Maskless Patterning of Vapor-Deposited Photosensitive Film and its Application to Organic Light-Emitting Diodes

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1. Introduction

Organic electronic devices mostly consist of multilayer of patterned thin films. Therefore, film formation and patterning are the most essential processes in device fabrication technology. The physical vapor deposition (PVD) provides a highly controllable method for preparing thin films of small molecules, and has been frequently employed for device fabrication. The authors have extended the PVD technique for depositing polymeric thin films by incorporating the polymerization reaction with the film formation [1]. Above all, the vapor deposition polymerization was effective in improving thermal stability of the deposited films.

Pattern formation by PVD has been conveniently achieved by depositing through a shadow mask. However, with increasing demand for fabricating large-scale devices, shadow-mask technique has encountered such the difficulties as mask alignment and contamination. The authors has proposed to eliminate the shadow masks for vapor deposition by associating polymerization reaction with the vapor-deposited films. A photosensitive film was prepared by coevaporating monomers and photoinitiators, which was locally polymerized by ultraviolet (UV) irradiation, and then developed in an organic solvent [2]. Carbazole polymer thin films have been patterned to a line width of 10 μ m with this method [3]. This paper investigates an application of this patterning technique for organic light emitting diodes (OLEDs), with an emphasis to assess possible damage to the device characteristics caused by the patterning process.

2. Experimental Method

Photopatterning

Photopatterning of carbazole polymer thin films was achieved first by preparing a photosensitive film by coevaporating carbazole monomer, 9H-carbazole-9-ethylmethacrylate (CEMA) with 5 wt% of photoinitiator, 4dimethylamino benzophenone (DABP). The chemical structures of these materials are shown in Fig. 1. The film was exposed to UV light of 60 mW/cm² at 355 nm for 1 min through a photomask in the air. It has been confirmed that the UV exposure induces polymerization of the codeposited film. The film was then immersed in tetrahydrofuran (THF) to develop a negative pattern of the UV exposure by dissolving the non-polymerized area.

OLED fabrication

OLEDs were prepared by using the photopatterned carbazole film as an emissive layer (EML). The basic structure of an OLED is as follows. On an indium-tin oxide (ITO) surface, a 30 nm-thick hole transporting layer (HTL) of *N*,*N*,*N*'-triphenyl-*N*'-(4-vinylphenyl) biphenyl-4, 4'-diamine (DvTPD) was deposited, and then annealed in vacuum at 150°C for 1 h to polymerize this layer. On this surface, a 30-thick nm EML was prepared by codepositing CEMA, DABP, and an emissive dopant of vinyl-tris(2phenylpyridine) iridium [vIr(ppy)₃] shown in Fig. 1. The dopant concentration was 5 wt%. The EML can be photopatterned as described above. On the EML, a 40 nm-thick electron transport layer (ETL) of bathocuproin was deposited, followed by vapor deposition of a LiF electron injection layer and an Al cathode.

Figure 2 shows the process flow chart for preparing the OLEDs. As a control device, an OLED was prepared without photopatterning the EML as shown in Fig. 2 (a) (device A). A single element device was prepared by photopatterning the EML to a size of 4x3 mm as shown in Fig. 2 (b) (device B). A multiple element device was prepared as shown in Fig. 2 (c), where a 2nd EML was deposited on the first EML after photopatterning it. After photopatterning the 2nd EML, the ETL and cathode were deposited to cover each EML pattern. Device C1 is constructed with the 1st EML that has underwent the deposition and development processes of the 2nd EML, while device C2 was prepared on the HTL that had



Fig. 1 Chemical structures of the deposited materials.



underwent development of the first EML. The devices were operated in the air without encapsulation.

3. Results and Discussion

Devices B, C1 and C2 gave green emission peaked at a wavelength of 510 nm, which is characteristic to the triplet emission of Ir(ppy)₃ dopant, while device A exhibited yellowish emission peaked at 545 nm. These results suggest that the device A consists of monomer EML whose dopant has extended π structure due to the vinyl group attached to the Ir(ppy)₃ dopant. On the other hand, devices B, C1 and C2 have polymer EML due to the photopolymerization during the patterning process. The polymerization led to break the π conjugation of the vinyl group, making the emission spectra the same as the non-conjugated Ir(ppy)₃.

Figure 3 shows the current-luminance characteristics of the devices described in Fig. 2. It is obvious that device A, which had an as-deposited EML without photopatterning, was inferior to other devices that had photopatterned EML. It is considered that this result reflects the fact that the EML of device A consists of monomers while the patterned devices have polymerized EML. The improvement of OLED characteristics by polymerization has also been reported in connection with the vapor deposition polymerization [4]. It is notable that in spite of the UV irradiation and rinsing in THF, the patterned EML was not deteriorated compared to the as-deposited EML.

At this moment, it is not known why the devices C1 and C2 gave higher luminance than device B. It is considered



that EMLs in devices C1 and C2 have been polymerized more completely during the additional patterning process. On the other hand, device B endured higher driving current, giving a higher maximum luminance before the device broke down. It is remarkable that both devices C1 and C2 exhibited almost the same luminescence characteristics although the EML of device C1 has underwent vapor deposition and patterning process of the second EML that was used to prepare device C2. This result indicated that the pattern formation process for the second EML did not damage the first EML, and reflects the fact that the patterns are generated as stable polymer thin films.

3. Conclusions

The new patterning method using the vapor-deposited photosensitive film was successfully applied for preparing OLEDs. This method consists of the conventional vapor deposition and the photolithographic processes, eliminating the use of shadow mask or photoresist. The patterns are obtained as stable polymer thin films. Moreover, the patterning process did not damage the device characteristics. It is expected that complicated film patterns or multicolor devices can be prepared by sequentially repeating this process.

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