Highly transparent organic light-emitting diodes with a metallic top electrode: the dual role of a Cs$_2$CO$_3$ layer

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Abstract: Highly transparent organic light-emitting diodes (TrOLEDs) are demonstrated using damage-free top cathodes of Cs$_2$CO$_3$/Ag capped with ZnS layers. The presence of ultrathin Cs$_2$CO$_3$ layers not only improves the electron injection properties but also makes Ag thin films more continuous and uniform, resulting in ideal top electrodes with low sheet resistance and high transmittance. The combination of the uniform Ag morphology enabled by Cs$_2$CO$_3$ and the optimized thickness of ZnS capping layers results in TrOLEDs that have a peak transmittance as large as 80% with a luminous transmittance of 76.4%. These TrOLEDs exhibit a low turn-on voltage of 2.6V due to injection improvement by the Cs$_2$CO$_3$ layers.

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References and links

1. Introduction

One of the many advantages of organic light emitting diodes (OLEDs) over other types of displays is that they can be easily adapted to transparent displays [1]. Considering the typical structure of OLEDs, which consist of a transparent anode of indium tin oxide (ITO) film, thin organic layers, an inorganic buffer layer (optional), and a metallic cathode, transparent OLEDs (TrOLEDs) with the most straightforward structure would be those in which the metallic cathode is replaced with ITO or similar transparent conductive oxides (TCO) [2, 3]. However, the deposition process of ITO or common TCOs, based mostly on RF sputtering, can damage the underlying organic layers. This sputtering damage may be alleviated to some degree by using a buffer layer, but complete protection is still regarded as challenging. Moreover, obtaining highly transparent TCOs with high conductivity often requires a high-temperature annealing process [4, 5] that is inapplicable to OLEDs due to the relatively low service temperature of organic materials. Another candidate that can be relatively free from deposition-induced damage is semitransparent thin metal layers deposited by thermal evaporation. They have been used as a top electrode typically in top-emission OLEDs [6–9] and also in transparent OLEDs (TrOLEDs) [10, 11], often in association with a buffer layer for injection improvement. In TrOLEDs using a metal top electrode, however, obtaining a high transmittance is challenging due to the relatively large reflection and absorption of metallic thin films. Reflection from a metal electrode may be reduced to a certain degree by the appropriate use of a capping layer [12], but absorption has not been easy to suppress. Hence the transmittance of TrOLEDs with a metal top electrode has been typically below 60–70% at best. In this work, we present a combinatorial approach that can reduce both the reflection and absorption of a thin silver layer and, at the same time, can improve its sheet conductance as well as its electron injection properties, so as to realize efficient, highly transparent OLEDs. In particular, emphasis is given to a thermally evaporated thin Cs2CO3 layer that plays a dual role as the electron injection layer and the nucleation-promoting layer for Ag.

2. Experiment

The proposed TrOLEDs are based on a conventional multilayer geometry using N,N′-bis(naphthalen-1-yl)-N,N′-bis(phenyl)-benzidine (NPB) as the hole-transporting layer (HTL) and tris(8-hydroxy-quinolino) aluminum (Alq3) as the emission/ electron-transporting layer.
(EML/ETL). ITO glass substrates were cleaned in an ultrasonic bath and treated by air plasma using a plasma cleaner (PDC-32G, Harrick Plasma) prior to deposition of the organic materials [13]. Optional Cs₂CO₃ layers with a nominal thickness of 1.5 nm were deposited on top of the Alq₃ layers primarily for an electron-injecting layer (EIL). Ag layers with a thickness in the range of 9-15nm were used as the top cathode. The Cs₂CO₃ layers were chosen because ultrathin Cs₂CO₃ layer had recently been shown to work as an electron injecting/collecting buffer layer in both OLEDs [14] and organic solar cells [15]. In contrast to a common EIL of LiF, which is known to work rather exclusively with Al, Cs₂CO₃ layers were shown to work comparably well with Al, Ag, and ITO [14, 15], indicating that the effectiveness of Cs₂CO₃ layers is relatively insensitive to the choice of a metal layer used together. Such insensitivity can be beneficial in that a choice of a metal electrode does not need to be limited by the injection capability of the metal itself and thus one can focus more on other aspects such as optical transparency and sheet conductance. Some devices had an additional layer of thermally evaporated ZnS (Alfa Aesar, 99.99%) as an optical capping layer. The current density-voltage-luminance (J-V-L) characteristics of the TrOLEDs were measured in an N₂-filled glove box directly connected to the thermal evaporation chamber using a source-measure unit (Model 2400, Keithley), a calibrated photodiode (FDS100-CAL, Thorlab), and a fiber-optic spectrometer (EPP-2000-UV-VIS-NIR, StellarNet). The transmittance was measured with a UV-VIS spectrometer (SV2100, K-MAC). The morphology of the top Ag layer was analyzed using scanning electron microscopy (SEM) (Nova NanoSEM 230, FEI Company) and its optical constant was characterized using the spectroscopic ellipsometer (M2000D, Woollam). For a fair comparison, samples with Ag films used for basic characterizations were prepared in the same batch as the OLED devices.

### 3. Results and discussions

#### 3.1 Improving the transmittance and sheet conductance of Ag thin films: the role of a Cs₂CO₃ layer as a nucleation promoter

To realize highly transparent OLEDs with a metal top electrode, it is crucial to first minimize the absorption from the metallic layer. Absorption from a metal layer being proportional to the product of refractive index \( n \) and extinction coefficient \( k \), Ag and Au are the most preferred choice due to their relatively low \( n \) and \( k \) values [16]. In principle, absorption below 5% could be achieved with 15-nm-thick Ag layers. However, the optical properties of metallic layers in this thickness range can be highly dependent on the microscopic morphology of the films. Before metal layers become thick enough to exhibit uniform, continuous morphologies, the effect of scattering and surface plasmon resonance on their optical constants can be significant [17, 18]. With Ag, scattering has been shown to mainly increase \( n \) [17], and surface plasmon resonance has been shown to mainly increase \( k \) [18]. Note that the \( nk \)-product and thus absorption are increased in both cases with respect to that of films with a continuous morphology, which may be described by the optical constants of bulk Ag. It is noteworthy that the critical thickness \( (d_{critical}) \) at which a metal layer begins to exhibit continuous morphologies can differ depending on the conditions of the surface onto which the metal layer is deposited. Hence the morphology of a metal layer needs to be identified on a case-by-case basis and has to be improved, if possible, in order to achieve the maximal transmittance that can be offered by the given metal.

Figure 1 shows the transmittance of OLED devices \( (T_{OLED}) \) with the structure of ITO/NPB (50nm)/ Alq₃ (50nm)/ x/ Ag (9, 12, and 15nm) with \( x \) being either Cs₂CO₃ (1.5nm) or nothing. With a Cs₂CO₃ layer, \( T_{OLED} \) increases as the thickness of the Ag layer \( (d_{Ag}) \) decreases, as expected for bulk-like, uniform thin films. Without a Cs₂CO₃ layer, however, \( T_{OLED} \) varies little with \( d_{Ag} \). In particular, \( T_{OLED} \) values of devices with 9-nm and 12-nm-thick Ag layers are virtually identical within the error bound. This strongly suggests that the overall transmission of the devices without the Cs₂CO₃ layers is limited by the morphological imperfections of the Ag layers.
The scanning electron microscopy (SEM) images of Ag layers shown in Fig. 2 confirm that Ag films deposited directly on Alq₃ layers exhibit morphologies with more grain boundaries than those deposited on the Cs₂CO₃ layer. With 9-nm-thick Ag films, both cases show grainy morphologies, but those grown on Cs₂CO₃/Alq₃ show morphologies with larger grains and less grain boundaries than those grown on Alq₃ layers. With 12-nm-thick Ag films, the difference becomes much more significant: Ag layers grown on Cs₂CO₃-covered Alq₃ layers exhibit compact, uniform morphologies virtually free of grain boundaries while those grown directly on bare Alq₃ layers still exhibit grainy features, confirming the importance of Cs₂CO₃ layers in growing high-quality Ag films. The feasibility of using seed layers that improve wetting to result in continuous thin metal films has been well recognized by Kaiser, and the role of Cs₂CO₃ layers may be understood in the same context [19].
both \(n\) and \(k\) values are higher for Ag films grown on Alq\(_3\) than those on Cs\(_2\)CO\(_3\)/Alq\(_3\) in most of the wavelength range studied. In particular, the difference in refractive indices \((n)\) is more significant than that in extinction coefficients \((k)\), indicating that the scattering effect is more dominant than the effect of surface plasmon resonances in the Ag films under study. The latter is known to be more significant when Ag films are composed of numerous island-like aggregates of silver atoms [18, 20]. Since the Ag films under investigation do not show island-like morphologies in all cases, the surface plasmon effect is expected to be weak.

![Image](image_url)

Fig. 3. (a) The optical constant of the 15-nm Ag on Cs\(_2\)CO\(_3\)/Alq\(_3\) or Alq\(_3\). (b) Measured and calculated transmittance of the 15nm-thick Ag on x/Alq\(_3\) (50nm)/glass with x either being Cs\(_2\)CO\(_3\) (triangle) or nothing (square).

From the practical point of view, successful transparent electrodes should not only exhibit a high transmittance but also have a high sheet conductance \((G_{SH})\), or equivalently, a low sheet resistance \((R_{SH})\). As shown in Table 1, \(R_{SH}\) values of Ag films on Cs\(_2\)CO\(_3\)/Alq\(_3\) are also smaller in all cases than those of Ag films deposited directly on Alq\(_3\). For example, \(R_{SH}\) of the 12-nm-thick Ag film on Cs\(_2\)CO\(_3\)/Alq\(_3\) is as low as 5.6 \(\Omega/\text{sq.}\), while that of the 12-nm-thick Ag film on Alq\(_3\) is 7.4 \(\Omega/\text{sq.}\). This result is consistent with the trend observed in \(T_{OLED}\) and SEM experiments in that the scattering of carriers at grain boundaries induces a larger effective resistivity in thin films than those expected for bulk materials of the same kind [21].

<table>
<thead>
<tr>
<th>Ag thickness (nm)</th>
<th>Sheet resistance ((\Omega/\text{sq.}))</th>
<th>Average transmittance (%) (400-700nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>On Alq(_3)</td>
<td>On Cs(_2)CO(_3)</td>
</tr>
<tr>
<td>9</td>
<td>8.8</td>
<td>7.1</td>
</tr>
<tr>
<td>12</td>
<td>7.4</td>
<td>5.6</td>
</tr>
<tr>
<td>15</td>
<td>5.8</td>
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The OLEDs in a structure shown in the inset of Fig. 1.

From the series of experimental results mentioned above, we can recognize that the Cs\(_2\)CO\(_3\) layer acts as a nucleation-promoting layer that reduces \(d_{critical}\), thus leading to Ag films with both high transparency and low sheet resistance even at relatively low nominal thickness.

3.2 Further enhancement in the transmittance of transparent OLEDs by high-index capping layers

Once the absorption by a metal layer is suppressed as discussed in the previous section, the reflectance has to be minimized to further enhance \(T_{OLED}\). In modulating the transmittance of
metal-based transparent electrodes, dielectric capping layers have been popular for their simplicity [12, 22]. The overall TrOLED structure with such a capping layer shown in the inset of Fig. 1a may be considered as a dielectric-metal-dielectric (DMD) structure as a whole in which the organic layers and ITO layers below its metal layer can be viewed effectively as a single dielectric layer. In a DMD structure, the right combination of the thicknesses of its two dielectric layers can result in matching of the optical admittance between the DMD multilayer stacks and the ambient medium, leading to a so-called “zero-reflection” condition [17, 23]. Because such a condition is met only at a specific wavelength, however, the average quantity weighted for the human photopic response is typically adopted as an optimization key. We adjusted the thickness of the capping layer or the outer dielectric layer (= \( d_{\text{cap}} \)) so that it maximized the luminous transmittance (\( T_{\text{lum}} \)) of OLEDs defined by

\[
T_{\text{lum}}(d_{\text{cap}}) = \frac{\int T_{\text{OLED}}(\lambda; d_{\text{cap}}) f_{\text{photopic}}(\lambda) d\lambda}{\int f_{\text{photopic}}(\lambda) d\lambda}
\]  

(1)

where \( f_{\text{photopic}}(\lambda) \) is the photopic luminosity function given at a wavelength \( \lambda \) [17]. It has to be noted that the maximum \( T_{\text{lum}} \) achievable with optimized \( d_{\text{cap}} \) can be further improved if a dielectric material with a higher \( n \) is used for the capping layer [See Fig. 4(a)]. With this in mind, ZnS, having an \( n \) of 2.2-2.4, was chosen as a capping layer in this study [22].

Figure 4(b) shows the calculated \( T_{\text{lum}} \) for TrOLEDs containing a ZnS capping layer as a function of the thickness of the ZnS layer (= \( d_{\text{ZnS}} \)). It is noted that \( T_{\text{lum}} \) of TrOLEDs with or without Cs\(_2\)CO\(_3\) layers vs. the thickness of the ZnS layer (\( d_{\text{ZnS}} \)) used as the capping layer. Without a Cs\(_2\)CO\(_3\) layer, the highest \( T_{\text{lum}} \) achievable in devices with a Cs\(_2\)CO\(_3\) layer is smaller by ~15% than that achievable in devices with a Cs\(_2\)CO\(_3\) layer. Figure 4(c) presents the contour plots of \( T_{\text{OLED}} \) as a function of both \( \lambda \) and \( d_{\text{ZnS}} \) for TrOLEDs with or without Cs\(_2\)CO\(_3\) layers. \( T_{\text{OLED}} \) greater than ~70% can be obtained at a \( d_{\text{ZnS}} \) of 30±10 nm over a wide spectral range in the
presence of Cs$_2$CO$_3$ layers, while such a high $T_{\text{OLED}}(\lambda)$ is obtained only within a limited spectral range in devices without Cs$_2$CO$_3$ layers, which explains the difference in $T_{\text{lum}}$ in those devices.

Figure 5 presents the transmittance spectra of actual OLEDs fabricated with 37-nm-thick ZnS-capping layers. It is clear that the experimental data are in a quantitative agreement with the calculation result. Using Eq. (1), $T_{\text{lum}}$ of 76.4% is estimated for the device having both Cs$_2$CO$_3$ and ZnS layers, while $T_{\text{lum}}$ of 66.7% is estimated for the device having a ZnS layer but no Cs$_2$CO$_3$ layer. Along with the calculation results outlined in Fig. 3, this result demonstrates the validity of the proposed combinatorial method based on a nucleation-promoting Cs$_2$CO$_3$ layer and a ZnS capping layer, in which the former suppresses absorption and the latter minimizes the reflection from the Ag layer.

![Fig. 5. Measured and calculated transmittance ($T$) of TrOLED devices in a structure of ITO/ NPB (50nm)/ Alq$_3$ (50nm)/ x/ Ag (15nm)/ ZnS (37nm) with x being either Cs$_2$CO$_3$ (1.5nm) (triangle) or nothing (square). $T$ of a glass substrate (diamond) and ITO-coated glass substrate (circle) are also presented for comparison.](image)

3.3 Device characteristics of the proposed transparent OLEDs (TrOLEDs)

Transparent electrodes used in OLEDs have to fulfill the requirements for carrier injection as well as those for transmittance and sheet conductance. It is often challenging to satisfy those requirements all at the same time. For example, ultrathin Al was shown to improve the morphology of Ag thin films and thus $G_{\text{SH}}$ [24], but it might not be so effective for transparent devices due to the relatively high light absorption of Al. Other multilayers or composite electrode structures such as Ca/Ag or Mg: Ag that are used for better electron injection also suffer from similar problems with limited transmittance. A Cs$_2$CO$_3$ layer was previously shown to enhance electron injection due to highly effective n-doping effect near the organic/ Cs$_2$CO$_3$ interface [25], and thus it may be regarded as an ideal candidate for a layer that can help injection of the desired carriers and, at the same time, can promote formation of uniform Ag layers as shown in the previous section. (For further details on the mechanism of electron injection enhancement by Cs$_2$CO$_3$, please refer to the work by Wu et al. [25] and Huang et al. [26])

Comparison of J-V characteristics of TrOLED devices with or without the 1.5-nm-thick Cs$_2$CO$_3$ layer indeed confirms that electron injection is greatly improved upon insertion of the Cs$_2$CO$_3$ layer [Fig. 6(a)]. Clearly, the J-V curve of the devices with the Cs$_2$CO$_3$ layer is shifted toward a lower voltage by approximately 4V with respect to that of the devices without it. Figure 6(b) presents the luminance ($L$) - voltage ($V$) characteristics of a device in a geometry of glass/ ITO/ NPB (50nm)/ Alq$_3$ (50nm)/ Cs$_2$CO$_3$ (1.5nm)/ Ag (15 nm)/ ZnS (37 nm or nothing) for both top and bottom emission directions. One can easily see that the electron injection enhancement due to the Cs$_2$CO$_3$ layer leads to a low turn-on voltage ($V_T$; defined as a voltage for $L$ of 1 cd/m$^2$) of 2.6V, which is comparable to the $V_T$ of conventional OLEDs in a configuration of glass/ ITO/ NPB (50nm)/ Alq$_3$ (50nm)/ LiF/Al [20].
The TrOLED device with both ZnS and Cs$_2$CO$_3$ layers exhibits luminous efficacy $\eta_{cd}$ of 2.3 cd/A for ITO-side emission and 1.2 cd/A for Ag-side emission, respectively. (See Fig. 7(a)) Note that the luminous efficacy for the total emission is 3.5 cd/A, which is also comparable to the conventional NPB/Alq$_3$-based OLEDs [20]. The asymmetry in $\eta_{cd}$, observable in Figs. 6(b) and 7(a), is considered to come from the finite internal reflection of the generated light from the Ag layer and is a phenomenon characteristic of TrOLEDs containing a metal-based electrode on one side and an ITO or similar transparent electrode on the other side. A degree of asymmetric light-emission may be tuned by varying $d_{ZnS}$ depending on the requirements of the target application, as we demonstrated in semitransparent organic solar cells [27]. As shown in Fig. 7(b), $d_{ZnS}$ of 37nm, which almost maximizes $T_{lum}$, corresponds to a situation in which the internal reflection ($R_{int}$) at the organic/Ag interface is suppressed to yield an emission that is relatively well balanced for both directions.

Hence, changing $d_{ZnS}$ to enhance the emission in a certain preferred direction would require a compromise in $T_{lum}$ to some degree. A good example is in fact the light emission characteristics of a TrOLED device without the ZnS layer. This device does have a relatively high $R_{int}$ as Fig. 7(b) shows, to yield a highly asymmetric light emission in which ITO-side emission is enhanced as Fig. 7(a) shows at the cost of a reduced $T_{lum}$. [Recall that the $T_{lum}$ of TrOLEDs without ZnS layers is limited to approximately 40%.]
4. Conclusions

We proposed a strategy for highly transparent OLEDs based on a combinatorial approach using a ZnS layer as a high-index capping layer and a Cs₂CO₃ interlayer as a nucleation-promoter and an electron injection layer. The former effectively enhances the transmittance of OLEDs by suppressing reflectance with appropriate optimization of thickness. The latter helps form a uniform, continuous Ag film even at a low nominal thickness, suppressing the absorption and thus improving the overall transmittance. The latter also helps to mitigate the scattering-induced decrease in sheet conductance of the Ag thin films, eventually to enable the Ag layers to have both high transparency and low sheet resistance. With the proposed method, we demonstrated efficient transparent OLEDs having a luminous transmittance of 76.4% and peak transmittance of 80%. The origin of the observed asymmetric light emission in the proposed TrOLEDs was also discussed including its relation to the luminous transmittance. We believe the work presented here provides a logical route to develop highly transparent OLEDs based on a metal-based top electrode, which has advantages over ITO electrodes due to its large-area compatibility and damage-free nature.

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