Photovoltaic Effects in CuPc/C₆₀ and ZnPc/C₆₀ Depending on the Organic Layer Thickness

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Organic photovoltaic properties were studied in CuPc/C₆₀ and ZnPc/C₆₀ heterojunction structure by varying the organic layer thicknesses. Current density-voltage characteristics of organic photovoltaic cells were measured using Keithley 236 source-measure unit and a 500 W xenon lamp (ORIEL 66021) for a light source. From the analyses of current-voltage characteristics such as short-circuit current density, open-circuit voltage and power conversion efficiency, optimum thickness of the organic layer were obtained.

Keywords: Photovoltaic effects, CuPc, ZnPc, C₆₀, Exciton blocking layer

1. INTRODUCTION

Since the main source of energy in industry is the oil and the amount of oil in nature is limited, a development of substituted energy is needed. One of the possible substituted energies is a solar energy, because the solar energy is unlimited, pollution-free, and low-cost. An energy converting device from the solar energy to the electrical energy is a photovoltaic cell, normally called a solar cell. There are two types of photovoltaic cells made out of either organic and inorganic materials; bulk type and thin-film type.

Recently, there is a growing concern in organic thinfilm photovoltaic cells due to a rapid development of light-emitting diodes in display[1-7]. A basic mechanism of organic photovoltaic cells is the opposite process of organic light-emitting diodes. However, an energy conversion efficiency of photovoltaic cells is quite low, which is about few %. Basically, the organic photovoltaic cells use materials which effectively create electrons and holes by the illumination of light. In a point of cell structure, there are mixed type of materials, heterojunction type, and dye-sensitized type. In 1986, Tang obtained energy conversion efficiency of about 1 % using the heterojunction type of organic photovoltaic cell[1]. In 2001, Peumans et al., reported a photovoltaic cell having a power conversion efficiency of 3.6 %[2]. Reported values of exciton diffusion length of CuPc (copper phthalocyanine), ZnPc(zinc phthalocyanine) and C_{60} (fullerene) are 10 nm, 30 nm, and 40 nm, respectively[3]. Since the exciton diffusion length depending on the materials, the organic thickness should be optimized in photovoltaic cells. In this paper, we studied organic photovoltaic properties and exciton blocking effects in heterojunction structures of CuPc/ C_{60} and ZnPc/ C_{60} depending on the organic layer thicknesses.

2. EXPERIMENTAL

The Indium-tin-oxide(ITO) glass, having a sheet resistance of $15\Omega/\Box$ and 170 nm thick, was received from Samsung Corning Co. A 5 mm wide ITO strip line was formed by selective etching in vapor of solution made with hydrochloric acid(HCl) and nitric acid(HNO₃) with a volume ratio of 3:1 for $10 \sim 20$ minutes at room temperature. The patterned ITO glass was cleaned by sonicating it in chloroform for 20 minutes at 50 °C. Then the ITO glass was heated at 80 °C for 1 hour in a solution made with second distilled deionized water, ammonia water and hydrogen peroxide with a volume ratio of 5:1:1. We sonicated the substrate again with a chloroform for 20 minutes at 50 °C and in deionized water

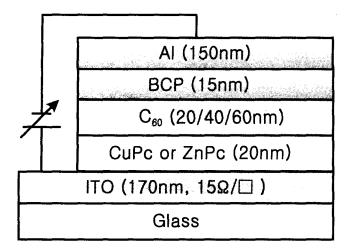
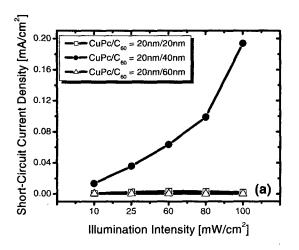


Fig. 1. Device structures of ITO/CuPc or ZnPc/C₆₀/with or without BCP/Al.



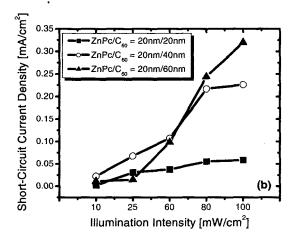
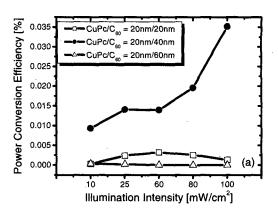


Fig. 2. Short-circuit current density as a function of illumination intensity in (a) ITO/CuPc (20 nm)/ C_{60} (20 nm, 40 nm, 60 nm)/BCP/ Al, and (b) ITO/ZnPc (20 nm)/ C_{60} (20 nm, 40 nm, 60 nm)/BCP/Al.



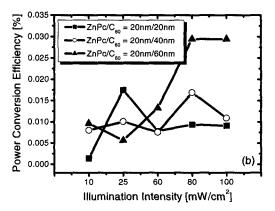


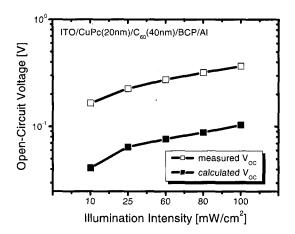
Fig. 3. Power conversion efficiency as a function of illumination intensity in (a) ITO/CuPc/ C_{60} / BCP/Al and (b) ITO/ZnPc/ C_{60} /BCP/Al devices for several thicknesses of CuPc/ C_{60} , and ZnPc/ C_{60} .

for 20 minutes at 50 °C. After sonicating the substrate, it was dried with N₂ gas stream and stored under vacuum.

Figure 1 shows a heterojunction device structure of ITO/CuPc or ZnPc/ C_{60} /BCP/Al. A layer thickness of CuPc and ZnPc was fixed to be 20 nm and the layer thickness of C_{60} was varied to be 20 nm, 40 nm, and 60 nm

The organic materials were successively evaporated under 10^{-6} torr at a rate of about $0.5\sim1$ Å/s. And Al cathode (150 nm) was deposited at 1.0×10^{-5} torr using thermal evaporation as well. An active cell area of device was made using a shadow mask to be 3 mm \times 5 mm.

Photovoltaic effects of organic photovoltaic cells were measured using Keithley 236 source-measure unit and a 500 W xenon lamp (ORIEL 66021). Light intensity on the device was measured by radiometer/photometer of International Light Inc (IL14004). The light intensity of the beam was adjusted to be 10, 25, 60, 80 and 100 mW/cm². All measurements were carried out at room temperature.



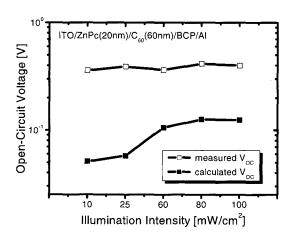


Fig. 4. Open circuit voltage as a function of illumination intensity in optimized (a) ITO/CuPc(20 nm)/ C_{60} (40 nm)/BCP/Al and (b) ITO/ZnPc(20 nm)/ C_{60} (60 nm)/BCP/Al device.

3. RESULTS AND DISCUSSION

Figure 2 shows a short-circuit current density $J_{\rm SC}$ as a function of the intensity of illuminated light for (a) CuPc/C₆₀ and (b) ZnPc/C₆₀ heterojunction devices. Maximum short-circuit current density was obtained when the layer thickness of CuPc/C₆₀ and ZnPc/C₆₀ are 20 nm/20 nm, 20 nm/40 nm, and 20 nm/60 nm, respectively.

Figure 3 shows a power conversion efficiency as a function of the intensity of illuminated light for (a) CuPc/C_{60} and ZnPc/C_{60} heterojunction devices. Maximum conversion efficiency was obtained when the layer thickness of CuPc/C_{60} and ZnPc/C_{60} are 20 nm/40 nm(3.5 %) and 20 nm/60 nm(3.0 %), respectively.

An open-circuit voltage $V_{\rm OC}$ has a following relation [8,9] with a reverse-biased saturated current.

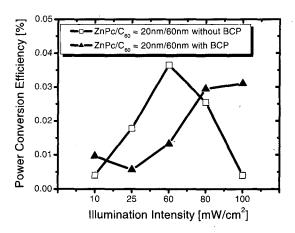


Fig. 5. Power conversion efficiency as a function of illumination intensity in optimized ITO/ZnPc(20 nm)/ $C_{60}(60 \text{ nm})/(a)$ without, (b) with BCP(15 nm)/Al device.

$$V_{OC} = \frac{kT}{q} \ln(\frac{I_L}{I_S} + 1) \tag{1}$$

, where k is a Boltzmann constant, T is an absolute temperature, and q is an electronic charge. I_S and I_L refer the reverse-biased saturation current under the dark and light condition.

Figure 4 shows a relation between the open-circuit voltage $V_{\rm OC}$ and the intensity of the illuminated light in the optimized structure of CuPc(20 nm)/C₆₀(40 nm) and ZnPc(20 nm)/C₆₀ (60 nm) device. In the figure, open squares are measured values and the solid squares are the calculated ones using Eq. (1).

The open-circuit voltage $V_{\rm OC}$ is mainly from the work function difference of the electrodes between ITO and Al. Measured open-circuit voltage is about 4 times higher than the expected value. It is thought that this difference comes from the relatively high value of $I_{\rm S}$, which is the reverse-biased saturation current under dark condition.

Figure 5 shows power conversion efficiency as a function of illumination intensity in optimized ITO/ZnPc $(20 \text{ nm})/C_{60}(60 \text{ nm})/(a)$ without, (b) with BCP(15 nm)/Al device.

In the device (a) without BCP, power conversion efficiency is increased until 60 mW/cm² of illuminated intensity, but quietly decreased over 60 mW/cm². In the other hands, as the illuminated intensity increases, the power conversion efficiency increases as well, because of increased the short-circuit current density. The BCP has a function of transport electrons to the cathode from the adjoining acceptor layer while effectively blocking excitons in the lower-energy-gap acceptor layer from recombining at the cathode. As the light intensity increases, there is a big improvement of conversion efficiency of the device with a use of BCP layer as is

seen in the Fig. 5(b).

4. CONCLUSION

Organic photovoltaic cell was studied by varying the organic layer thicknesses in ITO/CuPc/C₆₀/BCP/Al and ITO/ZnPc/C₆₀/BCP/Al heterojunction structure. Maximum energy conversion efficiency was obtained in the layer thickness of CuPc(20 nm)/C₆₀(40 nm)-3.5 % and ZnPc(20 nm)/C₆₀(60 nm)-3.0 %. We found that the short-circuit current density affects on the device efficiency and the measured open-circuit voltage is about four times higher than the theoretically expected one.

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