The Influence of Bottom Layer on the Performance of Perovskite LEDs

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ABSTRACT

We found the interface mixing could be occurred when a hydrophilic interlayer is utilized. To solve this problem we tried to change the perovskite precursor materials to exclude interlayer. As a result, we found that we could skip the interlayer by changing a composition of perovskite.

1 INTRODUCTION

Recently, perovskite light-emitting diodes (PeLEDs) have attracted noticeable attention because of their excellent properties such as extremely high efficiency, photoluminescence quantum low cost processability, easy color tenability, etc. As a result, much research has been conducted to increase the efficiency. The representative approach is control the perovskite layer from 3D to 2D structure. Besides, nanocrystal pinning (NCP) process such as solvent-based NCP (S-NCP) or additive-based NCP (A-NCP) method [1] is widely utilized to obtain small nano-grain size. In addition, an introduction of interlayer that may increases the surface coverage to improve the uniformity of the perovskite film is the other good approach to realize highly efficient PeLEDs, more than 20% of EQEs was already reported by many researchers [1]-[3] add the reference). Especially, we could also confirm that the device characteristics can be dramatically improved through the introduction of polyvinylepyrrolidone (PVP) interlayer between PEDOT:PSS and perovskite layer [4]-[6]. Indeed, it helps to form a uniform perovskite layer because of its hydrophilic properties, but it can also lead to serious level of interface mixing because PEDOT:PSS, PVP, and perovskite materials are all hydrophilic. In fact, their solubility is very high in common solvent such as dimethylsulfoxide (DMSO).

In this study, we report about the method to get rid of interface mixing problem by changing the perovskite composition to solve it. From this approach, we could achieve highly efficient PeLEDs even though we didn't use interlayer in between HIL and perovskite layer.

2 **EXPERIMENT**

An ITO patterned glass with an active area of 3mm x 3mm was utilized as an anode. The substrate was cleaned by acetone and isopropyl alcohol respectively.

Then it was irradiated by UV-O₃ treatment equipment to eliminate all the organic impurities and improve the wettability of substrate. A PEDOT:PSS was spin-coated onto ITO substrate at 3500 rpm for 40 s and annealed at 150°C for 15 min. A 0.5 wt% PVP solution dissolved in DMSO was spin-coated onto PEDOT:PSS layer at 2000 rpm for 1 min, followed by annealing at 100°C for 15 min. First, we prepared a perovskite precursor solution consist of CsBr, MaBr, PbBr2 and PEABr (Cs_{0.87}MA_{0.13}:PEABr:PbBr₂=4:2:5) to form PEA₂(Cs_{0.87}MA_{0.13})₄Pb₅Br₁₆ in DMSO and spin-coated at 2500 rpm in 45 s. Secondly, one consist of PbBr₂, FABr and PEABr (PbBr2:FABr:PEABr=3:2:2) to form PEA₂FA₂Pb₃Br₁₀ in DMSO was spin-coated at 500 rpm for 5 s and 3000 rpm for 1 min 40 s. During spin-coating process of perovskite, S-NCP or MA-NCP was also proceeded quickly right after a spinning of 35s; then substrates were annealed at 90°C in 10 min. After those we processes, TPBi (ETL), LiF (EIL), and AI cathode were applied by thermal evaporation under a pressure of ~5 x 10⁻⁷ Torr, respectively. Finally, all of devices were encapsulated and analyzed.

3 RESULTS

As mentioned earlier, we have fabricated devices with the structure shown in Fig. 1. Perovskite was fabricated in quasi-2D structure to prevent leakage current and to form nano-grain of appropriate size. In particular, precursor were formulated so that n = 3 or n = 5. The device structure we fabricated and used in this study is shown below.

Device B: ITO / PEDOT:PSS (60nm) / PVP (6nm) / PEA₂(Cs_{0.87}MA_{0.13})₄Pb₅Br₁₆(n= 5) (150nm)/ TPBi (50nm) / LiF (1nm) / AI (200nm)

Device C: ITO / PEDOT:PSS (60nm) / PEA₂FA₂Pb₃Br₁₀(n=3) (300nm)/ TPBi (40nm) / LiF (1nm) / AI (100nm)

First, Device A and Device B were prepared by adjusting the composition of perovskite to $PEA_2(Cs_{0.87}MA_{0.13})_4Pb_5Br_{16}$. In particular, it was deposited directly on the PEDOT:PSS for Device A and after forming a thin PVP (~6nm) on the PEDOT:PSS for Device B, respectively.

However, unlike Device A, in the case of Device B, both PVP and perovskite use a solution made by suing DMSO, so there is concern about interface mixing. As a result of the HOD, the hole current density decreased by more than an order of magnitude when PVP was introduced between PEDOT:PSS and perovskite layer ITO/PEDOT:PSS (60nm) / PVP (HOD: (6nm) $/PEA_{2}(Cs_{0.87}MA_{0.13})_{4}Pb_{5}Br_{16}(6nm) / MoO_{3} (10nm) / AI)$ although it's hardly detectable from the SEM image as shown in Fig. 2 due to its very thin thickness. However, as shown in Fig. 2, the cross-sectional SEM view clearly shows that the PEDOT:PSS and perovskite layers are properly formed in Device B. Incidentally, it was found that perovskite having а composition of PEA₂(Cs_{0.87}MA_{0.13})₄Pb₅Br₁₆can be modified to give moderate efficiency when A-NCP is applied during thin film formation.

Nevertheless, we thought that the use of same solvent for PVP and perovskite precursor may cause a problem associated with a repeatability or reproducibility. So, we tried to modify the perovskite composition which does not need an interlayer underneath during spin coating process. As a result, Device C was prepared by adjusting the composition of perovskite to PEA₂FA₂Pb₃Br₁₀ and toluene was used to proceed to S-NCP.

As a result, we found the size of nano-grain of $PEA_2FA_2Pb_3Br_{10}$ (n = 3) was basically smaller than that obtained from $PEA_2(Cs_{0.87}MA_{0.13})_4Pb_5Br_{16}$ (n = 5). Especially, we could form much more uniform perovskite film by using FA based perovskite solution as shown in the SEM image.

Fig. 3 shows the J-V and L-V characteristics of fabricated green PeLEDs and the representative results are summarized in Table 1. At a given constant voltage of 6.0 V, current density values of 215.3, 284.0, 6.1 mA/cm² are observed in the fabricated Devices A, B and C, respectively. The driving voltage to reach 1000 cd/m² is 4.1, 3.7 and 7.0 V for the Devices A, B and C, respectively (Table 1). The relatively high turn-on voltages of 3.0, 3.0 and 3.5 V were observed for the Devices A, B and C, respectively. At a given constant luminance of 1000 cd/m², the current efficiency is 3.9 cd/A for the Device A, 5.1 cd/A for the Device B, 5.2 cd/A Device C, respectively (See also Fig 3. and Table 1). These efficiency data correspond to 1.0, 1.3 and 0.79 % external quantum efficiencies of Devices A, B and C, respectively. The maximum current efficiency is 7.3 cd/A for the Device A, 8.5 cd/A for the Device B, 5.9 cd/A for the Device C, respectively.

Besides, the color coordinates at 1,000 cd/m² were (0.13, 0.79), (0.13, 0.78), (0.19, 0.74) for Devices A, B, and C, respectively.

Since the PeLED fabricated with $PEA_2FA_2Pb_3Br_{10}$ (n = 3) is very unstable in brightness and efficiency characteristics than PeLED prepared with $PEA_2(Cs_{0.87}MA_{0.13})_4Pb_5Br_{16}$ (n= 5) formed on the interlayer, we tried to improve the film condition by changing the dripping solvent to chloroform during S-NCP process.

Fig. 4 shows the J-V and L-V characteristics of fabricated green PeLEDs (see also Table 1). At a given constant voltage of 6.0 V, current density values of 6.1 and 98.4 mA/cm² are observed in the fabricated Devices C and D, respectively. The driving voltage to reach 1000 cd/m² is 7.0 and 4.0 V for the Devices C and D, respectively (Table 1). The turn-on voltages of 3.5 and 3.0 V were observed for the Devices C and D, respectively. The current efficiency characteristics of fabricated Devices are shown in Fig. 4. At a given constant luminance of 1000 cd/m², the current efficiency is 5.2 cd/A for the Device C, 13.5 cd/A for the Device D, respectively. These efficiency data correspond to 0.79 and 3.3 % external quantum efficiencies of Devices C and D, respectively. The maximum current efficiency is 5.9 cd/A for the Device C, 18.4 cd/A for the Device D, respectively.

In addition, the current efficiency was shown to be different depending on the type of solvent, especially in the case of Device D was able to obtain the current efficiency of 18.4 cd/A. This is similar to Device B using an interlayer. The color coordinates at 1,000 cd/m² were (0.19, 0.74), (0.20, 0.74) for Devices C and D respectively.

4 CONCLUSIONS

We have achieved improved device characteristics with the introduction of interlayers. However, there is an interface mixing problem between the interlayer and perovskite layer when we use PVP for interlayer. So we tried to change the perovskite precursor methylammonium cation to formamidinium cation. As a result, we obtained the smaller grain size with improved device characteristics without interlayer.

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Fig. 1 Structure of perovskite LEDs



Fig. 2 Scanning electron microscope (SEM) images (a) top view of perovskite layer (Device A and B), (b) cross sectional view corresponding to PEDOT:PSS / PVP / perovskite (for Device B), (c) top view of perovskite layer (for Device B and C), and (d) cross sectional view corresponding to perovskite (for Device C and D)





Fig. 3 J-V-L and Current efficiency characteristics of Device A, B, and C



Fig. 4 J-V-L and Current efficiency characteristics of Device C and D



Fig. 5 EQE of Device A, B, C, and D

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Table. 1 Comparison of device characteristics

	Device A	Device B	Device C	Device D
Turn-on voltage (1 cd/m²)	3.0	3.0	3.5	3.0
Operating voltage (1,000 cd/m ²)	4.1	3.7	7.0	4.0
Efficiency (1,000 cd/m ²)	3.9	5.1	5.2	13.5
Efficiency (max)	7.3	8.5	5.9	18.4
CIE (xy) (1,000 cd/m²)	0.13, 0.79	0.13, 0.78	0.19, 0.74	0.20, 0.74
E.Q.E (1,000 cd/m ²)	1.0	1.3	0.79	3.3