

Nondestructive Measurement of Carrier Mobility in Conductive Polymer PEDOT:PSS using Terahertz and Infrared Spectroscopy

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Abstract

Novel method to evaluate the density and mobility of carriers in conductive polymers is presented. The method utilizes the broadband spectral information of THz and infrared region. Terahertz-time domain spectroscopy revealed that the strong carrier scattering induced the weakly localized carrier behavior in conductive polymer poly(3, 4-ethylenedioxythiophene):poly(styrene sulfonate acid) (PEDOT:PSS) thin films. However, it is impossible to determine the carrier density and mobility uniquely only from the spectral information in THz range (0.1-4THz) when the carrier scattering rate is much larger than the THz frequency. We successfully determine the mobility of carriers in PEDOT:PSS thin films by the simultaneous fitting of THz conductivity and infrared reflectivity spectra. The dc conductivity increase by the secondary doping can be attributed to the mobility enhancement induced by the improvement of the disorder in PEDOT:PSS thin films. Under the assumption of the effective mass $m^*=0.3$, the obtained carrier mobility of PEDOT:PSS thin film with and without the secondary dopant of ethylene glycol are 9.77 and 0.77 cm^2/Vs , respectively.

1. Introduction

Terahertz (THz) spectroscopy allows a material's far-infrared optical properties to be determined as a function of frequency. This information can yield insight into material characteristics for a wide range of applications [1]. The dynamics of free carriers in solids are intensively studied in this research field. Due to its sensitivity of amplitude and phase information, THz time domain spectroscopy (THz-TDS) has become a powerful tool for the nondestructive measurement of the carrier density N and mobility μ in semiconductors [2]. The amplitude and phase information obtained from THz transmission or reflection measurement of conducting materials enable to determine the complex refractive index ($n-i\kappa$) and complex dielectric constant ($\epsilon_1-i\epsilon_2$) in THz region. These are related to the complex conductivity $\sigma(\omega)$ by

$$\begin{aligned}\sigma(\omega) &= \sigma_1(\omega) - i\sigma_2(\omega) = \epsilon_0 \omega \epsilon_2(\omega) - i\epsilon_0 \omega (\epsilon_b - \epsilon_1(\omega)), \\ \epsilon(\omega) &= \epsilon_1(\omega) - i\epsilon_2(\omega) = n^2 - \kappa^2 - i2n\kappa\end{aligned}\quad (1)$$

where, ϵ_0 is the dielectric constant of vacuum, ϵ_b is the dielectric constant of the sample without free carriers. In moderately doped semiconductors, Drude model well describes the frequency dependent $\sigma(\omega)$ by,

$$\sigma(\omega) = \sigma_1(\omega) - i\sigma_2(\omega) = \frac{\epsilon_0 \omega_p^2}{\Gamma + i\omega}, \quad (2)$$

$$\omega_p = \sqrt{\frac{Ne^2}{\epsilon_0 m^*}}, \quad (3)$$

where ω_p is the plasma frequency and Γ is the carrier scattering rate [2]. By fitting σ_1 data with the real part of the equation (2), ω_p and Γ can be obtained. These parameters give the carrier density and mobility $\mu = e\tau/m^*$ of the sample by assuming m^* . Actually, when the scattering rate Γ of free carriers is comparable to THz frequency, $\sigma_1(\omega)$ shows strong frequency dependence in THz frequency range and the plasma frequency ω_p and Γ can be obtained uniquely. This situation is applicable to the high crystalline semiconducting materials [2]. However, when Γ is much larger than

THz frequency, it results in the constant conductivity $\sigma_1(\omega) = \epsilon_0 \omega_p^2 \tau$ and it is impossible to obtain ω_p and Γ uniquely by the curve fitting of $\sigma_1(\omega)$ in THz region. On the other hands, $\sigma_2(\omega)$ is proportional to ω in the case of $\omega < \Gamma$, which also prevents from determining ω_p and Γ uniquely by $\sigma_2(\omega)$ curve fitting and the assumption of ϵ_b is also required.

Conductive polymers have been intensively studied for the variety of applications such as solar cell, transparent electrode from the discovery of the tremendous increase of dc conductivity realized by iodine doped poly acetylene [3]. However, their carrier transport mechanisms are not fully understood. Several groups reported THz complex conductivity of the conductive polymers using THz-TDS [4,5]. Their results show the partially localized carrier behavior and very high carrier scattering rate Γ . As mentioned above, such large Γ makes it difficult to obtain ω_p and Γ uniquely only from THz conductivity and the fitting by the theoretical model to the data required the trial and error [4].

In this paper, we proposed and demonstrated the novel nondestructive method to measure the carrier mobility of conducting polymers by assuming effective mass m^* using THz (0.1-4 THz) and infrared (20-250 THz) spectral information, complementally (THz-IR spectroscopy). The infrared reflectivity measurement shows the high reflectivity region due to the plasma oscillation of free carriers, which is useful for estimating ω_p of conducting polymers. This method is suitable for evaluating the carrier mobility of conductive polymers which have carrier densities of the orders between 10^{19} - 10^{20} /cm³ and high carrier scattering rate. Poly(3, 4-ethylenedioxythiophene):poly(styrene sulfonate acid) (PEDOT:PSS) thin films were used as samples because PEDOT:PSS is one of the best known π -conjugated polymers due to its excellent electrical conductivity and electro-optic properties, as well as processability. By using THz-IR spectroscopy, we successfully determine the carrier mobility of PEDOT:PSS thin films with and without the secondary dopant of the ethylene glycol (EG) which increase the dc conductivity. The results indicate that the increase of the dc conductivity of PEDOT:PSS by adding EG can be attributed to the enhancement of the carrier mobility, which results from the improvement of the disorder.

2. Experimental

The method utilizes the THz conductivity and infrared reflectivity spectra to estimate the carrier mobility. We used conventional THz-TDS and FT-IR spectrometer to measure the THz transmittance (0.1-4THz) and infrared reflectivity spectra (20-250THz=666-8325 cm⁻¹). PEDOT:PSS thin films with approximately 800 nm thickness were fabricated on half the area of the quartz substrate (thickness 1mm) using spinning coating technique from the PEDOT:PSS aqueous solution (3 %). The 3% PEDOT:PSS aqueous solution was obtained from the pristine solution (1.3 % concentration HC Starck Clevios PH1000) using the freeze dry technique. Dc conductivity of the PEDOT:PSS were enhanced by more than 50-fold on adding EG (15 %) to PEDOT:PSS solution. We prepared two samples with and without EG to investigate the secondary doping effect. Transmission and phase shift of the sample in THz frequency were measured by the conventional THz-TDS system. The area without PEDOT:PSS film was used for the reference measurement. Infrared reflectivity of PEDOT:PSS films were measured by Fourier transformed infrared spectrometer (FT/IR-4000, JASCO).

3. Results and Discussion

Figure 1 shows the transmittance of the PEDOT:PSS thin films with and without EG. The quartz substrate was used for the reference measurement. The transmittance of PEDOT:PSS without EG is higher than that with EG, which indicates the difference of the optical conductivity between samples. By analyzing the transmittance and phase shift, the complex conductivity $\sigma(\omega)$ of both samples in THz region were obtained as shown in Fig. 2 (a) and (b). For both samples, $\sigma_1(\omega)$ decrease with decreasing frequency and $\sigma_2(\omega)$ are negative, which is not simple Drude like behavior. Figure 2 (c) and (d) show the infrared reflectance spectra of PEDOT:PSS thin films. The reflectivity spectra in far-infrared and near IR-ultra violet region are also shown in Fig. 2 (c) and (d). Although the optical conductivities are quite

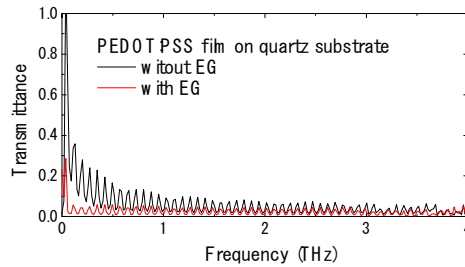


Fig. 1 (a) THz transmittance of the PEDOT:PSS thin films with and without EG.

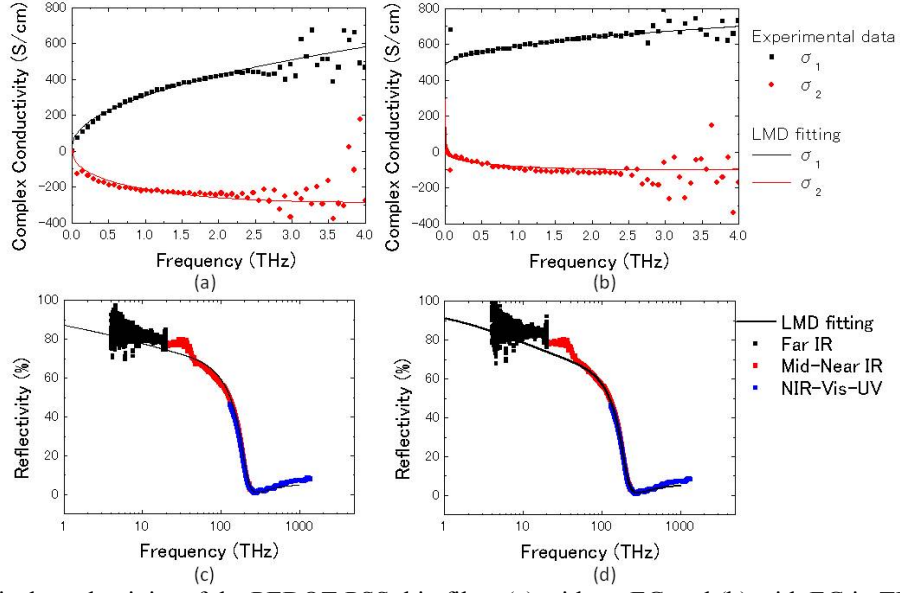


Fig. 2 Optical conductivity of the PEDOT:PSS thin films (a) without EG and (b) with EG in THz range. The infrared spectra of the PEDOT:PSS thin films with and without EG.

different, no difference in the infrared reflectivity between the samples can be seen. These results indicate that the plasma frequencies of the samples with and without EG are almost same and the difference of dc conductivity can be attributed to the degree of the sample's disorder. The dynamics of weakly localized carriers in polypyrrole films were studied by the localization modified Drude (LMD) model [6]. Other group also investigated ion-doped conducting poly-3-hexylthiophen (P3HT) using Drude-Smith model [5]. Our results indicates that THz conductivity in PEDOT:PSS is well fitted by LMD model which indicates that PEDOT:PSS is the disordered metal near metal-insulator transition [6]. In the case of LMD model, the complex conductivity is given by

$$\begin{aligned}\sigma_{1LMD}(\omega) &= \frac{\varepsilon_0 \omega_p^2}{\omega^2 + \Gamma^2} \left[1 - \frac{C}{(k_F v_F)^2} \Gamma^2 + \frac{C}{(k_F v_F)^2} \Gamma^{1.5} (3\omega)^{0.5} \right] \\ \sigma_{2LMD}(\omega) &= \frac{\varepsilon_0 \omega_p^2 \omega}{\omega^2 + \Gamma^2} \left[-1 + (1 - \sqrt{6}) \frac{C}{(k_F v_F)^2} \Gamma^2 + \frac{C}{(k_F v_F)^2} \Gamma^{2.5} (3/\omega)^{0.5} \right]\end{aligned}\quad (4)$$

where k_F is Fermi wavenumber, v_F is Fermi velocity, C is an order of unity. The $\sigma_{2LMD}(\omega)$ is not given in the literatures [6] and we analytically calculated $\sigma_{2LMD}(\omega)$ by Kramers-Kronig transformation of $\sigma_{1LMD}(\omega)$. If the complex conductivity is given, the complex refractive indices and reflectivity spectra of both samples in the infrared region can be calculated by eq. (1) and Fresnel equations. To utilize both THz and infrared spectral information to determine the fitting parameter, we define the error function defined by

$$Error(\omega_p, \Gamma, P) = |\sigma_{1LMD}(\omega_p, \Gamma, P) - \sigma_{1exp}| + \alpha |R_{LMD}(\omega_p, \Gamma, P) - R_{exp}| \quad (5)$$

where $P = C/(k_F v_F)^2$, α is the weighting factor, σ_{1exp} is the optical conductivity obtained by THz-TDS, R_{1LMD} is the calculated reflectivity and R_{1exp} is the reflectivity obtained by FT-IR spectrometer. We successfully determined the LMD parameters (ω_p , Γ , P) which gives the minimum value of eq. (5) using the Simplex method. The calculated THz complex conductivity and infrared reflectivity spectra using the fitting parameter are well reproduced as shown in Fig. 2. Figure 4 shows the calculated optical conductivity spectrum of PEDOT:PSS thin film with EG from THz to ultraviolet frequency region. Carrier density N is related to the optical conductivity spectra by

$$N = \frac{2m^*}{\pi e^2 A} \int_0^\omega \sigma(\omega') d\omega' \quad (6)$$

where, $A=1$ for Drude model and $A=1+(6^{0.5}-1)P\Gamma^2$ for LMD model. Using eq. (6), we can determine m^* by assuming the carrier density of the highly conductive PEDOT:PSS thin films [6, 7]. The carrier density of the PEDOT:PSS can

simply be calculated using a geometrical consideration. For highly conductive PEDOT:PSS, the ratio of PEDOT to PSS is 12.5 by weight. The density of solid films is approximately 1 g/cm^3 . Owing to the molecular weight of the monomeric units of PEDOT and PSS with 140 and 182 g/mol respectively, the density of EDOT monomer can be estimated to be approximately $1 \text{E}21/\text{cm}^3$. From electrochemical measurement, the level of oxidation per monomer unit is known to be approximately 1 charge per 3 EDOT units. Consequently, the carrier density of holes in PEDOT:PSS films can be estimated to be $3 \times 10^{20}/\text{cm}^3$ which leads to the effective mass of the PEDOT:PSS with EG is $0.3m_0$ from eq. (6). By assuming the effective mass $m^*=0.3m_0$, the carrier mobility μ ($= e(1-PT^2)/m^*\Gamma$) of the samples with and without EG are 9.7 and $0.77 \text{ cm}^2/\text{Vs}$, respectively. The carrier density of the PEDOT:PSS thin films without EG is $2.25 \times 10^{20}/\text{cm}^3$. The results indicate that the enhancement of the dc conductivity by the secondary dopant EG was caused by the improvement of the carrier mobility. For further qualitative evaluation of the carrier mobility, the information of the density or effective mass of carriers is needed to experimentally. However, we could not obtain the carrier density of PEDOT:PSS thin films by Hall measurement, which might be caused by the barriers between the electrode and films. Non-contact THz-Hall measurement might enable to escape this situation.

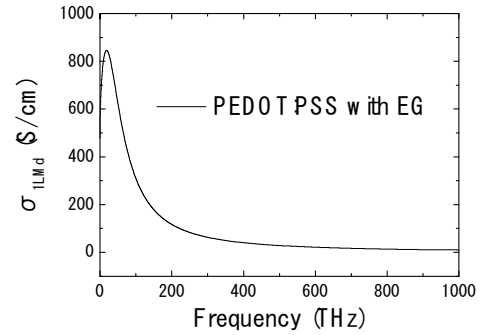


Fig. 3 (a) The calculated optical conductivity $\sigma_1(\omega)$ using LMD model.

4. Conclusion

We have proposed and demonstrated the novel method for evaluating the carrier mobility in conducting polymers. The method utilizes the simultaneous fitting THz and infrared spectral information of PEDOT:PSS using LMD model because it is difficult to determine the carrier scattering rate only from THz complex conductivity when the scattering rate is much larger than THz frequency, which is applicable for most of conductive polymers. Assuming $N=3.0 \times 10^{20}/\text{cm}^3$ and $m^*=0.3$ for highly conducting PEDOT:PSS thin films, the carrier mobilities of PEDOT:PSS with and without EG additives 9.7 and $0.77 \text{ cm}^2/\text{Vs}$, respectively. These values are much larger than compared with that of semiconducting polymers such as poly 3-hexylthiophen ($0.1 \text{ cm}^2/\text{Vs}$). However, the recent study on the organic field effect transistor based on benzothiophenes (Cn-BTBT) reported the field effect carrier mobility of $5 \text{ cm}^2/\text{Vs}$. Further studies to investigate the carrier density of conducting polymers are expected to improve this situation.

5. References

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