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Effect of thermal annealing on the structural and optical properties of spin coated copper phthalocyanine thin films

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ABSTRACT

Low cost sol–gel spin coating was used to deposit copper phthalocyanine (CuPc) thin films on both fused quartz and glass substrate. The prepared films were studied before and after thermal annealing at 350 °C for 1 h in air. X-ray diffraction (XRD) and field emission scanning electron microscope (FESEM) were used to study the structural properties. From the structural characterization results, the films transformed from the metastable α-phase to the stable β-phase. Refractive index, absorption coefficient, and lattice dielectric constant were evaluated before and after annealing for the first time for spin coated CuPc thin films using spectrophotometric measurements in the spectral range 200–2500 nm. The values of the direct optical band gap of the as deposited film at 1.52 eV and 2.85 eV were redshifted to 1.4 eV and 2.42 eV for the annealed film. This shift is significant for near infrared photonics. The third order nonlinear susceptibility was presented at lower photon energy for the CuPc films showing higher value for the annealed film.

1. Introduction

Recently, there is an increasing interest in the properties of organic semiconductors and their various applications in the field of optoelectronics [1–7]. Metal phthalocyanines (MPcs) are well-known organic semiconductors [8,9] and one of the most promising candidates, since these materials possess advantageous attributes such as appropriate band gap and chemical and thermal stability [10,11]. The most popular polymorphic phases of MPcs are metastable α- and stable β-forms [12,13]. Attempts have been made to use thin films of MPcs as molecular components in a number of electronic and optoelectronic devices [14–21].

Among the metal phthalocyanines, copper phthalocyanine (CuPc) has been found to have superior properties [22–25]. CuPc is a square planar molecule, which in bulk forms a number of different polymorphs with varying molecular arrangement and orientations along the stacking direction [26–28]. The change in crystalline phase and the optical property of CuPc thin films with annealing temperature has been observed [29]. CuPc is very interesting because of its potential applications in photovoltaic cells [30], photodetectors [31], field effect transistors [32], light emitting diodes [33], gas and chemical sensors [34,35], optical recording [36], organic memories [37], and optical limiting [38].

Thin films of CuPc are typically fabricated by thermal evaporation [39,40] because of their poor solubility in organic solvents. Few references have been reported the fabrication of CuPc thin films using spin coating technique [41–44]. In this article, we report the fabrication of CuPc thin films by spin coating technique. The structural and optical properties were studied for both the as deposited and annealed films. The optical properties in the spectral range 200–2500 nm were presented for the first time for the spin coated CuPc thin films.

2. Experimental details

The CuPc powder ($C_{32}H_{16}CuN_8$), diethanolamine ($NH(CH_2CH_2OH)_2$), and n-butyl alcohol (C_4H_9OH) were purchased from Strem USA, Scharlau, and British Drug Houses, respectively. All chemicals were utilized without further purification. Thin films was spin coated using spin coater, model Spin-1200D, Midas System Co.

CuPc powder of 30 mg was dissolved in 6 mL n-butyl alcohol mixed with 2.5 mL diethanolamine. The films were deposited on fused optically flat quartz substrates for optical measurements and

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glass substrates for structural characterizations. For the substrate cleaning, it was rinsed in hot acetone followed by hot isopropanol and finally it was rinsed in boiling distilled water and then was dried for 10 min to be ready for the deposition process. CuPc films were deposited from the prepared solution on the substrates by spin coating technique with spin speed 2500 rpm for 30 s. The as-coated film was heated at 225 °C for 10 min to evaporate the solvents. These procedures were repeated more than one time to get thicker film and to obtain films of different thicknesses. The thickness of the studied films was estimated from cross-sectional view of SEM and was found to be 117 nm. Annealing was carried out at temperature 350 °C for 1 h to obtain the stable β-phase.

The CuPc powder, as deposited, and annealed films were characterized by X-ray diffraction (XRD) for the structural properties using a Philips X-ray diffractometer model X′ Pert with CuK_α (1.5406 Å) radiation operated at 40 kV and 25 mA.

The field emission scanning electron microscope (FESEM) images of the as deposited and annealed CuPc thin films were recorded using scanning electron microscope (FEI, model Quanta 250 FEG) with accelerating voltage up to 30 KV and magnification up to 1,000,000 x.

The optical transmittance and reflectance spectra of the as deposited and annealed films were recorded at normal incidence in the wavelength range 200–2500 nm by a double beam spectrophotometer (JASCO model V-570 UV–Vis–NIR). The absolute values of transmittance and reflectance were calculated from the measured transmittance and reflectance [45].

3. Results and discussion

3.1. Structural characterizations

The XRD patterns of CuPc in its powder form, as deposited film, and 350 °C annealed film are shown in Fig. 1 a, b and c, respectively. The powder XRD pattern (Fig. 1a) illustrates many peaks with different intensities and positions identical to α-phase [12,46,47]. A broad hump at around $2\theta = 23°$ in Fig. 1b and c may be originated from the glass substrate on which the CuPc films were coated. The XRD pattern of the as deposited film (Fig. 1b) shows two diffraction peaks at $2\theta = 6.78°$ and 7.32° coinciding with the powder values. These peaks are corresponding to the (200) and $(0\,0\,\bar{2})$ planes of the metastable α-phase [12,48]. When the film was annealed at 350 °C (Fig. 1c), two diffraction peaks at $2\theta = 7.04°$ and 9.18° appeared, corresponding to the $(\bar{1}\,0\,1)$ and (101) planes of the stable β-phase [48,49]. This confirms the phase transformation by annealing from α-phase to β-phase.

Fig. 2 shows FESEM images of the as deposited (a) and annealed at 350 °C (b) CuPc thin films. The FESEM image of the as deposited CuPc thin film (Fig. 2a) shows a distribution of nanosized particles of estimated average size 10 nm. The FESEM image of the annealed film (Fig. 2b) show bigger particles of size ranging from 15 nm to 30 nm. There is an increase in the particle size by thermal annealing.

3.2. Optical characterizations

The transmittance $T(\lambda)$ and the reflectance $R(\lambda)$ of the as deposited and annealed CuPc thin films of thickness 117 nm are shown in Fig. 3. The spectra can be divided into two regions: (I) at wavelengths $\lambda < 1000$ nm, the total sum of $T(\lambda)$ and $R(\lambda)$ is less than unity, absorption region, implies the existence of absorption and (II) at longer wavelengths, $\lambda > 1000$ nm, the films become non-absorbing and no light is scattered or absorbed, $T + R \approx 1$.

The absorption coefficient α and the refractive index n were calculated for the as deposited and annealed films using the following equations [45]:

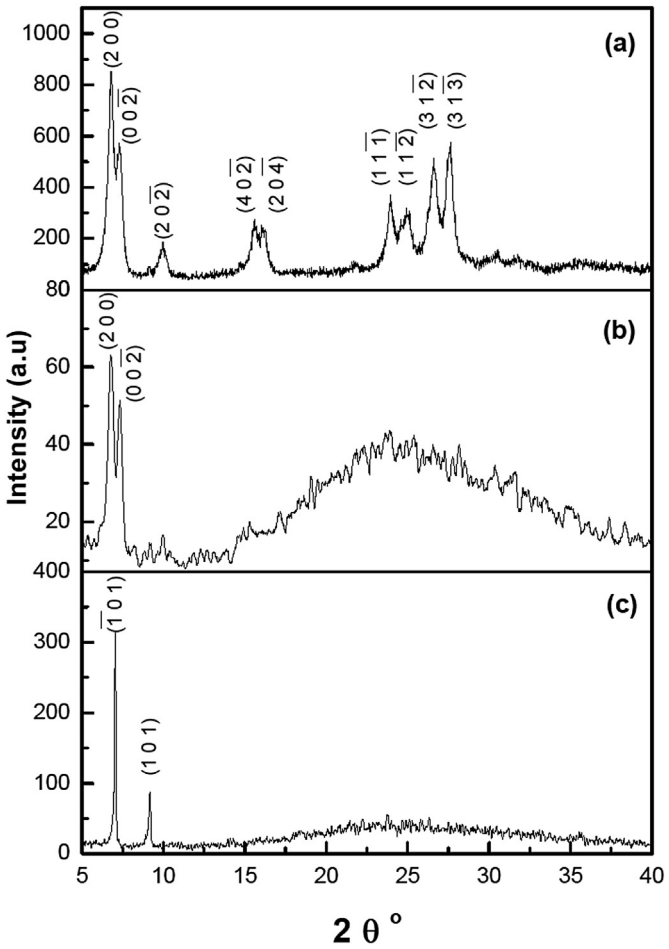

Fig. 1. XRD patterns of CuPc in its powder form (a) and for the as deposited (b) and annealed at 350 °C (c) films.

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

$$k = \frac{\alpha\lambda}{4\pi}, \tag{2}$$

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

with k known as the absorption index and d is the film thickness. Fig. 4 shows the variation of refractive index n and absorption coefficient α in the spectral region from 200 to 2500 nm for the as deposited and annealed CuPc thin films. The spectral dependence of the refractive index shows multi-oscillation peaks in the absorption region (strongly dispersive) at wavelengths $\lambda < 1000$ nm (anomalous dispersion), but changes slowly over the spectral range $\lambda > 1000$ nm (normal dispersion).

The absorption curve shows absorption bands in the near UV region with peak at 360 nm (3.44 eV) for the as deposited film and shifts to 390 nm (3.18 eV) for the annealed film (this band is known as Soret band or B-band), and in the red spectral region with peaks at 625 nm (1.98 eV) and 720 nm (1.72 eV) for the as deposited film and shift to 650 nm (1.91 eV) and 754 nm (1.64 eV) for the annealed film (the so-called Q-band). The Q-band has a doublet due to Davydov splitting [29]. The value of Davydov splitting (the energy