Thin Film Photovoltaics
Device Fabrication and Characterization

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Abstract

In the last couple of years, the manufacturing costs of silicon solar cell technology has declined substantially resulting into high driving efforts by industries and governments to establish solar power as a cornerstone for planet earth's demand of power. At the Optical Materials Engineering Laboratory at ETH, we built photovoltaic cells in order to understand the process of energy generation in semiconductors. In fact, the light-harvesting active layers we utilized for our evaluation was a perovskite structured compound named Methylammonium Lead Halide. We evaluated the electrical characteristics of a commonly used solar cell compared to the assembled perovskite solar cells and found profound differences between both cells - quantitatively and qualitatively.

1. Introduction

Every year the demand for energy continues to rise, due to worldwide population and economic growth. As our supply of fossil fuels are finite and peak oil is around the corner, the search for alternative sustainable energy sources is one of the most important challenges of the twenty-first century. Solar energy is a very promising solution to this problem. In order to convert solar into electrical power, photovoltaics (PV) emerged as a market in the last two decades. The core component of PV is the solar cell, which uses the photoelectric effect to turn light into electricity. Meanwhile there are a handful of different types of solar cells, the most common kind is made of single crystalline silicon. As it has its disadvantages, such as high fabrication costs, due to the required purity of the silicon, poor mechanical characteristics or limited efficiencies, we are going to compare it to perovskite solar cells in this practicum.

In modern research the term perovskite describes all materials that have a similar structure to calcium titanate, which means its chemical formulae have an ABX3 pattern. In this case A and B represent a cation and X stands for an anion (as seen in Fig. 1).

In the most commonly studied perovskite structures, X is also a halogen atom. Depending on the halide content, the optical bandgap is between 1.5 and 2.2 eV, which means perovskite cells have a finely tunable continuous bandgap, a big advantage compared to silicon cells
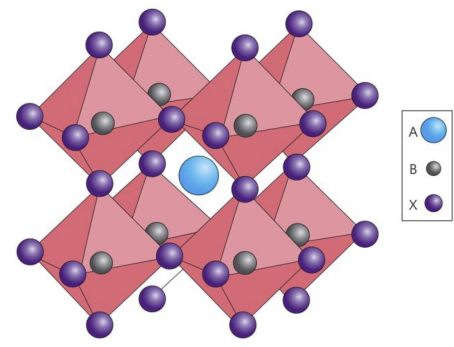

Figure 1: Crystal Structure of a Perovskite Compound

[Eperon et al. (2014)].

The perovskite layer however, is only responsible for absorbing the incidental radiation. In this experiment we use Titanium dioxide, which is an electron selective material, on the anode side of the cell. On the cathode side of the perovskite layer we use Copper thiocyanate as a hole selective contact material. When light hits the perovskite and consequently charges are generated, the electrons and the holes of the excitons are transported through the perovskite layer to charge their respective selective contacts and prevent them from recombining. This process only works in one direction, which means the solar cell acts as a diode. In order to produce solar power we connect the anode and the cathode through an external circuit where the electrons and the holes can then recombine.

It is very expensive to produce silicon solar cells, due

to processes which need to be conducted in clean room facilities in a vacuum at very high temperatures. Perovskite cells however, can be manufactured much simpler in wet laboratory conditions. The production can be scaled up easily as well, due to the techniques used to produce the main components (methylammonium and formamidinium lead trihalides).

One of the big disadvantages of perovskite solar cells is their short and long-term stability. External environmental factors such as moisture or oxygen in addition to process variables like temperature and ultraviolet influence are the main contributors to instability. Moisture leads to the decay of perovskite cells as the organic materials on the absorbing element are water-soluble [Bryant et al. (2016)] [Chun-Ren Ke et al. (2017)].

A lot of advancements have been made resulting in cells that perform stable for up to 10000 hours. The cell we made for this practicum is rather primitive in the sense that the overall lab-environment was loosely set at ambient conditions. The effect of these conditions therefore had to be accounted for as well in the later analysis of our photovoltaic cells.

2. Materials and Methods

Preparation of a Perovskite Solar Cell

As a base for our cell, we use FTO (Fluorine doped Tin Oxide) coated glass slides. This material is optically transparent for letting the light hit the perovskite layer and conductive to pass generated currents through external wiring. As aforementioned the cell is highly sensitive to environmental influences which is why we need to clean the FTO slides with isopropanol in an ultra sonicator. We cover a quarter of the slides with tape in order to save some space to clamp the wires to after we assembled the cell. Next, we spin coat Titanium Isopropoxide on the FTO slide of the glass, which will act as the electron selective contact layer on the anode side of the cell. After we bake the slides in the furnace we apply the perovskite precursor solution in droplets onto the TiO2-coating. A hot plate solidifies the precursor, which is then subjected to drops of a Copper Thiocynate (CuSCN) solution. Finally, after hardening the hole selective contact layer, we spread some carbon powder on to the assembly and finish by attaching a second FTO covered glass slide with metal clips. Figure 2 illustrates the final products which are now prepared for the final examination.

Experimental Setup

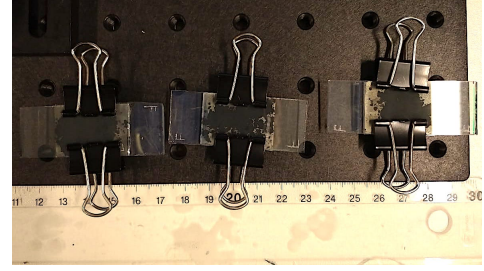The tools and parameters which are used for the evaluation of the electrical characteristics are as follows:

Figure 2: An Arrangement of Probes prepared for this Experiment

Table 1: Apparatus for the Experimental Setup

Tool	Specifications
Oriel Xe Lamp	300 W, collimated light
Filter	AM 1.5 global spectrum corresponds to an irradiance of $100 \frac{mW}{cm^2}$
Newport 818P-001-12	High sensitivity thermophile sensor
Keithley 2400	Semiconductor parameter analyzer
Origin	Data and analysis software

The stimulation of the reference solar cell as well as the assembled, three similar perovskite cells is achieved by the lamp and the filter. The filter has its purpose in simulating the solar spectrum. Since incoming light of the sun does not perpendicularly hit our solar cells, we assume that the air mass of 1.5 - that is 1.5 times the atmosphere thickness and therefore a net power density of $P_{inc} = 100$ mW/cm^2 - would be considered a good approximation. As a consequence, the thermophile sensor measures the light's intensity and the semiconductor parameter analyzer obtains the electrical data, connected to both terminals of the device under test. In total, four measurement sweeps are made and summarized in one spreadsheet file from the "Origin" data software.

Methods and Evaluation Process

The theoretical basis for the evaluation process is given by following characteristic parameters

- The current density J, which depends on the measured current and the area of each device

$$J = \frac{I}{A} \tag{1}$$

- The open voltage V_{OC}, which corresponds to the potential difference between both terminals while the device is disconnected from any circuit

- The short-circuit current I_{SC}, the current which flows through the solar cell when the potential between both terminals is zero (short-circuited) and ideally represents the light generated current

Usually, the short-circuit current depends on five key factors (as seen in Tab. 2)

Table 2: Key Factors contributing to the Short-Circuit Current

Tool	Specifications
Device Area	The higher the area, the higher the current
Number of incident Photons	The higher the incident power/irradiance of the light, the higher the number of protons
Spectrum of incident light	The intensity depends on the light's wavelength
Optical properties	The light absorption and reflection depends on the active-layer used
Probability of charge collection	Since the p-n junction cannot collect all incoming photons, the resulting current is rather probabilistic

In order to minimize the effect of all parameters to our problem, we eradicate the effects of different device areas by normalizing the current and observing the current density. In addition, we leave the number of photons i.e. the incident light as a constant in our experimental setup as well as the spectrum of the incident light by issuing a AM 1.5 spectrum via the filter. Therefore, the only key factors contributing to potential differences in each photovoltaic cell are the effect of absorption from the active layers and the charge collection probability from the p-n junction.

Efficiency of Solar Cells

One key selling point of energy generating devices is the efficiency. It also serves as a simple value to define the ratio between the energy output and the energy invested into the system. The calculations are the following:

$$FF = \frac{J_{max}V_{max}}{J_{SC}V_{OC}} \qquad (2)$$

The "Fill Factor" FF describes the ratio between the highest achieved, measured net power and the theoretically achievable power if the photovoltaic cell could operate from an open-circuit voltage and a short-circuited current. Graphically, it can interpreted as the ratio of two rectangular areas in a $J - V$ plot. FF is often referred as the "quality" of solar cells [National Instruments (2012)].

The power conversion efficiency is evidently given by the ratio of the measured, maximum power P_m and the "invested" power, coming from our light source.

$$\eta_{PV} = \frac{J_{SC}V_{OC} \cdot FF}{\left(\frac{P_{inc}}{A_{device}}\right)} \qquad (3)$$

From the obtained data, our goal is to determine what contributions the factors of chosen active-layer and collection of charge probability do make qualitatively. As well, we determine quantitative differences of the Fill Factor and efficiency between perovskite photovoltaic cells and commonly used photodetectors.

In addition to the measurement at AM 1.5 conditions, we also measure an electrical sweep while the devices are not under illumination. The obtained currents while applying voltages at these conditions are referred to as dark currents [Wikipedia (2017)]. Even though no photon should be entering the device - according to theory - electrons and holes would still be able to diffuse into the p-n junction. These measurements could give us a good estimation of the stability of our perovskite cells.

In order to interpret the data correctly, we have to first think about what the effects of the voltage sweep would cause if we modeled our perovskite cell as p-n diodes. When no voltage is applied, the holes and the electrons in the perovskite cell are diffusing into their respective counterpart. With our built-in selective materials, the recombination is suppressed. This creates a voltage between both the P and N region. The exposure to sunlight generates new carriers and therefore increases the voltage. The arising potential difference can then be used for electricity. By connecting the analyzer, we apply voltage in both directions and measure the resulting currents. The width of the depletion layer increases for negative applied voltage and decreases while applying positive voltages. Consequently, the measured current should be very small (ideally zero) for negative voltages and very high for positive currents. In theory, a reverse bias would result into a leakage current (since the p-n diode is not ideal) and to a breakdown due to overheating, which results into a strong negative current. In the case of forward bias, the smaller width of the depletion zone causes a small voltage between both P and N region. The small resistance would convert into a short current for sufficiently high applied voltages, with a breakdown (also known as the knee) of the depletion layer at very high voltages. The cell J-V characteristics should therefore be similar as illustrated in Fig. 3.

3. Results and Discussion

From the obtained electrical sweeps, we calculated our looked for values, as seen in Tab. 3. The corresponding power densities are highlighted in Fig. 4 - 9 while Fig. 7 and 9 are zoomed in since they are not clearly visible in the most general curves. One can see a far stronger rise in the perovskite cell data in comparison to the reference
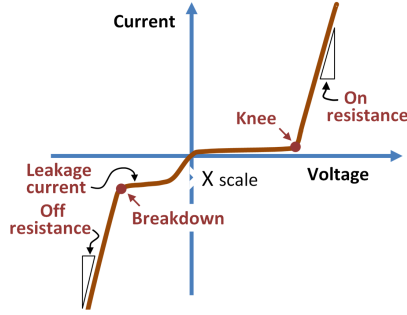
Figure 3: Typical behavior of a non-ideal p-n diode [Brews Ohare (2011)]

Table 3: Obtained Characteristics for the Reference Diode and all three Perovskite Solar Cells from the Measurement Sweeps

	Ref	S	P	X
J_{SC} $[\frac{mA}{cm^2}]$	−117.653	0.140	0.084	0.063
V_{OC} $[V]$	0.593	−0.390	−0.084	−0.371
Area $[cm^2]$	1	1.5	1.75	2
J_{max} $[\frac{mA}{cm^2}]$	−103.600	0.095	0.047	−0.039
V_{max} $[V]$	0.424	−0.390	−0.084	−0.371
FF $[\ ]$	0.629	0.419	0.258	0.371
η_{PV} $[\%]$	27.637	0.0344	0.00285	0.0174

Figure 4: Measurements of the Reference Photodiode under Illumination (green) and without any Illumination (blue)

Figure 5: Measurements of the "S"-Perovskite Solar Cell under Illumination (green) and without any Illumination (blue)

Figure 6: Measurements of the "P"-Perovskite Solar Cell under Illumination (green) and without any Illumination (blue)

silicon cell, this is especially visible in the P Cell (Fig. 6). One can observe a stark drop in current, after reaching the respective activation voltage, this is similar to the effect visible very well in the reference cell where the current stays constant and then changed after reaching the activation voltage. In the P and X Cell one can observe a hump around -0.75 V (Fig. 6 and 8), this is not visible in either the reference (Fig. 4) or the S Cell (Fig. 5). The calculated fill factors are similar to the values one would expect which is around 0.8 for most silicon cells. Even though the fill factor is not bad, the efficiency is very poor. Especially if compared to commercially available silicon cells which are around 25%. This is in one part due to the way we calculated it, which did not normalize for the power of the light bulb that hits the surrounding. This might also be due to strong manufacturing defects as well as the oxidation of the perovskites. These effects contribute to the factors we tried to isolate in the beginning. The decay of the active layer causes a lower probability to collect charges of any kind. In addition, the difference between the active layers used caused disparities between the devices tested. The photodiode does not show any kind of break down characteristics. At a far more negative voltage, we might be able to see a potential breakdown.
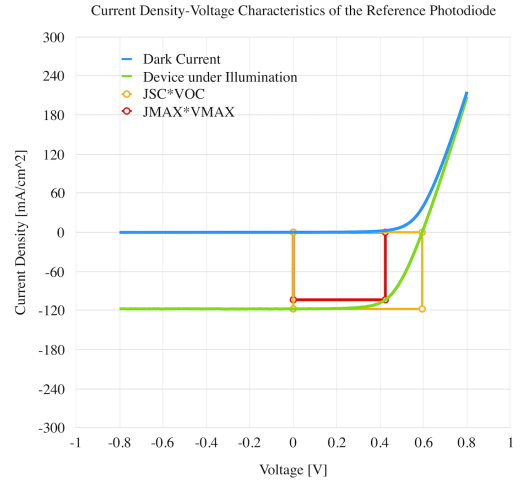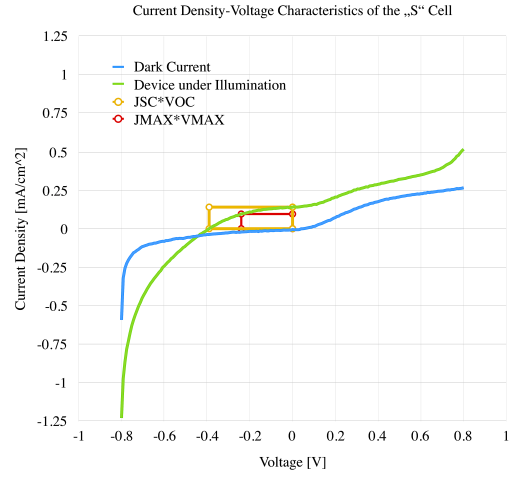
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Figure 7: Measurements of the "P"-Perovskite Solar Cell under Illumination (green) and without any Illumination (blue), magnified by scaling

Figure 8: Measurements of the "X"-Perovskite Solar Cell under Illumination (green) and without any Illumination (blue)

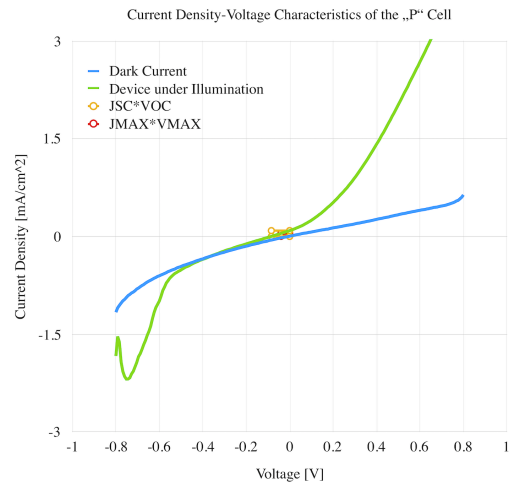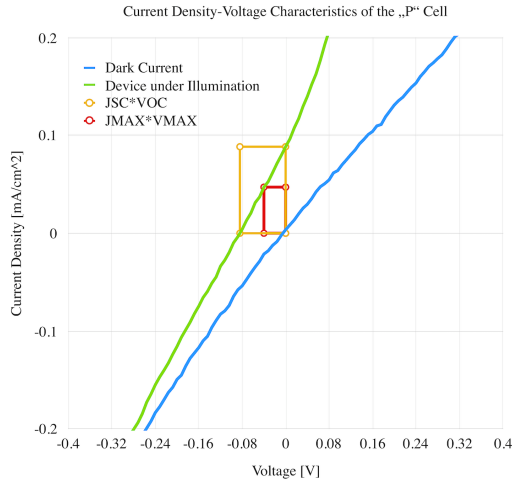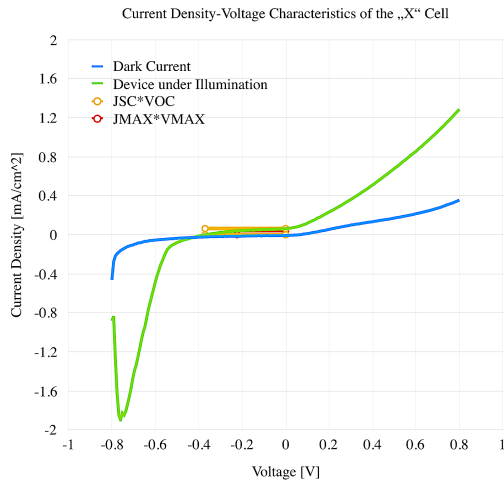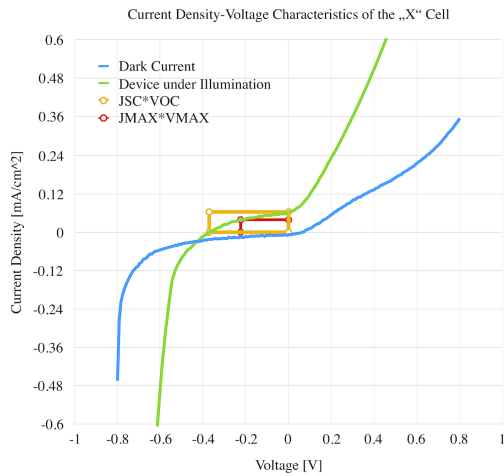Figure 9: Measurements of the "X"-Perovskite Solar Cell under Illumination (green) and without any Illumination (blue), magnified by scaling

4. Conclusions and Outlook

In general, we could observe major differences between the industry-fabricated silicon photodiode and the ones we produced in the laboratory. On one hand, the data for the photodiode follows a very strict relationship between the applied voltage and resulting current. The change after reaching activation voltage is very well visible and there is almost no ohmic part of the resistance. This is very different in the Perovskite cells, where in some parts the ohmic part strongly dominated the behavior, a small part increase was still visible after reaching the activation voltage. From this one can conclude that the Perovskite cells already were oxidizing and by far not perfect diodes anymore. This in part explains the very poor efficiency compared to the silicon cell. Other parts might stem from imperfect cristallization and defects that formed during the baking process, as our method was quite primitive and not meant to produce identical perfect cells. This can also be observed in the strong deviation of the different Perovskite cells even though there were produced in the same batch. Optimization potential would be to apply the heat in the baking process better. Also a machine coating of the chips would be better than doing so by hand, because this lead to big differences that could be observed with the eye already. Even though our measured efficiencies were low, the technology of Perovskite cells still has a lot of potential to help improve the cost effectiveness and energy effectiveness of solar power generation. If the problems with toxic materials and rapid oxidation can be handled and long term stability assured, this technology is more than just promising and might revolutionize renewable energy.

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5. References

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