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Fabrication and characterization of Ag film with sub-nanometer surface roughness as a flexible cathode for inverted top-emitting organic light-emitting devices

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An ultra-smooth Ag film with sub-nanometer surface roughness on a flexible substrate has been fabricated by a template-stripping process and its effect on the carrier injection and transport in organic light-emitting devices (OLEDs) has been investigated. The use of the ultra-smooth Ag film as an electrode results in both enhanced carried injection due to the improved contact between the electrode and the organic layer and enhanced carrier transport due to the larger grain size of the deposited organic layer on it. The ultra-smooth Ag film on the flexible substrate has been applied in inverted top-emitting OLEDs (ITOLEDs) as cathode, which exhibit improved efficiency due to the enhanced electron injection and transport. The maximum current efficiency of the ITOLEDs on the flexible substrate is 9.72 cd A^{-1}, whereas it is 6.03 cd A^{-1} for the devices on the conventional Si substrate, which corresponds to about a 62% enhancement. Moreover, the flexible ITOLEDs keep their good performance under a small bending radius and after repeated bending.

1. Introduction

Organic optoelectronic devices, such as organic light-emitting devices (OLEDs)[1–8] and organic solar cells[9–12] have attracted much attention due to their advantages of being light weight, low cost, having material abundance, requiring low power consumption, and, in particular, being sufficiently ductile for the organic material to undergo significant stress without cracking. The flexibility of the organic devices becomes a very attractive feature and has potential applications in flexible optoelectronic systems such as electronic newspapers, wearable displays and light collectors.[1,2,9,13] Highly conductive and flexible electrodes on the flexible substrate are the key issues for flexible optoelectronic devices. In general, indium–tin oxide (ITO) has been by far the most commonly used transparent electrode material because of its high work function, high transparency and availability. However, ITO is not an ideal choice for fully flexible electronic devices because of its poor mechanical robustness, and incompatibility with the plastic substrate due to the high-temperature deposition process needed. Conducting polymers, carbon nanotubes, graphene films, metal nanowires, metal grids, and ultrathin metal films have been explored as alternatives to the transparent ITO anode. Among them, the ultra-thin metal film is a potential candidate due to its combined characteristics of high electrical conductivity and good mechanical ductility, and, especially, it has good compatibility with most organic materials and can be simply deposited by thermal evaporation. The surface morphology of the electrode, such as the roughness, grain size and continuity, plays an important role in the performance of organic optoelectronic devices. Unfortunately, a metallic film deposited on the substrate by thermal evaporation has a rough surface, which is adverse to its application in flexible devices.

In this communication, we have demonstrated that an ultra-smooth Ag film on a flexible substrate can be fabricated by a template-stripping process combined with the evaporation process.[14–16] Compared to the as-evaporated Ag film, the template-stripped Ag film has lower roughness down to the sub-nanometer scale, a larger grain size and better continuity. The ultra-smooth Ag film has been applied as a cathode in flexible inverted top-emitting OLEDs (ITOLEDs). The flexible ITOLEDs have shown higher luminance and efficiency compared to conventional ITOLEDs due to the enhanced electron injection and electron transport induced by the ultra-smooth surface of the Ag cathode. The maximum current efficiency of the ITOLEDs on a flexible substrate is 9.72 cd A^{-1}, whereas it is 6.03 cd A^{-1} on s conventional Si substrate, which corresponds to an enhancement of about 62%. Moreover, the flexible ITOLEDs have also shown superiority in both flexibility and mechanical robustness.

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2. Experimental details

2.1. Fabrication of an ultra-smooth Ag film on a flexible substrate

The fabrication process of the ultra-smooth Ag electrode on a plastic substrate is shown in Fig. 1. At first, a cleaned silicon (Si) template was loaded into a thermal evaporation chamber. An Ag film was deposited on the Si template at a rate of 1 Å s^{-1} at a base pressure of 5 × 10^{-4} Pa. Then, a photopolymer (NOA63, Norland) film was spin coated 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. Finally, a pair of pre-cleaned tweezers was used to prise up an edge of the cured photopolymer film from the Si template, then the film was peeled off from one edge toward another slightly and the flexible substrate with the ultra-smooth Ag was obtained. Although the evaporated metal film has a rough surface after deposition, the smoothness of the opposite interface is near that of the Si templates. This method exhibits particular advantages in flexible optoelectronic devices, not only because the metal smoothness can be improved, but also since the backing layer itself is flexible and can be used as the substrate. The optimal thickness of the substrate is around 400–500 μm. The surface morphology of both the as-evaporated Ag film on the Si substrate and the template-stripped Ag film on the photopolymer substrate were measured using atomic force microscopy (AFM, iCON™, Veeco).

2.2. Fabrication and characterization of hole-only and electron-only devices and ITOLEDs

The hole-only devices, electron-only devices and ITOLEDs with both the as-deposited Ag films on the conventional Si substrate and the ultra-smooth template-stripped Ag films on the peeled off photopolymer substrate were fabricated. After the deposition of the Ag electrode, the Si and polymer substrated were loaded into a thermal evaporation chamber. Then the organic layers and top contact were grown layer by layer at a rate of 1 Å s^{-1} and a base pressure of 5 × 10^{-4} Pa. The stack structure of the hole-only device is Ag (80 nm)/MoO_3 (4 nm)/4,4′,4′′-tris(3-methylphenylphenylamino)triphenylamine (m-MTDATA) (30 nm)/*N*,*N*′-diphenyl-*N*,*N*′-bis(1,1′-biphenyl)-4,4′-diamine (NPB) (70 nm)/Ag (20 nm). MoO_3 is a commonly used anodic buffer in OLEDs. m-MTDATA and NPB are hole-injection and hole-transport layers, respectively. The stack structure of the electron-only device is Ag (80 nm)/fullerene (C_{60}) (120 nm)/Ag (20 nm). C_{60} as an ordinarily used electron acceptor in organic solar cells is employed to fabricate the electron-only device to confirm that the ultra-smooth Ag film is applicable to the organic solar cells. In ITOLEDs, tris(8-hydroxyquinoline)aluminum (Alq_3) was used as the emitting and electron-transport layer. The detailed structure is Ag (80 nm)/Al (1 nm)/LiF (1 nm)/Alq_3 (48 nm)/NPB (26 nm)/m-MTDATA (26 nm)/MoO_3 (4 nm)/Ag (20 nm). Here, the

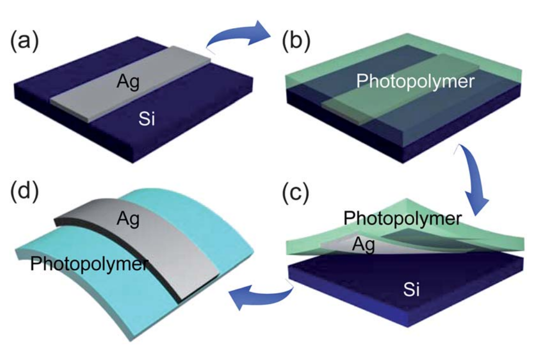

Fig. 1 Scheme of ultra-smooth Ag film fabrication by template stripping. (a) Deposition of the Ag film onto the Si substrate by thermal evaporation. (b) Spin-coating of the photopolymer as a backing film. (c) The Ag film adhered to the cured photopolymer film is stripped off. (d) Flexible substrate with the ultra-smooth Ag film.

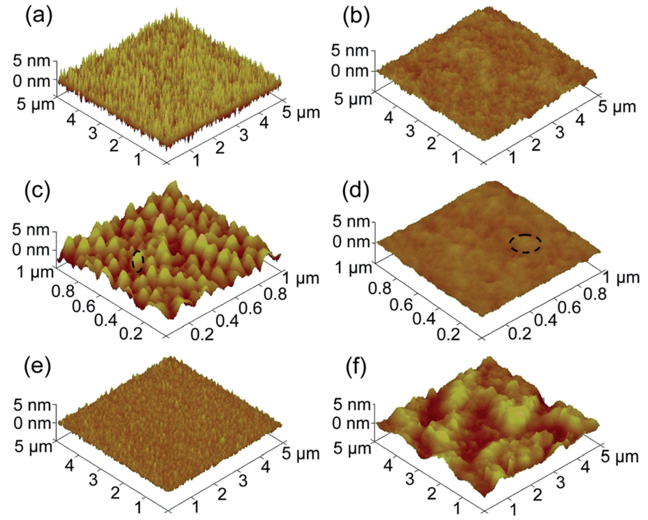

Fig. 2 Surface morphologies of the Ag film. AFM images in a scan area of 5 μm × 5 μm for the as-evaporated Ag film (a) and template-stripped Ag film (b). Enlarged AFM images in a scan area of 1 μm × 1 μm for the as-evaporated Ag film (c) and template-stripped Ag film (d). Surface morphologies of the organic layer on the as-evaporated Ag film (e) and template-stripped Ag film (f).

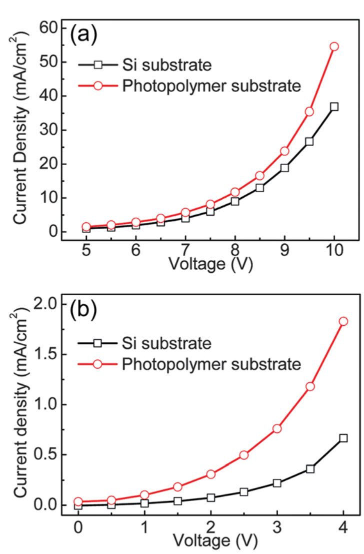

Fig. 3 Current density–voltage characteristics of hole-only devices (a) and electron-only devices (b).

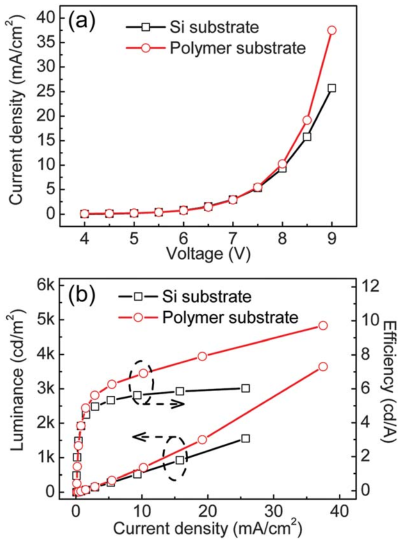

Fig. 4 EL performances of ITOLEDs on Si and photopolymer substrates. Current density–voltage (a) and luminance–current density–efficiency (b) characteristics.

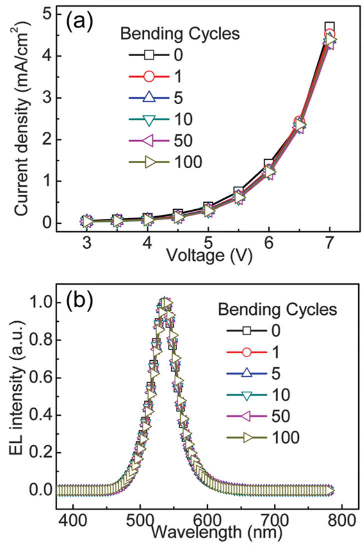

Fig. 6 Comparison of *J*–*V* characteristics (a) and EL spectra (b) before and after repeated bending.

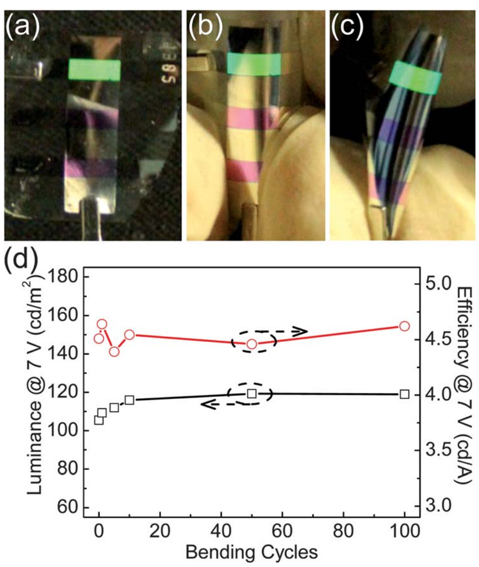

Fig. 5 Flexibility and mechanical robustness of the flexible ITOLEDs. Photographs of the flexible ITOLEDs before bending (a) and after bending at different bending angles (b) and (c). (d) Luminance and efficiency at 7 V as a function of the number of bending cycles.

active area of the device is 2 mm × 2 mm. The electroluminescence (EL) performance of the devices was measured using a Keithley 2400 programmable voltage–current source and a Photo Research PR-655 spectrophotometer. All of the measurements were conducted in air at room temperature.

3. Results and discussion

The surface morphology of the deposited metal films plays a fundamental role in the behavior of the produced devices, in the case where they are used as electrodes in OLEDs. The surface morphology of both the as-evaporated Ag film on the Si substrate and the template-stripped Ag film on the NOA63 flexible substrate has been investigated by AFM and is shown in Fig. 2. The surface roughness of the template-stripped Ag film is much improved compared to that of the as-evaporated Ag film as can be seen in Fig. 2(a) and 2(b). The root mean square (rms) roughness of the as-evaporated Ag and the template-stripped Ag surfaces are 1.04 nm and 0.322 nm, respectively. This improvement in the surface roughness is beneficial to the carrier injection by improving the contact between the metallic electrode and the organic layers. Generally, organic molecules are in form of large clusters when they are deposited on an electrode by thermal evaporation, and they can not fill the depressions of the rough electrode surface. Therefore, the contact area between the electrode and the organic layer will decrease with the increased surface roughness of the bottom electrode.[17,18] In case that the ultra-smooth Ag film is used as the electrode, the contact area between the electrode and the organic layer must be increased, so that the carrier injection from the Ag cathode into the organic layer can be enhanced. Moreover, the use of the ultra-smooth Ag film would reduce the possibility of short circuits between the anode and the cathode of the device owing to the lowered presence of asperity and spikes on the metallic film.

On the other hand, the ultra-smooth surface of the Ag film may influence the carrier transport through improved continuity and larger grain size formation of the Ag film. The enlarged AFM images with a 1 μm × 1 μm area are shown in Fig. 2(c) and 2(d), which clearly indicate that the template-stripped Ag film has much better continuity and a larger grain size. While the organic material is evaporated, the film grows through a process in which isolated crystals nucleate on the substrate and then grow to impinge and coalesce to form a continuous film. This type of growth is known as the Volmer–Weber mode for film growth, and is the process through which most polycrystalline and many epitaxial films form.[19–21]

Therefore, the surface morphology of the electrode is of great importance to nucleation and growth kinetics of the organic layer deposited on it, and which further influence the electrical property of the organic film.[19–23] The surface morphology of m-MTDATA on the as-evaporated Ag and template-stripped Ag films has been investigated to verify the difference in morphology on the different electrodes. During the process of nucleation and growth, grains and spikes on the Ag film may play a role as molecular capture centers. With more spikes and smaller grains on the Ag film, the m-MTDATA molecule may tend to form more and smaller grains. The AFM images of the m-MTDATA on different Ag films were shown in Fig. 2(e) and 2(f). A much larger grain size of the m-MTDATA film on the template-stripped Ag film can be observed compared to that on the as-evaporated Ag film. Generally, charge transport in an organic film is determined by the scattering of conduction electrons at defects, grain boundaries, and surfaces. The charge transport within a single grain is easier and faster than that through the grain boundaries. The number of the boundaries will be increased for the films with the smaller grain size, so that the ability of the charge transport in these films is restrained. In contrast, charge transport will be improved distinctly because of fewer grain boundaries for the films with a larger grain size. To further clarify the effect of the ultra-smooth surface morphology of the Ag film on the electrical performance of the organic devices, both hole-only and electron-only devices have been fabricated to investigate their current density (J)–voltage (V) characteristics. It can be seen from Fig. 3 that the current density of the devices with the ultra-smooth Ag anode is obviously higher than that of the devices with the as-deposited Ag anode in both hole-only and electron-only devices. Both increased carrier injection due to the improved contact between the ultra-smooth electrode and the organic film and the increased carrier transport due to the larger gain size of the organic film on the ultra-smooth electrode may contribute to the enhanced current density.

Inverted OLEDs architectures are more preferable in AMOLED (active-matrix OLED) devices.[24–29] The ultra-smooth Ag film on the NOA63 flexible substrate has been applied to flexible ITOLEDs as the bottom cathode to investigate its effect on the device performance. It can be seen from Fig. 4 that the EL performance of the ITOLEDs fabricated on the peeled off photopolymer substrate exhibits obvious improvement. Its maximum current efficiency is 9.72 cd A^{-1}, whereas it is 6.03 cd A^{-1} on a conventional Si substrate, which corresponds to about a 62% enhancement. This enhancement obviously originates from the enhancement in both the electron injection and electron transport as a result of the improvement of the surface morphology of the Ag cathode.

A bending test has been conducted to evaluate the flexibility of the ITOLEDs. The photographs of the devices operating at 6 V before and after bending are shown in Fig. 5(a)–(c). The bending radius is 8 mm in Fig. 5(b), and the substrate almost completely folded bending in Fig. 5(c). There are no cracks or dark spots observed on the operating devices. The mechanical robustness of the flexible ITOLEDs is further investigated by measuring their EL performance after repeated bending. As shown in Fig. 5(d), no obvious deterioration can be observed in the luminance and efficiency after repeated bending. Moreover, the EL spectra and J–V curves are almost identical over up to 100 bending cycles as shown in Fig. 6. The above results demonstrate that the ITOLEDs with the ultra-smooth Ag cathode on the peeled off photopolymer substrate are not only highly flexible but also highly mechanically robust.

4. Conclusions

In conclusion, an ultra-smooth Ag film on a flexible substrate has been fabricated by a template-stripping process and its effect on the carrier injection and transport has been investigated. Compared to the as-evaporated Ag film, the surface roughness, grain size and continuity of the template-stripped Ag film are all improved. A highly flexible and efficient ITOLED has been realized by using the ultra-smooth Ag film as the cathode. Compared to a conventional device, the flexible ITOLEDs exhibit enhanced efficiency due to the improved electron injection and transport induced by the improved surface morphology of the ultra-smooth cathode. In addition, the high mechanical robustness of the flexibility of the ITOLEDs has been demonstrated by conducting a bending test. From this research, we have confirmed that template stripping is an efficient and convenient method to realize an ultra-smooth Ag film on a flexible substrate as an electrode, providing promising candidates for realizing flexible optoelectronics applications in manufacturing industries.

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