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Displacement Current Induced by Electron Spin Resonance in Organic Semiconductor

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A current induced by electron spin resonance (ESR) transitions is investigated for polymer diodes using electrically detected magnetic resonance techniques. Polymer diodes under photoexcitation are shown to exhibit a strong ESR-induced current. The ESR current exhibits a spiked time response for modulation of the resonance condition and is concluded to result from a displacement current. The magnitude of the displacement current is found to vary depending on polymers used for active layers. Trapping and de-trapping processes of carriers are expected to determine the time profile of the displacement current, suggesting that materials with shallow trap levels would be suitable for applications to spin-based devices.

Keywords EDMR; displacement current; polymer diodes; ESR

I. Introduction

Organic semiconductors are known to exhibit a current at the moment of electron spin resonance (ESR) [1]. The ESR-induced current attracts much attention because it directly associates the electron spin with electric signals and can be applied to spintronics. The ESR-induced current has indeed been employed to realize spin-based quantum devices such as spin resonance transistors [2,3], a spin memory [4] and spin-based quantum computers [5–8]. However, such ESR-induced currents are usually very small and typically much less than one percent of the steady-state current, which degrades their functionality as a spintronic tool. Therefore, to expand the applicability of the ESR current, systems that can give much higher current are required.

We recently reported that an anomalous photocurrent comparable to its steady-state current is induced by ESR from polymer semiconductor diodes of poly′2-methoxy-5-(2′-ethyl- hexyloxy)-1,4-phenylene vinylene] (MEH-PPV) used as an active layer [9]. The ratio of the ESR-induced current to the steady-state photocurrent, as high as 80%, was the largest value, although closely similar results were reported following our report [10]. The ESR-induced current was found to be attributed to a displacement current caused by changes in polarization electric fields at ESR [9]. This system can thus be applied to controlling dielectric properties using magnetic resonance techniques. For considering a variety of future applications, fundamental properties of the ESR-phenomena

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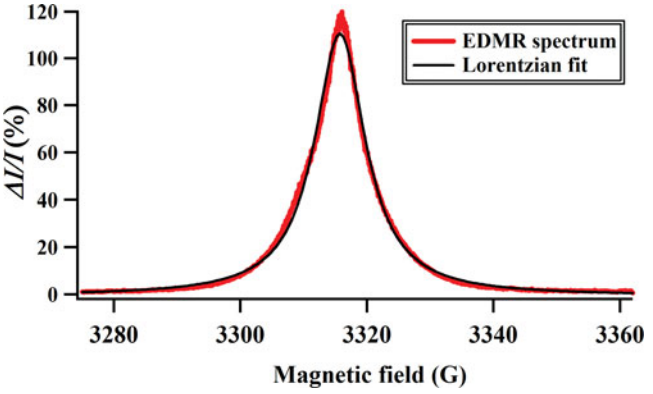

Figure 1. Electrically detected magnetic resonance (EDMR) spectra of SY-PPV diodes. The intensity of the EDMR signal (ΔI) is normalized against that of the steady-state photocurrent measured simultaneously (I). The photoexcitation intensity was 40 mW. The black solid curve indicates the result of spectral fit using a Lorentzian lineshape.

should be investigated. In this article, we show that similar type of displacement current induced by ESR is observed also from a diode based on a PPV-based copolymer, termed super-yellow (SY) PPV, which is well-known as an efficient electroluminescent PPV derivative for practical applications [11,12]. The ESR-induced displacement current is studied by an electrically detected magnetic resonance (EDMR) technique. Although a similar EDMR response is identified between MEH- and SY-PPVs, the time-constants of the response are found to be obviously different between the polymers. From the observation, we discuss the element to determine the magnitude of the ESR-displacement current.

II. Experimental

For the active polymer layer, alkoxyphenyl substituted poly(1,4-phenylene vinylene) dubbed super yellow PPV (SY-PPV) (Merck) was used [11]. The SY-PPV diodes were fabricated by spin-casting SY-PPV dissolved in chlorobenzene onto an indium-tin-oxide (ITO)-coated glass substrate (anode) and the subsequent deposition of an Al electrode by vacuum evaporation (cathode). The diode was then air-exposed in two weeks. The active area of the diode was 2 mm $\times$ 3 mm. The diode was loaded into a 5 mm diameter glass tube for EDMR measurements.

The EDMR experiments were carried out under photoexcitation with no applied bias (short circuit condition) using an X-band ESR spectrometer by modulating a microwave power (typically, 200 mW) with a PIN modulator (500 Hz). A diode-pumped solid-state (DPSS) laser with cw 473 nm output (CNI) was used for photoexcitation (40 mW). EDMR spectra were measured by recording the modulation current using a lock-in amplifier. Time resolved EDMR signals were measured with a digital oscilloscope for modulated resonant microwave power (50 Hz). All EDMR measurements were performed at room temperature under N_2 gas flow to minimize interactions with oxygen that could affect the paramagnetic spins in the film.

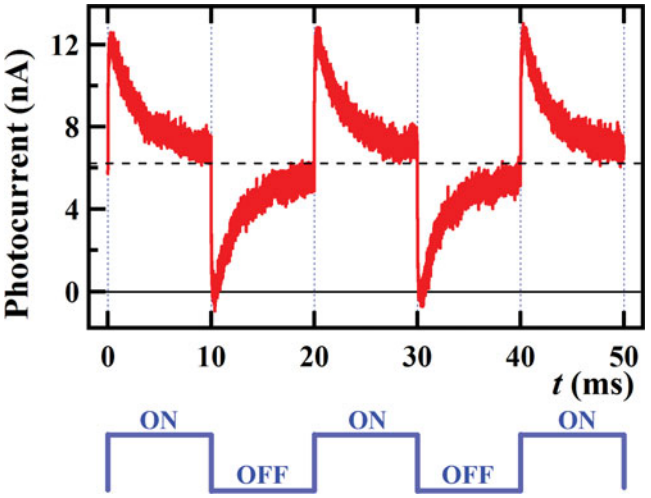

Figure 2. Time profile of photocurrent under resonance condition (3318 G) for the SY-PPV diode when repeatedly switching the ESR-resonant microwave power on and off, as shown in the bottom. The horizontal broken lines represent a steady-state photocurrent.

III. Results and Discussion

The EDMR spectrum under photoexcitation of the SY-PPV diode is shown in Fig. 1. The g-value determined from the peak position was approximately 2.002, indicating that the origin of the signals is π electrons of SY-PPV. The intensity of the EDMR signal was normalized with respect to the magnitude of the steady-state photocurrent (PC) measured simultaneously. The peak intensity of the signals is approximately 100%, which is beyond the value for MEH-PPV reported previously (80%) and indicates that the ESR-induced current is comparable with its steady-state PC. Figure 1 also shows the result of spectral fit using Lorentzian curves for the EDMR spectrum. It demonstrates that the spectrum can be nearly reproduced by a single Lorentzian curve with the full width at half maximum (FWHM) of 9.7 G. The Lorentzian line shape indicates that the EDMR line shape is not distorted by the strong microwave power used in the measurements. It has been well documented that carriers generated by chemical doping in conjugated polymers exhibit a Lorentzian lineshape and a narrow linewidth, typically less than a few gauss of the peak-to-peak width ΔH_{pp} in differential ESR spectra [13], because of the motional narrowing effect. The observed FWHM in the present study, corresponding to ΔH_{pp} of 5.6 G, is much larger than the case of motional narrowing. The influence of the motional narrowing is thus relatively small in the EDMR system, although the observed Lorentzian lineshape indicates the presence of non-negligible effects of spin motion. Previously, the FWHM attributed to the hyperfine interaction with protons was calculated to be 6.1 G for MEH-PPV [14]. Therefore the observed EDMR line shape with the 9.7 G- FWHM could be determined by a weak motional narrowing effect given by modulation of local magnetic fields primarily resulting from hyperfine couplings with protons.

Figure 2 presents the time-profile of EDMR signals measured at the resonance peak (3318G) for the SY-PPV diode. In this measurement, the microwave power was repeatedly switched on and off under the resonance condition as shown in the bottom of Fig. 2. The time profile exhibits positive and negative spike currents, when the microwave power is

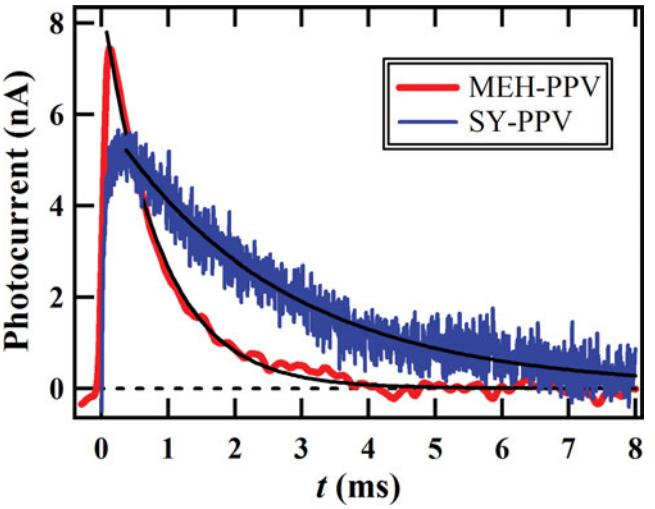

Figure 3. Comparison of the time trace in the ESR-induced current at the moment of the microwave-irradiation between MEH-PPV and SY-PPV diodes. The contribution of the steady-state photocurrent was removed in the traces. The black solid curves are the results of fit using a single exponential decay function, which determined the decay time constants to be 0.85 ms and 2.6 ms for MEH-PPV and SY-PPV diodes, respectively.

switched on and off, respectively. The feature of spike response is typical of a displacement current, which is induced by a change in the polarization electric field within the film and flows between two electrodes outside the film [15]. The observed spike feature is similar to the result of MEH-PPV [9]. In the case of MEH-PPV, the spike current was also observed when the diode was insulated by inserting an insulating layer between the MEH-PPV layer and the Al-electrode, providing the evidence of a displacement current. Therefore, the ESR-induced current in the SY-PPV diode similar to that of MEH-PPV is also concluded to be a displacement current.

The result of Fig. 2 suggests that the displacement current induced by ESR could be a feature commonly observed from conjugated polymers under photoirradiation. However, the displacement current is expected to include some features that are different among the materials used in the active layer. The transient time profile of the displacement current was thus compared between the cases of MEH-PPV and SY-PPV. The result of the comparison is shown in Fig. 3 and indicates that the time response of the displacement current in SY-PPV is much slower than that of MEH-PPV. The time profile was roughly approximated by a single exponential function and found to be 2.6ms and 0.85ms for SY-PPV and MEH-PPV, respectively. These time constants are much longer than typical circuit time constants of polymer diodes $\sim 1\mu$s. Therefore, the time constants of the ESR-displacement current are likely to be determined by very slow processes occurring in the diode. We particularly note that PPV derivatives are known to have a plenty of trapped carriers [16]. Therefore trapping and de-trapping processes of carriers are expected to determine the time profile of the ESR-displacement current. This is consistent with the less mobile features identified from the EDMR spectrum in Fig. 1. In the previous report, we proposed a model that the ESR transition decreases the density of carriers and thereby polarization electric fields formed by carrier pairs and/or trapped carriers within the diode are reduced, leading to generation of the displacement current [9]. From the model, we expect that the change of the polarization

field would be determined by the rate of trapping and de-trapping processes, and the rate is different between SY-PPV and MEH-PPV. The difference probably results from a difference in the trapping level depth; SY-PPV has deeper trapping sites. Such trapping sites could result from the copolymer structure of SY-PPV. When considering applications of the ESR-induced current to devices, systems that induces a strong and rapid displacement current are desired. From the result of the present study suggesting the influence of trapped carriers, material systems with shallow trap levels are expected to be suitable for the application because of their expected rapid trapping and detrapping processes.

IV. Conclusions

In summary, we have demonstrated from EDMR techniques that the SY-PPV diode exhibits a large ESR-induced current under photoexcitation. The ESR current was shown to exhibit a spiked time response for modulation of the resonance condition and concluded to result from a displacement current caused by changes in the polarization electric field within the diode. The time response of the displacement current in the SY-PPV was much slower than that in MEH-PPV. The trapping and de-trapping processes of carriers are thus expected to determine the time profile of the ESR-displacement current, suggesting that material systems with shallow trap levels would be suitable for applications to spin-based devices.

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