TOWARDS ULTRA-HIGH EFFICIENT PHOTOVOLTAICS WITH PEROVSKITE/CRYSTALLINE SILICON TANDEM DEVICES

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ABSTRACT: Perovskite/crystalline silicon tandem solar cells are one of the most promising approaches to reach conversion efficiencies beyond 30% at reasonable costs. In the present paper, we present our research directions and recent results. This includes fundamental studies on the perovskite material properties such as sub-band gap absorption and complex refractive index, as well as the development of a broadband transparent rear electrode. The electrode development enabled the fabrication of semitransparent perovskite cells with efficiencies up to 14.7%, which then translates to four-terminal tandem measurements with total stabilized efficiency of up to 22.8%. Furthermore, we present first results on monolithic perovskite/silicon tandems with total current of 32.25 mA/cm^2 on a flat wafer and finally provide optimization guidelines with optical simulations.
Keywords: Perovskite, silicon heterojunction, tandem, TCO, simulation

1. INTRODUCTION AND MOTIVATIONS

With over 90% of the market share, crystalline silicon (c-Si) wafer-based solar cells have been dominating the photovoltaic market for already several decades. C-Si cells reach efficiencies of up to 25.6% [1], which is already very close to both the practical efficiency limit of 26% and to the theoretical maximum efficiency of 29.4% [2]. Ultra-high efficiencies at affordable costs are however necessary and represent the most simple way to decrease the material consumption per Watt, the overall cost of photovoltaic systems and consequently also the price of electricity for the end-users. A promising approach to circumvent these efficiency limitations of single-junction cells is to combine a silicon solar cell (acting as the bottom cell) with an efficient and low-cost wide-band gap solar cell (top cell) in a tandem solar cell, where each sub-cell is optimized for a specific part of the incoming light spectrum.
Until very recently, no photovoltaic technology could meet the requirements for this wide-band gap top cell, which include high performance, high photocurrent, low cost and easy processing. The situation has recently changed with the rise of the perovskite solar cell.
Metal halide perovskite solar cells have recently made tremendous progress, with record efficiencies beyond 20% [3]. Interestingly, perovskite solar cells are not only very efficient, but also have a high and tunable band gap. This, together with the fact that they can be fabricated with low-cost processing techniques, makes them highly interesting for application in tandem cells. In such a device, the perovskite cell acts as the top cell, absorbing the visible light and letting through photons in the near-infrared part of the solar spectrum, which are harvested by the silicon solar cell with its narrower band gap.
In this paper, we present some of our recent results, covering a wide range of research necessary to make perovskite/c-Si tandem devices: from the understanding of material properties and characterization systems to the realization of real experimental devices, including both four-terminal and monolithic tandems. Finally, simulations and modeling are providing guidelines for further optimization.

2. PEROVSKITE MATERIAL PROPERTIES

For application in perovskite/c-Si tandem cells, the perovskite absorber layer has to be highly transparent at photon energies below its band gap. Any light absorbed

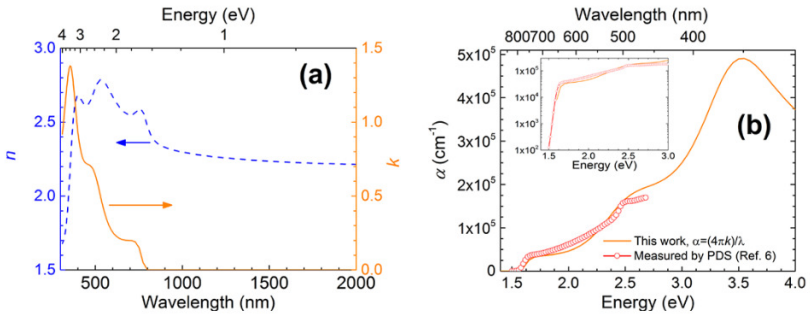

Figure 1: a) Refractive index and b) absorption coefficient of $CH_3NH_3PbI_3$. Reprinted with permission from Löper *et al.* J. Phys. Chem. Lett. 2015, 6, 66-71. Copyright 2015 American Chemical Society

in this sub-bandgap energy range would neither contribute to the photocurrent of the perovskite solar cell nor be transmitted to the silicon bottom cell, and therefore would severely limit tandem performance. We conducted highly sensitive photothermal deflection spectroscopy and Fourier-transform photocurrent spectroscopy to investigate absorption near and below the perovskite band edge [4]. The absorption edge of the $CH_3NH_3PbI_3$ perovskite material was found to be steep, with no observable sub-band gap absorption, as shown in the inset in Figure 1b. The lack of sub-band gap absorption and high transparency for wavelengths larger than 825 nm confirm that perovskites are suitable for tandem applications.

To further understand the optical and dielectric properties of perovskite absorber materials, the complex refractive index was studied by variable angle spectroscopic ellipsometry [5]. Figure 1a shows the refractive index of $CH_3NH_3PbI_3$. Note that its real part has a value of 2.61 at a wavelength of 633 nm. Consequently the perovskite layer is also well suited to act as an antireflective coating for silicon solar cells. This finding is particularly interesting for monolithic tandem devices, where the perovskite top cell is directly grown on top of the silicon bottom cell.

3. BROADBAND TRANSPARENT ELECTRODE

In order to be used in a tandem device, the perovskite top cell needs to feature large sub-band gap transmittance. Therefore the opaque rear contact (usually an evaporated metal such as Au, Ag or Al) has to be replaced by a broadband transparent electrode. In the last year, several groups have reported various potential material candidates, such as laminated carbon nanotubes [6], polymer-embedded metal grids [7], silver nanowires [8], graphene [9] or transparent conductive oxides (TCOs) [10]–[12]. For tandem applications, this rear electrode needs to be highly transparent particularly in the near infrared, to minimize the sub-band gap absorption in the top cell and maximize the amount of light that can be harvested by the bottom cell. So far, only silver nanowires and TCOs have proven to meet this requirement, while keeping good electrical properties [8], [11]. TCOs, deposited by radio-frequency sputtering, combine high transparency, high conductivity and large availability and excellent reproducibility. We started the transparent electrode development with indium tin oxide (ITO) [10], which showed only sub-optimal electrical and optical properties, as high process temperatures necessary for optimal ITO crystallization would harm the sensitive materials of the perovskite cells. We chose therefore to move to an amorphous TCO, namely indium zinc oxide (IZO). It can be deposited at room temperature and low power, and can provide high carrier mobilities with low carrier densities, minimizing free-carrier absorption in the NIR, while still maintaining good conductivity [13]. We applied IZO layers as transparent rear electrodes in mesoscopic perovskite solar cells and reached efficiencies of up to 9.7% in a semitransparent device [11]. However, the damage to the underlying layers was significant. This could be mitigated by introducing a thin molybdenum oxide (MoO_x) layer as a buffer layer between the sensitive organic hole transport layer and the sputtered TCO. As shown in Figure 2, this IZO/MoO_x electrode allowed us to make semitransparent perovskite solar cells with up to 10.3% efficiency, showing no FF or V_{oc} losses [11]. With further improvements to the perovskite cell fabrication process, following a method described in [14], we could recently improve the efficiency of semitransparent cells up to 14.7%. This value was obtained from current-voltage (*I-V*) scans when sweeping the voltage from 1.2 V to 0 V (reverse scan). A stabilized efficiency of 13.4% was obtained with a maximum power point tracking system, measuring for 400 s.

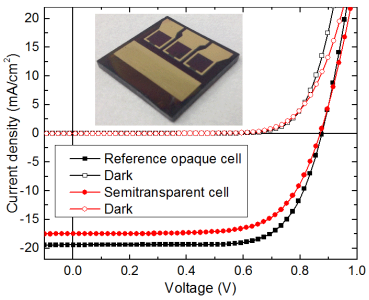

Figure 2: Semitransparent perovskite solar cell as presented in reference [11].

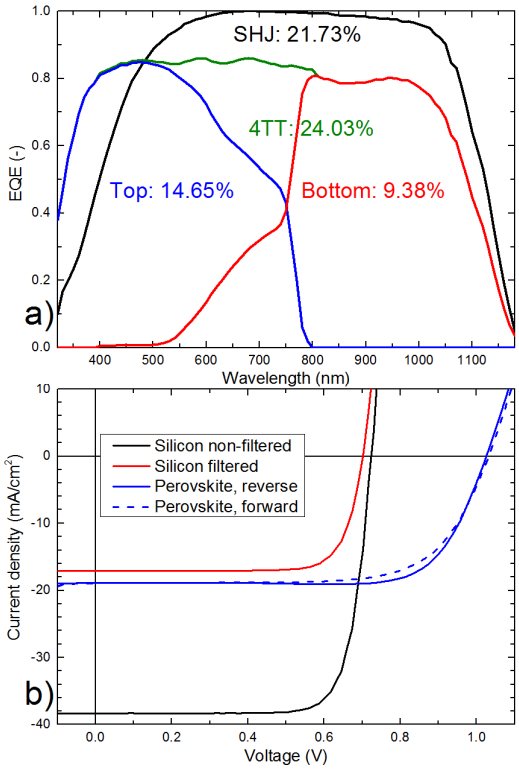

Figure 3: a) External quantum efficiency measurements of the semitransparent perovskite top cell (blue curve), the silicon heterojunction bottom cell when the incident light is filtered by the top cell (red curve) and the non-filtered silicon heterojunction cell (black curve). b) Current-voltage curves for both sub-cells compared to the non-filtered silicon cell.

4. FOUR-TERMINAL TANDEM

In a four-terminal tandem cell, the two sub-cells are fabricated independently and then mechanically stacked together. The characterization is then also carried out independently for each sub-cell. Since the first report of a four-terminal tandem with an efficiency of 13.4% [10], important progress has been made by several groups: 17% on a multicrystalline silicon cell [8], 19.5% on CIGS [12] and 19.6% on silicon heterojunction solar cells [11]. With our recent improvements in the semitransparent perovskite cell performance (up to $14.7\%_{reverse}$, $13.7\%_{forward}$, $13.4\%_{mpptracker}$), we could improve the four-terminal tandem efficiency up to $24\%_{reverse}$ ($23\%_{forward}$; $22.8\%_{mpptracker}$), as shown in Figure 3, with a silicon heterojunction bottom cell with an efficiency of 21.73% when measured as a single-junction cell.

5. MONOLITHIC TANDEM

In contrast to the mechanically stacked tandems, in a monolithic tandem the two sub-cells are processed on top of each other, connected by an intermediate recombination layer. This type of architecture allows for the reduction of fabrication steps and therefore the overall manufacturing costs. Furthermore only one highly transparent TCO is required, as compared to 2-3 in a four-terminal tandem, depending on the type of bottom cell. This is important in terms of costs, process simplicity and potential to reduce parasitic absorption. Monolithical integration however requires a process compatibility between the sub-cells. For example, solution-processed perovskite top cells require a sufficiently flat bottom cell surface, such that in the case of c-Si bottom cells, polished wafers have to be used at the expense of optical properties. Also silicon heterojunction solar cells are known to be sensitive to temperature higher than 200°C, which makes them incompatible with standard mesoscopic perovskite cells.

To date, perovskite-based monolithic tandems have been demonstrated on kesterite CZTS [15] and crystalline silicon homojunction solar cells [16]. In the latter, a silicon-based tunnel junction was developed to connect the two sub-cells and allowed for a maximum efficiency of 13.7% with a V_{oc} of 1.58V.

We have started our research on monolithically integrated tandems by working with high-temperature stable planar float zone silicon wafers featuring p- and n-contacts made by boron and phosphorous diffusion, on which a mesoscopic perovskite cell was deposited, hence including a 500°C annealed TiO_2 scaffold. We could reach efficiencies up to 10.9% with a V_{oc} of 1.43V on a cell with 1.19 cm^2 aperture area. Although this performance is still low, the EQE curves shown in Figure 4 show a total current of 32.25 mA/cm^2, with relatively high peak EQE values and still strong limitations from the top cell.

6. PARASITIC ABSORPTIONS

The rather low EQE values (<90%) shown in Figures 3a and 4 demonstrate that both four-terminal and monolithic tandems suffer from parasitic absorption that limits the quantum efficiency of the bottom cell. Reducing this parasitic absorption in the top cell will be an important challenge to succeed in making efficient perovskite/c-Si tandems.

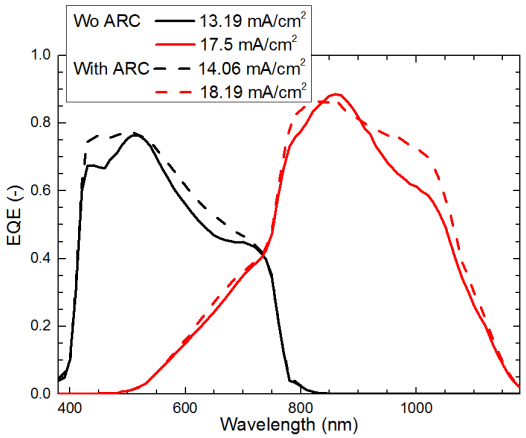

Figure 4: External quantum efficiency measurements of a monolithic tandem with high temperature mesoscopic perovskite top cell on boron diffused silicon bottom cell. Measured with and without antireflection coating.

Monolithic tandems have an advantage concerning this aspect, as they require fewer doped TCO layers, with typically significant parasitic absorption. In monolithic tandems, the sub-cells are also ideally optically coupled, with an intermediate layer whose thickness can be adjusted to shift the absorption maxima and thus tune current matching.

In the case of four-terminal tandems, the standard front electrode used in perovskite cells, namely FTO, is the main contributor to the top cell's sub-band gap parasitic absorption. As shown in Figure 5, the increased absorptance in the red and near-infrared spectral region due to larger free-carrier density in FTO translates directly in the bottom cell's EQE by a loss of 3-4 mA/cm^2 compared to a measurement with a similar perovskite cell using ITO as front electrode. We can however see that even with ITO, having lower free-carrier absorption, further improvements are still some necessary to match the non-filtered silicon cell. These losses can be attributed to parasitic absorption in other charge transport layers, such as the traditionally used hole transport layer spiro-MeOTAD.

Indeed, the high doping of the spiro-MeOTAD layer makes it parasitically absorb over the entire spectral range, and particularly for wavelengths below 400nm. The consequence of this absorption can be observed in a semitransparent perovskite cell illuminated from the rear spiro side (instead of the common illumination through the front glass side). As shown in Figure 6, the J_{sc} loss due to this parasitic absorption corresponds to about 2.4 mA/cm^2. This loss is highly detrimental for monolithic tandems, as in this architecture the perovskite top cell deposited on the silicon bottom cell has to be illuminated from the spiro-MeOTAD side.

For monolithic tandems, it becomes therefore crucial to find a replacement for spiro-MeOTAD with lower parasitic absorption.

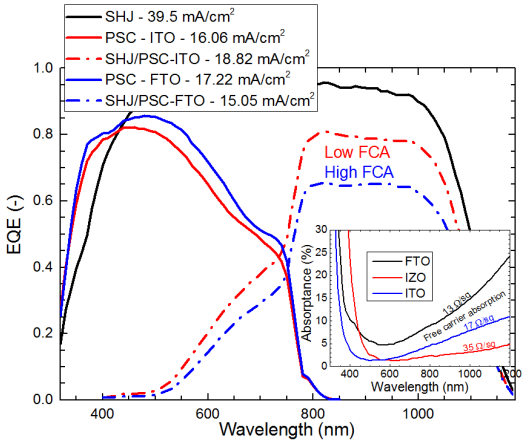

Figure 5: External quantum efficiency measurements of semitransparent perovskite cells (PSC) with ITO (red curve) and FTO (blue curve) front electrode and the corresponding curves for the filtered silicon heterojunction (SHJ) bottom cell, showing the effect of free carrier absorption. The inset gives the absorptance spectra for FTO, ITO and IZO.

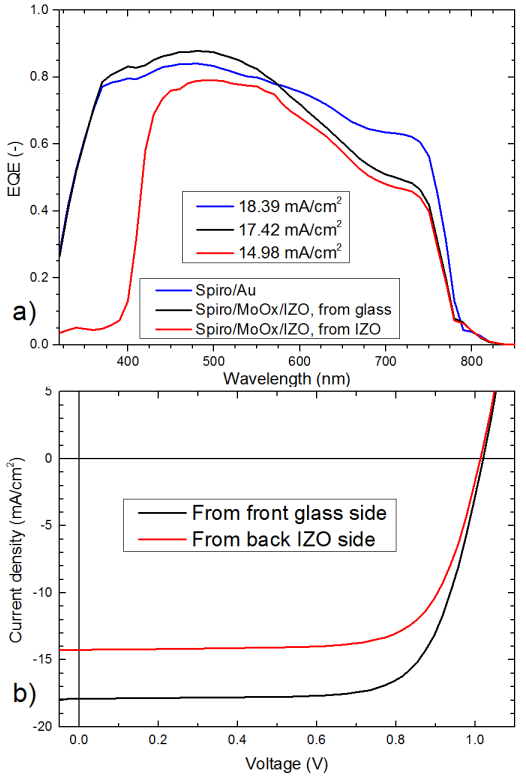

Figure 6 a) External quantum efficiency and b) current density-voltage measurements of a semitransparent perovskite cell with illumination from the front glass side (black curves) and with illumination from the rear spiro side (red curves).

7. SIMULATIONS AND MODELLING

In order to optimize four-terminal and monolithic tandems, optical simulations and modelling are useful tools to provide guidelines on layer thicknesses, device architecture, appropriate light management schemes and materials choices to ensure minimal parasitic absorption and current matching between sub-cells.

The upper efficiency limit of a perovskite/c-Si tandem can be estimated by assuming no parasitic absorption losses and equals to 37.04% in the case of a four-terminal tandem with a top cell with Lambertian light trapping and step-function back reflector [17]. In the case of a monolithic tandem, the efficiency limit is 35.67%, with current matching and optical coupling. The monolithic case is shown as more practically feasible, compared to the idealistic step-function back reflector necessary in a four-terminal tandem [17]. However as it has been shown in the previous sections, parasitic absorption losses are inherent to a real device. It is then interesting to assess the loss mechanisms and estimate the potential of a given solar cell if these losses could be removed. Using this approach, the efficiency limit of a perovskite/c-Si four-terminal tandem cell was estimated at 31.6% [10].

Numerical optical simulations of monolithic and four-terminal tandem cells can then provide guidelines on the choice of materials, layer thicknesses and effects of a texture [18]. This study showed that the parasitic absorption losses in spiro-MeOTAD are so strong that it will have to be replaced by a more transparent material to reach monolithic tandem efficiencies beyond the single-junction silicon cell record value of 25.6%.

Finally, the optimal top cell should have a band gap of 1.75 eV (compared to ~1.55eV of the commonly used $CH_3NH_3PbI_3$ perovskite material) when combined to a silicon bottom cell having a band gap of 1.12 eV. This combination would ensure maximal efficiency in a monolithic tandem.

8. CONCLUSIONS

In conclusion, we have shown that perovskite materials are excellent top cell candidates for tandem applications, having a sharp band edge with low sub-bandgap absorption. We developed a broadband transparent electrode using a sputtered TCO to replace the opaque metal rear contact and could show efficiencies of up to 14.7%$_{rev}$ for semitransparent perovskite solar cells. We then presented four-terminal tandems with total efficiencies of up to 24%$_{rev}$ and stabilized at 22.8%$_{mpptracker}$, surpassing both sub-cell single performances. In monolithic tandems, first results with high-temperature mesoscopic cells were presented on silicon homojunction solar cells. Finally, we presented device optimization guidelines and efficiency limits by optical simulations and modelling. This work represents a further step towards tandem cells with performance beyond the current single-junction silicon record efficiency at affordable costs.

9. ACKNOWLEDGEMENTS

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