Improved light extraction efficiency in organic light emitting diodes with a perforated WO$_3$ hole injection layer fabricated by use of colloidal lithography

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Abstract: We present an organic light emitting diode with a perforated WO$_3$ hole injection layer to improve the light extraction efficiency. The two-dimensionally perforated WO$_3$ layer was fabricated by use of colloidal lithography. The light extraction efficiency was improved due to Bragg scattering of waveguide modes and surface plasmon polaritons, and the operating voltage was also decreased. As a result, the external quantum efficiency and the power efficiency were increased as compared with those of conventional organic light emitting diodes without WO$_3$ layer. The angular dependence of emission characteristics was investigated by measuring radiant intensity profiles for emission angles and azimuthal angles.

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References and links

1. Introduction

Due to recent progress in studies of materials and devices for organic light emitting diodes (OLEDs), OLEDs have begun to be commercially used in display markets and have drawn attention as a next-generation lighting device. In order to ensure the success of OLEDs in the display and lighting markets, an improvement in the luminous efficiency is one of several crucial issues. The major reason which causes the low luminous efficiency of OLEDs is the low light extraction efficiency, which is only around 20% in a conventional OLED structure [1, 2]. A large part of the light from OLEDs, which typically consist of a transparent conducting oxide (TCO) layer, organic layers and a metal cathode on a glass substrate, is trapped as substrate guided mode and waveguide modes that occur due to the differences in reflective index between each layer [1–3]. Some light is also trapped in the form of surface plasmon polaritons (SPPs) at the interface between the organic layers and the metal cathode [1, 3]. The well-known methods to extract the trapped substrate guided mode in the glass substrate are to introduce a surface modification [4, 5] or to insert a micro-lens array [6–8] on the back side of the glass substrate. The waveguide modes trapped in the TCO layer and in the organic layers can be extracted through Bragg scattering by introducing a periodic grating structure with a period of several hundred nanometers [9–18]. If the metal cathode also has a grating structure, the trapped SPPs can be extracted through a similar mechanism [15–19].

There are a few disadvantages in these methods proposed to improve the extraction efficiency of OLEDs. One of the problems is the complexity of fabrication. Another problem is the angular dependence of the emission enhancement; the emission enhancement ratio can spontaneously reduce the dependence of the emission on the change of the azimuthal angle, which is the typical problem in OLEDs that have periodic nano-structures. Extracting the waveguide modes and the SPPs was reported to improve the light extraction efficiency, and the decreased operating voltage was achieved by the insertion of the perforated WO$_3$...
The angular dependence of the emission of OLEDs with a perforated WO₃ layer was investigated.

2. Calculation: waveguide and surface plasmon modes in OLED

The waveguide modes and the surface plasmon formed in the OLED can be extracted to the light by the periodic nanostructure if the grating period of the nanostructure corresponds to the grating period required to satisfy the Bragg scattering condition [3, 9, 11, 15, 19]. To determine the period of the perforated pattern, we calculated the dispersion relation and the field profile of the waveguide modes and the surface plasmon in the planar OLED structure without the perforated pattern, which consists of the glass substrate, the indium tin oxide (ITO) layer (150 nm), N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) layer (50 nm), tris(8-hydroxy-quinolinato) aluminium (Alq₃) layer (50 nm), and Al layer. The transfer matrix method was used for this calculation, and the thicknesses of the glass substrate and the Al layer were assumed to be infinite. The refractive indices of ITO, Alq₃ and Al were obtained from the literature [3]. 1.53 and 1.79 were used for the refractive indices of glass and NPB [11]. The proposed OLED structure, which will be fabricated by the method detailed in Section 3, has a hexagonal grating. The Bragg scattering condition of the hexagonal grating structure is governed by the following equations,

\[
\begin{align*}
    k_{\text{inplane}} &= k_{\text{air}} \sin \theta \\
    k_{\text{guide}} &= m g1 + n g2 = k_{\text{inplane}} \\
    g1 &= \left( \begin{array}{c}
        \frac{2\pi}{\Lambda} \\
        \frac{-2\pi}{\sqrt{3}\Lambda}
    \end{array} \right),
    g2 = \left( \begin{array}{c}
        0 \\
        \frac{4\pi}{\sqrt{3}\Lambda}
    \end{array} \right)
\end{align*}
\]

where \( k_{\text{air}} \) is the wavevector of the free space photon, \( \theta \) is the emission angle, \( k_{\text{inplane}} \) is the inplane component of \( k_{\text{air}} \), \( k_{\text{guide}} \) is the wave vectors of the waveguide mode, \( \phi_{\text{guide}} \) and \( \phi_{\text{inplane}} \) are the azimuthal angles of the propagations of the waveguide mode and the inplane component of the free space photon, \( \Lambda \) is the grating period of the hexagonal pattern, and \( m \) and \( n \) are integers. Based on the calculated dispersion relation and on Eqs. (1)-(3), the hexagonal grating period required to extract the waveguide modes in normal emission (where \( k_{\text{inplane}} \) is 0) was calculated for the emission wavelength, as shown in Fig. 1(a). There are a transverse electric (TE₀) waveguide mode, a transverse magnetic (TM₁) waveguide mode and a surface plasmon mode (TM₀) around the emission wavelength of 530 nm, which is the main emission wavelength of the Alq₃ layer. The normalized electric field intensity profile of the waveguide modes is shown in Fig. 1(b). The electric field of the surface plasmon mode is strongly confined to the interface between the organic layer and the metallic cathode; and, it is expected that the corrugated metallic structure of device D can more effectively extract the surface plasmon mode than can the TE₀ or TM₁ waveguide modes [15]. Therefore, based on the calculation shown in Fig. 1(a), we selected a grating period of 330 nm (represented as the dotted horizontal line in Fig. 1(a)), which is expected to effectively extract the surface plasmon mode at around the main emission wavelength of Alq₃ layer. Moreover, the grating period of 330 nm is also suitable for the extraction of the TE₀ waveguide mode at around the emission wavelength of the Alq₃ layer.
3. Fabrication

The proposed structure of the OLED with the perforated hole injection layer is shown in Fig. 2(e). We used the colloidal lithography process to fabricate the perforated hole injection layer, as shown in Fig. 2(a)-2(d). WO$_3$ was selected as a material for the perforated hole injection layer. The use of an inorganic material, not an organic material, for the perforated hole injection layer makes the colloidal lithography process easier. Also, WO$_3$ has been known to be an effective hole injection material in OLEDs [20, 21]; therefore, the selection of WO$_3$ as the material for the perforated hole injection layer can prevent a degradation of the hole injection characteristic, which may be caused by inserting a patterned nano-structure between the ITO layer and the hole transport layer [17]. The detailed fabrication process of the perforated WO$_3$ layer is as follows. PS nanosphere monolayer was formed on an ITO-coated glass substrate, as shown in Fig. 2(a); the diameter of the PS nanosphere was 330 nm and the thickness of the ITO layer was 150 nm. To form a close-packed and well-ordered PS nanosphere monolayer, we used a method to lift up the PS monolayer, which was floating on a water surface, to the substrate; this method was previously reported in references [22, 23]. The close-packed monolayer array was transformed into a non-closely packed monolayer array shown in Fig. 2(b) after reducing the size of the PS nanospheres via air-plasma etching, which was performed using a plasma cleaner (PDC-32G-2, Harrick Plasma). Then, a WO$_3$ layer with a thickness of 50 nm was thermally deposited on the PS nanosphere monolayer, as shown in Fig. 2(c). After removing the PS nanosphere monolayer with sonication in ethanol, we were able to obtain hexagonally perforated WO$_3$ layer on ITO layer, as shown in Fig. 2(d).
Figure 2. Graphical representation of the fabrication process of OLED with the perforated WO₃ layer: (a) self-assembled polystyrene monolayer, (b) non-closely packed self-assembled polystyrene monolayer after the air-plasma etching, (c) WO₃ layer deposited on the self-assembled polystyrene monolayer, (d) a perforated WO₃ layer, and (e) a structure of the OLED with the perforated WO₃ layer.

Figure 3(a) shows a scanning electron microscopy (SEM) image of the top view of the fabricated PS nanosphere monolayer on the ITO layer. A close-packed PS nanosphere monolayer was successfully fabricated. The fabricated PS nanosphere monolayer spontaneously developed a well-ordered hexagonal periodicity in individual domains with sizes of a few or a few tens of μm², due to the material’s self-organization properties. Increasing the domain size of the PS nanosphere array can be achieved by using the methods suggested in references [22, 23]. However, such an increase is not necessary in our application to OLEDs; and, on the contrary, the dependence of the emission enhancement on the change of the azimuthal angle can be reduced when the perforated WO₃ layer is fabricated using a PS nanosphere monolayer with domain size of a short range order of less than a few tens of μm²; the details will be discussed in Section 4. Figure 3(b) shows an SEM image of the top view of the perforated WO₃ layer with the hexagonally periodic nano-pattern. One period of the perforated pattern was 330 nm, which is the same as the original size of the PS nanosphere; and the diameter of the perforated hole was approximately 255 nm. The depth of the perforated pattern was 50 nm, which is the same as the thickness of the evaporated WO₃ layer.
The fabricated WO$_3$ layer on the ITO-coated glass substrate was cleaned by sonication in acetone and in isopropyl alcohol, and via an air-plasma treatment. Then, an OLED with a perforated WO$_3$ layer (device D) was fabricated by successive thermal evaporation of NPB layer of 50 nm as a hole transport layer, Alq$_3$ layer of 50 nm as an emissive layer and as an electron transport layer, an LiF layer of 1 nm as an electron injection layer, and an Al layer of 100 nm as a cathode metal, on the perforated WO$_3$ layer. The structure of the OLED with the perforated WO$_3$ layer (device D) is shown in Fig. 2(e). The inset of Fig. 3(b) shows a focused ion beam-type SEM (FIB-SEM) image of the cross section of the fabricated OLED. The organic layers and the metallic cathode of the fabricated OLED also had a corrugated structure due to the inserting of the perforated WO$_3$ layer on the ITO layer.

### Table 1 Structure and Thicknesses of Each Layer of the Fabricated Devices

<table>
<thead>
<tr>
<th>Device Type</th>
<th>Type of WO$_3$ layer</th>
<th>Thickness of each layer (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Device A</td>
<td>-</td>
<td>150 - 50 - 50 - 1 - 100</td>
</tr>
<tr>
<td>Device B</td>
<td>planar WO$_3$ layer</td>
<td>150 - 5 - 50 - 50 - 1 - 100</td>
</tr>
<tr>
<td>Device C</td>
<td>planar WO$_3$ layer</td>
<td>150 - 50 - 50 - 50 - 1 - 100</td>
</tr>
<tr>
<td>Device D</td>
<td>perforated WO$_3$ layer</td>
<td>150 - 50 - 50 - 50 - 1 - 100</td>
</tr>
</tbody>
</table>

For the comparison and evaluation of the device characteristics, we also fabricated an OLED device without a WO$_3$ layer (device A) and OLED devices with a planar WO$_3$ layer, of which the thickness was 5 nm or 50 nm (device B and C). The ITO layer of device A was treated by air plasma before the evaporation of the organic layers, and the ITO layers of devices B and C were also treated by air plasma before the evaporation of the WO$_3$ layer. The structure and the thicknesses of each layer of the fabricated devices are presented in Table 1. The active area of the fabricated devices was 2×2 mm$^2$.

### 4. Results and discussion

The device characteristics were measured as shown in Fig. 4. A Keithley 2400 sourcemeter was used for the measurement of the current density and the voltage. The luminance and the emission spectrum were measured by using a spectroradiometer (CS-2000, Konica Minolta); in order to obtain the external quantum efficiency (EQE) and the power efficiency, the measurements were performed at emission angles ($\theta$) of 0°, 10°, 20°, 30°, 40°, 50°, and 60°, while the azimuthal angle ($\phi$) was varied from 0° to 360° at increments of 15°; the emission spectra and the intensities at all emission and azimuthal angles, required to calculate the EQE.
and the power efficiency, were obtained by an interpolation method. The current density-voltage characteristics of devices A, B, C and D are shown in Fig. 4(a). The operating voltages of device D, having the perforated WO$_3$ layer, were lower than that of device A. When the nano-patterned layer is inserted between the anode and the organic layers, the operating voltage can be increased because the inserted nano-patterned layer inhibits the hole injection from the anode [17]. However, in our proposed structure of device D, we used WO$_3$ as the material for the nano-patterned layer; it is well known that WO$_3$ can yield an efficient hole injection property in OLED [20, 21]; therefore, the operating voltage can be reduced by inserting a WO$_3$ layer as a hole injection layer. The interesting point is that the operating voltage of device D was lower than that of device C, which had a thick and planar WO$_3$ layer (50 nm). In a corrugated OLED structure, the partial reduction of the organic layer thickness between an anode and a cathode is known to reduce the operating voltage [14]. However, such a reduction is unlikely in our proposed structure because it contains corrugated organic layers and a metal cathode on the planar ITO layer; an electric field enhancement effect at the region of the organic layer with the partially reduced thickness is hardly expected. It is thought that the increased interface area of the organic and metal layers, which is due to the insertion of the perforated WO$_3$ layer, is a major reason to reduce the operating voltage in our case. On the other hand, the operating voltage of device B, which had a thin WO$_3$ layer (5 nm), was increased as compared with that of device A. The reason for this phenomenon was not deeply investigated in this experiment; however, a similar phenomenon was reported in a previous work [21], and it is suspected that the surface morphology of the very thin WO$_3$ layer affects the hole injection characteristic.

Figure 4(b) shows the measurement results for current efficiency of devices A, B, C and D in normal emission. The current efficiency of device C was reduced by around 17.2% and that of device B was slightly increased at a current density of 90 mA/cm$^2$, as compared with that of device A. It seems that the altered hole injection property after the insertion of the planar WO$_3$ layer affected the charge balance characteristics of devices B and C. The current efficiency of the proposed structure, device D, was increased by approximately 52.7% at a current density of 90 mA/cm$^2$. This increment results from the increased light extraction due to the Bragg scattering, which was induced by the inserted two dimensional nano-structure, as was explained in Section 2. Figures 4(c) and 4(d) show the measurement results of the EQE and the power efficiency of devices A, B, C, and D. The EQE of device D was around 39.3% higher than that of device A. The reason that the enhancement ratio of the EQE was lower than that of the current efficiency in normal emission is that the emission enhancement ratio slightly decreased as the emission angle increased; the details will be discussed later. The power efficiency of device D was increased by approximately 60.2% as compared with that of device A at a current density of 90 mA/cm$^2$, due to the improved light extraction efficiency and the decreased operating voltage.
Figure 5 shows the emission spectra from devices A and D in normal emission. The emission enhancement from device D occurred with a broader peak in comparison with those in previous works [15, 18], because the perforated pattern of the WO₃ layer fabricated by use of colloidal lithography had imperfections in the hexagonal periodicity, as shown in Fig. 3(b). And yet, the emission enhancement from device D was clearly observed at around 550 nm. This corresponds to the expected wavelength at which the hexagonal grating period of 330 nm extracts the surface plasmon mode (TM₀), as can be seen in the calculation in Section 2. As we expected, it is thought that the corrugated metallic cathode of the proposed structure, device D, could effectively extract the surface plasmon mode.
Figures 6(a) and 6(b) show the radiant intensity profiles of devices A and D at all emission angles and azimuthal angles; these values were obtained by the interpolation method, based on the measurement data at emission angles of 0°, 10°, 20°, 30°, 40°, 50°, and 60°, while the azimuthal angle was varied from 0° to 360° at increments of 15°. The radiation pattern of device D was very similar to that of device A, except that a more enhanced radiant intensity was observed from device D; no dependency on the azimuthal angles was observed in the radiation pattern of device D. Generally, when a periodic nano-structure is adopted in an OLED device in order to improve the light extraction efficiency, the far-field radiation pattern is significantly influenced by the pattern of the periodic nano-structure [10, 11]. This phenomenon is a critical problem in information display applications. The perforated WO$_3$ layer of the proposed structure, device D, also had a well-ordered periodicity in the individual domains with a size under a few tens of μm$^2$. However, each domain faced another with randomized orientation in the long range order, as was mentioned in Section 3. Due to this randomized characteristic in the long range order, the far-field radiation pattern of device D was not affected by changes of the azimuthal angle, and a radiation pattern similar to that of device A was observed for device D.

Figure 6(c) shows the radiant intensity profiles of devices A and D for the emission angles at the fixed azimuthal angle. The Bragg scattering condition of the hexagonal grating structure is governed by Eqs. (1)-(3), and is a function of the emission angle. Therefore, the emission enhancement ratio of the OLED with the grating structure changes with the variation of the emission angle [10, 11, 16]. A similar characteristic was observed in device D: the emission enhancement ratio of device D was slightly reduced as the emission angle was increased. For the same reason, the color coordinates of the OLED with the grating structure were also affected by the variation of the emission angle. In our experiment, a CIE color coordinate change for the emission angle in device D was more severe than that in device A. When the emission angle was increased from 0° to 60°, the CIE color coordinates of device A changed from (0.3436, 0.5511) to (0.3212, 0.5614), while those of device D changed from (0.3777, 0.5314) to (0.3359, 0.5511). The variations of the x color coordinate were 0.0224 (6.52%) in device A and 0.0418 (11.07%) in device D. The variations of the y color coordinate were 0.0103 (1.87%) in device A and 0.0197 (3.71%) in device D. Though the variation of the color coordinates was higher in device D, this variation is expected to decrease if we properly adjust the wavelengths at which the emission enhancement occurs by optimizing the period of the grating nano-structure.
Fig. 6. Radiant intensity profiles of (a) device A and (b) device D at all emission ($\theta$) and azimuthal ($\phi$) angles. (c) Radiant intensity profiles of devices A and D for the emission angles while the azimuthal angle was fixed; dotted lines indicate the radiation profiles of a Lambertian source.

5. Conclusions

To improve the light extraction efficiency, an OLED having a perforated WO$_3$ hole injection layer between the ITO layer and the organic layers was proposed. The perforated WO$_3$ layer was fabricated via colloidal lithography using a self-assembled PS monolayer. The loss from the waveguide modes and the surface plasmon mode was recovered by Bragg scattering, and the EQE was increased by approximately 39.3% at a current density of 90 mA/cm$^2$. Furthermore, in the proposed structure, the perforated WO$_3$ layer has the function of a hole injection layer. The operating voltage of the OLED with the perforated WO$_3$ layer significantly decreased. The power efficiency of the proposed OLED structure increased by around 60.2% as compared with that of a conventional OLED. The angular dependency was also evaluated. In the proposed OLED, the far-field radiation pattern was not affected by changes of the azimuthal angle. Judging from the above considerations, we believe that the proposed structure, which has a perforated WO$_3$ layer, can be a useful and practical solution allowing us to improve the light extraction efficiency of OLEDs in lighting applications as well as in display applications.

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