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Effect of thermal annealing on structural and optical properties of titanyl phthalocyanine thin films

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ABSTRACT

Thin films of titanyl phthalocyanine (TiOPc) have been deposited on both fused quartz and glass substrates by the thermal evaporation technique. The structural and optical properties of the as-deposited and annealed films have been reported. The structural features of the as-deposited and annealed films have been studied by X-ray diffraction (XRD), field-emission scanning electron microscopy (FESEM), and Fourier-transform infrared (FT-IR) technique. The optical constants (refractive index, n, and absorption index, k) of the films have been presented for the first time in the wavelength range 200–2500 nm by using spectrophotometric measurements at nearly normal incidence. The band gaps of the as-deposited film at 1.48 eV and 2.5 eV corresponding to Q-band and B or Soret band were red-shifted to 1.15 eV and 2.19 eV, respectively, when the film annealed at 433 K.

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1. Introduction

Metal-free and metallophthalocyanines (Pcs) compounds have been extensively investigated as enabling materials in various electronic and photonic devices [1]. Phthalocyanines have attracted much attention in the field of organic electronics because of their good photoelectrical properties associated with their chemical and thermal stability [2,3]. They are widely used in organic photovoltaic devices and in many modern applications such as liquid crystals, electrochromic and electroluminescent displays, gas and chemical sensors and non-linear optics [4–9].

The organic photoconductive materials comprising phthalocyanine pigments (TiOPc), which have the similar photoconductive characteristics like a-Si and bulk-heterojunction polymers, have been widely used as an electrophotographic sensitive member in the laser printer [10–12].

Although all transition metals can coordinate to Pc ligands, only a few of them (Zn, Ti, and Pd) can form highly photoactive complexes, such as titanyl phthalocyanine (TiOPc) and zinc phthalocyanine (ZnPc), owing to the closed shell nature of the electronic configuration of Ti^{4+} or Zn^{2+}, similar to that of main group metal ions. Other transition metal Pc complexes usually show very short lifetime for their S_1, T_1 state and very low fluorescence emission efficiency [13].

Titanyl phthalocyanine (TiOPc) is a typical non-planar phthalocyanine. It has five polymorphs with different preparation and treatment procedures [14]. It is one of the best

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sensitive organic photoconductors in the NIR. Its absorption spectrum, photoconductivity, and charge transport properties all depend on a variety of phases [15]. Due to its excellent photosensitivity and electrical properties, TiOPc has been used in various applications including photodetectors [16], photovoltaic cells, non-toxic organic photoconductors in electrographic, printing devices [17,18], organic thin-film transistors [19], and in CD-R optical data storage [20].

The rapid progress of new photovoltaic devices based on organic semiconductors, demands a better understanding of the structural and optical properties of these materials. Remarkable efforts have been made to choose appropriate materials with the proper optical properties in order to use them in the field of novel optoelectronic devices. Thus, the elucidation of the relation between structural and optical properties is of both scientific and technological importance. This work reports the deposition of good quality TiOPc thin films by the thermal evaporation technique and carries out experimental studies of the structural and optical properties of TiOPc thin films with the emphasis that red-shift of the band gap occurs when the thin films are annealed at 433 K.

2. Experiment

TiOPc powder (photosensitivity $C_{32}H_{16}N_8OTi$) was obtained from Sigma-Aldrich Chem. Co. and was used without further purification. Thin films of TiOPc were prepared by using a high vacuum coating unit “Edward E306A” under vacuum of 4×10^{-5} Pa. The films were deposited on fused optically flat quartz substrates for optical measurements and on glass substrates for structural characterizations. The evaporation of the material was carried out using a quartz crucible heated by a tungsten coil. The evaporation rate (2.5 nm/s) as well as the film thickness of the evaporated films were controlled by using a quartz crystal monitor FTM6. The film thickness was determined after deposition by using multiple-beam Fizeau fringes in reflection [21]. Thermal annealing was carried out in atmospheric pressure at temperature 433 K for about four hours to obtain the α-phase. Another film was annealed at 523 K for about three hours to improve the crystal quality of the film. The X-ray diffraction (XRD) patterns were recorded using Philips X-ray diffractometer model X' Pert with CuKα (1.5406 Å) radiation operated at 40 kV and 25 mA. The patterns were recorded automatically with scanning speed of 2 deg/min.

The Scanning Electron Microscope images for the as-deposited and annealed thin films were recorded using SEM Model Quanta 250 FEG (Field Emission Gun) attached with EDX Unit (Energy Dispersive X-ray Analyses), with accelerating voltage up to 30 KV, magnification14x up to 100,0000 and resolution for Gun.1n). FEI Company, Netherlands.

The chemical structure characterizations of the powder, as-deposited, and annealed films were investigated by the Fourier-transform infrared (FT-IR) technique. The IR spectra for the powder mixed with KBr and the as-deposited film onto optically flat KBr single crystal substrates were determined using a Nicolet 6700 infrared spectrophotometer in the spectral range 400–4000 cm^{-1}. The spectral resolution of the IR spectrophotometer was ±1 cm^{-1} throughout the experiment.

The optical characterizations of the deposited thin films were performed at normal incidence in the wavelength range 200–2500 nm by a double beam spectrophotometer (JASCO model 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 the transmittance T and the reflectance R are given by [22–24].

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

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

$$R=\left(\frac{I_{fr}}{I_m}\right)R_m\left(1+[1-R_q]^2\right)-T^2R_q, \tag{2}$$

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. Assuming smooth, dense and homogeneous films, the optical constants were calculated using the following equations [25, 26]:

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

$$k=\frac{\alpha\lambda}{4\pi}, \tag{4}$$

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

where α is the absorption coefficient and d is the film thickness. The experimental errors in the calculated values of n and k with accuracy better than $\pm4\%$ [27]; Taken into account, measuring the film thickness was taken as $\pm2\%$, and in T and R as $\pm1\%$.

3. Results and discussion

Fig. 1 shows the XRD patterns of TiOPc in its powder form (a), as-deposited film (b), annealed film at 433 K (c), and annealed film at 523 K (d). The powder XRD pattern illustrates many peaks with different intensities indicating that the material is polycrystalline in nature. For the as-deposited thin film, the structure is almost amorphous (Fig. 1. b). When the film was annealed at 433 K (Fig. 1 c), diffraction peak at $2\theta=7.46^\circ$ appeared. These peaks are attributed to α-phase [14,28]. Thus the annealing changed the structure from amorphous to α-phase, which is in agreement to a published work [14]. At annealing temperature of 523 K, the intensity of the peak at $2\theta=7.46^\circ$ increased further.

Fig. 2 shows the field-emission scanning electron microscope (FESEM) images of the as- deposited and annealed (at 433 K for 4 h) TiOPc thin films on glass substrates. It can be

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