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RESEARCH ARTICLE

Structural Studies on Quaterthiophene (QT) Thin Films

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Abstract

Quaterthiophene (QT) thin films are prepared by vacuum vapour deposition method. The X-ray diffraction pattern for QT films deposited at room temperature (RT) and various annealing temperatures are studied. Their grain size and inter planar spacing are determined for various annealing temperatures. The QT thin films are reported to have a maximum inter planar spacing and minimum grain size at RT. Also reported that the grain size increases and the inter planar spacing decreases with increase in annealing temperatures. Indexing of prominent peaks is carried out and peaks are identified.

INTRODUCTION

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 bonded to form quaterthiophene-4T. Since it has high vapour pressure, it is possible to form thin films by vapour deposition at reduced temperatures. It also has good solubility which makes it, to use widely in organic electronics [1-2], in device fabrications, especially OFETs [3-6], OPVs [7] OLEDs [8-9], and ECDs. Since it has relatively low optical energy gap two polymorphs are known for quaterthiophene. They are low temperature (4T/LT) and high temperature (4T/HT) polymorphs. Both polymorphs show monoclinic structure.

Organic semiconductors are on high demand because of their suitability for microelectronics and nanotechnology applications. Among them, α-oligothiophenes (α-nT) are widely discussed. α-4T, which is one of the ologomers of thiophene, some of which are highly promising for application in thin film transistor devices. Major studies done are based on the polycrystalline form of α-oligothiophenes but both single crystals and oriented films are required for many applications. They are suitable for optical and electrical devices also. The greater solubility of α-4T makes it a more likely candidate for solution phase film deposition. The possibility to dissolve α-4T in most common organic solvents at room temperature is an unquestionable advantage in terms of processability of the organic semiconductor. For α-4T, two polymorphs of the bulk phase are known, α-4T/LT (low temperature) and α-4T/HT (high temperature) and single crystals can be grown by vapor transport and solution techniques.

Siegrist et. al [10] presented crystal structure data obtained from single crystals of the two polymers of α-4T. Extended Huckel Theory band structure calculations are presented, which shows that the α-4T polymorphs are indirect band gap semiconductors with the valence band maximum at Γ. Various structural studies on single crystals of oligomers of thiophene are referred in this work, that includes terthophene, dimethylquaterthiophene, sexithiophene and octithiophene. From those studies, they assumed that structural studies of the tetramer were based on Rietveld method using powder diffraction data and crystal growth has proven difficult. Also the investigations in

crystal growth of α-6T produced platelet shaped crystals of both polymorphs with lateral dimensions up to centimeters and thickness of the order of few micrometers to 10 micrometer. By making use of the growth method devised for α-6T, they suggest the growth of suitable single crystal of α-4T.

II. EXPERIMENTAL

Thin films of Quaterthiophene were deposited on chemically cleaned glass substrates kept at room temperature by thermal vacuum deposition method using HIND HIVAC coating unit (12A, 4D India) under a high vacuum of 10^{-6} Torr. 96% pure Quaterthiophene (from Sigma Aldrich India) was used as the source material. It was evaporated in Molybdenum boat at an evaporation rate of 20 Å/s to form thin films of thickness 1500 Å. The deposition rate and thickness were controlled by a digital quartz crystal thickness monitor. The RT prepared films were annealed at 80^0C, 100^0C and 120^0C below the glass transition temperature. X-rays (Cu K_α radiation) of wavelength 1.5409 Å was used in diffractometer. The X-ray diffraction patterns of the films were taken using Shimadzu 610 A diffractometer. Diffractograms with intensities verses angle of diffraction over a wide range of 2θ from 3^o to 50^o at RT and different annealing temperatures were plotted . XRD pattern of thin films with pre and post annealing treatment were analyzed. The grain Size and inter planar spacing were estimated using Scherrer formula and Bragg's equation. Prominent peaks were indexed and identified.

III. RESULTS AND DISCUSSIONS

During the formation of thin films by vacuum vapour deposition, the vapours are formed at high temperature and get deposited on a substrate maintained comparatively at a low temperature. Due to the sudden change in temperature during the formation of film, mechanical stresses will be developed with in the film. This makes the atoms arranged less orderly within the film. It makes it more brittle. In order to avoid the mechanical stresses formed during the preparation the thin film samples are annealed. To make the study more systematic, the prepared samples are annealed at different temperatures ($80\ ^0$C, $100\ ^0$ C, and $120\ ^0$ C) below the glass transition temperature.

The intensity of the x-ray diffracted beams are determined by Braggs equation $2d\sin\theta = n\lambda$. Variation of intensity versus angle of diffraction for RT film and films annealed at 80 ^{o}C, 100 ^{o}C and 120 ^{o}C are shown respectively in Figures 3 to 6. At RT, the first prominent peak corresponds to $2\theta = 5.915^o$. At annealed temperatures of 80 ^{o}C, 100 ^{o}C and 120 ^{o}C the first prominent peak corresponds to 5.845^0, 5.847^0 and 5.828^0 respectively. In X-Ray diffractogram the indexing of prominent peaks of Quaterthiophene are carried out and the peaks are identified [11]. From the XRD spectra it is obvious that at RT the prominent peaks are respectively in (002), (004), (006) and (008) directions corresponding to $2\theta = 5.915^o$, 11.688^o, 17.604^o and 23.397^0. The prominent peaks obtained are in good agreement with the reported results. The position of prominent peaks obtained at RT and at different annealing temperatures are tabulated and presented in Table.1. It is seen that the positions of prominent peaks almost remain unaltered with the pre and post annealing treatment. The intensities of prominent peaks, pre and post annealing treatments are given in Table.2.

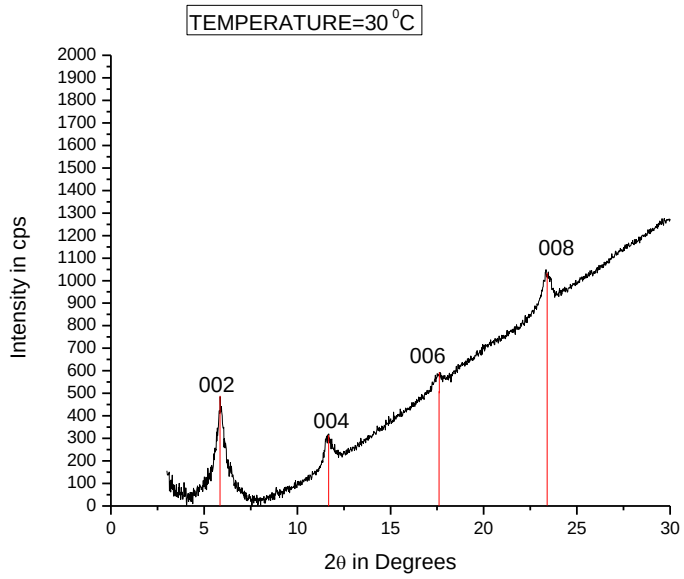

Figure 1: X-ray diffraction pattern of a RT deposited Quaterthiophene thin films with indexed

prominent peaks .

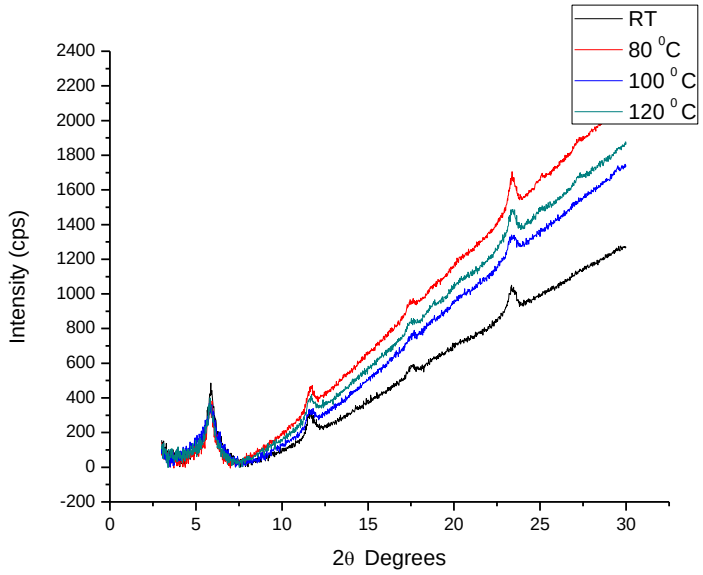

Figure 2: X-ray diffraction pattern of RT deposited Quaterthiophene thin films at RT and various Vacuum annealed temperatures.

Serial No.	Temperature ^{0}C	Position of prominent peaks(2θ)- Degrees			
		Peak(002)	Peak(004)	Peak(006)	Peak(008)
1	30	5.915	11.688	17.604	23.397
2	80	5.845	11.599	17.467	23.307
3	100	5.847	11.622	17.576	23.326
4	120	5.828	11.608	17.553	23.409

Table 1: Positions of prominent peaks (pre and post annealing treatment)

Serial No.	Temperature ^{0}C	Intensity of prominent peaks-Cps			
		Peak(002)	Peak(004)	Peak(006)	Peak(008)
1	30	489.05	322.72	590.70	1043.50
2	80	378.06	470.44	969.30	1689.88
3	100	368.92	341.20	783.34	1337.79
4	120	402.33	420.81	855.13	1483.51

Table 2: Intensity of prominent peaks (pre and post annealing treatment)

By using the equation $2d\sin\theta = n\lambda$, the inter planar spacings are calculated shown in table 3. This is found to be maximum at RT. As the annealing temperature increases from 80 ^{o}C to 120 ^{o}C the inter planar spacing decreases. It is very obvious that the value of Grain size is found to be the minimum at RT. It is also observed that the Grain size increases with the increase in the annealing temperatures from 80 ^{o}C to 120 ^{o}C. This is attributed to the ordering of the grain size with annealing temperature.

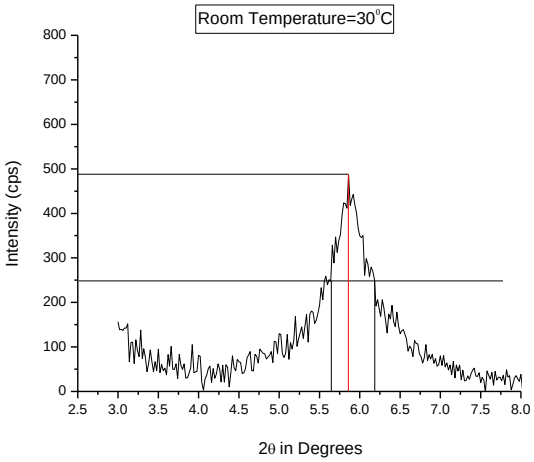

Figure 3: X-ray diffraction pattern for a RT deposited Quaterthiophene thin films.

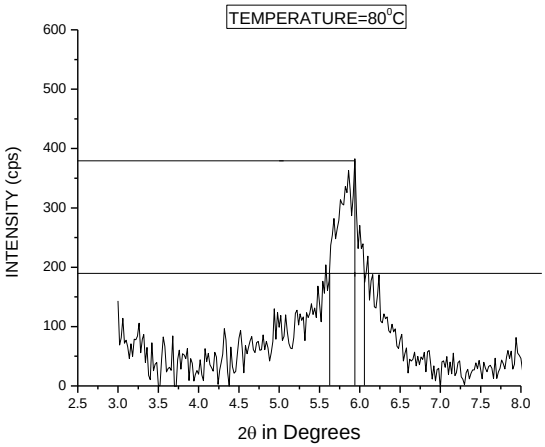

Figure 4: X-ray diffraction pattern for a RT deposited Quaterthiophene (vacuum annealed at 80 °C) thin films.

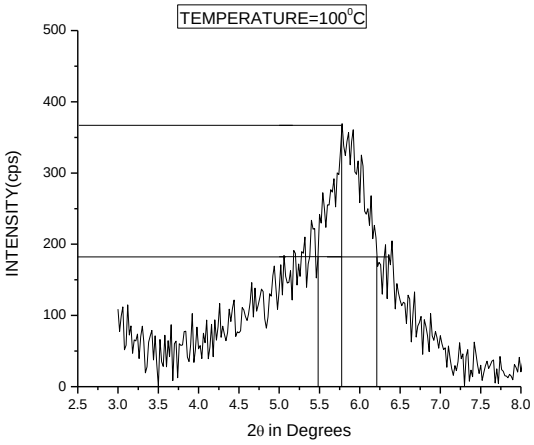

Figure 5: X-ray diffraction pattern for a RT deposited Quaterthiophene (vacuum annealed at 100 °C) thin films.

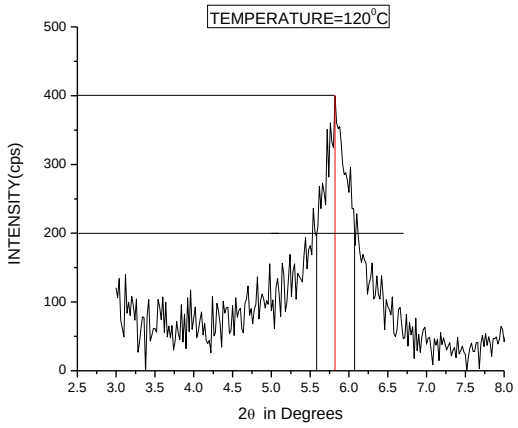

Figure 6: X-ray diffraction pattern for a RT deposited Quaterthiophene (vacuum annealed at 120 °C) thin films.

The inter planar space as calculated using the equation $d = n\lambda/(2\text{Sin}\theta)$ and grain size as calculated from the Scherrer formula, $D = (0.94\lambda)/(\beta_{1/2}\cos\theta)$ are tabulated in Table 3.

Annealing temperature				**FWHM/2**	**Grain size**	**Inter planar space**
	X1	X2	2θ	$\beta_{1/2}$	$D=(0.94\lambda)/(\beta_{1/2}\text{COS}\theta)$	$d=n\lambda/(2\text{Sin}\theta)$
Degree Centigrade			Degrees	Radians	Angstrom units	Angstrom units
30	5.65	6.18	5.91	0.103	14.047	4.212
80	5.63	6.06	5.85	0.102	14.215	3.547
100	5.48	6.21	5.84	0.102	14.212	3.555
120	5.58	6.07	5.83	0.102	14.256	3.416

Table 3: Structural parameters of vacuum annealed QT thin films

IV. CONCLUSIONS

Structural characteristics of thermally evaporated and vacuum deposited Quaterthiophene thin films were investigated. The Quaterthiophene thin films have maximum inter planar space and minimum grain size at RT. From the results it is seen that the grain size increases with increase in annealing temperature and the inter-planar space decreases the increase in annealing temperature which may be attributed to the ordering of the grain size with annealing temperature. In the x-ray diffraction pattern, the indexing of prominent peaks of Quaterthiophene were carried out and the peaks were identified for (002), (004), (006) and (008) directions. The position of the prominent peaks are found to be unaltered with the annealing treatments.

References

[1] A. L. Briseno, T. W. Holcombe, A. I. Boukai, E. C. Garnett, S.W. Shelton, J. J. M. Frechet, and P. D.

Yang, "Oligo- and polythiophene/ZnO hybrid nanowire solar cells" Nano Lett. 10 **(2010) 334–340.**

[2] K.N. Narayanan Unni, Remi de Bettignies, Sylvie Dabos-Seignon and Jean-Michel Nunzi, "A nonvolatile memory element based on a quaterthiophene field-effect transistor", Mater. Lett. 59 **(2005) 1165-1168..**

[3] E.Katz, Organic molecular solids as thin film transistor semiconductors. J. Mater. Chem. **7** (1997) 369-376.

[4] H. Meng. J. Zheng. A.J. Lovinger, B.-C. Wang. P.G. Van Pattern, Z. Bao, Chem. Mater. **15** (2003) 1778.

[5] A. Facchetti, M. Mushrush, H.E. Katz, T.J. Marks, Adv. Mater. **15** (2003) 33.

[6] D.M. Delongchamp, S. Sambasivan, E.K.L. Fischer. P. Chang, A.R. Murphy, J. M. J. Frechet, V. Subramannian, Adv. Mater. **17** (2005) 2340.

[7] K. Hara. M. Kurashige, Y. Dan-Oh, C. Kasada, A. Shinpo, S. Suga, K. Sayama, H. Arakawa, New J. Chem. **27** (2003) 783.

[8] M. Paisini, S. Destri, W. Porzio, C. Botta, U. Giovanella, J. Mater. Chem. **13** (2003) 807.

[9] M. Suzuki, M. Fukuyama, Y. Hori, S. Hotta, J. Appl. Phys**. 91** (2002) 91, 5706

[10] T. Siegrist, C. Kloc, R.A. Laudise, H.E. Katz, R.C. Haddontrs, Adv. Mater. **10** (1998) 379.

[11] Matteo Tonezzer, Optimization of nanostructured materials towards gas sensing, Doctoral Thesis**,(2012)** 112.