Enhanced photoconductivity and trapping rate through control of bulk state in organic triphenylamine-based photorefractive materials

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Abstract

In organic optical semiconductors, it is rather challenging to achieve precise control of photoconductivity and charge trapping, which determines the device performance. This paper reports on enhanced photorefractive response rate through control of the photoconductivity and trapping rate in organic triphenylamine-based photorefractive materials by means of bulk state tuning. The bulk state in organic triphenylamine-based photorefractive composites was controlled through a rapid cooling process from various melting temperatures during sample fabrication. The photoconductivity and trapping rate were determined from photocurrent measurements. Fabrication at lower melting temperatures enhanced the trapping rate for deep traps, whereas it reduced the trapping rate for shallow traps. As a result, a faster photorefractive response was obtained.

Keywords

Charge transport; Trapping rate; Photoconductivity; Organic photorefractive materials; Triphenylamine derivatives

Introduction

The performance of various organic electro-optic devices, including organic photovoltaic (OPV) cells [1-3], organic field-effect transistors (OFETs) [4-6], and organic photorefractive (PR) materials [7-12], is strongly affected by their conductive and charge trapping properties. These properties are affected by the fabrication conditions for semi-crystalline organic semiconductors of OPV cells [13-16] and OFETs [17-20] through changes in the bulk states. Organic PR composites typically consist of amorphous photoconductive polymers, crystalline nonlinear optical (NLO) chromophores, and other low-molecular materials such as sensitizers and plasticizers [21,22], and thus, there has been increasing interest in the effects of the bulk state of PR composites on photorefractivity.

Triphenylamine derivatives are recognized as high-hole mobility photoconductors with high optical transparency in the visible wavelength region because of their low reorganization energy [23] and are used as PR host polymers [24-26]. However, it is challenging to control the trapping rate and enhance the photorefractivity in triphenylamine-based PR materials since the nature of their trap sites, which is an important aspect of the PR process, has not yet been fully understood.

This paper presents the effects of the bulk state on PR response rate and photoconductivity of PR composites. The bulk state is tuned by controlling the melting temperatures, which refers to the temperature set during sample fabrication. Sample fabrication involved heating at the melting temperature followed by rapid cooling to prevent crystallization of the PR composites [27,28] that exhibit low glass

transition temperature (T_g). Control of the melting temperature enhanced the performance of the PR composites without affecting their chemical composition. This enhancement resulted from the formation of the space-charge field. We also discussed the effects of shallow and deep traps on space-charge field formation. Finally, we suggest a correlation between the properties of the traps and the bulk state.

Experiment

The PR composites consisted of poly(4-diphenylamino)styrene (PDAS) (59 wt.%) as a triphenylamine-based photoconductive amorphous host polymer, 4-homopiperidino-2-fluorobenzylidene malononitrile (FDCST) (20 wt.%) as a crystalline NLO chromophore, 9-(2-ethylhexyl)carbazole (EHCz) (20 wt.%) as a liquid plasticizer [29-31] to decrease T_g of the composites, and [6,6]-phenyl C_{61} butyric acid methyl ester (PCBM) (1 wt.%) as a sensitizer. To evaluate the effect of FDCST and EHCz, Butyl benzyl phthalate (BBP) (20 wt.%) was used as an inert liquid plasticizer [7] instead of FDCST or EHCz. Hereafter, the PR composites are referred to as REGULAR (PDAS/FDCST/EHCz/PCBM), W/O FDCST (PDAS/BBP/EHCz/PCBM), and W/O EHCz (PDAS/FDCST/BBP/PCBM). A solution of the materials in toluene/cyclohexanone (4/1 by volume) was stirred for 24 h, and the mixture was evaporated at 40 °C in vacuum after filtration. After the solvent evaporation, the resulting film was melted between two indium tin oxide (ITO) glass plates for 10 min at 100 °C, 105 °C, 110 °C, 120 °C, 130 °C, and 140 °C, and then cooled rapidly at 5 °C. The film layer thickness was controlled to be 50 μm using spacers. We found that

all samples maintained good optical transparency, with no dim portions due to recrystallization visible by the naked eye during the measurements (more than 2 weeks). However, at a certain tilt angle, the REGULAR (100 °C) sample exhibited yellow-green color due to scattering, which could not be observed for the REGULAR (140 °C) sample. It should be noted that the yellow-green color was not due to fluorescence emission. This result indicates that very small scattering centers appear in the REGULAR (100 °C) sample due to recrystallization, as will be explained below.

The diffraction signals for the evaluation of the PR response rate were measured using a four-wave mixing (FWM) technique [10]. The samples were irradiated by two *s*-polarized writing beams (He-Ne laser, 633 nm, 130 mW/cm²) and a *p*-polarized reading beam (laser diode, 808 nm, 180 μW) with counter propagation. Photocurrent experiments were performed using a laser diode operating at a wavelength of 640 nm and an intensity of 140 mW/cm². In the FWM techniques as well as the photocurrent experiments, fresh samples that were not exposed to either an external field or light illumination were used. A constant external field of 30 V/μm was applied for 30 min before the measurements to reduce the effect of dark current including mobile charges such as ionic ones [32]. The pumping duration for the samples was 1 s in both the experiments.

Results and Discussion

The FWM techniques were carried out for the REGULAR samples to demonstrate the effect of the melting temperatures. The diffraction beam powers from all samples reached plateau levels around 300 mW after irradiation by the writing beams. Moreover, the evolution of diffraction power followed a single exponential form [21]. The inset of Fig. 1 shows the typical growth of diffraction power fitted by the single exponential form for the REGULAR (140 °C) sample. As can be seen in Fig. 1, the PR response rates obtained from the single exponential fitting increased with a decrease in the melting temperatures, whereas the diffraction efficiencies at the plateau level exhibited almost constant values. The reproducibility of the trends of the response rate and diffraction efficiency with respect to the melting temperatures was confirmed with several sets of new samples. It should be noted that the values were slightly different from batch to batch by as much as $\pm 15\%$. The PR response rate and diffraction efficiency are generally determined by the NLO chromophore orientation and the formation of a space-charge field [8,22,33,34]. The degree and rate of NLO chromophore orientation evaluated by a transient Mach-Zehnder interferometer [35] were similar between the REGULAR (100 °C) and REGULAR (140 °C) samples, which exhibited the largest difference in the PR response rates; the NLO chromophore orientation times were on the order of a few milliseconds. Accordingly, the PR response time was dominantly limited by the formation rate of the space-charge field. The fact that the diffraction efficiency and the degree of NLO chromophore orientation (effective electro-optic coefficient) were

similar between the REGULAR (100 °C) and REGULAR (140 °C) samples indicates that the magnitude of the equilibrated space-charge field was similar. In other words, the difference in the PR response found in the REGULAR samples originated only from the different response of the space-charge field.

To explain the tendency of the space-charge field accompanied with the change in the melting temperatures, transient photocurrent measurements were carried out. Figure 2(a) shows the photocurrent values for six types of REGULAR samples. These samples were melt-pressed at 100 °C, 105 °C, 110 °C, 120 °C, 130 °C, and 140 °C. The reproducibility of the photocurrent trends as well as the photorefractive response with respect to the melting temperatures was confirmed. The photocurrents for the REGULAR samples increase linearly in the initial time range through ~0.4 ms with a similar slope, except for the REGULAR (100 °C) sample. This result indicates that charge trapping should be negligible in the early period [8]. In addition, the products of the charge drift mobility and the photogeneration factor [8] are expected to be similar among the samples, except for the REGULAR (100 °C) sample. In contrast, when the trap begins to be filled effectively with photocarriers, the photocurrent can shift from linearity. The effect of trapping on photocurrent dynamics in PR polymers can be well described by Schildkraut's model [8,36]; the photocurrent trace shows a shoulder or a continuous decrease depending on the trap depth or the detrapping rate. Such a shoulder appears around 1 ms in the photocurrent traces for the REGULAR samples, except for the REGULAR (100 °C) sample, owing to shallow trap filling, and a continuous decrease appears after 50 ms owing to deep trap filling. These shoulders have a tendency to be

gentler and the photocurrent exhibits higher levels with decreasing melting temperatures. In the REGULAR (100 °C) sample, the photocurrent steeply increased with irradiation time, showing no apparent shoulder due to the shallow trap, and two different kinds of photocurrent decay were observed after a peak around 4 ms. The abovementioned results indicate that the fabrication conditions at higher melting temperatures cause more shallow traps, which can result in a shoulder in the photocurrent change at around 1 ms.

Since shallow trap filling occurred much faster compared to the PR response time, as opposed to deep trap filling, it should not directly contribute to the development of the space-charge field. Therefore, deep trap filling was subsequently investigated. According to the Schildkraut model, the decreasing rate of photocurrent at the vicinity of the photocurrent peak in Fig. 2 shows the deep trapping rate given by the following relation,

$$\left. \frac{dj}{dt} \right|_{t=t_{peak}} \propto - \left. \frac{dM^+(t)}{dt} \right|_{t=t_{peak}} \propto -\gamma_M \cdot M \cdot j(t_{peak}). \quad (\text{Equation 1})$$

Here, $j(t_{peak})$ is peak photocurrent value, t is time, γ_M is the deep trapping coefficient, and M is the deep trap density. This evaluation assumes that the number of filled deep traps is negligibly small near the photocurrent peak. Figure 2(b) is plotted for a decreasing photocurrent rate. The slope, or the deep trapping rate, increases with a decrease in the melting temperatures, indicating a good correlation with the

PR response shown in Fig. 1. The value of $\gamma_M \cdot M$ calculated from Eq.1 increases with a decrease in the melting temperature, as shown in Fig. 2(b). These results indicate that the increase in the deep trapping rate is caused by an enhancement of both $\gamma_M \cdot M$ and $j(t_{\text{peak}})$. Moreover, as mentioned above, the equilibrated space-charge field strength was similar among the REGULAR samples, or in other words, all M values of the REGULAR samples were similar. Thus, the change in $\gamma_M \cdot M$ is determined only by γ_M ; the deep trapping coefficient increased with a decrease in the melting temperatures. It therefore seems reasonable to conclude that the enhanced PR response rate was attributed to the increase in the photocurrent peak and the enhancement of the trapping coefficient.

The photocurrent measurements of the W/O FDCST and W/O EHCz samples were carried out to determine the origin of the shallow and deep traps, and the corresponding results are shown in Fig.3 and Fig.4, respectively. Figure 3 shows that the W/O FDCST (100 °C) sample exhibits a similar photocurrent trace as that of the REGULAR (100 °C) samples: the appearance of no clear shoulder around 1 ms due to shallow traps, and two kinds of decay after the peak. The W/O FDCST (140 °C) sample does not show a shoulder, as in the case of the REGULAR (140 °C) sample. In contrast, it is clear from Fig. 4 that the W/O EHCz (140 °C) exhibits the shoulder, as in the case of the REGULAR (140 °C) sample. Moreover, the W/O EHCz (100 °C) sample shows two kinds of decay after the peak, as in the case of the REGULAR (100 °C) sample.

We first focus on the effects of FDCST addition. A comparison of the REGULAR, W/O FDCST, and W/O EHCz samples reveals that FDCST induces the shoulder in the photocurrent due to the filling of shallow traps. As a result, the addition of FDCST leads to the generation of shallow traps. Secondly, all REGULAR, W/O FDCST, and W/O EHCz samples demonstrate the effect of deep traps, which means the origin of deep traps is related to the PDAS itself.

Finally, a differential scanning calorimetry (DSC) thermal analysis was used for evaluating the state of crystallinity in the REGULAR (100 °C) and REGULAR (140 °C) samples. The DSC curves were measured using a DSC822e (Mettler-Toledo International). The shift of positive and negative peaks toward lower temperatures for REGULAR (100 °C) in Fig. 5 indicates that the REGULAR (100 °C) sample was relatively unstable and easily recrystallized at lower temperatures, compared with the REGULAR (140 °C) sample. It should be noted that both REGULAR samples exhibited the same change in heat capacity around 50 °C. These changes could be attributed to PDAS and/or EHCz, because the change around 50 °C was also confirmed in the W/O FDCST (100 °C) and W/O FDCST (140 °C) samples. Thus, the positive peak of recrystallization in the REGULAR samples is attributed to the FDCST crystallinity.

Changes in crystallinity can affect both the physical and optical properties of materials. We provide some explanations about the origin of the decrease in shallow traps and the increase in the trapping

coefficient for deep traps at low melting temperatures. The HOMO level of PDAS, FDCST, and EHCz are -5.7 eV, -6.0 eV, and -5.9 eV, respectively, which were estimated by photoelectron yield spectroscopy in air using an AC-3 spectrometer (Riken Keiki). The HOMO level of the FDCST is lower than that of the PDAS, and thus, the FDCST does not generally work as a trap site. However, it has been shown that the presence of shallow traps due to the addition of FDCST decreases the photocurrent, and the samples fabricated at lower melting temperatures have fewer shallow trapping sites.

In organic disordered semiconducting materials, the Gaussian density of states (DOS) well explains the mechanism of charge transport [37-39]. The width of DOS can be affected by the dipolar disorder including energetic and positional disorders. In our composites, the dipole density per unit concentration would reduce with a decrease in the melting temperature, owing to the crystallization of FDCST. The decrease in the dipole moments reduced the width of DOS, decreasing the overlap of the DOS edges between the PDAS and the FDCST. As a result, the effects of shallow traps of REGULAR (100 °C) and W/O EHCz (100 °C) samples were remarkably suppressed compared with the REGULAR (140 °C) and W/O EHCz (140 °C) samples, respectively. As mentioned above, these composites do not include any components that function as an energetic trap in terms of the HOMO level. However, the conformational traps due to inhomogeneity in polymers have been reported [40], and all our samples including the PDAS exhibited a continuous decrease in photocurrent due to deep trap filling. Hence, the structural traps of PDAS worked as deep traps in the composites. In terms of the deep traps, the trapping coefficient was

changed, whereas the trap density was constant. This enhancement of the trapping coefficient might be induced by the change in the PDAS structure. The PR composites mainly consisted in PDAS exhibit heterogeneous structures of the FDCST crystal and PDAS itself. Heterogeneous structures generally become larger at lower melting temperatures. This phenomenon would decrease the energy barrier of trap sites and thus increase the trapping coefficient in samples fabricated at lower melting temperatures.

Conclusion

We showed that bulk-state tuning improved the PR response rate in low- T_g PR composites through the accelerated buildup of the space-charge field. Our results indicate that the improvement in the PR response rate is caused by the enhanced deep trapping rate in samples fabricated at lower melting temperatures with rapid cooling. The enhanced deep trapping rate is a result of the increase in the deep trapping coefficient, which is assisted by the suppression of the shallow trapping rate resulting in an enhanced photocurrent. We suggest that such modifications of charge trapping are caused by the recrystallized FDCST chromophore and the change in the heterogeneous structures of PDAS.

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Figure captions

Fig. 1. Photorefractive response rate and diffraction efficiency for REGULAR samples as a function of melting temperature.

Fig. 2. (a) Photocurrent for the REGULAR samples fabricated at different melting temperatures (100 °C, 105 °C, 110 °C, 120 °C, 130 °C, and 140 °C) as a function of irradiation time. (b) The product of decreasing rate of photocurrent and $\gamma_M \cdot M$ calculated from Eq.1 as a function of melting temperature.

Fig. 3. Photocurrent for the W/O FDCST (100 °C) and W/O FDCST (140 °C) samples as a function of irradiation time.

Fig. 4. Photocurrent for the W/O EHCz (100 °C) and W/O EHCz (140 °C) samples as a function of irradiation time.

Fig. 5. DSC thermogram of the REGULAR (100 °C) and REGULAR (140 °C) samples at a heating rate of 20 °C/min.

Fig. 1.

Fig. 2.

Fig. 3.

Fig. 4.

Fig. 5

Melt @ 100 °C
+
Quench @ 5 °C

Melt @ 140 °C
+
Quench @ 5 °C