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Rapid Communication

Low temperature effects on electrical and optical properties of TTBNc thin films

I. Dhanya [a,*], T.G. Gopinathan [b], Nisha S. Panicker [a], C.S. Menon [a]

[a] School of Pure and Applied Physics, Mahatma Gandhi University, Priyadarshini Hills, Kottayam, Kerala 686 560, India
[b] Post Graduate Department of Physics, K.E. College, Mannanam, Kottayam, Kerala, India

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ABSTRACT

Electrical and optical properties of thermally evaporated air annealed Tetra-Tert-Butyl 2,3 Naphthalocyanine (TTBNc) thin films are studied. From the Arrhenius plot, the thermal activation energy is calculated for intrinsic and extrinsic region. Different hopping conduction parameters are tabulated using the Variable Range Hopping (VRH) model in the low temperature region. The studies on the optical absorption spectra lead to the determination of optical band gap energy and Urbach's energy of TTBNc thin films. Also the temperature dependence of steepness parameter is explained.

1. Introduction

Naphthalocyanines (Nc's) are phthalocyanine derivatives, with an extended network of 56 conjugated Π electrons. They have found numerous applications in materials science and advanced technologies especially in the field of linear and non linear optical materials, semiconducting technology, photosensitizers and in Photo Dynamic Therapy (PDT) of cancer treatments [1–5]. There are a variety of applications for this material due to its ease of synthesis, which lead to various structural variations due to the difference in the number of peripheral substitutions and adatoms like axial ligands [6]. It is being advantageous on an economic basis by providing an optical recording layer comprising a specified phthalo (naphthalo) cyanine coloring matter on a transparent substrate [7]. Compounds of naphthalocyanines are dyes and IR absorbers and can be used for optical information storage systems employing diode lasers [8]. Tert-butyl addition to the Nc's enhances the synthesis of materials, improves its stability which in turn causes a pronounced shift of Q bands towards the longer wavelength due to the increase of fundamental benzo units [9]. This results in the extra stability of tetra tert substituted naphthalocyanines apart from Nc's. There are earlier reports on the photo emission, luminescence and Raman spectroscopic properties of Tert-butyl substituted Nc's [10,11]. The basic structure of 2,11,20,29 Tetra–Tert-Butyl 2,3 Naphthalocyanine (TTBNc) used as the source material for the present study is as shown in Fig. 1. There are various techniques for the preparation of thin films like sputtering [12], spray pyrolysis [13], reactive thermal evaporation [14] etc.

Here we employed Physical Vapor Deposition (PVD) technique [15] for the fabrication of TTBNc thin films. Since the TTBNc, like other organic semiconductors, has lower melting point, low temperature studies on them are more significant. The present work is an attempt to study the post deposition air annealing on the optical and electrical properties of TTBNc thin films (Scheme 1).

2. Experimental

The source material for the study, 2,11,20,29 Tetra-Tert-Butyl 2,3 Naphthalocyanine (TTBNc) powder (97.56% purity) is originally procured from Sigma Aldrich, USA. Thin films of TTBNc are deposited onto thoroughly cleaned micro glass substrates kept at room temperature, at a pressure of 1×10^{-5} Torr using Hind Hivac 12 A4 coating unit. The evaporation was performed by resistive heating of TTBNc powder from a molybdenum boat connected to the respective electrodes. The thickness of the film was directly measured as 825 nm ± 5 nm by thickness profilometer [16]. Further it is confirmed by the Fizeau fringe method [17,18]. For the thickness measurements we have prepared a number of identical samples. Observations cannot be repeated on the same samples so the average values of number of observations made on identical samples. Films are annealed in air by keeping them in a furnace at temperatures 323, 373, 423 and 473 K. Electrical conductivity measurements are done for the five samples (A-as deposited; B-323 K, C-373 K, D-423 K and E-473 K air annealed) using the standard two-probe method with a programmable Keithley electrometer (Model No. 617) and a constant current source [19]. Pre-evaporated silver is used as ohmic contact. To avoid any type of contamination, measurements are done in a subsidiary vacuum system at a pressure of 10^{-3} Torr using a conductivity cell in the temperature range 300–523 K and resistance is noted at regular intervals of 5 K.

* Corresponding author. Tel.: +91 9847709457.
E-mail address: dhanya.iv@gmail.com (I. Dhanya).

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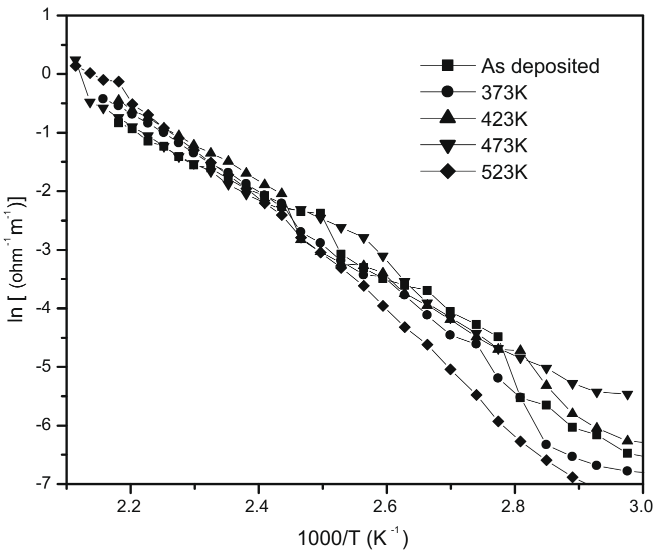


Fig. 1. lnσ vs. 1000/T for different TTBNc thin films.

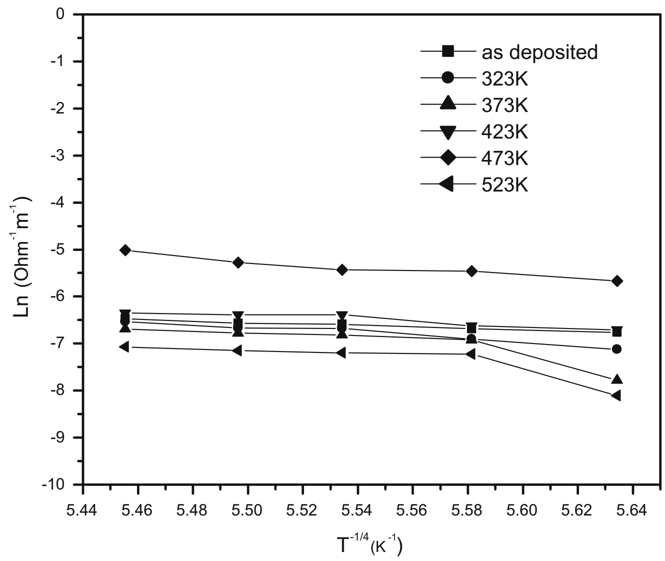
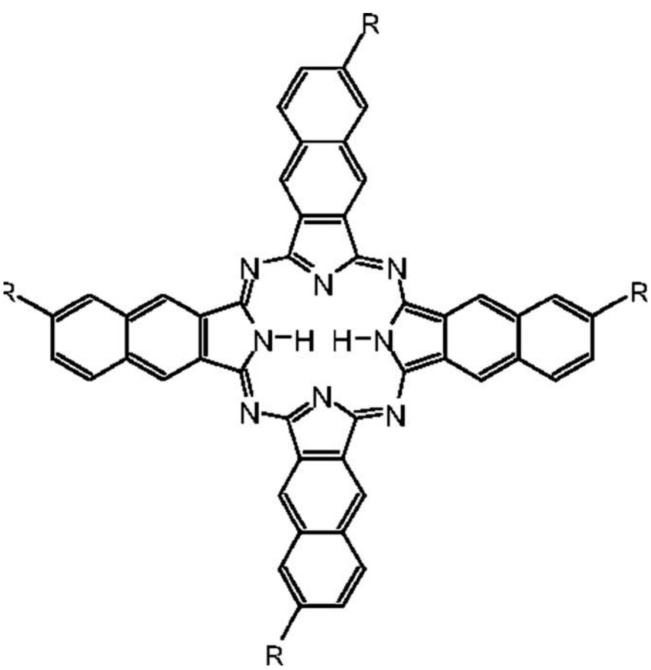


Fig. 2. lnσ vs. $T^{-1/4}$ for different TTBNc thin films.



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

UV–vis absorption spectra are recorded using a Shimadzu 240 UV–vis spectrophotometer.

3. Results

3.1. Electrical conductivity studies

Semiconducting properties are originally observed for bulk phthalocyanines, and TTBNc thin films are not much studied. So it is worth to investigate the electrical properties of these new materials. Hot probe method [20] is employed within the film to find the type of conductivity and are found to be n-type. The thermal activation energy of the films is calculated from the Arrhenius plot (Fig. 2) using the relation:

$$\sigma = \mathrm{A}\exp\left(\frac{-E_1}{kT}\right) + \mathrm{B}\exp\left(\frac{-E_2}{kT}\right) + \mathrm{C}\exp\left(\frac{-E_3}{kT}\right) + \cdots\cdots \quad (1)$$

where E_1, E_2, E_3 etc., are the thermal activation energies in different straight line regions corresponding to trap level impurities of the compound [21], A,B,C 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

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

The activation energies E_1, E_2 and E_3 are given in Table.1.

As annealing temperature increases from 323 K, the activation energy E_1, is found to fall to a value of 0.48 at 473 K and at 523 K, it rises to a value of 0.53.

In DC electrical conductivity studies a Variable Range Hopping (VRH) conduction mechanism can be fitted at low temperatures. From these studies we can measure the parameters like the density of states at Fermi level $N(E_F)$, and the hopping distance (R). The conduction mechanism at low temperature region can be expressed as [22].

$$\sigma(T) = \sigma_1 \exp\left[\left(\frac{-T_0}{T}\right)^{1/4}\right] \quad (3)$$

Mott described this behavior as VRH and can be applied to the TTBNc thin films at lower temperature region of conductivity and are plotted as in Fig. 2.

Table 1
Activation energy values of TTBNc thin films (t = 825 nm) air annealed at different temperatures.

Annealing temperature	Activation energy		
	$E_1 \pm 0.01$ (eV)	$E_2 \pm 0.01$ (eV)	$E_3 \pm 0.01$ (eV)
As deposited	0.47	0.47	0.12
323 K	0.84	0.6	0.29
373 K	0.81	0.59	0.12
423 K	0.57	0.53	0.05
473 K	0.48	0.27	0.07
523 K	0.53	0.23	0.03