Effects of the Film Thickness on the Photocurrent Generation from Polythiophene-fullerene Thin Films Containing of Silver Nanoparticles

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1. Introduction

Recently, organic thin film solar cells have attracted more attention, as the next generation of solar cells. In particular, the combination of poly(3-hexylthiophene) (P3HT) (electron donor) and [6,6]-phenyl-C₆₁-butylic acid methyl ester (PCBM) (electron-acceptors) has been widely investigated as typical photovoltaic conversion film in organic solar cell¹.

In solar cells, the internal quantum efficiency (η_{IQE}) is determined by absorption efficiency (η_A), exciton diffusion efficiency (η_{ED}), charge transfer efficiency (η_{CT}), and charge collection efficiency (η_{CC}). As to the ideal organic photovoltaic cells, the efficiencies of charge collection and transfer commonly approach 100%²⁾, if one choose the excellent pair of donar (D) - acceptor (A) pair and the heterojunction interface is employed, Generally, however, there seem to be alternative approaches to improve the charge-collection efficiency. As to η_A and η_{ED} , they can be determined from exciton diffusion length (L_D), and optical absorption length $1/\alpha$. It is also clear that η_A linearly increases with the film thickness (d), while η_{ED} linearly decreases with d. In the organic solar cell, it is basically important to investigate the effects of the film thickness of organic layer even in the case of mixed system of D and A. However, the most important issue to be studied and improved is that how to effectively absorb the incident light in the organic film by making the most of optical configuration and by enhancing the photo-molecule interactions.

On the other hand, gold and silver nanoparticles (AuPs and AgPs) generate enhanced electric fields due to localized surface plasmon resonance (LSPR) by coupling visible light. They can increase interactions between photons and molecules, and consequently, luminescence and photocurrent can be enhanced³⁾. Previously, we found that AgPs could enhance the photocurrent efficiency in thin P3HT:PCBM photocells. In order to improve the performance of the cells, it is important to investigate the effects of thickness of organic films as well as the effects of the two-dimensional nanostructure consisting of deposited AgPs.



Fig. 1. Schematic illustration of prepared electrodes.

In this study, we investigated the effect of film thickness on photocurrent of P3HT:PCBM film with and without AgPs.

2. Experimental Procedure

Here we used same method reported before to fabricate samples which structures are ITO/P3HT:PCBM and ITO/AgP/P3HT:PCBM (Fig. 1)⁴⁾. Fluorescence spectra were measured on JASCO FP-6500 spectrophotometers. The film thickness of P3HT:PCBM layer was controlled through change the concentration of P3HT:PCBM chlorobenzene solution. Photocurrents measurements were carried out with our three-electrode photo-electrochemical cell. Film thickness was determined through atomic force microscopic (AFM). The P3HT:PCBM film thicknesses of samples with structure of ITO/P3HT:PCBM are 230 \pm 3 nm, 86 \pm 2 nm, 74 \pm 1 nm, 40 \pm 4 nm, 19 \pm 2 nm, 13 \pm 1 nm, 9.6 \pm 2 nm, respectively. With



Fig. 2. Fluorescence emission spectra of P3HT:PCBM films with (solid lines) and without AgPs (dotted lines); Here, from(a) to (d) are the spectra of samples fabricated with the concentration of P3HT:PCBM chlorobenzene solution of 2.5 mg/ml (a), 5 mg/ml (b), 10 mg/ml(c), 20 mg/ml (d) and 40 mg/ml (e), respectively.

same method, the P3HT:PCBM film thicknesses of samples with structure of ITO/AgP/P3HT:PCBM are 129 ± 2 nm, 124 ± 1 nm, 45 ± 1 nm, 18 ± 1 nm, 12 ± 3 nm, respectively.

3. Results and Discussion

Figure 2 shows fluorescence emission spectra of ITO/P3HT:PCBM and ITO/AgP/P3HT:PCBM based on the fluorescence from excited P3HT (excitation wavelength: 530 nm). The thicker P3HT:PCBM film with AgPs exhibited less emission intensity. It suggested that enhancement effect of LSPR in the thick films should not be observed accurately.

Figure 3 shows the relationship between P3HT:PCBM film thickness and incident photon to current conversion efficiency (IPCE %). Here, the IPCE % were obtained through the photocurrent measured by 3 electrodes systems⁵⁾.

In the case of without AgPs, the film thickness less than ca. 100 nm resulted in an increase in the IPCE %. It was in accordance with the previous report.⁶⁾ They concluded the appropriate thickness for P3HT:PCBM bulk-heterojunction solar cells was around 100 nm.

On the other hand, in the case of with AgPs (as shown in figure 4), the P3HT:PCBM film over ca. 120 nm exhibited quite low IPCE %. These results suggested that the appropriate thickness of P3HT:PCBM film with AgPs should be thinner than without AgPs.

4. Conclusions

As to the P3HT:PCBM film without AgPs, the appropriate film thickness in our system was estimated around 100 nm. On the other hand, the appropriate thickness of P3HT:PCBM



Fig. 3. Relationship between P3HT:PCBM film thickness and average IPCE % at 500, 550, 600 nm of ITO/P3HT:PCBM electrode without AgPs.



Fig. 4. Relationship between P3HT:PCBM film thickness and average IPCE % at 500, 550, 600 nm of ITO/AgP/P3HT:PCBM electrode.

film with AgPs should be thinner than without AgPs.

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