# Surface Electronic Structures of Polythiophene Derivatives

*X. T. Hao,*[*1] *T. Hosokai,*[2] *N. Mitsuo,*[2] *S. Kera,*[2] *K. Sakamoto,*[1,2] *K. K. Okudaira,*[1,2] *N. Ueno*[1,2]

**Summary:** We report the surface electronic structures of polythiophene derivatives (including polythiophene, poly(3-butylthiophene), poly (3-hexylthiophene)(P3HT)) thin films observed by ultraviolet photoelectron spectroscopy and Penning ionization electron spectroscopy. He$^*$-impact-surface-modification was applied on the P3HT surface to control the distribution of the electron density.

**Keywords:** conjugated polymers; PIES; surface electronic properties

## Introduction

Polythiophene and its derivatives are the first conducting polymers that are stable toward oxygen and moisture. Studying surface electronic structures in these conjugated polymers is extremely necessary for their application to organic devices, such as thin film transistors, solar cells etc.[1,2] To achieve efficient charge transfer in these layer-structured devices, it is crucial that $\pi$ electronic wave functions overlap between these underlying polymer layer and the overlayer molecules. In this context, to observe the electronic states tailing outside the conjugated polymer surface is critically essential. The ordinary spectroscopic techniques using photons like ultraviolet photoelectron spectroscopy (UPS) (Figure 1) can probe the electronic density distributed at the top ~1 nm layer inside surface. Penning ionization electron spectroscopy (PIES) using metastable atoms as probes,[3] can observe the outermost surface electrons selectively since metastable atoms do not penetrate into the bulk of solid (Figure 1).

In this study, surface electronic structures of polythiophene derivatives (including polythiophene (PT), poly(3-butylthiophene) (P3BT), poly(3-hexylthiophene) (P3HT)) thin films were observed by UPS and PIES. Furthermore, He$^*$-impact-surface-modification was applied on the P3HT thin film with different conformations to control the distribution of electron density at the outermost surface.

## Experimental Part

The polythiophene derivatives were purchased from Sigma-Aldrich Co. Ltd and used without further purification. The PT thin films were vacuum deposited by evaporating the powder onto the Au/SiO$_2$/Si substrates and measured without breaking vacuum. The P3BT and P3HT powder were dissolved into chloroform and were then spin cast onto the Au/SiO$_2$/Si substrates. The solution concentration for P3BT and P3HT was 5mg/mL and the thin films were spin coated with speed of 3000 rpm. Another P3HT thin film was also spin coated by solution with concentration of 0.5mg/mL and spin speed of 400 rpm to get different conformation. The spin coated thin films were then loaded into the UHV chamber immediately and kept for several hours to remove the solvent residual before measurement. The samples were also annealed

---

[1] Faculty of Engineering, Chiba University, Chiba 2638522, Japan
Fax: +81-43-207-3796
E-mail: xt-hao@restaff.chiba-u.jp; dr.xthao@gmail.com

[2] Graduate School of Science and Technology, Chiba University, Chiba 2638522, Japan

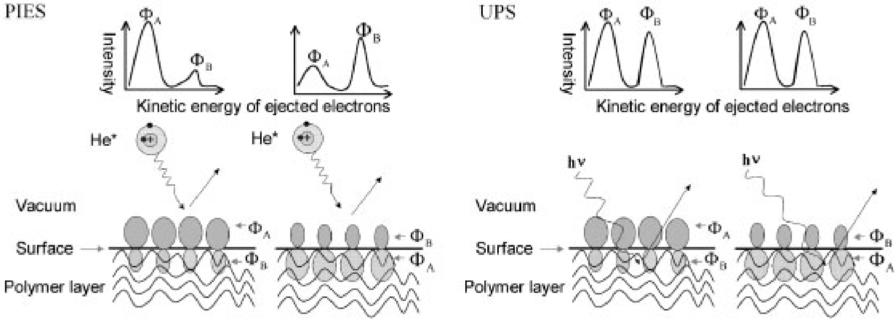

*Figure 1.*
Schematic diagrams showing working mechanism of Penning Ionization Electron Spectroscopy (PIES) and Ultraviolet photoelectron spectroscopy (UPS) on polymer surface.

at 453 K for one hour to further remove the contamination and improve the crystallinity. UPS and PIES spectra were measured by an ultrahigh vacuum electron spectrometer[4,5] with a newly equipped 180° hemispherical deflection-type analyzer (PHOIBOS 100).

## Results and Discussion

The distribution of the electronic states near surface (~1nm) and outermost surface of the polythiophene derivatives can be observed by UPS and PIES, respectively. Figure 2 (a) gives the UPS spectra of different polythiophene derivatives. From the spectra, it can be seen clearly that the electronic structure in the low binding energy (0–5 eV) has very similar feature for all the thin films. This indicates that attaching long flexible side alky chains to polythiophene (PT) could increase the solubility and processiblity of the polymer without significantly changing the $\pi$ electronic structure.[6] The stronger peak located at about $3 \sim 5$ eV corresponds to the localized $\pi$ states contributed from S 3p and

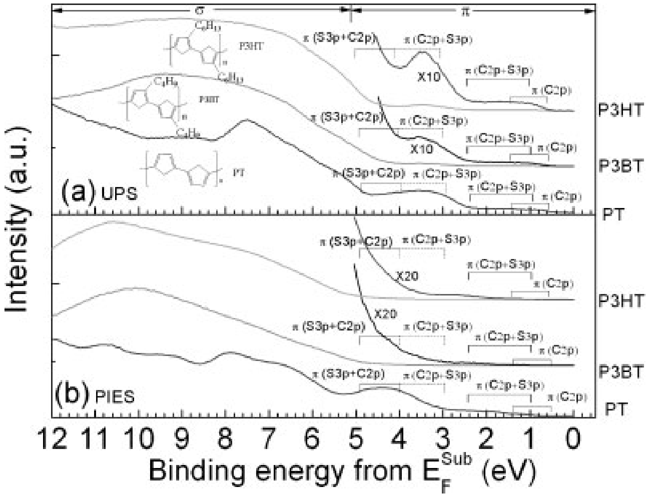

*Figure 2.*
The HeI UPS spectra (a) and PIES spectra (b) of polythiophene derivative thin films on Au/$SiO_2$/Si substrates. S3p+C2p denotes that states contributed from S 3p AO give more contribution than C2p to the feature in the spectra, while C2p+S3p gives the reverse meaning.

C 2p atomic orbitals (AOs). The observed $\pi$ states whose feature located around ~0.5 ~1 eV in UPS spectra is due to the strongly delocalized nature of HOMO state of C 2p AOs, while the feature around ~1 to ~2.5 eV comes from contribution of C 2p and partly contribution S 3p AOs. No clear discernable features appear for the spin-coated samples between 5 to 12 eV which are related to the $\sigma$ states from the main chain and the hexyl side groups due to the complexity of the polymer structure. The $\sigma$ states of the main chain can be observed clearly for the vacuum deposited PT films due to the better crystallinity and no influence of alkyl side chains.

Figure 2 (b) depicts the PIES spectra of different polythiophene derivatives. Considering the surface sensitivity of PIES, the observed features should be dominated by the electron density tailing outside the polymer surface. Clear features can be seen in the whole region of the spectra for PT thin film since the vacuum deposited film has well ordered crystalline structure and no alkyl chains. For P3BT and P3HT, the $\pi$ states (~1 ~ 2.5eV) and (~3 ~ 5 eV) contributed by C 2p and S 3p AOs are shown clearly in the spectra, indicating that the related electronic wave function is spreading outside the surface rather than shielded by the alkyl-chain. Correspondingly, the HOMO molecular orbital whose feature should be located at ~0.5 to ~1 eV is believed to be facing to the vacuum at the polymer surface although it cannot be detected by He* metastable atoms because S 3p AO spread more widely and may screen the interaction between He* and HOMO electronic wave function. Otherwise, the peak position difference between UPS and PIES may be due to the difference of AO distribution at surface region and the outermost surface. Comparing the spectra of PT, P3BT and P3HT thin film in the low binding energy (0–5 eV), the $\pi$ electronic structure is found to be conserved approximately after attaching the side alkyl chain onto the polymer backbone. The difference in the higher binding energy region (larger than 5 eV) comes from the effect of the $\sigma$ electronic states brought by the attached alkyl chains.

Apparently, $\pi$ electronic states from polymer backbone extending outside the surface can easily form $\pi$–$\pi$ wavefunction overlap with overlayer molecules. To get the $\pi$ electronic states exposed outside the surface, He*-impact-surface-modification[7] was employed on the P3HT film with different molecular orientation to remove the side chains that block these $\pi$ electronic states. A ''pure'' surface reaction is expected using He*-metastable-atom-beam to cut the side chains at outermost surface without penetrating inside the surface. On the other hand, it has been reported that the molecular orientation for P3HT thin films can be controlled by adjusting the coating parameters.[8,9] PIES was employed to observe the variation of the $\pi$ electronic states distribution at the outermost surface after He* surface modification on P3HT thin films with face-on conformation (concentration: 5mg/mL; spin speed: 3000 rpm) and edge-on conformation (concentration: 0.5mg/mL; spin speed: 400 rpm).[9]

Figures 3 and 4 give the PIES spectra of P3HT thin films (face-on and edge-on conformation, respectively) showing surface modification effects. Insets are the corresponding UPS spectra. It can be seen from the spectra that features related to $\pi$ states in the low binding energy region (0–5eV) becomes clearer and more intense for thin films with both conformations after surface modification. Note that the HOMO state of C 2p (~0.5 to ~1 eV) cannot be observed because widely spreading S 3p AO may screen the interaction between He* and HOMO electronic wave function. The substraction of weak bonded hydrogen atoms may mainly occur in the hexyl side chains due to the bombardment of He*, followed by the formation of new chemical bonds (C=C double bonds).[7,10] For the face-on conformation, the newly formed C=C bonds may change the zigzag conformation of the alkyl side chains to a conformation that gives the $\sigma$ states with stronger intensity along these side-chains showing more intense shoulder in the range

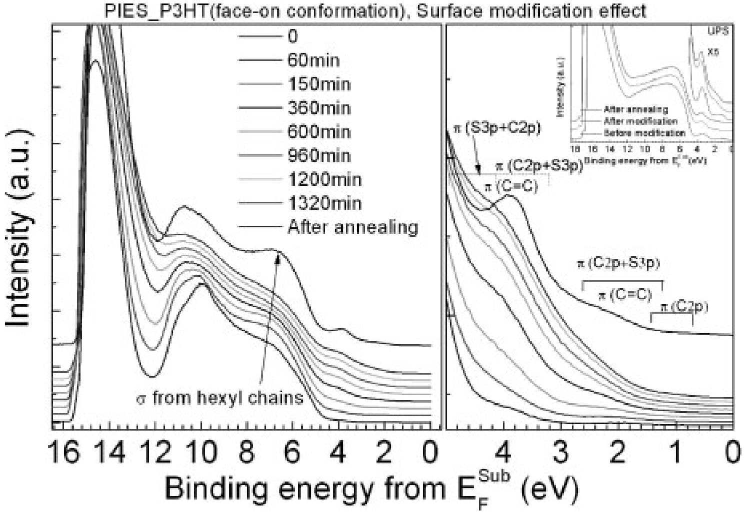

***Figure 3.***
The PIES spectra of P3HT thin films (face-on conformation) showing surface modification effect. Inset is the corresponding UPS spectra.

of 6–8 eV. On the other hand, for the sample with edge-on conformation, the changing of the alkyl side chain conformation would also possibly alter the main chains to be face-on conformation at the surface region since π states from the polymer backbone and the σ states along the alkyl side chains can be observed clearly by PIES. The newly formed bonds may induce disorder to the stacking lamella

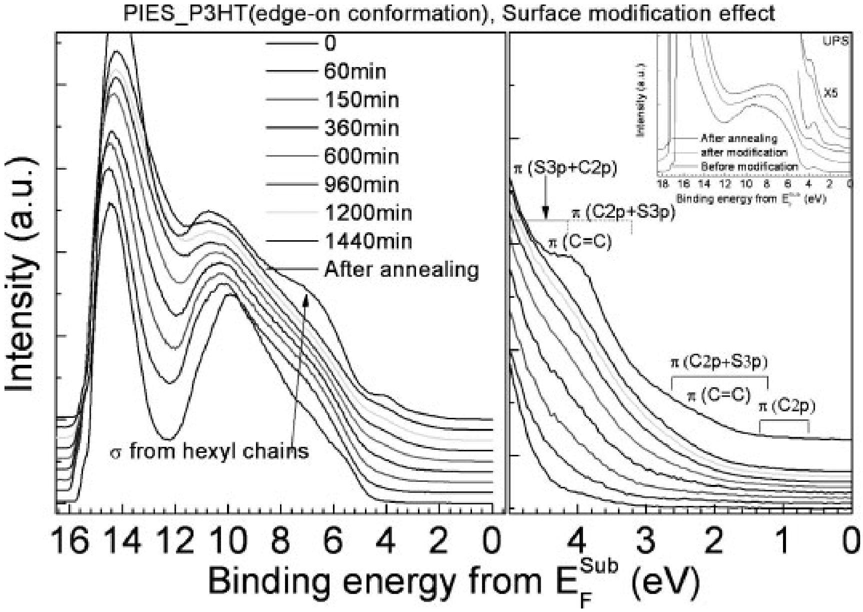

***Figure 4.***
The PIES spectra of P3HT thin films (edge-on conformation) showing surface modification effect. Inset is the corresponding UPS spectra.

structure of P3HT thin films, which results in the peak broadening of the features in the spectra. However, it could possibly be recovered by annealing the samples at 453 K for one hour Therefore, PIES spectra give clear features for the $\pi$ states derived from C 2p and S 3p, and $\sigma$ states from side chains after annealing as shown in the top curves of Figures 3 and 4. In addition, it is noteworthy that the AOs of the newly formed C=C double bonds may also partly contribute to the stronger intensity of the $\pi$ states in the range of $\sim$1$\sim$2.5 eV and $\sim$3$\sim$5 eV.[7,10]

## Conclusions

In summary, UPS and PIES were employed to observe the surface electronic structures of conjugated polythiophene derivatives. Especially, PIES was adopted to probe the electronics density tailing outside conjugated polymer surface. The spectra were measured and compared for different polythiophene derivatives (including PT, P3BT and P3HT). The He$^*$ metastable surface modification was employed on the P3HT surface with different conformations to get the $\pi$ electron density tailing outside the polymer surface.

[1] A. J. Cascio, J. E. Lyon, M. M. Beerbom, R. Schlaf, Y. Zhu, S. A. Jenekhe, *Appl. Phys. Lett.* **2006**, *88*, 062104.

[2] H. Sirringhaus, P. J. Brown, R. H. Friend, M. M. Nielsen, K. Bechgaard, M. M. W. Langeveld-Voss, A. J. H. Spiering, R. A. J. Janssen, E. W. Meijer, P. Herwig, D. M. Leeuw, *Nature* **1999**, *401*, 685.

[3] Y. Harada, S. Masuda, H. Ozaki, *Chem. Rev.* **1997**, *97*, 1987.

[4] K. K. Okudaira, S. Kera, H. Setoyama, E. Morikawa, N. Ueno, *J. Electron Spectros. Relat. Phenom.* **2001**, *121*, 225.

[5] X. T. Hao, T. Hosokai, N. Mitsuo, S. Kera, K. Sakamoto, K. K. Okudaira, N. Ueno, ICSM Conference**2006**, F11, Dublin, Ireland.

[6] A. O. Patil, A. J. Heeger, F. Wudl, *Chem. Rev.* **1988**, *88*, 183.

[7] H. Setoyama, S. Kera, K. K. Okudaira, M. Hara, Y. Harada, N. Ueno, *Jpn. J. Appl. Phys.* **2003**, *42*, 597.

[8] D. M. Delongchamp, B. M. Vogel, Y. Jung, M. C. Gurau, C. A. Richter, O. A. Kirillov, J. Obrzut, D. A. Fisher, S. Sambasivan, L. J. Richter, E. K. Lin, *Chem. Mater.* **2005**, *17*, 5610.

[9] X. T. Hao, T. Hosokai, N. Mitsuo, S. Kera, K. Mase, K. K. Okudaira, N. Ueno, *Appl. Phys. Lett.* **2006**, *89*, 182113.

[10] F. Amy, C. K. Chan, W. Zhao, J. Hyung, M. Ono, T. Sueyoshi, S. Kera, G. Neshe, A. Salomon, L. Segev, O. Seitz, H. Shpaisman, A. Scho1l, M. Haeming, D. Cahen, L. Kronik, N. Ueno, E. Umbach, A. Kahn, *J. Phys. Chem. B*, **2006**, *110*, 21826.