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Gamma radiation-induced changes on the structural and optical properties of aluminum phthalocyanine chloride thin films

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ABSTRACT

Thin films of aluminum phthalocyanine chloride (AlPcCl) were prepared by thermal evaporation technique under high vacuum at room temperature. The prepared films were divided into two groups for study; the first was the as – deposited films, the second group was irradiated in gamma cell type ^{60}Co source in air at room temperature with different absorbed doses (20–60 kGy). The surface morphology of γ-irradiated film was observed with a higher aggregation compared with as-deposited film with an average particles size of (10–28 nm). The optical parameters were obtained using spectrophotometric measurements of the transmittance and reflectance at normal incidence of light in wavelengths range of 200–2500 nm. The type of optical transition was found to be an indirect allowed transition, the band gaps decrease with increasing γ-irradiation doses. The calculated dispersion parameters of AlPcCl films decreased with increasing the γ-irradiation dose. The disagreement between the obtained values of ε_∞ and ε_L may be attributed to the lattice vibration and free carrier contribution.

1. Introduction

Organic semiconducting materials are of particular interest, since they possess a prosperous optoelectronic, electrical and processing properties for designing and fabrication of electronic devices [1]. Among these materials, a series of phthalocyanines represents a large family of heterocyclic conjugated molecules with high chemical stability. Phthalocyanines as a class of organic materials are generally thermally stable and can easily be deposited as thin films with high quality by thermal evaporation without dissociation. Metal phthalocyanines (MPc's) have gained considerable attention in recent years because they have been successfully applied in many applications such as gas sensors [2,3], solar cells [4–6] and light emitting diodes [7,8]. Optical absorption studies of MPc's thin films have attracted the researchers over the last few years [9,10]. Relatively few studies have focused on the halogenated MPc's although there is evidence that they may exhibit properties suitable for gas sensing applications [11]. It has also been shown that the halogenated Pc's exhibit remarkable morphological and thermal stability over a larger temperature range compared to unhalogenated Pc's [12].

One of the most halogenated MPc's derivatives is aluminum phthalocyanine chloride (AlPcCl), which is the focus of our study. It has a chemical formula of ($C_{32}H_{16}AlClN_8$). The present work aims to study the induced changes in the structure of (AlPcCl) thin films and estimate the related optical and dispersion parameters of these films before and after exposure to γ-radiation with different doses (20–60 kGy). Studying the optical properties like energy gap has an important role especially in the photovoltaic technology where the efficiency of the devices depends mainly on it.

2. Experimental details

The AlPcCl powder ($C_{32}H_{16}AlClN_8$) was obtained from Sigma–Aldrich Chem. Co. Thin films of AlPcCl with thicknesses 115 nm was prepared by thermal evaporation technique, using a high vacuum coating unit (Edward, E306A). Thin films were evaporated from quartz crucible source charged by AlPcCl and heated by a tungsten coil in a vacuum of 10^{-4} Pa during deposition. The films were deposited onto pre-cleaned quartz substrates maintained at room temperature and the deposition rate was controlled by using a quartz crystal thickness monitor (Edwards, FTM6). Film thickness was determined after deposition by using multiple-beam Fizeau fringes in reflection [13].

The investigated samples were irradiated in a gamma cell type ^{60}Co source in air at room temperature with different doses (20–

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60 kGy). The structural characterizations were investigated by using X-ray diffraction patterns (XRD). A Philips X-ray diffractometer (model X'Pert) was used for the measurements utilized monochromatic Cu Kα radiation operated at 40 kV and 25 mA. The diffraction patterns were recorded automatically with a scanning speed 2° min^{-1} in the 2θ range. The surface morphology of the AlPcCl thin films was studied by the scanning electron micrograph images obtained from field emission scanning electron microscope model – quanta 250 FEG (FEI-Company). Infrared spectroscopy of AlPcCl in powder and thin film forms was performed using ATI Mattson (Infinity series FTIR) infrared spectrophotometer in the spectral range 4000–400 cm^{-1}. A disk shaped from AlPcCl powder was mixed with vacuum dried grade KBr in percentage of 2:98, respectively. The FTIR measurements for thin film were come out for the films deposited on circular KBr single crystal substrate.

For optical measurements, the transmittance, T, and the reflectance, R, of films were measured at normal incidence in the spectral range 200–2500 nm using a double-beam spectrophotometer (JASCO, V-570 UV–VIS–NIR). The spectral data obtained directly from the spectrophotometer were transformed to absolute values by making a correction to eliminate the absorbance and reflectance of the substrate. The absolute values of $T(\lambda)$ and $R(\lambda)$ are given by [14]:

$$T = \left(\frac{I_{ft}}{I_q}\right)(1 - R_q) \quad (1)$$

where I_{ft} and I_q are the intensities of light passing through the film-quartz system and that passing through the reference quartz, respectively and R_q is the reflectance of the quartz substrate, and

$$R = \left(\frac{I_{fr}}{I_m}\right) R_m (1 + \lfloor 1 - R_q \rfloor^2) - T^2 R_q \quad (2)$$

where I_m is the intensity of light reflected from the reference mirror, I_{fr} is the intensity of light reflected from the sample and R_m is the mirror reflectance. The absorption coefficient, α, the absorption index, k, and the refractive index, n, can be calculated by using the following equations [14–16]:

$$\alpha = \frac{1}{d} \ln \left[\frac{(1-R)^2}{2T} + \sqrt{R^2 + \frac{(1-R)^4}{4T^2}} \right] \quad (3)$$

$$k = \frac{\alpha\lambda}{4\pi} \quad (4)$$

$$n = \left(\frac{1+R}{1-R} + \sqrt{\frac{4R}{(1-R)^2} - k^2} \right) \quad (5)$$

where α is the absorption coefficient and d is the film thickness. The experimental error in measuring the film thickness was taken as ±2%, ±1% in T and R and ±4% in the calculated values of n and k [17].

3. Results and discussion

3.1. Structural characterization

X-ray diffraction spectrum of AlPcCl in powder form is shown in Fig. 1(a), which indicates that the powder material is polycrystalline. Fig. 1(b) shows the diffractogram of as – deposited thin film of thickness 115 nm, the figure shows only two significant peaks around 2θ° = 25.19° and 31.76° and background of amorphity in the range of 15–35°, which is an indicator of nanostructure embedded in amorphous microstructure [18]. Diffraction pattern of γ-irradiated thin film, irradiated with 60 KGy is shown in Fig. 1(c); we noticed that the intensity of the two significant peaks was decreased in addition to increasing ripples. This observation suggesting that γ-irradiation results in changes in microstructure. The micrographs appeared in Fig. 2(a and b) confirmed the effect of γ-irradiation on the film topology, where the particles size

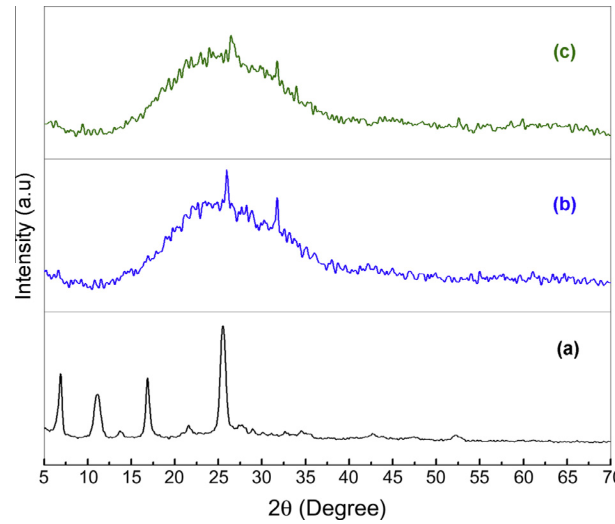

Fig. 1. The diffractograms (XRD) for AlPcCl: (a) in powder form, (b) as-deposited film, (c) γ-irradiated (60 kGy) thin film.

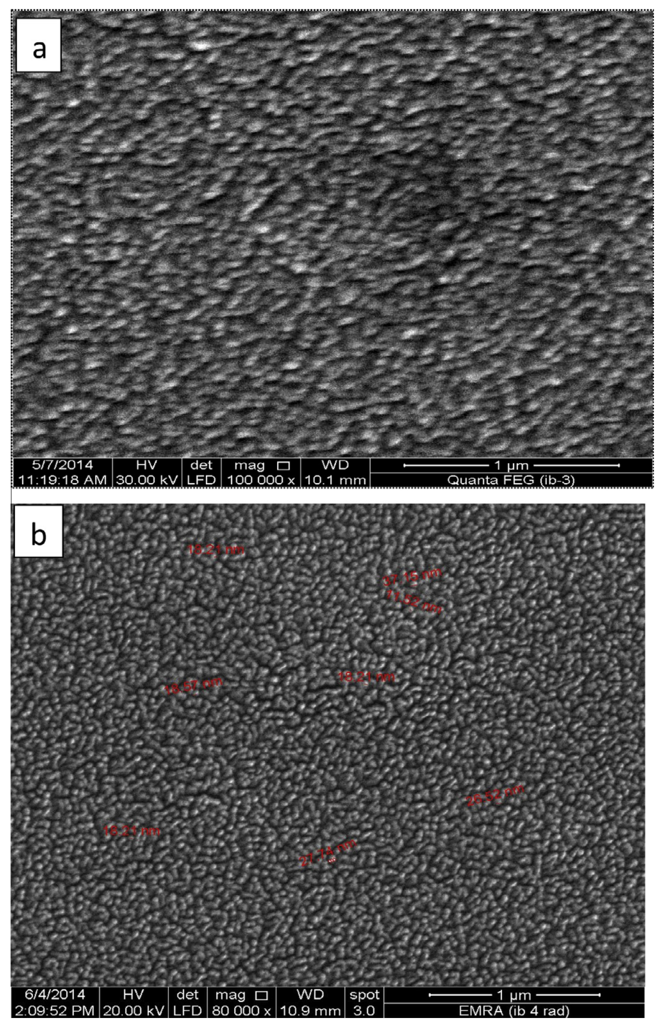

Fig. 2. FESEM images for (a) as-deposited, (b) γ-irradiated (60 kGy) AlPcCl thin films.