Effect of Thickness on Structural and Optical Properties of Tetra-tert-butyl-2, 3-naphthalocyanine Thin Films

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Abstract: Amorphous tetra-tert-butyl-2, 3-naphthalocyanine thin films have been deposited using physical vapor deposition technique under a varied thickness by adjusting the coating time. By analyzing the x-ray diffraction, the structure of as deposited films is found to be non-crystalline. Different optical properties of these thin films have been investigated by means of optical absorption and reflection spectra. Various optical constants like band gap energy, E_g the width of band tails of localized states into the gap, E_U and steepness parameter, β gets calculated and the variation of different optical parameters like refractive index, extinction coefficient, dielectric constants, optical conductivity and surface and volume energy losses with photon energy are estimated.

Keywords: Naphthalocyanines, Non-crystalline, Bandgap energy, Optical constants, Optical conductivity

Introduction

More complex options to porphyrines, naphthalocyanines have been extensively used as potential materials for optoelectronic and electronic devices for solar cells¹⁻³. Tert-butyl substituted naphthalocyanine, as one of phthalocyanine derivatives is known for frequency and time domain spectral hole burning optical storage devices⁴ due to the presence of large inhomogeneous broadening, relatively narrow holes at low temperatures and a built in proton photo transformation mechanism between different tautomers. Several free based naphthalocyanine derivatives exhibit a strong O-O absorption band region in the region 800 nm matching the wavelength of most semiconductor diode lasers and Ti-Sapphire lasers. Most studies related to phthalocyanine derivatives are addressed to the structural aspects of the molecular arrangement in thin films and in solution phase using UPS, XPS or NEXAFS⁵⁻⁸.

There are little studies on determination of various optical constants of naphthalocyanine compounds especially in thin film configuration even though some optical studies exist^{9,10}. Here we are intended to prepare 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine (TTBNc) thin films and monitored the x-ray diffraction pattern, absorption and luminescence spectra. TTBNc is absolutely a metal free porphyrine with the ligands are not co-ordinate to any central metal ion, the electronic states are exclusively of porphyrine ligand origin.

Due to high fluorescence quantum yield (0.01-0.4) of metal free TTBNc with respect to their metal centered compounds¹¹ and a strong fluorescence spectrum is observed in these compounds especially in thin film states. Here thin film samples of TTBNc with varied thickness are investigated.

Experimental

The raw material for thin film sample preparation is 2,11,20,29-tetra-tert-butyl-2,3-naphthalocyanine (TTBNc) powder, procured from sigma-aldrich chemicals, USA. TTBNc thin films were deposited onto thoroughly cleaned micro glass substrate at room temperature, at a base pressure of 1×10^{-5} torr using a Hind Hivac 12A4 coating unit. The evaporation was carried out by resistive heating of TTBNc powder from a molybdenum boat kept at a distance of 7 cm from the substrate by means of respective copper electrodes. Two sets of thin films are obtained on the same pressure condition by successive sets of coating. The thickness of the films is measured using thickness profilometer and is cross checked by Tolansky's method¹². The thicknesses are 825 nm and 195 nm for two sets of samples under investigation by varying their time of evaporation as 10 minutes and 2 minutes respectively with a variation of ± 15 nm. Thin film nature of these samples has been well established through a series of spectroscopic methods including x-ray diffractogram, UV-Visible spectrum and photoluminescence techniques and there by various optical constants gets calculated.

The structure properties are investigated by means of an x-ray diffractometer PAN analytical (X'pert Pro) with Cu K α radiations ($\lambda = 1.5405 \text{ \AA}$) in the range of 2θ between 10° and 40° . The optical measurements of the films like absorbance A, reflectance R of the films are carried out at room temperature using a Shimadzu UV-VIS 2450 spectrophotometer in the wavelength range from 190 to 900 nm. The photoluminescence spectrum is taken using Horiba Jobin Yvon Fluorolog 3 modular spectrofluorometer with 450 watt Xenon lamp and having a Hanafpu R 928-28 photomultiplier tube.

Results and Discussion

Structural characterization

The crystal structure of the TTBNc thin films under different thickness is investigated by x-ray diffraction (XRD) patterns. Figure 1 shows the diffraction patterns of as deposited TTBNc thin films of varied thickness and are found to be almost non crystalline in nature.

Optical band gap and Urbach energy

The optical absorbance and reflectance of the films are shown in Figure 2. The maximum absorbance is corresponding to B band for the two films with a varying wave length of 310 nm for 825 nm thick film and 340 nm for 195 nm thick film. In the absorption spectra the Q bands having a splitting of Q_x and Q_y and is prominent while thickness increases.

Figure 1. X-ray diffraction patterns of different TTBNc thin films

Figure 2. Optical absorbance (a) and reflectance (b) spectra of different TTBNc thin films. From the absorbance spectra, the absorption coefficient, α and extinction coefficient, k are found out using the expressions^{13,14}

$$\alpha = \frac{2.303 \times A}{t} \quad (1)$$

and

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

Where A , the absorbance; t , the thickness of thin films and λ is the wavelength range. Graphs of α vs. $h\nu$ and k vs. $h\nu$ are plotted and shown in Figure 3.

Figure 3. Absorption coefficient, α vs. photon energy and extinction coefficient, k vs. photon energy for TTBNC thin films of different thicknesses

The optical band gap E_g can be calculated from the following relationship^{15,16}

$$\alpha = \alpha_0 (h\nu - E_g)^n \quad (3)$$

Where $n=1/2$ for direct allowed transition. Graph of α^2 vs. $h\nu$ is plotted and is shown in Figure 4. Extrapolation of the plot to $\alpha^2=0$ determines the optical band gap. The band gap energy of TTBNC thin film is found to be 3.02 eV and is invariant with thickness variation.

Figure 4. Typical plot of α^2 vs. $h\nu$ of TTBNC thin film

The absorption coefficient near the fundamental absorption edge for as deposited TTBNC thin film is exponentially dependent on the incident photon energy and obeys the empirical Urbach relation, where $\ln \alpha$ varies as a function of $h\nu$. The Urbach energy can be calculated by the following relation¹⁷

$$\ln \alpha = \alpha_0 \exp \left[\frac{h\nu - E_t}{E_U} \right] \quad (4)$$

Where E_l and α_0 are constants and E_U is the Urbach energy, which refers the width of the exponential absorption edge. Figure 5 represents the Urbach plot of TTBNc thin film and E_U can be calculated from the slope of the graph. Urbach energy values of the films found to increase with increase in thickness due to the increase in the width of localized states in optical bands.

Figure 5. Typical Urbach plot of TTBNc thin film

From the Urbach plot, the steepness parameter β can be empirically determined using the relation,

$$\alpha = \alpha_0 \exp \left[\frac{\beta}{KT} (E - E_l) \right] \quad (5)$$

Where β , the steepness parameter, which characterizes the broadening of the absorption edge due to the electron-phonon interaction or exciton-phonon interaction¹⁸. From the above graph, the β values suggest that the absorption edge changes with the variation in thickness.

The refractive index and dielectric constants of TTBNc thin films

In the optical parameters, dispersion plays an important role in the research for optical materials, because of its significance in optical communication and in designing devices for spectral dispersion. The reflectivity of an absorbing medium of indices n and k in air under normal incidence is given by¹⁹

$$R = \frac{(n-1)^2 + k^2}{(n+1)^2 + k^2} \quad (6)$$

and the optical properties of any solid material is characterized by the complex refractive index ($N=n-ik$) and the complex dielectric constant ($\mathcal{E} = \mathcal{E}_1 - i\mathcal{E}_2$). Here the dispersion relates to the real part $\mathcal{E}_1$ and $\mathcal{E}_2$ is a measure of the dissipative rate of the wave in the medium. The real and imaginary part of dielectric constants are related to n and k values through the relations,

$$\mathcal{E}_1 = n^2 - k^2 \quad (7)$$

$$\varepsilon_2 = 2nk \quad (8)$$

Figure 6 & 7 represent the refractive index and ε_1 , ε_2 dependence of films with their photon energy¹⁹. The maximum value of refractive index is found to be 2.35 and 2.27 for 825 nm and 195 nm thick films respectively with their ε_1 , ε_2 variation are almost linear.

Figure 6. Refractive index variation as a function of photon energy for TTBNc thin films

Figure 7. Variation of ε_1 and ε_2 as a function of photon energy for TTBNc thin films

Optical conductivity of TTBNC thin films

The optical conductivity parameters, σ_1 and σ_2 are real and imaginary components respectively with their dependence on ε_1 & ε_2 can be described as²⁰

$$\sigma_1 = \omega \varepsilon_2 \varepsilon_0 \text{ and } \sigma_2 = \omega \varepsilon_1 \varepsilon_0 \quad (9)$$

Where ω is the angular frequency, ε_0 is the free space dielectric constant. The dependence of real σ_1 and imaginary σ_2 parts of optical conductivity with photon energy is as shown in Figure 8. The increase in photo conductivity due to the variation of photon energy is in a linear manner and is due to the excess electrons emitted by means of photon energy.

Figure 8. Real (σ_1) and imaginary (σ_2) part of different TTBNC thin films

Surface and volume energy loss functions of TTBNC thin films

The obtained results of optical conductivity can be further analyses through graphical representations of volume energy loss and surface energy loss as a function of photon energy (in Figure 9) to detect the existence of any possible allowed optical transition. Volume energy loss can be represented as²¹

$$\left[-\text{Im}\left(\frac{1}{\varepsilon}\right) \right] = \frac{\varepsilon_2}{(\varepsilon_1^2 + \varepsilon_2^2)} \quad (10)$$

and the Surface energy loss

$$\left[-\text{Im}\left(\frac{1}{(\varepsilon+1)}\right) \right] = \frac{\varepsilon_2}{[(\varepsilon_1+1)^2 + \varepsilon_2^2]} \quad (11)$$

Figure 9. Typical (a) volume energy loss and (b) surface energy loss of TTBNC thin film as a function of photon energy

Both the two energy losses have a linear variation with the corresponding photon energy and found a maximum energy loss near the optical band gap energy. By increasing the amount of deposition, there is an effect of variation in optical constants and most of them in linear. This variation can be discussed in terms of defects present in the composition, due to the presence of localized states in the optical band gap. The different optical constants with respect to their thicknesses are listed in Table 1.

Table 1. Different optical constants of TTBNC thin films of varied thickness

Thickness of film ± 15 nm	E_g ± 0.01 (eV)	E_u ± 0.01 (eV)	β $\times 10^{-2}$	Max. Ref. Index
195 nm	3.02	0.66	3.91	2.14
825 nm	3.01	0.78	3.30	2.43

Photoluminescence studies

In contrast to the porphyrazines, TTBNC films show usually broad but distinct emission bands centered at the given maxima ($\lambda_{\text{lum}}=417$ nm and 399 nm for $t=195$ nm and $\lambda_{\text{lum}}=410$ nm and 392 nm for $t=825$ nm). TTBNC thin films are the first ever porphyrazines found to exhibit two luminescence peaks in the solid state²². Even though the excitation wave length gets varied to 5 nm from 300 nm, there is no further shift in peaks at 392 nm ($t=825$ nm) and 399 nm ($t=195$ nm). With the increase in thickness, the intensity in emission peak get decreases from 9×10^6 ($t=195$ nm) to 5×10^6 ($t=825$ nm) at a wave length of 415 nm while there is a blue shift observes. This type of emission may be due to the presence of oxygen related defects, non bridged oxygen hole centers and organic bonds in form of $-\text{O}-\text{C}-\text{O}^{23}$. The fluorescence spectra of naphthalocyanine with different thickness are shown in Figure 10.

Figure 10. Luminescence spectra of TTBNC thin films as a function of wavelength for different thicknesses

Conclusion

The optical properties of amorphous tetra-tert-butyl naphthalocyanine thin films have been investigated. Using optical method, the values of different optical parameters like optical bandgap, E_g , Urbach energy, E_U and Steepness parameter, β are calculated. The increase in thickness scarcely changes the direct band gap, where as more deposition of material in thin film form changes the optical constants like refractive index, Urbach energy, extinction coefficient, dielectrical constants, optical conductivity and surface and volume energy losses. The fluorescence emission of TTBNC thin films shows strong broad and distinct bands with two resonance peaks. Further there is no considerable shift in peaks for single thickness film with different excitation wavelengths. As the thickness increases, it is found that there is a blue shift in the peaks.

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