

Local Electronic Structure of EG treated PEDOT : PSS Thin Films

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1 Introduction

Poly (3,4ethylenedioxythiophene) : poly (4styrene sulfonate) (PEDOT: PSS) has attracted considerable attention due to its superior electrochemical stability and transparency, which can be used as a possible alternative to ITO(Indium Tin Oxide). [1] As-prepared film from the PEDOT:PSS dispersion typically has a conductivity of $\sim 0.1 - 1$ S/cm, which is three or four orders of magnitude lower than that of ITO. Recently It was reported that the conductivity of the PEDOT:PSS thin film could be increased by 2 to 3 orders of magnitude by adding certain additives into the dispersion prior to film deposition or by treating the films with certain solvents or acids post deposition such as ethylene glycol (EG), diethylene. [2]

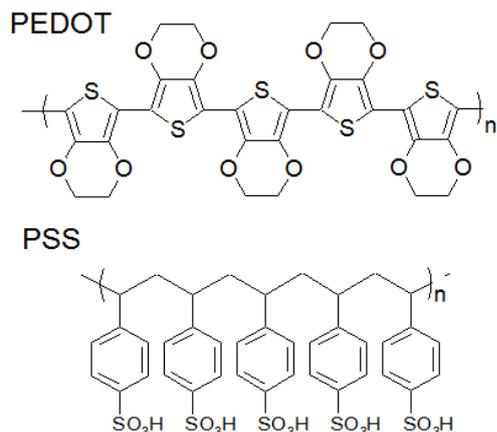


Fig.1 Molecular structure of PEDOT and PSS

The electrical conductivity strongly depends on the electronic structure of the valence region. It is important to clarify the electronic structure of valence of PEDOT, which is responsible for conductivity of PEDOT:PSS system

In this paper, we report on the surface-site-selective sulfur (S) L VV Auger electron spectroscopy, S 2p photoelectron spectroscopy (PES) and Auger photoelectron coincidence spectroscopy (APECS) of PEDOT:PSS system. The S L VV-S 2p APECS indicated that the electronic structure of valence band in the vicinity of the S atom not only in PEDOT but also PSS.

2 Experiment

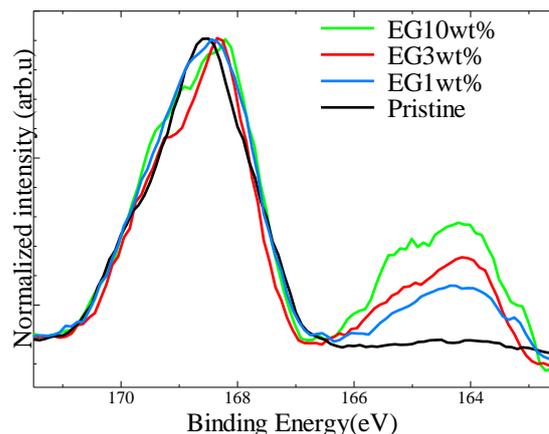
The PEDOT:PSS films were spin cast from the PEDOT:PSS aqueous dispersion (Clevios P AI4083, weight ratio of PEDOT to PSS = 1:6) onto ITO, which

were sonicated in acetone 10 min. The deposited PEDOT:PSS films were immersed in EG solution at various concentration (1wt%, 3wt%, and 10wt%).

The sample was irradiated with p-polarized SR with an incidence angle of 84° from the surface normal at the beamline 11C of the SR facility in KEK [Photon Factory (PF)]. A coincidence analyzer that can be used for Auger, PES, and APECS. Auger, PES, and APECS were observed at $h\nu = 203\text{eV}$. The energy resolution ($E/\Delta E$) of both the ASMA and the DP-CMA is ~ 36 in the electron kinetic energy range of 20–100 eV [3]

3 Results and Discussion

Figure 2 shows sulfur (S) (2p) PE spectra of PEDOT:PSS films dipped EG solution. The spectra display two contributions. The S(2p) signal for PSS appears at higher binding energy (BE) of 168.5eV due to the three electronegative oxygen atoms withdrawing the electron density of the S atom. The S(2p) doublet at 164.2 eV comes from PEDOT. The probing depth of the spectroscopy is defined by the inelastic mean free path of the S(2p) photoelectrons, is several Å for a kinetic energy of about 30eV. Upon increasing EG concentration the amount of PEDOT at the film surface increases. Furthermore, it is found that the difference of peak position of S(2p) of PSS at a BE of 168eV and that of PEDOT at about 164eV becomes smaller upon increasing EG concentration due to the promotion of charge transfer from PEDOT to PSS. (doping)

Fig.2 Sulfur (2p) PE at $h\nu = 203.3$ eV of PEDOT:PSS pristine and after treated (dipping EG solution with various concentration) films

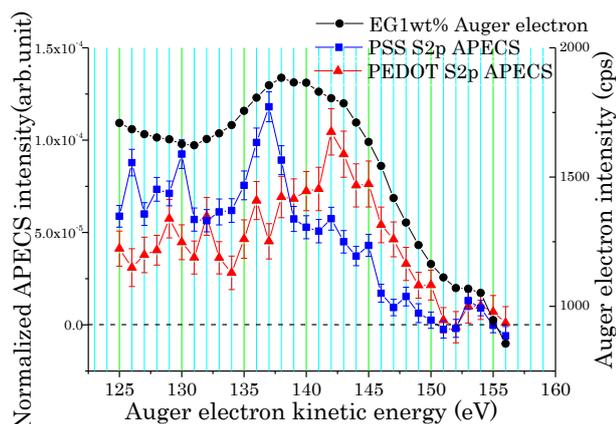


Fig.3 Sulfur(S) L VV-S 2p APECS of PEDOT:PSS film (dipping to EG solution with concentration of 1wt%) measured in coincidence with S 2p photoelectrons at a BE of 168.5eV (PSS) (■) and of 164.2 eV (PEDOT) (▲)

Figure 3 shows S L VV-S 2p APECS of PEDOT:PSS film (dipping to EG solution with concentration of 1wt%) measured in coincidence with S 2p photoelectrons at a BE of 168.5eV (PSS) and of 164.2 eV (PEDOT). The spectral feature of APECS in coincidence with S2p photoelectrons from PSS is largely different from that from PEDOT. The strong peak of APECS in coincidence with S 2p photoelectrons from PEDOT appear at about kinetic energy (E_k) of 143eV, which is larger than that of APECS in coincidence with S 2p photoelectrons from PSS. It reflects the difference between the electronic structure at the vicinity of S atoms in PEDOT, where the S atoms consist of π conjugated system, and that of S atoms in PSS, where the S atoms are part of sulfo group. It shows large density of states distributed in the vicinity of S atoms in PEDOT at relatively lower binding energy region.

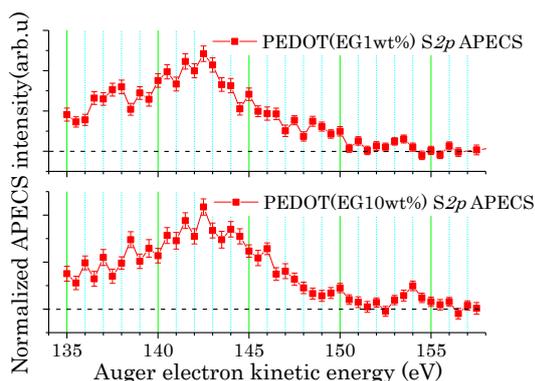


Fig. 4 Sulfur (S) L VV-S 2p APECS of PEDOT:PSS film (dipping to EG solution with concentration of 1wt% (upper panel) and 10wt% (lower panel)) measured in coincidence with S 2p photoelectrons at a BE of 164.2 eV (PEDOT).

Figure 4 shows S L VV-S 2p APECS of PEDOT:PSS film (dipping to EG solution with concentration of 1wt% and 10wt%) measured in coincidence with S 2p photoelectrons at a BE of 164.2 eV (PEDOT). The

APECS of PEDOT:PSS film by dipping to 10wt% EG solution shows a stronger peak at E_k of 154 eV for the comparison with that of PEDOT:PSS film by dipping 1wt% EG solution. It indicates that the new states distributed in the vicinity of S atom of PEDOT by dipping to high concentration EG solution appears near the top of valence region. The conductivity of PEDOT:PSS by dipping to 10wt% EG solution becomes higher by 2-3 orders magnitude than that by dipping to 1wt% EG solution. The states distributed in the vicinity of S atom in PEDOT at near valence band top can be considered to be related to the high conductivity of treated PEDOT:PSS.

4 Conclusion

The local electronic structure of valence region in the vicinity of S atom of PEDOT:PSS film surface can be obtained by APECS. It is found that the electronic structure in the vicinity of S atoms of PEDOT is different from that of PSS. The states in the vicinity of S atoms in PEDOT for high concentration EG treated PEDOT PSS film can be detected at most valence top region and are related to the origin of high conductivity of PEDOT:PSS film.

Acknowledgements

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References

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