Wavelength-Selectivity of Organic Photoconductive Devices by Wet Process

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1. Introduction

Organic photoconductive devices have attracted much attention from both practical and physical points of view. A photocurrent multiplication phenomenon of up to 10,000 times has been observed, and this has been ascribed to an interaction between an organic layer and an Au electrode [1]. In addition, an efficient high-speed photoconductive device has been demonstrated using multilayer structure composed of donor-acceptor alternating layer [2]. Recently, a transparent organic photodiode for polarized light detection using aligned layer of organic molecules was reported [3].

By virtue of the superior wavelength selectivity of organic molecules, organic photoconductive devices with blue (B), green (G), and red (R) sensitivity were fabricated [4]. In addition, a new type of image sensor overlaid with three organic photoconductive films of such B, G, and R sensitivity was reported [5]. Those devices were fabricated by a thermal evaporation process with high reliability and high device performances. In order to improve larger area productivity with lower cost, however, we need to develop solution-processed devices at the same time.

In this study, we demonstrated B, G, and R sensitive organic photoconductive devices based on solution process. We report on the fabrication process and photoconductive characteristics of these devices.

2. Experimental

Figure 1 shows the cross sectional view of fabricated devices and molecular structures of organic materials used in this study. When an incident light reaches an organic film through a glass substrate and an indium tin oxide (ITO) anode, it is absorbed by the organic film to generate carriers. The photo-generated carriers are accelerated by an electric field and finally read out from ITO and Al electrodes as a photocurrent.

At first, a glass substrate covered with a patterned ITO was cleaned with solvents. Then, three-types of organic photoconductive materials were spin-coated on the glass substrates at a rotation speed of 1000 rpm for 60 second. We Poly(dioctylfluorenyl-co-benzo-thiadiazole used [F8BT], 50mol% Rhodamine6G [R6G]: Poly(dioctylfluorene) [PFO], and 108mol% Nickeltetrakis-(tert-butyl)phthalocyanine [Ni(t-Bu)₄Pc]:PFO as B, G, and R light sensitive photoconductive molecules, respectively. These organic materials were dissolved in chloroform as the content of 15 g/l for F8BT and R6G:PFO, and 10g/l for Ni(t-Bu)₄Pc:PFO. Then, the solvent was removed by baking the samples in air at 100 degree for 10 min. Finally, LiF and Al were evaporated successively. The device structures are summarized in Table 1.



(b) Molecular structures of organic materials

Fig. 1 (a) Cross sectional view of devices A, B, and C with F8BT, R6G:PFO, and Ni(*t*-Bu)₄Pc:PFO as photoconductive layers and (b) molecular structures of organic materials used in this study.

Color	Device structure
Blue	Glass/ITO (150 nm)/F8BT (160 nm)/
(device A)	LiF (0.5 nm)/Al (150 nm)
Green	Glass/ITO (150 nm)/R6G:PFO (270 nm)/
(device B)	LiF (1.0 nm)/Al (150 nm)
Red	Glass/ITO (150 nm)/ Ni(t-Bu) 4Pc:PFO
(device C)	(210 nm)/LiF (1.0 nm)/Al (150 nm)

3. Results and Discussion

Figure 2 shows photocurrent spectra of fabricated devices with photoconductive layers of F8BT (at 2.5 V)

R6G:PFO (at 5.0 V), and Ni(*t*-Bu)4Pc:PFO (at 2.0 V), respectively. In the case of device A, there was a peak of photocurrent at 465 nm but it kept down at the wavelength region above 500 nm. Therefore, this device has sensitivity at B-region with little response of G and R regions. The center wavelength of device B, on the other hand, was 554 nm, and the photocurrent decreased in both shorter and longer wavelength sides. As a result, the incident light of G region is detected by the device B. The photocurrent spectrum of the device C had the peak at 610 nm with the full width at half maximum of about 70 nm as shown in Fig. 2, showing the sensitivity only R region.

These results clearly indicate that we can obtain selective B, G, and R sensitivity by using F8BT, R6G;PFO, and Ni(*t*-Bu)₄Pc:PFO, which can be fabricated by wet process.



Fig. 2 Spectral photoresponse characteristics of three-types of fabricated devices with F8BT, R6G:PFO, and Ni $(t-Bu)_4$ Pc:PFO as photoconductive layers.

Figure 3 represents the external quantum efficiency (EQE) defined as the number of photoelectrons divided by the number of irradiated photons. The EQE was estimated from measured current density-voltage characteristics while irradiating light to organic photoconductive layers through a glass substrate. The center wavelengths of irradiated light were 469 nm, 530 nm, and 619 nm for devices A, B, and C, respectively. In addition, the bias voltage with 50 ms pulse duration was also applied to the device during the current

density-voltage measurement.

The EQEs of all the devices increased constantly with increasing electric field, which was estimated as the applied pulse voltage divided by the thickness of organic photoconductive layer. The maximum EQE of device A was 0.1% at the electric field of 2.2×10^5 V/cm, implying approximately 10 and 100 times higher than devices B and C. The EQEs of devices B and C were 0.009 at 1.5×10^5 V/cm and 0.001 at 1.7×10^5 V/cm, respectively.



Fig. 3 External quantum efficiencies of devices A, B, and C with F8BT, R6G:PFO, and $Ni(t-Bu)_4Pc:PFO$ as photoconductive layers as a function of electric field.

4. Summary

We demonstrated color-sensitive polymer-based organic photoconductive devices fabricated by spin-coating process. The photocurrent spectra of all the devices showed good spectral selectivity, which enables us to move toward a high-resolution, high-efficiency and lightweight image sensor.

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