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Abstract: The indium–tin-oxide-free organic solar cells (OSCs) have been fabricated using a semitransparent Au film as anode. A comparative study between the OSCs with different metal cathodes shows that formation of an ideal ohmic contact at low-workfunction Ca and the organic interface reduces series resistance and increases the carrier collection. Moreover, a periodic corrugation was introduced into the device structure, which leads to an enhanced light absorption in the OSCs by elongating the optical path of the incident light inside the absorber material. The highest power conversion efficiency of an optimal OSC with a Au anode and a corrugated Ca/Ag cathode is 1.4%, which is significantly improved in contrast to 0.61% for the OSC with a planar Al cathode.

Index Terms: Organic solar cells (OSCs), low-workfunction metal, periodic corrugation, Au anode.

1. Introduction

Organic solar cells (OSCs) are potential candidates for the next generation of photovoltaic devices because of their advantages over their inorganic counterparts: they are low-cost, flexible, and appropriate for large-scale applications [1]–[4]. Indium–tin oxide (ITO) is the most commonly used transparent electrode material in OSCs because it provides a combination of transparency and conductivity. However, a global shortage of indium, more than 80% of the fabrication cost [5], and poor compatibility with flexible substrates have limited its commercial applications. A roll-to-roll process is compatible to ITO-free OSCs on the flexible substrates [6]–[9]. Transparent flexible conductive materials such as conducting polymers [10]–[12], carbon nanotube films [13]–[15], graphene [16], random networks of metallic nanowires and nanometallic/micrometallic grids [17], [18] have been shown to be promising alternatives to ITO. Unfortunately, very few of these electrodes have yielded OSCs with performances comparable to those utilizing ITO.

Recently, Au has attracted attention as an electrode material to replace ITO in OSCs [19]–[22] because of its high workfunction, high conductivity, simple fabrication process, and compatibility with flexible materials [23]. Moreover, Au is more easily extracted from the earth crust and can also be applied very thin, so that a short energy payback time is expected [24]. In this paper, a semitransparent Au film instead of the ITO is used as the anode in the OSCs. The performance of
the Au-based OSCs has been improved using an ultrathin low-workfunction metal Ca modified thick Ag as cathode and introducing the periodic corrugation into the device. We demonstrated that an ideal ohmic contact at the Ca/organic interface increases the carrier harvest and reduces the series resistance of the OSCs. Moreover, light trapping and more efficient capture and separation of excitons at the interface between the donor and the acceptor induced by the introduction of the periodic corrugation have played an important role in improving short-circuit current. As a result, the power conversion efficiency (PCE) of optimally corrugated OSCs is significantly improved.

2. Experimental Details

2.1. Preparation of Periodically Corrugated Substrate

A two-beam laser interference microfabrication system was set up, as shown in Fig. 1(a). A continuous laser with a wavelength of 266 nm (MBD E-200, Coherent Inc., USA) was used as the light source. Before the fabrication of the cells, the glass substrates were precleaned sequentially by acetone, ethanol, and deionized water in an ultrasonic bath for 10 min and finally dried in a N\textsubscript{2} stream. A 120-nm-thick layer of photoresist (NOA-68, Norland Inc., USA) was spin-coated onto the cleaned glass substrates and exposed by two beams, which were split from the UV laser and had a beam diameter of \( \frac{\text{C24}}{\text{C26}} \) mm. After the exposure, the samples were baked for 1 min at \( \frac{\text{C24}}{\text{C25}} \) Co na and then developed in acetone. By controlling the writing angle and exposure time, 1-D corrugations with a period of \( \frac{\text{C22}}{\text{C23}} \) m and groove depths of 20, 35, and 45 nm were achieved. The morphologies of the microstructures were characterized by atomic force microscopy (AFM, Digital Instruments Nanoscope IIIA, Veeco Inc., USA) in tapping mode, and the AFM images of the 20-, 35-, and 45-nm grooves are shown in Fig. (b)–(d), respectively.

2.2. Fabrication and Characterization of OSCs

The OSCs were fabricated on both glass substrates coated with the corrugated photoresist and bare glass substrates. Then, the substrates were immediately loaded into a thermal evaporation chamber. A 20-nm-thick Au layer (\( \sim 10 \ \text{\Omega/sq} \)) was deposited onto the substrates by thermal evaporation through a shadow mask. An electron donor layer of copper phthalocyanine (CuPc, 35 nm), an electron acceptor layer of fullerene (C\textsubscript{60}, 70 nm), and an exciton-blocking layer of bathocuproine (BCP, 10 nm) were evaporated sequentially. As shown in Fig. 2(a), devices A, B, C, and D were
fabricated on a bare substrate with Al (80 nm), LiF/Al (1 nm/80 nm), Mg/Ag (3 nm/80 nm), and Ca/Ag (3 nm/80 nm) cathodes, respectively. Devices E, F, and G were fabricated on corrugated substrates with 20-, 35-, and 45-nm groove depths, respectively, so that the periodic corrugations were formed throughout the device structure, as shown in Fig. 2(b). The cathode of all the corrugated devices is Ca/Ag. All organic and metallic films were thermally evaporated under high vacuum ($5 \times 10^{-4}$ Pa). All organic materials were purchased from LumTec. Corp. and used as received. The active area of the device is $2 \times 2$ mm$^2$. The thickness of each layer was monitored by quartz crystals and calibrated by a spectroscopic ellipsometer (J. A. Woollam Co., Inc., USA). The current density–voltage ($J$–$V$) curves of the OSCs were measured by a Keithley 2400 sourcemeter under 1 sun (100 mW/cm$^2$) simulated AM 1.5-G illumination. The reflectance spectra of the samples were measured by a UV-vis spectrophotometer (UV-2550, SHIMADZU Co., Inc., Japan). All values herein are given without mismatch correction.

3. Results and Discussion

3.1. Optimization of the Cathode Structure

First, the Au-based OSCs using Al (A), LiF/Al (B), Mg/Ag (C), and Ca/Ag (D) cathodes were fabricated and characterized to obtain an optimized cathode structure. The workfunction of Al, Mg, and Ca is 4.28, 3.6, and 2.9 eV, respectively. The $J$–$V$ characteristics of the prepared OSCs are shown in Fig. 3. The detailed results are given in Table 1. The interface between the electrode and the organic active layer plays an important role in the carrier collection and interfacial resistance [25]–[27]. From the $J$–$V$ curves, it can be seen that the short-circuit current ($J_{sc}$) of the OSCs is strongly dependent on the workfunction of the cathode. The OSC with Al cathode (A) shows poor photovoltaic behavior ($V_{oc} = 0.42$ V, $J_{sc} = 2.83$ mA/cm$^2$, PCE = 0.61%). When Al was modified by LiF, slightly higher $J_{sc}$ (3.33 mA/cm$^2$) and PCE (0.74%) were obtained. Mg and Ca with a further lower workfunction of 3.6 and 2.9 eV, respectively, were used in devices C and D. As a result, the highest $V_{oc}$ (0.46 V), photocurrent (5.12 mA/cm$^2$), and PCE (1.27%) were observed for device D using Ca/Ag as cathode. The PCE is increased by 1 time over the PCE of device A with Al cathode.

The major contributing factor to the obvious increment is the formation of an ideal ohmic contact at the organic/cathode interface due to the very good matching of the Fermi levels of Ca (2.9 eV) to the lowest unoccupied molecular orbital of the BCP (2.9–3.0 eV) [28], [29], which reduce the series resistance and enhance the carrier harvest. On the other hand, a large workfunction difference between the anode of Au (5.1 eV) and the electrode of Ca (2.9 eV) forms a strong built-in electric field in active layers, which promotes the separation of excitons and reduces the recombination of carriers. In both cases, a high photovoltaic performance can be achieved.
3.2. Performance of the OSCs with Corrugated Structure

The corrugations with various groove depths were introduced into the planar device with the optimal Ca/Ag cathode to further improve its properties. The $J–V$ characteristics of these OSCs (devices E, F, and G) are shown in Fig. 4, and the detail performance is summarized in Table 2. Comparing with the planar device with the same cathode (device D), the photocurrent of corrugated OSCs increases with increasing groove depth. The $J_{sc}$ of corrugated device G with a 45-nm groove depth is 5.57 mA/cm$^2$, which is higher than that of planar device D (5.12 mA/cm$^2$). The PCE increases from 1.27% for planar devices to 1.4% for device G with a groove depth of 45 nm, corresponding to an enhancement of 10%.

To verify that this efficiency enhancement is induced by the corrugation, the absorption spectra of the corrugated devices with various groove depths were compared with that of the planar device, as shown in Fig. 5. The light is incident through the semitransparent Au anode, and the reflection spectra have been measured. Absorption spectra are obtained from the complementary relation between reflection and absorption. The peaks at 645 and 710 nm correspond to the intrinsic absorption of CuPc, while the peak at 550 nm is due to the resonance of the microcavity formed by the two metallic electrodes. The absorption significantly increases with the groove depth in the short-wavelength region (less than 500 nm) and also in the absorption region of CuPc, which indicates that more light is trapped in the OSCs with the corrugated structure. The increased trapping of light results in the grating depth-dependent enhancement of light absorption and $J_{sc}$.
The period of 1.5 μm is much larger than the wavelength scale; therefore, the effect of surface plasmons promoting better absorption can be ruled out. The elongated optical path of the incident light inside the absorber material due to the structured metal electrode surfaces is the most probable mechanism for the absorption enhancement [30]. The light reflected by the microstructured
back cathode is no longer normal to the substrate plane; thus, it crosses the absorber layer at a greater angle on the way back. Therefore, the path for absorption is elongated, and light is concentrated in the absorber. In addition, the larger junction interface area induced by the corrugation may also contribute to the increased efficiency [31]–[33] because the number of excitons generated in CuPc within a diffusion length of the junction interface increases proportionately to the junction area.

4. Conclusion

In summary, the performance of OSCs with Au anode has been improved by employing a low-workfunction and periodically corrugated Ca/Ag cathode. The experimental results show that the performance of planar devices is dependent on the workfunction of the cathode. The PCE of the planar OSC with an optimal Ca/Ag cathode exhibits 2 times enhancement compared with that of the device with Al cathode. Moreover, the performance of Au-based OSCs has been further improved by employing corrugated structures. The corrugated metal electrode surfaces can increase the length of the optical path of the incident light inside the absorber material and enhance light trapping. The increased junction interface area induced by the corrugation also contributed to the increased efficiency by improving the capture of the excitons at the corrugated interface. As a result, the PCE exhibits a further increment of 10% comparing with that of the planar device.

References


