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Effect of Film Thickness and Post Deposition Annealing Temperature on Dislocation Density, Strain and Full Width at Half Maximum of -quaterthiophene (-4T) Thin Films

V. Sasidharan
School of Technology and Applied Sciences, Mahatma Gandhi University Regional Centre, Pullarikunnu, Malloosserry. P.O, Kottayam, Kerala, India.
C.S. Menon
School of Pure and Applied Physics, Mahatma Gandhi University, Priyadarshini Hills P.O,
Kottayam, Kerala, India.
K. Shreekrishna Kumar
School of Technology and Applied Sciences, Mahatma Gandhi University Regional Centre, Pullarikunnu, Malloosserry. P.O, Kottayam, Kerala, India.

ABSTRACT

-quaterthiophene (-4T) thin film of various thicknesses are prepared by thermal evaporation method. X-ray diffractograms of the as-deposited and annealed films are recorded using X-ray diffractometer (XRD-6000 Shimadzu, Japan). The dependence of dislocation density, strain and fullwidth at half maximum (FWHM) on film thickness and post deposition annealing temperature of -4T thin films have been studied from the X-ray diffractograms. Dislocation density and strain are found to decrease with increase in film thickness and annealing temperature. FWHM is found to decrease with increase in film thickness and annealing temperature.

Keywords

-4T; thermal evaporation; annealing; dislocation density;strain and FWHM

1.INTRODUCTION

Oligothiophenes are widely considered as an interesting material in organic electronic industry because of their high stability to withstand oxidation [1]. Oligothiophenesattract 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, -quaterthiophene (-4T) is widely studied because of its promising applications in organic electronic industry.

Quaterthiophene (-4T) is a good photosensitive organic material which shows considerable absorption in the short wavelength region of the UV-visible spectrum. -4T thin film is suited for organic and optoelectronic device applications. Organic semiconductors [2-11] are useful in microelectronics and nanotechnology. -oligothiophenes [12-13] (-Nt) are oligomers of thiophenes. Among them -4T [14-15] is highly promising for applications in thin film transistor devices [16]. The solubility of -4T makes it a more potential candidate for solution phase film deposition. The capability of -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 bonds via its α carbon atoms to form oligomers of thiophene. Four thiophene sub units are bonded to form -quaterthiophene (-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].

2. EXPERIMENTAL DETAILS

-Quaterthiophene powder of 96% purity from Sigma Aldrich has been used as source material in the preparation of -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 -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. -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. -4T thin films have been deposited at deposition rate of 2 Å/sec till the thickness monitor indicates the formation of -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 ºC, 80 ºC, 100 ºC and 120 ºC. The dependence of dislocation density, strain and FWHM of -4T thin film on the film thickness and post deposition annealing temperature have been estimated and studied using X-ray diffractograms. The variations of dislocation density, strain and FWHM with film thickness and annealing temperatures have been tabulated in tables 1and 2.

3. RESULTS AND DISCUSSION

X-ray diffractogram of -4T thin film of thickness 100 nm annealed at 80 º C is shown in Fig.1.

The chemical and physical properties of thin films (Senthilarasu*et al.*) [42] are strongly influenced by Strain and dislocation density. Dislocation density and strain (Chowdhury *et al.*) [43] have been estimated using equations 1 and 2

The dislocation density ( ) =1/D^2 1

where D is the grain size.

Dislocation density ( ) is defined as the length of dislocation lines per unit volume of the crystal.

Strain ( ) = $_{1/2}$Cos /4 2

where $_{1/2}$ is FWHM and is the angle of diffraction

For films of various thicknesses and tabulated in tables 1 and 2. For thin film of sample of thickness 50 nm, it is seen that dislocation density of as deposited sample decreases from 83.25 x $10^{-4}$to 13.11x 10^{-4}as the annealing temperature increases from 60 ºC to 100 ºC then increases to 79.44 x10^{-4}as the annealing temperature increases to 120 ºC.

In the case of film of thickness 50 nm, the strain of as deposited film sample decreases from 52.68 x 10^{-4}nm^{-2} to 13.04x 10^{-4}nm^{-2} as the annealing temperature increases to 100 ºC. In the case of film of thickness 100 nm, the strain of as deposited film sample decreases from 9.86 x 10^{-4}nm^{-2} to 7.84x 10^{-4}nm^{-2} as the annealing temperature increases to 80 ºC then increases to10.33 x10^{-4}nm^{-2}. In the case of film of thickness 200 nm, the strain of as deposited film sample decreases from 9.27 x10^{-4}nm^{-2} to 7.63x 10^{-4}nm^{-2} as the annealing

temperature increases to 80 ºC then increases to 8.83 x $10^{-4}nm^{-2}$. This increase may be due to re-sublimation. Decrease in strain with film thickness may be due to difference in film morphology.

For thin film of sample of thickness 100 nm, it is seen that dislocation density of as deposited sample decreases from 7.42 x$10^{-4}nm^{-2}$ to 5.98 x$10^{-4}nm^{-2}$ as the annealing temperature increases from 60 ºC to 100 ºC then increases to 11.42 x $10^{-4}nm^{-2}$ as the annealing temperature increases to 120 ºC. For thin film of sample of thickness 200 nm, it is seen that Dislocation density of as deposited sample decreases from 6.57 x $10^{-4}nm^{-2}$ to 5.36 x $10^{-4}nm^{-2}$ as the annealing temperature increases to 60 ºC then increases to 10.98 x $10^{-4}nm^{-2}$ as the annealing temperature increases to 120 ºC.Dislocation density is found to decrease with increase in film thickness. Variations in dislocation density may be due to difference in film morphology.

Variations of Full Width at Half Maximum (FWHM) have been estimated and tabulated in table 2. It is found that FWHM decreases with increase in film thickness and increase in annealing temperature. Sharpening of prominent peak is observed with increase in film thickness and increase in annealing temperature, which shows a better lattice quality and crystallinity [44].

Table1: Variations in Dislocation density of as deposited andannealed thin with film thickness

Temperature	Film Thickness	Grain Size	Dislocation Density x 10^{-4}
(ºC)	t (nm)	D (nm)	δ (nm^{-2})
30	50	10.96	83.25
	100	36.7	7.42
	200	39.02	6.57
60	50	19.48	26.35
	100	37.87	6.97
	200	43.19	5.36
80	50	26.48	14.26
	100	41.39	5.84
	200	42.05	5.66
100	50	27.62	13.11
	100	35.03	8.15
	200	40.9	5.98
120	50	11.22	79.44
	100	29.59	11.42
	200	30.18	10.98

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Table 2: Variations in Strain of as deposited and annealed thin films with film thickness

Temperature	Film Thickness	FWHM	Strain x 10^{-4}
(°C)	(nm)	(radians)	ε
30	50	2.15×10^{-2}	52.68
	100	4.03×10^{-3}	9.86
	200	3.79×10^{-3}	9.27
60	50	7.59×10^{-3}	18.58
	100	4.17×10^{-3}	9.56
	200	3.43×10^{-3}	8.38
80	50	5.54×10^{-3}	13.57
	100	3.20×10^{-3}	7.84
	200	3.12×10^{-3}	7.63
100	50	5.33×10^{-3}	13.04
	100	4.22×10^{-3}	10.33
	200	3.61×10^{-3}	8.83

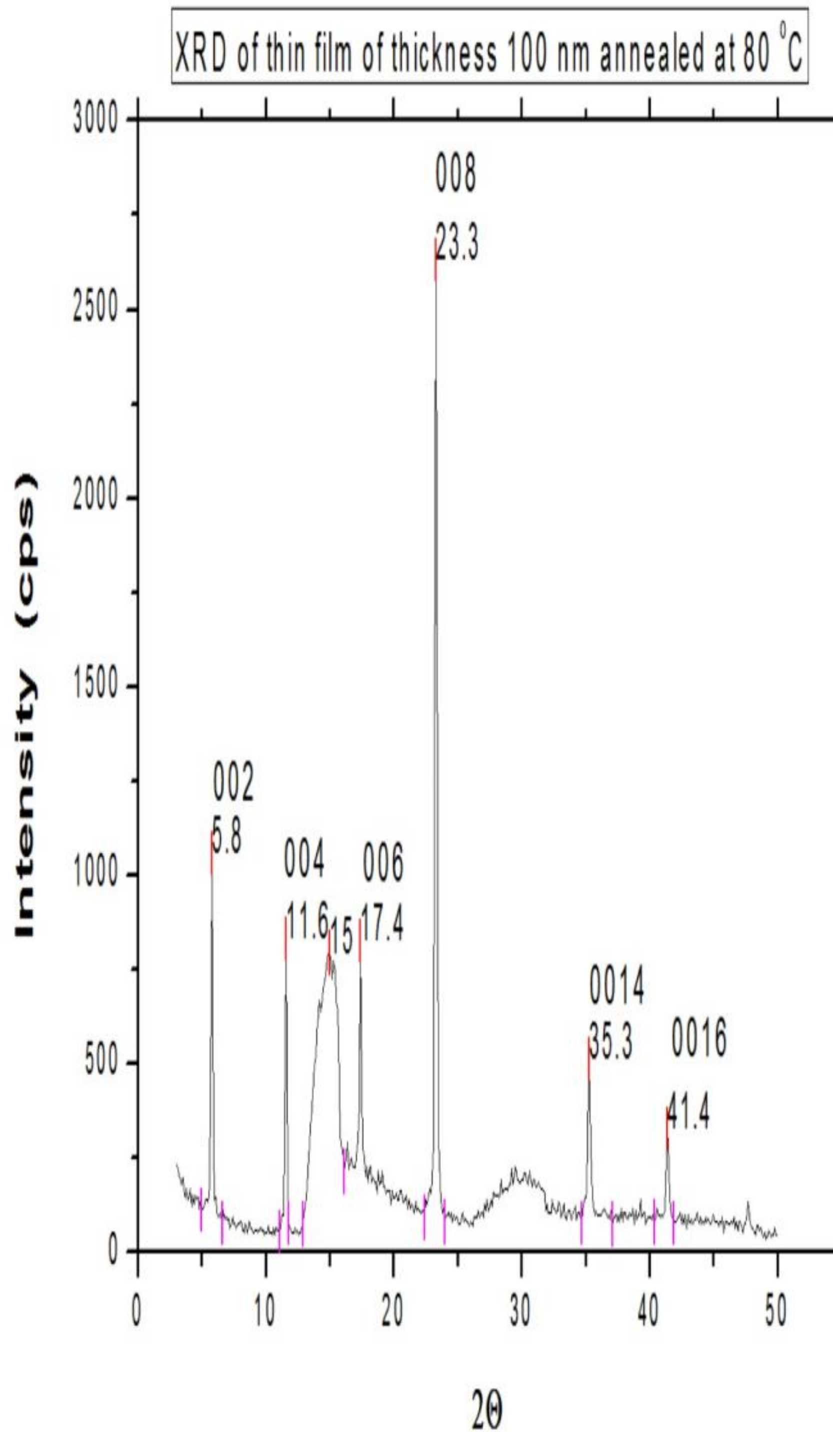

Figure 1: X-ray diffractogram of -4T thin film of thickness 200 nm annealed at 80 ºC

Temperature (^{o}C)	Film Thickness (nm)	Grain Size (nm)
30	50	10.96
	100	36.70
	200	39.02
60	50	19.48
	100	37.87
	200	43.19
80	50	26.48
	100	41.39
	200	42.05
100	50	27.62
	100	35.03
	200	40.90
120	50	11.22
	100	29.59
	200	30.18

Temperature (^{o}C)	Film Thickness (nm)	Grain Size (nm)
30	50	10.96
	100	36.70
	200	39.02
60	50	19.48
	100	37.87
	200	43.19
80	50	26.48
	100	41.39
	200	42.05
100	50	27.62
	100	35.03
	200	40.90
120	50	11.22
	100	29.59
	200	30.18

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4. CONCLUSIONS

Dislocation density and strain are found to decrease with increase in film thickness. Variations indislocation density may be due to difference in film morphology.It is found that FWHM decreases with increase in film thickness and increase in annealing temperature. Sharpening of prominent peak is observed with increase in film thickness and increase in annealing temperature, which shows a better lattice quality and crystallinity

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