Characteristics of organic light-emitting diodes with conducting polymer anodes on plastic substrates

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The fabrication of conducting polymer films by a screen-printing method and characterization of an organic light-emitting diode (OLED) implemented using these films as an anode on plastic substrates are reported. Organic transparent electrode materials containing poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (PEDOT:PSS) were used after the modification by a unique nanoparticle binder design. The electro-optical properties as well as mechanical stabilities of these films were measured. The OLED performances when employing these films were comparable to that of OLEDs using indium tin oxide (ITO) despite their relatively poor conductivity. An external quantum efficiency of the OLED using this anode is ~3.5%, which is about twice as that of OLEDs using ITO. These results show that the organic transparent electrode of a conducting polymer film patterned by the screen-printing method is a potential candidate for an electrode of the flexible OLED. © *2008 American Institute of Physics*. [DOI: 10.1063/1.2840053]

I. INTRODUCTION

There has been a rapid progress in the area of flexible electronics because of their numerous applications including organic electronic devices and displays. To realize such devices, especially for commercialization, it is required to achieve a high mechanical flexibility and low fabrication cost.[1,2] Flexible electronics and displays require flexible electrode materials, which are electrically conducting and optically transparent. Also, those materials should be comparable to indium tin oxide (ITO), which has been widely used as powerful transparent electrodes in many electronic applications, because they combine attractive properties with respect to visible transparency and electrical conductivity.[3] Indium tin oxide is not suitable for flexible applications because the film cracks lead to a decrease of the electrical conductivity abruptly when bent repeatedly. It has a very high sheet resistance and surface roughness when deposited at a low temperature for the compatibility with plastic substrates, and indium migration from the surface causes device failure.[4,5]

As an alternative to ITO, a promising candidate for flexible electrode materials is a conducting polymer containing a dispersed nanoparticle such as poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (PEDOT:PSS), which has excellent electro-optical properties.[6] However, PEDOT:PSS has some drawbacks such as a low water resistance, low electrochemical stability, and low mechanical strength of printed films; few reports can be found on organic light-emitting diodes (OLEDs) with PEDOT:PSS electrodes.[6] For practical applications, it is indispensable to study how to manage those disadvantages in order to use the PEDOT as electrodes.

PEDOT:PSS, an organic polymer material, is vulnerable to water, chemicals, and high-temperature processes. Therefore, the photolithography process is not a suitable method as it employs spin-coating, high temperature, and chemical processes. The printing method is a process which has many advantages for the paste PEDOT:PSS, and is regarded as a proper process for the polymer solutions. In order to apply PEDOT:PSS material to the electrode formation, it is necessary to develop a printing method which makes a direct patterning possible.

Kafafi *et al.* have demonstrated that an OLED device with PEDOT:PSS patterning as an anode can be realized,[7] but there was a limit for the photolithography process. Jabbour *et al.* reported an OLED fabricated by inkjet printing.[8,9] Inkjet printing is a competitive technique for high-resolution patterning to micron-size, but it needs time for commercialization because the nozzle of the head is still apt to be clogged and only solutions with a low viscosity can be used for a successful process.

Compared with that, the screen-printing method is a promising process for industrial purposes because the patterning is simultaneous with the coating without a novel

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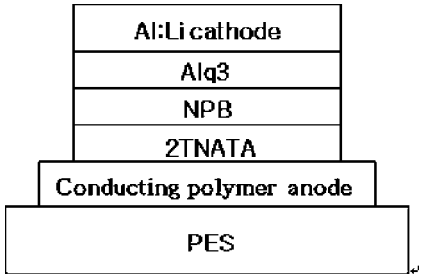

FIG. 1. Structure of the CP-OLED device.

vacuum process, and it is an easy, soluble processing technique scalable to very large substrates. This method is applicable to print films in various areas, e.g., the active layer in OLEDs,[10] electrodes in organic thin film transistor (OTFT),[11] and the active semiconducting polymer layer for photodetector applications.[12]

In recent trends, screen printing is processable up to 20 μm resolution; this shows the potential of this method for device fabrication. Jabbour *et al.* first reported OLED applied to active layers except an electrode, fabricated using the screen-printing method. If the organic materials can be processed in solution as electrodes as well as active layers, low-cost large area electronics with flexible plastic substrates for display can be realized by using only a printing technique.[13–15]

In this work, we report on the fabrication and characterization of an organic transparent electrode (OTE) using a screen-printable conducting paste which is composed of PEDOT:PSS (designed by unique nanoparticle binders), and the flexible OLED using OTE as an anode, which implies that this OTE film and screen-printing method could be employed for many flexible device applications.

II. EXPERIMENTAL DETAILS

The flexible electrode material used in this work is a screen-printable conducting polymer (CP) paste with high stability based on PEDOT:PSS (PriMet-P, DPI Solutions, Inc.). PriMet-P was composed of PEDOT:PSS and nanoparticle binders, which provide high durability without any loss of conductivity. While the conventional CP electrode printed by PEDOT:PSS itself or modified PEDOT:PSS formulation shows a low durability due to its deficient water and chemical resistance, the environmental stability of OTE printed by PriMet-P is improved by a unique binder design. PriMet-P was screen-printed on a transparent plastic substrate, e.g., a polyethersulfone (PES) sheet produced by I-component Corporation with a thickness of ~200 μm. An OLED device with an ITO anode was fabricated using a commercial ITO-coated glass substrate for comparison.

The structure of the OLED device employed in this work is shown in Fig. 1. In the figure, the organic structures consisted of a 150 nm 4,4′,4″-Tris[2-naphthyl(phenyl) amino]triphenylamine (2TNATA) hole injection layer (HIL), a 50 nm *N*,*N*′-bis-(1-naphthyl)-*N*,*N*′-diphenyl-1,1-biphenyl-4,4′-diamine (NPB) hole transport layer (HTL), 50 nm tris-(8-hydroxyquinoline) aluminum (Alq_3) electron transport and emission layers (ETL and EML) deposited at 1–2 Å/s in a thermal evaporator with a low base pressure of 10^{-6} Torr. The cathode is an Al:Li layer with a thickness of 100 nm, which was formed by the evaporation process. After all depositions, the devices were hermetically sealed with adhesives and cover plates, such as PES for flexible devices and glass for rigid devices. The active area for both of the OLEDs fabricated with CP paste (hereafter referred to as CP-OLED) and the OLED with ITO (hereafter referred to as ITO-OLED) was 5×5 mm.

The screen mask used in the experiment was made of nylon fabric with 325 mesh count/in., which means that the thread diameter is 28 μm and the opening size is 50 μm. After being printed, the polymer films were annealed at 120 °C for 30 min to remove excessive H_2O and free solvent after 30 min of a drying process employed to suppress any unexpected effect from the bubble formation.

The film thickness was obtained using a stylus profilometer (Tencor Alpha-Step). The sheet resistance was measured by the four-point probe method. The work function of the film was determined by UV photoelectron spectroscopy (UPS; EscaLab 220-IXL). The UPS spectra were recorded using nonmonochromated He I (21.2 eV) radiation from a helium discharge lamp. The sample was biased at −5.0 V for observing the low-energy secondary electron cutoff. The work function (Φ) was determined by the following relation: $\Phi = h\nu - E_{\text{cutoff}} + E_{\text{Fermi}}$, where E_{cutoff} and E_{Fermi} are the binding energies of the secondary electron cutoff and Fermi level, respectively. Optical spectra such as transmittance and absorbance were measured using an UV-visible spectrophotometer (UV-3101PC, Shimadzu Co.). The refractive indices of the anode films were analyzed by spectroscopic ellipsometer (VUV-VASE™ VU-302, J. A. Woollam Co., Inc.). Atomic force microscopy (AFM) (XE-100, PSIA) and scanning electron microscopy (SEM) (XL30 ESEM, Philips) were used to evaluate the surface morphology of the CP anode. For a wettability test, the contact angle between the CP paste and the substrates was measured by a contact angle analyzer (phoenix-450, SEO).

To investigate a mechanical tolerance of the films, we performed a cyclic bending test. We measured the dependence of the resistance variation on mechanical stress (compressive stress) of a CP film on a polyethersulfon (PES) substrate. We also used an ITO film on a polyethylene terephthalate (PET) substrate, which is a touch panel grade commercial product, for comparison. Each film was prepared on a plastic substrate of 40×80 mm without pattern. During the cyclic bending test, both of the films on the plastic substrates directed toward the mandrel surface were bent with a stroke of 40 mm and the change in electrical resistance of the films was continuously measured by a computer system with an Agilent 34401A6 1/2 digital multimeter.

The *J*-*V*-*L* characteristics of the OLED devices were measured using the Keithley 2400 source-measurement unit. The luminance was measured using a PR-650 Spectrascan photometer.

III. RESULTS AND DISCUSSION

The film morphology is shown in Fig. 2. Figures 2(a) and 2(b) show the morphology of films coated on a glass

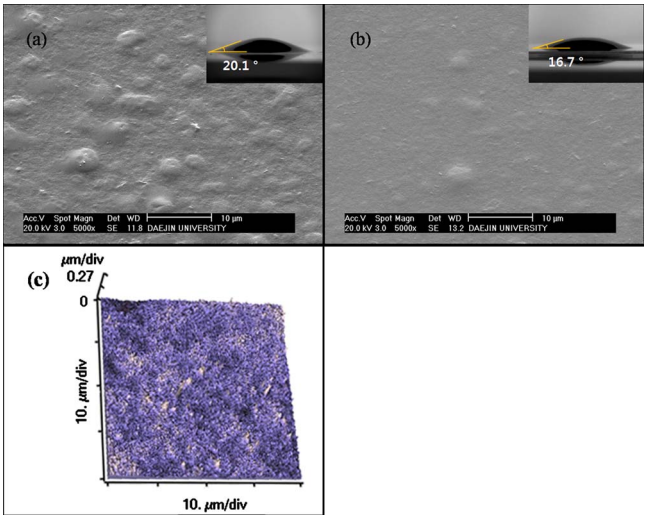

FIG. 2. (Color online) Surface morphology of a conducting polymer film observed by using SEM (inset: contact angle images) (a) on glass substrate; (b) on plastic substrate; and (c) an AFM image on plastic substrate.

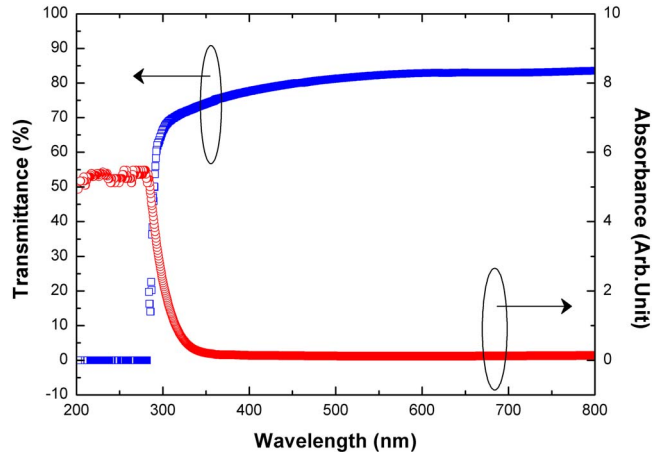

FIG. 3. (Color online) Optical transmittance and absorbance of conducting polymer film.

substrate and on a plastic substrate, respectively. The film on the glass shows a rough surface with many bubblelike shapes, the diameters of which are ~5 μm. On the contrary, the film on the plastic substrate has a smoother surface with fewer bubblelike shapes than the glass case. A wettability test was performed in order to find the reason for the difference in the surface morphology. As shown in the insets of Figs. 2(a) and 2(b), the contact angle between the paste and the substrate for the plastic films is about 16.7°, which is smaller than 20.1° for the glass case. Better wettability for the plastic substrate, which is assumed from the smaller contact angle than for the glass substrate, seems to result in fewer bubbles on the surface.

Figure 2(c) shows the AFM result of the film on a plastic substrate. As shown in the figure, the rms (root-mean-square) surface roughness of the film on a plastic substrate is ~150–200 Å. There were no spikes inducing a short between the anode and cathode on the film surface and only smooth hill-shaped features, although the surfaces of film fabricated by the screen-printing method have a tendency to be rough. In OLED devices, the control of the surface morphology of the anode film is regarded as one of the most important matters, because a smooth surface morphology of the anode is required to fabricate an OLED with a long lifetime and without a short circuit. In addition, because all the functional organic thin films are deposited on the anode film, the surface morphology of the anode film is directly transferred to the morphology of the organic layers. Therefore, the uneven surface of the anode can provide a negative effect for device performance. Regarding this aspect, anode films by the screen-printing method could be processed more easily on a plastic substrate than on a glass. The results show the possibility of a realization of flexible displays, even though the device characteristics which could be degraded by a rough surface should be improved. The surface sheet resistance of the conducting polymeric layer was ~2000 Ω/sq when we considered the average thickness of the film, ~2000 Å. The physical parameters and values of the CP film are shown in Table I, and compared to those of an ITO layer.

To determine the applicability of this film to a flexible device, we analyzed the film characteristics intensively. Regarding the optical properties of the CP film, the transparency and absorbance properties are shown in Fig. 3. As the film transmittance is 80–85% without any absorption of the light in the visible spectrum region, we can conclude that the requirement for the transparent electrodes through which light is extracted was satisfied.

The refractive index of the film was ~1.6 in the range of 400–700 nm, which is lower than that of ITO (1.8–2.0).[16] The work function of this CP film was about 4 eV, which is a little bit lower than that of ITO (4.4–4.9 eV),[17] and seems to be appropriate for a cathode instead. In addition, it is different from that revealed in previous reports.[18–26] These reports described that PEDOT:PSS film is available for the transparent anode or hole injection layer in organic light-emitting diodes because it exhibits a large work function (~5 eV) comparable to that of ITO. However, some reports[27,28] may support our result. They revealed that the work function of PEDOT:PSS film might vary according to the dopant concentration and the surface morphology or near-surface molecular arrangement. From these viewpoints we may say that certain factors related to surface properties made a work function of PEDOT:PSS film low. Although it

TABLE I. Electro-optical properties of conducting polymer film and ITO layer.

	Thickness (nm)	Sheet resistance (Ω/sq)	Transmittance (%)	Refractive index	Work function (eV)
CP film	200	2000	80–85	1.6	4.0
ITO film	180	9	>90	1.8–2.0 (Ref. 16)	4.4–4.9 (Ref. 17)

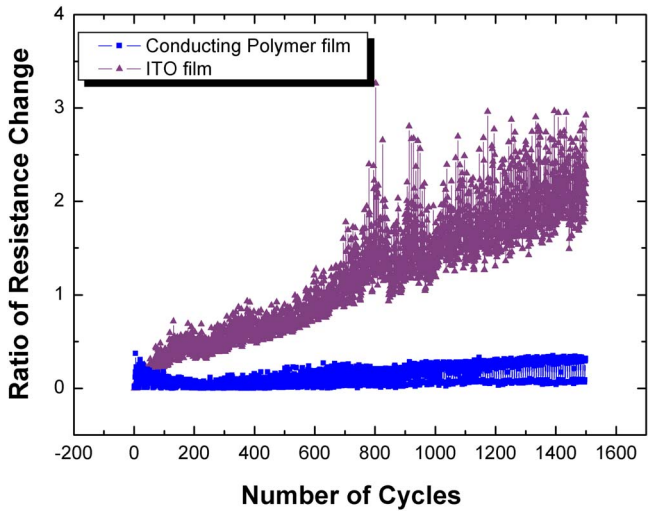

FIG. 4. (Color online) Resistance change in the conducting polymer film, and commercialized ITO film for comparison under the cyclic bending test.

is not clear yet and needs further study, our experimental results of the low work function of CP film can be explained by the effects of PSS doping concentration or surface morphology induced by adding nanoparticle binders to the PEDOT:PSS paste or applying the screen-printing method. The low work function of the anode electrode is disadvantageous for hole injection; this leads to an increase of the turn-on voltage of the OLED (Ref. 14) and a decrease in efficiency. Despite the demerit as an anode, this result shows a potential application to the bottom cathode in inverted bottom-emitting OLEDs (IBOLEDs) (Refs. 29 and 30) instead of ITO. Since ITO has a high work function, the efficient electron injection from ITO into the organic has been a tenacious issue to resolve in IBOLEDs. IBOLEDs will likely become more important in the future, particularly for large, active matrix OLED (AMOLED) displays such as future TV applications, where a large-scale *a*-Si TFT is readily available and free from the uniformity problem of the rival low-temperature polysilicon TFT.

Figure 4 indicates a better mechanical stability of the CP film, compared with a commercialized ITO film on the PET substrate. The resistance of the film increases continuously with increasing the number of cyclic bending operations. An increase of the ratio of resistance change in the CP film after 1500 cycles is below 0.5, while that in the ITO film is 2–3. This indicates that the CP film has a good mechanical tolerance, which is indispensable to commercialization. Although CP film has a higher sheet resistance than ITO, it shows more stable electrical characteristics and suitability to flexible display applications, as it is more flexible to external shocks than ITO.

Figure 5(a) shows the turn-on voltages of both devices. Despite the large difference in the sheet resistances between the CP film ($\sim$2000 Ω/sq) and ITO film (9 Ω/sq), the measured turn-on voltage for the CP-OLED is 17 V, which is higher than that for the ITO-OLED, 9 V. This is attributed to the relatively poor conductivity and large energy band barrier induced from the low work function between the anode and organic material. A considerably high sheet resistance of the

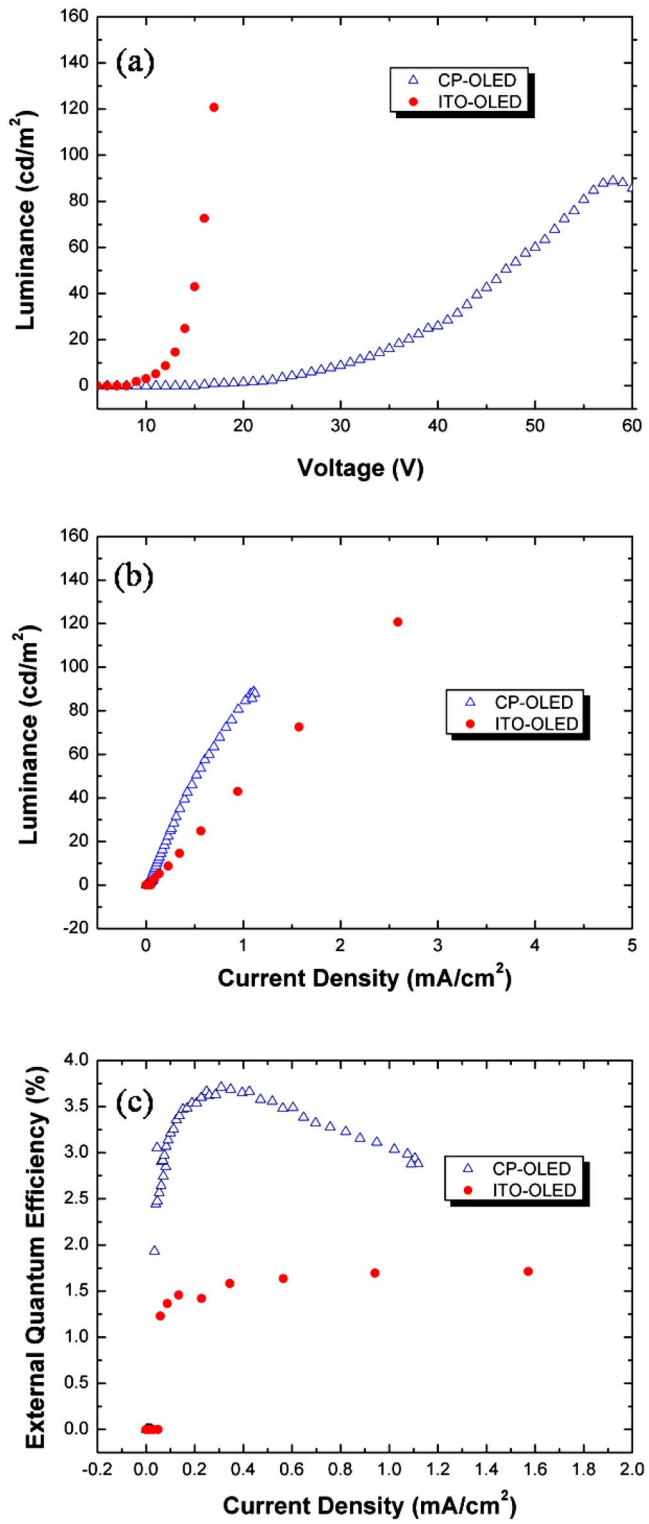

FIG. 5. (Color online) (a) Applied voltage vs luminance. (b) Current density vs luminance of CP-OLED and ITO-OLED. (c) External electroluminescence quantum efficiency as a function of current density measured for CP-OLED and ITO-OLED.

CP film limits the current flow through the OLED device. The highly shifted driving voltages in both cases are also due to their thick hole-injection layer.

Figures 5(b) and 5(c) are plots of the luminance and external electroluminescence quantum efficiency (η_{EL}) with respect to the current density. Although CP-OLED has draw-

TABLE II. Refractive indices and the ratio of the optical energy of each layer in OLED devices using conducting polymer film and ITO as an anode.

	Refractive index			Ratio of the optical energy transmitted		
	n_1	n_2	n_3	$2B_{12}$	$2B_{23}$	$2B_{13}(2B_{12}\times 2B_{23})$
CP-OLED	1.71	1.60	1.65	0.65	1	0.65
ITO-OLED	1.71	1.80	1.51	1	0.46	0.46

backs such as a relatively poor electrical property and low work function, it shows a better light extraction at the same applied current per unit area than ITO case [see Fig. 5(b)]. This result is consistent with the η_{EL} obtained in CP-OLED, up to ~3.5%, while that of an OLED using an ITO anode was ~1.5% [see Fig. 5(c)].

First, the results can be explained by the charge balance between holes and electrons. A high η_{EL} for CP-OLED means that the charge recombination at the emitting layer of the device is efficient. An increase of the hole-injection barrier with a low work function of the anode makes hole injection difficult. However, as the hole mobility becomes higher than the electron mobility by 2–3 orders of magnitude, the hole-injection property is balanced with the electron injection property. Second, the refractive indices of the anode and the substrate are different from each other. A simple ray-optics model explains the degradation in the external EL quantum efficiency of device with the waveguiding loss which results from the difference of the refractive indices of the layers on the light propagation from the active region to the outside. In order to evaluate the loss, the optical energy ratio, $2B$, is calculated. The ratio of the optical energy transmitted from material I into material J with refractive indices n_I and n_J ($n_I > n_J$) to the total energy emitted is given as $2B_{IJ}=\{1-[1-(n_J/n_I)^2]^{1/2}\}$.[31,32] Refractive indices and the ratio of the optical energy of the each materials are shown in Table II. In the case of ITO-OLED, $n_1=1.71$ (emitting layer, Alq_3), $n_2=1.80$ (ITO), $n_3=1.51$ (Ref. 13) (soda-lime glass), and $2B_{13}=0.46$. As the light generated in the active layer, Alq_3, propagates to ITO with little loss, and 46% of the light propagates from ITO to the glass substrate, the ratio of the optical energy transferred from the active layer to the substrate seems to be around 46%. On the other hand, in the case of the CP-OLED, $n_1=1.71$ (emitting layer, Alq_3), $n_2=1.60$ (CP), $n_3=1.65$ (PES film), and $2B_{13}=0.65$. In the same manner, as 65% of the light generated in the Alq_3 layer propagates to the CP layer, and the light propagates from ITO to the PES substrate with little loss, the ratio of the optical energy transferred from the active layer to the substrate seems to be around 65%. The higher ratio of the optical energy transfer with CP than ITO explains the higher external quantum efficiency.

IV. CONCLUSION

We studied a CP film formed on a plastic substrate by the screen-printing method, and investigated characteristics of an OLED with a CP flexible anode. The electrical and optical properties of a CP film were studied, and a sheet resistance of 2000 Ω/sq, a transmittance of 80–85%, a refractive index of 1.6, and a work function of 4.0 eV were measured for a 2000 Å thick film. A better surface morphology of the CP film is shown on a plastic substrate than the glass case, and a mechanical stability of the film is demonstrated by a cyclic bending test. The performance of CP-OLED when using these films is comparable to that of ITO-OLED despite their relatively poor electrical conductivity and low work function. A high external EL quantum efficiency of ~3.5% was obtained in CP-OLED. These results indicate that the transparent CP film patterned by the screen-printing method is a potential candidate for an electrode of the flexible OLED. Also, it is expected that the polymer electrode fabricated by a screen printing could be employed for a low-cost and large panel process in the area of touch panels, and illuminations such as backlight units.

ACKNOWLEDGMENTS

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