph. It was reported that the α-form of MPc can be characterized by a band around 720 cm^{-1}.

Moskalev and Kirin [8] found an intense band 1006-1008 cm^{-1} and Stymne et al [9] observed an NH vibration band at 1539 cm^{-1}, which are characterized for metal-free phthalocyanine, H_2Pc. In the present spectrum the absence of these bands indicates that the two hydrogen atoms were replaced by other metal as in the sample under investigation. The bands at 1605.45, 1407.78 and 1118.51 cm^{-1} are belonged to C-C benzene ring stretching vibration, while the bands at 1170.58 and 1337.39 cm^{-1} are pyrrole stretching. The band at 1287.25 cm^{-1} is associated to isoindole stretching and the band at 1455.6 cm^{-1} is associated to macro-ring stretching.

Table 1. Absorption frequencies in 500-2000 cm^{-1} infrared region for the powder, the as-deposited and the annealed thin film of $SnPcCl_2$ at 623 K.

Powder	As-deposited film	Annealed film	Assignment[7]
		1646.91	Pyrrole stretching
1605.45	1607.38		Benzene stretching
		1541.81	Pyrrole stretching
	1486.85		Isoindole stretching
1455.6	1466.6	1467.56	Macroring stretching
1407.78	1407.78	1407.78	Benzene stretching
1337.39	1338.36	1338.36	Pyrrole stretching
1287.25	1282.43	1286.29	Isoindole stretching
1170.58	1162.87	1164.79	Pyrrole stretching
1118.51	1116.58	1119.48	Benzene stretching
1082.83	1084.76	1084.76	C-H bending
1057.76	1059.69	1060.66	C-H bending
958.448			Isoindole deformation
889.023	889.023	891.916	M-N stretching
778.136	777.172	776.208	C-H wagging
747.281	747.281	749.209	Isoindole deformation
721.247	719.318	723.175	C-H wagging
	688.463		Macroring breathing
571.79	573.719		Benzene deformation
496.58	499.473		Isoindole deformation

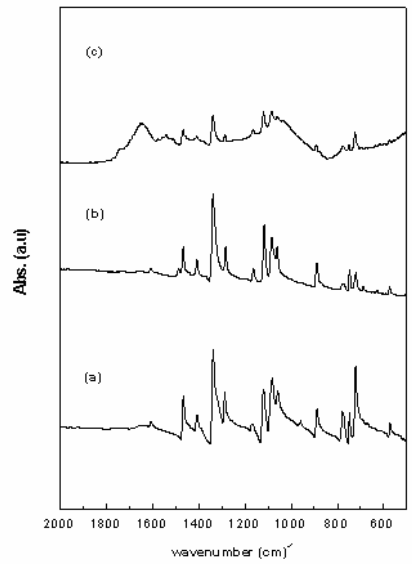


Fig. 2. The IR absorption spectra of $SnPcCl_2$ (a) powder, (b) as-deposited thin film at 303 K and (c) annealed thin film at 623 K for 2h.

One medium band at 889.023 cm^{-1} appears to be consistent with the metal ligand (M-N) vibration bands observed at frequencies in the range, 888 and 919 cm^{-1} for the Fe, Co, Ni, Cu, Zn, Pd and Pt series of phthalocyanines, indicating the extra ordinary stability of the metal phthalocyanines due to the strong bonding between the metal ion and the four surrounding nitrogen atoms in the pyrrole rings [10].

3.2-X-ray analysis of $SnPcCl_2$

The original powder material of $SnPcCl_2$ was identified by using an X-ray diffraction as shown in Fig. 3. The XRD pattern has many diffraction lines with different intensities, thus indicating that the powder of $SnPcCl_2$ is a polycrystalline material. The unit cell parameters of $SnPcCl_2$ were determined by using the CRYSFIR computer program [11]. The values of Miller indices, *hkl*, and Lattice spacing, d_{hkl}, that corresponding to each diffraction line in the XRD pattern was indexed using CHECKCELL program [11] and collected in Table 2. The analysis indicates that $SnPcCl_2$ has monoclinic structure. The calculated lattice parameters are a = 20.816 Å, b = 9.487 Å, c = 14.142 Å and β = 97.9°. The values of these parameters are in a good agreement with those reported for $SnPcCl_2$ crystals [4].

Table 2. X-ray diffraction data of the powder $SnPcCl_2$.

No.	$d_{measured}$	$d_{calculated}$	$2\theta_{measure}$	$2\theta_{calculated}$	I/I_o	*hkl*
1	10.29182	10.309	8.58450	8.57	100	200
2	7.80570	7.807	11.32652	11.325	6.87	201
3	7.13925	7.159	12.38782	12.353	0.79	111
4	6.47943	6.494	13.65503	13.624	0.53	$\bar{2}11$
5	6.02400	6.028	14.69288	14.683	6.09	211
6	5.59283	5.595	15.83261	15.826	2.48	$\bar{1}12$
7	5.38971	5.382	16.43331	16.457	2.20	$\bar{3}11$
8	5.30362	5.289	16.70196	16.749	0.81	112
9	5.18667	5.192	17.08134	17.064	5.90	$\bar{2}12$
10	4.73977	4.744	18.70572	18.691	2.75	020
11	4.48783	4.492	19.76609	19.749	10.01	$\bar{2}03$
12	4.19615	4.189	21.15532	21.19	3.65	013
13	3.93284	3.928	22.58976	22.621	1.86	022
14	3.80580	3.805	23.35427	23.362	0.88	122
15	3.63687	3.637	24.45542	24.455	1.23	303
16	3.44917	3.449	25.80861	25.81	4.40	$\bar{6}01$
17	3.32671	3.326	26.77603	26.782	1.14	$\bar{5}03$
18	3.26567	3.268	27.28604	27.268	12.25	$\bar{6}02$
19	3.10758	3.107	28.70314	28.708	7.33	$\bar{5}21$
20	3.04972	3.037	29.25981	29.382	1.14	131
21	2.94211	2.945	30.35525	30.32	1.11	700
22	2.81336	2.813	31.78033	31.784	1.33	710
23	2.71158	2.71	33.00663	33.02	1.48	$\bar{1}15$
24	2.62751	2.623	34.09447	34.157	1.31	$\bar{1}33$
25	2.53567	2.534	35.36933	35.389	2.27	$\bar{8}02$
26	2.42747	2.428	37.00161	36.998	2.78	$\bar{5}32$
27	2.28417	2.285	39.41575	39.402	1.23	106

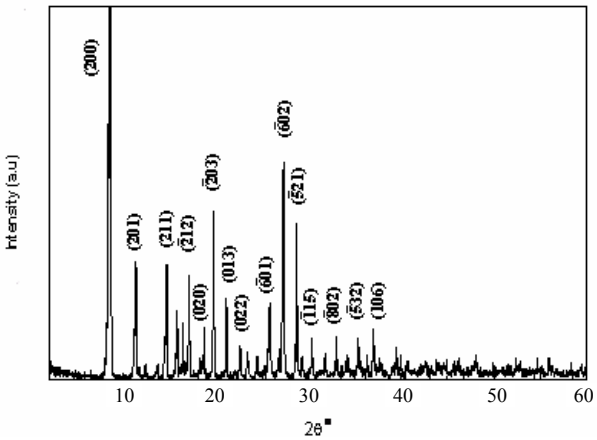


Fig. 3. XRD pattern for $SnPcCl_2$ powder.

Fig. 4 shows X-ray diffraction patterns for $SnPcCl_2$ thin films of different thickness, ranged from 70-615 nm. The presence of hump in the films emphasizes the as amorphous nature of $SnPcCl_2$ films. Several diffraction peaks appeared with the increase of the film thickness. This behaviour indicates that the crystallinity degree was improved with the increase of the film thickness. For the $SnPcCl_2$ thin film of thickness 615 nm, the dominant diffraction peak appeared at 2θ° = 26.57°, corresponding to $(\bar{5}03)$ plane of $SnPcCl_2$.

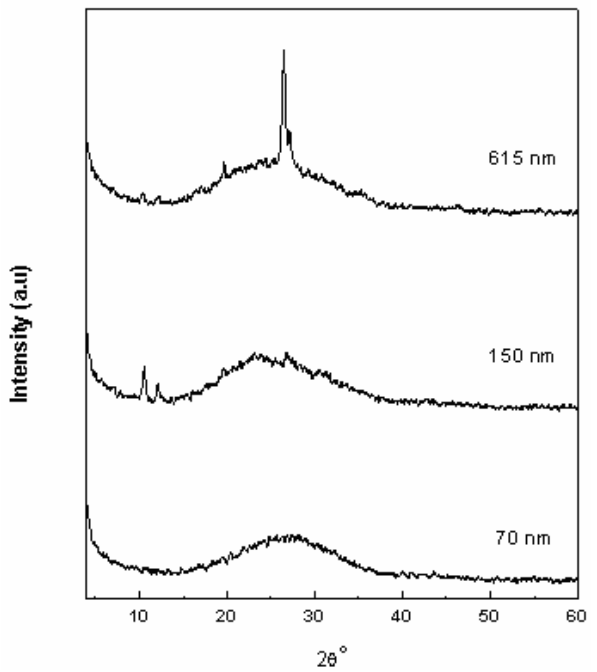


Fig. 4. XRD pattern for $SnPcCl_2$ thin films of different thickness.

Fig. 5 shows X-ray diffraction patterns for $SnPcCl_2$ thin film of thickness 615 nm which annealed at 523 K for 2h. The ($\bar{5}03$) plane is found to be the preferred orientation for annealed film of thickness 615 nm.

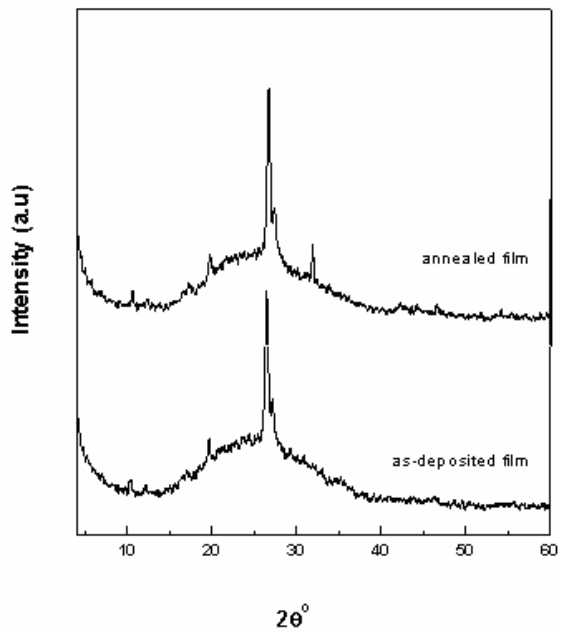


Fig. 5. XRD pattern for $SnPcCl_2$ thin film of thickness 615 nm (as-deposited at 303 K and annealed at 523 K for 2h).

The mean crystallite size, L, was estimated by using the Scherrer's expression [13]:

$$L = \frac{K_s \lambda}{\beta' \cos \theta} \quad (1)$$

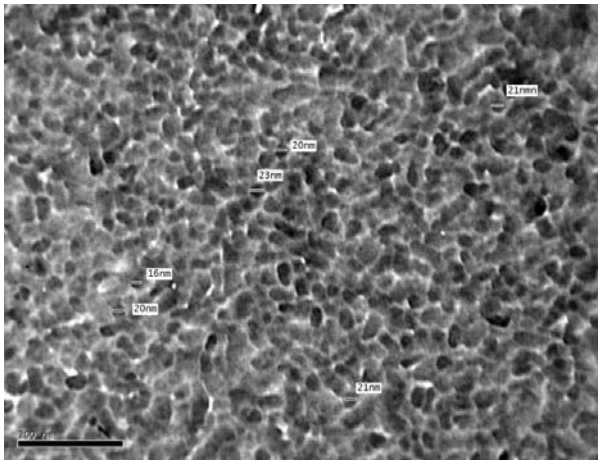
$$\beta' = \sqrt{(\beta_f)^2 - (\beta_p)^2} \quad (2)$$

where K_S is the Scherrer's constant and is of the order of unity ≈ 0.9 [14], λ is the X-ray wavelength of CuKα (1.54056 Å), β_f and β_p are the width of the strong peak at half maximum intensity for the thin film and the powder, respectively) and θ is the corresponding Bragg's angle.

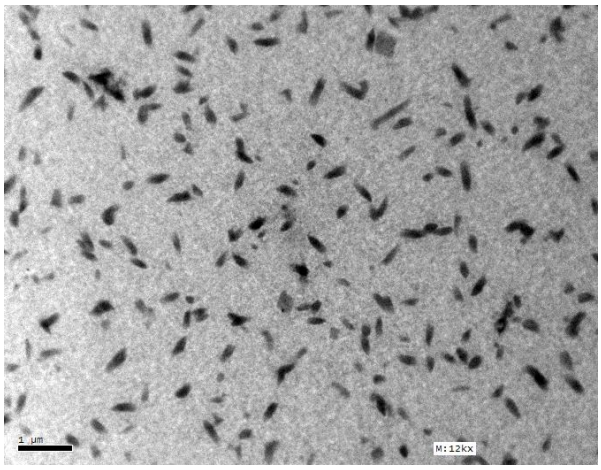
The values of L are calculated for the as-deposited and annealed $SnPcCl_2$ film of thickness 615 nm which was found to be 53.21 nm and 55.63 nm, respectively. The observed values of L are found to be in a good agreement with those calculated for other phthalocyanines such as; CuPc [15], H_2Pc [16] and MgPc [17].

3.3. Electron microscope investigations

Fig. 6(a) shows the microstructure for the as-deposited $SnPcCl_2$ film of thickness 70 nm using transmission electron microscope (TEM) technique. As observed from the figure, the film was made of homogeneous small round nanoparticles with an average size of 20 nm. The film was exposed to heat-treatment process. The $SnPcCl_2$ film was annealed at 523 K for 2h. TEM of the annealed film is shown in Fig. 6 (b). The annealing condition led to distinct growth in the nanoparticles of $SnPcCl_2$ film. Its average size was being about of 100 nm after annealing with rod particles.



(a)

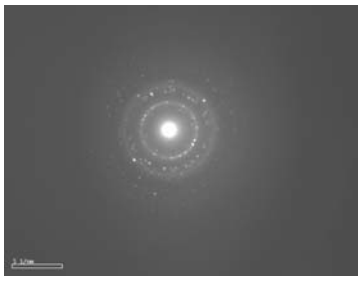


(b)

Fig. 6. TEM micrographs for $SnPcCl_2$ film of thickness 70 nm (a) as deposited at 303 K and (b) annealed at 523 K for 2h.

The electron diffraction pattern of the as-deposited $SnPcCl_2$ film of thickness 70 nm is shown in Fig. 7 (a). As shown from the figure, the pattern consists of halos that confirming the amorphous nature of $SnPcCl_2$ film. This behaviour shows a good agreement with the X-ray diffraction pattern for this film. Figure 7 (b) shows the electron diffraction pattern for the annealed $SnPcCl_2$ film at 523 K for 2h. The pattern consists of spotty rings, which have the reflection planes ($\bar{6}01$) and (106). This indicates that the heat-treatment process results in a change in the degree of crystallinity for $SnPcCl_2$ film.

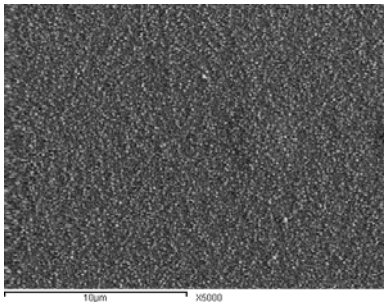
(a)



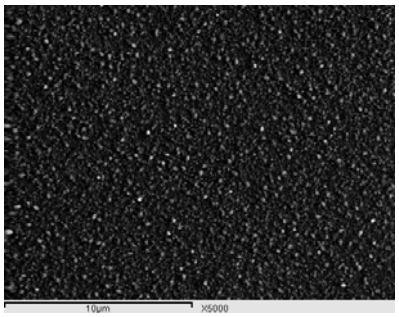
(b)

Fig. 7. DEM for $SnPcCl_2$ film of thickness 70 nm (a) as-deposited at 303 K and (b) annealed at 523 K for 2h.

Fig. 8 shows the scanning electron micrograph (SEM) of a typical film of $SnPcCl_2$ with thickness 615 nm. The image of as-deposited $SnPcCl_2$ film is shown in Fig. 8 (a), which shows clearly almost uniform distribution of some nanosized particles. The growth of $SnPcCl_2$ particles have been found after the film being annealed at 523 K for 2h as shown in Fig. 8 (b).



(a)



(b)

Fig. 8. SEM for $SnPcCl_2$ film of thickness 615 nm (a) as-deposited at 303 K and (b) annealed at 523 K for 2h.

Thus it was concluded that the growth of particles and the corresponding surface morphology depend on the temperature and annealing condition as observed for CuPc thin films [2]. This behaviour was confirmed by X-ray for the film as shown in Fig. 5, and the value of the mean crystallite size for as-deposited and annealed films.

4. Conclusions

The structural properties of tin phthalocyanine dichloride, $SnPcCl_2$, thin films have been investigated. FTIR spectral analysis confirmed that $SnPcCl_2$ is chemically and thermally stable up to 623 K. Also, the powder and thin film of $SnPcCl_2$ have α-polymorph as a crystalline nature. The XRD obtained for $SnPcCl_2$ in the powder form confirms that the material is polycrystalline with monoclinic structure. Miller indices, ***hkl***, values were calculated for each diffraction peak. The obtained XRD for $SnPcCl_2$ thin films show a preferential orientation in the $(\bar{5}03)$ plane. The heat-treatment process for $SnPcCl_2$ thin films leads to an increase in the value of mean crystallite size, L. TEM for $SnPcCl_2$ thin films indicates that the film was made of homogeneous small round nanoparticles with an average size of 20 nm. The SEM showed smooth growth morphology of $SnPcCl_2$ film which was deposited at 303 K. Also, there is an increase in the growth rate and change in the crystallinity degree and surface morphology with the annealing process.

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*Corresponding author: hend2061@yahoo.com