pH effect on carrier transport in conducting polymer PEDOT:PSS investigated by terahertz and infrared-visible spectroscopy

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Abstract— The pH effect on the carrier transport of conducting polymer PEDOT:PSS has been studied by terahertz and infrared-visible spectroscopy. The neutralization of conducting polymer poly (3, 4 ethylenedioxythiophene):poly (stylene sulfonate) (PEDOT:PSS) decreased the carrier concentration and mobility, which lowered the electrical conductivity of PEDOT:PSS by five orders of magnitude with increasing pH from 1.7 to 11.7.

I. Introduction

Poly (3, 4 ethylenedioxythiophene):poly (stylene sulfonate) (PEDOT:PSS) is expected as a key materials for flexible and/or printed electronics, solar cell and thermoelectric devices because of its excellent properties such as high and stable electrical conductivity, transparency and solubility. The realization of such devices requires the control of carrier concentration and mobility of PEDOT:PSS. However, there are few reports on the control of the carrier concentration and mobility of PEDOT:PSS because of the difficulty of its characterization. In Ref. [1], we have reported the characterization of carrier transport property of PEDOT:PSS by the combination of terahertz (THz) and infrared-visible (IR-Vis.) spectroscopy. In this study, we investigated the pH effect on the carrier transport property of PEDOT:PSS by using THz and IR-Vis spectra.

II. Results

Figure 1(a) and (b) show pH dependence of the IR-Vis reflectance of the pristine and EG of PEDOT:PSS films, respectively. By increasing the pH, the plasma reflectance region becomes narrower and lower. We determined the plasma frequency $\omega_p=(Ne^2/\varepsilon_0 m^*)^{0.5}$ and carrier scattering rate Γ by fitting the data with Drude model. The plasma frequency ω_p increases with the addition of EG and decreases with increasing pH. On the other hands, the Γ increases with increasing pH, which agrees with the lower crystallinity observed by XRD [2]. de Kok, et al. [3] proposed that pH effect originate from a change in the relative stability of localized polarons with and delocalized bipolarons on the doped thiophene that is induced by the replacement of PSS-H with PSS-Na. From the pH dependence of ω_p, it is estimated that the carrier concentration of pristine and EG15 film decreased 27% and 17%, respectively.

Figure 1 (c) and (d) show the pH dependence of the THz conductivity spectra $\sigma(\omega)$ normalized by the DC conductivity $\sigma_D(0)=\varepsilon_0\omega_p^2/\Gamma$ obtained from Drude-fit of IR-Vis spectra. $\sigma(\omega)/\sigma_D(0)$ of both pristine and EG15 films decrease with decreasing frequency indicating the weakly localized carrier state due to the disorder. The $\sigma(\omega)/\sigma_D(0)$ of the pristine films rapidly drop down and approaches to zero below 1 THz and decreases by increasing pH. On the other hands, $\sigma(\omega)/\sigma_D(0)$ of EG15 at pH 1.5 and 5.9 show the nearly flat spectra and that at pH=11.8 also drop down to near zero conductivity below 1 THz. The decrease of the electrical conductivity the by pH effect is attributed to the lower carrier mobility due to the lower PEDOT crystallinity. The relative carrier mobility μ calculated by σ_{DC}/ω_p^2 were obtained. Compared to the pristine at pH 11.4, the N and μ of EG15 at pH 1.5 becomes 47% and more than 500 times higher, respectively. The results indicate that the electrical conductivity change by pH effect is dominated by the change of μ.

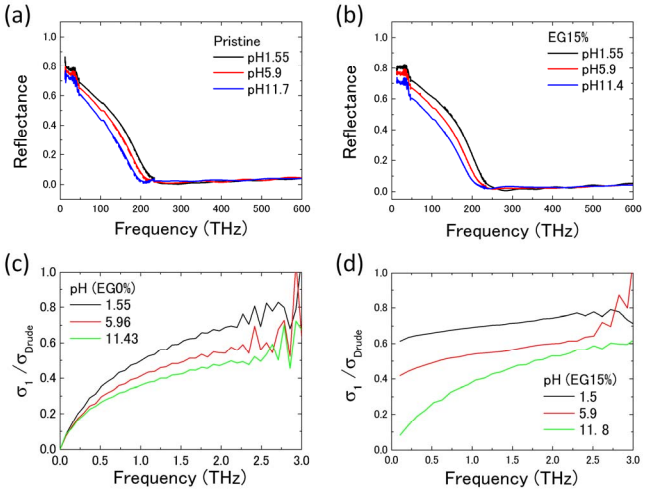

Fig. 1 The IR-Vis reflectance of PEDOT:PSS (a) without and (b) with the addition of EG. The normalized THz optical conductivity of PEDOT:PSS (c) without and (d) with the addition of EG.

References

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