Influence of Titania Thin Film Morphology on the Photovoltaic action of Hybrid Titania-P3HT Solar Cell

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Abstract. We report the effects of surface properties of a titania (TiO2) interconnected network structure for photovoltaic applications of organic thin-film solar cell. The electron acceptor layer was obtained by annealing after spin coating of mixture of polyethylene glycol (PEG), Poly(3-hexylthiophene) (P3HT) and Poly(methylmethacrylate) (PMMA) with titania sol-gel solution. The fabrication method was simple and efficient for the increase of titania surface area. The size and height of nanocrystal titania was controlled by spin-coating speed of mixed solution and components of mixed polymer. The bulk-heterojunction solar cells consist of a nanocrystalline titania. In addition, P3HT solar cell showed strong dependence upon surface morphology and the best performance of cell was produced an open circuit voltage of 0.55 V, a short circuit current density of 0.78 mA/cm2, a fill factor of 0.51 and corresponding to a power efficiency of 0.22 % (air mass 1.5).

1. Introduction

Organic thin-film solar cells are a promising alternative to conventional inorganic solar cells because of the advantages of large area, low cost fabrication, flexible shape, easy processing, and light weight [1-2]. The photovoltaic effects of the solar cell based on organic material have been studied extensively, including dye sensitized, organic/inorganic hybrid, conjugated polymer/C60-delivered, inorganic compounds. However, the power conversion efficiencies of all reported organic photovoltaic devices are still low in comparison to typical inorganic photovoltaic cells. It can be attributed to the low stability of the organic material, inconsistency between the solar and polymer absorption spectrum, and the low mobility of excited electron or hole [3]. One potential solution to overcome the low mobility of carriers is by using nanostructured inorganic materials in the capacity of electron acceptor. Typically, nanostructured titania (TiO2) is one of the promising candidates as an electron recipient mediums due to its stability, easy control of size and shape, proper band-gap and low cost [4]. The ideal structure of electron acceptor has straight path way for the electron transfer such as nanorods, nanotubes and nanopores [5-7]. But fabrication of these titania nanostructures is relatively difficult compared with hybrid solar cell made by spin-coating method. A comprehensive solution for easy fabrication and the low mobility is utilizing of nanocrystalline structure which is commonly made by annealing after mixing of various polymer with titania sol-gel solution. Heeger et al. reported a very
low incorporation of polymers of ~0.5% in nanocrystalline titania (nc-titania) electrode [8]. In that case, the interface may result in the presence of more defective sites that can increase the recombination of excitons in photovoltaic cell. McGehee et al. suggested heating the cell in a nitrogenous atmosphere in order to infiltrate the conjugated polymer into the ordered titania pores with diameter of 20 nm [9]. His group also investigated the hole mobility of polymer into the straight nanopores of anodic alumina with pore diameter of 20–120 nm and observed that the highest mobility at diameter of 75 nm and similar hole mobility with flat film at 20 nm [10]. It is noticed that small diameter pore for increasing surface area causes a low hole mobility. Therefore, there should be an optimization between pore diameter and carrier mobility. In this work, we study structures based on titania substrate of different morphology which were made by annealing after mixing of polyethylene glycol (PEG), Poly(methylmethacrylate) (PMMA) and Poly(3-hexylthiophene) (P3HT) with titania sol-gel solution. It is found that the optimized titania morphology with infiltrate polymer dose not need additional process steps such as heat treatment. In addition, it is proved by measuring characteristics of hybrid photovoltaic cells using nc-titania and P3HT as the electron acceptor and donor, respectively.

2. Experimental

The titania sol-gel solution was prepared from a mixture of titania (IV) ethoxide, HCl and isopropanol. All samples were prepared on indium tin oxide (ITO) coated glass substrate, which were first cleaned by ultrasonic agitation in acetone and isopropanol. The cleaned substrate was then spin-coated (2000 rpm, 10 sec) with titania sol-gel solution that prevent direct contact of polymer with ITO. The titania neat films were obtained by sintering at 500 °C for 1 h in air and the process was repeated twice. Then the nc-titania films were accomplished by the same sintering method after titania sol-gel:various polymer mixture spin-coating on the titania neat film. The each mixed solution was obtained by mixing ratios of titania with PEG, P3HT (in chlorobenzene, 6 g/l) and PMMA(in chlorobenzene, 7 wt%) are 43 g/l, 25 ml/l and 125 ml/l, respectively. The nc-titania film thickness and morphology were controlled by 1000~3000 rpm spin-coating speed. Flat films titania cell was also prepared for a reference. After spin-coating P3HT (1000 rpm, 10 sec) on the nc-titania or flat film, the gold counter electrode was deposited by vacuum evaporation. The films thickness of the P3HT and gold electrode were about 80 nm and 100 nm, respectively. We inspected the surface morphology of the nc-titania with atomic force microscopy (AFM). Optical properties of the nanoporous titania and P3HT were investigated via UV-VIS absorption spectral measurements. Power conversion efficiencies were estimated from current-voltage (I-V) characteristics under solar simulated light (AM 1.5, 100 mW/cm²) irradiation. I-V characteristic was measured using a semiconductor parameter analyzer (Keithley 236) at room temperature in air.

3. result and discussion

For conventional flat titania-P3HT photovoltaic cells, the device structure (thickness of each layer, spin coating speed, sinter condition etc.) were optimized. The best device performances for the flat cell (open circuit voltage ($V_{oc}$)=0.52 V, short circuit current ($I_{sc}$)=0.277 mA/cm², power conversion efficiency ($\eta$, PCE)=0.056%) were obtained with spin-coating at 2000 rpm for 10 sec. Figure 1(d) shows the AFM images of the flat titania surface which had extremely smooth area that having rms roughness below 1.4 nm.

The nc-titania films were prepared by spin-coating a titanium ethoxide with various polymer mixture on the previous flat titania layer. Figure 1(a) show the AFM image that spin-coating (2000 rpm, 10 sec) of PEG:titania mixture and sintered at 500 °C for 1h. It is shows a higher roughness compared to the flat titania film. Film thickness and morphology by spin-coating at 1000, 1500, 2000, 2500 and 3000 rpm, the rms roughness becomes 8.1, 10.9, 12.2, 13.0 and 17.6 nm, and film thickness is 110, 80, 50, 40 and 30 nm, respectively. The film thickness decreases with increase of spin-coating speed, but the film roughness increases (figure 2(a)). As shown figure 2(b), it was observed that $V_{oc}$ nearly did not change in all devices roughness (figure 2(a)). As shown figure 2(b), it is observed that $V_{oc}$ nearly did not change in all devices but $I_{sc}$ increased at coating speed between 1000 rpm and 2000
rpm and then decreased at more than 2500 rpm. One possible reason for the result might be the increased contact area between the polymer film and the nc-titania with higher surface roughness, which may result in a more efficient charge collection at the interface. But efficiency was decreased at higher roughness (more than 2500 rpm). The reason with the higher roughness at the interface may result in the presence of more defect sites that can increase series resistance and recombination rate of electron-hole pair, thereby decrease $I_{sc}$ and FF [11]. It is known that the diffusion length of charge carrier in P3HT is only a few nanometers [12-13]. The best efficiency is obtained for the device with the spin-coating at 2000 rpm 10 sec. This cell produced $V_{oc}$ of 0.55 V, $I_{sc}$ of 0.78 mA/cm$^2$, fill factor (FF) of 0.51 and power conversion efficiency (PCE) of 0.22 % (figure 2(c)). In order to confirm this effect, we made nc-titania film with P3HT blend. Figure 1(b) show the AFM image for sample that nc-titania were made from P3HT precursor. From figure 1(b), it can be observed that the surface morphology similar with figure 1(a). From measurement of films thickness and morphology, spin-coated at 1000, 1500, 2000, 2500 and 3000 rpm, the rms roughness becomes 14.0, 13.4, 12.6, 11.9 and 10.6 nm, and film thickness is 100, 70, 65, 60 and 50 nm, respectively. In this case, it can be observed that the rms roughness decreases when coating speed increases. As shown figure 3(b), observed that $V_{oc}$ did nearly not change but $I_{sc}$ increased at coating speed between 1000 rpm and 2000 rpm and then decreased at more than 2500 rpm. This is nearly same results with previous work, which showed highest efficiency at ~12 nm rms roughness at 2000 rpm. The device performances at 2000 rpm are $V_{oc}$ of 0.56 V, $I_{sc}$ of 0.657 mA/cm$^2$, FF of 0.48 and PCE of 0.18 %. The best power efficiency of P3HT:titania blend cell slightly lower than PEG:titania blend cell. It is believed that nc-titania layer by
Figure 3. Nc-titania films characteristics made by various coating speed with P3HT:titania blend. (a) films thickness (left) and rms roughness (right); (b) I-V curves; (c) PCEs.

PEG:titania absorbed lights over the higher wavelength range 375 ~ 575 nm than nc-titania layer made by P3HT:titania as shown figure 1(e). Higher absorption and an increase of the carrier mobility are most likely the reasons for the higher efficiency with PEG [14]. To investigate the effect of nc-titania roughness, we made PMMA:titania blend cell at 2000 rpm. Which had roughness of 76.2 nm and the absorption over the wavelength range 450 ~ 625 nm higher than PEG:titania blend cell. However it showed very low efficiency (V oc=0.05 V, I sc=0.034 mA/cm 2, FF=0.30, PCE=0.0005). It has been demonstrated that the morphological properties of nc-titania layer in an inorganic-organic hybrid solar device strongly influences the overall efficiency of the photovoltaic cell.

4. conclusion

In conclusion, the photovoltaic cells based on nc-titania:P3HT by optimizing the films morphology were fabricated and tested. The best roughness of nc-titania for the bulk-heterojunction device without any post-treatment is approximately 12 nm. AFM images were used to study the nc-titania film morphology and the surface roughness that effected charge collection efficiency at the nc-titania/P3HT interface. As a result, power conversion efficiency of the best devices was 0.22 %.

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References

[1] Coakley K M and McGehee M D 2004 Chem. Mater. 16 4533
[2] Taima T, Chikamatsu M, Yoshida Y, Saito K and Yase K. 2004 Appl. Phys. Lett. 85 6412
[3] Brabec C J, Sariciftci N S and Hummelen J C 2001 Adv. Funct. Mater. 11 15
[4] Alberius P C A, Frindell K L, Hayward R C, Kramer E J, Stucky G D and Chmelka B F 2002 Chem. Mater. 14 3284
[5] Huynh W U, Dittmer J J and Alivisatos A P 2002 SCIENCE 295 2425.
[6] Yoon J H, Jang S R, Vital R, Lee J and Kim K J 2006 J. Photochem. Photobiol. A 180 184
[7] Kim S S, Jo J, Chun C, Hong J C and Kim D Y 2007 J. Photochem. Photobiol. A 188 364
[8] Bartholomew G P and Heeger A J 2005 Adv. Funct. Mater. 15 677
[9] Coakley K M and McGehee M D 2003 Appl. Phys. Lett. 83 3380
[10] Coakley K M, Srinivasan B S, Ziebarth J M, Goh C, Liu Y and McGehee M D 2005 Adv. Funct. Mater. 15 1927
[11] Taima T, Toyoshima S, Hara K, Saito K and Yase K 2006 Japan. J. Appl. Phys. 45 L217
[12] Bozano L, Carter S A, Scott J C, Malliaras G G and Brock P J 1999 Appl. Phys. Lett. 74 1132
[13] Friend R H, Denton G J, Hall J M and Harrison N T 1997 Solid State commun 102 249
[14] Li G, Shrotriya V, Yao Y and Yang Y 2005 J. Appl. Phys. 98 043704-1