Synthetic Metals 195 (2014) 110–116

Contents lists available at ScienceDirect

Synthetic Metals

journal homepage: www.elsevier.com/locate/synmet

Structural, absorption and dispersion characteristics of nanocrystalline copper tetraphenyl porphyrin thin films

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ARTICLE INFO

Article history:
Received 15 February 2014
Accepted 14 May 2014
Available online 11 June 2014

Keywords:
CuTPP thin film
Energy gap
Dispersion parameters

ABSTRACT

Thin films of tetraphenyl porphyrin (CuTPP) were prepared by thermal evaporation technique under vacuum. The surface morphology and crystalline structural characteristics of CuTPP were achieved by atomic force microscopy (AFM). The crystalline structure of CuTPP thin films was investigated by using X-ray diffraction. The average crystallite size, D, was calculated using the modified Scherrer's equation. Optical constants (refractive index, n, and absorption index, k) of CuTPP films were estimated by using spectrophotometric measurements of transmittance and reflectance in the spectral range from 200 to 2500 nm.

The optical constants of CuTPP are independent of film thickness in the thickness range 400–1270 nm. The dependence of absorption coefficient on the photon energy was determined and the analysis of the result showed that the optical transition in CuTPP films is allowed and indirect. The onset and optical energy gap for are 1.80 and 2.30 eV, respectively. The UV–vis absorption spectrum was analyzed in terms of both molecular orbital and band theories. The optical dispersion parameters of CuTPP thin films such as oscillator energy, E_o, dispersion energy, E_d, the lattice dielectric constant, ε_L, the high frequency dielectric constant, ε_∞, and the ratio of the free charge carrier concentration to the effective mass, N/m^* were investigated. Moreover, third order nonlinear susceptibility, $\chi^{(3)}$ of CuTPP films was also considered.

1. Introduction

Organic semiconducting materials are of particular interest, since they possess advantageous electrical, optical, optoelectronic and processing properties for design and fabrication of novel class of the semiconductor-based devices such as diodes, photovoltaic devices [1,2]. These materials have advantages of low cost, ease of processing, and the ability to modify their structure to obtain the desired electrical and optical characteristics when compared with conventional inorganic semiconductors [1–4].

Organic molecules that are colored contain delocalised electrons spread over a number of atoms is known as conjugated systems [5]. The π-conjugated electron system has all the essential electronic features of organic materials: light absorption and emission, charge generation and transport [6,7].

Porphyrin dyes are a class of conjugated macrocyclic compounds in which four pyrrole rings are linked to each other in cyclic fashion through meso-carbon bridges [6]. There is currently considerable concern about photoprocesses porphyrins, metalloporphyrins and related compounds due to the applicability of these molecules in playing an essential function in many biological processes; oxygen transport to photosynthesis, catalysis to pigmentation changes, laser sciences optoelectronic techniques and electronic devices [6–8].

Porphyrins and other metalloporphyrins thin films can easily be prepared by chemical or physical methods. These methods include thermal evaporation, vapor deposition, spin coating and Langmuir Blodgett (LB) deposition techniques [6,9,10].

As an extension for studying the family of porphyrin compounds by our scientific group and the little information in the literature concerning the optical characterization of CuTPP films confirms the significance of this investigation. Moreover, to the best of our knowledge there is no thorough study of its optical properties, as reported here. Therefore, the objective of this study is to investigate the structural and optical properties of thermally evaporated thin

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http://dx.doi.org/10.1016/j.synthmet.2014.05.013
0379-6779/

Table 1
AFM parameters of CuTPP film using XEI software.

Statistics value	Mean radius (nm)	Surface area (μm^2)	Volume (nm^3)	Roughness (nm)
Average	80	0.025	3.74×10^6	1.421
Standard deviation	29	0.017	2.53×10^6	0.43

films of CuTPP including the absorption and dispersion characteristics refractive over the spectral range 200–2500 nm, and check the effect of thickness on their structural, morphological and optical properties.

2. Experimental details

CuTPP was purchased from Aldrich Chem Co. and was used as received without any further purification. The different thicknesses of CuTPP thin films are prepared by conventional thermal evaporation technique, using a high vacuum coating unit (Edwards Co. model E306A, England), under a pressure of about 4×10^{-5} Torr and the rate of deposition (2.5 nm/s). The evaporation rate is controlled by quartz crystal monitor (FTM4, Edwards). The glass and quartz optical flat substrate was used for structure and optical measurements respectively.

Surface morphology of nanocrystalline CuTPP films was studied using atomic force microscope (AFM, WET-SPM-9500-J3, Shimadzu, Japan).

The crystal structure of the different thickness was investigated by using a Philips X-ray diffractometer (model X' pert) with utilized monochromatic Cu K_α radiation ($\lambda = 1.5418$ Å).

The transmission electron microscope model (TEM) JEOL JEM - 123 has been used for investigate the crystalline structure of CuTPP thin film. JASCO spectrophotometer, model V-570 UV–VIS–NIR, was used to measure the optical transmittance (T), and reflectance (R) of different thickness of CuTPP thin films in the range of wavelength 250–2500 nm.

The refractive index, n, the absorption index, k, and the absorption coefficient, α, can be calculated by using the following equation [4,8]:

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

$$k = \frac{\alpha \lambda}{4\pi} \quad (2)$$

$$n = \left(\frac{1+R}{1-R} + \sqrt{\frac{4R^2}{(1-R)^2} - k^2} \right) \quad (3)$$

3. Results and discussion

3.1. Surface morphology and crystalline structure characterization

2-D and 3-D atomic force microscope (AFM) images of CuTPP films are shown in Fig. 1(a) and (b) for studying the surface morphology and surface roughness. Accompanied XEI software was used for the data processing and analyzing of the extracted parameters such as the average values and the standard deviations of roughness and particles sizes. The average and standard deviation values of the mean radius, surface area values roughness and the particles sizes are calculated and listed in Table 1. The AFM results indicate that a nearly homogeneous deposition is obtained for films, except the upper corner of the film, under the thermal evaporation conditions. A rough characteristic for the film surface is favorable for solar cell applications because the rough surface will trap more light [11].

XRD patterns of CuTPP film onto glass substrates are shown in Fig. 2. Miller indices of the main preferred orientation peaks along (0 2 0) and (1 2 1) are matched with those published before by El-Nahass et al. [12]. The obtained patterns indicate that the CuTPP film is partially crystallized and no change on the position of the diffraction peaks. The analysis also indicates that CuTPP has the triclinic form with space group ($P-1$) and lattice constants of $a = 12.905$ Å, $b = 20.994$ Å and $c = 9.82$ Å.

Moreover, the diffracted peaks are observed to be broad at half maximum. Broadening of diffracted peaks is mainly due to lattice microstrain and smaller crystallite size. The average crystallite size, D, was calculated using the modified Scherrer's equation [13]:

$$D = \frac{K\lambda}{\sqrt{\beta_1^2 - \beta_2^2 \cos\theta}} \quad (4)$$

where λ is the X-ray wavelength, K is a constant (~0.94), β_1 and β_2 are the width at half maxima of the broadened peaks of CuTPP and a

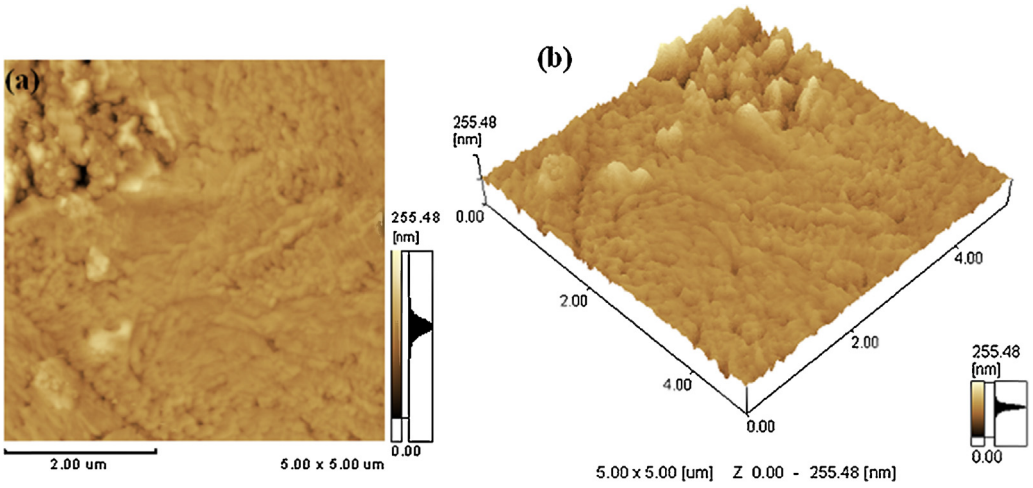

Fig. 1. AFM images of surface topography of CuTPP thin film (a) 2-D image, (b) 3-D image.