Optoelectric properties of amorphous Tert-Butyl substituted Zinc Naphthalocyanine thin films

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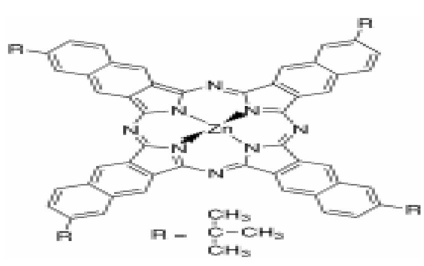
Structural analysis, Electrical conductivity and optical properties of thermally evaporated air annealed Zinc Tetra Tert-Butyl 2, 3 Naphthalocyanine (ZnTTBNc) thin films are reported in this paper. As deposited ZNTTBNc thinfilms are noncrystalline in nature while crystallinity increases with annealing temperature. Thermal activation energy and optical band gap energy at different transition levels are determined from the respective Arrhenius plots and optical absorption spectra. A deep red absorption band is present in these films and a blue shift of 60 nm is observed in the Q bands due to post deposition heat treatment.

(Received November 3, 2010; accepted November 29, 2010)

Keywords: Zinc naphthalocyanine, Thin films, semiconductor

1. Introduction

Naphthalocyanines are a class of organic semiconducting materials with proved potential in optoelectronic applications. They have long been known as infra red dyes and more recently have been investigated for use in gas sensors, molecular level electronics and optical limiters [1, 2]. For device fabrication studies of naphthalocyanines, it is necessary to study the excited state electronic properties in solid level structures or in thin film form. It makes the basic electrical studies of these materials more significant and paves the way to identify the detection of majority charge carrier concentration and distribution of Fermi level energy. More over to the best of our knowledge, there is no other previous reports on the type of conductivity and electrical properties of ZnTTBNc thin films. The addition of a central metal atom like Zinc and the tert-butyl substitution to the fourth position of Naphthalocyanine group enhances their relevance due to ease of synthesis and chemical stability [3]. Metal substitution at the centre of naphthalocyanine ring and other peripherally substituted groups determine the electrical conductivity and thermal activation energy [4]. In this paper, the influence of post deposition air annealing on the electrical conductivity, thermal activation energy and optical band gap for ZnTTBNc thin films are investigated.



Sc. 1. Structure of Zinc 2, 11, 20, 29 Tetra Tert -Butyl 2, 3 Naphthalocyanine.

2. Experimental

Zinc 2,11,20,29 Tetra Tert-Butyl 2, 3 Naphthalocyanine (ZnTTBNc-basic structure is shown in Sc.1) thin films used in the present study is prepared by thermal evaporation technique. ZnTTBNc powder imported from Sigma Aldrich (USA) is used as raw material. The material is sublimed at a pressure of 10^{-5} Torr in a Hind Hivac 12A4D vacuum coating unit. Pre cleaned glass substrates are placed vertically above at a height of 12 cm from the molybdenum boat used as the heating element. The rate of deposition is adjusted to be 1 Å/S. The thickness of the film is simultaneously checked as 300nm by a digital thickness monitor of model no. DTM-101 and the temperature inside the coating unit are set to be at room temperature (30 ^{o}C). Samples of equal thickness are annealed in air at 50 ^{o}C, 150 ^{o}C and 250 ^{o}C for one hour. Structural properties of thinfilm samples are studied from the X-ray spectrum obtained from Siemans-EQBCL015 X-ray Diffractometer (Model No. D5005). Silver electrodes are deposited on two sides of the films and thin copper strands are fixed using silver paste for ohmic contact. The electrical conductivity studies are carried out in a temperature range 50-200 ^{o}C and the resistance is noted at regular intervals of 5 ^{o}C using a programmable Keithley electrometer (model no. 617). Temperature is monitored by a chromel-alumel thermocouple fixed to the substrate. UV-visible absorption spectra of these films are recorded using a double beam spectrophotometer CARY 5000 (Version no. 109).

3. Results and discussion

Structural properties of ZnTTBNc thinfilms are analysed using X-ray analysis shown in Fig. 1. It is find that as deposited sample is noncrystalline with a hump peak and crystalline nature increases with the raise of temperature.

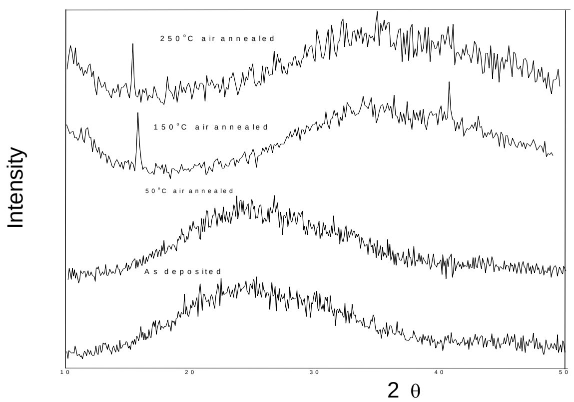


Fig. 1. XRD diagram of different ZnTTBNc thinfilms.

The thermal probe technique is used to find the type of conductivity [5]. Using this method the majority charge carriers in the ZnTTBNc thin film is found to be electrons and it belongs to n-type semiconductors. The activation energy of the films are calculated from the slope yield value of the Arrhenius plot of conductivity (Fig. 2) using the relation

$$\sigma = A\exp\left(\frac{-E_1}{kT}\right) + B\exp\left(\frac{-E_2}{kT}\right) \quad (1)$$

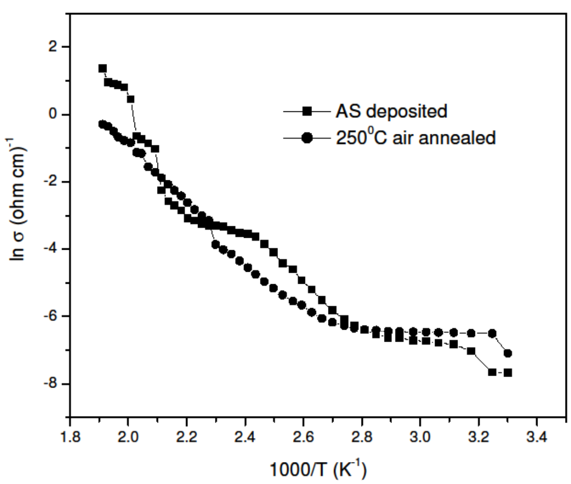


Fig. 2. Plot of lnσ vs. 1000/T for different ZnTTBNc thinfilms.

where E_1 and E_2 are the thermal activation energies in intrinsic region and corresponding to trap level impurities of the compound [6], A and B are constants, k is the Boltzmann constant and T is the absolute temperature. The resistance of the film is measured using a Keithley digital electrometer. The resistance R, length l, breadth b, and thickness t and the electrical conductivity of the film are related by

$$\sigma = \left(\frac{l}{Rbt} \right) \quad (2)$$

The activation energies E_1 and E_2 are given in Table1.

Table 1. Activation energy of ZnTTBNc thin films (t=300 nm) annealed in air at different temperatures.

Annealing Temperature	Activation energy	
	E_1±0.01(eV)	E_2±0.01 (eV)
As deposited	0.57	0.09
50°C	0.76	0.05
150 °C	0.81	0.06
250 °C	0.71	0.02

From the table, it is observed that the intrinsic activation energy E_1 increases with annealing temperature up to 150 °C. The decrease in the value of E_1 at 250 °C may be assigned to a phase change [7]. On the other hand the extrinsic level activation enthalpy E_2 is found to decrease with annealing temperature.

On analyzing the optical band gap energy, there are two levels of conduction; one in fundamental absorption level and other a trap level impurity absorption type. The optical absorption spectrum for as deposited and 250 °C air annealed ZnTTBNc are plotted in Fig. 3.

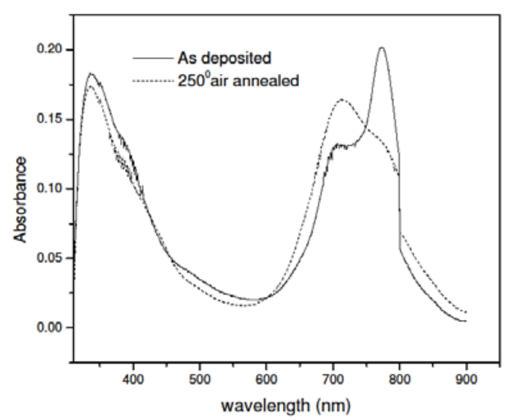


Fig. 3. Optical absorption spectra of different ZnTTBNc thin films.

There is a deep red Q band in the absorption spectrum and its intensity is found to decrease on annealing while there is a shift in maximum peak of 60 nm towards shorter wavelength side from 773 nm to 713 nm. There is no shift in B band due to air annealing. The splitting of Q band to Qx and Qy at 704 nm and 773 nm respectively is present in the as deposited ZnTTBNc thin films. The splitting decreases on annealing and is found to disappear in the maximum annealed sample with a broad single peak at 713 nm.

The optical band gap E_g can be calculated from the following relationship [8, 9]

$$\alpha = \alpha_0 \left(h\upsilon - E_g \right)^n \tag{3}$$

where n =1/2 for direct allowed transition. From the absorbance spectra, the absorption coefficient α is calculated from absorbance A and film thickness t, using the expressions [10]

$$\alpha = \frac{2.303 \times A}{t} \tag{4}$$

Graph of α^2 vs. hν is plotted and is shown in Fig. 4.

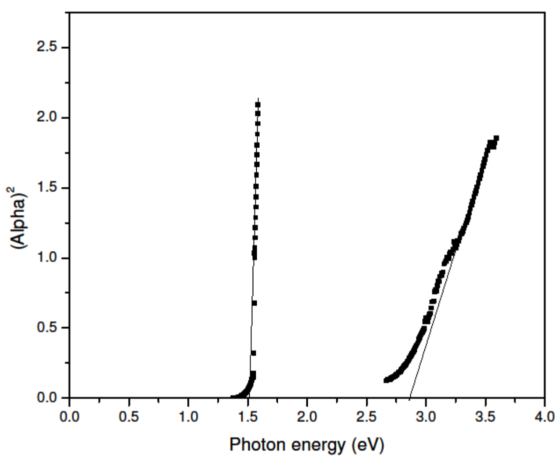


Fig. 4. Typical plot of α^2 vs. hν for as deposited ZnTTBNc thin films.

Extrapolation of the straight line region of the plot to α^2=0 determines the optical band gap. The fundamental band gap energy, E_{g1} is found to be 2.85 eV and corresponding to sublevel E_{g2} is 1.49 eV for as deposited ZnTTBNc thinfilms. Optical band gap energy for different ZnTTBNc thin films at two energy levels are listed in Table 2.

Table 2. Optical band gap energy of ZnTTBNc thin films (t=300 nm) annealed in air at different temperatures.

Annealing Temperature	Band gap energy(E_g)	
	E_{g1}±0.01(eV)	E_{g2}±0.01 (eV)
As deposited	2.85	1.49
50^{o}C	2.75	1.48
150 ^{o}C	2.56	1.48
250 ^{o}C	2.49	1.47

As the annealing temperature increases, the optical band gap energy is found to decrease from 2.85 eV to 2.49 eV. Narrowing of fundamental optical band gap due to annealing effects is observed here with the creation of sublevels at almost similar energy levels. The evidence of similar band gap levels is early reported for different phthalocyanines [10]. This is for the first time that such a lower value of optical band gap energy is observed in naphthalocyanines.

4. Conclusions

Structural, Electrical and optical properties of ZnTTBNc thin films have been studied with respect to post deposition air annealing treatment. The room temperature sample shows amorphous nature while the crystallinity increases with annealing temperature and the structure is not defined because of standard JCPDF data for such complex materials. In the thermal activation process of these films, there are two different conduction mechanisms found to involve; one in intrinsic level at high temperature region and other by active role of impurities in lower temperature region. Thermal activation energy increases up to 150 ^{o}C and thereafter there is a decrease at 250 ^{o}C which can be due to a phase change. Optical studies show deep red level absorption band and splitting of Q band which decreases with annealing temperature. Further there is a significant change in the energy band gap from 2.85 eV to 2.49 eV showing a narrowing of band gap.

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