OPEN-CIRCUIT VOLTAGE IMPROVEMENT OF WIDE-BADNGAP PEROVSKITE SOLAR CELLS

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ABSTRACT

Xingjian Ying: Open-circuit Voltage Improvement of Wide-bandgap Perovskite Solar Cells (Under the direction of Jinsong Huang)

To make photovoltaic technology more competitive in the market, the levelized cost of electricity (LCOE) must be sufficiently low. Currently, other costs of the solar system dominate the price, instead of modules, so that making improvements in efficiency of solar cells becomes an effective way for further lowering LCOE. While single-junction solar cells have nearly reached their efficiency limits, tandem structures have become a practical choice. Perovskite is a promising material to serve as the wide-bandgap component in tandem devices. However, open-circuit voltage (V_{OC}) of wide-bandgap perovskite solar cells still suffers from a significant deficit. In this thesis, perovskite/ C_{60} interface is identified as a major source of additional non-radiative recombination. Sub-bandgap states could form after perovskite contact with C_{60} , leading to additional recombination losses. Insertion of a thin interlayer helps passivate the perovskite surface and reduce non-radiative recombination at the interface, resulting in device V_{OC} up to 1.284 V for 1.67-eV-perovskites.

To my parents and friends.

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LIST OF ABBREVIATIONS

2-T	two-terminal
4-T	four-terminal
ALD	atomic layer deposition
BCP	2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline
BOS	balance of system
CTLs	charge transport layers
DLCP	drive-level capacitance profiling
DMF	N, N-Dimethylformamide
Eg	bandgap
EQE	external quantum efficiency
ESS	energy storage system
ETL	electron transport layer
FA^+	formamidinium
FF	fill factor
НОМО	highest occupied molecular orbital
HTL	hole transport layer
IEA	International Energy Agency
ICL	interconnection layer
\mathbf{J}_{SC}	short-circuit current
LCOE	levelized costs of energy/electricity
ITO	indium tin oxide
LUMO	lowest unoccupied molecular orbital
MA^+	methylammonium
NDC	Nationally Determined Contribution

NMP	N-methyl-2-pyrrolidone
PCE	power conversion efficiency
PEDOT: PSS	poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate)
PL	photoluminescence
PLQY	photoluminescence quantum yields
PMMA	poly(methyl methacrylate)
PSCs	perovskite solar cells
РТАА	poly(triarlyamine)
PV	photovoltaics
QFLS	quasi-Fermi level splitting
SAMs	self-assembled monolayers
SQ	Shockley-Queisser
SRH	Shockley–Read–Hall
ТСО	transparent conductive oxide
TPBi	2,2',2"-(1,3,5-Benzinetriyl)-tris(1-phenyl-1-H-benzimidazole)
TRPL	time-resolved photoluminescence
UV-Vis	ultraviolet-visible
Voc	open-circuit voltage

CHAPTER 1. BACKGROUND FOR WIDE-BANDGAP PEROVSKITE SOLAR CELLS

1.1 Solar photovoltaics

Human activities, principally through emissions of greenhouse gases, have unequivocally caused global warming, with global surface temperature reaching 1.1°C above 1850-1900 in 2011-2020.¹ Governments all over the world are beginning to formulate policies for emission reduction. The United States' Nationally Determined Contribution (NDC) aims to reduce greenhouse gas emissions by 50-52% from 2005 levels by 2030, putting the United States on a path to achieve net zero emissions no later than 2050.² To achieve the decarbonization goal, clean energy technology should be deployed widely to replace fossil fuel. Solar energy is one of the most attractive options as it is an inexhaustible resource combined with versatile, silent, efficient and increasingly cost-effective technologies. According to a report by International Energy Agency (IEA), solar photovoltaics (PV) will surpass coal in 2027 to become the largest installed electricity capacity worldwide (**Figure 1.1**).³



Figure 1.1 Share of cumulative power capacity by technology, 2010-2027.³

1.2 Levelized cost of electricity (LCOE)

The levelized costs of energy/electricity (LCOE) is a widely used evaluation metric to compare the cost of generating power by various technologies over their entire lifespan, which is also a powerful tool for project evaluation for investment decision making.⁴ Therefore, lower LCOE will greatly enhance the market competitiveness of photovoltaic technologies. Currently, the reduction of costs has been mainly due to falling module prices and other costs like balance of system (BOS) has come to dominate the total cost of the system.^{5,6} As shown in **Figure 1.2**, even in the utility-scale, solar modules account for about 30% of the cost, which will be even lower if taking energy storage system (ESS) into consideration. Since other costs dominate the price, simply driving down module price is not an effective way. Therefore, improving the module efficiency could be a major approach to further lower the cost by increasing energy yield per unit area.⁷As single junction crystalline silicon solar cell is approaching its detailed balance limit, multijunction solar cells based on silicon bottom cell is now found to be one of the most practical technologies that could overcome the single junction cell efficiency limit so that keep driving down LCOE of PV technology.



Figure 1.2 Utility-scale Q1 2023 U.S. benchmarks (100-MWdc PV, 240-MWh ESS).⁶ Here, MSP stands for minimum sustainable price and MMP stands for modeled market price.

1.3 Tandem solar cells

As for an ideal single junction solar cell, large fraction of energy is wasted because of thermalization and spectrum mismatch.⁸ Stacking junctions with different E_g in optical series could mitigate the energy loss so that surpass the S-Q limit of single junction cell. Several structures of the multijunction tandem solar cell are developed. Typically, for double-junction perovskite/silicon tandem devices, there are two commonly used configurations: two terminal (2-T) tandem and four terminal (4-T) tandem. As shown in Figure 1.3, 4-T tandem is the structure where the wide bandgap perovskite cell and silicon solar cell are mechanically stacked together. Several different concepts of 4-T tandem devices are demonstrated, like spectral splitting⁹ and reflective tandems.¹⁰ Due to the relatively high-cost optical components and the rather complex system integration, most researchers focus on regular architecture. In terms of 4-T tandem device, two subcells could be fabricated separately and work at its own maximum power output point regardless of current match, which widely expands the choice of subcells. Although this configuration is relatively simple in fabrication and operation, the additional two electrodes and power electronics, e.g., inverters will result in high cost.^{11,12} According to a study about accelerating photovoltaic market entry, independently developed wide bandgap perovskite module might be able to enter the PV market earlier for 4-T tandem cells.¹³ As for 2-T tandem cells, two subcells are fabricated on a single substrate sequentially with an interconnection layer (ICL) in between (Figure 1.3). Compared with 4-T configuration, the limitation on the bandgap choice for wide bandgap cell and fabrication process make 2-T tandem more challenging to fabricate but could avoid extra cost. Many groups have devoted efforts in 2-T silicon/perovskite tandem solar cell and a record efficiency of 33.7% has been achieved on 1 cm2 cell¹⁴ and 28.6% for full-size (258.15 cm²) tandem cell recently¹⁵, implying the promising potential in future PV application.



Figure 1.3 Schematics of several perovskite/silicon tandem architectures: a) four-terminal mechanically stacked; b) two-terminal monolithically integrated; c) four-terminal optical spectral splitting; d) four-terminal reflective tandem.¹⁶

1.4 Wide-bandgap perovskite solar cells

1.4.1 Perovskite

Perovskite is a group of materials that have the same crystal structure as the mineral calcium titanium oxide. Generally, perovskite compounds have a chemical formula ABX₃ as shown in **Figure 1.4**. As for photovoltaic applications, A refers to a monovalent cation like methylammonium (MA⁺), formamidinium (FA⁺) or caesium (Cs⁺); B refers to a divalent cation like Pb²⁺ or Sn²⁺; and X refers to a halide anion (I⁻, Br⁻ or Cl⁻). Halide perovskites have attracted the attention of researchers around the world due to its promising optoelectronic properties like high absorption coefficient, small carrier effective mass, excellent defect tolerance¹⁷, widely tunable bandgap¹⁸ and solution processability.



Figure 1.4 Cystal structure of perovskite.¹⁸

1.4.2 Perovskite solar cells

Perovskite solar cells (PSCs) architecture arose from the typical solid-state dye-sensitized solar cells (DSSCs), in which the compact TiO₂ (c-TiO₂) and mesoporous-TiO₂ layers act as hole blocking layer and ETL, respectively. Since the discovery of the long charge carrier diffusion length and the ambipolarity nature of halide perovskites made by the Snaith group^{19,20}, it has become possible to prepare an efficient PSC without mp-TiO₂ layer and planar PSC was developed. Now there are three commonly used architectures for halide perovskite solar cells and planar structures received great attention due to the simplicity in processing.

Mesoporous architecture refers to devices with structure: transparent conductive oxide (TCO) /blocking or compact electron transport layer (ETL) (e.g. c-TiO₂)/mesoporous metal oxide (e.g. mp-TiO₂)/perovskite/ hole transport layer (HTL)/ back electrode (**Figure 1.6a**). Here, mp-TiO₂ transport electrons to TCO before back-recombination and the compact layer blocks holes and the direct contact between the forward contact and the perovskites. However, the complex process and high processing temperature of this ETL hinder the commercialization of this architecture.

Stranks et al. demonstrated that $CH_3NH_3PbI_{3-x}Cl_x$ has much longer electron-hole diffusion length (~1000 nm) than $CH_3NH_3PbI_3$ (~100 nm)²⁰. This work indicated that mesostructured is no longer a necessity and efficient planar heterojunction perovskite solar cells is achievable, which is now the most widely adopted architecture. According to the relative location of HTL and ETL, planar structure can be categorized into conventional (n-i-p) and inverted (p-i-n) as shown in **Figure 1.6b** and **Figure 1.6c**, respectively. Here, TCO is transparent conductive oxide (e.g. ITO, FTO); ETL is an n-type semiconductor (e.g. compact TiO₂, SnO₂, C₆₀ and its derivatives); HTL is a p-type semiconductor (e.g. spiro-OMeTAD, poly(triarlyamine) (PTAA), poly(3,4-ethylenedioxythiophene)-poly(styrenesulfonate) (PEDOT: PSS), NiO_x and et. al); rear electrode could be metal (e.g. Au, Ag and Cu), carbon or transparent conductive oxides (e.g. ITO, IZO, AZO). Recently, a group of self-assembled monolayers (SAMs) based on carbazole and organic phosphonic acids are developed as more advanced hole selective contact²¹ and most state-of-the-art devices are based on SAMs. Since p-i-n structure device tends to have

better stability, scale-up capability and easy integration for tandem applications, many great improvement of perovskite solar cells and perovskite-related tandem solar cells are based p-i-n structure. ²²



Figure 1.5 Schematic structures of PSCs. (a) Mesoporous. (b) Planar n–i–p. (c) Planar p–i–n.²³

1.4.2 Bandgap of wide-bandgap perovskites

For 2-T tandem devices, the bandgap of perovskite is of great importance since the current matching of the top and bottom cell is required to ensure the overall device current is not limited by the subcell with lower current. As calculated by Moritz H. Futscher and Bruno Ehrler, the optimal bandgap (E_g) for the top perovskite solar cell is 1.73eV under standard test conditions (AM1.5G, 1kW/m², 25°C) for limiting efficiency of 45% ²⁴. However, when it comes to outdoor field-testing conditions in which the operation temperature is above 25°C, the bandgap of perovskite could be lower than 1.73eV due to the red-shift of silicon Eg with temperature and the blue-shift of perovskite E_g with temperature²⁵. Their model suggested that 2-T tandem devices with perovskite E_g around 1.68eV delivers the highest energy yield. Moreover, the optical imperfection like parasitic absorption and reflection also has the effect of lowering the optimal bandgap of perovskites²⁶. However, according to their energy yield model, when it comes to realistic irradiation conditions (Phoenix and Portland), the optimal bandgap returns to around 1.69-1.71eV due to the variation of spectral irradiance over the course of a year and average photon energy of local spectra.

1.4.3 Achieving wide bandgap

In lead halide perovskites, the electronic and optical properties are largely determined by lead halide bonds.²⁷ Generally, the wide bandgap perovskite is realized by mixing the Br and I, like for FAPbI_yBr_{3-y}, bandgap from 1.48 eV to 2.23 eV could be achieved.¹⁸ This bandgap difference could be mainly attributed to the distance change of Pb-X bond due to different ionic radius of halide anions. Moreover, mixing different A site cations could also tune the bandgap in terms of different ionic radius, local strain, "hollow" perovskite and PbX₆ octahedral tilting.^{28,29}

However, there is an empirical limit when choosing different A site cations and X site anions: Goldschmidt tolerance factor (t):

$$t = \frac{R_A + R_X}{\sqrt{2}(R_B + R_X)} \tag{1}$$

where R_A , R_B , and R_X are the radius of the A site cation, B site cation, and X site anion, respectively. An orthorhombic, cubic, and hexagonal structure will form when t < 0.8, 0.8 <t < 1, and t > 1, respectively.³⁰ There are only three cations (Cs⁺, MA⁺, FA⁺) have been found that could form cubic structure for APbI₃, but it is also found that mixing ions with different size could tune the effective tolerance factor to form stable cubic structure, which makes it possible to incorporate some other cations into the lattice.³¹

Currently, most wide-bandgap perovskites are achieved by mixing I- and Br-. A-site cations are majorly modified for stability concern though they can also tune the bandgap. As for B-site, Sn^{2+} is vulnerable by oxidation³², so it's rare to see Sn^{2+} in wide-bandgap perovskite.

CHAPTER 2. OPEN-CIRCUIT VOLTAGE DEFICIT OF WIDE-BANDGAP PEROVSKITE SOLAR CELLS

According to a database of perovskite solar cells reports, the wider bandgap perovskite solar cells generally suffer from a larger V_{OC} deficit compared to the narrower-bandgap counterpart.³³ Generally, there is still a large room for V_{OC} improvement for further efficiency improvement.



Figure 2.1 V_{OC} vs. Bandgap literature reports of perovskite p-i-n cells in www.perovskitedatabase.com.³³ The black dotted line indicates the material bandgap and the black solid line the theoretical radiative V_{OC} .

2.1 Open-circuited voltage (Voc) of solar cells

Basically, when a solar cell is illuminated by the sunlight, electron-hole pairs will be generated in the absorber. In this condition, the Fermi level of the semiconductor in the thermal equilibrium is no longer suitable and therefore quasi-Fermi levels are introduced. The Fermi level will be split into electron quasi-Fermi level (E_{Fn}) and hole quasi-Fermi level (E_{Fp}). The difference between E_{Fn} and E_{Fp} is called quasi-Fermi level splitting (QFLS) and that's the highest achievable V_{OC} of the solar cell. Generally, nonradiative recombination could reduce the QFLS and energy level misalignment between different layers could result in mismatch between internal QFLS and V_{OC} of the device. In terms of classical diode equation, V_{OC} could be expressed by equation:

$$V_{OC} = \frac{n_{id}kT_{cell}}{q}\ln\left(\frac{J_{SC}}{J_0} + 1\right)$$
(2)

Where n_{id} is the ideality factor, k is Boltzmann constant, T_{cell} is the temperature of the solar cell, q is the elementary charge, J_{SC} is the short-circuit current and J_0 is the saturation current. This is derived from the basic diode equation of p-n junction solar cells when J=0:

$$J = J_{SC} - J_0 \left[\exp\left(\frac{qV}{n_{id}kT_{cell}}\right) - 1 \right]$$
(3)

2.2 Current status of Voc for wide-bandgap perovskites

As for 2-T Si/perovskite tandem solar cells, the most suitable bandgap of perovskite is around 1.68eV based on the state-of-art tandem devices and simulation. Most of the wide-bandgap perovskites are over 1.60eV, so here I will just focus on reports of the perovskites with bandgap over 1.60eV.

In 2015, Jonathan et al. reported the first 2-terminal Si/perovskite solar cells with efficiency reaching 13.7%. Their perovskite sub-cell's V_{OC} can reach to 1.05 V approximately.³⁴ Afterwards, researcher around the world dramatically improved the sub-cells and as well the tandem device. Currently, the highest efficiency of Si/perovskite tandem solar cells with certification is 34.6% but no more details released.³⁵ The state-of-the-art devices with literature report can reach up to 33.7% and 33.9%.^{14,36} Jiang Liu et al. achieved V_{OC} of 1.27 V for 1.69-eV-bandgap cell and realized the tandem efficiency of 33.9%.³⁶ As for V_{OC} , 1.27 V in this report is actually not the highest value. Silvia Mariotti et al. achieved V_{OC} of 1.28 V for 1.68-eV-bandgap perovskite cell and the final tandem V_{OC} reached up to 2.00 V.³⁷ Wang et al. recently reported V_{OC} of 1.30 V for 1.66-eV bandgap perovskite cells, which represented the lowest V_{OC} deficit (0.36 V) in wide-bandgap perovskite solar cells.³⁸ Based on the Shockley-Queisser (SQ) Limit, V_{OC} limit of 1.66-eV bandgap material is 1.365V and 1.30V has already surpassed the 95% of the limit.³⁹

$2.3 V_{OC}$ deficit from ideal models

Ideally, solar cell performance is estimated based on SQ model.⁴⁰ However, in real-world many assumptions in this model could not be fulfilled and therefore leading to the power losses. **Figure 2.2** shows the gap between the ideal cells and real cells. In SQ model, it is assumed that only photons with energy $E > E_g$ is absorbed by the active layer, whereas photons with energy $E < E_g$ do not interact with the solar cell at all (assumption 1), which means that the absorptivity A(E), is a step function, 0 for $E < E_g$ and 1 for $E > E_g$. However, none of the real solar cell has such step function because of band tails, resulting from structural disorder⁴¹ or simply a finite cell thickness and finite absorption coefficients. In addition, average number of photogenerated electron–hole pairs per absorbed photon could be reduced to <1 due to parasitic absorption of photons in contact layers or by free carriers in the optical absorber, which violated the assumption that an absorbed photon generates precisely one electron–hole pair that contributes to the short-circuit current J_{SC} (assumption 2). The violation of assumptions 1 and 2 decreases the external photovoltaic quantum efficiency so that leads to the reduction of J_{SC}. According to the Equation (2) and (3), the V_{oc} will also drop because of J_{SC} as shown in **Figure 2.2**.

Assumption 3 is that the electron-hole pair loses (to the absorber material's lattice) all excess energy above E_g , that is, the pair relaxes on sub-picosecond timescales to the average energy of a thermalized electron-hole pair (in thermal equilibrium with the cell at T_{cell}), where the underlying is that in the solar cell all relaxed electron-hole pairs are at the same temperature T_{cell} .⁴² It could be violated under field conditions where temperature of the solar modules is over 25°C which is normally use to rate efficiency. Generally, the elevated temperature will mainly reduce V_{OC} as well as other parameters. In this dissertation, temperature will be considered the same so there are no temperature-related effects.

Assumption 4 states that the generated electrons and holes either are collected at their respective contacts or recombine radiatively by emission of a photon, which is the only allowed recombination. Part of the emitted photons will be reabsorbed so there is only a fraction of photons being emitted to the ambient.⁴³ However, in real-world cells, electron and holes would engage in non-radiative recombination

in the bulk and at the interface, which is a major loss channel as shown in **Figure 2.2**. Here, in this dissertation, non-radiative recombination will be the major challenge to overcome.

Assumption 5 states that each contact is ideal because each exchanges only one carrier type (electrons or holes) with the absorber (selective contact) and because it has negligible resistance.⁴² In a simplest case of violating this assumption, like shown in **Figure 2.2**, the additional resistive element reduce the fill factor (FF) while hardly affect J_{SC} and V_{OC} .

Consequently, other than the imperfect absorption of the materials in real world, which could be partially improved by light management, the major factor that deviates the V_{OC} from the ideal V_{OC} is non-radiative recombination.





2.4 Non-radiative recombination

Non-radiative recombination is a decisive factor for V_{OC} in final devices. This could include several different types like defect-assisted recombination, Auger recombination, and interface

recombination. Auger recombination is a multi-charge non-radiative process and strongly depends on the charge carrier density. Fortunately, auger recombination is negligible in lead iodide perovskite solar cells.⁴⁴ Band-tail states emerge due to continuous energetic disorder, which results from the rotational freedom of polar organic cations like FA^+ and MA^+ in the perovskite structure.⁴⁵ Band-tail recombination is associated with charge-carrier relaxation from the energy-band edges to the band-tail states via the release of photons, which results in a loss of V_{OC} output.⁴⁶ On the other hand, defect-assisted recombination are proved to be significantly and universally affect the V_{OC} and attracted more attention of the field.⁴⁷ Therefore, later part will be mainly focused on defect-assisted recombination and especially the interface recombination.



Figure 2.3 Electron (hole) charge current density as a function of free energy.⁴⁸ Solid lines represent the electron (hole) current $J_{e(h)}(\mu) = J_{sun} - J_{rec}$. The dotted lines mark the point of maximum extraction of electrical power. Red curves and circles: electron (hole) current density in the double heterojunction; recombination is dominated by interface electron and hole annihilations. Cyan curves and circles: electron (hole) current density in the single hybrid perovskite layer; recombination is due to electron and hole SRH annihilations alone. Dashed lines: $J_{e(h)}(\mu)$ in the SQ limit.⁴⁸

2.4.1 Defect-assisted recombination

In solar cells, sufficiently long lifetimes are needed to get the photo-generated charge carriers to be collected by the electrodes before the non-radiative recombination occurs. One of the most common ways that accelerates non-radiative recombination is defect. Those with a thermal activation energy

higher than $k_{\rm B}T$ (where $k_{\rm B}$ is the Boltzmann constant), which are called deep-level defects, are the predominant traps sources for non-radiative recombination losses. In perovskite films, there are intrinsic point defects like vacancies (V_{MA} , V_{Pb} and V_I), interstitials (MA_i , Pb_i and I_i), cation substitutions (MA_{Pb} and Pb_{MA}) and antisites (MA_I, Pb_I, I_{MA} and I_{Pb}) (Figure 2.3a, b).⁴⁹ Yin et al. identified eight of them as having low energy of formation (V_{MA}, V_{Pb}, V_I, MA_i, I_i, MA_{Pb}, Pb_{MA} and MA_I).⁴⁹ Halide vacancies (such as V₁) are widely considered to be major contributors to deep-level traps that induce nonradiative recombination.⁵⁰ The I_i defect is also of considerable importance owing to its redox chemistry, which can be easily oxidized to the corresponding I_i^+ defect at Fermi energies close to valence band maximum (VBM).⁵¹ These defects act as charge traps: I_i^- captures photogenerated holes, while I_i^+ captures electrons, forming the neutral I_i^0 defect.^{52,53} As a consequence, the formation of I_i^0 could lead to subsequent formation of I₂, which can escape spontaneously from the perovskite.⁵¹ Zhenyi et al. identified and through combining thermal admittance spectroscopy (TAS) and drive-level capacitance profiling (DLCP) technique, which offered a feasible way of tracking those defects.⁵⁴ Together with other works, iodine interstitials are demonstrated to be universal traps in MA-based perovskites and also MA-free perovskites.^{54,55} In case of wide-bandgap perovskite with bromide, the iodine interstitials are still found to be the main source of deep charge traps.⁵⁶ The introduction of bromide leads to an increase in the Pb-Br-Pb angle by 13° compared with that of Pb–I–Pb in MAPbI₃ and as a consequence Br…Br (or Br…I) distance increased compared with I···I, which makes it easier to form I_i^+ between Br···Br or Br···I (Figure 2.3c).⁵⁶



Figure 2.4 The transition energy levels of (a) intrinsic acceptors and (b) intrinsic donors in MAPbI₃.⁴⁹ (c) Geometrical structures of MAPbI₃ and MAPb($I_{0.8}Br_{0.2}$)₃ with iodide interstitials.⁵⁶

2.4.2 Interface-induced recombination

Perovskite solar cells are based on p-i-n or n-i-p structures that include at least four different interfaces (two electrode/charge transport layers (CTLs) interface and two perovskite/CTLs interface), among which perovskite/CTLs interface plays a relatively vital role in determining charge extraction and non-radiative recombination loss. As a practically more attractive one, p-i-n structure has two perovskite/CTLs interface: perovskite/HTLs on the bottom and perovskite/ETLs on the top. Ideally, the perfect interface must selectively extract the majority charge carriers while blocking the minority charge carriers with minimal defects that induce non-radiative recombination. However, mismatched energy-level, surface defects and interfacial recombination could result in additional non-radiative recombination. **Figure 2.4** shows interface-related loss mechanisms.



Figure 2.5 After (1) carriers transport to the interfaces without significant losses, then at the interface, carrier extraction can be impaired by (2) interfacial energy barriers due to inadequate band alignment, (3) defect-induced surface (interface) recombination, and (4) back recombination of extracted carriers, which still reside in the interface region.⁵⁷

Energy-level alignment is one of the major aspects that cause the V_{OC} loss.⁵⁸ In this case, carriers will lose part of their free energy once they transferred from the perovskite to CTLs resulting in mismatch between internal QFLS and V_{OC} . Martin Stolterfoht et al. directly related energy offset with the resulting difference between the QFLS and device V_{OC} .⁵⁸ By using ultraviolet photoelectron spectroscopy (UPS) with background illumination they flattened surface band bending that allows them to directly compare the energy levels of transport layers and perovskite bulk and they attributed the V_{OC} loss of PEDOT-or P3HT-based devices to the energy-level misalignment based on the energy diagram, which shows the superiority of PTAA and poly-TPD as HTLs (**Figure 2.5a, b**).^{58,59} However, perovskites with different compositions could show different energy level especially for wide-bandgap perovskite since they normally will alloy iodide and bromide. ⁶⁰ Fortunately, another new group of materials called SAMs could be developed to optimize the energy level alignment for wide-bandgap perovskite solar cells which tend to have deeper VBM after mixing iodide with bromide.²¹ However, energy-level alignment between PTAA and wide-bandgap perovskite for perovskite/Si tandem does not seem to be a serious issue when comparing the HOMO of PTAA and VBM of perovskite.^{61,62} Therefore, the improvement from the replacement of PTAA with SAMs actually relates to other factors like passivation and effective hole extraction. As for perovskite/ETL interface, the dominant ETL used in p-i-n is fullerene and its derivatives due to appropriate alignment of their LUMO to many popular perovskites and high electron affinity and mobility. Until now, the state-of-the-art p-i-n devices are still based on fullerene or its derivatives.^{36,63,64} So in terms of electron extraction, fullerene seems to be the best choice for now though the energy alignment is not ideal.⁶⁵



Figure 2.6 (a) J-V characteristics of the p-i-n cells with different HTLs. (b) Plots of energy level alignment between perovskite and different HTLs.⁵⁸

Compared to interface energy-level alignment, reducing non-radiative interfacial recombination is of greater importance in further V_{OC} improvement.⁶⁶ As shown in **Figure 2.4**, other than energy-level misalignment, there are two major physical process that may induce potential loss: (3) defect-induced surface (interface) recombination and (4) back recombination of extracted carriers, which still reside in the interface region.⁵⁷

Perovskite/HTL interface, in case of p-i-n structure, is relatively more complicated since it does not only induce potential interface recombination but also significantly influence the crystallization process of the perovskite films. Simple modifications of PTAA layers could help further improve the interface quality, like addition of poly[(9,9-bis(3'-((N,N-dimethyl)-N-ethylammonium)-propyl)-2,7fluorene)-alt-2,7-(9,9-dioctylfluorene)] (PFN-Br) or poly(methyl methacrylate) (PMMA).^{67,68} Another typical electron transport material BCP is also found to be effective due to its chelation property.⁶⁹ It is found that 2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline (BCP) could break the Pb-Pb dimer structure on the surface, which induce gap states.⁶⁹ As a result, one of the most stable and efficient perovskite minimodules was achieved based on BCP-doped PTAA. Other than widely-used PTAA, a group of carbazolebased SAMs starts to shine in p-i-n devices after 2-(9H-carbazol-9-yl)ethyl]phosphonic acid) (2PACz) showing up.²¹ SAMs, in principle, could covalently bind to the TCO and autonomously form a functional layer in a self-limiting process. More importantly, SAMs delivers great opportunity of forming a conformal thin HTL on top of textured silicon cell which provides higher energy yield and avoids extra manufacturing cost from chemical-mechanical polishing.⁷⁰ In 2020, Amran Al-Ashouri et al. then designed a molecule called Me-4PACz ([4-(3,6-dimethyl-9H-carbazol-9-yl) butyl] phosphonic acid) (Figure 2.6a) as hole-selective layer, which not only passivates perovskites but also enhances hole extraction, resulting in 1.68-eV-perovskite with device $V_{OC} > 1.23 V.^{61}$ Simple modification of aliphatic chain length and substitution groups significantly influence the device performance (Figure 2.6b,c).⁶¹ Despite SAMs promise, it's still hard to achieve a high-density, closely packed monolayer and the formed monolayer could be washed off by the typical solvents used in perovskite precursors (Figure 2.6d).^{71,72}



Figure 2.7 (a) Typical carbazole-based SAM molecule structure, with R denoting a substitution, like a methoxy group, a methyl group or nothing; the number 2 or 4 denotes the number of the linear C atoms between the phosphonic acid anchor group and the conjugated carbazole main fragment.⁶¹ (b) J-V characteristics of the devices based on SAMs with different aliphatic chain length.⁶¹ (c) J-V characteristics of the devices based on SAMs with methyl group substitution and different aliphatic chain length.⁶¹(d) Schematic depiction of deposition and desorption of SAM on ITO surface–connected hydroxyls rinsed sequentially by ethanol then DMF. Dotted line represents a weak hydrogen bond.⁷²

Perovskite/ETL interface is another source of interfacial non-radiative recombination. Fullerene and its derivatives have been widely used in organic solar cells as acceptors during the past decades and now they dominate in p-i-n perovskite solar cells. At beginning, fullerene layers are found to be effective in passivating the charge traps at the surfaces and grain boundaries of perovskite thin films, which significantly suppressed the notorious current–voltage hysteresis and increased the PCE of the perovskite solar cells.⁷³ Though fullerenes greatly improved the performance of perovskite solar cells, the main contributors are J_{SC} and FF, instead of V_{OC} .^{73–75} Later, energy disorder of fullerenes is to blame for the V_{OC} deficit.⁷⁶ Usually, the amorphous fullerene layer is subject to a wide distribution of band tail states originating from their structural, chemical, and dynamical disorder, which will reduce the QFLS.⁷⁷

Therefore, the V_{OC} of perovskite solar cells were essentially determined by the energy disorder in the fullerene layer, rather than the LUMO of fullerenes.⁷⁷ Simple solvent annealing has been tested to be effective in enhancing phenyl-C₆₁-butyric acid methyl ester (PCBM) structural ordering so that the energy disorder decreased.⁷⁶ In addition, rational modification of PCBM also facilitate energy ordering. Jiang et al. connect fullerene to terpyridine with alkyl chains, in which the chelation effect and π -stacking of terpyridine improve the molecular ordering resulting in reduced energy disorder.⁷⁸

In perovskite/silicon tandem solar cells, C₆₀ has become the standard ETL and yielded the highest-efficiency devices. However, the Voc of those devices are found to be limited by the nonradiative recombination at the perovskite/ C_{60} interface.^{58,66,79} By using the density functional theory (DFT) calculations, Liu et al. argued that C_{60} could induce the formation of deep trap states within perovskite bandgap, which could be suppressed by increasing the contact distance (Figure 2.7a).⁸⁰ Warby et al. directly reveal the presence of the interface traps which is sub gap states (Figure 2.7b) and identified that the non-radiative recombination at the perovskite/ C_{60} interface is an across-interface recombination, where the electron extracted to the C_{60} recombine with a hole in the perovskite via trap states.⁷⁹ However, they suggests that those traps are either low lying states created by broadened C_{60} density of states (DOS) or charge transfer states (Figure 2.7c).⁷⁹ Though the origin of the traps that induce perovskite/C₆₀ interfacial non-radiative recombination is still not clear, the strategies used in the field are kind of the same—by inserting an interlayer between perovskite and C_{60} . Wang et al. fabricated a thin layer of insulator between perovskite and C₆₀ to form tunneling contact so that the back recombination of extracted carriers decreased.⁸¹ The insertion of an ultra-thin (≈ 1 nm) LiF interlayer between the perovskite and C₆₀ has also been reported to significantly improve the V_{OC} while keeping the FF.^{58,66} This ultra-thin interlayer has been revealed that it could reduce hole concentration on both sides of the interface and decouple the energy level of perovskite and C₆₀, which is also known to be field effect passivation in silicon solar cells.^{82,65} However, the deliquescent behavior and high ion diffusivity of Li salts may result in reduced device stability.^{83,84} Therefore, alternative fluorides were investigated, like

 MgF_{x} .⁸⁰ Insulating AlO_x, deposited by atomic layer deposition (ALD) which is also compatible with textured surface, has been shown to effectively improve the performance of PSCs.⁸⁵⁻⁸⁷ Though the process of ALD may negatively affect the performance, by keeping a slight PbI₂-excess near the surface the universal improvement of device V_{OC} is observed.⁸⁷ Organic molecules have also been investigated to be feasible to boost the interface.^{37,88,89} Piperazinium iodide (PI) recently attracts many groups and proved to be an effective choice.^{37,90,91} PI is designed to have two different passivation ends: -NH as an electron donor and NH²⁺ as an electron acceptor to react with different surface defects.⁹⁰ However, this molecule is then found to form a dipole at the interface to form more favorable energy-level alignment and reduced non-radiative interface recombination, which eventually attribute to the V_{OC} improvement, instead of chemical passivation.³⁷ As a result PI helped improve V_{OC} of 1.68-eV-perovskite solar cell up to 1.28 V. Low-dimensional perovskites are also tested to passivate the interface.^{92,93} However, typical cations that's been used to form low-dimensional perovskites are found to be detrimental to operational stability.⁹⁴ Usually, usage of those organic molecules are still based on small-area devices and therefore their compatibility with scaled-up manufacturing still needs to be further investigated.



Figure 2.8 (a) Schematic model and density of states (DOS) of a wide-bandgap perovskite as a function of the distance d to the C_{60} molecule. The inset of the enlarged DOS shows the induced mid-gap states when C_{60} is in close proximity to perovskite.⁸⁰ (b) Sensitive external quantum efficiency (EQE) measurements of triple cation perovskite solar cells plotted as a function of photon energy and compared for the case with (blue) and without (red) a LiF layer, highlighting the presence of deep traps at low EQEs (10^{-7}) .⁷⁹ (c) Proposed mechanism of across-interface non-radiative recombination induced by C_{60} in contact perovskites.⁷⁹

In conclusion, the interface quality is of vital importance in further improving the device V_{OC} . Emergence of SAMs not only passivates perovskite/HTL interface and enhances charge extraction. However, the coverage of SAMs and robustness are still problematic. Though many reports suggest that perovskite/C₆₀ interface shows additional interface non-radiative recombination, the origins of those traps that induce recombination are still not clear yet. Interlayers that slightly separate the perovskite and C₆₀ are demonstrated to be effective in reducing non-radiative recombination and choice of materials and fabrication methods determine its final improvement and scale-up compatibility.

2.5 Photoluminescence quantum yields (PLQY) for QFLS characterization

The actual location of the quasi-Fermi levels is generally not accessible, but fortunately the QFLS could be determined directly by means of absolute PL measurements. This methodology has been proven to be an efficient approach for quantifying recombination losses in the neat perovskite, multilayer stacks or even complete cells.^{66,95} The following formula derivation process was reported by Pietro Caprioglio et al.⁹⁵

This method relies on the assumption that all PL stems from the radiative recombination of free charges in the perovskite. Then, the quantum yield of the PL radiation is the ratio between the emitted photon flux φ E from free carrier recombination on the perovskite and the absorbed photon flux φ A or, equivalently, as the ratio between the total radiative recombination current J_{rad} and the generation current J_G. At open-circuit conditions, the net current flowing in the device is zero and J_G is equal to the recombination current J_R, which is composed of the radiative (J_{rad}) component and all nonradiative recombination processes (J_{non-rad}) in the perovskite and all other layers and interfaces.

$$PLQY = \frac{\phi E}{\phi A} = \frac{J_{rad}}{J_G} = \frac{J_{rad}}{J_R} = \frac{J_{rad}}{J_{rad} + J_{non-rad}}$$
(4)

On the other hand, for quasi equilibrium under steady state illumination, the density of free carriers in the valence and conduction band of the perovskite is related to the QFLS (or the sum of the chemical potentials of free electron-hole pair, μ) as follows⁹⁶:

$$n^{2} = N_{C}N_{V} \cdot e^{\left(\frac{E_{C}-E_{V}}{k_{B}T}\right)} \cdot e^{\left(\frac{E_{F,e}-E_{F,h}}{k_{B}T}\right)} = n_{i}^{2} \cdot e^{\left(\frac{QFLS}{k_{B}T}\right)}$$
(5)

where N_C and N_V are the effective density of states in the conduction band and the valence band respectively, T is the temperature, k_B is the Boltzmann constant, E_C and E_V are the conduction and valence band energy levels respectively, n_i is the intrinsic carrier density in the dark. We relate now equation (3) to the radiative recombination current $J_{rad} = edR = edkn^2$, which is the current originated exclusively from bimolecular radiative recombination in the perovskite, and to the dark radiative recombination current $J_{0, rad} = edkn_i^2$, which is the current due to radiative recombination of carriers in the dark. The latter is related to the absorption of the background black body radiation by the detailed balance principle.⁹⁷ Then:

$$J_{rad} = J_{0,rad} \cdot e^{\left(\frac{QFLS}{k_BT}\right)} \tag{6}$$

Furthermore, equation (6) can be combined with equation (4) to derive a direct relation between the PLQY and the QFLS:

$$QFLS = k_B T \cdot ln\left(\frac{J_{rad}}{J_{0,rad}}\right) = k_B T \cdot ln\left(PLQY \cdot \frac{J_G}{J_{0,rad}}\right) = QFLS_{rad} + k_B T \cdot ln(PLQY)$$
(7)

 FLS_{rad} is the radiative limit of semiconducting material, setting the maximum achievable splitting of the quasi-Fermi levels, hence the V_{OC} .

CHAPTER 3. IMPROVING $V_{\rm OC}$ WITH INTERLAYER MODIFICATION OF PEROVSKITE/C_{60} INTERFACE

3.1 Introduction

As discussed in Chapter 2, the device V_{OC} of wide-bandgap perovskite solar cells still lags behind its narrower-bandgap perovskite counterparts. Non-radiative recombination is one of the main factors that deviates the device V_{OC} from the ideal case. Defect-assisted recombination and interfacial recombination have been proved to be decisive. Recently, more attention has been focused on the interfacial quality of perovskite solar cells, which could help further enhance device performance.

In this work, we demonstrated that perovskite/ C_{60} interface is the limiting factor of the QFLS, and insertion of thin interlayer could mitigate the non-radiative recombination at the interface. By comparing PLQY of perovskite bulk, stacks of perovskite/HTL (PTAA) and perovskite/ETL (C_{60}) at open-circuit condition, the perovskite/ C_{60} contact shows almost a magnitude lower PLQY while perovskite/PTAA contact does not induce additional recombination. Typical ETLs, like 2,2',2"-(1,3,5-Benzinetriyl)-tris(1phenyl-1-H-benzimidazole) (TPBi) and BCP are tried to perform as a thin interlayer between perovskite and C_{60} to minimize the PLQY loss and maintain the charge transport effectiveness. Those ETLs thin interlayers are tested to be effective in reducing interfacial non-radiative recombination. However, maybe due to unfavorable energy alignment, they usually decrease FF of the device though they improve the V_{OC} of the device. BCP interlayer, due to its chelation property shows better passivation effect so that the final V_{OC} is higher. With 2.5 nm BCP interlayer, V_{OC} of 1.67-eVwide-bandgap perovskite single junction solar cell could reach up to 1.284V but with the trade-off of FF. 3.2 Materials and methods

3.2.1 Materials

Lead (II) iodide (PbI₂, 99.99% trace metals basis) and TPBi (>98%(HPLC)) are purchased from TCI. Formamidinium iodide (FAI, 99.99%), 4-fluoro-phenethylammonium iodide (4-F-PEAI, >99%) anddodecylammonium iodide are purchased from GreatCell Solar. Benzylhydrazine hydrochloride (BHC, 95%) was purchased from AmBeed. Lead bromide (PbBr₂), caesium iodide (CsI,), BCP, *N*,*N*-Dimethylformamide (DMF), isopropanol (IPA), bathocuproine (BCP), L- α -phosphatidylcholine (LP, >99%), 2-Phenylethylamine hydrochloride (PEACl), PTAA, toluene and *N*-methyl-2-pyrrolidone (NMP) are purchased from Sigma-Aldrich. C₆₀ were purchased from NANO-C. All purchased chemicals are used as received without further purification. 5% v/v FAH₂PO₂ (synthesized in our lab). Methylhydrazine iodide (MHyI) is synthesized by lab mate Zhifang Shi as reported in recent publication.⁹⁸

3.2.2 Device fabrication

Patterned ITO glass substrates were cleaned by acetone and then UV-ozone treated for 15 min before use. First, the 2 mg mL⁻¹ mixed-SAMs (2PACz and [2-(9-ethyl-9H-carbazol-3-yl) ethyl] phosphonic acid (EtCz3EPA)) in methanol was blade coated on ITO substrate with blade gap of 200 μ m followed by annealing at 130 °C for 5 min. When the substrates were cooled down to room temperature and washed in methanol, 2.2 mg mL⁻¹ PTAA in toluene was blade coated on substrates with slight N₂ flow. Perovskite composition is MHy0_{0.05}Cs_{0.25}FA_{0.75}Pb(I_{0.82}Br_{0.15}Cl_{0.3})₃. 1.46 M perovskite was dissolved in DMF with FAH₂PO₂, LP, dodecylammonium iodide, phenylethylammonium chloride, 4-F-PEAI, BHC and 20 mol% of NMP (compared with lead) and then blade coated on top of mixed-SAMs/PTAA with N₂ knife (20 psi) and blade gap of 250 μ m at a coating speed of 20 mm s⁻¹. The annealing is conducted in air with relative humidity ~25% at 130 °C for 2 min and then at 100 °C for 6 min. The single junction widebandgap perovskite solar cells is finished by thermally evaporating C₆₀ (30 nm), BCP (6 nm), and Cu (150 nm).

3.2.3 Device characterization

I-V characteristics of solar cells and mini-modules were performed using a Xenon-lamp based solar simulator (Oriel Sol3A, Class AAA Solar Simulator) and the power of the simulated light was calibrated to 100 mW cm-2 by a silicon reference cell (Newport 91150V-KG5). All devices were measured using a Keithley 2400 source meter without temperature controller. External quantum efficiency (EQE) was conducted on the system from Newport. PLQY was conducted on homemade system with spectrometer (QEPRO, Ocen optics), integration sphere, laser source (LRS-0532-PFM-00100-03, Laserglow Technologies) tuned to 1-sun equivalent intensity and OceanView software. Time-resolved photoluminescence (TRPL) studies were conducted with a HORIBA Dleta Flex TCSPC fluorescence lifetime system. UV-Vis absorption spectroscopy studies were conducted with Evolution 201 UV-Visible Spectrophotometer from Thermo Scientific.

3.3 Experiments and results

The perovskite composition used in this dissertation is MHy_{0.05}Cs_{0.25}FA_{0.75}Pb(I_{0.82}Br_{0.15}Cl_{0.3})₃. **Figure 3.1a** shows the absorption spectrum and PL spectrum of this wide-bandgap perovskite film. **Figure 3.1b** indicates the basic device structure used in this dissertation, where mixed-SAMs and PTAA act as double-layer HTL. **Figure 3.1c** shows the typical EQE curve, from which the bandgap of 1.67eV is derived from the 1st derivative of EQE.



Figure 3.1 Basic information of $MHy_{0.05}Cs_{0.25}FA_{0.75}Pb(I_{0.82}Br_{0.15}Cl_{0.3})_3$ wide bandgap perovskite. (a) Absorption spectrum and photoluminescence (PL) spectrum. (b) Device structure. (c) Device EQE and 1st derivative of EQE.

3.3.1 Preliminary PLQY test of perovskite and half stack of device

PLQY has been proved to be a practical contactless method to measure QFLS loss: $\Delta E_F = \Delta E_F^{rad} + kTln(PLQY)$.^{66,79} Here we use our system to test PLQY of the films and half stacks of the devices (glass/ITO/HTL/perovskite and glass/ITO/HTL/perovskite/ETL (C₆₀)). Here, the 532-nm laser intensity is tuned to 1-sun equivalent with a spot diameter around 2 mm. The schematic illustration is shown in **Figure 3.2a.** The results are consistent with what many others have reported that the PLQY drop dramatically when perovskite and C₆₀ are in contact under the 1-sun equivalent illumination. As shown in **Figure 3.2b**, PLQY drops a little when in contact with double-layer HTL. To eliminate the effect of HTL tuning the crystallization of perovskite layer, we coated another thin layer of PTAA on top of perovskite layer with the same blade coating method used in fabricating bottom HTL and there is no significant influence on the PLQY value but even makes it a little higher. However, when there is C₆₀ in contact with perovskite, the PLQY of perovskite drops almost one magnitude from ~ 1% to 0.1%, which indicates that there is more non-radiative recombination happening between perovskite and C₆₀ than between the perovskite and HTL. The calculated QFLS loss for those stacks is 0.11 eV, 0.12 eV, 0.11 eV and 0.17 eV.



Figure 3.2 (a) Schematic illustration of PLQY test (b) PLQY test results of different stacks.

3.3.2 Origins of interface traps

Though many literatures report additional non-radiative recombination at the perovskite/ C_{60} interface, the origins of this non-radiative recombination is still not clear.^{79,80} Warby et al. suggests that it is because of the across-interface recombination and they suspect this comes from the non-uniform statistic charge distribution of perovskite surface that broadening the energy band of C_{60} eventually resulting in increased interface recombination. Therefore, the actual mechanism behind the additional recombination still needs further investigation.

This thesis tried to identify the perovskite/ C_{60} interface induced traps by using UV-Vis absorption spectroscopy since normally the trap states are difficult to distinguish in luminescence studies but absorption studies. However, in samples fabricated as they are in real devices, the interface signal could be negligible compared to the perovskite bulk signal. Therefore, we tried to mix perovskite and C_{60} well to create more interfaces that could contribute more signal to the final results. We tried to dissolve C_{60} into the perovskite precursor and as expected the solubility of C_{60} in DMF is very low though still a little bit is dissolved as indicated by the color change (**Figure 3.3a**). The solution is prepared by mixing excess C_{60} in DMF with ultrasonic, followed by filtration. Perovskite precursor was mixed with C_{60} solution waiting for film fabrication and absorption measurement. As shown in **Figure 3.3b**, the film prepared by mixed solution has obvious sub-bandgap absorption which may indicate the contact between perovskite and C_{60} could induce additional gap states that may consequently result in increased non-radiative recombination and V_{OC} loss.



Figure 3.3 (a) Photos of pure DMF (left), filtered C_{60} /DMF solution (middle left) and perovskite precursor (middle right) and mixture of perovskite and C_{60} (right). (b) Absorption spectrum of film fabricated using pure perovskite precursor and mixture of perovskite precursor and C_{60} .

3.3.3 Interlayer modification of perovskite/C₆₀ interface with TPBi

Since the contact between perovskite and C_{60} will induce additional trap states, we decided to slightly separate the perovskite and C_{60} with a thin interlayer. TPBi is one of the most widely used ETL in optoelectronic devices with relatively high carrier mobility⁹⁹ so that we hope the insertion of TPBi thin layer could mitigate the charge blocking effect shown in insulating materials. The molecule structure is shown in **Figure 3.4a**. Compared with the typical interlayer used in the field like LiF, the insertion of TPBi shows a similar effect in reducing interface non-radiative recombination, indicated by the PLQY measurement shown in **Figure 3.4b**. By calculating the QFLS loss, the insertion of the interlayer could help mitigate the losses by around 10 meV. However, in our case, when it comes to devices, TPBi interlayer obviously enhanced the device V_{OC} while the LiF insertion did not show any improvements of V_{OC} (**Figure 3.4c**). Considering the uniformity of the thin interlayer, we decided to use thermal evaporation to deposit TPBi on top of perovskite for further optimization. After depositing 2.5 nm of TPBi between perovskite and C_{60} , the device V_{OC} could be improved from around 1.250 V to over 1.265 V (**Figure 3.4d**). Representative J-V curves of devices with different TPBi thickness are shown in **Figure**

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3.4e. We also conducted TRPL studies, the results of which indicate that the insertion of TPBi interlayer increase carrier lifetime meaning reduced charge traps at the interface (**Figure 3.4f**).



Figure 3.4 (a) TPBi molecule structure. (b) PLQY test of different stacks: perovskite, none, LiF and TPBi represent glass/ITO/HTL/perovskite, glass/ITO/HTL/perovskite/C₆₀, glass/ITO/HTL/perovskite/1 nm LiF/C₆₀ and glass/ITO/HTL/perovskite/TPBi/C₆₀, respectively. (c) Device V_{OC} with different thin interlayers. (d) Device V_{OC} with different TPBi interlayer thickness. (e) J-V curves of devices with TPBi interlayer. (f) TRPL results with TPBi interlayer (perovskite films were fabricated on top of glass/ITO/HTL substrates).

3.3.4 Interlayer modification of perovskite/C₆₀ interface with BCP

Though TPBi is tested to be a relatively effective interlayer choice, it is demonstrated to just have physical contact with perovskite.¹⁰⁰ Another typical ETL BCP is reported to have strong binding with perovskite due to the chelation property, which can effectively passivate the perovskite.⁶⁹ Therefore, we tried to use BCP as interlayer expecting better passivation on perovskite as well as further improvement of device V_{OC} . Here we deposit BCP thin layer between perovskite and C_{60} by thermal evaporation method which provides great uniformity and industry compatibility. We first deposited thick (~15 nm) TPBi or BCP layer on top of perovskite to compare the passivation effectiveness and BCP outperforms TPBi as PLQY results indicated in Figure 3.5a. Then we tracked the PLQY value of glass/ITO/HTL/perovskite/BCP stack when varying BCP thickness to determine the minimum thickness that will fully passivate the perovskite surface. The data in Figure 3.5b indicates that at least 8-nm deposition is needed to fully passivate the surface of perovskite which may suggest that at least 8-nm deposition could fully cover the perovskite surface. Afterwards we added C_{60} on top of this stack to check how BCP interlayers influence the non-radiative recombination at the interface. The PLQY track (Figure **3.5c, d)** suggests that 8-nm BCP could almost recover the PLQY to status that before the deposition of C_{60} . TRPL study is also conducted to further investigate the effect of BCP interlayer. Like TPBi, BCP interlayer also prolonged the carrier lifetimes (Figure 3.5e). As suggested by Kirchartz et al, we calculated differential lifetime $(\tau(t) = -(\frac{dln(\emptyset_{PL}(t))}{dt})^{-1})$ from the decay curve to distinguish the charge transfer process and interfacial recombination.¹⁰¹ Figure 3.5f indicates that BCP interlayer effectively reduce the non-radiative recombination at interface since the plateau after charge transfer is dominated by interfacial recombination according to their simulation.¹⁰¹



Figure 3.5 (a) PLQY results of perovskite with and without 15nm TPBi/BCP treatment. (b) PLQY trends of perovskite film with different BCP layer thickness. (c) PLQY trends of glass/ITO/HTL/perovskite/BCP/ETL stack with different BCP thickness. (d) PLQY ratio of glass/ITO/HTL/perovskite stack before and after deposition of C₆₀ with different BCP thickness. (e) TRPL results of glass/ITO/HTL/perovskite/ETL stack with and without 2.5 nm BCP interlayer. (f) Computed differential lifetimes from fits to the transients in (e).

However, in real device fabrication, only 2.5 nm thick BCP interlayer could already induce an obvious FF drop as shown in **Figure 3.6c** mainly due to the increased series resistance which can be attributed to the BCP's blocking effect of electron extraction as its band energy level does not match well with perovskite. Eventually, a 2.5 nm thick BCP interlayer could enhance the device V_{OC} up to 1.284V, higher than TPBi-modified devices.



Figure 3.6 Statistics of parameters of devices with 2.5 nm BCP interlayer. (a) Open-circuit voltage. (b) Short-circuit current. (c) Fill factor. (d) Power conversion efficiency.

Since BCP interlayers obviously induce FF loss, we also adopted DLCP to characterize the interlayer effect in devices. In DLCP measurement, we can always get the double-U shape curves when there is BCP interlayer at the interface as shown in **Figure 3.7a**, which may indicate that the thin BCP interlayer acts as insulating material at the interface. Considering the complexity, it can hardly be used to derive trap density of perovskite surface. To understand the double-U shape curve, the device could be regarded as two different junctions after thin BCP layer deposition and the final curve is the combination of the results from both junctions, which though may affect the interpretation of the depth profile. This result actually implies that evaporated BCP forms islands on top of perovskite, similar to the PERC structure in silicon solar cells.¹⁰² PMMA is a widely used insulator for interface modification for electronic devices and it can form discontinuous film when coating it with very low concentration.⁷⁹ We

also test DLCP curve of devices that coated with thin PMMA layer at perovskite/ C_{60} interface and the double-U shape curve also occur (**Figure 3.7b**), which could also prove that the evaporated BCP acts as insulating islands between perovskite and C_{60} as shown in **Figure 3.7c**.



Figure 3.7 (a) DLCP depth profiling of the device with 2.5 nm BCP interlayer. (b) DLCP depth profiling of the device with thin PMMA layer. (c) Schematic illustration of devices structure when BCP interlayer is deposited on top of perovskites.

In conclusion, we identified that perovskite/ C_{60} interface is a main source of non-radiative recombination in our wide-bandgap solar cells. The contact between perovskite and C_{60} could induce sub bandgap states which could be responsible for the additional non-radiative recombination at interface. Other typical ETL like TPBi and BCP are tried as interlayer between perovskite and C_{60} , which significantly reduce the non-radiative recombination at interface. With better passivation effect, BCP interlayer finally improved the device VOC up to 1.284 V for 1.67-eV wide-bandgap perovskite solar cells though induced slight FF loss.

CHAPTER 4. CONCLUTIONS AND OUTLOOK

4.1 Conclusions

In this work, we first introduced the importance of developing efficient tandem devices to keep driving down the LCOE of solar photovoltaic systems. As promising alternatives for wider bandgap subcells in tandem devices, metal halide perovskites attract dramatic attention in the field. However, device V_{OC} of wide-bandgap perovskite solar cells suffers a larger deficit compared to their narrower-bandgap counterparts. Non-radiative recombination is the main reason for high V_{OC} loss. According to the literature, intrinsic defects in perovskites and interface-induced non-radiative recombination have often been cited as the primary causes. Two perovskite-related interfaces are of vital importance in further improving device performance. As a bottom layer, HTL does not only affect interfacial recombination but also affect crystal growth of perovskite layer. Fullerene, as a dominant ETL material in p-i-n device induces severe additional non-radiative recombination at perovskite/ETL interface, which requires more efforts from the field.

Fullerene-induced non-radiative recombination is also identified in our wide-bandgap perovskite solar cells. The absorption spectrum indicates that the contact between perovskite and C_{60} could result in increased sub-band states which are proposed to be responsible for additional non-radiative recombination at perovskite/ C_{60} interface. TPBi and BCP are tried as thin interlayer between perovskite and C_{60} to mitigate the interface non-radiative recombination. Both of them effectively improved the PLQY of half stack and lead to higher device V_{OC} . TPBi thin interlayer enhanced V_{OC} to over 1.265 V, while BCP boost V_{OC} up to 1.284 V due to better passivation effect on perovskite surface. However, the V_{OC} improvement comes with compromise of FF since BCP interlayer is found to performs as an insulator at the interface, which inhibits the charge extraction from perovskite to C_{60} .

4.2 Outlook

As shown in this thesis, though interlayer modification could help boost device V_{OC}, there is usually a compromise with FF. This trade-off effect should be avoided because both parameters affect final efficiency. Since slightly separating the perovskite and C_{60} is shown to be effective, tunneling layers like those used in silicon solar cells could be further investigated when transferred to perovskite solar cells. Inspired by SAMs, forming a conformal electron-selective monolayer on top of perovskite as an ETL could be an ideal case, which also help avoid the parasitic absorption of fullerene when light illuminates from ETL side and weak physical bonding between C_{60} and perovskite. Rylene diimides are a robust, versatile class of polycyclic aromatic electron-transport materials with excellent thermal and oxidative stability, high electron affinities, and, in many cases, high electron mobilities; they are, therefore, promising candidates for a variety of organic electronics applications.¹⁰³ The derivatives from this class have seldom been investigated in perovskite solar cells, which suggests great potential for further interface modification or even replacing the fullerene. N-type semiconducting metal oxides are another alternative as ETLs in p-i-n devices. ALD SnO_x has already been tried, demonstrating extraordinary operational stability, but the efficiency still lags behind C₆₀-based devices.¹⁰⁴ By further optimization of the perovskite/ETL interface and SnO_x, efficiency of SnO_x-based p-i-n devices are very likely to be comparable to or surpass C₆₀-based devices.

Another major problem of mixed-halide wide-bandgap perovskites is phase segregation, which could be detrimental to photovoltaic performance of the perovskite solar cells and the tandem solar cells. Wide-bandgap perovskites for perovskite/silicon tandem do not need extremely wide bandgap to maximize efficiency so by mixing only different A-site cations may also fulfill the bandgap requirement. In that case, the wide-bandgap perovskite could be achieved by pure iodide, avoiding halide segregation. Inorganic β -CsPbI₃ exhibit_s relatively suitable bandgap of 1.68 eV for perovskite/silicon tandem applications, in which both segregation of A-site cations and halides could be totally avoided. However, the phase instability at ambient conditions and the rareness of Cs may limit further practical investigation.

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Last but not least, considering that the textured surface could improve light management and avoid the polishing cost of silicon wafer, future perovskite/silicon tandem will also be textured to maximize LCOE. Widely adopted solution-processed method in perovskites field is difficult to form conformal perovskite layer. The thermal evaporation method could be a promising candidate for forming a uniformly conformal perovskite layer with good compatibility for manufacturing.

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