

Fabrication and Characterization of Perovskite-based LEDs (PeLEDs)

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Abstract: Perovskite-based Light Emitting Diodes (PeLEDs) are the fastest-growing new generation of cost-effective and efficient multicolor LEDs. This work shows different deposition techniques involved in the manufacturing of PeLEDs and the making of a fully functional device. Individual layers have been characterized morphologically by optical microscopy and scanning electron microscopy (SEM) and optical properties have been measured by UV-Vis spectroscopy and PL spectra. Complete device performance has been analyzed by comparing its I-V curves. Short-term stability analysis has been carried out by monitoring current and electroluminescence (EL) at constant voltage over time. Treating the devices under controlled humidity conditions seems to improve PeLED performance. Results notify that post treatment might be a necessary step in elevating device efficiencies.

I. INTRODUCTION

Over the last decades, the presence of light-emitting diodes (LEDs) has increased significantly and they indeed play a pivotal role in a myriad of applications. In this regard, an evolution towards higher luminance, more efficient and cost-effective LED technology is predicted. Literature shows that PeLEDs have promising characteristics that can fulfill the growing demands and revolutionize future lighting and display technologies.

An LED is a PN or PIN heterojunction device in which the emitting layer is a direct band-gap semiconductor, where electrons and holes recombine radiatively, i.e. accompanied by the emission of a photon, with no intermediate phonon transitions (as in indirect bandgap semiconductors)[1]. In a PeLED, the light emitting layer (EML) is a thin layer of perovskite (referring to those materials with an ABX_3 type crystal structure). As recent studies have shown that PeLEDs have an extraordinary performance with efficiencies exceeding 20% [3], metal halide perovskites are to be considered as an excelling optoelectronic material for solid-state light emitting applications. In addition to perovskites being direct band-gap semiconductors, they have other magnificent intrinsic properties such as high carrier mobility, bandgap tunability, high quantum photoluminescence yield and high emission colour purity (narrow full-width at half maximum) [4] [5].

Despite the above-mentioned advantages, producing efficient and highly stable PeLEDs is a challenge. Its sensitivity to moisture and O_2 is a major bottleneck to improve device performance and increase durability. Thus, most PeLEDs are reported being fabricated inside a completely inert atmosphere (mostly in a N_2 filled glovebox).

In addition to the perovskite layer, PeLEDs contain charge transport layers (CTLs) —in perovskite jargon, P

and N layers are called hole and electron transport layers, respectively —and charge injection layers (CILs). Thus, individual layer quality together with interfaces play a major role in determining the device performance and its stability. As forerunners in inkjet printing technology, our group have successfully published an article on defect-free inkjet-printed perovskite layer processed in an ambient atmosphere [2].

This work presents the results that have allowed the development and production of a fully functional inkjet-printed green LED based on lead halide perovskite (LHP) layers (in particular, $CsPbBr_3$). The CTLs are deposited using techniques such as spin coating and e-beam/thermal evaporation. They are structurally analysed through SEM and UV-Vis spectroscopy. The entire device performance is compared between fresh and aged devices. Results suggest that a post treatment might be a beneficial step to enhance the device performance of PeLEDs.

II. EXPERIMENTAL

The device can be of two type architectures namely "P-I-N" or "N-I-P", where "P" and "N" represent the hole (HIL) and the electron (EIL) injection layers, respectively, while "I" stands for the intrinsic light emitting layer (EML). Regarding the CTLs, hole (HTL) and electron (ETL) transport layers, transport and limit (by introducing an energy barrier) the injected charges to the EML, where they recombine radiatively. As CTLs with perovskite form heterojunctions, work functions, band-gap alignment and band-gap offsets between layers are essential parameters to take into account when designing the device structure.

The devices are fabricated on a commercially bought glass substrate from the company called Ossila. These substrates come with a patterned transparent conductive coating of indium tin oxide (ITO) whose resistance is $20 \Omega/square$. First step in device fabrication is the cleaning of the substrates. It is important to have a clean,

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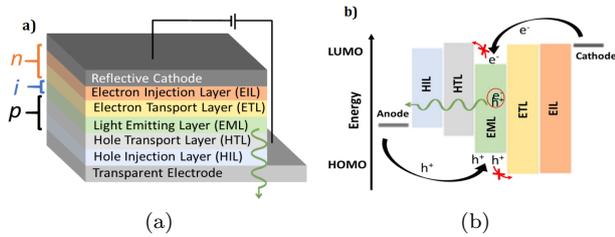


FIG. 1: Cross section of the structure (a) and energy band diagram (b) of an LED. When injected charges recombine radiatively, photons are emitted (green arrow). [5]

dust-free surface with low surface tension to achieve smooth, defect-free layers.

Initially, the substrates are introduced into a 3% soap solution in DI water at 100°C (3 mL of the concentrated liquid solution *Hellmanex III* in 300 mL of water). It is ultrasonicated for 5 min. Further steps include ultrasonication of the substrates in DI water, acetone and isopropanol, in this order for 5 min each. Finally, the substrates are dried with the nitrogen gun.

For NIP architecture, commercially bought SnO_2 (Alfa Aesar) diluted in DI water is used. For PIN architecture, NiO_x (from Avantama) and PEDOT:PSS (from Hereaus) have been spin coated. To improve the wettability of SnO_2 and PEDOT:PSS on ITO, the substrates are subjected to UV-ozone treatment for 20 min. In case of PEDOT:PSS, the solution is filtered ($0.22\ \mu\text{m}$ CA filter) and ultrasonicated for 20 min before usage.

A. Deposition techniques

For deposition of CTLs, spin coating and e-beam/thermal evaporation technique have been used. For spin coating, the substrate is attached to a holder connected to a rotor. The solution of interest is dropped onto the substrate. As a result of centrifugal force during rotation, a thin homogenous film will be achieved. By controlling the amount of solution together with the speed and time of rotation, the thickness of the resultant thin films can be controlled. In case of e-beam evaporation, the electron beam causes the target atoms to transform into the gaseous phase (under high vacuum of $< 10^{-4}$ mbar). The atoms then attach to the substrate forming a compact, uniform, pinhole free layer. The thickness is controlled by the duration of process. For depositing the active layer of CsPbBr_3 , inkjet printing technique is used where the thickness is controlled by drop spacing and the number of layers printed. It is to note that all processes have been carried out in ambient atmosphere, even the deposition of the perovskite layer.

B. Characterization

The characterization of the deposited layers has been done using different techniques:

Structural Characterization:

To observe the morphology, thickness and look for pinholes or other nanoscale defects. The following instruments were used for that purpose:

- (1) Optical microscope
- (2) Scanning Electron Microscopy (SEM)–Jeol 7100

Optical Characterization:

- (1) UV-Vis spectroscopy: to analyze the transparency of the layer from UV to NIR wavelengths (350 nm to 900 nm) which in turn aids in calculating the bandgap energy through Tauc plot (plot of $\sqrt{\alpha E}$ vs E , where α represents the absorption coefficient and E the photon energy; extrapolating the linear region to the abscissa yields the optical bandgap).
- (2) Photoluminescence spectroscopy: to identify the emission wavelength, its intensity and full width half minimum (FWHM) value.

Electrical Characterization:

- (1) I-V curves: Current response to applied voltages helps us to understand charge injection, charge transport, turn-on voltage, series resistance and other electrical parameters of importance in the complete devices.
- (2) Electroluminescence (EL): generation of photons of a particular wavelength (depending on the active material) when the applied voltage is greater than its bandgap energy.

III. RESULTS AND DISCUSSION

N-I-P and P-I-N are the two proposed architectures as shown in Fig. 2a and 2b. Structural and optical properties are critical points in quality control. Differences in morphology directly impact the performance of the PeLED. For this reason, our investigation started with analyzing the layer qualities before fabricating the perovskite layer. Thereby, SnO_2 on ITO (N-I-P) and NiO_x on ITO (P-I-N) were spin coated. We noticed that the surface tension of ITO was high while spin coating SnO_2 layers. To reduce the surface tension, the ITO substrates were exposed to 20 min of UV-ozone. However, this step was not required in case of NiO_x . SEM images in Fig. 2 (c) and (d), show successfully coated pinhole free, uniform and compact layers.

The energy band diagram of all the CTLs and the active layer is shown below in Fig. 3. The losses in PeLEDs mainly happen in the trap sites at perovskite/ETL or perovskite/HTL interface. To reduce losses, many works in literature suggest the use of small molecule transport and/or blocking layers whose metal cation radius is smaller than that of the perovskite. Thus, the lattice vacancies contributing to the traps are filled. In this work, *1,3Bis(3,5dipyrid-3-ylphenyl)benzene* (BmPyPhB) acts as an ETL and additionally as a hole blocking layer with deeper valence band level at -6.8 eV. Likewise, *N,NDi(1naphthyl)N,Ndiphenyl(1,1biphenyl)-4,4-diamine*

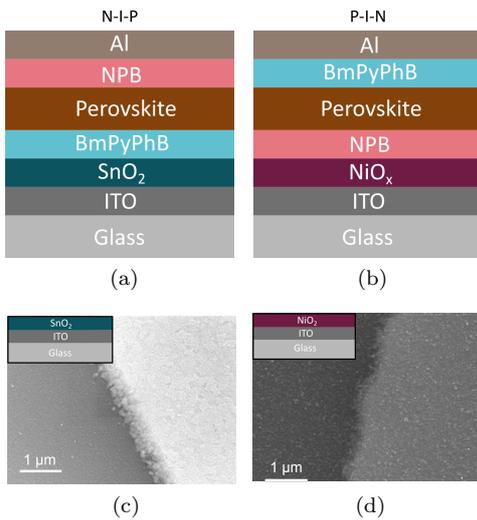


FIG. 2: Cross section of the device architecture of an NIP-type (a) and PIN-type (b). SEM images of spin coated layers of SnO_2 and NiO_x are shown in (c) and (d), respectively.

(NPB) acts as HTL and as an electron blocking layer having higher conduction band energy level at -2.8 eV. In this way, electrons and holes are confined in the active layer, assisting radiative recombination.

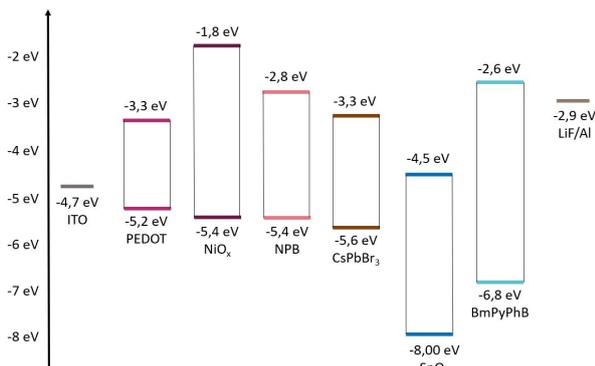


FIG. 3: Energy band diagram.

Small molecule (SM) layers were fabricated using spin coating. BmPyPhB was dissolved in tetrahydrofuran (THF) and NPB was dissolved in toluene at a concentration of 1 mg/mL. They were spin coated on SnO_2 and NiO_x , respectively. Table I contains both the spin conditions and those of the subsequent annealing process.

UV-Vis spectroscopy measurements were carried out to determine the optical properties of these layers. Fig. 4a shows that all the layers show excellent optical properties with $> 85\%$ transmittance in the visible spectrum. Negligible percentage of light is absorbed indicating that there are no optical losses in these layers (Fig. 4b). Thus, together with suitable energy band levels and transparent optical properties, SnO_2 , NiO_x , BmPyPhB and NPB are promising candidates for further device fabrication.

TABLE I: Experimental conditions to deposit each material by spin coating.

	Solute (μL)	Spin coating		Annealing	
		v (rpm)	t (s)	T ($^{\circ}C$)	t (min)
SnO_2	75	5000	30	200	20
BmPyPhB	60	5000	30	110	15
NiO_x	75	5000	60	170	30
NPB	60	3500	30	110	15

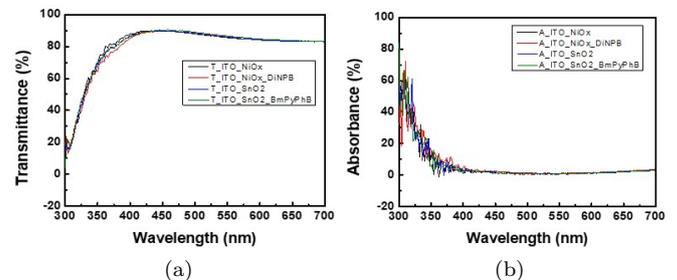


FIG. 4: Optical characterization of CTLs and CILs in (a) and (b) and PL spectra of three different thermal post-processes of the $CsPbBr_3$ printed thin films [2] in (c).

Following the method in G. Vescio *et. al.*, $CsPbBr_3$ was successfully inkjet-printed on SnO_2 and NiO_x : Fig. 4c shows that the analyzed samples present very similar PL wavelength (524 nm). Consecutively, NPB and BmPyPhB were spin coated onto the perovskite layer. Fig. 5 shows the PL emission of a $SnO_2/CsPbBr_3$ interface which was excited using a laser pointer of 405 nm. It emits in green colour which is the expected for $CsPbBr_3$ (524 nm). However, when NPB was spin coated on $CsPbBr_3$ layer, the intensity of the green emission was very low visibly (encircled in Fig. 5b). Worse, the emission was lost when BmPyPhB was spin coated on the active layer (encircled in Fig. 5c). We speculate that the lost in emission is either due to the large amount of solvents used for spin coating or due to the non-orthogonality of the solvents used in NPB and BmPyPhB to the $CsPbBr_3$ layer. Thus, solution processing technique is not advised onto the perovskite layer.

To narrow down and deepen the investigation, we follow the widely used P-I-N architecture with PEDOT:PSS

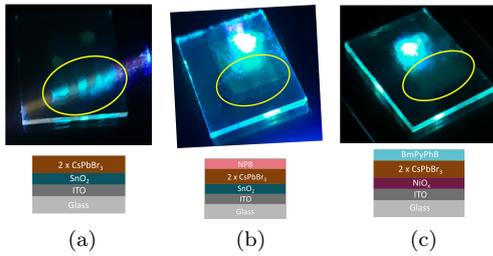


FIG. 5: PL emission seen when excited with laser pointer of 405 nm for (a) $\text{SnO}_2/\text{CsPbBr}_3$ (b) $\text{SnO}_2/\text{CsPbBr}_3/\text{NPB}$ and (c) $\text{NiO}_x/\text{CsPbBr}_3/\text{BmPyPhB}$.

as HIL with inkjet-printed CsPbBr_3 . Subsequently, we move to thermal evaporation of BmPyPhB as ETL and e-beam evaporation of Al for the top contact. Fig. 6a shows the pictorial representation of the device architecture. A shadow mask is used during the evaporation of Al. Thus, the active area of each pixel is set to be 0.045 cm^2 (6 pixels in one substrate as shown in Fig. 6b).

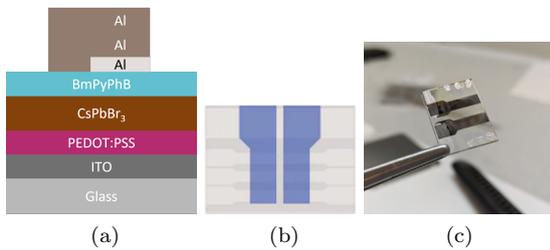


FIG. 6: Cross section of the PIN type architecture developed (a), sketch of the device top view (b) and image of the fabricated device (c).

Fig. 7a shows the I-V curves of two devices with the above-mentioned architecture (Fig. 6a). At forward bias, only a few microamperes of current have been reached indicating a higher series resistance in the device. This could be because of the poor contact of CsPbBr_3 nanocrystals with the CTLs. To check the shelf life of these devices and to observe if the devices improve over time, device 1 and 2 were stored in the glovebox (N_2) for 14 days. I-V curve (Fig. 7b) shows that there is improvement in the current by 1 order of magnitude (at $=+5\text{V}$). Inspired by post treatments (PT) on perovskite solar cells, one of the devices (device 2 – blue curve) was subjected to controlled relative humidity of 45 – 50% inside a vacuum setup for 13 hours. Surprisingly, the current increased further one order of magnitude (at $=+5\text{V}$).

Short-term stability measurements were carried out on these devices, as shown in Fig. 8. The current and corresponding EL intensity were measured at a constant voltage of 18V. The results show that, even though improvements were noticed in the I-V curves, the current and the EL started to decrease within few seconds for the device that was only stored in GB. Contrarily, post treated device showed 56% improvement from its initial

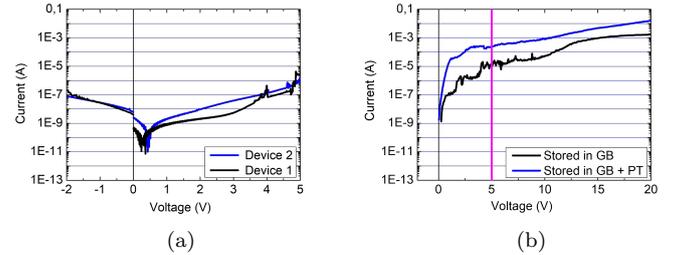


FIG. 7: I-V curves of the fresh device in (a) and the stored devices during 14 days, with and without PT, in (b). These I-V curves correspond to pixel 4 of the devices.

current value together with EL by a factor of 2. They showed stable performance for over 75s. We speculate that perovskite crystals require some time to make better contact with the charge transport layers. Thereby, series resistances at the perovskite/CTL interfaces are reduced. However, treating them under controlled $\text{RH}\%$ for 13h seems to fasten this process. Nonetheless, further investigations are needed to confirm this hypothesis.

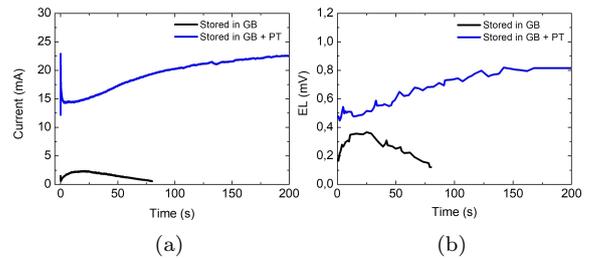


FIG. 8: The dependence of the current with time in (a) and the dependence of the electroluminescence (EL) with time in (b) are represented, when applying a constant voltage of 18 V to the devices.

IV. CONCLUSIONS

In this work, the processing of various organic and metal oxides layers has been shown. SEM images show that the resultant thin films (SnO_2 and NiO_x) are smooth and pinhole free layers. Metal oxide layer together with small molecule layers (BmPyPhB and NPB) shows excellent optical properties with $> 85\%$ of transmittance. It suggests that there will be negligible optical losses when these layers are incorporated into the complete devices.

Despite having good optical properties, the solvent used in the preparation of small molecule layers is not compatible to the underlying perovskite layer. It leads to faster degradation of perovskite nanocrystals losing its photoemission. Thus, it is not advisable to use solution processing technique to fabricate layers after perovskite. New devices with spin-coated PEDOT:PSS and ther-

mal evaporated BmPyPhB (PIN architecture) showed promising results. Although lower forward currents were noticed in the fresh devices, storing them in a N_2 environment improved their performance. Further treating them in a controlled relative humidity (40 – 50%) in vacuum seems to drive the reaction faster. Thereby, increased and stable current and EL are observed. It is presumed that the improvement in performance is due to the better contact of perovskite nanocrystals with charge transport layers over time. Additionally, post treatment is postulated to achieve improved results with stable performance. Thus, post treatment might be a vital step to be considered to improve PeLEDs performance.

The results of this work have helped the group to eventually manufacture a fully functional inkjet-printed green PeLED based on $CsPbBr_3$.

Finally, I would like to include that this work has been complemented and fed back with the studied subjects of Physical Electronics and Micro and Nanotechnology,

achieving a greater understanding and a more global learning.

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- [1] Schubert, Erdmann Fred. *Light-Emitting Diodes*. Cambridge Univ. Press, 2014.
- [2] Vescio G, Frieiro J L, et. al., *High Quality Inkjet Printed-Emissive Nanocrystalline Perovskite $CsPbBr_3$ Layers for Color Conversion Layer and LEDs Applications*. Adv Materials Technologies 210 15-25, 2022.
- [3] Lin K, Xing J et. al., *Perovskite light-emitting diodes with external quantum efficiency exceeding 20 per cent*. Nature 562 245–8, 2018.
- [4] Adjokatse S et. al., *Broadly tunable metal halide perovskites for solid-state light-emission applications Materials*. Today 20 413–24, 2017.
- [5] Prakasam, V., *Metal Halide Perovskites for Light-Emitting Applications*. Ph.D. Institut de Ciència Molecular, Universitat de València, 2019.