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Enhancing Performances of Hybrid Perovskite Light Emitting Diodes with Thickness Controlled PMMA Interlayer

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Abstract

Solution processed organic-inorganic halide perovskites emerged as efficient materials for the fabrication of light-emitting diodes (LEDs). Spin coating of perovskites on solid support for device integration leads to poor morphology with pinholes and leakage current through electrical shunt paths thereby decreasing the device efficiency. Here, we report a facile route to improve the performance of MAPbBr₃ perovskite based LEDs by incorporating a poly(methyl methacrylate) (PMMA) interlayer in the device structure at the interface of ZnO and MAPbBr₃ layer. The thickness of PMMA interlayer was varied to achieve optimal device performance by overcoming the leakage current and reduced non-radiative recombination pathways. LEDs with optimal PMMA thickness showed a significant enhancement in device performance comparison to the devices without PMMA interlayer. The perovskite LEDs with ~ 7 nm PMMA interlayer exhibits a maximum luminance of ~ 3450 cdm⁻², current efficiency of ~ 11.88 cdA⁻¹, external quantum efficiency of ~ 2.82% and power efficiency of ~ 4.4 lmW⁻¹ showing robust LED properties with ~ 6-fold enhancement compared to the device without PMMA. Our route provides a convenient way to improve the efficiency of perovskite LEDs by controlling device structure with planar PMMA interlayer, which can be extended to other perovskite LEDs.

Keywords: Hybrid Halide Perovskites, Light Emitting Diodes, PMMA Interlayer.

1. Introduction

Organic-inorganic halide (MAPbX₃, MA=CH₃NH₃, X=I, Br, Cl) perovskites have received extensive attention in optoelectronic device applications.¹⁻⁸ Excellent photovoltaic properties with power conversion efficiencies up to ~ 22% have been achieved in a short span.⁹ In addition to the efficient photovoltaic properties, MAPbX₃ emerged as an excellent light emitting material showing broad color-tunability, high color purity with narrow full width at half maxima (FWHM), high photoluminescence (PL) quantum yield.¹⁰⁻¹⁴ These features make MAPbX₃ as promising luminescent material for the fabrication of LEDs. Several recent reports showed that the bright and color-tunable electroluminescence (EL) can be achieved from hybrid perovskite LEDs, which provides a platform for the preparation of various kind of displays and lighting applications.¹⁵⁻³⁸ A breakthrough is achieved from the

MAPbBr₃ based LEDs producing a bright luminance of ~ 364 cdm⁻² at room temperature.¹⁵ Recently, high efficiency LEDs have been fabricated by optimizing the fast crystallization process of MAPbBr₃ through “nanocrystal pinning” (NCP) process showing EQE of ~ 8.53%.²⁴ Yuan et al. and Wang et al. have achieved near-infrared perovskite LEDs with EQE of ~ 8.8% and ~ 11.7% respectively using solution process routes.^{25,26} Highly efficient emitters are prepared by coating the perovskite grains with longer-chain organic cations to yield EQE of ~ 10.4%, 9.3% for MAPbI₃ and MAPbBr₃ based LEDs.²⁷ Although, high efficiency LEDs have been fabricated using hybrid halide perovskite nanocrystals, however, direct spin coating of perovskite precursor solution for the preparation of active thin film for the device fabrication often contain non-uniform surface coverage, pin holes and defects. These lead to leakage current through electrical shunt paths lowering luminance and overall device efficiency.²⁸

One way to overcome the leakage current and defects is to use blends of the perovskites with different polymers. Various composites have been prepared by blending the perovskites with polymers like ionic conductor (Poly(ethylene oxide)), poor ionic conductor (PVDF), ionic insulating polymer (PS) and aromatic polyimide (insulator) precursor (PIP).^{28,29} However, blending insulating polymers with hybrid halide perovskites for the device fabrication leads to an increase in the overall resistance of the device, which offers high potential barrier to the charge carriers. Recently, LEDs of hybrid-mixed cation perovskite Cs_{0.87}MA_{0.13}PbBr₃ have been fabricated using insulating polyvinyl pyrrolidone (PVP) polymer in between the ZnO and perovskite layer showed EQE of ~ 10.4%.³⁰ Several reports have shown that the presence of an additional planar insulating layer within the device structure improves the device performance instead of using perovskite-polymer blends as active emissive layer.^{30,31} The use of the planar insulating layer with controlled thickness overcomes the leakage current problem, reduces the non-radiative recombination centers at the interface and supports balancing the charge injection into perovskite emissive layer. However, a detailed study by varying the interlayer thickness at the interface for improving the device performance is still lacking. Hence, it is necessary to control and optimize the thickness of the planar insulating interlayer within the device structure in order to achieve improved LED performance.

Here we report on the fabrication of efficient MAPbBr₃ based LEDs by incorporating additional PMMA interlayer

within the device structure. Controlled morphology of MAPbBr₃ crystals with reduced grain size have been achieved by NCP process and using excess MABr molar ratio in the perovskite composite solution. Introduction of optically transparent and electrically insulating PMMA interlayer in between the ZnO and perovskite MAPbBr₃ emissive layer suppresses the leakage current, improves the injected charge density into emissive layer, and significantly reduces the non-radiative recombination. We optimized the thickness of the PMMA interlayer in a controllable way to optimize the performance of the LEDs. The devices with ~ 7 nm PMMA interlayer thickness shows the optimal device performance with maximum luminance of ~ 3450 cdm⁻², current efficiency (CE) of ~ 11.88 cdA⁻¹, EQE of ~ 2.82%, and power efficiency (PE) of ~ 4.4 lmW⁻¹. These results represent a way to achieve improved MAPbBr₃ LED performance using a facile PMMA interlayer by avoiding complex device architectures.

2. Experimental

Experimental Materials. Hydrobromic acid (HBr, 48% in water, Merck), Methylamine (CH₃NH₂, 40 wt.% in H₂O, TCI Chemicals), PbBr₂ (99.999%, Aldrich, trace metals basis), Poly(9-vinylcarbazole) (PVK, average M_w ~25,000-50,000, Aldrich), N,N'-Di-1-naphthyl-N,N'-diphenylbenzidine (NPD, 98%, TCI Chemicals), poly(methyl methacrylate) (PMMA, average M_w ~350,000, Aldrich) were used as received.

Preparation of MAPbBr₃ Precursor Solution. Methylammonium Bromide (MABr) was synthesized according to the reported method with trivial modifications.¹⁶ In brief, MABr was synthesized by reacting 50 mL of hydrobromic acid (48% in water) added dropwise to the 30 mL of methylamine (40% in methanol) at 0 °C for 2 h while continuous stirring in a round bottom flask. Following this, the solvent in the reaction solution was removed by rotary evaporation at 50 °C for 1 hr. Purification of the products was conducted by dissolving in ethanol, recrystallizing from diethyl ether, and drying at room temperature in a vacuum oven for 24 hr. The washing and recrystallization process was repetitively done to obtain high-purity crystals. Further, the MAPbBr₃ precursor solutions (30 wt.%) were prepared by dissolving the MABr (94.2 mg) and PbBr₂ (205.8 mg) with 1.5:1 molar ratio in 1 ml of anhydrous N, N-dimethylformamide (DMF) at 60 °C while continuous stirring for overnight.

Perovskite Thin Film Preparation - Nanocrystal Pinning (NCP) Process. The MAPbBr₃ thin films were prepared by using spin coating technique - NCP process.²⁴ The NCP process involves the two steps. At stage one, the perovskite precursor solution in DMF was loaded onto the targeted substrate and accelerated to a speed of ~ 500 rpm. After 10 sec of the 1st stage, the rotation speed was further accelerated to ~ 3000 rpm and maintained for 90 sec. After completion of 25 sec, nanocrystal pinning process was initiated by dripping the chloroform solution onto the spinning substrate. During the next 65 sec, the residual solvent was evaporated, which induces the fast crystallization of perovskite nanocrystals. The films were further annealed at 70 °C for 5 min under continuous N₂ flow chamber.

LED Fabrication using MAPbBr₃. Initially, the indium tin oxide (ITO) coated glass substrates were patterned accordingly with the scotch tape, zinc powder and HCl. The patterned ITOs were cleaned with soap solutions and deionized (DI) water. Further, the ITOs were cleaned with acetone, ethanol and isopropyl alcohol for 10 min sequentially by sonication process and then placed on a hot plate at 120 °C to evaporate the residual solvent. The cleaned ITO substrates were subjected to UV-ozone treatment for 15 min to make the

surface hydrophilic. At first, the ZnO nanoparticles (loading ~ 30 mg/ml) were spin coated on ITO – coated glass substrate at a speed of ~ 2500 rpm for 45 sec and films were annealed at ~ 130 °C for 30 min under N₂ flow to obtain a uniform layer. On top of ZnO layer, an ultrathin layer of PMMA in dichloroethane solution was spin coated at ~ 3000 rpm for 30 sec and films were annealed at 100 °C for 10 min under N₂ flow to evaporate the solvent. The surface was rinsed twice with DMF solution. To prepare MAPbBr₃ thin film, MABr:PbBr₂ composite solution was spin coated on top of the ITO/ZnO/PMMA layer by employing the NCP process. The substrates were then annealed at 70 °C for 5 min under continuous N₂ flow. Particularly, MAPbBr₃ nanoparticle layers were fabricated by using the NCP process, which use the dripping of chloroform solution onto the spinning layers during spin-coating of MAPbBr₃ solution. Further, poly(9-vinylcarbazole) (PVK) – chlorobenzene solution (10mg/ml) was spin coated on to the top of MAPbBr₃ layer. The films were annealed at 70 °C for 5 min under continuous N₂ flow. The PVK layer acts as a hole transport layer and effective electron blocking layer. Further, the substrates were transferred into a high vacuum thermal evaporator (~ 10⁻⁶ mbar). The fabrication of perovskite LEDs successfully completed by thermally evaporating the N,N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine (NPB/NPD) (working as a hole injection layer), and aluminum (Al) top electrode sequentially through a shadow mask without breaking the high vacuum within the thermal evaporator deposition chamber. The active device area was 6 mm² (2 mm × 3 mm) defined by the overlapping area of the ITO and Al electrodes. All the samples were prepared and device fabrication was done at room temperature in ambient conditions.

Materials Characterization Techniques. Absorption spectrum of the MAPbBr₃ thin films deposited on glass substrates were carried out by using the Agilent UV-vis spectrophotometer. X-ray-diffraction (XRD) measurements were carried out by the Bruker D8 Advance powder diffractometer using Cu K-α (λ = 1.5418 Å) as the incident radiation. Field Emission Scanning Electron Microscopy (FESEM) measurements were performed by using the JEOL JSM-6700F instrument operating at an accelerating voltage of 5 kV. The PL and EL spectra were recorded with NanoLog spectrofluorometer (HORIBA JobinYoun). The PL time resolved spectroscopy measurements were carried out by Edinburgh PL spectrophotometer (FLS 980) with 373.8 nm picosecond (ps) pulse diode laser with pulse width of ~ 70.5 ps (Model EPL 375). The current versus voltage characteristic measurements of fabricated LEDs were conducted by using a LABVIEW program based computer-controlled source measurement unit (Keithley 2420 SMU) and the luminance-voltage measurements were carried out by Konica Minolta CS-200 Chroma meter. The EQE measurements were carried out with help of silicon photodiode from the calibrated light source. All the LED devices fabricated under room temperature under ambient conditions until unless mentioned.

3. Results and Discussion

Composition of MABr and PbBr₂ molar ratio have been reported to plays a crucial role in LEDs device performance.^{24,32} We have prepared MAPbBr₃ precursor solution (30 wt.%) by dissolving MABr and PbBr₂ at a molar ratio of 1.5:1.0 in anhydrous N, N-dimethylformamide (DMF) at 60 °C while continuous stirring for 12 hrs. Generally, an excess amount of Pb atoms remains owing to the incomplete reaction between MABr and PbBr₂ or unintended losses of Br atoms when MABr and PbBr₂ are mixed in 1:1 molar ratio.²⁴

Hence, we have used excess amount of MABr, which suppresses the exciton quenching and improves the steady-state PL significantly.^{24,32} Additionally, we have adopted NCP process for the fabrication of MAPbBr₃ thin films.²⁴ In NCP, the perovskite precursor in higher boiling point DMF solution spin coated onto the targeted substrate followed by the nanocrystal growth initiated by dripping the chloroform solution. Higher boiling point of the DMF allows a slow evaporation, which leads to the formation of larger grains. Hence, excess DMF is washed out by dripping the chloroform onto the spinning substrate. Faster evaporation rate of the chloroform initiate pinning of nanocrystals through fast crystallization process. Hence, reduced grain size and uniformity of MAPbBr₃ grains have been achieved by rising solvent evaporation time using chloroform.²⁴

Figure 1. (a) XRD of MAPbBr₃ thin film on glass substrate. (b-c) FESEM morphology images of MAPbBr₃ thin films at different magnifications. (d) UV-vis absorption (red curve) and PL (green curve) spectra of MAPbBr₃ thin film.

X-ray diffraction (XRD) pattern of the MAPbBr₃ films shows sharp peaks corresponding to (100), (110), (111), (200), (210), (211), (220) and (300) planes (Figure 1a) and peak positions match well with the previously reported cubic Pm m phase.^{16,20,21,29,33,34} The morphology of the thin film was analyzed by using Field Emission Scanning Electron Microscopy (FESEM). Figure 1b-c show FESEM images of perovskite thin films with different magnification prepared using the NCP process. FESEM images reveal compact and uniform perovskite layer covering a large area on substrate (Figure 1b). An average dimension of ~ 600 nm of the nanocrystals is measured from the FESEM image (Figure 1c). UV-vis absorption spectrum (Figure 1d) shows a peak at ~ 510 nm. We have calculated the band gap of ~ 2.3 eV using Taut plot by obtaining the threshold of the absorption spectrum (Supporting Information (SI), Figure S1), which matches with the previously reported MAPbBr₃ nanocrystals.^{16,33} The PL spectrum exhibits an intense peak at ~ 536 nm with a FWHM of ~ 31 nm. A considerable overlapping between the absorption and PL spectra is evidenced suggesting a reduced Stokes shift.

We have fabricated LEDs in an inverted structure configuration using MAPbBr₃ as active emissive layer. The LED device structure consisting of indium tin oxide (ITO)/ZnO/PMMA/MAPbBr₃/PVK(Poly(9-vinylcarbazole))/NPD(N, N'-Di(1-naphthyl)-N,N'-diphenyl-(1,1'-biphenyl)-4,4'-diamine)/Al (Figure 2a). All layers within the device structure were deposited using solution processed route via spin coating technique except NPD/Al layers. The PMMA layer was

deposited from the dichloroethane solution by spin coating process. We used insulating interlayer of PMMA of different thicknesses to engineer the device structure to improve performance. The solution-processed ZnO nanocrystals were employed as electron-transporting layer (ETL) and hole-blocking layer due to their high electron mobility, excellent optical transparency, and a deep valence-band energy level that effectively blocks the holes. The PVK layer was employed as a hole-transporting layer (HTL) and electron-blocking interlayer. The NPD-layer was used as a hole injecting layer. Figure 2b shows the energy level band diagram with respect to vacuum level respectively.^{18,34,39} The combination of effective hole-blocking nature of ZnO, electron-blocking nature of PVK and their appropriate energy levels allow effective charge carriers injection into the active MAPbBr₃ layer for radiative recombination. A cross-sectional FESEM image of a LED device structure is shown in Figure 2c. From the cross-sectional FESEM image, the thicknesses of the ZnO, PMMA, MAPbBr₃, PVK, NPD and Al top-electrode layers are found to be ~ 70 nm, 7 nm, 100 nm, 30 nm, 30 nm and 100 nm respectively.

Figure 2. (a) Schematic representation of device architecture of the perovskite LEDs. (b) Flat energy-level band diagram of the multilayered perovskite LED. (c) Cross-sectional FESEM image showing different layers of a LED device.

One of the motivations of the present work is to introduce PMMA layer with an optimum thickness within the device to reduce the leakage current through shunt paths. We have varied the thickness of PMMA layer within the LED device to achieve optimal LED device performance. To quantify the thickness of the PMMA layer used within the device structure, we have prepared PMMA thin films on silicon substrate under the same condition of device fabrication. The PMMA film thickness was varied by different loading concentrations. Atomic force microscopy (AFM) images of the PMMA thin films prepared from the ~ 1.8 mg/ml loading concentration on silicon substrates are presented in the Figure 3. The thickness of the films was measured by making an ultrafine scratch on the thin films (Figure 3a). Figure 3b shows the 3D image of the step of the scratch drawn on the PMMA film. The line-scan profile shows a step height of ~ 7 nm (Figure 3c). The PMMA thin film shows a surface roughness of ~ 1 nm (inset of Figure 3d). The thickness of the PMMA thin films are found to be ~ 5 nm, 10 nm, 12 nm with the loading concentration of ~ 1.2 mg/ml,

2.7 mg/ml and 3.3 mg/ml respectively (SI, Figure S2).

Figure 3. (a) The AFM image of the PMMA thin film deposited on silicon substrate with a loading of ~ 1.8 mg/ml in dichloroethane. (b) Three-dimensional representation of an ultrafine scratch on the thin film. (c) Line scanning height profile of the PMMA thin film showing a step height of ~ 7 nm. (d) AFM image of PMMA thin film along with the roughness profile showing the average roughness of ~ 1 nm (inset).

We studied the steady-state PL of MAPbBr₃ thin films deposited at different conditions (Figure 4a). MAPbBr₃ films deposited directly onto ZnO layer shows green emission peaking at ~ 536 nm. Interestingly, PL spectra of ZnO/PMMA/MAPbBr₃ with different PMMA layer thickness enhance the pristine MAPbBr₃ PL intensity. An increase of PL intensity is observed with increasing layer thickness of PMMA retaining the PL peak position. Notably, a saturation of PL intensity is observed upon using ~ 12 nm thick PMMA layer. The enhancement of PL intensity arises from the reduced non-radiative recombination centers at the interface of the MAPbBr₃ and ZnO layer through the passivation of ZnO surface defects by PMMA at the interface.³⁰ These observations reveal that optimized PMMA thickness is necessary to passivate the surface defect states of the ZnO layer along with a simultaneous control over the efficient charge injection to obtain enhance performance of the LED devices. The solid-state PL image of the ZnO/PMMA/MAPbBr₃ thin film of ~ 7 nm PMMA under ~ 365 nm UV light exposure shows green emission (Inset, Figure 4a). We carried out Time-Correlated Single Photon Counting (TCSPC) measurements of the MAPbBr₃ thin films embedded within the device architecture (Figure 4b). The time-resolved PL decay curves are best fitted to bi-exponential function. We observed that the PL lifetime of the MAPbBr₃ thin films increases upon PMMA passivation. The average PL lifetime for the ZnO/MAPbBr₃ is calculated to be ~ 23.92 ns, while the ZnO/PMMA/MAPbBr₃ films show lifetimes of ~ 43.29 ns, ~ 54.63 ns, ~ 65.16 ns and ~ 65.93 ns for PMMA layer thickness of 5 nm, 7 nm, 10 nm and 12 nm respectively. A similar increase in the PL lifetime of the perovskite film had been observed previously after PVP modification, which was attributed to the reduction of bulk defects.³⁰ The modification of the interface between the ZnO – MAPbBr₃ by insertion of a thin PMMA layer increases the lifetime initially with the layer thickness. However, no significant change in the lifetime was observed above the thickness ~ 10 – 12 nm of PMMA layer. These results indicate

that the insertion of the additional PMMA layers with an appropriate thickness helps in reducing the surface defect states at ZnO/MAPbBr₃ interface and enhances emissive properties of the MAPbBr₃ thin film, which is beneficial for LED fabrication.^{30,31}

Figure 4. (a) Steady-state PL spectra of MAPbBr₃ thin films deposited on Glass/ZnO, Glass/ZnO/PMMA with different thickness of the PMMA layer. Inset shows the PL image of the MAPbBr₃ thin films prepared with ~ 7 nm PMMA under 365 nm UV light excitation. (b) Comparison of PL time decay curves of MAPbBr₃ thin films on ZnO and ZnO/PMMA with different PMMA layer thickness.

We tested the performance of MAPbBr₃ LEDs containing PMMA layers with different thicknesses. The LED devices consisting of ~ 7 nm PMMA layer show the strong green EL at ~ 540 nm, which replicates PL spectrum of the MAPbBr₃ perovskite thin film (Figure 5a). The EL peak intensity increases significantly with increasing applied bias voltage while retaining the same peak position. The true color photographic image of the glowing LED shows EL uniformly distribute across the entire active device area without any inhomogeneity (Figure 5b). Corresponding Commission Internationale de l'éclairage (CIE) chromaticity coordinates diagram depicts EL at (0.22, 0.72), which closely matches with the CIE coordinates (0.21, 0.73) for PL of MAPbBr₃ thin film (Figure 5c). These observations clearly signify that the EL solely originates from MAPbBr₃ active layer. Figure 5d shows the current density and luminance versus voltage characteristics of device with 7 nm PMMA interlayer. The luminance versus voltage characteristics of the devices show LED responses with an effective threshold voltage below 5 V (Figure 5d). Above the turn-on voltage, the luminance versus voltage plot is mostly linear (Figure 5d). Luminance is detectable starting from a threshold voltage of ~ 5 V showing a maximum value of ~ 3450 cdm⁻². The device shows maximum CE of ~ 11.88 cdA⁻¹ (Figure 5e), EQE of $\sim 2.82\%$ (Figure 5f) and PE of ~ 4.4 lmW⁻¹ (Figure 5g).

In addition to the enhancement of the PL, the use of PMMA interlayer suppresses the flow of leakage current in between the ETL and HTL which is beneficial for the LED performance. Because of the presence of PMMA interlayer, the charge carriers experience a finite potential barrier and the injected charge carrier density into the active MAPbBr₃ emissive layer can be controlled.^{28,30} Recently, polyethyleneimine (PEI) modified ZnO is used as cathode interlayer for the fabrication of near-infrared (NIR) and visible green LEDs.³¹ High quality perovskite thin film with crystalline features, long PL lifetimes, good surface coverage and improved device performance have been achieved by the

Figure 5. (a) Comparison of EL spectra of the devices operated under different bias voltages from ~ 5 V to ~ 15 V with the solid state PL spectra of MAPbBr₃ thin film. (b) The true color photographic image of the green color LED device under operation. (c) CIE chromaticity coordinates of the solid state PL and EL of LED. (d) Current density versus voltage and luminance versus voltage curves. (e) Current efficiency versus current density plot. (f) EQE versus voltage plot. (g) Power efficiency versus voltage plot.

additional PEI interlayer. Similarly, a blend of perovskite and a polyimide precursor dielectric (PIP) solution is used to prepare the perovskite nanocrystals within a thin-film matrix of PIP for the fabrication of LEDs.²⁸ This report suggests an improvement in the device EQE by two orders of magnitude to ~ 1.2% when PIP was used. Single-layer LEDs fabricated from the perovskite– poly (ethylene oxide) (PEO) composite thin films with different weight ratios by spin coating process, exhibited a bright-maximum luminance of ~ 4064 cd m⁻², CE of ~ 0.74 cd A⁻¹ and EQE of ~ 0.165%.²⁹ When PEO is replaced by PVDF or PS, a drastic reduction in the luminance and increase in the turn on voltage have been observed. Alternatively, single layered LEDs fabricated from MAPbBr₃ and PEO composite thin film prepared by doctor blade technique showed low turn on voltage of ~ 2.6 V, maximum luminance of ~ 21014 cd m⁻² and EQE of ~ 1.1%.³³ However, LEDs with high luminance are exhibiting lower efficiency possibly because of the presence of shunt paths and the leakage current. High EQE of ~ 8.53% for MAPbBr₃ LEDs have been obtained using fast crystallization NCP process.²⁴ Recently, LED device performance has been improved by using a composite solution of (PVK) : 1,3,5-tris(1-phenyl-1H-benzimidazol-2-yl)benzene (TPBi) : MAPbBr₃, which exhibits maximum luminance of ~ 7263 cd m⁻² and EQE of ~ 2.28%.³⁴ These reports show that the LED

device efficiency can be improved using polymer interlayer at the interface of organometallic perovskites. Our modification using thin PMMA interlayer at the ZnO/perovskite interface balance charge injection into emissive layer, minimizes leakage current, reduce the surface defect states and shows comparable device performance with the above sets of literatures (SI, Table S1).

We investigated the performance of LEDs by varying the PMMA interlayer thickness from 5 nm to 12 nm. All the devices were fabricated in a similar configuration except the variation of PMMA layer thickness. As the thickness of the PMMA layer in the device increases, the current density is decreased gradually at each operating voltage (Figure 6a). The PMMA layer acts as a finite potential barrier, passivating the shunt paths and controlling the injected charge density as well as leakage current. Luminance versus voltage characteristic curve shows a turn ON voltage of ~ 4.5 V (defined at ~ 1 cd m⁻²) for the device without PMMA interlayer. The turn ON voltage is increases slightly upon using PMMA interlayer, which acts as a finite potential barrier for charge carriers. Luminance from the devices changes significantly with the PMMA thickness. Luminance gradually increases from ~ 2519 cd m⁻² (without PMMA) to ~ 3450 cd m⁻² for ~ 7 nm PMMA interlayer, which drops down to ~ 1402 cd m⁻² and ~ 215 cd m⁻² for ~ 10 nm and ~

Figure 6. Device performance characteristic curves of MAPbBr₃ LEDs fabricated without and with additional PMMA interlayer with thickness of ~ 5 nm, 7 nm, 10 nm and 12 nm. The colour codes are indicated in the inset. (a) Current density versus voltage and luminance versus voltage curves. (b) Current efficiency versus current density plots. (c) External quantum efficiency versus voltage plots. (d) Power efficiency versus voltage plots.

12 nm PMMA layers respectively. At higher PMMA thickness, the charge carriers experience a higher resistive potential barrier affecting the charge injection into the emissive perovskite layer, which results in decrease in overall luminance of the LED device. The current density reduces and luminance increases at a specific applied bias voltage with the optimized thickness of PMMA interlayer. For example, a current density of ~ 3.0 mA cm⁻² is required to produce a luminance of ~ 200 cd m⁻². However, larger current densities of ~ 18.3 mA cm⁻², ~ 10.3 mA cm⁻², ~ 4.7 mA cm⁻², ~ 29.3 mA cm⁻² are needed for the devices without PMMA and with other PMMA thickness-controlled devices like ~ 5 nm, ~ 10 nm and ~ 12 nm respectively to produce a luminance of ~ 200 cd m⁻². Similarly, higher voltage is required to generate a luminance of ~ 200 cd m⁻² for the device with increased PMMA interlayer. At optimized PMMA thickness of ~ 7 nm, the device shows significantly low turn ON voltage, maximum luminance and less current density compared to other controlled devices (Figure 6a). These results suggest that an optimized thickness of the PMMA interlayer is necessary to achieve improved performance of the LED devices.

We further measured the characteristic parameters like CE,

EQE, and PE of the MAPbBr₃ LEDs (Figure 6b-d). All the measured characteristic parameters of the LEDs are presented in table S2 (SI, Table S2). All the LED parameters like luminance, CE, EQE and PE are found to increase in presence of an additional PMMA interlayer with optimum thickness. Initially, CE is found to be ~ 2.26 cd A⁻¹ without PMMA, which increases for the optimal PMMA interlayer thickness and decreases at higher thickness of PMMA. The LED device CE is found to be ~ 2.26 cd A⁻¹ (without PMMA), ~ 3.56 cd A⁻¹ (~ 5 nm), ~ 11.88 cd A⁻¹ (~ 7 nm), ~ 5.23 cd A⁻¹ (~ 10 nm), and ~ 1.32 cd A⁻¹ (~ 12 nm). Similar trend is observed for both the EQE and PE of the LEDs. The EQE is found to be ~ 0.45% (without PMMA), ~ 0.78% (~ 5 nm), ~ 2.82% (~ 7 nm), ~ 1.12% (~ 10 nm) and ~ 0.28% (~ 12 nm) respectively. Hence a six-fold enhancement in EQE has been achieved by using ~ 7 nm PMMA interlayer in comparison to the devices without PMMA. The PE are found to be ~ 0.70 lm W⁻¹, 1.20 lm W⁻¹, 4.4 lm W⁻¹, 1.73 lm W⁻¹, and 0.44 lm W⁻¹ for the devices without PMMA and with 5 nm, 7 nm, 10 nm and 12 nm PMMA layers respectively. These results emphasises comparable device performance with the previously reported MAPbBr₃ based LEDs using a simple PMMA interlayer.

4. Conclusion

In conclusion, we have demonstrated a simple and efficient route to improve the overall performance of solution processed MAPbBr₃ based LEDs by introducing an insulating additional planar PMMA interlayer in between the ZnO and perovskite emissive layer. PMMA interlayer successfully eliminated the shunt paths and non-radiative defect states, thereby improving the device efficiency. We optimized the device structure by controlling the thickness of the PMMA interlayer to improve the LED device performance. PMMA interlayer with ~ 7 nm thickness shows a six-fold enhancement of the device performance in comparison to the devices without PMMA. The best performing devices showed the improved luminance of ~ 3450 cdm⁻², CE of ~ 11.88 cdA⁻¹, EQE of ~ 2.82% and PE of ~ 4.4 lmW⁻¹. Our results using a simple planar PMMA layer within the device structure is comparable with the reported MAPbBr₃ based LEDs. Our work demonstrates an effective way to reduce the leakage current by controlling the interface of the device architecture and reduction of surface states to reduce non-radiative transitions, which could be beneficial for the development of high performance perovskite LEDs.

Supporting Information (SI)

The file contains additional Figures, experimental methods, tables.

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