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Determination of band energy levels of α-quaterthiophene (α-4T) thin films from its optical absorption spectrum

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Abstract: *α-4T thin film of various thicknesses are prepared by thermal evaporation method. The absorption spectra of the as-deposited and annealed films are recorded using UV-Vis-NIR spectrophotometer. The dependence of absorption coefficient on photon energy has been studied. Optical band energy levels of annealed thin films of various thickness have been estimated. The fundamental optical band energy gap slightly decreases with increase in film thickness. There is no appreciable change in optical band energy levels on annealing.*

Keywords*: α-4T; thermal evaporation; annealing: optical band energy levels*

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I. Introduction

Oligothiophenes are widely considered as an interesting material in organic electronic industry because of their high stability to withstand oxidation [1]. Oligothiophenes attract remarkable attention as an organic semiconductor. It shows nonlinear optical, electrical, and liquid crystalline properties. These properties are dependent on various film deposition parameters. Their physical properties can be attained by incorporating minor structural modifications by altering parameters like deposition rate, film thickness, substrate temperature, annealing temperature and annealing time. Among oligothiophenes, α-quaterthiophene (α-4T) is widely studied because of its promising applications in organic electronic industry.

Quaterthiophene (α-4T) is a good photosensitive organic material which shows considerable absorption in the short wavelength region of the UV-visible spectrum. α-4T thin film is suited for organic and optoelectronic device applications. Organic semiconductors [2-11] are useful in microelectronics and nanotechnology. α-oligothiophenes [12-13] (α-Nt) are oligomers of thiophenes. Among them α-4T [14-15] is highly promising for applications in thin film transistor devices [16]. The solubility of α-4T makes it a more potential candidate for solution phase film deposition. The capability of α-4T to dissolve in organic solvents at room temperature is advantageous. Hence it can be used easily to process organic semiconducting material.

Oligothiophene consists of thiophene sub units bonded each other by σ bonds via its α carbon atoms to form oligomers of thiophene. Four thiophene sub units are bonded to form α-quaterthiophene (α-4T) molecule. Since it has high vapour pressure, it is possible to form thin films by thermal evaporation[17] by vapour deposition technique on sublimation in high vacuum. It has good electrical characteristics suitable for the fabrication of organic field effect transistors (OFETs) [18-24], organic photovoltaics (OPVs) [25-26], organic light emitting diodes (OLEDs) [27-30], solar cells [31-37] and electro chromic devices (ECDs). Organic electronics is an emerging field in electronic industry where organic semiconductors can be used in the fabrication of electronic devices [38-41].

II. Experimental details

α-Quaterthiophene powder of 96% purity from Sigma Aldrich has been used as source material in the preparation of α-4T thin films. Hind Hivac coating unit (Model 12A4-D) has been used for the preparation of thin films. Thermal evaporation technique has been employed in vacuum coating unit for the deposition of thin films. The thin films of α-4T of thicknesses 50 nm, 100 nm, 169 nm and 200 nm have been deposited on thoroughly cleaned glass substrates of dimensions 75 mm x 25mm x 1.35 mm. substrates are cleaned well in light soap solution and soaked well in dilute nitric acid. It is washed thoroughly in distilled water and subjected to ultrasonic agitation in acetone for 2 to 5 minutes. Thereafter it is rinsed with isopropyl alcohol and dried using hot air. It is further subjected to HT cleaning provided with vacuum coating unit for 2-5 minutes. These glass substrates which are totally free from any sort of contamination have been used for the deposition of thin films. α-4T powder has been placed in pre-cleaned molybdenum boat of dimension 23 x 13 x 11 mm and the cleaned glass substrates are placed at distance of 20 cm above the boat and well enclosed by the bell jar of the coating unit. Using rotary pump, a fore vacuum of 10^{-3} m.bar as measured by pirani gauge has been created inside the vacuum chamber to fulfil the pre-requisite vacuum for the operation of diffusion pump. A high vacuum of 10^{-6} m.bar as indicated by penning gauge has been produced using diffusion pump. α-4T thin films have been deposited at deposition rate of 2 Å/sec till the thickness monitor indicates the formation of α-4T thin film of required thickness. The prepared thin films of thicknesses 50 nm, 100 nm and 200 nm have been annealed in vacuum at 60 °C, 80 °C, 100 °C and 120 °C. The dependence of absorption coefficient (α) with photon energy (hυ) has been studied. The optical band energy levels of as deposited and annealed α-4T thin films have been estimated from $(\alpha h\upsilon)^2$ vs. hυ plots.

III. Results and discussion

Optical energy levels of as deposited and annealed thin film samples have been estimated from the hν–$(\alpha h\nu)^2$ plots. Estimated values of energy levels of as deposited and annealed thin films of thicknesses 50 nm, 100 nm and 200 nm are tabulated in the table 1. It is seen from the table that fundamental energy gap of as deposited thin film is 3.88 ± 0.01 eV, 3.87 ± 0.01 eV and 3.73 ± 0.01 eV as the film thickness increases from 50 nm to 100 nm and 200 nm respectively. The fundamental energy level of thin films annealed at 60 °C and of thickness 50 nm is 3.89 ± 0.01 eV, 3.88 ± 0.01 eV and 3.74± 0.01 eV as the film thickness increases to 100 nm and 200 nm respectively. It is seen that the fundamental energy gap of films annealed at 80 °C and of thickness 50 nm decreases from 3.88 ± 0.01 eV to 3.70 ± 0.01 eV as the film thickness increases to 200 nm. The fundamental energy gaps of films annealed at 100 °C and of thickness 50 nm decreases from 3.90 ± 0.01 eV to 3.87 ± 0.01 eV and 3.84 ± 0.01 eV as the film thickness increases to 100 nm and 200 nm respectively. Also seen that the fundamental energy level of thin films annealed at 120 °C and of thickness 50 nm decreases from 3.90 ± 0.01 eV to 3.82 ± 0.01 eV as the film thickness increases to 200 nm. As the film thickness increases dislocation density and strain decreases which increases grain size which in turn slightly decreases the fundamental energy gap. As the film thickness increases the strain and dislocation density decreases which may be attributed to the difference in the film morphology [42]. The observed energy levels agree with the energy gap obtained by Jose` et. al., [43]. $(\alpha h\nu)^2$– hν plots of as deposited and annealed thin film of thickness 50 nm, 100 nm and 200 nm are drawn for the estimation of energy gaps. The optical absorption spectrum of α-4T thin film at room temperature (RT) is shown in Fig. 1. $(\alpha h\nu)^2$ vs. hν plot for thin films of thickness 50 nm at room temperature (RT) is shown in Fig. 2.

Table 1. Optical band energy levels of as deposited and annealed α-4T thin films

Thin film thickness (nm)	Temperature (°C)	Energy level 1 ± 0.01 eV	Energy level 2 ± 0.01 eV	Energy level 3 ± 0.01 eV
50	30	3.88	2.67	2.44
50	60	3.89	2.68	2.45
50	80	3.88	2.66	2.44
50	100	3.90	2.60	2.36
50	120	3.90	2.75	-
100	30	3.87	3.40	2.45
100	60	3.88	3.41	2.44
100	80	3.88	3.40	2.44
100	100	3.87	3.31	2.39
100	120	3.90	3.06	-
200	30	3.73	2.78	2.48
200	60	3.74	2.77	2.48
200	80	3.70	2.77	2.45
200	100	3.84	2.94	2.38
200	120	3.82	2.84	2.37

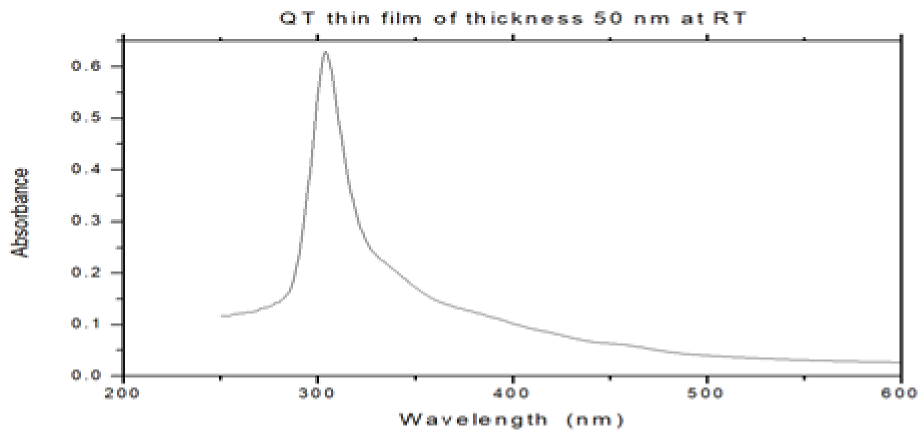

Fig. 1. Absorbance spectrum of α-4T thin film of thickness 50 nm at room temperature

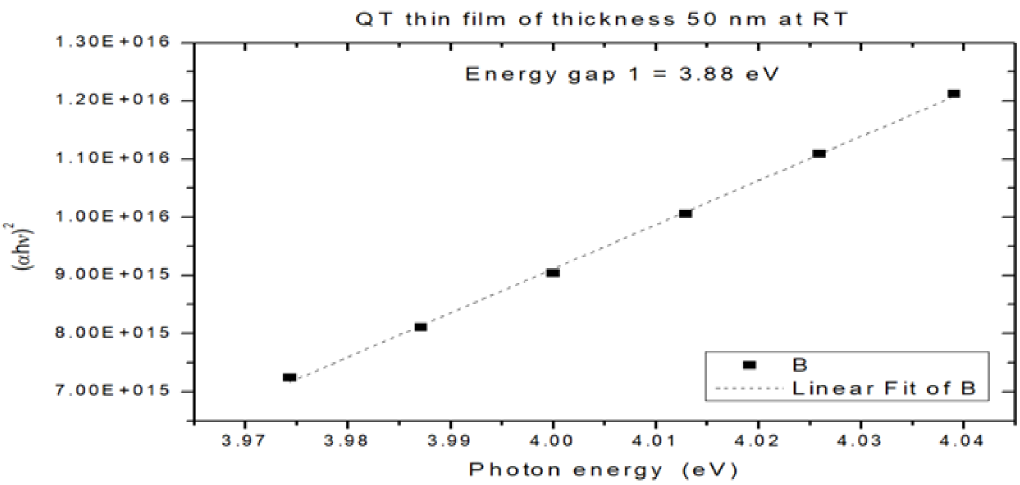

Fig. 2. $(\alpha h\upsilon)^2$-hυ plot of α-4T thin film of thickness 50 nm at room temperature

IV. Conclusions

$(\alpha h\nu)^2$– hν plot at the band edge is found to be a straight line. It is observed that the absorption coefficient is estimated to be ≥ 10^3 cm^{-1}. Hence α-4T thin films are found to have direct energy gap. Fundamental band energy level of α-4T thin films depend slightly on film thickness. Optical band gap is found to decrease slightly with increase in film thickness and vice versa. There is no observable change in the optical energy levels on annealing.

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