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Intense pulsed light annealed buffer layers for organic photovoltaics

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ABSTRACT

The effect of intense pulsed light (IPL) annealing on the fabrication of OPV buffer layers was investigated. In order to avoid causing damage with the high intensity light, an inverted OPV structure was used. Sol–gel type ZnO was annealed by IPL and used as an electron extraction layer. The effects of controlling a variety of parameters, including the voltage, pulse duration, and distance between the substrate and the light source, on the device fabrication process were studied. In order to obtain better energy level matching between the work function of the cathode and the LUMO of the semiconducting acceptor, polyethylenimine ethoxylated was used. The most homogenous ZnO nanoparticle layer was obtained with 30 IPL pulse treatments, resulting in an optimum electron extraction layer. IPL annealed ZnO devices showed enhanced performance compared to thermally annealed ZnO devices. OPV devices with IPL-treated ZnO coated with PEIE showed a ~10% enhancement in the conversion efficiency compared to devices with thermally annealed ZnO coated with PEIE.

1. Introduction

Research and development of electronic devices based on organic materials began several years ago and have led to the advanced flexible devices that we see today. The fact that many polymers are readily soluble makes them favorable for use in flexible device manufacturing processes that are aided by printing technologies. Even though organic-based devices cannot completely replace conventional inorganic devices because of their relatively poor performance, they have attracted significant attention due to their potential for use in an extensive variety of applications. In particular, the mechanical flexibility of polymeric materials and their solution processing capabilities make them naturally compatible with printing methods that use plastic substrates. Organic photovoltaic (OPV) devices have several advantages over traditional silicon-based or other inorganic solar cells. These benefits include the fact that they are light weight, inexpensive, easily processed, and can be manipulated to obtain a tailored structure. Thus, OPVs have been accepted as a new way of obtaining clean renewable energy. Recent rapid improvements in the power conversion efficiency have elicited expectations for commercial OPV devices in the near future [1–4]. Organic solar cells produced by roll-to-roll systems have strongly improved the possibility of obtaining commercially-available OPVs [5–10].

Intense pulsed light (IPL) has been utilized for device fabrication through “sintering” (nano-sized metal particles absorb the UV spectrum of light from a xenon flash lamp and instantly melt to make a bare metal film) or “annealing” (removal of the organic ligands from a metal oxide ink, which causes crosslinking of the polymeric dielectric and improves the crystallinity of the organic semiconductor) [11–13]. When a xenon flash lamp is used, a wide spectrum range (from UV to IR) can be utilized to a variety metals and inorganic materials depending on the absorption characteristics of the material. In addition, the high photon intensity of the xenon lamp allows for a very short exposure time and the line light source characteristics of the xenon lamp allow for a wide range of substrate widths (up to 500 mm). These conditions mean that IPL is compatible with roll-to-roll systems, which enables the use of less expensive substrates by reducing the thermal burden. By controlling a variety of simple parameters (e.g. the voltage, pulse duration, and distance between the substrate and the light source), the IPL technique can also simplify the device fabrication process [14]. Some other techniques utilizing light have also been reported [15,16].

For the preparation of inverted OPVs, ZnO has been widely used because of its high transparency, high electron mobility, and simple fabrication procedure [17–19]. In particular, fabricating the ZnO layer can be divided into two types of methods: 1) drying the solvent from a pre-synthesized ZnO nanoparticle solution and 2) oxidizing Zn by using a sol–gel process. Both methods, which

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require either a high temperature or a long drying and annealing time, are not suitable for roll-to-roll processes using polymer substrates (which are susceptible to thermal damage). However, the flash lamp annealing method has the advantages of reducing the risk of thermal damage to the substrate and a shorter annealing time. In this study, we investigated the effects of pulsed light annealing for the fabrication of the buffer layer of OPVs.

2. Materials and methods

The electron buffer layers were prepared from PEIE (polyethylenimine ethoxylated), a bare ZnO solution, and a PEIE solution coated on ZnO nanoparticles. 0.4 g of PEIE was dissolved in 2-methoxyethanol (100 g) and the resulting solution was stirred for 24 h. A 20 wt% ZnO sol–gel stock solution (purchased from Ditto Technology in Korea) was diluted with methanol to 1, 3, 5, and 10 wt%. The resulting solutions were spin coated on top of ITO-coated glass at 5000 rpm for 40 s. The PEIE solution was dried in a convection oven at 110 °C for 10 min. For thermal ZnO annealing, the 1, 3, 5, and 10 wt% ZnO film samples were dried on a hot plate at 250 °C for 10 min. For IPL annealed samples, 5 wt% samples were annealed with an external bias of 500 V for 2 ms at a frequency of 10 Hz. The gap between the lamp and the sample was 5 mm.

The photoactive layer was fabricated by spin coating a 4 wt% solution of poly(3-hexylthiophene) (P3HT) and [6,6]-phenyl C_{60} butyric acid methyl ester (PCBM) (1:0.8 by weight) in 1,2-dichlorobenzene. The spin coating rate was 1000 rpm for 40 s. This was followed by annealing in a convection oven at 110 °C for 10 min. Then, PEDOT:PSS ink (Agfa EL-P5010) was screen printed and annealed in a convection oven at 110 °C for 10 min. Finally, the electrode layer was screen printed with silver paste (purchased from TOYO), UV cured for 30 s, and annealed in a convection oven at 110 °C for 7 min.

The device size was 0.25 cm^2 and the device performance was measured under an illumination of 100 mW/cm^2 with an AM 1.5G solar simulator (Newport Oriel). Measurements were not corrected for reflection loss or light absorption in the ITO electrode. The *I–V* characteristics were determined with a Keithley 2400 source-measurement unit. The thickness of the coated film was measured with a surface profiler (TENCOR®, P-10 α-step). The IPL system is composed of a xenon lamp (Heraeus, Model: P3780, 1 kW) with a high power supply and a remote controller (developed by EESYS).

3. Results and discussions

In this study, the effect of using IPL annealing for the fabrication of electron extraction layers was studied. Due to the high intensity (i.e., high depth of light penetration) of IPL, an inverted OPV structure was used, as shown in Fig. 1. Inverted OPVs have been widely studied due to their extended lifetime compared to the normal OPV structure [20,21]. Ever since OPVs containing PEIE (as a modified, low work function electrode) were first reported by Zhou et al. [22], many studies have been performed due to the difficulty of energy level matching between the work function of the cathode and the LUMO of the semiconducting acceptor. The addition of ZnO between the ITO electrode and PEIE has also been widely studied in an attempt to enhance the OPV efficiency by lowering the work function of ZnO [23].

In order to obtain the highest efficiency OPVs with ZnO/PEIE as an n-type buffer layer, we determined the optimal ZnO film thickness by using thermal annealing. When the 1 wt% sol–gel solution was spin coated (thickness of ZnO layer was 20 nm), devices showed the highest current density, but the fill factor was the lowest; therefore, the overall power conversion efficiency was lower than the device coated with the 5 wt% sol–gel solution (thickness of ZnO layer was 40 nm). Fig. 1 shows the *I–V* characteristics of typical devices. As the ZnO film thickness increased (i.e., the concentration of the stock solution increased), the current density decreased. An optimum value was observed when the 5 wt% stock solution (coated film thickness was about 40 nm) was used. Since ZnO acts as a resistor, we expected the extracted current density to decrease as the thickness of ZnO increases. However, when the 10 wt% ZnO sol–gel solution was spin coated, the resulting ZnO film thickness was about 90 nm and showed a current value between the 5 wt% and 3 wt% solutions. Additionally, the open circuit voltages and fill factors were not significantly affected by the thickness of the ZnO film. The device performances for different ZnO film thickness are summarized in Table 1. As shown in Fig. 1, the ZnO layer coated from the 5 wt% sol–gel solution showed the best conversion efficiency. This might be caused by the formation of a more homogenous film due to thermal annealing the films with the optimum thickness. From these results, the 5 wt% sol–gel solution film (thickness of ZnO layer was 40 nm) was determined to have the optimum ZnO film thickness. The optimum thickness of PEIE (10 nm), which was used for lowering the work function of ZnO, was based upon the results reported in another study [22].

Next, the influence of the irradiation conditions on ZnO annealing was studied by varying the number of pulses. In general, the process parameters of the IPL system for millisecond annealing are the output power (or voltage), pulse duration time, frequency, and number of pulses. Gebel et al. showed that when the duration time of a single pulse is increased, while the other process parameters are fixed, the temperature gradient along the depth profile is decreased [24]. This causes homogeneous annealing of the sample. However, this method requires a high output power, which increases the substrate temperature and affects the substrate properties after prolonged periods of time. We have studied the effects of the various process parameters on our IPL system and found that the optimum annealing conditions occur at a reduced output power and duration time and an increased pulse number. At these conditions, the substrate temperature was not

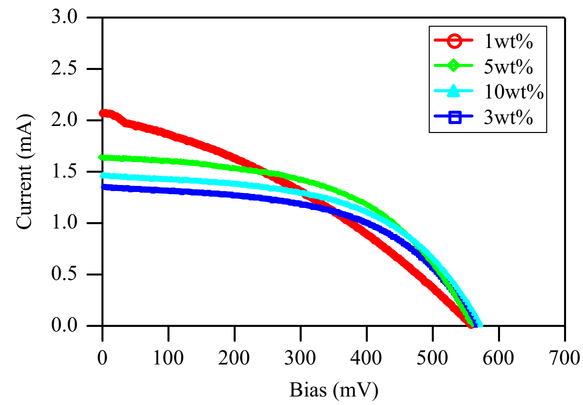

Fig. 1. The *I–V* characteristics of devices with different ZnO thicknesses.

Table 1
Summary of OPV device performances with different ZnO thickness.

Number	*W/T*(%)	J_{sc} (mA/cm^2)	I_{sc} (mA)	V_{oc} (mV)	FF (%)	Eff (%)
ZnO	1	8.524	2.063	559	34	1.5
	3	5.564	1.391	561	51	1.5
	5	6.643	1.661	565	51	1.9
	10	5.996	1.489	567	50	1.7