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Fabrication of silica glass thin films containing organic emissive materials and application to multi-layer organic light-emitting diodes

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ABSTRACT

Organic-inorganic hybrid films are fabricated by applying a sol-gel method using perhydropolysilazane (PHPS), which are then applied on the active layers of quadruple-layer structure organic light-emitting diodes (OLEDs). All organic layers are fabricated using wet-process. In the quadruple-layer OLEDs consisting of the active layer without the sol-gel reaction, electroluminescence (EL) emissions from the active layer is not observed. This is because the electron-transporting layer and the adjacent active layer are mixed. However, if the sol-gel reaction is performed the EL emissions from the active layer are clearly observed. This is because the active layer is not destroyed due to its insolubility.

KEYWORDS

organic-inorganic hybrid films; sol-gel; PHPS; electroluminescence; OLEDs

1. Introduction

Recently, organic light emitting diodes (OLEDs) have been energetically investigated for applications to flat panel displays [1–5] and novel illumination light sources [6–11] because in comparison with inorganic LEDs they are more advantageous. In particular, polymer LEDs (PLEDs) have the advantage of low-cost production because they can be easily fabricated by using wet-process. However, since OLEDs are greatly damaged by moisture and oxidant effect, the operating lifetime is shorter than inorganic LEDs [12]. Very recently, they were successfully fabricated by applying the sol-gel method organic-inorganic hybrid thin films which contain organic emissive materials [13,14]. Consequently, the photoluminescence (PL) emission from the fabricated organic-inorganic hybrid film demonstrated much longer operating lifetime without the sealing process. This is due to the fact that the organic emissive materials are protected against the oxidant effect by the sealing effect of the inorganic material SiO_2. In this paper, the organic-inorganic hybrid films are applied to multi-layer structure OLEDs because the hybrid films have the advantage of arising from their insolubility. Due to the insolubility, the active layer is not mixed with the adjacent organic layers during the wet-process.

2. Experimental

2.1 Sample fabrication

All organic layers of the multi-layer white OLEDs are fabricated by applying spin-coating method. A hole-injection layer (HIL) is fabricated on indium-tin-oxide (ITO)-coated glass

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substrate using poly(3,4-ethylenedioxythiophene)-polystyrene sulfonic acid (PEDOT:PSS). Then, a hole-transporting layer (HTL) is fabricated on HIL using poly(4-butylphenyl-diphenyl-amine) (Poly-TPD). Then, an organic-inorganic hybrid film is fabricated on HTL as an active layer by applying the sol-gel method. In the active layer, perhydropolysilazane (PHPS) is used as a sol-gel reaction accelerator, and 5,6,11,12-Tetraphenylnaphthacene (rubrene) is used as an emissive material. In addition, poly(9,9-dioctyl-fluorene-co-N-4-butylphenyl-diphenylamine) (TFB) is used as a host material. To fabricate PHPS solution containing the organic materials, rubrene and TFB are added in PHPS as their density is adjusted to be 30 wt%. The mass ratio of both rubrene and TFB is adjusted to be 10:1. Moreover, the PHPS solution is attenuated to be 3.5 wt% in xylene. Then, a thin film of the solution containing PHPS, TFB, and rubrene is fabricated on HTL, which then it turns into the organic-inorganic hybrid film by applying the sol-gel reaction, which is accelerated by annealing at 50 degrees and humidification of 90%RH for 60 minutes in a constant temperature and humidity chamber [13]. In order to fabricate quadruple-layer OLEDs for improving the electron injection into the active layer, what is more a thin film of tris(8-hydroxyquinolinato)aluminium (Alq3) is additionally fabricated on the active layer of the hybrid film as an electron-transporting layer (ETL). Finally, aluminum (Al) is vacuum deposited as a cathode metal. The thickness values of HIL, HTL, EML, and ETL are about 50 nm.

2.2 Experimental setup

Transmission electron microscope (TEM) observation is performed using JEM2100F (JEOL). Also a Fourier-transform infrared (FT-IR) spectroscopy is performed with a JASCO FT/IR-4100. The photoluminescence (PL) spectra are recorded using a multi-channel spectroscope (Ocean Optics USB-2000), and a pulsed N_2 laser is used to photoexcite the samples. Electroluminescence (EL) properties are evaluated by executing a combination system of an integrating sphere and a multi-channel photodetector (PMA-12, HAMAMATSU). Finally all measurements take place in the atmosphere and at room temperature.

3. Results and discussion

3.1 TEM observation of the organic-inorganic hybrid films

In previous research on fabricating organic-inorganic hybrid films using PHPS as a sol-gel reaction accelerator, only TFB are used as organic materials [13]. In this case, TFB is found to be distributed in the middle layer intermediated by SiO and SiO2 layers. Thus, TFB is not being exposed to the air resulting longer PL operation time. However at the present work, the distribution of organic materials in the hybrid films must be evaluated, because rubrene is used with TFB in the hybrid films. Figure 1(a) shows a cross-sectional TEM image of the fabricated hybrid film by the sol-gel method using PHPS on an Al film. It is clearly observed that the fabricated hybrid film consists of three stacked layers. It is then confirmed that the thicknesses of the three stacked layers are uniform within the 7-μm width of the cross section. According to the energy-dispersive X-ray fluorescence spectroscopy (EDS) observation shown in Fig. 1(b), carbon atoms are concentrated in the middle layer (Layer B), while oxygen and silicon atoms are concentrated in layers A and C. This concludes that organic materials, rubrene and TFB are concentrated in layer B, while layers A and C are SiO_2 fabricated by the sol-gel reaction. This is the same as the previous result [13]. This result indicates that the lifetime of the light emission becomes longer because organic emissive materials are

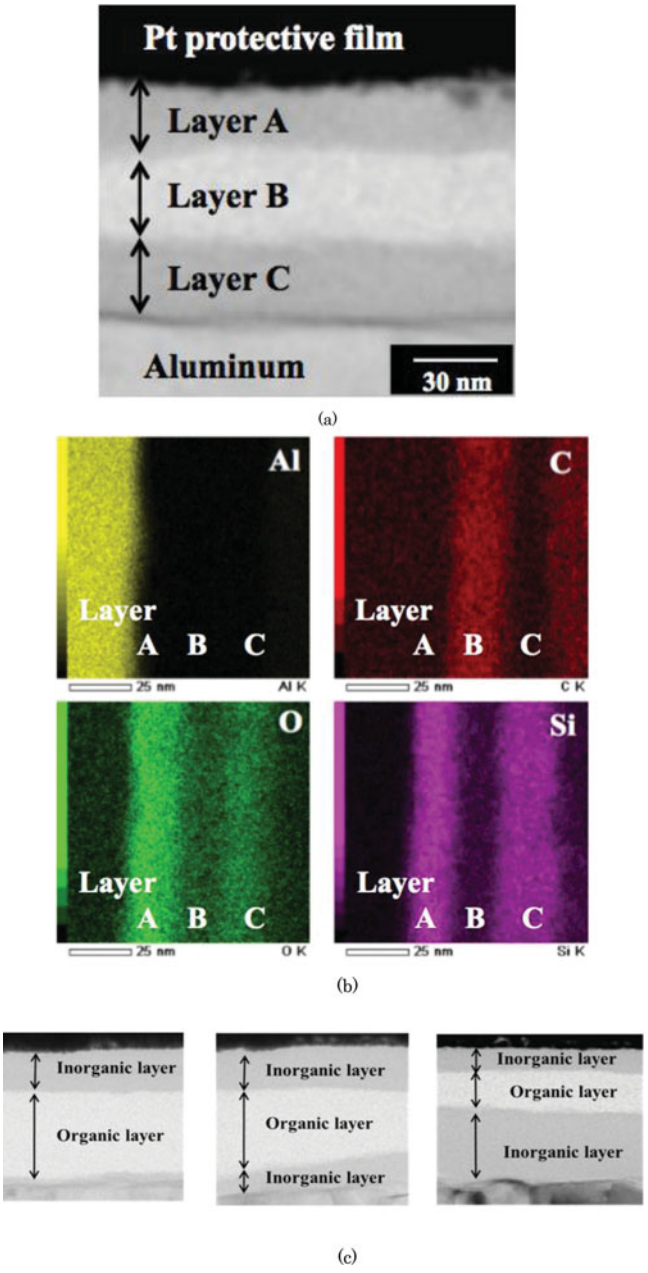

Figure 1. (a) cross-sectional TEM image of the hybrid film fabricated by applying the sol-gel method using PHPS on an Al film. Three stacked layers are clearly observed. (b) cross-sectional EDS images of the distribution of four atoms; aluminum (upper left), carbon (upper right), oxygen (lower left), and silicon (lower right). The layers A, B, and C correspond to the same layers shown in Fig. 1(a). The brightness is proportional to the density of the four atoms. From the upper right figure, it is clear that the carbon atoms are concentrated in layer B. (c) Cross-sectional TEM images are observed at some different points of the hybrid film fabricated by using sol-gel reaction without the humidification of 90%RH.

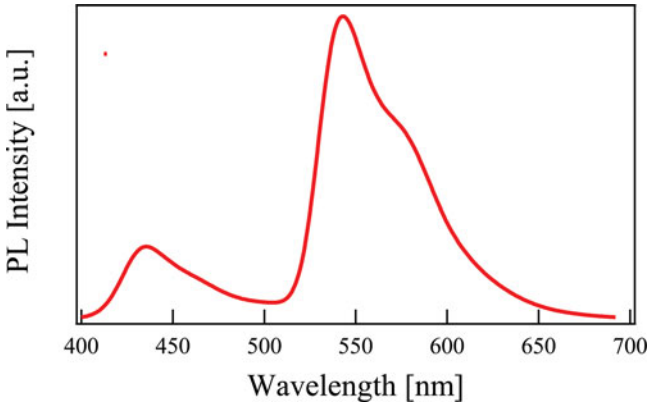

Figure 2. PL spectrum of PHPS solution containing rubrene and TFB after the sol-gel reaction. A PL emission from rubrene is clearly observed.

protected against oxidation and moisture by the SiO_2 layers. Figure 1(c) demonstrates other cross-sectional TEM images observed at different points of the hybrid film fabricated using sol-gel reaction without the humidification of 90%RH. It is very clear that the thicknesses of the organic materials and SiO_2 are not uniform. This indicates that in order to fabricate hybrid films with uniform thickness distribution, a moderate humidification is required.

3.2 PL properties of rubrene after sol-gel reaction

It has to be confirmed that the emissive material has not been destroyed during the sol-gel reaction. This is because both high-temperature and humidity are necessary to accelerate the sol-gel reaction. Figure 2 displays the PL spectrum of rubrene after the sol-gel reaction. The shape of the PL spectrum has not been changed, indicating that the rubrene has not been destroyed by the sol-gel process.

To evaluate the sealing effect of the hybrid film, the variation of the PL intensity of the rubrene embedded in SiO_2 is observed. Figure 3 shows the variation of normalized PL intensity over time from the hybrid films after and before the sol-gel reaction. It is clear that the PL intensity of the sample without the sol-gel reaction suddenly decreased in the first three

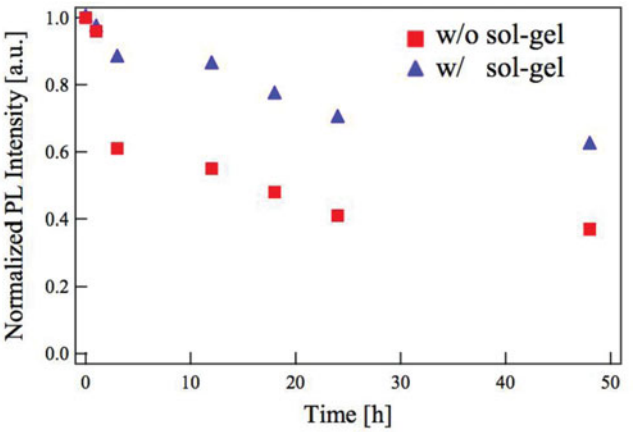

Figure 3. Variation of the normalized PL intensity over time from the hybrid films after (blue triangle) and before (red square) the sol-gel reaction.

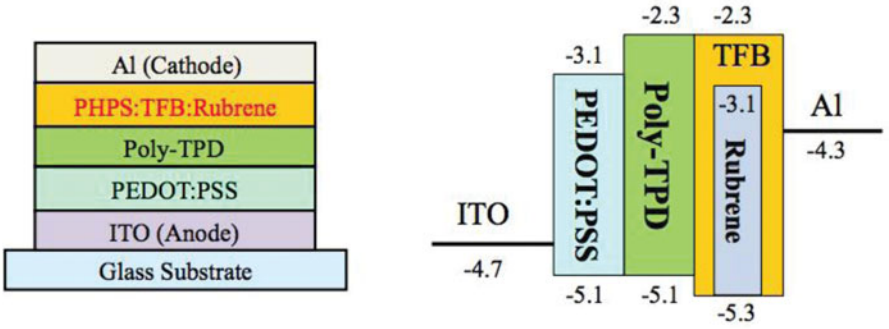

Figure 4. Schematic illustrations of the cross-sectional sample structure (left) and the energy diagram (right) of triple-layer structure OLEDs.

minutes. This demonstrates that the most of rubrene was destroyed by oxidation and moisture in a short period of time. On the contrary, the sample with the sol-gel reaction does not demonstrate the same rapid decrease of the PL intensity. This means that rubrene is protected against the oxidation and moisture because it is intermediated by SiO_2 layers as shown in Fig. 1(a). Due to this, the PL intensity of the sample with the sol-gel reaction after 48 hours is more than 65% of the initial PL intensity. In contrast, the sample without the sol-gel reaction reveals the large decrease of the PL intensity, resulting 48 hours later in about 40% of the initial PL intensity. The result concludes the importance of sealing effect of the organic-inorganic hybrid films.

3.3 EL properties of triple-layer structure OLEDs

Figure 4 shows schematic illustrations of the cross-sectional sample structure and the energy diagram of the triple-layer structure OLEDs. It is noted that they do not contain an ETL, thus the discrepancy between the Lowest Unoccupied Molecular Orbital (LUMO) level of TFB and the work function of Al cathode is about 2.0 eV. Figure 5 shows EL spectra of the triple-layer structure OLEDs before and after the sol-gel reaction. It is clear that the EL emissions from rubrene are successfully observed from both samples. The applied voltage, observed

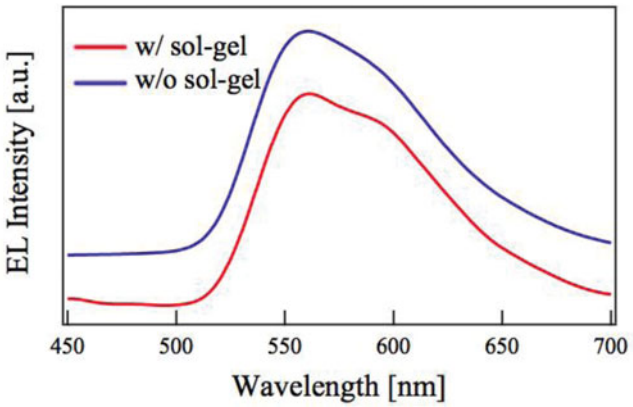

Figure 5. EL spectra of the triple-layer structure OLEDs with the sol-gel reaction (red line) and without the sol-gel reaction (blue line).

Table 1. Applied bias voltage, observed luminance, and external quantum efficiency of the triple-layer structure OLEDs with and without the sol-gel reaction.

	Voltage [V]	Luminance [cd/m^2]	External quantum efficiency [%]
w/ sol-gel	26	50	0.01
w/o sol-gel	8	40	0.09

luminance and the external quantum efficiency are listed in table 1. The OLED with the sol-gel reaction needs 20 V to emit light because the resistance of SiO_2 layers fabricated by using sol-gel reaction is much larger.

3.4 EL properties of quadruple-layer structure OLEDs

Figure 6 shows schematic illustrations of the cross-sectional sample structure and the energy diagram of quadruple-layer structure OLEDs. It is noted that they have an ETL using Alq3 between the active layer and the Al cathode. Thus, the electron injection into the active layer can be improved because the LUMO level of Alq3 is located between the LUMO level of TFB and the work function of Al cathode. Figure 7 shows EL spectra of the quadruple-layer structure OLEDs before and after the sol-gel reaction. The EL emission from rubrene is clearly observed from the sample with the sol-gel reaction at around 550 nm. However, the sample without the sol-gel reaction demonstrates an EL emission with a different peaking-wavelength which is approximately 530 nm. This corresponds to the emission wavelength of Alq3. The result implies that the active layer without the sol-gel reaction is mixed with the adjacent ETL consisting of Alq3 during the wet-process. Thus, Alq3 does not affect electron-transportation but affects the emissive material. On the other hand, the active layer with the sol-gel reaction is insoluble with the adjacent layer. Consequently, Alq3 layer functions as a fine ETL improving electron injection into the active layer. The applied voltage, the observed luminance, and the external quantum efficiency are listed in table 2. In that case, the applied voltage to the sample with the sol-gel reaction can be reduced to 10 V, which leads to the improvement of the external quantum efficiency. On the other hand, the sample without the sol-gel reaction requires a larger applied voltage in order to emit light, which leads to the smaller external

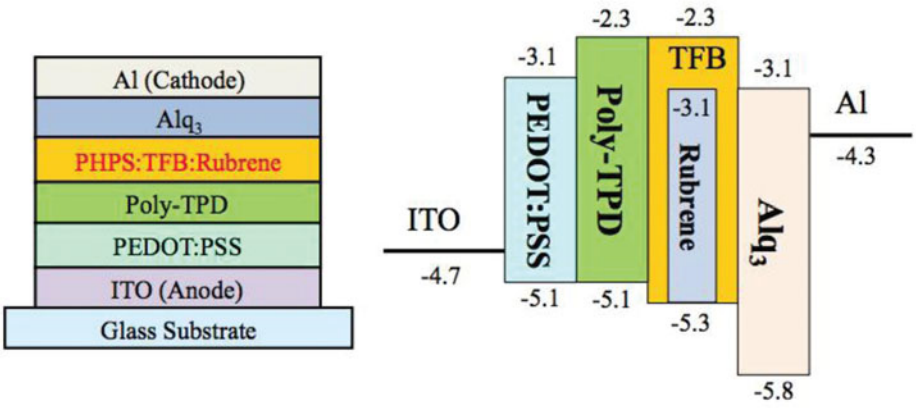

Figure 6. Schematic illustrations of the cross-sectional sample structure (left) and the energy diagram (right) of quadruple-layer structure OLEDs. In comparison with the triple-layer structure OLEDs, an electron-transporting layer is placed between the active layer and the Al cathode electrode to improve electron injection.

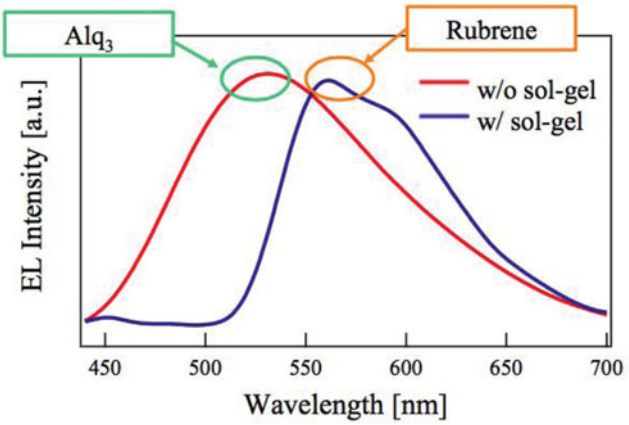

Figure 7. EL spectra of the quadruple-layer structure OLEDs with the sol-gel reaction (blue line) and without the sol-gel reaction (red line). An EL emission from rubrene is observed in the sample with the sol-gel reaction, while an EL emission from Alq3 in the electron-transporting layer is observed in the sample without the sol-gel reaction.

Table 2. Applied bias voltage, observed luminance, and external quantum efficiency of the quadruple-layer structure OLEDs with and without the sol-gel reaction.

	Voltage [V]	Luminance [cd/m^2]	External quantum efficiency [%]
w/ sol-gel	10	30	0.07
w/o sol-gel	24	80	0.03

quantum efficiency. This is probably due to the fact that large amount of resistance supplied by the inhomogeneous interface between the active layer and ETL.

4. Conclusion

Organic-inorganic hybrid films containing organic emissive materials are fabricated by applying sol-gel method using PHPS and applied to OLEDs as active layers. In the quadruple-layer structures, the active layer without the sol-gel reaction is mixed with the adjacent ETL during the wet-process. Thus, the ETL does not improve the electron injection. On the other hand, the active layer with the sol-gel reaction is insoluble with the ETL. Consequently, the external quantum efficiency is improved because the ETL improved the electron injection into the active layer. The results demonstrate that the organic-inorganic hybrid films are crucial for fabricating multiple-layer structure organic devices by applying wet-process.

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