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Citation: Applied Physics Letters **101**, 133303 (2012); doi: 10.1063/1.4755774
View online: http://dx.doi.org/10.1063/1.4755774
View Table of Contents: http://scitation.aip.org/content/aip/journal/apl/101/13?ver=pdfcov
Published by the AIP Publishing

Highly flexible inverted organic solar cells with improved performance by using an ultrasmooth Ag cathode

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(Received 27 July 2012; accepted 13 September 2012; published online 26 September 2012)

Inverted organic solar cells (OSCs) with high efficiency and flexibility have been demonstrated. A thick Ag film with ultrasmooth morphology fabricated on a photopolymer substrate by template-stripping process and a semitransparent Ag film has been employed as cathode and anode of the top-illuminated OSCs, respectively. An improved performance has been obtained compared with that of the OSCs deposited on Si substrate due to the enhanced charge extraction and reduced charge loss resulted from the employment of the ultrasmooth cathode. Moreover, the flexible OSCs obtained by this method keep good performance under a small bending radius and after repeated bending. © *2012 American Institute of Physics*. [http://dx.doi.org/10.1063/1.4755774]

Organic solar cells (OSCs) as possible next-generation solar energy-harvesting devices have attracted much attention due to their low-energy consumption in fabrication, low-cost manufacturing, and particular mechanical flexibility.[1–5] In flexible OSCs,[6–8] a crucial aspect is the fabrication of high performance electrodes on flexible substrates because surface morphology of electrodes can affect efficiency and stability of devices. Recently, plastic film, e.g., polyethylene terephthalate (PET)[6–8] is the most commonly used flexible substrate and indium-tin-oxide (ITO) is the traditionally used transparent electrode material. Unfortunately, sputtering ITO is not an ideal choice because not only its high cost and complicated technology but also bring adverse impact on PET substrate due to high-temperature process. PET will suffer from thermal shrinkage when ITO is deposited.[8,9] In addition, the scarcity of indium reserves, intensive processing requirements, and highly brittle nature of metal oxides impose serious limitations on the use of these materials for applications in flexible devices. Metal thin films have been adopted as one of the candidates to replace ITO,[9,10] due to their high transparency, high conductivity, and their simple deposition by thermal evaporation. However, the inherently rough surface of the metal films deposited by evaporation due to polycrystallinity is an obstacle to high performance of the OSCs, because surface morphology of electrode is a key issue for both enhancement of charge extraction and reduction of charge loss at the electrode in the OSCs.

Template stripping has been demonstrated to be a simple and effective technique to generate smooth metallic films.[11–13] Typically, solids with ultrasmooth surface such as mica, glass, and silicon are used as master templates. With subsequent metal deposition on the templates, a smooth surface at the metal-template interface is formed, which can be peeled off using a backing layer. Although the evaporated metal film has a rough surface after deposition, the smoothness of the opposite interface is near that of the templates. This method exhibits particular advantage in flexible optoelectronic devices, because not only the metal smoothness can be improved but also the backing layer itself is flexible and can be used as the substrate. Highly flexible and efficient top-emitting organic light-emitting devices with ultrasmooth electrode have been demonstrated by using template stripping.[14] However, further application of this method in flexible OSCs has not yet been explored. In this letter, Ag film with ultrasmooth surface morphology has been fabricated on plastic substrate by employing the template stripping technique and has been used as the cathode in flexible top-illuminated OSCs. The inverted OSCs have shown superiority in both flexibility and mechanical robustness. Moreover, the power conversion efficiency (PCE) is 13% enhanced compared with a conventional OSC due to the enhanced electrons extraction at the ultrasmooth Ag/organic interface and reduced charge loss at the ultrasmooth Ag cathode.

The fabrication process of ultrasmooth Ag cathode on plastic substrate is shown in Figs. 1(a)–1(c). At first, a cleaned silicon (Si) template was loaded into a thermal evaporation chamber. An 80 nm thick Ag was grown at a rate of 1 Å/s at a base pressure of 5×10^{-4} Pa. Then, photopolymer (NOA63, Norland) was spin coated onto the template deposited with the Ag film for 20 s at 1000 rpm and exposed to an ultraviolet light source for 5 min. The power of the light source is 125 W. At last, the cured photopolymer film can be peeled off. Generally, the adhesion is proportional to the surface energy of the substrate.[15] The surface energies of Si and photopolymer substrates were measured by contact angle measurements (SL200B, Solon Tech.). The surface energy of Si substrate is 40.77 mJ/m^2, while it is 45.76 mJ/m^2 for photopolymer substrate. The higher surface energy of the photopolymer results in its better adhesion with the Ag film, so that the flexible substrate with ultrasmooth Ag was obtained. The optimum thickness of photopolymer is in the range of 0.3 to 0.8 mm. The repeatability of this process is fine over large areas. The surface morphology of both as-evaporated Ag film on Si substrate and template-stripped Ag film on photopolymer substrate was measured by atomic

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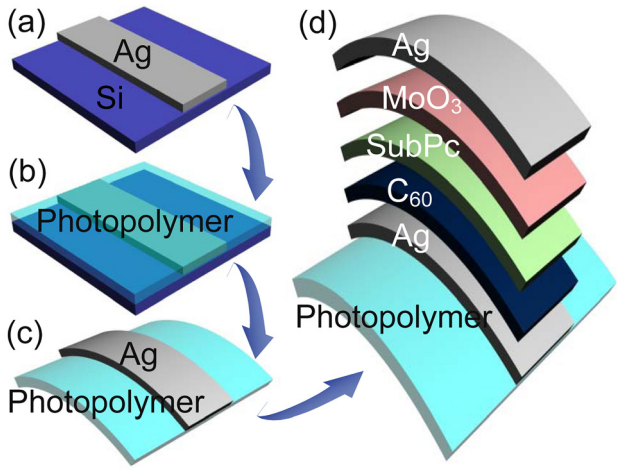

FIG. 1. Scheme of fabricating OSCs with ultrasmooth Ag film by template stripping. (a) Ag film is deposited onto the Si template by thermal evaporation. (b) Photopolymer is spin-coated as a backing film. (c) The Ag film adhered to the cured photopolymer film is stripped. (d) Organic layer and anode evaporated on Ag film.

force microscopy (AFM; iCON, Veeko). The AFM images of the surface morphology are shown in Fig. 2. The root mean square (rms) roughnesses for the as-evaporated Ag and the template-stripped Ag surfaces are 1.22 nm and 0.341 nm, respectively. The roughness of the template stripped Ag film is much improved compared with that of the as evaporated Ag film.

Inverted OSC was fabricated on the peeled-off substrate with the template-stripped Ag cathode. The structure of OSCs was shown in Fig. 1(d). An 80-nm thick Ag film obtained by the template stripping method was used as the bottom cathode. The surface resistance of the 80-nm thick Ag film measured by a *4*-point *probe* (ST-21H, 4probes Tech.) is 0.3 Ω/□. To demonstrate the effect of the ultrasmooth Ag cathode on the performance of the OSCs, the OSCs with the as-deposited cathode on the Si substrate were fabricated under identical process conditions for comparison. Fullerene (C_{60}) was used as electron acceptor. Boron subphthalocyanine chloride (SubPc)[16–18] was used as an electron donor material. It is a cone-shaped Pc molecule with 14π-electrons in its aromatic system, which has attracted attention since it can provide greater V_{OC} due to its low highest occupied molecular orbital. And 16-nm semi-transparent Ag film was used as the top anode. A MoO_3 buffer layer is deposited between SubPc and top Ag anode to prevent damage to the SubPc layer during Ag anode deposition.[18] The stack of device structure is Ag (80 nm)/C_{60} (40 nm)/SubPc (13 nm)/MoO_3 (10 nm)/Ag (16 nm). This inverted structure eliminates the need for a transparent ITO and glass substrates and it is more suitable to flexible devices design without sacrificing device active area.[18,19] Here, all layers were deposited by thermal evaporation in a high vacuum system at a rate of 1 Å/s at a base pressure of 5×10^{-4} Pa. The active area of the device is 2×2 mm^2. The current density-voltage (J–V) characteristics of devices were assessed with a Keithley 2400 programmable voltage-current source. A solar simulator was used providing an AM 1.5 G spectra at 100 mW/cm^2 for top illumination.

The J-V characteristics of OSCs are compared and shown in Fig. 3. It can be seen that the performance of the OSCs fabricated on the peeled-off photopolymer substrate exhibits obvious improvement. Its open-circuit voltage (Voc), short-circuit current density (Jsc), fill factor (FF), and PCE are 1.06 V, 5.74 mA/cm^2, 0.59, and 3.60%, respectively, while they are 1.02 V, 5.47 mA/cm^2, 0.57, and 3.19% on the conventional Si substrate. The parameters are summarized in Table I. For the PCE increasing from 3.19% to 3.60%, it arises from Jsc and Voc increasing while the FF almost remained constant. These improvements obviously originate from lowered surface roughness of the Ag cathode. Generally, organic molecules are in form of large clusters when they deposited on electrode by thermal evaporation, and they cannot fill the depression of the rough electrode surface. Therefore, the contact area between electrode and organic layer will decrease with the increasing surface roughness of the bottom electrode.[20,21] In case that the ultrasmooth Ag film is used as the cathode, the contact area between the Ag cathode and C_{60} must be increased, so that the charge extraction between C_{60} and Ag cathode can be enhanced, which results in the improved Jsc. The increased Voc owing to the reduction of charge loss at the cathode may also be contributed to the excellent surface morphology of Ag cathode. While the enhancement in FF is not very obvious, because the factor that charge transport and mobility balance associated with it has almost not been affected by the ultrasmooth Ag cathode.

The improvement of Voc and Jsc has been further clarified through comparing the dark current density of device on different substrates. The J-V curves are shown in Fig. 3(b). As we know, different part of dark J-V curves can imply different characteristics of solar cells.[22] Compared with the OSCs with Si substrate, the parallel resistance and injection of the OSCs fabricated on photopolymer substrate are both enhanced. Since the Voc was closely related to parallel resistance of devices, we can conclude that the increased Voc could be caused by the increased parallel resistance. In addition, the enhanced injection under the dark condition could provide an evidence for the improved charge extraction under illuminated condition, which is the origin of the increased Jsc.

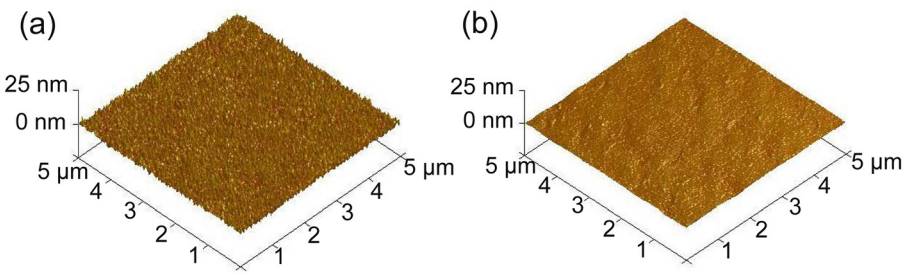

FIG. 2. AFM images of (a) as-evaporated Ag surface and (b) template-stripped Ag surface.

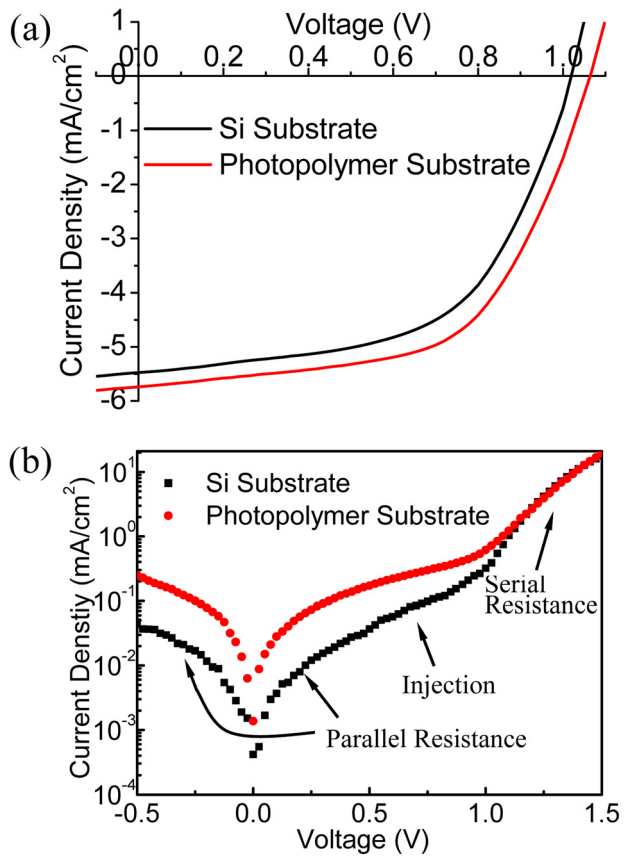

FIG. 3. (a) Photocurrent density and (b) dark current density-voltage (J-V) characteristics of OSCs on Si and peeled-off photopolymer substrates.

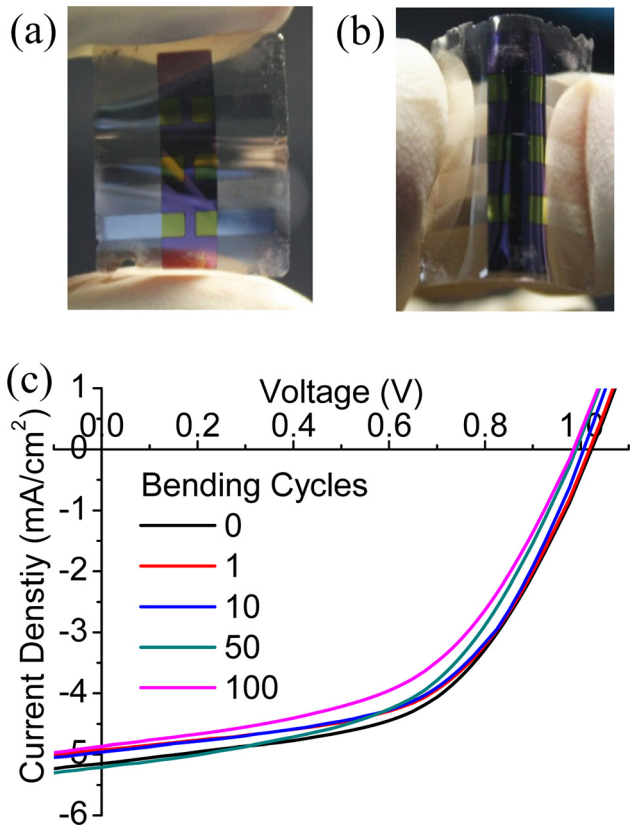

FIG. 4. Flexibility and mechanical robustness of the flexible TOLEDs. (a) and (b) Photographs of the flexible OSCs before and after bending. (c) Comparison of J-V characteristics before and after repeated bending.

TABLE I. Summary of the parameters of OSCs on different substrates.

Substrate	Jsc (mA/cm^2)	Voc (V)	FF	PCE (%)
Si	5.47	1.02	0.57	3.19
NOA	5.74	1.06	0.59	3.60

A bending test has been conducted to evaluate the flexibility of the OSCs. The photographs of the devices before and after bending are shown in Figs. 4(a) and 4(b). The mechanical robustness of the flexible OSCs is further investigated by measuring its J-V characteristics after repeated bending with a bending angle of about 180°. As shown in Fig. 4(c), no obvious deterioration can be observed in the J-V curves after repeated bending. The Jsc and Voc show very little variation over up to 100 bending cycles. The above results demonstrate that the OSCs are not only flexible but highly mechanically robust.

In summary, a template-stripping technique has been employed to create an ultrasmooth Ag cathode on a flexible substrate for realizing highly flexible and efficient top-illuminated inverted OSCs. The OSCs exhibit enhanced Jsc, Voc, and PCE due to the ultrasmooth cathode-induced improvement in the charge extraction between C_{60} and cathode and reduction in the charge loss at the cathode. The high mechanical robustness of the flexibility has been demonstrated by conducting the bending test. From this study, we have confirmed that template stripping is an efficient method to realize flexible OSCs with high performance, which are promising candidates for realizing flexible energy harvesting devices in manufacturing industries.

The authors gratefully acknowledge the financial support from the 973 Project (2011CB013005) and NSFC (Grant Nos. 61177024, 60977025, and 61107024).

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