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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.

1. 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,

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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.

2. 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/cm^2) 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/cm^2. 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.

3. 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 ms 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 ±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

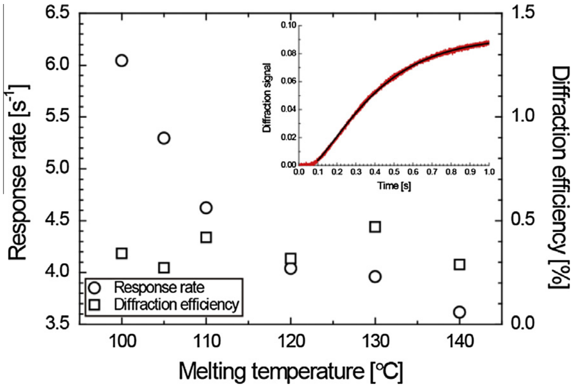

Fig. 1. Photorefractive response rate and diffraction efficiency for REGULAR samples as a function of melting temperature.