Improvement of Short-Circuit Current in Plasmonic Organic Solar Cells Based on Grating Structures

Akira Baba^{*}, Dai Murashima, Nobutaka Aoki, Kazunari Shinbo, Keizo Kato, Futao Kaneko

Center for Transdisciplinary Research and Graduate School of Science and Technology, Niigata University 8050 Ikarashi 2-nocho, Nishi-ku, Niigata, Japan *Phone: +81, 25, 262, 7260 E, meili shahe@one niigata u so in

*Phone: +81-25-262-7369 E-mail: ababa@eng.niigata-u.ac.jp

1. Introduction

Organic thin-film photovoltaic cells are one of the most promising candidates for inexpensive and flexible photovoltaic cells based on organic materials.^{1,2} An important challenge in the advancement of the organic thin-film photovoltaic cells is reducing their film thickness while maintaining their high efficiency. Hence, it is essential to develop a way to strongly absorb light in the thin-film layer. Because surface plasmon resonance (SPR) offers an enhanced optical field, i.e., increased absorption in the cell, there has been considerable interest in fabricating plasmonic-structured photovoltaic cells.³ The use of surface plasmons (SPs) in organic photovoltaic cells utilizing metal nanoparticles has been investigated as improved light absorption systems that provide high-efficiency cells.^{4–6} The prism-coupling method has also been used for the improvement of the organic photovoltaic cell.⁷⁻⁹ Although several SP-enhanced organic thin-film photovoltaic cells have been investigated to some extent with promising results,10 there have been a few reports on grating-coupled SP-enhanced organic thin-film photovoltaic cells. In particular, few working organic photovoltaic devices with plasmonic grating structures have been reported, whereas several important studies using finite-difference time-domain (FDTD) simulations have been reported recently.^{11,12} The grating-coupled technique is a prismless, convenient, propagating SPR excitation method.^{13,14} There have been reports that light scattering and light trapping can be obtained on the grating surface (without SP excitation), resulting in the improvement of the obtained photocurrent.¹⁵ Hence, in addition to the light scattering improvement effect, a remarkable improvement in the photocurrent of the cells might be obtained if the SP-enhanced field can be obtained on grating substrates. Recently, we demonstrated multimode SP excitations and enhanced photoluminescence properties of a metallic grating by using compact disc-recordable substrates.¹⁶

In this study, we demonstrate the fabrication of organic thin-film bulk-heterojunction photovoltaic cells on Blu-ray Disc recordable (BD-R) substrates for the excitation of grating-coupled SPs, which efficiently improve the photocurrent conversion. We also studied the distance dependence of the plasmon-enhanced photocurrent property by controlling the thickness of the P3HT:PCBM layer because the SP is an evanescent wave that exponentially decays as it moves away from the metal surface. Furthermore, in order to understand the experimental results, finite-difference time-domain simulations were performed by assuming that the organic thin-film photovoltaic cells had a grating structure. FDTD calculations indicated an increased electric field distribution in the cell, which corresponded well with the experimental results.

2. Experimental

Figure 1 depicts a schematic diagram of the fabricated bulk-heterojunction photovoltaic cell. The BD-R polycarbonate grating substrates were deposited with an ~150-nm-thick silver layer by vacuum evaporation. A procedure similar to the preparation technique reported in (17) was used to prepare the BD-R substrates. P3HT and PCBM were dissolved in trichloromethane with a P3HT:PCBM mass ratio of 1:1. The P3HT:PCBM thin film was deposited on silver/grating substrates by spin-coating the mixed solution at 2000 rpm for 1 min. The sample was then annealed at 100 °C for 1 h. ^Then, a multilayered film of low conductive PEDOT:PSS 10^{-5} (conductivity = 1 X S/cm) and poly(diallyldimethyl-ammonium chloride) (PDADMAC),¹⁷ which acted as a hole transport layer, was fabricated by the layer-by-layer (LbL) deposition technique.^{18,19} The P3HT:PCBM surface samples were then alternately immersed in aqueous solutions of PEDOT: PSS and PDADMAC for 15 min each until a10 bilayers were obtained. Between consecutive immersions, the samples were rinsed twice using deionized water for a duration of 2 min. Finally, high conductivity PEDOT:PSS (conductivity = 150 S/cm) was deposited on the PEDOT:PSS/PSS LbL film by spin-coating at 3000 rpm for 1 min; this acted as the anode. The sample was then annealed at 100 °C for 30 min.



Figure 1. Schematic drawing of the fabricated SPR-enhanced organic thin-film photovoltaic cell.

3. Results and Discussions

To study the effect of SP excitation, we investigated the short-circuit photocurrent properties both with and without SP excitation. We performed photocurrent measurements by irradiating collimated visible light from a 350-mW xenon lamp. Figure 2 shows the short-circuit photocurrent properties of the fabricated organic photovoltaic cells in which the thickness of the P3HT:PCBM layer is approximately 40 nm. For SP excitation measurements, the sample was irradiated with p-polarized light, whereas for non-SP excitation measurements, the sample was irradiated with s-polarized light. As shown in Fig. 2, for all cases, the short-circuit current with SP excitation increased more compared with that without SP excitation. This result clearly indicates that the grating-coupled SP excitation can enhance the photoelectric conversion in the cell. The current for the grating-coupled SP excitation increased up to two-fold more than that with no SP excitation. We plotted the enhanced factor p/s, i.e., the ratio of the current with SP excitation (p-polarization) to the current without SP excitation (s-polarization), as a function of the incident angle (Fig. 4) for each thickness of the P3HT:PCBM layer. It should be noted that the enhanced factor p/s increased with decreasing film thickness. Because the SP-enhanced optical field exponentially decayed as the distance from the silver surface increased, the increased current with the thinner P3HT:PCBM layer was caused by the stronger optical field in the wide range of the film. Furthermore, it should be noted that the short-circuit current increased at all incident angles, as exhibited by this plot. In all cases, the p/s factor was higher at higher incident angles. It should be noted that the p/s factor obtained using BD-R grating substrates showed the highest enhancement among all the other grating pitches, which were measured using Compact Disc recordable (CD-R) (A=1.6 $\mu m)$ and Digital Versatile Disc recordable (DVD-R) (A=740 nm) grating substrates.



Figure 2. Short-circuit photocurrent properties of the photovoltaic cell upon irradiation by visible light with SP excitation (p-polarization) and without SP excitation (s-polarization) (P3HT:PCBM = 40 nm).

3. Conclusions

In conclusion, we have demonstrated the fabrication of grating-coupled SPR-enhanced organic thin-film photovoltaic cells and their improved short-circuit current properties. Obvious increases in the short-circuit photocurrent can be obtained when the propagating-SP is excited on the silver gratings as compared to that without SP excitation. The FDTD simulation indicates that the electric field in the P3HT:PCBM layer can be effectively in-



Figure 3. Enhanced factor p/s, i.e., the ratio of the current with SP excitation (p-polarization) to the current without SP excitation (s-polarization).

creased using the grating-coupled SP technique. The demonstrated method should provide new opportunities to remarkably increase the efficiency of organic thin-film photovoltaic cells.

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