MERIT Self-directed Joint Research

Study of the carrier transport mechanism of conducting polymer PEDOT/PSS by terahertz spectroscopy

Makiko Ogino1, Zijing Guo2

1 Department of Applied Physics Takahashi laboratory

2 Department of Advanced Materials Science Okamoto Kida laboratory

Summary

Terahertz spectroscopy (1 meV ~ 10 meV) and broadband reflectivity spectroscopy (10 meV ~ 4 eV) have been performed on thin film samples to investigate the carrier transport mechanism of PEDOT/PSS, a typical conducting polymer. It is known that the DC conductivity of PEDOT/PSS changes with ethylene glycol treating, H^+ doping and de-doping. In this study, we measured the terahertz conductivity of four types of PEDOT/PSS thin films with and without ethylene glycol, H^+ doping, and de-doping. It is found that the relation between the four samples reflected in the obtain terahertz conductivity complies well with that in the DC conductivity, and carrier localization effect was observed in the film without ethylene glycol treatment. In addition to the terahertz conductivity, a broadband conductivity spectrum of the ethylene glycol treated thin film in the far-infrared to visible region was also obtained by measuring the broadband reflectivity spectrum and conducting Kramers-Kronig transformation to it. In the broadband conductivity spectrum, a Drude-like response was observed.

Introduction of authors

Makiko Ogino : Her specialized field is the optics of magnets. In this study, M. Ogino is responsible for the measurement and analysis of terahertz spectrum.

Zijing Guo : Her specialized field is broadband spectroscopy of conducting polymer. In this study, Z. Guo is responsible for the measurement of the spectrum from far-infrared to UV region and the analysis of Kramers-Kronig transformation of the full spectrum.

1． Introduction

Conducting polymers have been attracting attention as the electronic material for the next generation due to their advantages such as high conductivity, lightweight, flexibility, and ease of treatment. On the other hand, due to some advanced structures unlike solid crystals, their carrier transport mechanism remain unclear in most cases. One of the most representative conducting

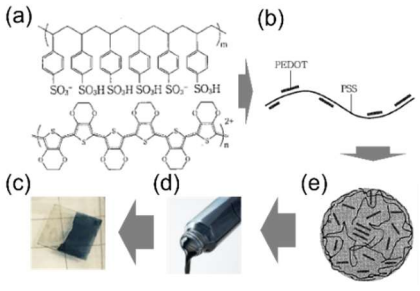

Figure 1 Hierarchical structures of the conducting polymer PEDOT/PSS.

polymers is (3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) (PEDOT/PSS). Figure 1(a) shows the molecular structure of PEDOT/PSS. PEDOT, an oligomer consisting of 6-18 EDOT (3,4-ethylenedioxythiophene) molecules, is oxidized by PSS, a chain polymer strong acid, and therefore becomes doped with carriers (holes). The binding of PEDOT and PSS molecules forms a chain-like secondary structure as shown in Figure 1(b). The chains aggregate to form the colloidal tertiary structure shown in Figure 1(e). This colloid is formed by a shell of PSS chains and an irregular arrangement of PEDOT molecules inside. The colloid can be uniformly dispersed in water (Fig. 1(c)), and thus thin films can be prepared by spin coating (Fig. 1(c)).

There are two representative examples of previous studies on the control of the conductivity of PEDOT/PSS, which contributes to the elucidation of the carrier transport mechanism. One of the studies reports that an addition of a small amount of ethylene glycol (EG) to the aqueous dispersion of PEDOT/PSS increases the electrical conductivity of the thin film by about 100 times, as shown in Figure 2(a) [1]. This is found to be caused by EG promoting the crystallization of the PEDOT molecules inside the colloid, which facilitate the intermolecular transferring of carriers. The second study increases the electrical conductivity of PEDOT/PSS by proton doping. Figure 2(b) shows the electrical conductivity obtained after alternated H^+-doping (sulfuric acid treatment) and de-doping (potassium hydroxide treatment) of EG-treated PEDOT/PSS thin films. When PEDOT/PSS is H^+-doped, a twofold increase from 500 S/cm to 1000 S/cm in electrical conductivity is shown. It is thought that protons become bound to the PEDOT molecules and holes are doped. The protons could also be withdrawn by de-doping, in which case the conductivity decreases to ~1 S/cm.

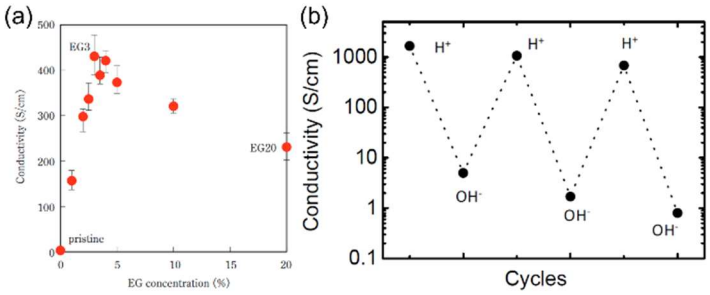

Figure 2 (a) PEDOT/PSS thin film's DC conductivity dependent on different concentrations of ethylene glycol treatment[1].
(b) Reversibility of H^+-doping and de-doping process on EG treated PEDOT/PSS thin film's conductivity. [2]

Although according to the above, conductivity controls in the conducting polymer PEDOT/PSS have been individually achieved, the carrier transport mechanism remains unclear. In this study, we investigated the carrier transport mechanism by observing the optical spectra in the terahertz to ultraviolet region.

2. Experiment

2．1．Sample preparation

The samples were PEDOT/PSS thin films prepared on silica substrates (Fig. 3) thanks to AIST Mukaida-Wei group. Four types of PEDOT/PSS thin films with different conductivity were used: untreated, EG-treated, sulfuric acid-treated (H^+-doped), and potassium hydroxide-treated (de-doped). Since terahertz spectroscopy requires the transmission waveforms of both the substrate and the the thin film+substrate, a part of the thin film sample was removed to allow simultaneous measurement of the transmission waveforms of the substrate and the thin film (Figure 3). Thin films with thicknesses of 100 nm and 800 nm were used.

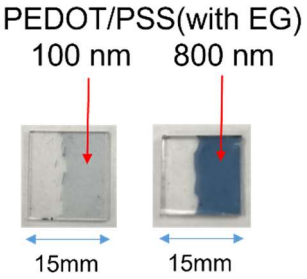

Figure 3 Thin film of PEDOT/PSS on silica substrate.

2．2．Terahertz spectroscopy measurement

We conducted terahertz time domain spectroscopy. A femtosecond laser with a wavelength of 800 nm and a time width of 100 fs was used as the light source. Two photoconductive antennas were used to generate and detect terahertz light. Figure 4 shows the time-domain waveform and the spectrum of the terahertz light used in this experiment. As shown in Fig. 4(b), optical spectrum down to around 10 meV can be measured using this system. Since the absolute intensity and phase of the transmitted electric field waveform could be obtained simultaneously in time-domain spectroscopy, the real and imaginary parts of the optical conductivity can be obtained at the same time.

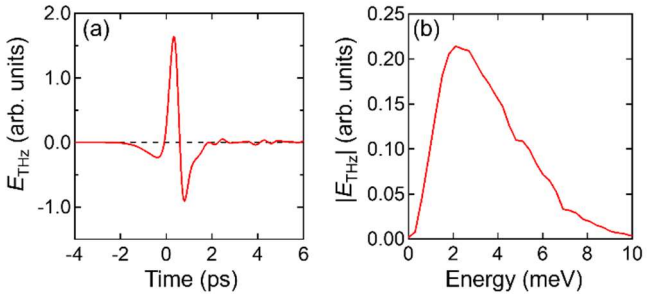

Figure 4 (a) Time domain waveform, (b) Fourier transformed spectrum of terahertz light used in the measurement.

3．Results and Discussion

3．1．Terahertz spectroscopy of PEDOT/PSS with conductivity control

On 4 different types of PEDOT/PSS samples on quartz substrates whose film thickness are about 100 nm: PEDOT/PSS (1) treated only with ethylene glycol (EG) (nondope), (2) without EG treatment (without EG), (3) treated with H_2SO4 after EG treatment (H^+ doped), (4) with treated with KOH after EG treatment (OH^- doped), terahertz time domain spectroscopy (THz-TDS) was performed. Transmittance waveform through vacuum (blank), transmittance waveform through substrate (substrate), transmittance waveform through substrate + sample (sample) were measured respectively for each sample.

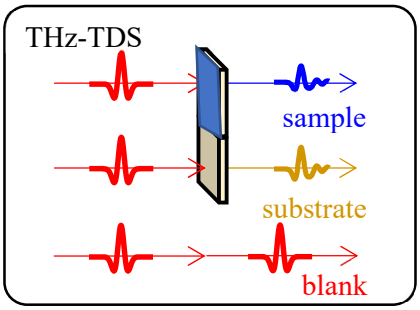

Fig. 5 Terahertz time domain spectroscopy (THz-TDS) on thin film samples.

As an example for detailed analysis, Figure 6 (a) shows the obtained electric field-time waveform when using the nondope PEDOT / PSS sample.

The transmittance spectra of the substrate and thin film of the nondope PEDOT / PSS sample calculated from the electric field-time waveform are shown in Fig. 6 (b) in yellow and blue lines, respectively.

As shown in Fig. 6 (b), the transmittance of synthetic silica, which is the substrate material, decreases toward the high frequency side in the THz region due to an absorption peak. On the other hand, the transmittance spectrum of the PEDOT / PSS thin film shows a relatively flat shape.

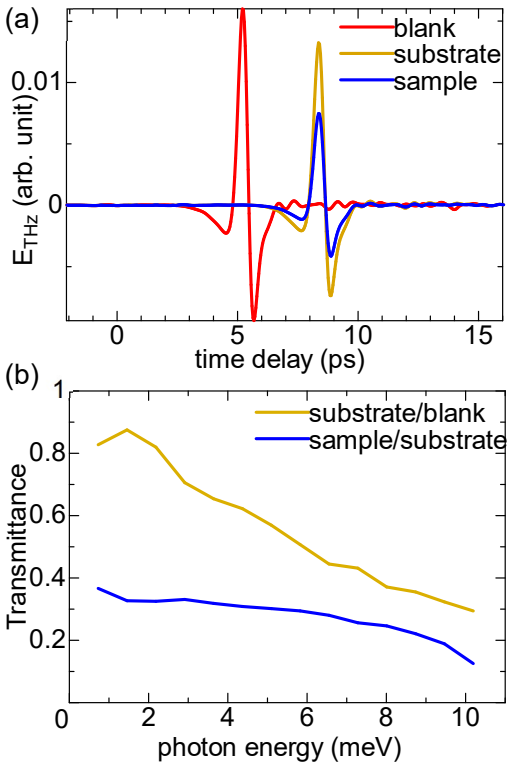

Fig. 6 (a) nondope 100nm PEDOT/PSS Electric field-Time waveform.
(b) nondope 100nm PEDOT/PSS transmittance.

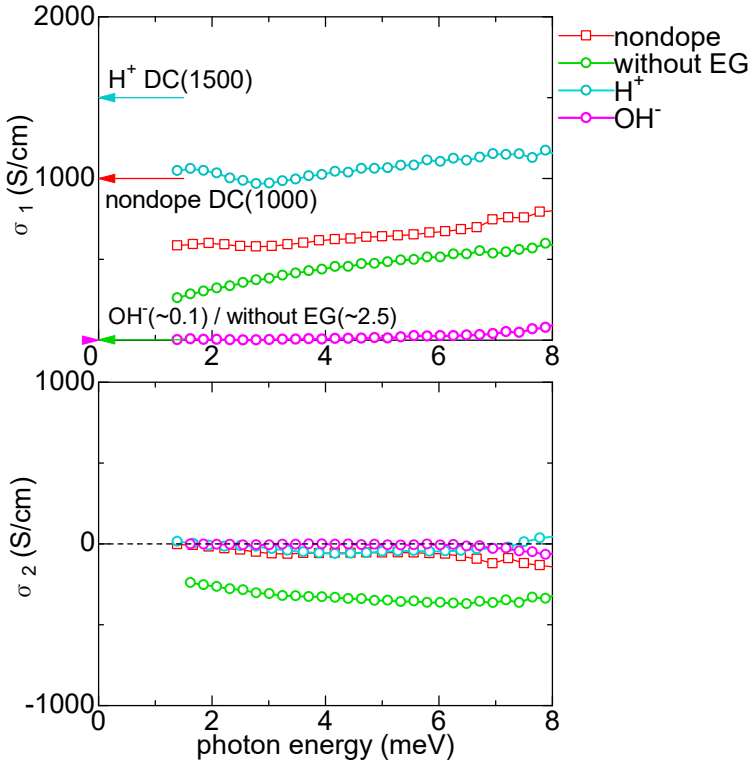

Fig. 7 Terahertz-region conductivity spectrum of PEDOT/PSS samples(film thickness 100 nm) under different conductivity control.

Conductivity was derived to evaluate carrier transport properties. Based on the complex transmittance, the Tinkham formula [3] (see below) for thin film analysis was used to obtain the conductivity spectra of four types of PEDOT/PSS. As shown in Figure 7.

$$t(\omega) = \frac{2N(1+N_S)\exp\left(\frac{i\omega(N-1)d}{c}\right)}{(N+N_S)(N+1)-(N-N_S)(N-1)\exp\left(-\frac{i2\omega Nd}{c}\right)} \quad ※\ N(\omega) = n(\omega) - i\kappa(\omega),$$

$$\sigma(\omega) = \sigma_1(\omega) - i\sigma_2(\omega)\ [E = E_0 e^{-ikx}]$$

In which $t(\omega)$ is the complex transmittance of the thin film depending on the angular frequency, N and N_s are the complex refractive indexes of the thin film and the substrate, respectively, d is the thickness of the thin film, and c is the velocity of light.

The order of conductivity values of the four types of PEDOT/PSS should be H^+ doped, nondope, without EG, and OH^- doped in descending order. This order is consistent with the order of DC conductivities measured formerly.

For the real part of conductivity, the spectrum of nondope sample shows a flat shape, whereas the without EG spectrum tends to decrease towards the low frequency side. For the imaginary part, the spectrum of the without EG sample seems larger than that of the nondope sample. Previous studies [4] observed a same tendency in optical conductivity spectra of samples with (nondope) and without EG (without EG). This is thought to be due to carrier localization in the without EG PEDOT/PSS sample by analysis using the Localization-modified Drude model (LMD). For the samples in this study, it shall also be able to be conjectured that carrier localization is stronger in the without EG sample than that in the H^+ doped or nondope sample.

3．2．Derivation of broadband optical conductivity spectrum of nondope PEDOT/PSS thin film

A broadband complex optical conductivity spectrum was measured for an EG-treated PEDOT/PSS thin film with a film thickness of 800 nm. In the terahertz region, the complex optical conductivity can be directly obtained by transmittance measurement. Since the absorption is large in the far-infrared region and above, only reflectivity measurement is possible. In this way, the complex optical conductivity spectrum is measured by Kramers-Kronig transformation of the broadband reflectivity spectrum.

Specifically, for each energy region, we used Takahashi Laboratory's THz-TDS device for 1.2 ~ 4 meV, Okamoto Laboratory's newly developed THz-TDS device for 4 ~ 10 meV, Fourier-transform infrared spectroscopy (FTIR) device with bolometer for 0.01 ~ 0.1 eV, FTIR with Mercury Cadmium Telluride sensor for 0.1 ~ 0.7 eV, and a visible-UV microspectroscopy device for 0.7 ~ 4 eV.

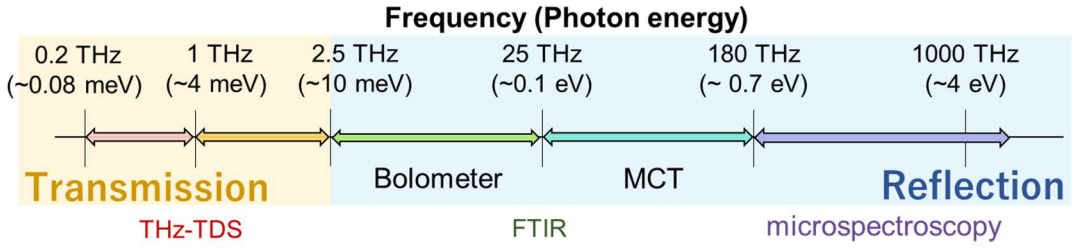

Fig. 8 Spectroscopic methods in each frequency domain.

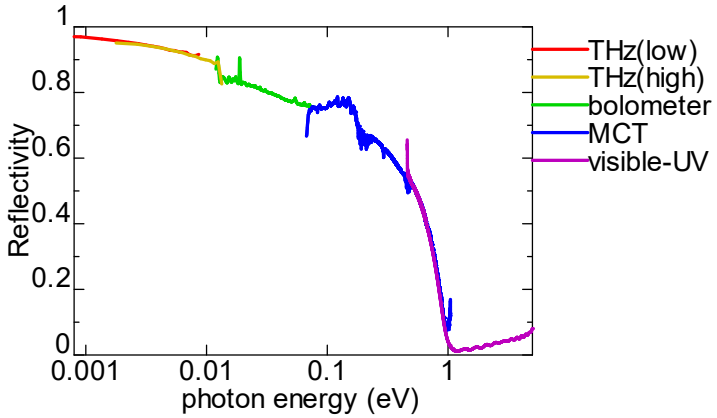

Fig. 9 Broadband reflectivity spectrum of nondope PEDOT/PSS (film thickness 800 nm).

The results of the reflectivity spectrum measurement are shown. The reflectivity spectra of each region are connected without contradiction. Then by applying Kramers-Kronig transformation to the broadband reflectance spectrum thus obtained, the following conductivity spectrum could be obtained. (Fig. 10)

The broadband optical conductivity spectrum obtained by Kramers-Kronig transformation is well consistent with the conductivity spectrum measured without approximation in the terahertz region. This spectrum is almost flat in the low energy region and the real part of the conductivity decreases toward 0 above about 0.1 eV. This behavior is consistent with the Drude model, which represents the optical conductivity of a conductor.

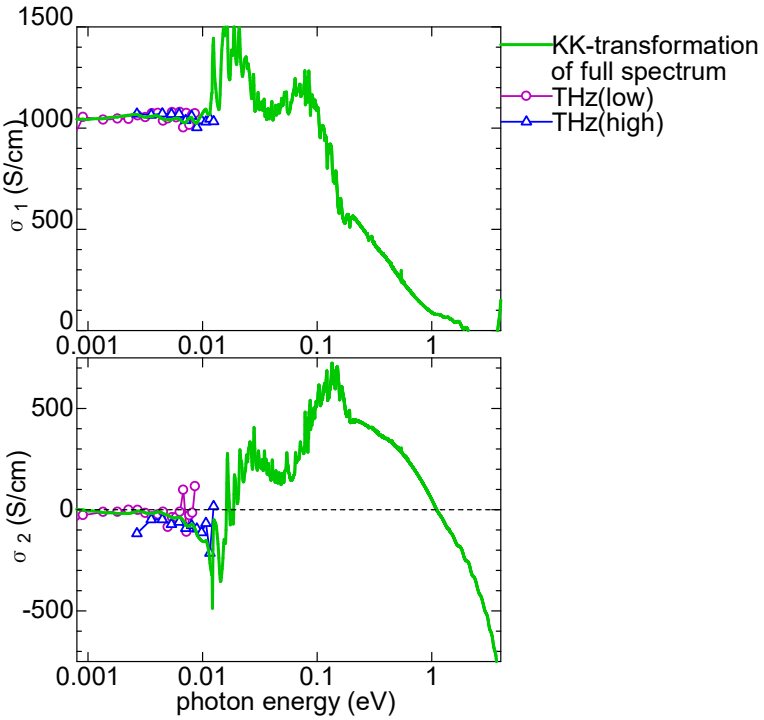

Fig. 10 Broadband optical conductivity spectrum of nondope PEDOT/PSS (film thickness 800 nm) by KK transformation.

Acknowledgement

We would like to express our sincere gratitude to our advisors, Assoc. Prof. Youtarou Takahashi and Prof. Hiroshi Okamoto, for their great support and guidance in the conduct of this research. We would also like to thank our secondary advisors, Prof. Hiroshi Okamoto and Prof. Junichi Takeya for their permission and

advice on this research proposal. Finally, We would like to express our gratitude to MERIT program for giving us the opportunity to do spontaneous fusion research.

References

[1] 奥崎秀典 PEDOT/PSS の階層構造と電気伝導度向上のメカニズム 応用物理 **83,** 834 (2014).

[2] S. He, M. Mukaida, K. Kirihara, L. Lyu, and Q. Wei Reversible Protonic Doping in Poly(3,4-Ethylenedioxythiophene) Polymers **10,** 1065 (2018).

[3] M. Tinkham Energy Gap Interpretation of Experiments on Infrared Transmission through Superconducting Films Physical Review **104,** 845 (1956).

[4] M. Yamashita, C. Otani, M. Shimizu, and H. Okuzaki Effect of solvent on carrier transport in poly(3,4-ethylenedioxythiophene)/poly(4-styrenesulfonate) studied by terahertz and infrared-ultraviolet spectroscopy Applied Physics Letters **99,** 143307 (2011).