Regular Paper

Efficiency and Lifetime Improvement of Organic Light-Emitting Diodes with a Use of Lithium-Carbonate-Incorportated Cathode Structure

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Enhancement of efficiency and luminance of organic light-emitting diodes was investigated by the introduction of a lithium carbonate (Li_2CO_3) electron-injection layer. Electron-injection layer is used in organic light-emitting diodes to inject electrons efficiently between a cathode and an organic layer. A device structure of ITO/TPD (40 nm)/Alq_3 (60 nm)/Li_2CO_3 (x nm)/Al (100 nm) was manufactured by thermal evaporation, where the thickness of Li_2CO_3 layer was varied from 0 to 3.3 nm. Current density-luminance-voltage characteristics of the device were measured and analyzed. When the thickness of Li_2CO_3 layer is 0.7 nm, the current efficiency and luminance of the device at 8.0 V are improved by a factor of about 18 and 3,000 compared to the ones without the Li_2CO_3 layer, respectively. The enhancement of efficiency and luminance of the device with an insertion of Li_2CO_3 electron-injection layer is thought to be due to the lowering of an electron barrier height at the interface region between the cathode and the emissive layer. This is judged from an analysis of current density-voltage characteristics with a Fowler-Nordheim tunneling conduction mechanism model. In a study of lifetime of the device that depends on the thickness of Li_2CO_3 layer, the optimum thickness of Li_2CO_3 layer was obtained to be 1.1 nm. It is thought that an improvement in the lifetime is due to the prevention of moisture and oxygen by Li_2CO_3 layer. Thus, from the efficiency and lifetime of the device, we have obtained the optimum thickness of Li_2CO_3 layer to be about 1.0 nm.

Keywords: Organic light-emitting diodes, Li_2CO_3, Electron-injection layer

1. INTRODUCTION

Organic light-emitting diodes (OLEDs) generate light by a recombination process of electrons and holes that are injected from the electrodes to an emission layer. It is self-emissive and it has advantages such as high contrast, excellent viewing angle, fast response time, and etc. Moreover, it also has a potential application to a flexible display. For a low-voltage operation and a low-power consumption of the device, an efficient charge-injection from the electrodes to the charge-transport layer is needed. The injected electrons and holes should also be efficiently recombined in the emission layer.

Since Tang and VanSlyke reported on efficient organic light-emitting diodes [1], a number of researches have led to the enhancement of the efficiency and luminance of the device out of the various structures and materials. One method of improving the efficiency of the organic light-emitting diodes is by using the low work function metals such as Ca, Mg, and Li. Kido et al. reported on the enhancement of the current density and luminance of the organic light-emitting diodes by doping low work function metals of Li, Sr, and Sm on the electron-transport layer [2]. Hung et al. reported on the enhancement of current density and efficiency of the device by introducing a lithium fluoride (LiF) layer near cathode [3]. It was explained that the LiF layer helps in the electron injection from the cathode to the emission layer by the lowering of an electron-injection barrier height. Jabbour et al. researched on the electrical properties of organic light-emitting diodes depending on the thickness of LiF electron-injection layer [4]. They achieved an external quantum efficiency of 3.2 % and 3.0 % with Mg and Al cathodes, respectively.

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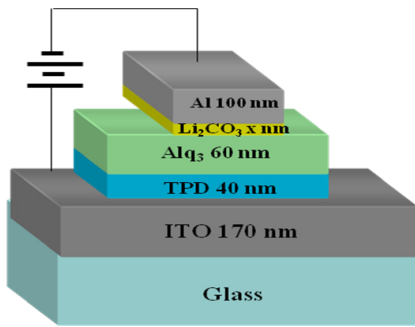
Fig. 1. The device structure of ITO/TPD/Alq$_3$/Li$_2$CO$_3$/Al used in our study.

Li$_2$CO$_3$ (lithium carbonate)
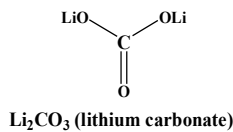
Fig. 2. Molecular structure and chemical formula of lithium-carbonate material.

Fig. 3. (a) Current density-voltage and (b) luminance-voltage characteristics of the ITO/TPD/Alq$_3$/Li$_2$CO$_3$/Al devices. The thickness of Li$_2$CO$_3$ layer was varied from 0 to 3.3 nm.

Recently, the performance of the organic light-emitting diodes is being researched with the use of electron-injection layer of carbonate materials [5-7]. Wu et al. reported an advantage of electron-injection layer of cesium carbonate (Cs$_2$CO$_3$) by comparing the performance of the devices with a use of Cs$_2$CO$_3$ and LiF layer [7]. They investigated on the electronic structures and electron-injection mechanisms by using photoemission spectroscopy. Li et al. reported that the evaporated Cs$_2$CO$_3$ decomposes to metallic cesium during a thermal evaporation. The deposited Cs layer functions as an electron-injection layer [7]. There are not many works that reported on the role of lithium carbonate (Li$_2$CO$_3$) in organic light-emitting diodes. Recently, Kao et al. used another carbonate material of Li$_2$CO$_3$ as an electron-injection layer. They performed an X-ray and photoemission study to see a reaction mechanism between the electron-injection layer and the emission layer [8].

The lifetime of the organic light-emitting diodes is being researched as an organic material is weak to an exposure of moisture and oxygen. There are dark spot and thermal aging in the degradation mechanism of the device [9]. In order to reduce a dark spot, prevention of moisture and oxygen to the device is needed. In order to reduce thermal aging, an improvement of the interface at an organic/metal is needed.

In this paper, we focus on a new electron-injection layer of Li$_2$CO$_3$, which is not widely used in the organic light-emitting diodes. We present an efficiency and lifetime improvement of the organic light-emitting diodes with the use of Li$_2$CO$_3$ layer in the device structure of ITO/TPD (40 nm)/Alq$_3$ (60 nm)/Li$_2$CO$_3$ (x nm)/Al (100 nm) by varying the Li$_2$CO$_3$ layer thickness.

2. EXPERIMENTS

Devices were fabricated inside a vacuum chamber by thermal evaporation. Figure 1 shows the manufactured structure of ITO (170 nm)/TPD (40 nm)/Alq$_3$ (60 nm)/Li$_2$CO$_3$ (x nm)/Al (100 nm) device. Here, Li$_2$CO$_3$ material was used as an electron-injection layer. The thickness of Li$_2$CO$_3$ layer varied from 0 to 3.3 nm. Figure 2 shows the molecular structure of Li$_2$CO$_3$ material. The molecular weight of this material is 73.89, a density is 2.110 g/cm^3, and a boiling point is 1,310℃. Indium-tin-oxide (ITO) substrate
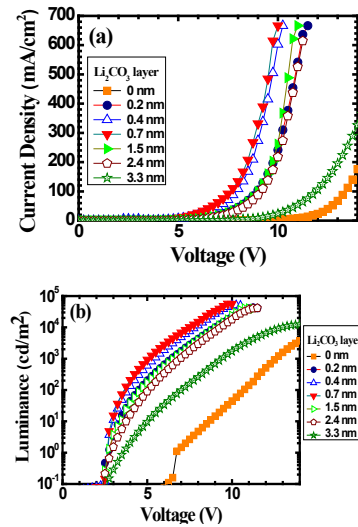
has a surface resistance of 10 Ω/sq. It was purchased from Samsung Cornings, and it was used as an anode.

An aluminum (Al) that has a purity of 99.99% was purchased from Aldrich Co. and it used as a cathode. N,N'-diphenyl-N,N'-di(m-tolyl)-benzidine (TPD) and tris(8-hydroxyquinoline) aluminium (Alq$_3$) were used as a hole-transport layer and an emission layer, respectively. Thermal evaporation of the materials were performed at a pressure of 5×10^{-6} Torr. Deposition rates for TPD and Alq$_3$, Li$_2$CO$_3$, and Al were 0.5~1.0 Å/s, 0.2 Å/s, and 0.5~5 Å/s, respectively. The size of the substrate was 20×20 mm^2, and the active area of the device was made to be 3×5 mm^2.

Thickness of Li$_2$CO$_3$ layer was obtained from the quartz oscillator thickness monitor (STM-100/MF) which calibrated with density and geometric factors, and it was also measured using Alpha-Step 200 surface profiler. Current density-luminance-voltage characteristics of the devices were measured as a function of voltage using Keithley 236 source-measure unit, Keithley 617 electrometer, and Si photodiode at room temperature.

3. RESULTS AND DISCUSSION

We have studied how the Li$_2$CO$_3$ electron-injection layer affects the performance of the organic light-emitting diodes. Electrical properties of the organic light-emitting diodes were studied depending on the thickness of Li$_2$CO$_3$ layer.

Figure 3 shows the (a) current density-voltage and (b) luminance-voltage characteristics of the ITO/TPD/Alq$_3$/ Li$_2$CO$_3$/Al devices for various thicknesses of Li$_2$CO$_3$ layer that ranges from 0 to 3.3 nm. Figure 3(a) shows that the current density-voltage characteristics. In general, it shows a strong rectification behavior. General behavior in this figure is the following. As the thickness of Li$_2$CO$_3$ layer increases in the device, the voltage-dependent current density of the device increases up to 0.7 nm thick Li$_2$CO$_3$ layer. Then it gradually decreases. For example, the current density at 8.0 V for the device with 0.7 nm thickness of Li$_2$CO$_3$ layer is increased by a factor of about 130 compared to the one for the device without the Li$_2$CO$_3$ layer. Figure 3(b) shows a corresponding voltage-dependent luminance of the same devices. In this figure, we can see that the use of Li$_2$CO$_3$ layer in the device causes an improvement in the luminance and turn-on voltage. The luminance of the device at 8.0 V with an insertion
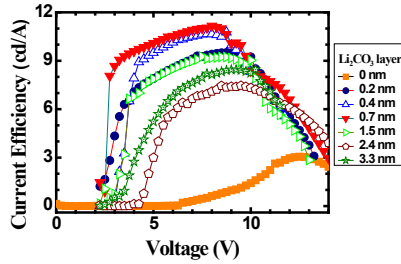
Fig. 4. Voltage-dependent current efficiency of the devices obtained from the data in Fig. 3.

of 0.7 nm thick Li_2CO_3 layer is about 3,000 times higher than the one without the Li_2CO_3 layer. There is also a dramatic reduction in the turn-on voltage of the device from 6 V to 2.5 V with the use of Li_2CO_3 layer compared to the one without the Li_2CO_3 layer. A thing to be pointed out is, irrespective of the Li_2CO_3 layer thicknesses that we have studied, the turn-on voltage of the device is almost the same.

Figure 4 shows the corresponding current efficiency of the devices as a function of voltage obtained from the data of Fig. 3. In general, the efficiency of the devices is improved by employing the Li_2CO_3 layer to the device. And there is a shift of the voltage where the maximum current efficiency occurs as the Li_2CO_3 layer thickness in the device changes. While the maximum current efficiency for the Al-only device occurs near 12 V, the maximum efficiency for the device with 0.7 nm Li_2CO_3 layer occurs near 8 V. However, when the Li_2CO_3 layer's thickness becomes 3.3 nm, the maximum efficiency occurs near 10 V. If the current efficiency of the device is compared under the same applied voltage, Fig. 4 shows that the current efficiency for Al-only device at 8.0 V is about 0.62 cd/A, and the one for the device with 0.7 nm Li_2CO_3 layer is about 11.2 cd/A. Therefore, with the use of a thin Li_2CO_3 layer there is an improvement in the efficiency by a factor of about 18 compared to the one for Al-only device.

In order to understand reason for the improvement in the efficiency of the device with the use of Li_2CO_3 layer, a Fowler-Nordheim tunneling conduction mechanism model is applied to the current density-voltage characteristics. This is given by the following relation.

$$J = AF^2 \exp\left(-\frac{B}{F}\right) \tag{1}$$

Here, J is the tunneling current density, F is an electric field, and B is a parameter relating to the shape of the barrier. If injected charges tunnel though a triangular shaped barrier formed at an interface between the electrode and the organic layer, then the parameter B is given by the following.

$$B = \frac{8\pi(2m^*)^{1/2}\phi^{3/2}}{3qh} \tag{2}$$

Here, ϕ is an energy-barrier height, q is an elementary electronic charge, m^* is an effective mass of the charge carrier, and h is the Planck constant.

In order to deduce an energy-barrier height at the interface of the device, a Fowler-Nordheim relation of ln (J/F^2) as a function of $1/F$ was plotted in Fig. 5(a) by using the data of Fig. 3(a). Using the linear relationship of this figure in a high electric-field region, where the tunneling conduction is assumed to occur, the parameter B is obtained. An electron-injection barrier height in
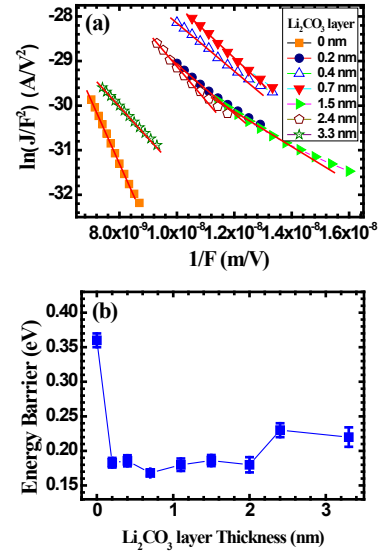

Fig. 5. (a) Fowler-Nordheim plot of the current density-voltage characteristics. The injection barrier height is obtained from the slope of the straight line indicated in the figure, (b) obtained electron energy-barrier height as a function of Li_2CO_3 layer thickness.
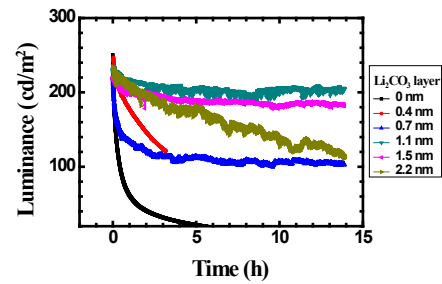

Fig. 6. Lifetime of the device depending on the thickness of Li_2CO_3 layer.

the organic light-emitting diodes is calculated from the value of parameter B by using Eq. (2). Figure 5(b) shows the obtained energy-barrier height of the device as a function of Li_2CO_3 layer thickness. From this figure, we can see that when the thickness of Li_2CO_3 layer is 0.7 nm, it has a lower energy-barrier height compared to others.

As the Li_2CO_3 layer thickness increases further, the energy-barrier increases a little. From this result, we can speculate that the electron-injection energy barrier is affected by a Li_2CO_3 layer in the organic light-emitting diodes.

Figure 6 shows that the lifetime of the device depends on the thickness of Li_2CO_3 layer. When the thickness of Li_2CO_3 layer is 1.1 nm, the device shows a relatively longer lifetime. As the thickness of Li_2CO_3 layer increased further in the device, the lifetime of the device decreased. The improvement in the lifetime is thought to be due to the protection of the device from moisture and oxygen by using Li_2CO_3 layer.

4. SUMMARY

Efficiency and lifetime improvement of the organic light-emitting diodes were studied by using an electron-injection layer of Li_2CO_3. The device was manufactured in a structure of ITO/TPD/Alq_3/Li_2CO_3/Al by varying the thickness of Li_2CO_3 layer

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from 0 to 3.3 nm. The current density, luminance, and current efficiency were measured as a function of voltage. For the device with a Li_2CO_3 layer thickness of 0.7 nm, the current efficiency of the device at 8.0 V was increased to more than 18 times than the one without the Li_2CO_3 layer. An analysis using Fowler-Nordheim tunneling conduction mechanism shows that the barrier height for the device with 0.7 nm thick Li_2CO_3 layer is lower than the others. It is thought that the Li_2CO_3 layer-incorporated cathode in the organic light-emitting diodes which lowers the electron energy-barrier height between the cathode and the organic layer. Thus, the electron injection is improved and the recombination of the holes and the electrons is thought to be improved as well. When the thickness of Li_2CO_3 layer is 1.1 nm, the lifetime of the device was relatively superior to others. It is thought that the Li_2CO_3 layer in the device acts as a protection layer from oxygen and moisture.

ACKNOWLEDGMENTS

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