Title of Article

High-efficiency transparent organic light-emitting diode with one thin layer of nickel oxide on transparent anode for the see-through-display application

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Abstract

Work function of different species of metal oxide has been investigated, and of nickel oxide was found to reach about 5.4 eV, much higher than those of other metal species and indium tin oxide (ITO). The transparent organic light-emitting diode using a thin oxidation of nickel film upon ITO as an anode and a thin MgAg layer as a cathode has been fabricated. Device performance was found to improve greatly due to an efficient hole injection from nickel oxide; moreover, the top-emitting intensity was nearly same as the bottom-emitting intensity of device. The current efficiencies of the bottom and top emissions reached about 4.1 and 3.2 cd/A, respectively.

1. Introduction

The transparent organic light-emitting diode (TOLED) has received much attention recently due to its wide application in see-through-display [1, 2]. However, there are still two problems to be solved for fabricating a high-performance TOLED. The local damage resulting from sputtering indium tin oxide (ITO) or indium zinc oxide (IZO) on organic layer as a cathode will lower the device efficiency. In addition, there are the differences in luminance and color purity for the emissions from both surfaces of device due to an asymmetric structure of light propagation.

A lot of researches have been done about the development of transparent buffer layer on the organic layer. Partharathy *et al.* successfully developed a TOLED using copper phthalocyanine (CuPc) as an electron injection layer, and the maximum transmission rate could reach about 85% in the visible region [3]. The formation of internal energy level by high-energy sputtering on CuPc was found to facilitate the electron injection [4]. However, there is strong absorption of CuPc during the region of 650 nm-700 nm, which will limit the performance of red OLED. Our research group used $Ni(acac)_2$ as a buffer layer between top transparent cathode and organic layer and achieved good performance [5].

In addition, two-layer structure of MgAg/ITO, LiF/Al/SiO_2:Al, and only single-layer of LiF/MgAg and Ca-Ag have been reported as a transparent cathode and could lower the damage from sputtering ITO on organic layers effectively [6-9]. However, the change in reflectivity due to the use of the metallic buffer of MgAg might lead to much difference in the outputting efficiency or spectra from the both surfaces of TOLED. This will limit the application of TOLED for see-through-display. The methodology for optimizing viewing characteristics of top-emitting OLEDs has been presented [10, 11]. In this paper, we have designed a TOLED with a symmetric structure, in which two metal layers was used next to the transparent electrodes and functioned as a hole injection and an electron injection layer, respectively.

2. Experimental

The ITO-coated glass substrates were cleaned with detergent solution, rinsed with methanol, and subjected to oxygen plasma treatment of 50 W for 5 minutes immediately before use. For comparison, 10 nm metal- and ITO/metal- coated glass substrates were also used as an anode. The Ni-coated substrates were treated by oxygen plasma for 2 minutes in the plasma chamber to prepare an oxidation of metallic film.

Devices were fabricated by utilizing vacuum thermal deposition system. We deposited 40 nm 4,4'-bis[N-(1-napthyl)-N-phenyl-amino]-biphenyl (NPB) as a hole transport layer, 20 nm 0.5-wt% coumarin 6 in tris(8-hydroxyquinoline)aluminum (Alq) as a light-emitting layer and 40 nm Alq as an electron transport layer, subsequently, upon ITO-, metal oxide (MO)-, or ITO/MO-coated glass substrates under a base pressure of lower than 5.5 $\times 10^{-6}$ Torr. The electron injection layer of 0.4 nm LiF and the cathode of 10 nm Mg:Ag (9:1 mass ratio) were evaporated on the top of organic layer. Finally, we employed the electron cyclotron resonance (ECR) sputtering to form a transparent cathode onto thin-film buffer layer of MgAg. The sputtering conditions are as followed: the gas flow of Ar and O_2 is 30 and 0.2 SCCM, respectively; both RF and μ radiation are 300 W; the calibrated deposition rate is 10 nm/min. The structure and schematic energy diagram of devices were schematically illustrated in Fig. 1.

Figure 1

The transmission of thin metal layer of MgAg and Ni has been measured. It was found that the transmission decreased exponentially from 98% at 5 nm to 55% at 10 nm and to 19% at 20 nm for MgAg film, and from 85% at 5 nm to 50% at 10 nm and to 16% at 20 nm for Ni film. In addition, it has been reported that the electrical conductivity of thin metallic films decreases as the film thickness increases due to the filling of the empty channels between the isolated islands of thin metallic films and the transformation of metallic films from discontinuous to continuous films [12]. Therefore, a 10 nm of metal layer was selected in this study for keeping both good electric conductivity and transmission.

We have measured the luminance-current density-voltage characteristics of devices with a source measure unit (HP4140B, Hewlett-Packard) and a luminance color meter (BM-7, TOPCON). The color meter was placed on the normal of the test device to measure the front luminance. Fluorescence spectra were recorded with a Jasco FP-75 spectrophotometer. The highest unoccupied molecular orbital level for the oxidation of metallic films measured with a Riken Keiki AC-3 photoelectron emission spectrometer.

3. Results

3.1. Work functions of metal and metal oxide

Table 1 shows the work function of metal species and their oxides. ITO is a non-stoichiometric compound, of which the chemical composition can be easily changed by the surface treatment. Using oxygen inductively coupled plasma, the decrease in Sn:In ratio and the increase in oxygen concentration of ITO are assumed to be closely related to the enhanced work function of the ITO [13]. As regards other metal species, the formation of oxidation of metallic film may lead to increasing pinning-free state, which is contributed to the increased work function of metal species. In addition, O_2 plasma treatment will change the flatness of atom level of metal surface, facilitating hole injection by changing Schotty barrier heights at metal/semiconductor interfaces. Some researcher have revealed that the use of Ag electrode treated by the UV-ozone as an effective reflecting anode for the top-emitting OLEDs can gives nearly identical operation voltage as the ITO [14]. It can be found that after O_2 plasma treatment, the work function of nickel can reach 5.4 eV, much higher than Ag and other species of metals as well as ITO. Thus the nickel oxide can function as both the conductive electrode and the hole injection layer, leading to an enhancement in device efficiency by facilitating the hole injection, as seen from energy diagram of devices in Fig. 1(b).

Table 1 Work function of several species of metals before and after O_2 plasma treatment

Species	Before plasma (eV)	After plasma (eV)
ITO	4.8	5.1
Zn	4.3	4.3
Cr	4.6	4.8
Ag	4.4	4.8
Ge	4.7	5.0
Ni	4.5	5.4

3.2. TOLED using IZO as a transparent cathode

Using ECR sputtering technology to fabricate transparent IZO on the organic layer, two devices with and without buffer layer have been fabricated. In this study, we used LiF/MgAg as buffer layer due to its good electron injection performance. Figure 2 shows that the top and bottom luminance is almost same for the device without buffer layer but quite different for device with buffer layer. The luminance from both surfaces of the device with a structure of ITO/Organic layers/IZO is 1600 cd/m^2 at about 100 mA/cm^2, 8600 cd/m^2 at 690 mA/cm^2. On the other hand, the bottom emission and the top emission for the device with a structure of ITO/Organic layers/LiF/MgAg(10nm)/IZO were 3800 and 528 cd/m^2 at the current density of 112 mA/cm^2, and 65300 and 3578 cd/m^2 at the current density of 720 mA/cm^2, respectively. The maximum ratio of the bottom emission with respect to the top emission can reach about 18 times.

[**Figure 2**]

The introduction of one buffer layer can prevent the damage from sputtering and thus improve the device efficiency. However, it was observed that the emission intensity from both surfaces of device was much different on the order of 18 times. The deposition of one transparent organic layer on the metallic layer can enhance the outcoupling efficiency [9]. Based on our experimental result, however, the introduction of metallic buffer layer affected the device performance, especially the luminance ratio of bottom surface with respect to top surface when sputtering IZO on the metallic layer. We ascribe this difference to the optical and/or electrical change of MgAg surface due to a local damage by ECR sputtering.

3.3. TOLEDs using thin metal as a transparent cathode

We have fabricated the TOLEDs using one thin MgAg film as a transparent cathode, while we changed the species of anodes, which are an ITO, a thin nickel film, and an ITO/nickel, respectively. The nickel oxide was formed on the substrates with nickel film after O_2 plasma treatment for 2 minutes. The luminance-current density and spectral characteristics of the devices were shown in Fig. 3.

[**Figure 3**]

It can be observed from Figs. 3a and 3b that the top emission was much weaker than the bottom emission for the devices with only ITO or only thin nickel as an anode. The ratios of bottom-emission luminance from glass side with respect to top-emission luminance from metallic side were about 6.4 and 3.6 times at the current density ranging from 10 to 120 mA/cm^2 for the devices with ITO and nickel as an anode, respectively. On the other hand, while depositing one thin layer of nickel on ITO and using it as anode after O_2 plasma treatment, the top-emission intensity was improved greatly and the ratio of bottom to top emission decreased to be about 1.4, as shown in Fig. 3(c).

The electrical and optical characteristics of devices were summarized into Table 2. It can be found that the turn-on voltage (the voltage when a luminance of 0.5 cd/m^2 was detected) for all transparent devices was almost the same, which is 2.7-2.8 V. However, it was found that the current efficiency and external quantum efficiency was the highest for the device with an anode of ITO/Ni, the next for the device with Ni as an anode, and the lowest for the device with ITO as an anode. This demonstrated that the nickel oxide had a better hole injection performance than ITO.

In addition, we have found that the EL of top emission was spectrally narrowing, as revealed in the right in the Fig. 3. Although the peak emission for both-surface emission may be unchanged, the full wavelength at half maximum (FWHM) for the top emission was about 4~6 nm narrower than the bottom emission due to a microcavity effect.

Table 2 The characteristics of devices used in the study

Bottom glass/anode		ITO150 nm		Ni10nm		ITO150nm/Ni10nm	
Top cathode (LiF/MgAg)		10 nm	150 nm	10 nm	150 nm	10 nm	150 nm
Turn-on voltage [a)] (V)	Bottom	2.7	2.6	2.8	2.6	2.7	2.6
	Top	3.0	-	3.0	-	2.8	-
Current efficiency [b)] (cd/A)	Bottom	4.8	6.8	5.0	9.8	4.1	11.1
	Top	0.7	-	1.4	-	3.2	-

External quantum efficiency [b] (%)	Bottom	2.1	3.13	2.3	5.1	1.4	5.7
	Top	0.2	-	0.5	-	1.2	-
Peak emission (nm)	Bottom	510	510	510	510	514	512
	Top	508	-	510	-	510	-
FWHM (nm)	Bottom	74	74	74	62	72	64
	Top	70	-	68	-	66	-

a) the voltage at the luminance of >0.5 cd/m^2;

b) at the current density of about 100 mA/cm^2.

It is worthy to note that the device performance of TOLEDs was lowered to some extend compared to the bottom-emitting device (the thickness of MgAg cathode was 150 nm), as seen in Table 2. For example, at the current density of about 100 mA/cm^2, the total current efficiencies for the TOLEDs with respect to those for the bottom-emission devices were 5.5 to 6.8 cd/A, 6.4 to 9.8 cd/A, and 7.3 to 11.1 cd/A for devices with ITO, Ni, ITO/Ni as an anode, respectively. This was contributed to the increase in turn-on voltage from 2.6 to 2.8 V due to relatively high resistance, as shown in Table 2. In addition, a refractive index mismatch between MgAg (n=4.3) /Air (n=1.0) may lead to a reflection loss of light, thus decreasing the outcoupling efficiency through the top surface too.

4. Conclusions

In summary, high work function of nickel oxide has been demonstrated. Using IZO or one thin MgAg layer as a cathode, the performance of two TOLEDs has been investigated. We concluded that the introduction of one thin nickel oxide layer on transparent ITO as one hole injection layer could improve device performance greatly and balance both sides' emission intensity. This was mainly contributed to good hole injection characteristics and high reflective effect of nickel oxide.

Acknowledgements

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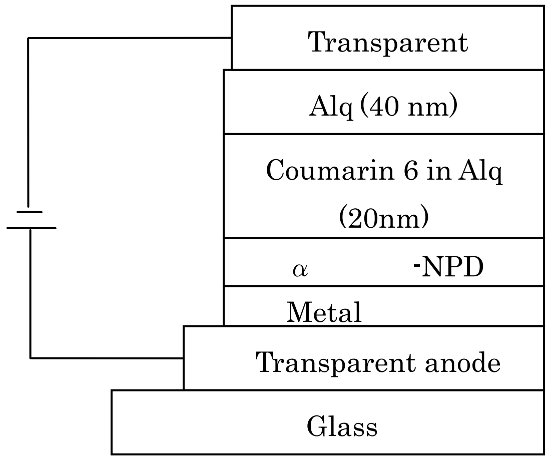
Figure Captions

Figure 1. The device structure of TOLEDs used in this study (a) and schematic energy diagram (b)

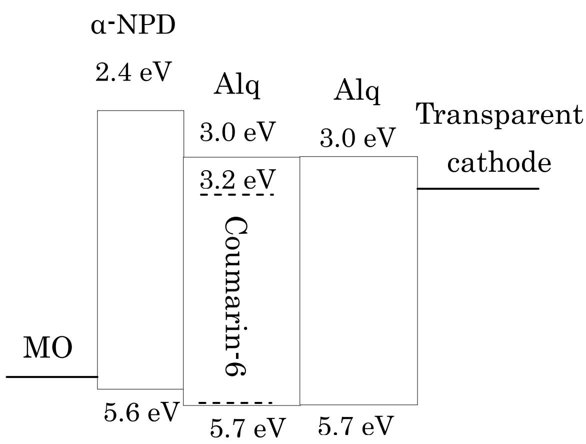
Figure 2. Luminance from top and bottom surfaces *vs.* current density for TOLEDs with IZO as a cathode

Figure 3. Luminance and spectra from the top-emission(T) and the bottom-emission(B) of devices with 10 nm MgAg as a cathode and different anodes: a) ITO as an anode; b) 10 nm of nickel as an anode; c) ITO/Ni as an anode.

FIG. 1


Transparent
Alq (40 nm)
Coumarin 6 in Alq
(20nm)
α -NPD
Metal
Transparent anode
Glass

(a)


α-NPD
2.4 eV
Alq
3.0 eV
Alq
3.0 eV
Transparent
cathode
3.2 eV
Coumarin-6
MO
5.6 eV
5.7 eV
5.7 eV

(b)

FIG. 2

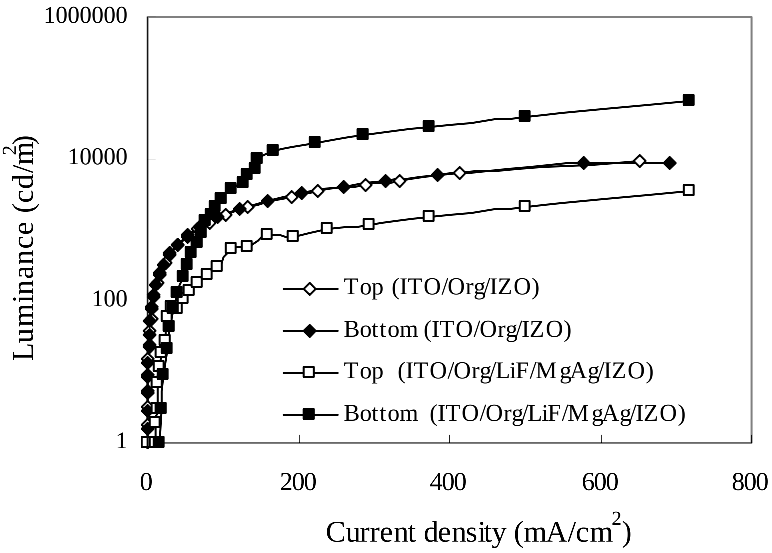
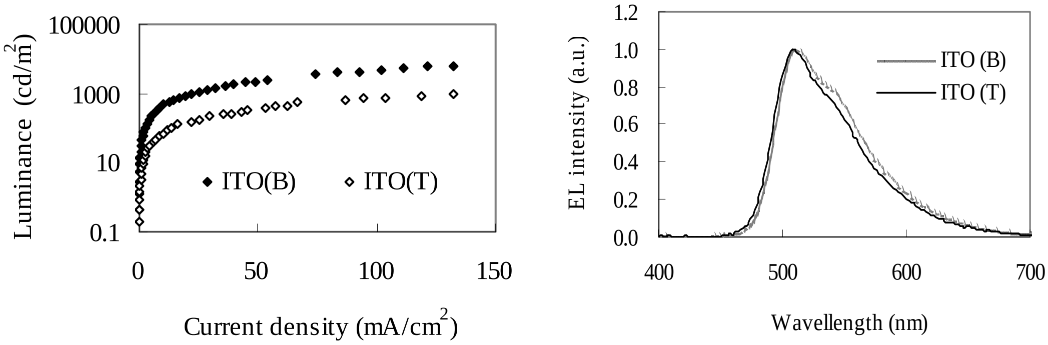
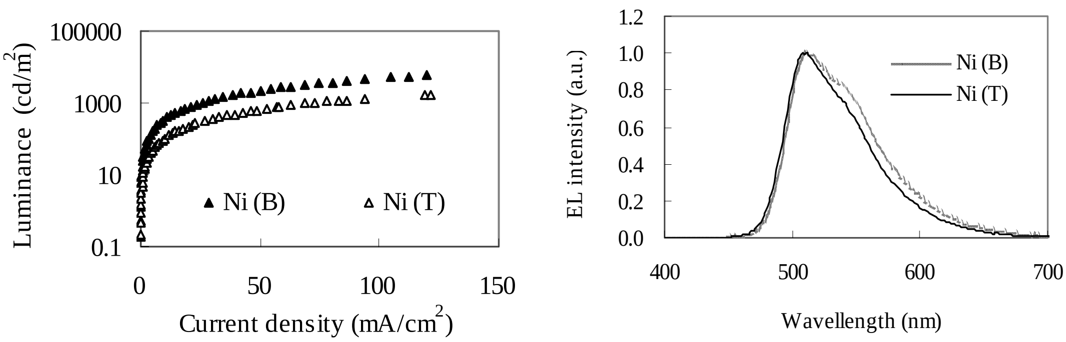

1000000
10000
100
1
Luminance (cd/m2)
0
200
400
600
800
Current density (mA/cm2)
Top (ITO/Org/IZO)
Bottom (ITO/Org/IZO)
Top (ITO/Org/LiF/MgAg/IZO)
Bottom (ITO/Org/LiF/MgAg/IZO)

FIG. 3



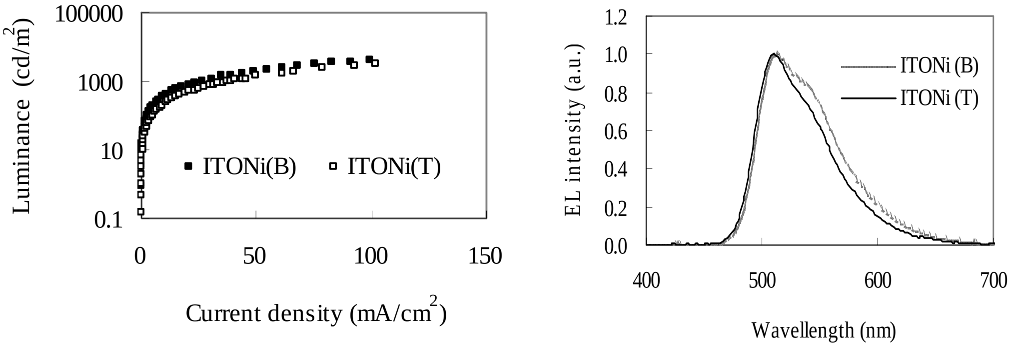
Luminance (cd/m²)
100000
1000
10
0.1
0
50
100
150
Current density (mA/cm²)
ITO(B)
ITO(T)
EL intensity (a.u.)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
Wavelength (nm)
ITO (B)
ITO (T)

(a)



Luminance (cd/m²)
100000
1000
10
0.1
0
50
100
150
Current density (mA/cm²)
Ni (B)
Ni (T)
EL intensity (a.u.)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
Wavelength (nm)
Ni (B)
Ni (T)

(b)



Luminance (cd/m²)
100000
1000
10
0.1
0
50
100
150
Current density (mA/cm²)
ITONi(B)
ITONi(T)
EL intensity (a.u.)
1.2
1.0
0.8
0.6
0.4
0.2
0.0
400
500
600
700
Wavelength (nm)
ITONi (B)
ITONi (T)

(c)