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# LOW TEMPERATURE EFFECTS ON ELECTRICAL AND OPTICAL PROPERTIES OF VACUUM ANNEALED ZINC TETRA- TERT- BUTYL 2, 3 NAPHTHALOCYANINE THINFILMS

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*Electrical and optical properties of thermally evaporated vacuum annealed Zinc* 2, 11, 20, 29 *Tetra -Tert -Butyl* 2, 3 *Naphthalocyanine (ZTTBNc) 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. Optical absorption spectra of ZTTBNc thinfilm reveals that B bands posses the same wavelength region while Q bands shift to* 165 *nm from as deposited to maximum vacuum annealed sample. Further the Q band splitting is also absent for* 523 *K vacuum annealed thinfilm. Also ZNTTBNc thinfilms have a wide optical bandgap with a consistant trap level energy as that of any other organic semiconductors.*

***Keywords:*** *ORGANIC SEMICONDUCTORS, NAPHTHALOCYANINE, THIN FILM, VARIABLE RANGE HOPPING, OPTICAL BAND GAP.*

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## 1. INTRODUCTION

Naphthalocyanines (Nc's) are phthalocyanine type organic semiconducting materials, 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 [1-4]. There are a variety of applications for this material due to it's ease of synthesis, which lead to various structural variations due to the difference in the number of peripheral substitutions and adatoms like axial ligands [5]. 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 [6]. 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 [7, 8]. There are various techniques for the preparation of thin films like sputtering [9], spray pyrolysis [10], reactive thermal evaporation[11] etc. Here we employed Physical Vapor Deposition (PVD) technique [12] for the fabrication of ZTTBNc thin films. Since the ZTTBNc, 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 vacuum annealing on the optical and electrical properties of ZTTBNc thin films.

## 2. EXPERIMENTAL

The source material for the study, Zinc 2, 11, 20, 29 Tetra-Tert-Butyl 2, 3 Naphthalocyanine (ZTTBNc) powder (90 % purity) is originally procured from Sigma Aldrich, USA. Thin films of ZTTBNc are deposited at a base pressure of $1 \times 10^{-5}$ Torr using Hind Hivac 12 A4 coating unit having thickness 300 nm by thickness profilometer [7]. Films are vacuum annealed at 323 K, 423 K and 523 K by keeping them in a subsidary vacuum system of pressure $10^{-3}$ Torr. Electrical conductivity measurements are done for samples using the standard two-probe method with a programmable Keithley electrometer (Model No. 617) [8]. UV-Visible absorption spectra are recorded using a Shimadzu 240 UV-VIS spectrophotometer.

## 3. RESULTS AND DISCUSSIONS

### 3.1 Electrical conductivity studies

Semiconducting properties are originally observed for bulk phthalocyanines, and ZTTBNc thin films are not much studied. So it is worth to investigate the electrical properties of these new materials. Hot probe method [17] 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. 1) using the relation:

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

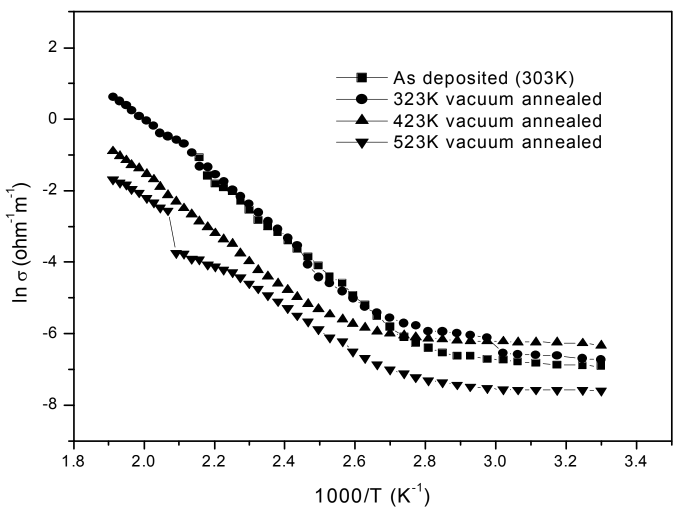


***Fig. 1*** – $\ln\sigma$ *Versus 1000/T for different ZTTBNc thin films*

where $E_1$ and $E_2$ are the intrinsic and extrinsic thermal activation energies in different straight line regions of the compound [18], $A$ 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,

$$\sigma = l/RbT \tag{2}$$

The activation energies $E_1$ and $E_2$ are given in Table 1. 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 ($R$).

***Table 1*** – *Activation energy values of ZTTBNc thin films ($t$ = 300 nm) vacuum annealed at different temperatures*

| Annealing temperature of ZTTBNc thinfilm camples | Activation energy | |
|---|---|---|
| | $E_1 \pm 0.01$, eV | $E_2 \pm 0.01$, eV |
| As deposited (303 K) | 0.72 | 0.08 |
| 323 K vacuum annealed | 0.69 | 0.12 |
| 423 K vacuum annealed | 0.66 | 0.05 |
| 523 K vacuum annealed | 0.55 | 0.02 |

The conduction mechanism at low temperature region can be expressed as [19],

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

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

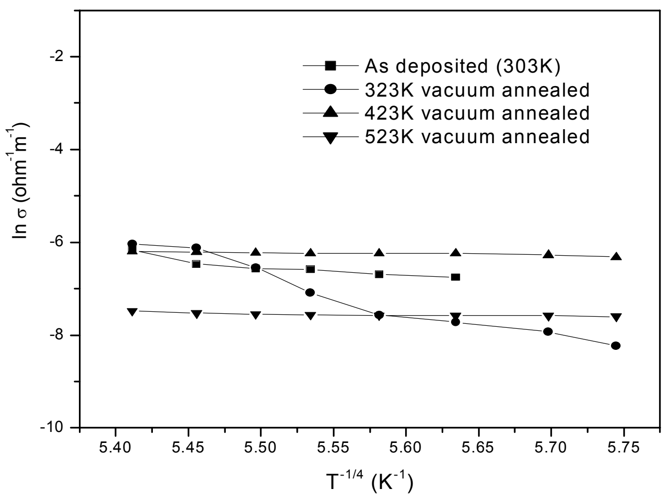


***Fig. 2*** – ln$\sigma$ *Versus* $T^{-1/4}$ *for different ZTTBNc thin films*

From equation (3), $T_0$ can be calculated using the relation:

$$T_0 = \frac{16}{N(E_F)kL_{loc}^3} \tag{4}$$

and,

$$R = \left[ \frac{9L_{loc}}{8\pi kTN(E_F)} \right]^{\frac{1}{4}} \tag{5}$$

Taking $L_{loc} = 10^{-7}$ cm [20], the values corresponding to VRH parameters can be calculated for ZTTBNc thin films and are collected in Table 2.

***Table 2*** *– Hopping conduction parameters of ZTTBNc thin films annealed in air at different temperatures*

| Samples | $T_0$ (K) | $N(E_F)$ ($m^{-3}eV^{-1}$) | $R(m)$ |
|---|---|---|---|
| As deposited (303 K) | $8.38 \times 10^{12}$ | $0.013 \times 10^{40}$ | $15.82 \times 10^{-8}$ |
| 323 K vacuum annealed | $0.241 \times 10^{12}$ | $0.481 \times 10^{40}$ | $6.51 \times 10^{-8}$ |
| 423 K vacuum annealed | $0.0095 \times 10^{12}$ | $12.27 \times 10^{40}$ | $3.14 \times 10^{-8}$ |
| 523 K vacuum annealed | $0.0078 \times 10^{12}$ | $14.75 \times 10^{40}$ | $10^{-8}$ |

### 3.2 Optical absorption studies

The UV VIS-NIR absorption spectra of ZTTBNc thin films of thickness 300 nm vacuum annealed at different temperatures are plotted in Fig. 4. The plots show B and Q bands. All the samples posses B bands at 334 nm but the Q band position gets varied from 775 nm (as deposited) to 610 nm (523 K vacuum annealed). The Q band is further splitted into two peaks $Q_x$ and $Q_y$ for 303 K and 423 K vacuum annealed samples with a splitting of 60-65 nm.

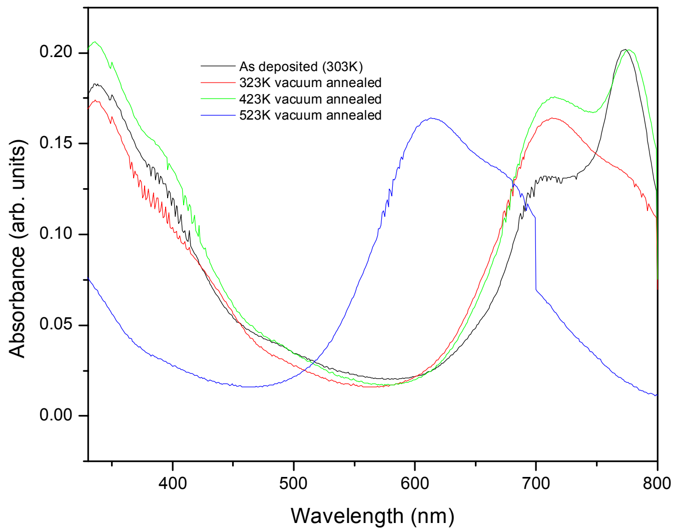


***Fig. 3*** *– Absorption spectrum of different ZTTBNc thin films*

The optical band gap energy is calculated using the relation [21, 22],

$$\alpha = \alpha_0 (h\nu - E_g)^n \qquad (6)$$

where $n = 1/2$ for direct allowed transitions, α the absorption coefficient, $E_g$ is the optical band gap and $h\nu$ is the photon energy. Fig. 4. shows the tipical $\alpha^2$ versus $h\nu$ graph for as deposited ZTTBNc thin film.

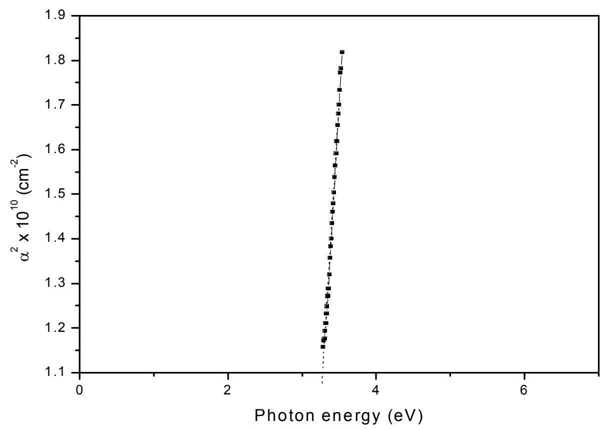


***Fig. 4*** *– Tipical $\alpha^2$ versus $h\nu$ graph for as deposited ZTTBNc thin film*

We have determined the band gap energy of the material as 3.27 ± 0.01 eV. There is a notable shift in bandgap energy as indecated by Table 3.

***Table 3*** *– Band gap energy($E_{g1}$) and trap level energy ($E_{g2}$) for different ZTTBNc thinfilms*

| Annealing temperature of ZTTBNc thinfilm camples | Bandgap energy | |
|---|---|---|
| | $E_{g1}$ ± 0.01, eV | $E_{g2}$ ± 0.01, eV |
| As deposited (303 K) | 3.27 | 1.54 |
| 323 K vacuum annealed | 3.19 | 1.52 |
| 423 K vacuum annealed | 3.12 | 1.50 |
| 523 K vacuum annealed | 3.09 | 1.50 |

## 4. DISCUSSIONS

Usually an exponential variation of electrical conductivity is observed for organic semiconductors. The hot probe treatment is used to determine the majority charge carriers in ZTTBNc thin films and are found to be electrons, and hence is proved to be an n-type semiconductor. ZTTBNc thin films show a negative Temperature Coefficient of Resistance (TCR) that the conduction mechanisms of these films are thermally activated. The existence of different activation enthalpy at different regions in each plot reveals the presence of both intrinsic charge carrier conduction and the conduction due to trap level impurities. Activation energy is found to decrease with annealing temperature up to 473 K and a sudden increase at 523 K may be assigned to a phase change or due to the colour center formation [23, 24]. Even though the material under thin film preparation is found to be pure and metal free, the freshly prepared samples may contain certain types of defects such as vacancies, grain boundaries and dislocation which can partially be annealed out by heat treatment resulting in the decrease of defect densities. Air moistures as well as other contaminants may act as donor or acceptor levels in the film, contributes as extrinsic carrier conductivity and results in hopping process. In low temperature region, the carriers gets trapped and cannot be excited into one of these allowed bands, the dominant conduction carried out through hopping type and is in localized states near the Fermi level.

The optical absorption spectrum reveals that in addition to the fundamental B band there are two excitonic energy levels $Q_x$ and $Q_y$ present for as deposited film. Vacuum annealing decreases the Q band splitting and is entirley absent for maximum annealed sample. Desorption of oxygen in the vacant site create a $\Pi$ to $\Pi^*$ transition [25, 26] which acts as trap level impurities corresponding to two excitonic energy levels in the ZTTBNc thin films. This material is having a direct allowed band gap with energy of $3.27 \pm 0.01$ eV and found decreases with vacuum annealing effects as that of any other n-type organic semiconductors.

## 5. CONCLUSION

Electrical conductivity and optical absorption studies on ZTTBNc thin films have been conducted with respect to post deposition vacuum annealing. These films are thermally stable over a wide range of temperature. The existence of trap levels is confirmed due to the presence of two different linear regions in the $\ln\sigma$ versus $1000/T$ plots. The VRH model is applicable in the low temperature region of conductivity and different hopping conduction parameters are gets calculated. The optical absorption study reveals the narrowing of band gap energy with annealing temperature.

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