

Transient Absorption Decay and Photoconductive Characteristics of NPh₃-Silole Doped Fluorene Blend Film

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1. Introduction

In general, an organic thin-film can be fabricated by a roll-to-roll solution process. Therefore, organic devices have been interesting for several applications, such as light-emitting diodes, photovoltaic cells, and field effect transistors. In addition, a color-selective organic photoconductive device has been also investigated for a stacked organic image sensor [1]. This is because several organic materials have the selective absorption band at visible wavelength regions (blue, green, and red) and the higher absorption coefficient compared to Si [2]. However, the solution-processed organic photoconductive device has lower performances than the multilayer device fabricated by a conventional thermal evaporation process [2,3].

To realize an organic photoconductive device with a low fabrication cost, we need to develop solution-processed organic photoconductive devices. However, the multilayer structure with the high device performance is difficult to fabricate by the conventional solution-process. Since most photo-excited carriers of the single layer device recombine in the organic layer before reaching electrodes as a photocurrent. One possible approach to reduce the carrier recombination probability is the doping technique like a bulk-heterojunction structure of organic photovoltaic cells [4-6]. In our previous papers, we demonstrated the drastically improved external quantum efficiency (EQE) and the reduced dark current density by doping several silole derivatives. Among the tested silole derivatives, 1,1-dimethyl-2,5-bis(*N,N*-dimethylamino-phenyl)-3,4-diphenylsilole has the lowest ionization potential. Therefore, the photo-induced carriers efficiently dislocates in the organic layer with poly(dioctylfluorenyl-co-benzo-thiadiazole (F8BT) as a blue-sensitive material [5,7].

In this study, we investigated another silole derivative with the low ionization potential to improve the device characteristics. We used 1,1-dimethyl-2,5-bis(*N,N,N*-tri phenylamine)-3,4-diphenylsilole (NPh₃-silole). At first, the charge carrier dynamics in the NPh₃-silole doped F8BT film was estimated by measuring the transient absorption decay spectrum. The transient absorption characteristics are useful to understand carrier dynamics in an organic material [8], and they were measured by the femtosecond pump-probe technique. And then, we also investigated the device performance by doping NPh₃-silole in F8BT.

2. Experimental

After dissolving F8BT into chloroform at a concentration of 1 wt%, NPh₃-silole was added into the resulting solution. The concentrations of NPh₃-silole:F8BT were 0, 30, 50, 70, and 100 wt%. After passing through the filter with 0.45 μm holes, the organic solution was spin-coated on a silica glass substrate. And then, the sample was annealed in nitrogen atmosphere at 70 $^{\circ}\text{C}$ for 1 hour. Finally, an encapsulating glass cap was covered to avoid the degradation of the organic layer during the measurement.

Figure 1 shows the schematic configuration of the experimental setup and molecular structures of F8BT and NPh₃-silole. Time-resolved absorption decay characteristics were measured using the Ti:sapphire femtosecond laser system. The detail of the measurement setup is described in the following paper [8]. The wavelength of pump light was 480 nm, and F8BT has the high absorption coefficient at this wavelength region [2]. The transient absorption spectrum was measured by changing the wavelength of the probe light from 550 nm to 1200 nm.

We also fabricated the organic photoconductive device. The device structure was indium tin oxide (150 nm)/NPh₃-silole:F8BT /Al (130 nm). The NPh₃-silole:F8BT layer was formed by a conventional spin-coating process. Photocurrent density-electric field characteristic were estimated using a DC voltage current source/monitor (ADCMT, 6241A) while irradiating the blue-light (470 nm and 0.7 mW/cm²).

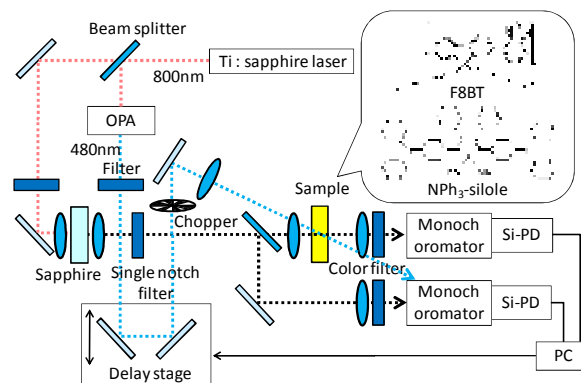


Fig. 1 Experimental setup of the femtosecond pump-probe technique. The inset shows molecular structures of NPh₃-silole and F8BT.

3. Results and Discussion

Figure 2 shows the transient absorption spectra of the NPh₃-silole doped F8BT thin films with different concentrations of NPh₃-silole. The optical density (ΔOD) was calculated from the optical intensities of transmitted with and without pump light. An absorption peak ranged from 900 to 1000 nm was observed by doping NPh₃-silole in F8BT, whereas this peak was not observed in the case of the neat films with NPh₃-silole and F8BT only. Therefore, we can conclude that the observed peak corresponds to the photo-induced carrier density in the NPh₃-silole doped F8BT layer. This result indicates that the carrier dislocation efficiency was improved by doping NPh₃-silole in F8BT. The ionization potential of NPh₃-silole was 5.53 eV, and it was much lower than that of F8BT (6.04 eV). Thus, the photo-induced hole was pulled toward silole side. This fact indicates the observed peak was considered to be the photo-induced hole density in the NPh₃-silole:F8BT layer.

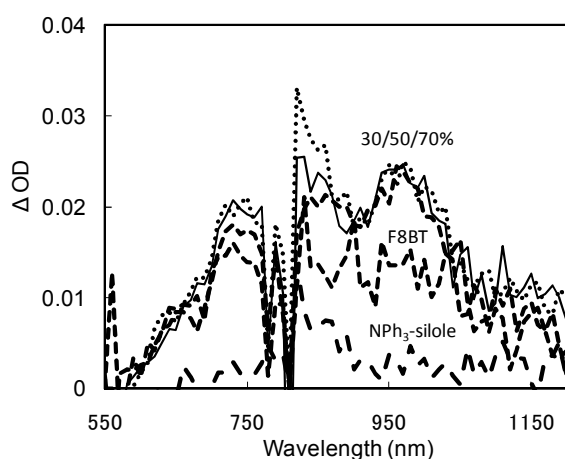


Fig. 2 Transient absorption spectra of NPh₃-silole doped F8BT thin films with different concentrations of NPh₃-silole.

Figure 3 shows the relationship between the applied electric field and the EQE of the devices with different concentrations of NPh₃-silole. The thicknesses of the NPh₃-silole:F8BT layers were 130 nm (0 wt%), 220 nm (30 wt%), 270 nm (50 wt%), and 340 nm (70 wt%). The EQE was drastically improved by doping the NPh₃-silole. Especially, the high EQE was obtained when the negative bias voltage was applied to the device. In general, the dark current density was important factor for image sensing applications, and the low dark current density was obtained for all the devices at the negative bias condition. Thus, the device performance while applying the negative bias voltage is important parameter. The maximum EQE of 52% was achieved at the concentration of 50 wt%.

The EQE roughly corresponds to the photo-excited carrier density in the organic layer. Therefore, this result indicates that the photo-induced carriers efficiently move to the electrode with the less carrier recombination probability by doping NPh₃-silole. This result is good agreement with the transient absorption characteristics, as shown in Fig. 2. The transient absorption spectrum shows the increased photo-

to-induced carrier density in the NPh₃-silole:F8BT layer, and this fact is considered to cause the high EQE of the organic photoconductive device. However, the EQE was reduced at the doping concentration of 70 wt%. The mechanism is not cleared; however, the one possible hypothesis is aggregated NPh₃-silole prevents the carrier transport.

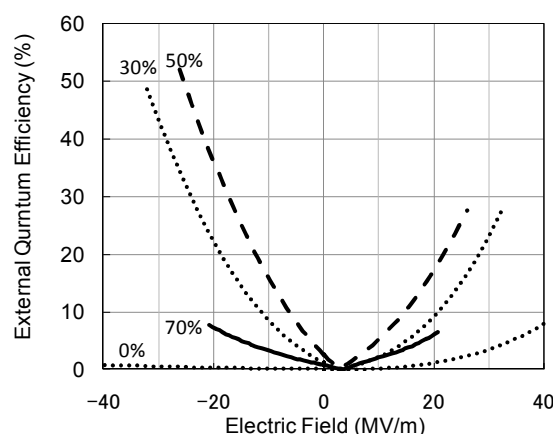


Fig. 3 Influence of the applied electric field on the EQE while irradiating the blue-light (470 nm).

4. Conclusions

In conclusion, we investigated the transient absorption characteristics of the NPh₃-silole doped F8BT thin film to understand the carrier dynamics. In addition, the organic photoconductive device with the NPh₃-silole doped F8BT layer was also estimated. These results indicate that the photo-induced carrier density was improved by doping NPh₃-silole in F8BT, resulting in the high EQE.

Acknowledgement

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