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Title	X線反射率測定によるポリヘキシルチオフェン超薄膜の構造評価
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Citation	
Issue Date	2006-03
Type	Thesis or Dissertation
Text version	none
URL	http://hdl.handle.net/10119/3228
Rights	
Description	Supervisor:佐々木　伸太郎教授，材料科学研究科，修士

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Structural evaluation of polyhexylthiophene ultra-thin films by X-ray reflectivity measurements

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March 2006

1. Introduction

π-Stacking is one of the central themes in recent organic, biochemical, and polymer chemistry[1]. Various planar aromatic molecules form the stacked structure, in which the plane-to-plane distance is in the range of 3.4－3.8 Å[1]. Thin films of π-conjugated polymers are widely used for the fabrication of optoelectronic and electronic devices. More detailed studies are needed for structure evaluation of thin films. It was recently reported that nondoped HT-P3HexTh molecules formed an ordered, stacked structure with the hexyl side chains oriented perpendicularly to the surface of a SiO_2/Si substrate when the polymer was spin-coated on the substrate.[8][9] The nanostructure of thin films of regioregular head-to-tail poly(3-hexylthiophene-2,5-diyl) (HT-P3HexTh) was studied by X-ray reflectivity measurements.

2. Experimental

HT-P3HexTh films were offered from Prof. Yamamoto (Chemical Resources Laboratory, Tokyo Institute of Technology). Five specimens (No. 1－5) of thickness less than 10 nm were prepared by spin-coating

method on Al_2O_3 (001) plates. Reflectivity profiles were measured with Cu Kα radiation (wavelength $\lambda = 1.5418$ Å) by using an ordinary XRD diffractmeter with the specular reflection condition at room temperature. The range of reflection angle (2θ) was 1－10 °. The interference pattern from surface of thin film and the film-substrate interface is expressed by

$$I(q) = q^{-4}\{K_1 + K_2\cos(qL)\} \cdot \exp(-q^2A^2) \qquad (1)$$

where $q = 4\pi \sin\theta / \lambda$, L is film thickness and A is surface roughness (square root of square average of deflection from height of average). K_1 and K_2 are constants. Thickness (L) and surface roughness (A) of the films were analyzed by Fourier transformation of X-ray reflectivity profiles. Surface images were obtained by atomic force microscopy (AFM), from which surface roughness was evaluated.

3. Results and Discussion

X-ray reflectivity profile and the Fourier transformation of sample No.1 is show in Figure 1, which gives $L = 1.7$ nm and $A \cong 0.3$ nm. This thickness corresponds to the size of the molecule (1.65 nm). The data are listed in Table 1. The roughness A = 0.3－0.4 nm increased with L. The roughness estimated by AFM was comparable to X-ray reflectivity data. The evaluated values of thickness were not discrete with a specific interval. The molecular chains were stacked without preferred orientation on the substrate.

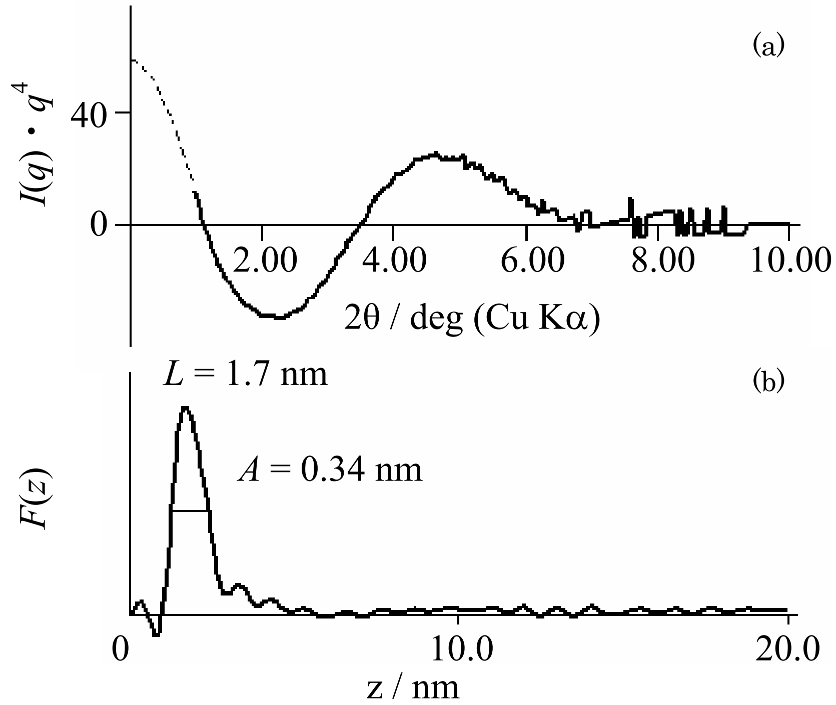


Figure 1. (a) X-ray reflectivity profiles of sample No. 1 and (b) the Fourier transform.

Table 1. Data of HT-P3HexTh thin films

No.	X-ray reflectivity		AFM
	thickness (L / nm)	roughness (A / nm)	roughness (A / nm)
1	1.7	0.34	0.30
2	2.8	0.37	0.40
3	4.2	0.42	0.40
4	5.1	0.51	0.49
5	6.5	0.43	0.44
substrate	−	0.17	0.08

Effect of heat treatments on L and A was investigated. The dependence of L and A on annealing temperature of No. 5 is show in Figure 2. Thickness has increased by 10—15 % while maintained during one year. This increase is due to the oxidation reaction which happens at C^{α} atoms of the side chains (Scheme 1.). The thickness of samples has decreased gradually by the stepwise heat treatment (Figure 2.). It was attributed to the thermal decomposition of the side chains.

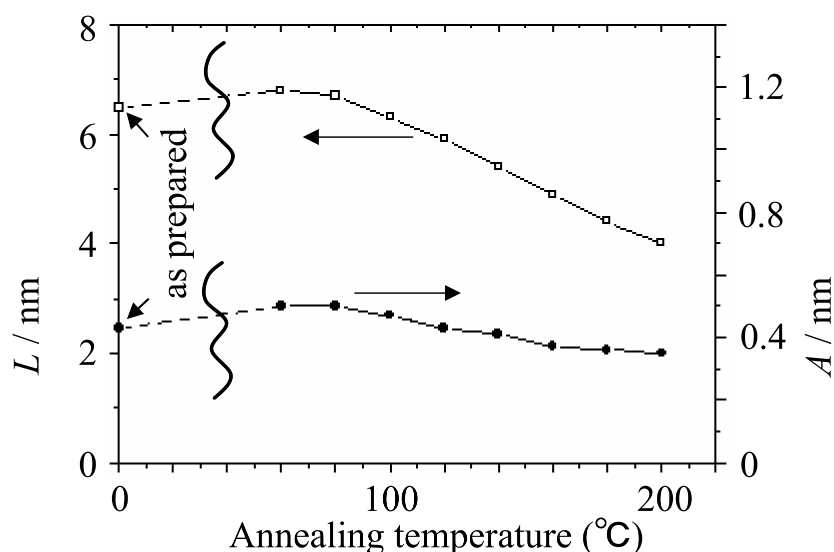
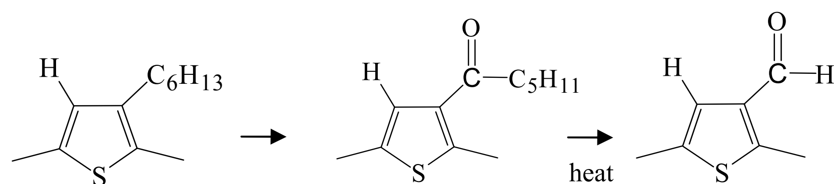


Figure 2. Effect of heat treatments on thickness (L) and surface roughness (A) of sample No. 5. The sample was annealed at each temperature for 1h in vacuum.



Scheme 1. Chemical change in thiophene unit.