Improved lifetime of highly flexible OLEDs based on multilayered transparent electrodes with enhanced barrier performance

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Abstract — Flexible organic light-emitting diodes (FOLEDs) showing enhanced barrier properties under repeated mechanical stress are reported. By combining metal-based multilayer transparent electrodes (MTEs) as highly flexible anodes replacing ITO electrodes and sol-gel organic–inorganic hybrimers which function as both planarizing films and barrier layers, the proposed FOLEDs not only exhibit a level of performance comparable to that of ITO-based reference devices but also show a superior mechanical flexibility with "after-bending" lifetime close to that of ITO-based devices.

Keywords — *Multilayered transparent electrode (MTE), water-vapor transmission rate (WVTR), flexible display, organic light-emitting-diode (OLED) lifetime.*

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1 Introduction

Flexible organic light-emitting diodes (FOLEDs) are attracting much attention as highly portable or conformable displays.[1] Due to the porous nature of many plastic substrates, the commercial viability of FOLEDs is expected to depend largely on the availability of an effective encapsulating structure which prevents permeation of ambient air and water.[2,3] Another important aspect is the mechanical flexibility of transparent electrodes. For example, ITO electrodes, which are used most often in OLEDs, are known to have relatively poor flexibility and crack under mechanical stress.[4] In that respect, we have recently demonstrated that a dielectric/metal/dielectric (DMD) multilayer system can become an effective alternative to ITO electrodes.[5] More specifically, a metal layer is responsible for sheet conductance in DMD electrodes, and thus a sheet resistance below ~10 Ω/□ is readily achieved. With the cooperative effect of the two high-index dielectric layers, transmittance can be increased to ~85% and can be varied in a relatively wide range if needed.[5] It turns out that DMD electrodes are highly flexible due to the ductile nature of a metal thin film and can lead to high-performance OLEDs with excellent flexibility. In order for this DMD technology to be truly successful in practice, its gas-barrier properties should also be identified for the reasons mentioned above. Hence, this work is devoted to characterizing the barrier properties of DMD electrodes used in FOLEDs particularly when they undergo repeated bending operation. We also discuss the potential role of sol-gel organic–inorganic hybrimers as a planarizing film and its additional role for enhancing the barrier properties of plastic substrates. The lifetime of FOLEDs based on DMD electrodes with the sol-gel hybrimer is also evaluated.

2 Experimental

The flexible OLEDs under study had a normal bottom-emission geometry and were based on N,N′-Bis-(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB) as a hole-transporting layer, Tris(8-hydroxy-quinolinato) aluminum (Alq_3) as an emitting and electron-transporting layer, and LiF/Al as a cathode [see Fig. 1(a) for the overall schematic of a device structure for OLEDs fabricated on flexible substrates]. The anodes of the FOLEDs were based on multilayered transparent electrodes (MTEs) consisting of thermally evaporated ZnS (40 nm), Ag (20 nm), and WO_3 (5 nm) (ZAW) layers.[5] 20-nm-thick Ag films were shown to provide a sheet resistance as small as ~6 Ω/□ Before deposition of ZAW layers, polyethylene naphthalate (PEN) substrates were solvent-cleaned in an ultrasonic bath and were treated by air plasma (PDC-32G, Harrick plasma) for 5 min. Immediately after the plasma treatment, the PEN substrates were planarized with polymeric films (SU-8; Kayaku Microchem) or with sol-gel hybrimers.[6] 5-μm-thick hybrimer layers were spin-coated at 2000 rpm for 30 sec from diluted cycloaliphatic epoxy oligosiloxane solution. The coated film was photopolymerized with a UV lamp (λ = 350–390 nm) in an air ambient. Commercially available ITO-coated PEN substrates (Peccell Technology; 200 μm thick, 15 Ω/□) were also used for reference samples. The same PEN substrates were used in all devices for a fair comparison.

Water-vapor transmission rates (WVTRs) of multilayered electrode coated substrates were measured using a calcium (Ca) corrosion test.[7] Figure 1(b) shows the schematic diagram of the Ca test. An Al-contact electrode (100 nm) and a Ca test layer (200 nm) were deposited on a cleaned glass substrate through a shadow mask by thermal evaporation. Then, the glass substrate with that Ca layer was covered by a PEN substrate with electrodes under test. They

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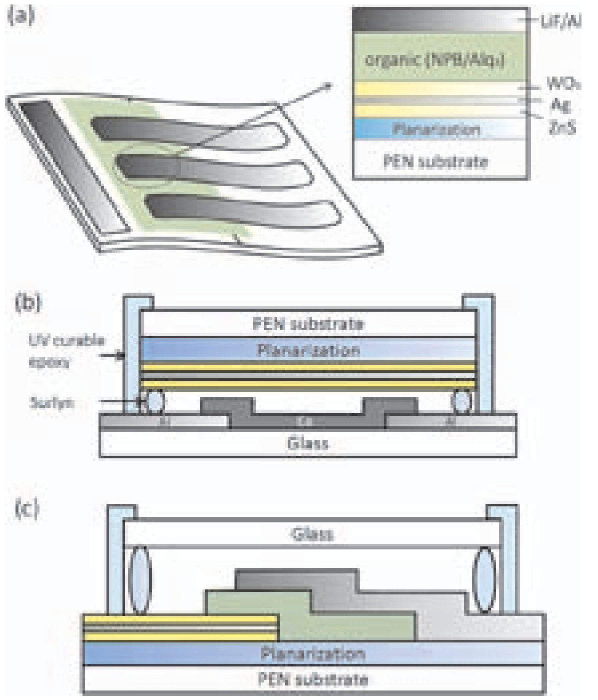

FIGURE 1 — (a) A schematic diagram of a device structure with multilayered transparent electrodes for normal bottom-emitting flexible OLEDs. The planarization layer consists of SU-8 or hybrimers. (b) The test structure used for Ca corrosion test. (c) The same for the lifetime measurement of flexible OLEDs. Structures shown here are for ZnS/Ag/WO_3 (ZAW) electrodes. Those with ITO electrodes were also tested as a reference. In such a case, ITO replaces the layers corresponding to ZAW and planarization layers in the figure.

were sealed in N_2-filled glove box with Surlyn (Solaronix SA, Swiss) and an additional UV-curable epoxy. The electrical resistance was monitored by using a precision multimeter (Hewlett Packard 34401A) with samples under test kept in the controlled-environment chamber (model TH-PE-025, JEIO Tech.). For the lifetime measurement of FOLEDs, they were encapsulated with a cleaned glass lid using the same sealants employed for the Ca test [Fig. 1(c)]. Current-density–voltage (J–V) and luminance–voltage (L–V) characteristics of OLED devices were also monitored while being kept in the same environment chamber using a source-measure unit (Keithley 238) and a calibrated photodiode (FDS100-CAL, Thorlab), respectively. For the test after mechanical stress, we used a custom-made bending tester which can perform a bending cycle test.

3 Results and discussion

3.1 Moisture barrier property of ZAW multilayer electrodes

Figures 2(a) and 2(b) show the oxidation of a Ca layer monitored by its electrical resistance that increased due to the water-vapor permeation through the ZAW-coated PEN and ITO-coated PEN, respectively. One can observe that the WVTR of the ITO-PEN increased from 4.0×10^{-3} to 3.7×10^{-2} g/m^2/day after repeated bending [5000 times at a radius of curvature (r_C) of 15 mm with tensile stress] due to a physical stress yielding the microcracks or pinholes.[8] It is noteworthy that the WVTR of the ZAW-coated PEN was almost invariant and changed only slightly under the same bending test regardless of the planarization layers, indicating that the barrier performance of the ZAW-coated PEN has a higher resistance to repetitive bending than ITO-coated PEN (see Table 1 for the WVTR in each case). These phenomena are expected to come mainly from (*i*) the ductile nature of metallic thin films and (*ii*) the multilayered geometry of a ZAW electrode on PEN that may litigate the

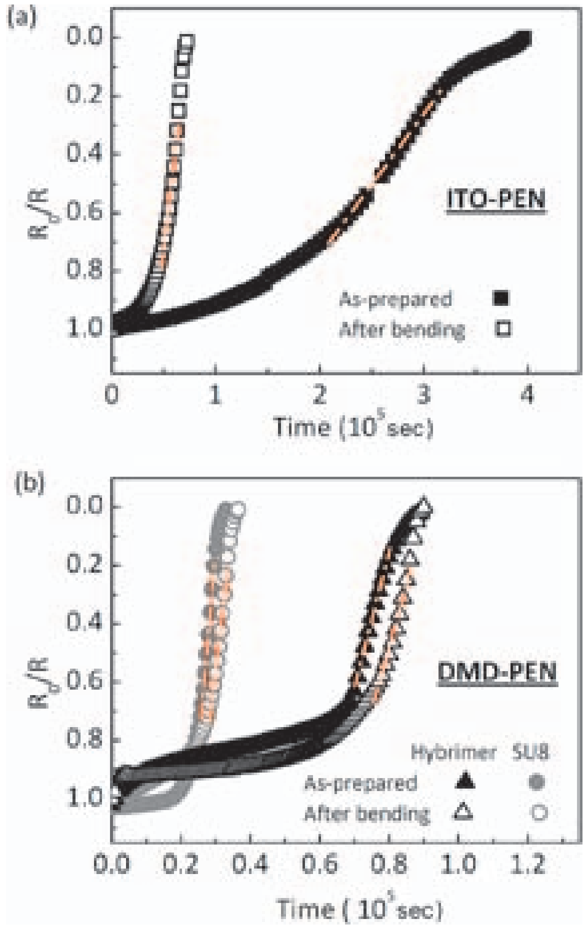

FIGURE 2 — Reciprocal of resistance (R) of a Ca layer (a) on ITO-based PEN and (b) on ZAW-based PEN coated with SU-8 (circle) or hybrimers (triangle) as a function of time measured for as-prepared samples (filled) and for those after repeated bending (5000 times at radius curvature r_C = 15 mm) (blank) at 38°C, 90% RH.

TABLE 1 — Water-vapor transmission rates (WVTRs) of transparent electrodes.

Substrate	WVTR (g/m^2/day)	
	As-prepared	After bending
ITO on PEN	4.0×10^{-3}	3.7×10^{-2}
ZAW on SU-8/ PEN	9.2×10^{-2}	9.9×10^{-2}
ZAW on Hybrimer/ PEN	4.0×10^{-2}	4.3×10^{-2}

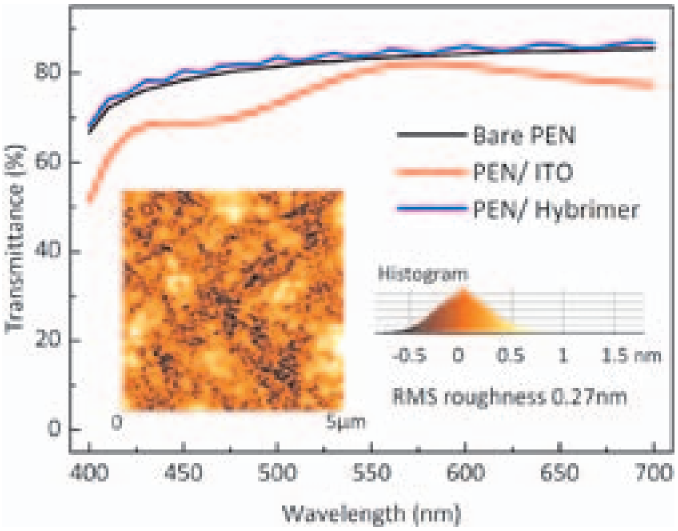

FIGURE 3 — Optical transmittance of the hybrimer barrier coating on a PEN substrate, ITO-coated PEN substrate, and bare PEN substrate. The inset shows the AFM image and height distribution for the top surface of a hybrimer-coated PEN substrate.

direct diffusion of gases by effectively decoupling the defects formed in each layer under mechanical stress.[8,9]

It is also noted that the barrier performance of the ZAW-coated PEN improved when organic–inorganic sol-gel hybrimer films instead of SU-8 films were used for planarization layers. It was previously reported that organic–inorganic hybrid materials have higher barrier performance than common, commercially available polymers since they are composed of photo-cross-linkable organic functional groups and highly condensed inorganic networks of Si–O–Si. The latter is expected to minimize pathways for water molecules and has hydrophobic characteristics. Also, hydroxyl groups, generated by the polymerization, can reduce the penetration of water molecules by polar–polar interaction.[6]

As for the basic properties as planarizing layers, the average transmittance of the hybrimer-coated PEN was shown to be almost identical to a bare PEN, and its surface roughness and peak-to-valley height was shown to be as small as 0.27 and 1.2 nm, respectively (see Fig. 3). Combination of this good planarizing function and barrier properties makes the sol-gel hybrimer coating an ideal choice for the planarizing films in flexible devices on plastic substrates.

3.2 Flexible OLEDs based on MTEs with hybrimer layers

Figures 4(a) and 4(b) show the current-density–voltage (J–V) and luminance–voltage (L–V) characteristics of bottom-emitting FOLEDs with ITO anodes and those with ZAW anodes with planarization layers based on hybrimers, respectively. It can be easily seen that FOLEDs based on ZAW-based PEN exhibit desirable OLED characteristics comparable to that of ITO-based FOLEDs.[5] This result confirms that the proposed organic–inorganic hybrimers can effectively planarize the rough polymer substrates. Planarization was shown to be critical for DMD electrodes in achieving the low sheet resistance and high transmittance.[10]

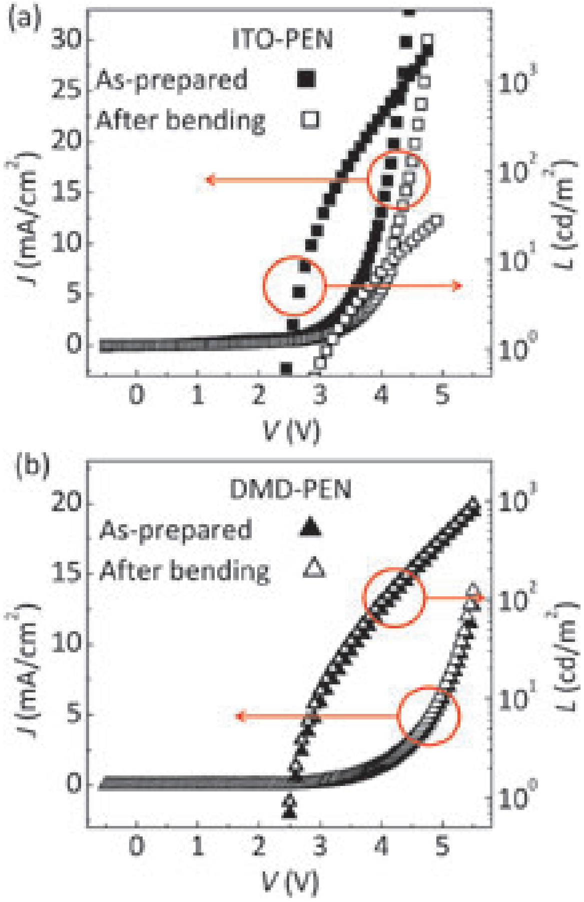

FIGURE 4 — Characteristics of bottom-emitting flexible OLEDs based on (a) ITO-based PEN and (b) ZAW-based PEN coated with hybrimers for as-prepared samples (filled) and for those after repeated bending (blank). Current density (*J*) *vs.* voltage (*V*) and forward luminance (*L*) *vs.* voltage (*V*) characteristics are shown.

Note that FOLEDs based on ZAW electrodes with hybrimer layers maintained their initial characteristics after repeated bending [3000 times at radius of curvature (r_C) of 18 mm with tensile stress], demonstrating their excellent reliability under mechanical stress. On the other hand, ITO-based FOLEDs exhibited considerable degradation; the initial luminance at 5 V severely degraded from 4720 to 31.3 cd/m^2 after the same bending test.

3.3 Lifetime of FOLEDs under study

As a next step, we have tested the environmental reliability of ZAW-based and ITO-based OLEDs on PEN substrates for both as-prepared samples and samples after repeated bending (r_C = 18 mm; bending 3000 times]. Figures 5(a) and 5(b) show the change in luminance and voltage of each flexible OLED at a constant driving current of 1 mA under a relatively harsh environment (38°C, 90% RH).

As reflected in the moisture permeability characteristics of the previous section, the $t_{0.8}$ lifetime (the time that it takes for L to becomes 80% of its initial value) of

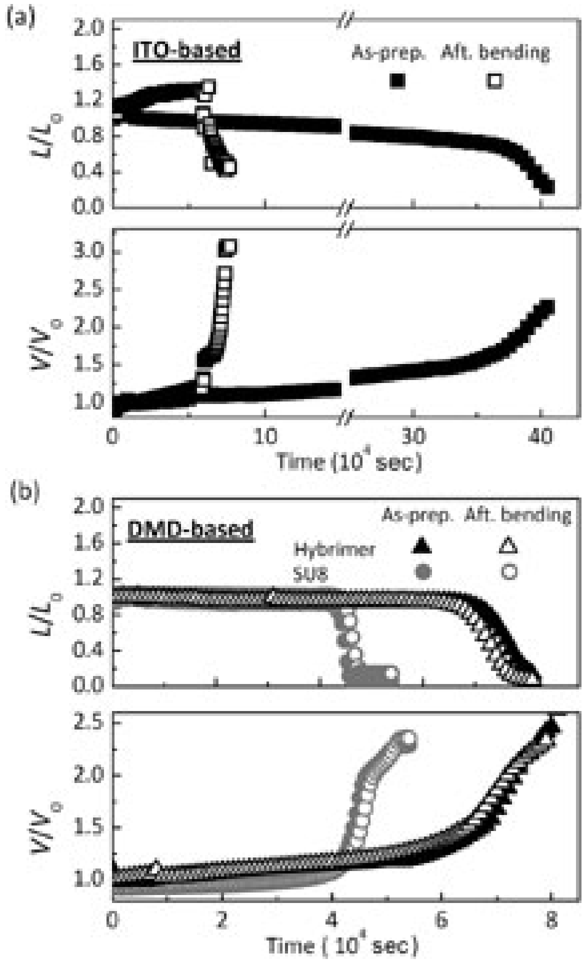

FIGURE 5 — Normalized luminance (L/L_0) and voltage (V_0/V) of (a) ITO-based flexible OLEDs and (b) ZAW-based flexible OLEDs on PEN substrates that are coated with SU-8 (circle) or hybrimers (triangle) as a function of time before (filled) and after (blank) repeated bending [3000-cycle bending at a radius curvature (r_c) of 18 mm] measured at a constant current of 1 mA (38°C, 90% RH).

ITO-based FOLEDs after repeated bending decreased roughly five fold from 3.1×10^5 sec to 6.4×10^4 sec when compared to as-prepared ITO-based FOLED devices. However, the lifetime of ZAW-based FOLEDs remain almost unchanged even after the aforementioned bending test. The $t_{0.8}$ lifetime of the ZAW-based FOLEDs device with SU-8 layers was about 4.5×10^4 sec in both cases. Use of the hybrimer-based planarization layers resulted in enhancement in the lifetime of ZAW-based OLEDs. The $t_{0.8}$ lifetime of ZAW-based FOLEDs device with hybrimer layers was about $(7–7.5) \times 10^4$ sec for both devices with and without the bending test. This $t_{0.8}$ lifetime value is comparable to that of ITO-based FOLEDs after the bending test and corresponds to a lifetime enhancement of over 60% with respect to the ZAW-based FOLEDs with SU-8 layers. These results indicate that the hybrimer coating not only planarizes the rough polymeric substrate effectively but also improves the barrier properties of PEN substrates against water and O_2 permeation.

It is noted that the lifetime of FOLED devices with electrodes under study exhibit a good correlation with the reciprocal of the WVTR for substrates with the corresponding electrodes, while device performance (Fig. 4) does not. For example, both ITO-based FOLEDs and ZAW-based FOLEDs with hybrimers have comparable WVTR values after bending, but ITO-based FOLEDs exhibit much poorer performance than ZAW-based FOLEDs after bending. This is because the WVTR of a substrate with a particular electrode-geometry mainly affects the long-term variation in the performance of a device fabricated thereon. Hence, it will mainly affect the lifetime of a device rather than the device performance measured at a specific time. For ITO-based devices, the bending-induced stress results in micro-cracks in the ITO electrodes. These cracks in turn increase the WVTR and at the same time leads to an increase in the sheet resistance.[4,5] The former (increased WVTR) leads to a reduced lifetime and the latter (increased sheet resistance) leads to a degradation in performance. Since the WVTR of ITO-coated PEN substrates that increased after bending was still comparable to that of a hybrimer-coated substrate with ZAW electrodes, FOLED devices with ITO and ZAW/hybrimer after bending exhibit comparable lifetimes. On the other hand, the bending-induced increase in sheet resistance of ITO is typically quite significant and often accompanied with the formation of inactive regions within the device area.[4,5] Both of these changes make FOLED devices made with ITO electrodes exhibit *L–V* characteristics that are significantly degraded.

4 Conclusions

In summary, $ZnS/Ag/WO_3$ (ZAW) coated on PEN substrates was shown to have a barrier performance that slightly changed under repeated bending-induced stress. The lifetime of flexible OLEDs based on these ZAW electrodes was also shown to remain almost unchanged after repeated bending, while that of FOLEDs based on ITO electrodes significantly degraded after the same level of bending test. In addition, it was shown that the organic–inorganic hybrimers can function as planarization layers for plastic substrates and simultaneously work as layers enhancing the gas-barrier properties. We believe the results obtained in this study provide the fundamental information important in realizing reliable, highly flexible OLEDs.

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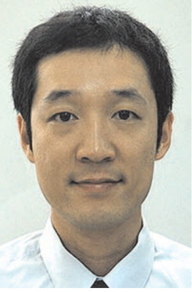

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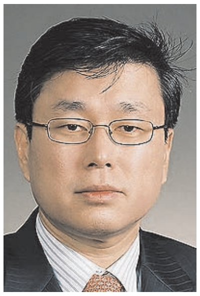

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