ABSTRACT

In recent years, perovskite solar cells (PSC) have grabbed huge attention among the PV technology community. Organic-Inorganic hybrid perovskites (OIHPs) have excellent optoelectronic properties including long carrier diffusion length, tunable band gaps, ease of processing. During the last decade, PSCs have seen tremendous increase in photo conversion efficiency from 3% to over 26%, challenging the dominance of silicon solar cells.

Despite the unprecedented rise in efficiency and relatively low cost, the perovskite absorber layer suffers from poor stability, which leads to faster degradation of device performance, which is the major roadblock to the commercialization of PSC. Several research groups are engaged in devising strategies to improve the stability of the perovskite absorber layers. Some of the suggested strategies include additive and solvent engineering (additives, co-solvent and dripping of antisolvent during processing), compositional and dimensional engineering (i.e. mixing of cations and mixed 2D/3D perovskite), defect passivation (introducing buffer layer at electron transport layer (ETL)/perovskite or perovskite/hole transport layer (HTL)) and interface engineering (i.e. inorganic ETL and HTL or bilayer ETL). The main aim of this thesis is to unravel the salient aspects of film formation and improve the stability of the organic-inorganic hybrid perovskite (OIHP) absorber layer.

The charge carrier transport and diffusion length depend on the microstructure of the absorber films. Poor film microstructure (pinholes and defects) leads to faster degradation and are active sites of recombination. The first part of the thesis investigates various strategies to control the microstructure of Pb and Sn-based perovskite, including the use to different additives, antisolvents, and annealing time. Using a mixed solvent dimethyl sulfoxide (DMSO): dimethyl formamide (DMF) (1:4) and dripping of antisolvent (chlorobenzene, CB) during the later stages of spin coating is found to help in achieving large-grained formamidinium methylammonium

lead bromine iodide $FAMAPb(I,Br)_3$ perovskite films. Perovskite films, which were radiative annealed (RA) in vacuum at a relatively low temperature of 120 ºC for just 60 seconds, remained stable for 60 days (at 60% RH). A PCE of 12.24% with open circuit voltage (V_{oc}) close to 0.9 V was achieved in the PSC fabricated using radiative annealed perovskite film. In the case of Sn-based perovskites, introducing additives SnX_2 (X=F, Cl) and dripping of CB improved the microstructure and stability of $FASnI_3$ by restricting the oxidation of Sn^{2+} to Sn^{4+}.

The electron transport layer (ETL) transports the electrons and block the holes to prevent shunting, which improves the performance of PSCs. TiO_2 is known to catalyse degradation of the perovskite layer. On the other hand, SnO_2 shows better conductivity, mobility and stability with perovskite. Bilayer ETL is an effective way to transcend the limitations of single-layer ETL, thus improving the performance and stability of PSC. The stability and charge transfer ability of formamidinium methyl ammonium lead iodide ($FAMAPbI_3$) films is studied on spray deposited TiO_2, SnO_2, and bilayer TiO_2-SnO_2 ETL. Factors such as wettability and roughness of the substrate decide the morphology and uniformity of the perovskite film. The absence of defects and discontinuities due to higher wettability and lower roughness of TiO_2-SnO_2 assisted in achieving compact and large grained film which improved the stability of perovskite films on bilayer ETL up to 60 days in ambient air (RH = 70%), at the same time, PL peaks showed greater quenching and more efficient electron extraction at the bilayer-ETL/perovskite interface. While the PSC based on bilayer ETL has shown better PCE of 13% than the TiO_2 and SnO_2 alone (10%).

In general, a single cation perovskite absorber layer (methylammonium lead iodide $MAPbI_3$ or formamidinium lead iodide $FAPbI_3$) suffers from unintentional phase transition to yellow or delta phase, which lowers the photovoltaic performance and thermal stability. Introducing triple cation cesium formamidinium methylammonium iodide ($CsFAMAPbI_3$) perovskite

could avoid phase segregation and suppress the delta phase formation. The last part of this thesis looked into the contribution of triple cation (TC) $CsFAMAPbI_3$ perovskite in improving the stability and performance of PSCs. The TC perovskite layer remained stable for up to 1000 hours without any hint of decomposition or phase change. The triple cation perovskite absorber film, along with spray-deposited TiO_2 (ETL), results in an efficient device having efficiency close to 18.60%, while the 1000 hours stored perovskite could still deliver a 12.2% device.

The insight gained from this work highlights the importance of perovskite composition engineering, solvent engineering, precursor preparation and annealing methods for improving device performance and stability. The improvements discussed here will be important for the development of stable and efficient PSC.

Keywords: *Perovskite solar cell; stability; lead-based perovskite; lead-free perovskite; organic-inorganic halide perovskite*