Dependence of refractive index and dielectric constant of α-quaterthiophene (α-4T) thin films on photon energy

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Abstract: α-Quaterthiophene (α-4T) thin films of various thicknesses are prepared by thermal evaporation method. The absorbance and reflectance of the as-deposited and annealed films are recorded using UV-Vis-NIR spectrophotometer. Refractive index, extinction coefficient, real and imaginary part of dielectric constant of as deposited and annealed thin films of various thicknesses have been estimated. Dependence of refractive index, extinction coefficient, real and imaginary parts of dielectric constant of α-4T thin film with photon energy have been studied. It is observed that when refractive index (n) attains maximum extinction coefficient (k) takes minimum and vice versa with variations in photon energy. Real and imaginary parts of dielectric constant ε1 and ε2 vary with photon energy in accordance with variations of refractive index.

Keywords: α-4T; thermal evaporation; annealing, refractive index; extinction coefficient; dielectric constant

Date of Submission: 29-01-2018
Date of acceptance: 20-02-2018

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-Ni) are oligomers of thiophenes. Among them α-4T [14-15] is highly 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 [31-36] and electro chromic devices (ECDs). Organic electronics is an emerging field in electronic industry where organic semiconductors can be used in the fabrication of devices [37-40].

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...
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thoroughly cleaned glass substrates of dimensions 75 mm x 25 mm x 1.35 mm. Substrates are well cleaned 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 the 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 absorbance and reflectance of the as-deposited and annealed films are recorded using UV-Vis-NIR spectrophotometer. Refractive index, extinction coefficient, real and imaginary parts of dielectric constant of as deposited and annealed thin films of various thicknesses have been estimated. Dependence of refractive index, extinction coefficient, real and imaginary parts of dielectric constant of α-4T thin films with photon energy have been studied.

III. Results and discussion

Extinction coefficients (k) and refractive indices (n) of the as deposited and annealed thin films have been estimated using equations 1 and 2 for wavelengths ranging from 300 nm to 1100 nm of films of thickness 50 nm, 100 nm and 200 nm. The variations of n and k with photon energy of as deposited thin film of thickness 50 nm is shown in the figure 1. It is seen from the plots that when n increases, k tends to decrease and vice versa. That is when n attains maximum, k becomes minimum and vice versa which is expected from equation 2.

From the plot, it is seen that initially as photon energy increases from 1 eV to 1.5 eV, n increases abruptly as reflectance attains maximum corresponding to photon energy 1.5 eV during which k decreases with increase in photon energy. As a result, n attains maximum at ≈ 1.5 eV. As photon energy increases from 1.5 eV to ≈ 3.8 eV, n decreases and attains minimum as reflectance rapidly attains minimum due to high absorption of energy by the material of the film at ≈ 3.8 eV. Rapid increase in absorption energy may be attributed to surface and volume imperfections [41] of the thin film. Thereafter n gradually increases due to occurrence of dispersion before the absorption edge followed by anomalous dispersion. Low refractive index may be attributed to the successive internal reflections or due to trapped photons within the grain boundary [42].

\[ k = \alpha \lambda /4\pi \]

where \( \alpha \) is the absorption coefficient and \( \lambda \) is the wavelength

\[ n = (1+R) / (1-R) + [(1+R) / (1-R)]^2 - (k^2+1)^{1/2} \]

where R is the reflectance and k is the extinction coefficient

Real part of dielectric constant is related with dispersion and imaginary part of dielectric constant gives a measure of rate of dissipation of the wave in the medium. The real and imaginary parts of dielectric constant of α-4T thin films of different thicknesses are estimated using equations 3 and 4. Variations of real and imaginary parts of dielectric constant with photon energy of as deposited thin film of thickness 50 nm is shown in the figure 2. From the plot, it has been noticed that \( \varepsilon_1 \) and \( \varepsilon_2 \) vary with photon energy according to the variations in n (as n>>k), as expected from equations 3 and 4. From the plot, it is seen that \( \varepsilon_1 \) and \( \varepsilon_2 \) decrease abruptly around \( h\nu \approx 2.4 \text{ eV}, 2.8 \text{ eV} \) and 4 eV as, k decreases due to rapid absorption of energy by the material of the film.

The real and imaginary parts of dielectric constants are respectively given by

\[ \varepsilon_1 = n^2 - k^2 \]

\[ \varepsilon_2 = 2nk \]
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Figure 1: Variation of refractive index and extinction coefficient with photon energy of $\alpha$-4T thin film of thickness 50 nm at room temperature

![Figure 1](image1)

Figure 2: Variation of real and imaginary part of dielectric constant with photon energy of $\alpha$-4T thin film of thickness 50 nm at room temperature

![Figure 2](image2)

IV. Conclusions

When refractive index attains maximum extinction coefficient takes minimum and vice versa. Real and imaginary parts of dielectric constant vary with photon energy in accordance with variation of refractive index. n-k plots show that the band gap of thin films consists of multiple energy levels.

References

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