Nanostructured Extremely Thin Absorber Solar Cells

**Master Thesis**

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Constance

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Related publication


Contribution through the measurement and analysis of impedance spectroscopy data.
1 Introduction and Fundamental Concepts
   1.1 Solar Power ......................................................... 1
   1.2 Working Principles of Heterojunction Solar Cells ................. 2
      1.2.1 Dye-Sensitized Solar Cells (DSSC) .......................... 5
      1.2.2 Solid State-Dye Sensitized Solar Cells (SS-DSSC) and Hybrid Solar Cells (HSC) ........................................... 6
      1.2.3 Organic Photovoltaic (OPV) and Bulk-Heterojunction (BHJ) Solar Cells .......................................................... 7
      1.2.4 Inorganic Heterojunction and Extremely Thin Absorber (ETA) Solar Cells ............................................................ 7
   1.3 Sb₂S₃-based Hybrid and ETA Solar Cells ............................ 8
   1.4 Chemical Bath Deposition of Sb₂S₃ ............................... 11
   1.5 Impedance Spectroscopy (IS) ....................................... 11
      1.5.1 Equivalent Circuits and Circuit Elements .................... 13
      1.5.2 Modeling and Data Fitting ...................................... 14

2 Experimental Methods and Characterization Techniques ............ 23
   2.1 Sb₂S₃ Growth ......................................................... 23
   2.2 Solar Cell Fabrication ............................................. 24
   2.3 Characterization Methods ........................................... 25
      2.3.1 Current-Voltage Characterization (I-V) ....................... 25
      2.3.2 External Quantum Efficiency (EQE) ............................ 28
      2.3.3 Absorption Measurements ...................................... 30
      2.3.4 Photo Voltage Decay (PVD) and Photo Current Decay (PCD) .. 31
      2.3.5 Impedance Spectroscopy ....................................... 32
      2.3.6 Film Thickness Measurements using Atomic Force Microscopy (AFM) 33

3 Fabrication of Sb₂S₃ Coatings .......................................... 35
   3.1 Flat Films on TiO₂ .................................................. 35
      3.1.1 Introduction ................................................... 35
      3.1.2 Experimental Methods ........................................ 35
      3.1.3 Results and Discussion ....................................... 37
   3.2 Coating of TiO₂ Nanostructures .................................... 39
      3.2.1 Introduction .................................................... 39
Abstract

The introduction of nanostructured metal oxides as electron acceptor resulted, among others, in the concept of extremely thin absorber cells. Thus, inorganic semiconductors like Sb$_2$S$_3$ can be utilized as sensitizer, which typically possess promising properties, such as a tunable band gap and a high extinction coefficient. Furthermore, low quality/crystallinity requirements of the layer due to a small thickness allow the application of low cost fabrication methods, such as chemical bath deposition. However, a detailed characterization of intrinsic properties is unavoidable in order to find the best device architecture and suitable material combinations for highly efficient solar cells.

This study focuses on the fabrication, optimization, and characterization of Sb$_2$S$_3$ coatings and Sb$_2$S$_3$ based solar cells. For this purpose, chemical bath deposition conditions and parameters, i.e., deposition temperature, positioning of the substrates, immersion time, and pre- and post-treatments have been examined and resulted in a detailed recipe for the fabrication of high quality Sb$_2$S$_3$ coatings. In combination with optimized layer thicknesses and crystallization conditions of Sb$_2$S$_3$ and P3HT, efficiencies of over 3.2% could be achieved with flat heterojunction solar cells.

In order to identify intrinsic limitations, which prohibit further improvement of efficiency, more detailed and comparative measurements with P3HT:PCBM cells have been done. Thus, revealing monomolecular recombination processes of excitons, a potential dependency of charge separation, and long charge carrier pathways as main loss mechanisms of fabricated flat heterojunction cells. Furthermore, investigation of several hole transport materials revealed a disadvantageous influence on charge generation due to the parasitic absorption of light by the hole transport material.

Based on the results obtained from Sb$_2$S$_3$ based flat heterojunction solar cells, the use of nanostructured metal oxides in combination with transparent hole transport materials is proposed to possibly overcome some of the found limitations.
# Abbreviations

<table>
<thead>
<tr>
<th>Symbol</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>$\eta$</td>
<td>power conversion efficiency</td>
</tr>
<tr>
<td>$\tau_{\text{PCD}}$</td>
<td>lifetime of charge carriers in photocurrent decay</td>
</tr>
<tr>
<td>$\tau_{\text{PVD}}$</td>
<td>lifetime of charge carriers in photovoltage decay</td>
</tr>
<tr>
<td>Ag</td>
<td>silver</td>
</tr>
<tr>
<td>AFM</td>
<td>atomic force microscope</td>
</tr>
<tr>
<td>Au</td>
<td>gold</td>
</tr>
<tr>
<td>BHJ</td>
<td>bulk heterojunction</td>
</tr>
<tr>
<td>CBZ</td>
<td>chlorobenzene</td>
</tr>
<tr>
<td>CuSCN</td>
<td>copper(I) thiocyanate</td>
</tr>
<tr>
<td>CdS</td>
<td>cadmium sulfide</td>
</tr>
<tr>
<td>CdSe</td>
<td>cadmium selenide</td>
</tr>
<tr>
<td>CdTe</td>
<td>cadmium telluride</td>
</tr>
<tr>
<td>CuInS$_2$</td>
<td>chalcopyrite copper indium sulfide</td>
</tr>
<tr>
<td>DPA</td>
<td>dipicolinic acid</td>
</tr>
<tr>
<td>EQE</td>
<td>external quantum efficiency</td>
</tr>
<tr>
<td>EtOH</td>
<td>ethanol</td>
</tr>
<tr>
<td>FF</td>
<td>fill factor</td>
</tr>
<tr>
<td>H$_2$O</td>
<td>water</td>
</tr>
<tr>
<td>HSC</td>
<td>hybrid solar cell</td>
</tr>
<tr>
<td>HOMO</td>
<td>highest occupied molecular orbital</td>
</tr>
<tr>
<td>HTM</td>
<td>hole transport material</td>
</tr>
<tr>
<td>$I_{\text{light}}$</td>
<td>photocurrent</td>
</tr>
<tr>
<td>$I_{\text{SC}}$</td>
<td>short circuit current</td>
</tr>
<tr>
<td>In-OH-S</td>
<td>indium hydroxy sulfide</td>
</tr>
<tr>
<td>IPCE</td>
<td>incident photon to current efficiency</td>
</tr>
<tr>
<td>IQE</td>
<td>internal quantum efficiency</td>
</tr>
<tr>
<td>ITO</td>
<td>indium tin oxide</td>
</tr>
<tr>
<td>KSCN</td>
<td>potassium thiocyanate</td>
</tr>
<tr>
<td>LiSCN</td>
<td>lithium thiocyanate</td>
</tr>
<tr>
<td>LUMO</td>
<td>lowest unoccupied molecular orbital</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>Poly[2-methoxy-5-(3′,7′-dimethyloctyloxy)-1,4-phenylenevinylene]</td>
</tr>
<tr>
<td>Abbreviation</td>
<td>Definition</td>
</tr>
<tr>
<td>--------------</td>
<td>------------</td>
</tr>
<tr>
<td>MPP</td>
<td>maximum power point</td>
</tr>
<tr>
<td>Na$_2$S$_2$O$_3$</td>
<td>sodium thiosulphate</td>
</tr>
<tr>
<td>N$_2$</td>
<td>nitrogen</td>
</tr>
<tr>
<td>NIR</td>
<td>near infrared</td>
</tr>
<tr>
<td>O$_2$</td>
<td>oxygen</td>
</tr>
<tr>
<td>OD</td>
<td>optical density</td>
</tr>
<tr>
<td>OPV</td>
<td>organic photovoltaics</td>
</tr>
<tr>
<td>P$_{\text{coll}}$</td>
<td>charge collection probability</td>
</tr>
<tr>
<td>P3HT</td>
<td>poly(3-hexylthiophene)</td>
</tr>
<tr>
<td>PBDTTT-C-T</td>
<td>poly([4,8-bis-(2-ethyl-hexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b’]dithiophene-2,6-diy1]-alt-[2-(2’-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diy1])</td>
</tr>
<tr>
<td>PC$_{60}$BM</td>
<td>[6,6]-phenyl-C$_{60}$-butyric acid methyl ester</td>
</tr>
<tr>
<td>PCD</td>
<td>photocurrent decay</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b’]dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)]</td>
</tr>
<tr>
<td>PEDOT:PSS</td>
<td>poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate)</td>
</tr>
<tr>
<td>PVD</td>
<td>photovoltage decay</td>
</tr>
<tr>
<td>R$_s$</td>
<td>series resistance</td>
</tr>
<tr>
<td>R$_{\text{sh}}$</td>
<td>shunt resistance</td>
</tr>
<tr>
<td>S</td>
<td>sulfur</td>
</tr>
<tr>
<td>SbCl$_3$</td>
<td>antimony trichloride</td>
</tr>
<tr>
<td>Sb$_2$S$_3$</td>
<td>antimony sulfide, stibnite</td>
</tr>
<tr>
<td>spiro-OMeTAD</td>
<td>(2,2’,7,7’-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9’-spirobifluorene)</td>
</tr>
<tr>
<td>TiCl$_3$</td>
<td>titanium(III) chloride</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>titanium dioxide</td>
</tr>
<tr>
<td>UV-Vis</td>
<td>ultraviolet-visible spectroscopy</td>
</tr>
<tr>
<td>V$_{\text{OC}}$</td>
<td>open circuit voltage</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>tungsten trioxide</td>
</tr>
</tbody>
</table>
1 Introduction and Fundamental Concepts

In the last 100 years, electricity and energy in general has become one of the main assets of modern civilization. In just the last 40 years, the global demand for energy and electricity has almost doubled and will double again with the current policy within the next 20 years.\cite{1} However, electricity is a form of energy and energy comes at a price. This is the reason why cheap fossil fuels are still the main source, even if renewable energies, such as wind, hydro, and particularly solar power have significant potential to produce cheap and clean electricity.

1.1 Solar Power

Assuming the contour of the earth as a circle with the diameter of the earth ($\sim 12000 \text{ km}$) and the mean incoming solar radiation, given by the solar constant ($\approx 1360 \text{ W/m}^2$)\cite{2}, the sun delivers an energy of about $10^5 \text{ TW}$ in every single second and therefore about $10^9 \text{ TWh}$ per year. This is $5 \cdot 10^4$ times more than the current world wide electricity generation and still about $1 \cdot 10^4$ times more than the world’s energy consumption in 2010, which was about 21431 TWh.\cite{1}

![Figure 1.1: Global direct normal irradiance of sunlight. \cite{3}](image)

Of course this is only a rough estimate and due to the losses in and to the atmosphere this is not the power that arrives on the ground. But even 10% of this light on 1% of the
1.2 Working Principles of Heterojunction Solar Cells

earth’s surface (the most promising areas are shown in Figure 1.1), converted with 10% efficiency would suffice to meet a large part of our energy demand.

The scope of this untapped potential has already been recognized with the presentation of the first silicon solar cell by Chapin et al. and the Bell Telephone Laboratories in 1954.\cite{4} Since then, many scientists have worked on silicon solar cells and improved the efficiency of initially 6%\cite{4} to near the detailed balance limit$^{1}$ of $\eta \sim 32\%$, as hypothesized by Shockley and Queisser in 1961.\cite{5} Current state-of-the-art single-crystalline Si cells show an efficiency of 25% and thin-film GaAs cells almost 29%.\cite{6} However, despite their high efficiencies, the fabrication of these solar cells is very expensive and environmentally unfriendly$^{2}$, reducing their environmental benefits and large-scale use.

The first known organic two-layer solar cell was introduced only a few years after the publication of Chapin et al., namely in 1958, by Kearns and Calvin.\cite{7} This was the cornerstone of organic and hybrid solar cells, with their huge advantages like solution processable layers, low energy and low temperature requirements (cheaper and less pollutant fabrication process), a potentially flexible design and in a wide range adjustable material properties. With the demonstration of by seven orders of magnitude increased polymer conductivities by Shirakawa et al., the subject became even more interesting.\cite{8} However, it took almost another 10 years before the first cell was presented, whose power conversion efficiency was at least in the range of 1%.\cite{9} The triumphal march of solar cells, which use the advantage of organic materials as photoactive material finally began in 1991 as Grätzel and O’Regan presented the first dye-sensitized solar cell with an efficiency of about 8%.\cite{10}

Since then, considerable effort has been done in this field of research and led to a multitude of different types of organic and hybrid solar cells, all of which have their specific advantages and disadvantages. Some of them will be explained in the following chapter in more detail.

1.2 Working Principles of Heterojunction Solar Cells

All types of solar cells must meet certain requirements to efficiently produce photocurrent, whether it is solar cells from silicon or organic material. They have to absorb light in order to generate free charge carriers, which are subsequently transported in preferred directions to the electrodes to avoid recombination processes.

In conventional silicon solar cells, these processes take place within a single layer of high crystalline silicon, which has a relatively high dielectric constant. While the high crys-
tallinity favors delocalization of charge carriers the dielectric constant decreases the potential wall of charge carrier separation.\[11\] Thus, absorption of incident light results almost instantly in creation of free charge carriers due to thermal separation of the low bounded (binding energy $\sim 10 \text{meV}$) Wannier-Mott excitons. Subsequently, separated charge carriers are transported to the electrodes by the internal electric potential difference, formed through the joining of the p- and n-doped regions of the crystal.

However, polymers used in hybrid and organic solar cells generally exhibit a low dielectric constant and poor crystallinity. Therefore, the absorption of light does not lead directly to free charge carriers, but rather to bound states called excitons. Figure 1.2 illustrates the generation, movement and recombination of excitons in organic solar cells.

![Figure 1.2: a) Generation, movement and b) recombination processes of Frenkel and charge-transfer (CT) excitons. (1) Frenkel excitons are generated throughout the absorbing layer and are moving by diffusive hopping transport (2). At interfaces or impurities they can relax into CT excitons (3) or completely dissociate into free charge carriers (4), which subsequently move towards the electrodes (5). Meanwhile recombination can occur at several steps, e.g., if the mean free path length of Frenkel excitons is shorter than their distance to the interface (6), when the separation time of CT excitons is sufficiently larger or they meet a surface defect (7) or when charge carriers of different excitons meet by chance at an interface (8). In nanostructured solar cells recombination additionally occurs in unconnected islands filled with one type of charge carriers (9).](image_url)

In organic solar cells absorption of light generates mainly Frenkel excitons, which are excited electron states localized on the absorbing molecule.\[12\] These excited states are generated (1) throughout the absorbing layer and can migrate within the material by diffusive incoherent hopping through the lattice, where they are scattered at each molecule and thus perform a random walk (2).\[12\]

Due to their high binding energy of about $0.25 - 0.35 \text{eV} \gg k_B T$ neither thermal energy nor internal electric fields are sufficient to separate them.\[11\] However, at interfaces and impurities Frenkel excitons can relax into charge-transfer (CT) excitons (3) or completely dissociate into free charge carriers (4), which subsequently are transported to the electrodes (5).
Nevertheless, recombination may occur until the charge carriers have reached the electrodes. Frenkel excitons generally recombine in the absorbing material if their mean free path length, typically about 10 nm, is shorter than their distance to an interface or impurity (6). At interfaces, recombination of CT excitons occurs, when the separation time is sufficiently larger or when these excitons meet a surface defect (7) while moving along the interface. Additionally, charge carriers of separately generated excitons can recombine with each other, e.g., when they meet by chance at interfaces (8) or when there are unconnected islands of one material in structured solar cells (9).

The most fundamental geometry of organic or hybrid solar cells is a flat heterojunction arrangement of two active layers, as it is schematically shown in Figure 1.3 a). Either the donor, the acceptor, or both materials absorb light and generate free charge carriers as described above. Due to a well-defined choice of materials and associated energy level alignment, electrons and holes are mainly injected in a preferred direction as visualized in Figure 1.3 b). This results in a high chemical potential energy gradient at the interface, which is simultaneously the main driving force of the charge carriers to the electrodes in organic solar cells, since they do not exhibit such a high internal electric field silicon solar cells do.[11]

The blocking layers support the diode like behavior by preventing the charge carriers of migration to the wrong electrode. They typically consist of metal oxides, such as titanium dioxide (TiO$_2$) [13] and zinc oxide (ZnO) [14] for hole blocking or tungsten trioxide (WO$_3$) [15] and molybdenum trioxide (MoO$_3$) [16] for electron blocking. In addition, migration of excitons to the electrode-interface is blocked, preventing them to dissociate into the opposite direction of favored charge transport.

Figure 1.3: a) Schematic of a flat bilayer heterojunction solar cell and b) corresponding energy diagram, with two active layers (acceptor and donor), two blocking layers, a transparent conductive oxide (TCO) layer, and metallic back- and front contacts.

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1 Introduction and Fundamental Concepts

In this geometry, only thin layers of the absorbing material contribute to the generation of photocurrent since the typical mean free path length of excitons is in the range of a few nm. Therefore, flat heterojunctions are undesirable due to their typically poor device efficiency. For this reason, different approaches have been pursued in order to maximize the interface and simultaneously minimize the distance excitons have to travel. This resulted in various types of organic and hybrid solar cells like dye-sensitized solar cells (DSSC), where only one monolayer of dye is absorbing light, bulk heterojunction solar cells (BHJ), which consist of a mixed phase of acceptor and donor, and extremely thin absorber solar cells (ETA), which utilize materials with high absorption coefficients but still sufficient conductivity. The most important types are explained in more detail.

1.2.1 Dye-Sensitized Solar Cells (DSSC)

The introduction of mesoporous TiO$_2$ in dye-sensitized solar cells by Grätzel and O’Regan in the early 1990s was a major step in the development of efficient excitonic photovoltaic. They took advantage of sintered TiO$_2$ nanoparticles to create a $10 \mu$m thick, high surface framework ($\sim 60\%$ porosity), and subsequently coated it with a monolayer of strongly absorbing Ruthenium complex dye. In addition, a liquid electrolyte was used to transport holes. This results in a high absorption of light and simultaneously efficient exciton dissociation, because all excitons are generated directly at the interface. For this reason, DSSCs were, until recently, the most efficient excitonic solar cells with $12.3\%$ efficiency. Figure 1.4 illustrates a schematic of a typical DSSC.

![Figure 1.4: Schematic illustration of a dye-sensitized solar cell, utilizing mesoporous TiO$_2$ to produce a high surface area, which is coated with a monolayer of strong absorbing dye. A liquid electrolyte is used for transportation of holes to the electrode.](image)

Advantages of liquid electrolytes are their high electrochemical stability and good solvent properties, such as the great ability to penetrate porous structures and short range charge screening. Specifically, the charge screening increases the extraction probability of charge carriers and prevents recombination at the TiO$_2$-dye-electrolyte interface due to a smaller attraction of opposite charges. However, solar cells with liquid electrolytes have to be sealed tightly, since leakage of most solvents is environmentally hazardous and, due to their operating principle, destroys them.
1.2 Working Principles of Heterojunction Solar Cells

1.2.2 Solid State-Dye Sensitized Solar Cells (SS-DSSC) and Hybrid Solar Cells (HSC)

To directly address the technical challenges of sealing DSSCs, research has focused on solid hole transport materials (HTM), such as poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS)\textsuperscript{[22]}, (2,2',7,7'-Tetrakis[N,N-di(4-methoxyphenyl)amino]-9,9'-spirobifluorene) (spiro-OMeTAD)\textsuperscript{[23–30]}, poly(3-hexylthiophene) (P3HT)\textsuperscript{[31–34]}, poly[2,6-(4,4-bis-(2-ethylhexyl)-4H-cyclopenta[2,1-b;3,4-b']-dithiophene)-alt-4,7-(2,1,3-benzothiadiazole)] (PCPDTBT)\textsuperscript{[35]}, poly[2-methoxy-5-(3',7'-dimethyloctyloxy)-1,4-phenylenevinylene] (MDMO-PPV)\textsuperscript{[36]}, poly([4,8-bis-(2-ethylhexyl-thiophene-5-yl)-benzo[1,2-b:4,5-b']dithiophene-2,6-diyl]-alt-[2-(2'-ethyl-hexanoyl)-thieno[3,4-b]thiophen-4,6-diyl]) (PBDTTT-C-T)\textsuperscript{[37, 38]} and many others, wherein P3HT, PCPDTBT, MDMO-PPV and PBDTTT-C-T serve not only as a HTM but also as a light absorber.

From this, solid state dye sensitized solar cells (SS-DSSC) and hybrid solar cells (HSC) have been developed, which have a similar configuration as DSSCs, as shown in Figure 1.4, except the electrolyte is replaced with the HTM. Specifically, in SS-DSSCs free charge carriers are generated only by the dye, whereas in HSCs both the dye and the HTM contribute to light absorption and generation of free charge carriers.

But even with the enhanced and complementary light absorption by the HTM\textsuperscript{[28, 39, 40]} and other benefits over DSSCs, SS-DSSCs and HSCs can still not compete due to their relatively low efficiencies of about 7%\textsuperscript{[22, 30]} and $\sim 3.8$%\textsuperscript{[28, 41]}, respectively.

Meanwhile, new structures, such as nanowires\textsuperscript{[42]}, nanotubes\textsuperscript{[28]} and inverse opal structures\textsuperscript{[43]} have been produced in order to improve charge carrier pathways and to address the challenges of pore-filling typically found in mesoporous TiO$_2$. Figure 1.5 illustrates schematics of these new structures. However, their efficiencies still trail mesoporous TiO$_2$.

![Schematic illustration of different nanostructured morphologies. a) Nanowires, b) Nanotubes and c) inverse opal structure.](image-url)

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1.2.3 Organic Photovoltaic (OPV) and Bulk-Heterojunction (BHJ) Solar Cells

Organic photovoltaics (OPV) have been developed parallel to the DSSC architecture, whereas TiO$_2$ is still used as hole blocking layer, leaving the part as electron acceptor to organic compounds like [6,6]-phenyl-C$_{60}$-butyric acid methyl ester (PC$_{60}$BM) or PC$_{70}$BM, which are commonly used C$_{60}$ and C$_{70}$ derivatives. In combination with one of the above mentioned absorbent HTMs as donor, organic photovoltaics are usually fabricated in a mixed-phase morphology, called bulk-heterojunction (BHJ) (Figure 1.6).

![Figure 1.6: Schematic illustration of an organic bulk heterojunction solar cell.]

The morphology of these mixed phases can be manipulated through selection of solvent, varying spin-coating parameters, or subsequent annealing procedures, but not directly controlled. Nevertheless, optimization of morphology and material combinations results in efficiencies of up to 9.2%.[^44^]

1.2.4 Inorganic Heterojunction and Extremely Thin Absorber (ETA) Solar Cells

Furthermore, inorganic semiconductors are suitable as sensitizers in solar cells. They can either replace organic dyes, due to their high absorption coefficient in the visible range[^35^], be used as a high conductivity[^3^] HTM as copper(I) thiocyanate (CuSCN)[^45^–^48^], or they can simultaneously be used in completely inorganic heterojunction solar cells. The latter was done by Boix et al. and Kaiser et al., offering the prospect of long-term stability.[^21^, ^49^]

The high absorption coefficient led to the new concept of extremely thin absorber (ETA) solar cells, wherein only the thin absorber layer contributes to charge generation and, thus, enhances fast charge separation and reduces recombination of opposite charge carriers.[^46^, ^50^] For this purpose promising materials, such as cadmium sulfide (CdS)[^48^, ^51^],

[^3]: compared to organic HTMs
chalcopyrite copper indium sulfide (CuInS$_2$)$^{[49]}$, cadmium telluride (CdTe)$^{[52]}$, cadmium selenide (CdSe)$^{[53]}$ and antimony sulfide (Sb$_2$S$_3$)$^{[35, 54-56]}$ have been investigated. These compounds have additional advantages over organic absorbers and frequently used dyes, as a large intrinsic dipole moment, uncomplicated ways of band-gap adjustment and even possible generation of multiple excitons out of a single photon.$^{[57]}$ Moreover, ETA cells exhibit lower crystallinity requirements due to the small thickness of the absorber and allows the use of low cost fabrication methods, such as chemical bath deposition (CBD).

Until recently, the highest efficiencies in this area was $\sim 6\%$ and was obtained with Sb$_2$S$_3$ on mesoporous TiO$_2$ in combination with PCPDTBT as HTM.$^{[35]}$ However, recent developments resulted in a new generation of mixed inorganic-organic sensitizers with perovskite structure, which are even able to outperform DSSCs and already result in efficiencies of $\sim 12\%$.\cite{18, 58}

1.3 Sb$_2$S$_3$-based Hybrid and ETA Solar Cells

The research on new materials brought forth antimony sulfide (Sb$_2$S$_3$), or stibnite as it is called in its crystalline form, as a promising candidate for high performance solar cells. Sb$_2$S$_3$ has a relatively high occurrence in the earth’s crust.$^{[59, 60]}$ Additionally, Sb$_2$S$_3$ has other favorable properties, such as a large intrinsic dipole moment$^{[55]}$, a suitable optical band gap ($\sim 1.7 - 1.9$ eV)$^{[35, 54, 55, 57, 60-65]}$, n-type behavior$^{[66]}$, a high dielectric constant (9.6 – 14.4, depending on the crystallinity)$^{[67, 68]}$, and a good band alignment in combination with various HTMs$^{[54]}$ (see Figure 6.1). While good band alignment is primarily beneficial for exciton dissociation and charge carrier transfer at the interface, a high dielectric constant allows separation of charge carriers directly inside the bulk, provided that the crystallinity is high enough.$^{[54, 69, 70]}

The high extinction/optical absorption coefficient of $1.8 \cdot 10^5 \text{ cm}^{-1}$ in the visible range$^{[35, 54, 57, 60, 62, 63]}$ further allows the production of extremely thin absorber cells, since the absorption of a 150 nm thick Sb$_2$S$_3$-film equals the light absorption of a 1 $\mu$m thick amorphous Si-film$^{[54]}$ and reduces production costs even further. Incident photon to conversion efficiency (IPCE) or external quantum efficiency (EQE) (see Section 2.3.2) exhibit values of $> 80\%$ across the whole visible region$^{[55, 57, 64]}$, whereas measurements in an integrative sphere reveal an absorption onset at $\sim 700 - 750 \text{ nm}$.$^{[63]}$

All these benefits led to the investigation of many different combinations of materials, morphologies, and deposition techniques in order to optimize performance and stability of fabricated solar cells. A brief overview of the last years of research is summarized in Table 1.1.
1 Introduction and Fundamental Concepts

Table 1.1: Summarized overview of research on Sb$_2$S$_3$ based solar cells of recent years.

<table>
<thead>
<tr>
<th>Metal oxide</th>
<th>Deposition method</th>
<th>HTM</th>
<th>Surface treatment</th>
<th>PCE @ 100 mW/cm$^2$</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD 5 – 10 nm</td>
<td>CuSCN</td>
<td>In-OH-S for TiO$_2$</td>
<td>3.37 %</td>
<td>[64]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD $\sim$ 1 – 3 nm</td>
<td>CuSCN</td>
<td>LiSCN for Sb$_2$S$_3$</td>
<td>3.7 %</td>
<td>[50]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD up to 20 nm</td>
<td>spiro-OMeTAD$^1$</td>
<td>In-OH-S for TiO$_2$</td>
<td>3.1 %</td>
<td>[55]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD</td>
<td>P3HT + PEDOT:PSS</td>
<td>DPA</td>
<td>5.13 %</td>
<td>[62]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD</td>
<td>CuSCN</td>
<td>KSCN for Sb$_2$S$_3$</td>
<td>3.25 %</td>
<td>[71]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD</td>
<td>P3HT</td>
<td>Mg$^{2+}$, Ba$^{2+}$, Al$^{3+}$ for TiO$_2$</td>
<td>4.1 %</td>
<td>[72]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>CBD</td>
<td>CuSCN</td>
<td>LiSCN for Sb$_2$S$_3$</td>
<td>2.6 %</td>
<td>[73]</td>
</tr>
<tr>
<td>TiO$_2$ nanowires</td>
<td>CBD 1060 nm</td>
<td>P3HT + PEDOT:PSS</td>
<td>-</td>
<td>4.65 %</td>
<td>[60]</td>
</tr>
<tr>
<td>flat ZnO</td>
<td>thermal evaporation 100 nm</td>
<td>P3HT 40 nm</td>
<td>-</td>
<td>2.4 %</td>
<td>[54]</td>
</tr>
<tr>
<td>ZnO array of nanowires</td>
<td>thermal evaporation</td>
<td>P3HT</td>
<td>-</td>
<td>2.9 %</td>
<td>[63]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>ALD$^2$ 9 nm</td>
<td>CuSCN</td>
<td>LiSCN for Sb$_2$S$_3$</td>
<td>2.6 %</td>
<td>[73]</td>
</tr>
<tr>
<td>mesoporous TiO$_2$</td>
<td>SILAR$^3$</td>
<td>polysulphide electrolyte</td>
<td>-</td>
<td>&lt; 0.3 %</td>
<td>[74]</td>
</tr>
<tr>
<td>TiO$_2$ nanowires</td>
<td>SILAR$^3$</td>
<td>polysulphide electrolyte</td>
<td>-</td>
<td>$\sim$ 1.5 %</td>
<td>[75]</td>
</tr>
</tbody>
</table>

$^1$ with 3 additives  
$^2$ atomic layer deposition  
$^3$ successive ionic layer adsorption and reaction
1.3 \( \text{Sb}_2\text{S}_3 \)-based Hybrid and ETA Solar Cells

Investigations include ZnO and TiO\(_2\) as flat and nanostructured electron acceptor, CuSCN, P3HT, PCPDTBT, spiro-OMeTAD, and liquid electrolytes as hole conductors, and various surface modifiers, such as indium hydroxy sulfide (In-OH-S), potassium thiocyanate (KSCN), lithium thiocyanate (LiSCN), and dipicolinic acid (DPA) in order to improve the interfaces.

In this case, TiO\(_2\) is by far the most frequently used metal oxide for mesoporous and nanowire structures, although coating of TiO\(_2\) by \( \text{Sb}_2\text{S}_3 \) is less than optimal due to a crystal lattice mismatch. Several groups demonstrated independently a homogeneous coating of TiO\(_2\) by \( \text{Sb}_2\text{S}_3 \) directly after chemical bath deposition\(^{[35, 55]}\) and atomic layer deposition (ALD)\(^{[73]}\). However, after annealing the initially amorphous layers, \( \text{Sb}_2\text{S}_3 \) crystallized into stibnite and formed clusters and particles rather than a homogeneous layer. In combination with CuSCN as HTM this was shown to result in enhanced charge carrier recombination at the TiO\(_2\)-\( \text{Sb}_2\text{S}_3 \)-CuSCN triple-interface due to surface states in the \( \text{Sb}_2\text{S}_3 \).\(^{[71]}\) Alternatively, scanning electron microscopy images of \( \text{Sb}_2\text{S}_3 \) on ZnO showed good surface coverage when deposited by thermal evaporation.\(^{[63]}\)

Apart from the expense and scalability for mass production, the deposition technique additionally appears to have a significant impact on the final efficiency of the solar cell. Since the deposition technique determines the coverage of the substrate as well as the crystallinity of the \( \text{Sb}_2\text{S}_3 \) after annealing, it plays an important role on both nanostructured electrodes and flat films. This draws attention to the interfaces of \( \text{Sb}_2\text{S}_3 \) and how they can be optimized.

As a result, several surface modifiers have been investigated. Specifically, indium hydroxy sulfide (In-OH-S) was proven to have a beneficial effect on the metal oxide-\( \text{Sb}_2\text{S}_3 \) interface, since it prevents \( \text{Sb}_2\text{S}_3 \) from oxidizing.\(^{[55, 64]}\) Investigations by Tsujimoto et al. also revealed general improvements in power conversion efficiencies by using Mg\(^{2+}\), Ba\(^{2+}\) and Al\(^{3+}\) as surface modifier, which enhance fill factor (FF) and open circuit Voltage (V\(_{\text{OC}}\)) of the solar cells. Alternatively, potassium thiocyanate (KSCN) and lithium thiocyanate (LiSCN) are frequently used surface modifiers of the \( \text{Sb}_2\text{S}_3 \)-HTM interface\(^{[50, 64, 71–73]}\), and lead to lower series resistance and higher V\(_{\text{OC}}\)\(^{[50]}\) when copper thiocyanate is used as HTM. For other HTMs, surface modification is less common since many polymers show a different behavior due to their molecular structure. This was particularly illustrated by the bonding of thiophene rings to \( \text{Sb}_2\text{S}_3 \) by Im et al.\(^{[35]}\)

Although efficiencies exceeding 4% have been achieved\(^{[76]}\), \( \text{Sb}_2\text{S}_3 \) in DSSCs seems to be a poor choice, since it is unstable in contact with liquid electrolytes.\(^{[55, 64, 74, 77]}\) Alternatively, Cardoso et al. could show that solid state \( \text{Sb}_2\text{S}_3 \) based solar cells with P3HT as HTM are stable for at least six months stored in ambient air.\(^{[60]}\)
1.4 Chemical Bath Deposition of Sb$_2$S$_3$

Compared to other deposition techniques like atomic layer deposition$^{[73]}$, successive ionic layer adsorption and reaction (SILAR)$^{[74]}$ and thermal evaporation$^{[63]}$, chemical bath deposition is technically easy to implement, less pollutant, least expensive, feasible at low temperatures and scalable for mass production.$^{[61]}$

First reports of CBD of Sb$_2$S$_3$ date back to the 1990s and describe the key factors for obtaining high quality films.$^{[61, 78]}$ These include concentration of the precursors, temperature and pH value of the deposition bath as well as subsequent annealing conditions.

Initially CBD was performed at room temperature utilizing potassium antimonyl tartrate, triethanolamine and ammonia as starting materials. Subsequently, the reaction was initiated by adding thioacetamide, leading to a slow release of Sb$^{3+}$ and S$^{2-}$, which combines to Sb$_2$S$_3$.$^{[61]}$

Further improvement of the reaction pathways by Nair et al. in 1998 and their adaptation by Messina et al. in 2007 resulted in a less complex procedure, which became the standard recipe for CBD of Sb$_2$S$_3$ as ETA.$^{[65, 79]}$ Therefore, a molar solution of sodium thiosulfate (Na$_2$S$_2$O$_3$) in 25 ml H$_2$O and antimony trichloride (SbCl$_3$) in 2.5 ml acetone has to be prepared and filled with water to make a volume of 100 ml.$^{[65]}$

However, the deposition temperature plays a significant role since the reaction speed and therefore the rate of release of Sb$^{3+}$ and S$^{2-}$ is temperature dependent, rendering processing temperatures below 10 °C favorable for deposition of homogeneous coatings. Additionally, a gradient in temperature was shown to be beneficial for adhesion of deposited films. In the study by Messina et al. films deposited at constant temperatures below 5 °C detached easily from the substrate during rinsing with water.$^{[65]}$

1.5 Impedance Spectroscopy (IS)

Impedance spectroscopy (IS) is a frequently used tool to gain more information about the internal physical processes of solar cells$^{[21, 41, 71, 80–83]}$ and their intrinsic properties, such as conductivity, mobility of charge carriers, or bulk generation-recombination rates.$^{[84, p.4]}$ Even the complete I-V curve can be reconstructed, if at least one point of it is known.$^{[85]}$

In order to measure an impedance spectra a small electric perturbation is applied, which can be done either by applying a known voltage or current to the cell, and the resulting signal is recorded.
In the standard technique, this is done by applying a sinusoidal single-frequency voltage

\[ V(t) = V_0 \cdot \sin(\omega t) \]  \hspace{1cm} (1.1)

where \( V_0 \) is the amplitude of the signal and measuring at the same angular frequency \( \omega \) the amplitude \( I_0 \) of the resulting current

\[ I(t) = I_0 \cdot \sin(\omega t + \varphi) \]  \hspace{1cm} (1.2)

which is additionally shifted by a phase angle \( \varphi \). After subsequent Fourier transformation \((FT\{\})\) of initial perturbation \( V(t) \) and measured current response \( I(t) \) from time into frequency domain, both signals can be easily associated with the impedance as

\[ Z(\omega) = \frac{FT\{V(t)\}}{FT\{I(t)\}} = \frac{V(\omega)}{I(\omega)} = Z' + iZ'', \]  \hspace{1cm} (1.3)

where \( i \) is the imaginary number and \( Z' \) and \( Z'' \) are the real and imaginary part of the impedance, respectively. Since the impedance is frequency dependent, this measurement is repeated usually for frequencies between \( 10^{-3} \) and \( 10^6 \) Hz.

However, a single impedance spectrum contains only a limited space for physical interpretation, which is why several measurements have to be performed at different steady-state conditions. Specifically, in solid state solar cells this can be done, i.e., by applying an additional DC voltage, illuminating the sample, or both.

By treating the system as linear and time-invariant in each single steady-state condition, the combination of several circuit elements mathematically simplifies in frequency domain to an Ohm’s law-like behavior. Otherwise, impedance would be dependent on the perturbation amplitude and solving differential equations as for capacities

\[ I(t) = \left( \frac{dV(t)}{dt} \right) C \]

and inductors

\[ V(t) = \left( \frac{dI(t)}{dt} \right) L, \]

or even an entire system of them would be necessary.

In practice linearity can be assumed if the applied perturbation is in the order of the thermal voltage, i.e., 25 mV or less.
1 Introduction and Fundamental Concepts

1.5.1 Equivalent Circuits and Circuit Elements

Analysis of impedance data can be done either by developing a reasonable physical theory with correct mathematical derivation or by comparing and fitting of equivalent circuits to the experimental data. The latter is a rather empirical but also very common method of analysis, wherein the interpretation is the challenging part.

An overview of the most frequently used elements is listed in Table 1.2. Among these are not only ideal elements such as resistors or capacitors, but also distributed elements such as constant phase elements (CPE and QPE) which can be justified by the fact that the different layers and interfaces in the cell are not homogeneous or have a certain extension.

Table 1.2: Common electrical circuit elements used in IS.\cite{86, p.15} Formulas for impedance containing imaginary number i, angular frequency $\omega = 2\pi f$ and the symbols for corresponding circuit elements. For ideal resistors $R$, capacitors $C$ and inductors $L$ and non-ideal capacities $T$ and $Q$ in constant phase elements.

<table>
<thead>
<tr>
<th>Circuit Element</th>
<th>Symbol</th>
<th>Impedance</th>
<th>Diagram</th>
</tr>
</thead>
<tbody>
<tr>
<td>Resistance</td>
<td>R</td>
<td>$R$</td>
<td>$\Box$</td>
</tr>
<tr>
<td>Capacitance</td>
<td>C</td>
<td>$\frac{1}{i\omega C}$</td>
<td>$\Box$</td>
</tr>
<tr>
<td>Inductance</td>
<td>L</td>
<td>$i\omega L$</td>
<td>$\Box$</td>
</tr>
<tr>
<td>Constant phase element (CPE)</td>
<td>$T_p$</td>
<td>$\frac{1}{(i\omega)^p T}$</td>
<td>$\Box$</td>
</tr>
<tr>
<td>Constant phase element (QPE)</td>
<td>$Q_n$</td>
<td>$\frac{1}{(i\omega Q)^n}$</td>
<td>$\Box$</td>
</tr>
</tbody>
</table>

These elements can be connected either in parallel, in series, or in a much more complicated way to fit the experimental data. However, rearranging circuit elements in equivalent circuits with 3 or more elements can still result in the same impedance at all frequencies as can be seen for the circuits in Figure 1.7. Therefore, the simplest possible equivalent circuit with best fit results should be used.\cite{84, p.93}

Figure 1.7: Same impedance at all frequencies possible in a) Voight-, b) Maxwell- and c) Ladder-representation of equivalent circuit, if values of the components are matching.\cite{84, p.92}
1.5 Impedance Spectroscopy (IS)

1.5.2 Modeling and Data Fitting

To find the most appropriate model is a challenging task. A common strategy to do this is by looking at the experimental data and identifying the necessary components in the Nyquist or impedance plane plot $Z'$ vs. $Z''$. Additionally, different representations for impedance and its corresponding functions and illustrations like admittance, bode plots\(^4\) or complex capacitance plane plots are very valuable and can provide additional information about the system.\(^{[84, p.7]}\)\(^{[86, p.14]}\) The most frequently used representations are listed in Table 1.3.\(^{[86, p.15]}\)

Table 1.3: Different representations and corresponding functions of impedance\(^{[86, p.15]}\), wherein $L$ and $A$ are the length and area of the sample.

<table>
<thead>
<tr>
<th>Impedance</th>
<th>$Z(\omega)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Phase angle</td>
<td>$\tan(\theta) = \frac{Z''}{Z'}$</td>
</tr>
<tr>
<td>Admittance</td>
<td>$Y(\omega) = \frac{1}{Z(\omega)}$</td>
</tr>
<tr>
<td>Complex capacitance</td>
<td>$C(\omega) = \frac{1}{i\omega Z(\omega)}$</td>
</tr>
<tr>
<td>Complex dielectric constant</td>
<td>$\epsilon(\omega) = \frac{LC(\omega)}{A}$</td>
</tr>
</tbody>
</table>

A few examples of basic equivalent circuits and their simulations will be discussed to demonstrate the interaction of individual components and their contribution to impedance. Simulations were performed with ZView for frequencies between 1 and $10^6$ Hz.

\(^{4}\)magnitude or phase of impedance vs. frequency
The basic behavior of ideal resistors and capacitors in AC circuits is illustrated best in a RC series combination, which is illustrated in Figure 1.8. As can be seen, an ideal resistor is independent of frequency and generates no imaginary part in impedance. Therefore, resistors only determine intersections and distances on the $Z'$-axis, which also can be seen by looking at the formal expression of impedance of a single resistor

$$Z(\omega) = R.$$  

(1.4)

Alternatively, an ideal capacitor is frequency dependent and only contributes an imaginary part to the impedance

$$Z(\omega) = \frac{1}{i\omega C}.$$  

(1.5)

When these two components are combined in series, the impedance will show the frequency dependence of the capacitor shifted by the value of the resistor. Thus, impedance can simply be written as the sum of the impedance of the individual components

$$Z(\omega) = R + \frac{1}{i\omega C}.$$  

(1.6)

Due to the capacitance, the circuit behaves like an open circuit at low frequencies, whereas at high frequencies the capacitor induces a short circuit behavior and only the contribution of the resistor remains, as if the capacitor no longer exists.

An important and widely used component in equivalent circuits of solar cells is the RC parallel combination.\(^{[21, 71]}\) It describes the "minimal IS model for solar cells"\(^{[86, p.27]}\), and is supposed to represent the recombination resistance of charge carriers and the chemical capacitance, which produces the voltage across the cell due to splitting of Fermi levels by photogenerated charge carriers.\(^{[86, p.27]}\) Adding an additional series resistor, this model takes also internal transport resistances into account and is already suitable for fitting experimentally gained data of conventional silicon solar cells.\(^{[83]}\) In that case, the expression for impedance can be written as

$$Z(\omega) = R_s + Z_1(\omega) = R_s + \frac{1}{R_1 + i\omega C_1} = R_s + \frac{R_1}{1 + i\omega \tau_1},$$  

(1.7)

whereas $Z_1(\omega)$ is the impedance of the RC parallel combination and

$$\tau = C_1 R_1$$  

(1.8)

is the relaxation time of this system.\(^{[86, p.16]}\)

\(^{5}\)Relative to the size of the capacitor. For capacitors with $C > 10^{-7}$ F, frequencies of $C > 10^5$ Hz are already sufficient to suppress their main contribution.
Therefore, impedance of the RC parallel combination was gained by utilizing the already-mentioned Ohm’s law-like behavior and the admittance representation

\[ Y(\omega) = \frac{1}{R_1} + i\omega C_1 = \frac{1}{Z_1(\omega)}. \]  

(1.9)

The simulation of a RC parallel combination results in an arc or semicircle in the impedance plane plot, which is illustrated in Figure 1.9, including the frequency dependency. The diameter of the semicircle is defined by the parallel resistor R₁, whereas the additional series resistor Rₚ is just shifting the semicircle along the Z’-axis to larger values (see Figure 1.10).

Figure 1.9: 3D illustration of a simulated RC parallel (R₁ and C₁) combination with preceding series resistor Rₚ by plotting Frequency vs. Z’ vs. Z”.

Figure 1.10: Simulation of a RC parallel (R₁ and C₁) combination with preceding series resistor Rₚ. a) Impedance plane and b) bode plot for fixed capacitance C₁ = 10⁻⁸ F and different series and parallel resistors (values in Ω).
The influence of the capacitor on the circuit response is illustrated in Figure 1.11, where each curve is shifted for a better comparison. Thus, changing the value of the capacitor does not change the shape of the semicircle but rather determines the range of it that is visible for a fixed range of frequencies. Therefore, high capacities limit the visible range of the curve to high, and low capacities to low frequencies.

Figure 1.11: Simulation of a RC parallel (R₁ and C₁) combination with preceding series resistor Rₛ. a) Impedance plane plot and b) bode plot for fixed resistances Rₛ = 500 Ω and R₁ = 5000 Ω and varying values of the capacitor (in F). For better comparison, each curve is shifted to the previous by 1000 upwards.

In the phase angle vs. frequency bode plots of Figure 1.10 b) and Figure 1.11 b) both components show a direct influence on the peak position of the phase angle, which is shifted inversely proportional to τ₁.

So far we have only considered ideal components and their combinations. However, to fit real systems the usage of these components is limited, particularly of ideal capacitors, since they are not able to fit compressed or shifted semicircles, as seen in Figure 1.12. A reasons for this behavior in real systems could be inhomogeneous or extended layer thicknesses or other unpredictable influences, such as impurities or trap states causing a dispersion in frequency. However, the unambiguous origin is still unknown.[86, p.22]

In order to fit experimental data with this behavior, constant phase elements like CPE or QPE can be used. Their individual impedance is given by

\[ Z_{\text{CPE}}(\omega) = \frac{1}{(i\omega)^\rho T} \]  

(1.10)
1.5 Impedance Spectroscopy (IS)

and

\[ Z_{\text{QPE}}(\omega) = \frac{1}{(i\omega Q)^n}, \quad (1.11) \]

respectively, and are very close related to a capacitor. In fact, for \( n = p = 1 \) they are indeed ideal capacitors, which is why the impedance of the equivalent circuits is the same as for a capacitor in Equation (1.7), except for the correction factor of the constant phase element.

Figure 1.12: Simulation of resistor-constant phase element parallel (R₁ and CPE/QPQ) combination with an additional preceding resistor Rₛ. a) Impedance plane plot and b) bode plot for fixed values of \( Rₛ = 500 \, \Omega \), \( R₁ = 5000 \, \Omega \). In addition, values \( Q = T = 10^{-8} \, \text{F} \) of the constant phase elements CPE and QPE are fixed and only \( n = p \) (see Table 1.2) is changing. Each curve is shifted by 1000 for a better comparison.

Figure 1.12 illustrates the comparison of the two constant phase elements for various values of \( n \) and \( p \), respectively, while the values of \( Q = T = 10^{-8} \, \text{F} \) are fixed. To fit the profile of the impedance in the impedance plane plot, the two elements are almost equivalent, since they differ mainly in their phase shift. A capacitor should be used as a comparison in order to find the circuit component to fit the experimental data. If the angular phase peak in the bode plot is shifted to higher or lower frequencies a CPE or QPE is required, respectively, instead of an ideal capacitor.

A combination of two RC parallel circuits in series and a preceding series resistor is shown in Figure 1.13. Keeping all resistors at predefined values ensures that only the ratio of the two capacitors \( c = C₁/C₂ \) determines the shape and the number of arcs. Therefore, the magnitude of the capacitors determines, which is the dominate component of the system. Specifically, if \( C₁ \) is much larger than \( C₂ \), a small and a large semicircle is visible, whereas
the small one is at low and the large one at high frequencies. Alternatively, if \( C_1 \) is much smaller than \( C_2 \) the frequency dependency of the arcs is vice versa. In case that both capacities are in the same order of magnitude only one arc is visible. Nevertheless, the new expression for impedance of two RC parallel combinations can be found as

\[
Z(\omega) = R_s + Y_1(\omega) + Y_2(\omega) = R_s + \frac{R_1}{1 + i\omega\tau_1} + \frac{R_2}{1 + i\omega\tau_2},
\]

(1.12)

by expanding the expression of a single RC parallel combination in Equation (1.7).

Figure 1.13: Simulation of two RC parallel \((R_1, C_1, R_2 \text{ and } C_2)\) combinations with an additional preceding resistor \( R_s \). a) Impedance plane plot and b) bode plot for fixed values of \( R_s = 500 \Omega, R_1 = 1000 \Omega \text{ and } R_2 = 5000 \Omega \) and varying values of ratio \( c = \frac{C_1}{C_2} \).

Diffusion processes are also frequently occurring phenomena in experimental data that can be modeled using a so-called transmission line. A general diffusion is represented by a transmission line including \( N \) resistors \( R_1...N \) and generic components \( \zeta_1...N \) as illustrated in Figure 1.14. In this case, the generic component is variable and represents different types of diffusion processes. A brief overview of some diffusion processes and their corresponding generic components \( \zeta \) is listed in Table 1.4.

Table 1.4: List of common diffusion processes and their corresponding generic components \( \zeta \) used in equivalent circuits.[86, p.58]

<table>
<thead>
<tr>
<th>Process</th>
<th>( \zeta )</th>
</tr>
</thead>
<tbody>
<tr>
<td>ordinary diffusion</td>
<td></td>
</tr>
<tr>
<td>anomalous diffusion</td>
<td></td>
</tr>
<tr>
<td>diffusion and recombination</td>
<td></td>
</tr>
</tbody>
</table>

Eugen Zimmermann
1.5 Impedance Spectroscopy (IS)

Figure 1.14 shows the simulation of an ordinary \((p = 1)\) and anomalous \((p < 1)\) diffusion for a different number \(N\) of repeating resistors and constant phase elements. A characteristic feature of transmission lines with a high number of repeating elements is the nearly linear behavior at high frequencies.

![Figure 1.14: a) Impedance plane plot and b) bode plot of a simulated transmission line for ordinary \((p = 1)\) and anomalous \((p < 1)\) diffusion (\(N\) repetitions of \(R_1\) (in \(\Omega\)) and \(\zeta_1 = \text{CPE}\) (in \(F\))).](image)

Finally, an inductive element will be discussed, which occasionally occurs in experimental data. Indications that an inductor is necessary in order to describe the measured data are positive values of \(Z''\) at low frequencies and an associated positive phase angle. Both can be seen in Figure 1.15, which illustrates simulations of the pictured equivalent circuit for different values of \(L\).

![Figure 1.15: Simulated behavior of an inductor \(L\) in a RC parallel \((R_1\) and \(C_1\)) combination. Fixed values for \(R_s = 500\,\Omega\), \(R_1 = 5000\,\Omega\), \(R_2 = 10000\,\Omega\) and \(C_1 = 10^{-8}\,\text{F}\). Varying values for \(L\) (in \(H\)).](image)
Increasing L leads to two perfectly formed semicircles, one with positive and one with negative $Z''$ values. However, by reducing the resistance $R_2$ the curve becomes more and more into a complete circle, no matter how large the magnitude of the inductance. The impedance of this circuit can be expressed by,$^{[86, p.21]}$

$$Z(\omega) = R_s + \frac{1}{Z_{\text{parallel}}(\omega)} = R_s + \frac{1}{\frac{1}{R_1} + \frac{1}{R_2 - i\omega L_2} + i\omega C_1}.$$  \hspace{1cm} (1.13)
2 Experimental Methods and Characterization Techniques

In this chapter, the sample preparation and characterization methods used for Sb$_2$S$_3$ films and solar cells will be discussed.

2.1 Sb$_2$S$_3$ Growth

Deposition of Sb$_2$S$_3$ films was performed by using CBD and the standard recipe described in Chapter 1.4. In detail, approximately molar solutions with 4 g of Na$_2$S$_2$O$_3$ in 25 ml deionized H$_2$O and 650 mg of SbCl$_3$ in 2.5 ml acetone have been prepared and mixed with additional 100 ml of completely deionized water. Therefore, precursor chemicals were weighed on a Pioneer PA214 analytic balance by OHAUS Corporation. Due to humidity variations in the laboratory and a fast water soaking of SbCl$_3$, the deviation of the material actually used was about 10%.

Beakers with the precursor solutions were sealed with parafilm and cooled for at least two hours. Initially, this was done on a KP281 cooling plate by Fryka. The set point for temperature was adjusted to $-1 \, ^\circ C$, leading to a temperature gradient from top to bottom inside the bath, even after several hours of cooling. For better control and a more uniform temperature distribution, the procedure was changed to a cool down in an ice bath, as shown for two simultaneous baths in Figure 2.1.

![Figure 2.1: CBD of antimony sulfide in an ice bath after a) 13 and b) 103 minutes of mixing precursors.](image)
The beakers were submerged to the upper edge in ice to ensure a homogeneous cooling over several hours and the time needed for the deposition process. Samples were placed tilted on Teflon holders as seen on the leftmost in Figure 2.2 a). The holder itself, was placed in the bath either directly after mixing the chemicals, or after the color change due to the reaction became visible. Figure 2.2 b) illustrates the color gradient, after the reaction becomes recognizable.

After deposition, the samples were rinsed with deionized water and dried in a nitrogen flow and ambient air. Finally the backside of the samples was cleaned with hydrochloric acid and all samples were transferred into a nitrogen glovebox for annealing.

2.2 Solar Cell Fabrication

Standard solar cells preparation was performed on commercially available 14 mm × 14 mm glass substrates by Kintec Company, which were covered with tin doped indium oxide (ITO) as transparent conductive oxide (TCO).

Initially, all substrates were cleaned in an ultrasonic bath by immersing them for at least 5 minutes each in deionized water with dishwashing detergent, followed by acetone, and a final isopropanol (IPA) step. Afterwards, TiO$_2$ was applied by spray pyrolysis on a hotplate at 450°C, using titanium di-isopropoxide bis(acetylacetonate) as precursor in a 1:10 diluted solution with ethanol. Sb$_2$S$_3$ was deposited by chemical bath deposition and subsequently annealed in a nitrogen filled glovebox.

Finally, the HTM was applied by spin coating and WO$_3$ and Ag by thermal evaporation by using a shadow mask, wherein the latter results in three solar cells per substrate. The thickness of WO$_3$ was varied from 5 to 8 nm. For Silver, layer thicknesses of 15 − 20 nm and 80 − 150 nm were used for semitransparent and regular solar cells, respectively.

Initially, also PEDOT:PSS was used as hole selective layer until it was completely replaced by WO$_3$. 

---

Figure 2.2: a) Teflon sample holder with as usually for deposition tilted and for comparison straight sample placement. b) Color gradient of the bath in two minute steps after Sb$_2$S$_3$ concentration is high enough for visual recognizability. Numbers represent minutes after pouring precursors into the water beaker.
A schematic of the final solar cell is illustrated in Figure 2.3, revealing in side view (a) the detailed stacking of the single layers and in top view (b) the arrangement of the back contact (bottom) and the separate pixels\(^2\), \(L\), \(M\) and \(R\), where each pixel represents an independent solar cell.

![Schematic of standard solar cell configuration. a) Side view with detailed stacking of layers. b) Top view of three independent solar cells/pixels. The dimensions are illustrating the predefined active areas of 12.5 mm\(^2\) each, when illuminated through the shadow mask.](image)

In order to avoid shortcuts by the measuring gold contacts, the ITO substrates are etched\(^3\) on one side. On the other side, the back/bottom contact to the ITO was established by scraping the overlying layers with a diamond scribe and filling with silver paste.

### 2.3 Characterization Methods

Several characterization methods are used to investigate overall solar cell performance, layer thickness, absorption spectra, recombination processes and intrinsic electric properties, which briefly will be discussed in the next sections.

#### 2.3.1 Current-Voltage Characterization (I-V)

Solar cell performance is primarily analyzed by current-voltage (I-V) measurements\(^4\), which are acquired by measuring the current flow for a given range of bias voltages. Simulated I-V curves under illumination and in dark are shown in Figure 2.4, pointing up the most important characteristics.

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\(^2\)left, middle and right as seen from the glass/ITO side (back contact at the bottom)  
\(^3\)already done by Kintec Company  
\(^4\)if the area is known: current density-voltage (j-V)-curves
2.3 Characterization Methods

Figure 2.4: Simulated I-V curves under illumination and in dark as described by ideal diode model of Equation 2.3. Most important characteristics are short circuit current $I_{SC}$ and open circuit voltage $V_{OC}$ of the theoretical maximum power point ($P_t$) as well as current $I_{MPP}$ and voltage $V_{MPP}$ of the maximum power point ($P_{max}$). Furthermore series resistance $R_s$ and shunt resistance $R_{sh}$ can be determined by analysis of the data.

These include

$I_{SC}$ measured current at short circuit condition of the electrodes
$V_{OC}$ open circuit (external) voltage $V_{OC}$ which completely compensates the built-in potential (open circuit condition) and reduces the current to zero
$P_t$ theoretical maximum power point $P_t = I_{SC} \cdot V_{OC}$
$P_{max}$ maximum power point (MPP) $P_{max} = I_{MPP} \cdot V_{MPP}$ of I-V curve, with corresponding current $I_{MPP}$ and voltage $V_{MPP}$
$R_s$ series resistance $R_s$ and
$R_{sh}$ shunt resistance $R_{sh}$.

Another significant characteristic of illuminated I-V curves is the fill factor (FF), which is given by the ratio of $P_{max}$ and $P_t$ as

$$FF = \frac{P_{max}}{P_t} = \frac{V_{MPP} \cdot I_{MPP}}{V_{OC} \cdot I_{SC}}$$  \hspace{1cm} (2.1)

and describes how much of the theoretical maximum power for fixed values of $I_{SC}$ and $V_{OC}$ can be achieved. Combining these characteristics and the illumination power ($P_{light}$) of the light source, the power conversion efficiency (PCE) can be expressed by

$$\eta = \frac{P_{max}}{P_{light}} = \frac{I_{MPP} \cdot V_{MPP}}{P_{light}} = \frac{I_{SC} \cdot V_{OC} \cdot FF}{P_{light}}.$$  \hspace{1cm} (2.2)
The diode-like behavior of the shown I-V curves is caused by the heterojunction architecture and supported by the blocking layers. Thus, leading to preferred directions of electron and hole transport, respectively. In this case, a reverse bias blocks and a forward bias favors electron transport, because the electron collecting electrode is lying on a higher or lower potential, respectively, compared to the hole collecting electrode.

In forward direction the current increases exponentially until it fades into linear behavior, which is mainly limited by the $R_s$ of the cell. Alternatively, the $R_{sh}$, which determines the slope of the curve in reverse direction, represents the internal loss mechanisms and blocks most of the current for moderate bias. However, further increasing the voltage leads to the breakdown of the diode and a much higher current flow. Since both resistances directly affect the FF and thus the PCE of the cell, small values of series and high values of shunt resistance are desirable in order to maximize current flow and minimize losses.

To simulate the curves shown above\(^5\), the generalized Shockley model is used. The model corresponds to a DC equivalent circuit, which is illustrated in Figure 2.5 and consists of at least one diode. In this case, the diode has a thermal induced saturation current $I_s$ and an ideality factor $n$. Other components of the equivalent circuit are an illumination induced photocurrent $I_{light}$ and series and shunt resistances, $R_s$ and $R_{sh}$, respectively, which can be assigned to the already known resistances, mentioned above.

The mathematical expression of this equivalent circuit is given by the generalized Shockley equation

$$I = \frac{R_{sh}}{R_s + R_{sh}} \left[ I_s \left( \exp \left( \frac{q \cdot V - q \cdot I \cdot R_s}{n \cdot k_B \cdot T} \right) - 1 \right) + \frac{V}{R_{sh}} - I_{light} \right],$$

(2.3)

where $k_B$ is the Boltzmann constant, $T$ the temperature and $V$ the voltage. Although this model is frequently applied to analyze organic and hybrid solar cells\[^{87-89}\] it was originally used to describe conventional solar cells. For this reason it is not suitable to provide an appropriate description of organic solar cells or is capable to fit them, without being extended.\[^{90}\] However, the main features of conventional and organic/hybrid solar cells can be expressed in the same way, so that the model is still sufficient to explain the basic working principle.

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\(^5\)except the break through behavior at large reverse bias
2.3 Characterization Methods

Data acquisition
Data acquisition is done with a LabView program in combination with a Keithley 2400 source meter unit and a LOT Oriel solar simulator, including an AM 1.5G filter equipped 150 W Xe-lamp. In order to get all important parameters a typical measurement has covered a scan range of $-0.8 \text{ V}$ to $+1.2 \text{ V}$ with $0.01 \text{ V}$ step size and $10 \text{ ms}$ per data point.

Measurements are performed in dark and under illumination, where the latter is normalized to $100 \text{ mW} \cdot \text{cm}^{-2}$ by a silicon reference solar cell certified by Fraunhofer Institute. To further improve the spectral match to natural sunlight an additional KG5 filter is mounted on the reference cell. The three independent solar cells/pixels were measured consecutively, while covered by a shadow mask with illuminated areas of $12.5 \text{ mm}^2$ each.

For measurements in dark, a lightproof overlay was used to ensure that no additional current is generated due to the absorption of light. However, because the measurement is carried out at room temperature or the sample is heated due to the light source, it is possible that thermally excited charge carriers contribute to the measured current.

In addition, light intensity dependent I-V measurements were performed by introducing neutral density filters in the optical path of the setup. Light intensities were subsequently calibrated using the same certified silicon reference solar cell mentioned before.

2.3.2 External Quantum Efficiency (EQE)

To analyze the detailed spectral composition of the photocurrent of I-V curves, external quantum efficiency (EQE) measurements can be performed. Therefore, the sample is held at short circuit condition (bias $0 \text{ V}$) and illuminated by monochromatic light while the current response is recorded. The EQE is defined as

$$
EQE(\lambda) = \frac{N_c}{N_{\text{photon}}(\lambda)} = \frac{I_{SC}}{e} \cdot \left( \frac{P_{\text{light}}(\lambda)}{h \nu} \right)^{-1}
$$

where $N_c/s = I_{SC}/e$ is the number of photogenerated free charge carriers per second, $N_{\text{photon}}(\lambda)/s = P_{\text{light}}(\lambda)/h \nu$ the number of incident photons of a certain energy $h \nu$ or wavelength $\lambda = c/\nu$ per second, $P_{\text{light}}$ the illumination power of the light source and $e$, $c$ and $h$ the elementary charge, speed of light and Planck constant, respectively. EQE is also called incident photon to charge carrier efficiency (IPCE), since it indicates how much of the total incident photons are converted into measurable current.

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6 Approximately terrestrial solar spectral irradiance at air mass 1.5 on a $37^\circ$ tilted surface. Illustrated in Figure 2.7.
7 Shunt resistance is sometimes difficult to obtain, due to charging/trap filling effects of the sample at the beginning of the measurement. Therefore a broader negative voltage range has to be measured to cut off the unnecessary part.
Alternatively, this also means EQE measurements do not take into account how many photons are actually absorbed. Therefore, internal quantum efficiency (IQE) measurements have to be done, wherein an integrative sphere simultaneously measures the reflected and scattered light in order to calculate the total absorption.

Despite these limitations, EQE allows the estimation of the upper limit of achievable short circuit current $I_{SC}$ using

$$I_{SC} = \int e \cdot EQE(\lambda) \cdot \frac{P_{light}(\lambda)}{h\nu} \cdot d\lambda = \int e \cdot EQE(\lambda) \cdot \frac{N_{photon}(\lambda)}{s} \cdot d\lambda.$$  

(2.5)

Thus, maximum currents of 26 and 33 mA cm$^{-2}$ can be achieved with absorption onsets of 800 and 900 nm, respectively, when every photon ($EQE = 100\%$) of the AM 1.5G solar spectrum is converted into free charge carriers.$^{[91, 92]}$

The EQE can be further written as a composition of individual efficiencies$^{[39, 93]}$

$$EQE = \eta_A \cdot \eta_{exc} \cdot \eta_{diff} \cdot \eta_{sep} \cdot \eta_{tr} \cdot \eta_{cc},$$  

(2.6)

where the components are

- light absorption efficiency $\eta_A$,
- generation of excitons $\eta_{exc}$,
- diffusion of excitons to an interface $\eta_{diff}$,
- dissociation/separation of excitons at the interface $\eta_{sep}$,
- charge transport to the electrodes $\eta_{tr}$ and
- charge collection by the electrodes $\eta_{cc}$.

However, the particular composition of the individual efficiencies has to be determined experimentally in a variety of experiments.

**Data acquisition**

Similar to acquisition of I-V curves, EQE spectra are recorded using a LabView program in combination with the same Keithley 2400 source meter unit and an equal LOT Oriel solar simulator$^8$. Additionally, a LOT-Oriel Omni 150 Monochromator was positioned between 150 W Xe-lamp and sample, which was placed in a light proof metal box. Typical measurements of EQE spectra are performed at wavelengths between 300 and 800 nm with 2 nm step size and 10 ms per data point.

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$^8$calibrated with a silicon reference solar cell certified by Frauenhofer Institute and a KG5 filter

Eugen Zimmermann

29
2.3.3 Absorption Measurements

Absorption spectra of individual and composed layers are recorded using a 8453 UV-Vis spectrometer by Agilent Technologies, which is monitoring optical density (OD)\(^9\) in response to the wavelength. A schematic of the used spectrometer is illustrated in Figure 2.6. A deuterium (190 to 800 nm) and a low-noise tungsten lamp (370 to 1100 nm) are installed as light sources. Both lamps together produce a measurement range of 190 to 1100 nm with a resolution of 1 nm. Prior to the measurement of the first absorption spectrum, the instrument was calibrated using a blank ITO substrate.

As for EQE spectra, maximum \(I_{SC}\) of the absorption spectra can be estimated by utilizing

\[
I_{SC} = \int e \cdot \text{Abs}(\lambda) \cdot \frac{N_{\text{photon}}(\lambda)}{s} \cdot d\lambda. \tag{2.7}
\]

In addition to the AM 1.5G spectrum, Figure 2.7 shows an absorption and EQE spectrum of a typically fabricated solar cell, where the colored areas correspond to the calculated values of \(I_{SC}\), using Equation 2.5 and 2.7, respectively.

\(^9\) Absorbance = \(1 - 10^{-\text{OD}}\)

Figure 2.7: AM 1.5G spectrum\(^9\) as well as absorption and EQE spectrum of a typically fabricated solar cell. Colored areas correspond to the calculated values of \(I_{SC}\), using Equation 2.5 and 2.7, respectively.
2 Experimental Methods and Characterization Techniques

2.3.4 Photo Voltage Decay (PVD) and Photo Current Decay (PCD)

Recombination and charge collection processes are investigated by photo voltage (PVD) and photo current decay (PCD) measurements, which both are acquired by monitoring the voltage response of the solar cell to a small disturbance\textsuperscript{10} by a laser pulse.

A schematic of the used setup is shown in Figure 2.8, including a Tektronix Tekscope digital oscilloscope, a pulsed laser, and the background illumination by a LOT Oriel solar simulator calibrated to approximately $100 \text{ mW/cm}^2$. The pulsed laser was set to a wavelength of 532 nm, an intensity of $\sim 5 \text{ mW/cm}^2$ and a repetition rate of $\sim 18 \text{ Hz}$, where each pulse-time is only a few nanoseconds. As for light intensity measurements, neutral density filters and the silicon reference solar cell were used for adjustment and calibration of the background illumination, respectively.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.8.png}
\caption{Schematic of the PVD/PCD setup.}
\end{figure}

For PVD measurements, quasi-open circuit conditions were established by using the $1 \text{ M}\Omega$ termination resistances of the oscilloscope.\textsuperscript{[96]} Thus, charge carriers are prohibited to flow to the electrodes and the built-in voltage $V_0$ can be measured, which is generated by the background illumination and corresponds to the open circuit voltage. Each absorbed laser pulse generates additional free charge carriers and results in an increase voltage signal. However, since charge carriers are not able to pass the termination resistance, the voltage signal decays with the rate of the internal recombination processes to equilibrium.

In contrast, PCD measurements are performed at quasi-short circuit condition by using the $50 \text{ \Omega}$ termination resistance of the oscilloscope.\textsuperscript{[97]} In this case, the additionally generated charge carriers are extracted by the electrodes, leading to a measurable voltage drop at the termination resistance, which can be converted into a current with the help of Ohm’s law.

\textsuperscript{10}in the Force
Due to the small perturbation by the laser, acquired PVD and PCD data\textsuperscript{11} can be fitted by a single exponential function\textsuperscript{96, 98, 99}

\[ X(t) = A \cdot \exp(k \cdot t) + X_0, \] (2.8)

where \( X(t) \) is the measured voltage \( V(t) \) or current \( I(t) \) response, \( X_0 \) the baseline voltage \( V_0 \) or current \( I_0 \), and \( A \) and \( k \) the amplitude and decay rate, respectively.

For PVD measurements, the decay rate is equivalent to an effective recombination rate, where the inverse gives the charge carrier/electron lifetime\textsuperscript{98, 99}

\[ \tau = \frac{1}{k}. \] (2.9)

Thus, under working conditions, small voltage decay rates or large charge carrier lifetimes are desirable for maximal charge extraction. Alternatively, it is desirable to have high decay rates for the PCD measurement since they indicate a quick charge extraction. Combination of both decay rates further allows to estimate charge collection efficiency\textsuperscript{100}

\[ \eta_{\text{coll}} = \frac{k_{\text{PCD}}}{k_{\text{PCD}}} \cdot k_{\text{PVD}}. \] (2.10)

\subsection*{2.3.5 Impedance Spectroscopy}

For acquisition of impedance spectra a Metrohm Autolab PGSTAT302N, a FRA2 module and the application NOVA were used. The solar cell was connected inside a metallic and lightproof cage (see Figure 2.9) to provide controlled conditions and protection from electric or magnetic interference of surrounding devices.

Via the external connection of the Autolab PGSTAT302N, an additional DC voltage could be applied to the sample. Measurements were carried out under illumination and in dark, wherein for light measurements a white light diode was utilized, which was approximately calibrated to 100 mW/cm\textsuperscript{2} using the same silicon reference solar cell as for calibration of I-V measurements. Small AC perturbations are generated by the Autolab PGSTAT302N with frequencies between 1 and 10\textsuperscript{6} Hz and a peak amplitude of \( 10 \cdot \sqrt{2} \text{mV} \), where the latter is well below thermal voltage at room temperature (\( \sim 25 \text{mV} \)) and should ensure linearity of the system (see Chapter 1.5).

Subsequent modeling of equivalent circuits and data fitting was performed with ZView.

\textsuperscript{11}Usually acquired as an average of \( \sim 200 \) decays.
2 Experimental Methods and Characterization Techniques

Figure 2.9: Schematic of the experimental setup for IS-measurements with a Metrohm Autolab PGSTAT302N and the cage containing a white light diode and the sample.

2.3.6 Film Thickness Measurements using Atomic Force Microscopy (AFM)

Film thickness of different polymers was measured by using a Digital Instruments Dimension 3100 Multimode AFM in tapping mode and Gwyddion for data processing and visualization.
3 Fabrication of Sb$_2$S$_3$ Coatings

Several studies have been reported on fabrication of Sb$_2$S$_3$ based solar cells, pointing out the importance of deposition parameters, such as deposition time, bath temperature and subsequent annealing conditions. However, to the best of my knowledge, no detailed or complete recipe has been published. This chapter gives an introduction in how Sb$_2$S$_3$ coatings by chemical bath deposition are fabricated. Moreover, it describes respective challenges of coating flat and nanostructured TiO$_2$ surfaces. Furthermore, the influence of TiO$_2$ surface treatments on growing conditions of Sb$_2$S$_3$ is investigated.

3.1 Flat Films on TiO$_2$

3.1.1 Introduction

A flat bilayer geometry was chosen for first investigations of Sb$_2$S$_3$ films. It is the least complex device geometry, easy to fabricate, and, therefore, should give the highest chance of reproducibility and comparability. In this experiment, two types of cooling mechanism, resulting in different deposition temperatures were used. Furthermore, various pre- and post-treatments of the substrate were examined to find a basic recipe for preparation of homogeneous Sb$_2$S$_3$ coatings.

3.1.2 Experimental Methods

Solar cells are prepared on ITO substrates with compact TiO$_2$ layers, which are processed as described in Chapter 2.2 and chemical bath deposition as in Chapter 2.1. The investigated parameters, which are assumed to have an influence on film quality, are summarized in Table 3.1. These include the deposition temperature of the bath, pre-treatments, sample position in the bath, immersion time and post-treatments.

The deposition temperature was varied by changing cooling of the solutions from a cooling plate to an ice bath. The former was set to $-1\,^\circ$C and cooled only the bottom, leading to an internal temperature gradient. However, the ice bath results in homogeneously distributed temperatures of $\sim 0\,^\circ$C, since the beakers were submerged to the upper edge. For both procedures, solutions were cooled for at least two hours prior deposition.
To improve the growth conditions, especially for samples which are immersed later (see below), the substrates were pre-wetted in H\textsubscript{2}O. This is expected to lead to a less abrupt transition and reduce the coating by large particles. However, pre-treatments can also increase the reproducibility, as was intended by cleaning the substrate in O\textsubscript{2}-plasma (7 minutes) or by annealing at 150°C (10 minutes) in order to remove contaminants. Due to these pre-treatments, older substrates can be used with comparative results to other experiments.

Immersion time of the substrates into the chemical bath was chosen either after the formation of Sb\textsubscript{2}S\textsubscript{3} becomes visible (visible color change of the bath) or right after mixing the precursors. Thereby, the former is dependent on the temperature of the bath and takes 30 to 60 minutes, from the point of mixing precursor solutions.

After deposition, substrates were carefully rinsed in deionized water flow of low and moderate pressure or dipped completely in deionized water to remove remaining unattached particles. Finally, samples are dried by a nitrogen flow and/or in ambient air. Therefore, samples were either placed flat on a table or remained standing upright in the sample holder.

Film quality was measured using UV-Vis and AFM while device performance was quantified through I-V and EQE characterizations. However, due to the variety of other parameters that arise in the production of solar cells, effects on film quality were mainly assessed qualitatively.
3.1.3 Results and Discussion

Initial experiments with deposition of Sb$_2$S$_3$ on a cooling plate proved to be very unreliable. This can be attributed to the temperature gradient, which is induced by this method and an additional large dependence on ambient temperature, leading to large scattered deposition temperatures and unrepeatable results. For this reason, subsequent deposition was carried out in an ice bath. By the complete confinement of the beakers in the ice, the deposition was isolated from external variations in temperature. However, the duration of the cooling is still important although not as large of an influence as with the cooling plate. While it took only about 30 to 40 minutes for the former type of cooling until formation of Sb$_2$S$_3$ becomes visible, the latter requires 45 to 60 minutes. Thus, resulting in a much slower release of Sb$^{3+}$ and S$^{2-}$ and, consequently, slower and more controllable deposition.

Investigation of plasma cleaning and annealing as pre-treatment did not reveal a significant influence on reproducibility. For this reason, these steps were skipped for substrates, which were processed immediately after spray pyrolysis of TiO$_2$. Alternatively, pre-wetting in H$_2$O showed a beneficial influence, since less holes and big particle agglomerates are visible on substrates, which are immersed after the reaction becomes visible. However, the immersion of samples directly after mixing the precursors improves the film quality in a much more significant manner and was a major leap in the production of high quality films (Figure 3.1 a)-d) vs. e)-f)).

![Figure 3.1: Comparison of different immersion times, sample positions and drying positions. Immersion time: direct immersion after mixing solutions a)-f) (105 minutes in bath) vs. immersion after Sb$_2$S$_3$-formation becomes visible e)-h) (55 minutes in bath). Sample position: tilted a), b), e), f) vs. upright c), d), g), h). Drying position: lying on a clean base a), d), e) h) vs. upright in the sample holder b), c), f) g).](image-url)
Such obtained films, especially in combination with a tilted sample position, exhibit a very homogeneous covering without any holes or agglomerates (Figure 3.1 a)). Thereby, the tilted position prevents most of the bigger particles from attaching to the surface, which happens much more often on upright positioned samples. Another benefit of the tilted position is a slightly greater area, which is covered by the chemical bath (upper left corner in Figure 3.1 c) & d)). This can be attributed to a better diffusion of the ions and chemicals in larger gaps, which, on the other hand, prevents efficient deposition on covered areas.

After the chemical bath, post-treatment of the samples proved to be another important production step. Therefore, both rinsing with water and drying of the samples have to be considered together, since the water, which remains on the surface, can dissolve the just made film. Worst results are obtained by dipping the synthesized film in H$_2$O for a brief moment or rinsing in water of moderate pressure. Thereby, the Sb$_2$S$_3$ film detaches due to these treatments, regardless of the subsequent process of drying. Thus, the film quality was determined to be the best when substrates are rinsed carefully in a deionized water flow of low pressure as opposed to the dipping and rinsing under moderate pressure.

Finally, the remaining water droplets have to be removed quickly, since otherwise the film is detaching exactly at these positions. This can best be accomplished by blowing the substrates with N$_2$ while they are placed on a clean base. Drying while the samples are in the holder bears the risk that the holder is still wet, causing a slow release of the films, starting from the edges.

In contrast to the basic recipe, provided by Messina et al. in [65], the bath temperature was not stepwise decreased from 10°C to the final deposition temperature, but rather fixed to the value, which was determined by the ice bath. Despite their prediction
\footnote{Messina et al. noted, that deposited antimony sulfide films detach from glass substrate when the temperature is not reduced gradually from $> 5$ °C.}, this did not inevitably lead to detachment of the films, if the substrates are post-treated properly. Also, circulation of the bath, which originally was part of the recipe, was avoided to prevent bigger particle agglomerates of attaching to the surface.

In summary, the best recipe was found as:

1. cooling of solutions in ice bath for at least 2 hours
2. no pre-treatment of substrates
3. tilted position in holder
4. direct immersion of substrates after mixing precursor solutions
5. rinsing substrates in a low pressure water flow
6. immediately drying samples in lying position on a clean base.
For further investigations, the surface of as prepared Sb$_2$S$_3$ films was characterized by AFM, revealing a very low mean surface roughness of about $\sim 10 \pm 5$ nm (see Figure 3.2) with occasional outliers.

![AFM picture of as prepared Sb$_2$S$_3$ films](image)

Figure 3.2: AFM picture of as prepared Sb$_2$S$_3$ films. Surface roughness/mean height across the image is about $\sim 21 \pm 3$ nm on profile 1 and $\sim 19 \pm 3$ nm on profile 2.

### 3.2 Coating of TiO$_2$ Nanostructures

#### 3.2.1 Introduction

Nanostructured surfaces offer higher surface areas compared to flat bilayer structures. Thus, substantially thinner absorber layers are sufficient in order to absorb most of the light, resulting in more efficient exciton and charge carrier pathways and less recombination. This was impressively demonstrated by the mesoporous TiO$_2$ structures of O’Regan and Grätzel in 1991.$^{[10]}$

As a result, other nanostructures, such as nanowires and nanotubes have been created to improve this approach, by generating predefined and ordered pathways for the charge carriers. However, fabrication of ordered structures is not ensured, leading to challenging coating conditions, i.e., filling of mesoporous and nanotube structures or cavities in nanowire arrays. Nevertheless, mesoporous structures have been successfully coated with Sb$_2$S$_3$ by several research groups.

#### 3.2.2 Experimental Methods

Substrates with TiO$_2$-nanowires are fabricated by hydrothermal growth and provided by a group member. A SEM image of a typically produced TiO$_2$-nanowire array as provided is illustrated in Figure 3.3. Structures are coated with Sb$_2$S$_3$ mainly as described by the previously found recipe for flat layers, however, not yet optimized. Characterization was done by eye and SEM.
3.2.3 Results and Discussion

Although deposited layers are more strongly attached to the sample, nanostructured samples have to be prepared as carefully as flat samples. Specifically, the better adhesion of the layer can be attributed to a protection of the coating by the structure.

However, prior investigation of flat layers indicated an inefficient coating of covered or narrow areas by CBD. This is confirmed by SEM cross section images of Sb$_2$S$_3$ coated nanowires in Figure 3.3 c), which are showing air inclusions between the wires.

![Figure 3.3: a) SEM top view on a typically produced TiO$_2$-nanowire array as well as SEM cross sections of a complete Sb$_2$S$_3$ based solar (ITO/TiO$_2$/145 minutes CBD Sb$_2$S$_3$/P3HT/PEDOT:PSS/Ag) cell b) broken by hand and c) cut by a focused ion beam.](image)

Nevertheless, additional experiments have to be done in order to optimize the coating process or to find a suitable structure, which combines a high surface area and good processability by CBD. But as a matter of time and complexity of fabrication of reproducible structures, no detailed investigations haven been performed on these challenges.

3.3 Influence of TiO$_2$ Surface Treatment on Sb$_2$S$_3$ Film Growth

3.3.1 Introduction

Various publications on Sb$_2$S$_3$ based solar cells are reporting on beneficial effects of surface treatment on cell performance and stability (see Table 1.1). However, no reports have been found on surface treatment of TiO$_2$ in order to improve the film growth. For this purpose, basic studies on different surface modifiers have been performed. As a used surface modifier 4-mercaptopyridine (4-MP) was investigated. It is known to improve efficiency of charge carrier separation at the TiO$_2$-P3HT interface since it induces a re-orientation of the polymer chains with respect to the TiO$_2$ and, therefore, enhances short circuit current $I_{SC}$.[101] Alternatively, HTM polymers, such as P3HT and PCPDTBT are very unique as surface treatment, since the energy level alignment is contrary to that desired (see Figure 6.1). However, both polymers have been shown to have a good binding to Sb$_2$S$_3$[35], holding the potential of an improved growth process.
3.3.2 Experimental Methods

Investigations include four different surface modifiers, different deposition techniques, deposition parameters and modifier concentrations. 4-MP was applied either by dipping substrates for 5 minutes into a bath or by spin-coating the solution at 500 and 1000 rounds per minute (rpm), respectively. P3HT was prepared as 0.4 and 1 mg/ml and PCPDTBT as 0.2 mg/ml solutions and spin-coated at 8000 rpm. As a final surface modifier, a mix of P3HT and PCPDTBT was prepared, which had an estimated concentration of 1 mg/ml and was also spin-coated at 8000 rpm. On flat substrates all prepared solutions were tested while only P3HT and 4-MP were used on nanowires. Subsequently, influence of the modifier was analyzed by I-V measurements.

3.3.3 Results and Discussion

P3HT, PCPDTBT and 4-MP did not show a visible effect on Sb$_2$S$_3$ growth and film quality, while a mix of P3HT and PCPDTBT becomes even repellent and big parts of the freshly deposited layers peel off right after samples are taken out of the bath. The latter is also clearly seen in I-V measurements, which confirm the as expected worst performance of the mixed polymer treated substrates. Figure 3.4 is visualizing power conversion efficiency of all experiments on surface treatment of (a, b and c) flat and (d) nanostructured TiO$_2$.

![Figure 3.4: Power conversion efficiencies of three surface modifier experiments on (a, b and c) flat and one experiment on (d) nanostructured samples. Data is acquired by I-V measurements, where each point represents a working pixel on a fabricated solar cell.](image-url)
Furthermore, I-V measurements of flat bilayer cells reveal a negative influence on PCE when pure P3HT or PCPDTBT are used as surface modifier. The lowered efficiency is caused either by decreased $I_{SC}$, $V_{OC}$, or both. This is assumed to be a result of the unfavorable energy band alignment, which prevents an efficient charge transfer from $\text{Sb}_2\text{S}_3$ to $\text{TiO}_2$ and leads to more recombination at the interface. This effect decreases with layer thickness of the modifier, which is indicated by the higher efficiencies of lower concentrated PCPDTBT modified solar cells in Figure 3.4 c), even though the estimated maximum layer thickness is only 1 – 2 nm. On $\text{TiO}_2$ nanowires, P3HT also decreased open circuit voltage but significantly increased short circuit current and, therefore, resulted in comparable efficiencies to untreated cells.

In contrast to polymer modifiers, the effect of 4-MP is more positive, although it is conventionally used to improve the interface of $\text{TiO}_2$-P3HT and not $\text{TiO}_2$-$\text{Sb}_2\text{S}_3$. While it has decreased the efficiency of fabricated solar cells in the first examination (a), it has shown beneficial effects in solar cells of further experiments. Specifically, improving short circuit current and fill factor and simultaneously keeping the open circuit voltage at the value of untreated substrates. This is true for both, flat $\text{TiO}_2$ substrates and nanowires.

I-V measurements of fabricated cells, which are stored in ambient air and in dark for several days are illustrated in Figure 3.5 and reveal another beneficial influence of P3HT and 4-MP as surface modifier. Specifically, both modifier reduce the necessity of aging of the cells (see Chapter 4.2), which is improving cell performance under normal storage conditions with time.

![I-V measurements of experiments on surface modified flat (left) and nanostructured (right) substrates, fabricated and measured on the same day and stored under same conditions until the next measurement. For each group the I-V curve of the best and simultaneously stable cell is shown.](image-url)
In summary, only surface modification by 4-MP is showing predominantly beneficial effects, such as an enhanced efficiency and stability of fabricated solar cells. However, no visible difference was seen between modified and unmodified layers. Therefore, it can not be determined whether these improvements are a result of better growing conditions of Sb$_2$S$_3$ or an improved interface as in the case of In-OH-S. The latter is frequently used as surface modifier of TiO$_2$ in combination with Sb$_2$S$_3$ in order to increase stability and to prevent oxidation of the Sb$_2$S$_3$ layer due to the catalytic effect of TiO$_2$.\textsuperscript{[64]}

However, the mean variation of these few experiments, especially on nanowires, is still to high, and no clear origin of either positive or negative effects can be discerned. In addition, no detailed informations are available on other possibly occurring effects, such as the influence of the organic solvent, or changed morphology or crystallization of Sb$_2$S$_3$ on such modified TiO$_2$ surfaces.
4 Optimization of Flat Junction 
\textbf{Sb}_2\textbf{S}_3-\textbf{P3HT} Solar Cells

This chapter provides experimental results of optimized layer thicknesses and crystallization processes of \text{Sb}_2\text{S}_3 and P3HT. \text{Sb}_2\text{S}_3 films were grown using the standard recipe described in the previous chapter. However, surface modifications were left out in order to keep the system as simple as possible. Optimization of \text{Sb}_2\text{S}_3 and P3HT layer thickness was performed alternately, resulting in varying preparation parameters of different experiments.

4.1 \text{Sb}_2\text{S}_3 Deposition Time

4.1.1 Introduction

If the chemical bath temperature is constant, the deposition time becomes the main parameter to regulate the thickness and, therefore, light absorption of the deposited \text{Sb}_2\text{S}_3 films, which is a major way to control and improve the photogenerated current $I_{SC}$.[35] Generally, thicker films allow a more complete light harvesting. However, the efficiency can already decrease before the absorption reaches its maximum due to the limited conductivity of most low quality materials\textsuperscript{1} typically used in ETA solar cells. For this reason, layer thickness has to be optimized to reduce recombination and transport losses, and to maximize the possible current.

4.1.2 Experimental Methods

Several experiments have been performed to find the optimal deposition time of \text{Sb}_2\text{S}_3, covering CBD times between 60 to 135 minutes, on flat films. Each experiment was carried out under slightly different conditions\textsuperscript{2}, so that the experiments are not directly comparable with each other. On nanowires, only one experiment was done in order to roughly estimate the basic deposition time and to see whether they are suitable at all.

\textsuperscript{1}Low quality compared to monocrystalline silicon.
\textsuperscript{2}Cooling times of solutions in the ice bath prior deposition were 115, 165 and 200 min, respectively.
Table 4.1 summarizes detailed informations about preparation parameters of the individual experiments. In addition, all samples were plasma cleaned before CBD, and annealed at 140°C for 60s after spin-coating P3HT and PEDOT:PSS, respectively. Subsequent characterization was done by UV-Vis, SEM, AFM, I-V and EQE measurements.

Table 4.1: Preparation parameters of time study experiments. For better filling of nanowires a spin-coating process with two steps was used.

<table>
<thead>
<tr>
<th>experiment</th>
<th>P3HT concentration</th>
<th>spin-coating parameter</th>
<th>hole selective material</th>
<th>top contact</th>
</tr>
</thead>
<tbody>
<tr>
<td>flat 1</td>
<td>20 mg/ml</td>
<td>2000 rpm</td>
<td>PEDOT:PSS + WO3 (5 nm)</td>
<td>Ag (100 nm)</td>
</tr>
<tr>
<td>flat 2</td>
<td>20 mg/ml</td>
<td>1000 rpm</td>
<td>PEDOT:PSS</td>
<td>semitransparent Ag (20 nm)</td>
</tr>
<tr>
<td>flat 3</td>
<td>20 mg/ml</td>
<td>2000 rpm</td>
<td>PEDOT:PSS</td>
<td>Ag (80 nm)</td>
</tr>
<tr>
<td>nanowires</td>
<td>40 mg/ml</td>
<td>50 rpm 1000 rpm</td>
<td>PEDOT:PSS</td>
<td>Ag (80 nm)</td>
</tr>
</tbody>
</table>

4.1.3 Results and Discussion

Efficiencies of experiments on fabricated flat bilayer solar cells are summarized in Figure 4.1, leading to different optimal deposition times of Sb₂S₃.

Figure 4.1: Compilation of Sb₂S₃ deposition time experiments, showing summarized efficiencies of fabricated flat bilayer solar cells. Each data point represents one pixel.
Experiment 1 (Figure 4.1 a)) shows increasing PCE values for deposition times up to 80 minutes and implies optimal times of $>80$ minutes. This is confirmed by the second experiment (Figure 4.1 b)), where the efficiencies further increase from 80 to 100 minutes and decrease for longer deposition times. Thus, indicating a maximum PCE for deposition times of $\sim 100$ minutes. In contrast, experiment 3 (Figure 4.1 c)) shows an inverse behavior. In this case, efficiencies already decrease for deposition times longer than 75 minutes.

Comparing these results with corresponding UV-Vis measurements, this behavior can be explained by different deposition rates, which are most likely caused by slightly varying bath temperatures. Figure 4.2 shows the absorption$^3$ of prepared films of the second and third experiment at different wavelengths and demonstrates the significant variation in absorption. Thus, experiments with the same deposition time are only partially comparable if no additional measurements are performed.

![Absorption Spectra](image)

**Figure 4.2:** Mean absorption of (annealed) Sb$_2$S$_3$ films at different wavelengths in respect to deposition time.

For this purpose, SEM cross section images of Figure 4.3 have been recorded. However, in most cases, the interface between Sb$_2$S$_3$ and P3HT could not be distinguished. Furthermore, layer thickness measurements were complicated by the fact that some layers detached during the SEM sample preparation. Nevertheless, rough estimates lead to Sb$_2$S$_3$ layer thicknesses of 60 – 80 nm for deposition times of 85 minutes of experiment 3.

$^3$Mean value of 2-4 substrates.
4.1 Sb$_2$S$_3$ Deposition Time

Figure 4.3: SEM cross sections of finished solar cells with the structure ITO/flat TiO$_2$/Sb$_2$S$_3$/P3HT/PEDOT:PSS/Ag, including annealing of Sb$_2$S$_3$. a) Sb$_2$S$_3$ CBD of 100 minute from experiment 2 and b) 85 minutes from experiment 3. c) another view on b) with estimated layer thicknesses of ITO, TiO$_2$, Sb$_2$S$_3$ + P3HT and PEDOT:PSS.

Alternatively, deposition of Sb$_2$S$_3$ on silicon results in very smooth surfaces, even after subsequent annealing of the substrate and allows a precise determination of the layer thickness. Figure 4.4 illustrates an AFM picture of such a sample, which was fabricated with a deposition time of 105 minutes and subsequent annealing. Fitting the height profile of the edge seen in this picture by a step function returns a value of $\sim 51 \pm 1$ nm for the height of the Sb$_2$S$_3$ layer, which fits to the layer thickness measurement of SEM cross sections.

Figure 4.4: AFM picture and corresponding height profile of Sb$_2$S$_3$ on silicon. The edge for determining the height of the Sb$_2$S$_3$ layer was formed by a strip, which has been masked prior to deposition.

Only considering the best achieved PCE on TiO$_2$ nanowires, I-V measurements of Figure 4.5 imply an optimal deposition time of about 145 minutes. Due to the much higher surface area of a nanowire array, this corresponds to very thin layer thicknesses of only a few nanometers, which is indicated in the SEM cross section of Figure 3.3 b).
However, only one experiment was performed on this investigation, since the manufacturing process of the wires itself was not yet optimized, leading to unreproducible results.

Figure 4.5: I-V curves (a) and summarized power conversion efficiencies (b) of solar cells, fabricated on TiO$_2$ nanowires.

4.2 Sb$_2$S$_3$ Crystallization Conditions

4.2.1 Introduction

Right after deposition, as prepared Sb$_2$S$_3$ layers result in an amorphous, smooth, and homogeneous coverage.[54, 65] However, subsequent annealing of the films above 250$^\circ$ C initiates crystallization of the film into islands of polycrystalline Sb$_2$S$_3$ with mean crystallite sizes of 38 – 40 nm.[54, 65] The crystalline structure leads to an improved conductivity in dark by one to two orders of magnitude$^4$ and higher absorption of up to $\sim$ 750 nm.[54, 73] The latter is illustrated in Figure 4.6 in respect to the thickness of the layer.

Figure 4.6: Absorption of amorphous (dashed lines 1-4) and polycrystalline (solid line 1’-4’) Sb$_2$S$_3$ with increasing film thickness from $\sim$ 33 nm (1 and 1’) to $\sim$ 132 nm (4 and 4’).[73]

$^4$before annealing: $\sim$ 3 $\cdot$ 10$^{-8}$ S/cm, after annealing: $\sim$ 1.5 $\cdot$ 10$^{-7}$ S/cm according to [54] before annealing: $\sim$ 4 $\cdot$ 10$^8$ $\Omega$cm, after annealing: $\sim$ 5 $\cdot$ 10$^6$ $\Omega$cm according to [61]
Consequently, annealing is not only desirable, but rather necessary in order to produce optimized solar cells. In this section, investigations on annealing temperature and annealing duration will be discussed.

### 4.2.2 Experimental Methods

All annealing experiments were performed on a Stuart SD160 hotplate by Bibby Scientific Limited in a N\textsubscript{2}-atmosphere of a MB-200B modular glovebox workstation equipped with a MB-200-G gas purifier by MBraun. Thus, a controlled environment could be established with an O\textsubscript{2} concentration below 10 ppm and a humidity of approximately 2.5\%.

The substrates are either annealed at constant temperature of 325\,°C or for a constant time of 35 min for investigation of annealing time or annealing temperature, respectively.

Solar cells for I-V measurements are fabricated with 20 mg/ml P3HT solution in CBZ, which was spin-coated at 2000 rpm and subsequently annealed at 140\,°C for 60 seconds. Finally, 5 nm WO\textsubscript{3} and 80 nm Ag were thermally evaporated on top.

### 4.2.3 Results and Discussion

Results of annealing time and annealing temperature experiments are summarized in Figure 4.7, 4.8 and 4.9, showing I-V curves of best pixels and key characteristics of all fabricated solar cells.

![I-V curves of best pixels of (a) annealing temperature and (b) annealing duration experiment. a) Constant duration of 35 minutes. b) Constant temperature of 325\,°C.](image-url)
I-V curves and corresponding characteristics of the annealing temperature experiment (Figure 4.7a) and 4.8), reveal a clear temperature dependency of short circuit current and open circuit voltage due to an improved crystallinity Sb$_2$S$_3$. Specifically, the current increases nearly by a factor of two by increasing annealing temperature from 265°C to 325°C, and reaches a maximum at temperatures around 310°C where no further improvement occurs. Meanwhile, open circuit voltage decreases slightly by $\sim 0.1$ V with increasing temperatures. However, the significantly increased current in combination with only slightly decreased voltage leads to optimal annealing temperatures around 310°C.

Figure 4.8: Characteristics $I_{SC}$, $V_{OC}$, and PCE of annealing temperature experiment.

Alternatively, investigation of annealing time (Figure 4.7b) and 4.9) does not indicate an effect on short circuit current any more, while the $V_{OC}$ still decreases, particularly for long annealing times. The latter was also found by Liu et al. and is assumed to be caused by electric shunts or specific energy level alignment variations of polycrystalline Sb$_2$S$_3$.\[^{54}\]

Figure 4.9: Characteristics $I_{SC}$, $V_{OC}$, and PCE of annealing temperature experiment.

Eugen Zimmermann
4.3 P3HT Layer Thickness Adjustment

Surface Oxidation of Sb$_2$S$_3$

Another important point which is related to the optimization process is the oxidation of Sb$_2$S$_3$ at the interfaces. This occurs due to ambient air, which is present during the transfer to the glovebox or the annealing process. This point was not investigated intentionally, since it is barely reproducible, but still significantly affects the production and the eventual performance of the solar cells. For this reason, a short summary will be given in combination with results found in literature.

While thicker layers of Sb$_2$O$_3$ are highly insulating, thin layers at the interfaces are beneficial for performance of the solar cell since they passivate the surface and, therefore, reduce recombination at the interfaces.$^{[54]}$ Angle resolved XPS measurements by Liu et al. reveal a ~ 0.5 nm thick oxidized layer at the interface, which is formed without special treatment. It is composed of approximately 60\% Sb$_2$S$_3$ and 40\% Sb$_2$O$_3$ and vanishes completely after in situ sputter-cleaning of the surface.$^{[54]}$

Thus, several reported effects can be associated to this oxide layer, such as improved PCEs of cells, which are annealed in N$_2$ and subsequently cooled in ambient air compared to cells which are annealed and cooled completely in N$_2$.$^{[60, 64]}$ Furthermore, cells are better performing, which are annealed in O$_2$ at 200\°C for 10 min additionally to the normal annealing procedure in N$_2$.$^{[64]}$

Another effect, which fits in this context is an improved performance through aging of the cells. Specifically, efficiency of fabricated solar cells improves under normal storage conditions$^5$ with time, which is assumed to result by a slow evaporation of the solvent used for CuSCN as HTM.$^{[64]}$ However, this effect was also typically seen in self made solar cells, produced with P3HT and CBZ as solvent and already shown in Figure 3.5.

However, uncontrolled oxidation of the Sb$_2$S$_3$ layer is unfavorable, since in most cases it decreases performance, as seen for cells which were kept too long in ambient air before annealing or were annealed in the glovebox under higher O$_2$ concentrations ($> 30$ ppm).

4.3 P3HT Layer Thickness Adjustment

4.3.1 Introduction

Another parameter, which has to be adjusted in order to achieve optimized solar cell performance is the thickness of the HTM layer. In this case, optimization was performed with P3HT, which has shown to be an appropriate HTM for Sb$_2$S$_3$ based cells. However, as most organic materials, P3HT exhibits low hole mobilities of only $10^{-5} \sim 10^{-3}$ cm$^2$/V$S$.$^{[54]}$

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$^5$ambient air in dark
For this reason, the layer thickness has to be thin enough to prevent unnecessary transport losses while still forming a dense layer for selective charge carrier transport. Below, the investigation on different layer thicknesses is described in more detail.

### 4.3.2 Experimental Methods

Layer thickness optimization of P3HT was done by varying the concentration of prepared solutions in a range from 2.5 to 20 mg/ml in CBZ. In order to achieve reproducible and homogeneous layers, all solutions were spin-coated at 2000 rpm for 60 seconds with an acceleration set to 10. Subsequently, samples were annealed at 120–140 °C for 60 seconds, which is known to improve charge carrier mobility of P3HT.\(^{[54, 102]}\)

Substrates were prepared with Sb$_2$S$_3$ deposition times of 85 and 105 minutes and subsequently annealed at 325 °C for 35 minutes. Characterization was done by I-V, EQE and IS measurements. Additionally, layer thickness of P3HT was determined using AFM.

### 4.3.3 Results and Discussion

Figure 4.10 summarizes power conversion efficiencies of several experiments performed in order to optimize layer thickness of P3HT. Compared to the deposition of Sb$_2$S$_3$, adjustment of P3HT layer thickness has a higher reproducibility and resulted in optimum concentrations of 5 – 10 mg/ml. Specifically, performance increases with decreasing concentration mainly due to improved $I_{SC}$ and FF of fabricated cells.

![Figure 4.10: Summarized PCE values of several experiments performed in order to find optimum layer thickness of P3HT.](image)

Eugen Zimmermann
However, reducing the concentration below 5 mg/ml results in more unstable cells and dramatically decreased FFs, which is assumed to be a consequence of insufficient coverage of the Sb$_2$S$_3$ layer by P3HT.

This is supported by AFM measurements of different P3HT concentrations spin-coated on glass substrates. Specifically, these measurements reveal layer thicknesses of 33 ± 4, 75 ± 3 and 156 ± 4 nm for concentrations of 10, 20 and 30 mg/ml, respectively, which are indicating a nearly linear decrease in layer thickness with decreasing concentration. Consequently, concentrations of 5 mg/ml and below should result in layer thicknesses of < 20 nm, which are in the same range as the measured surface roughness of Figure 3.2.

![Figure 4.11: P3HT layer thickness measurement using AFM, whereas the linear fit acts as a guide to the eye.](image)

I-V thickness dependency is also visible for flat TiO$_2$/squaraine dye/P3HT cells (Figure 4.12), which were produced for another experiment. This is especially true for the $I_{SC}$.

![Figure 4.12: I-V curves (a) and PCE values (b) of fabricated flat TiO$_2$-dye-P3HT solar cells.](image)
4 Optimization of Flat Junction Sb$_2$S$_3$-P3HT Solar Cells

Impedance spectra acquired from solar cells with different P3HT layer thicknesses on Sb$_2$S$_3$ are shown in Figure 4.13, confirming a reduced recombination resistance of cells with thicker polymer layers. This is in accordance with previously shown I-V curves of Sb$_2$S$_3$ and can be attributed mainly to the low conductivity of P3HT.

**Figure 4.13:** a) Nyquist plot of impedance spectra recorded for solar cells with different P3HT layer thickness under illumination. b) Equivalent circuit used for data fitting.

### 4.4 Conclusion

In summary, investigations on flat bilayer structures of this chapter resulted in optimal layer thicknesses of approximately 50 – 60 nm and ~ 30 nm for Sb$_2$S$_3$ and P3HT, respectively. These correspond to chemical bath deposition times of about 100 – 105 minutes, using the recipe described in the previous chapter and P3HT concentrations of approximately 5 – 10 mg/ml, spin-coated at 2000 rpm. Moreover, the P3HT layer indicates to be optimal if it is as thin as possible while still covering Sb$_2$S$_3$ completely. Literature values found for planar device configuration suggest slightly thicker layers of 100 and 40 nm of Sb$_2$S$_3$ and P3HT, respectively.\cite{54}

I-V curves of the highest quality devices that have been produced thus far (PCE was already shown in Figure 4.10 c)) are shown in Figure 4.14, exceeding power conversion efficiencies of 3.2%. Compared to rarely found publications on planar layer device configuration of solar cells using Sb$_2$S$_3$ as absorber as by Boix et al. (ITO/TiO$_2$/Sb$_2$S$_3$/P3HT with $\eta = 1.43\%$)\cite{21} or Liu et al. (FTO/ZnO/Sb$_2$S$_3$/P3HT with $\eta = 2.4\%$)\cite{54}, this is an improvement by more than 100 and 30%, respectively. Moreover, cells of this fabrication batch were yet to be optimized, leaving some space for further improvement.
Figure 4.14: I-V curves of solar cells with best so far optimized layer thicknesses of Sb$_2$S$_3$ and P3HT.
5 Comparison Of Optimized flat Sb$_2$S$_3$-P3HT and P3HT:PCBM BHJ Solar Cells

5.1 Introduction

After optimization of preparation parameters, more detailed characterization of optimized solar cells was done in order to examine internal processes, such as recombination, charge collection probability, and behavior under different illumination intensities. Also, a P3HT:PCBM bulk heterojunction was used as a reference, since it is a common and well investigated solar cell architecture with reproducible characteristics and typically not charge transport or recombination limited.

5.2 Experimental Methods

This experiment includes the Sb$_2$S$_3$ champion device of the last chapter and a standard P3HT:PCBM bulk heterojunction solar cell for comparison.

Sb$_2$S$_3$ based solar cell was prepared with a chemical bath deposition time of 105 minutes and subsequent annealing at 325 °C for 35 minutes. P3HT is applied by spin-coating a 10 mg/ml solution at 2000 rpm and annealing at 140 °C for ~60 seconds. Finally, WO$_3$ (8 nm) and Ag (125 nm) are thermally evaporated.

The P3HT:PCBM cell was prepared and provided by a group member, using the standard preparation method. Specifically, cleaning and TiO$_2$ deposition was mainly performed as described in Chapter 2.2. Subsequently, the P3HT:PCBM blend solution, consisting of a 1:1 volume ration of 30 mg/ml P3HT and 24 mg/ml PCBM in CBZ, and PEDOT:PSS were spin-coated at 1000 rpm for 60 seconds with an acceleration set to 15 and 1, respectively. After application of PEDOT:PSS, the substrate was annealed at 140 °C for 1 – 2 min. Ag contacts (150 nm) are thermally evaporated on top. Finally, cells are annealed in a glovebox at 140 °C for 10 minutes.
Characterization and comparison of these cells were made under AM 1.5G and with normal and light intensity dependent I-V, EQE, IS, and photo voltage and current decay measurements.

5.3 Results and Discussion

5.3.1 I-V and EQE measurements

Optimization of fabricated flat bilayer solar cells, as described in the last chapter, led to outstanding solar cell performances with external quantum efficiencies of $\sim 75\%$ in the region of highest global irradiance spectrum, which is illustrated in Figure 5.1. In this case, the EQE is slightly overestimated by the setup since the measurements are performed at low light intensities without background illumination. However, calculation of the maximal achievable current density $J_{SC,\text{theo}} \sim 9.7\text{ mA/cm}^2$ using Equation 2.5 indicates a good match to the measured current density $J_{SC} \sim 9.3\text{ mA/cm}^2$ of I-V, and confirms the measured EQE values.

![Figure 5.1](image-url)

Figure 5.1: a) Calculated amount of global irradiance contributing to the b) EQE spectra of highest quality Sb$_2$S$_3$ ETA and a reference P3HT:PCBM BHJ solar cell.

Moreover, a high EQE implies that most of the layer contributes to charge generation and not only a few nanometers near the interfaces as in the case of most organic materials like P3HT. This means, excitons exhibit either small binding energies and can be separate directly inside the bulk or long diffusion path lengths. The former is assumed due to the combination of relatively large crystallite sizes and a high dielectric constant of Sb$_2$S$_3$ after annealing. However, the size of the crystallites also supports long diffusion paths since excitons have less grain boundaries to pass.
Nevertheless, even with a complete layer contributing to charge generation, I-V measurements of Figure 5.2 indicate a less than optimal charge transport (worse FF) and higher recombination (lower shunt resistance) in Sb$_2$S$_3$, compared to the P3HT:PCBM reference. This can be mainly attributed to the flat bilayer structure in combination with low conductivity of Sb$_2$S$_3$. In P3HT:PCBM cells charge carrier pathways are better separated due to the phase separation of the bulk heterojunction.

![Figure 5.2: I-V curves and characteristics of Sb$_2$S$_3$ and P3HT:PCBM solar cells.](image)

**5.3.2 Light Intensity Depend I-V measurements**

In order to analyze performance limitations of fabricated cells, light intensity dependent I-V measurements were performed. These can be used to understand possible limitations by built-up space-charges and recombination processes or to calculate the probability of charge collection.

Space-charges are mainly affecting highly absorbing organic and (low quality) semiconducting materials at higher light intensities due to their generally low conductivities. Specifically, charge carriers are generated too fast to be extracted by the electrodes, building up space-charges, which attract complementary charge carriers and greatly enhance recombination. In a light intensity ($P_{\text{light}}$) vs. $I_{SC}$ log-log plot, such a limitation is indicated by a non-linear correlation of $I_{SC} \sim P_{\text{light}}^\alpha$ with $\alpha < 1$.\[103\]

Figure 5.3 a) shows this correlation for self made Sb$_2$S$_3$ and P3HT:PCBM based solar cells and reveals no limitations of this kind. Moreover, this is one of the reasons for high EQE, if reflection and absorption losses are minimized.\[104\]
5.3 Results and Discussion

Alternatively, Figure 5.3 b) shows the open circuit voltages as a function of light intensity ($P_{\text{light}}$), which can be described by

$$V_{\text{OC}} = \frac{E_{\text{gap}}}{q} - \frac{k_B \cdot T}{q} \cdot \ln \left( \frac{(1 - P) \gamma N_c^2}{PG} \right) \sim \frac{S \cdot k_B \cdot T}{q} \cdot \ln \left( P_{\text{light}} \right), \quad (5.1)$$

where $E_{\text{gap}}$ is the energy difference between the highest occupied molecular orbit (HOMO) of the electron donor and the lowest unoccupied molecular orbit (LUMO) of electron acceptor$^1$, $q$ the elementary charge, $k_B$ the Boltzmann constant, $T$ the temperature, $G$ and $P$ the generation rate and dissociation probability of electron-hole pairs, respectively, $\gamma$ the Langevin recombination constant$^2$, and $N_c$ the density of states in the conduction band.$^{106}$ This equation intentionally describes the case that only Langevin$^3$ recombination of free charge carriers occurs, which mainly depends on the particular charge carrier concentrations of electrons and holes and leads to a logarithmic light dependency of open circuit voltage ($S=1$).

Fits of own data result in slopes of $S \sim 1.9$ for both types of solar cells and indicate a stronger recombination process apart from Langevin recombination. One possibility is an additional electron trap state assisted recombination process at lower charge carrier concentrations, which in that case would be slightly higher for Sb$_2$S$_3$ based solar cells.$^{107}$ However, since both types of cells are showing a similar behavior, this enhanced recombination also could be caused by a common attribute, such as the TiO$_2$ blocking layer. This assumption is supported by the fact that in P3HT:PCBM cells the TiO$_2$ layer is known to be thinner due to a slightly different preparation process.

---

1 Origin of the built-in potential of organic and hybrid solar cells.$^{105}$
2 $\gamma = 2(\mu_n + \mu_p)$ with dielectric constant $\epsilon$ and electron ($\mu_n$) and hole ($\mu_p$) mobilities.$^{106}$
3 Stochastic recombination of free charge carriers (bimolecular recombination).
Furthermore, probability of charge collection

$$P_{coll}(V) = \frac{I_{light}(V) - I_{dark}(V)}{I_{saturation}}, \quad (5.2)$$

is highly related to recombination processes, where $I_{light}(V)$ and $I_{dark}(V)$ are the measured I-V curves under illumination and in dark, respectively, and $I_{saturation}$ the reverse saturation current at sufficiently large reverse bias voltages.$^{[108]}$

Figure 5.4 illustrates $P_{coll}$ for both absorber materials and reveals a nearly light independent collection probability of Sb$_2$S$_3$ based solar cells. In combination with the linear behavior of $I_{SC}$ in Figure 5.3 a) and, therefore, exclusion of space charge limitations, this leads to a mainly monomolecular recombination dominated loss mechanism.$^{[109]}$

Furthermore, the low FF of Sb$_2$S$_3$ can be explained by a potential dependent charge separation, which is in agreement with light intensity dependent measurements and the used flat bilayer structure. This is supported by measurements of Liu et al, which reveal a high recombination rate of charge carriers in the Sb$_2$S$_3$ layer due to the absence of HTM or metal oxide and therefore a decreased internal electric field in Sb$_2$S$_3.$^{[54]}$

![Figure 5.4: Visualized charge collection probabilities of a) Sb$_2$S$_3$ and b) P3HT:PCBM based solar cells by normalizing light intensity dependent I-V curves (inset) to an I-V curve measured in dark.](image)

Charge collection probability of P3HT:PCBM based solar cells, on the other hand, is clearly light dependent even at zero potential. This indicates mainly bimolecular recombination processes due to the highly charge carrier concentration dependent recombination rate, which is a result of the increased interface.
5.3 Results and Discussion

5.3.3 PVD/PCD

Photovoltage and photocurrent decay measurements, which are performed at different light intensities are illustrated in Figure 5.5 and reveal slightly higher charge carrier extraction rates but also faster recombination in P3HT:PCBM based cells compared to Sb$_2$S$_3$.

![Figure 5.5: Photovoltage and photocurrent decay rates of Sb$_2$S$_3$ and P3HT:PCBM solar cells.](image)

Both can be attributed to the morphology of P3HT:PCBM cells in combination with a thinner layer thickness of TiO$_2$. The improved BHJ morphology allows for the fabrication of solar cells with much better charge carrier pathways and therefore faster extraction. However, the increased interfacial area between P3HT and PCBM, and separated inclusions of one of these materials, enhance bimolecular recombination, which in light dependent measurements was found to be the dominant recombination process in this type of solar cells.

In contrast, the flat layer arrangement of Sb$_2$S$_3$ and P3HT results in less bimolecular recombination due to the single interface but instead in long charge carrier pathways.

5.3.4 IS

In order to analyze intrinsic electric properties of compared solar cell types, impedance spectroscopy measurements were performed. Acquired data for measurements under illumination at zero potential as well as corresponding fits are shown as Nyquist and bode plots in Figure 5.6, where data points below 100 Hz were excluded due to high deviation.
For both types of investigated cells the basic model of one series resistance $R_s$ and one RC parallel combination $R_{rec}$ and $C_\mu$ as described in Chapter 1.5 was chosen as starting point. The broadened peak of the phase angle in the bode plot of Sb$_2$S$_3$ indicates at least two overlapping processes with peaks at $\sim 3.5 \cdot 10^3$ and $\sim 4.8 \cdot 10^4$ Hz, respectively. Therefore, a second RC parallel combination was set in series to the basic model. Further improvement was achieved by replacing the capacitors by constant phase elements (QPE), which resulted in an adequate model with well matching fits. In this case, the RC parallel combinations were assigned to the respective interfaces of Sb$_2$S$_3$ to TiO$_2$ and P3HT, where the resistances can be associated with recombination processes and the capacities with interfacial trap states[85].

The phase bode plot of P3HT:PCBM cells shows in addition to the RC parallel element at $4.1 \cdot 10^4$ Hz a transmission line behavior at high frequencies, which is represented by a straight line. Thus, a transmission line$^4$ with length $L$ was included into the model instead of a second RC parallel combination. In this case, each generic component $\zeta_i$ represents a RC parallel combination, where the capacitor is replaced by a constant phase element (CPE). The length, $L$, originally was used to describe the length of a porous electrode$^{[110, 111]}$ and affects the absolute values$^5$ of the generic components $\zeta_i$ but not their ratio between different measurements.

Both models are illustrated in Figure 5.7 and exhibit relatively good fits with deviation of only a few percent.

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$^4$In ZView labeled as distributed element 'DX Type 12 - Bisquert #3' with length $L$ instead of repetition number $N$ mentioned in Chapter 1.5.

$^5$Fit parameter of fits with different $L$ values are not directly comparable to each other.
5.3 Results and Discussion

Figure 5.7: Equivalent circuits used for fitting acquired impedance spectra of a) Sb$_2$S$_3$ and b) P3HT:PCBM solar cells.

However, exponents of used constant phase elements occasionally slightly exceed the upper limit of 1, thus indicating insufficient data points for proper fits. All other simulated parameters are summarized in Table 5.1 and 5.2 for Sb$_2$S$_3$ and P3HT:PCBM based solar cells, respectively.

Table 5.1: Parameter of fitted impedance spectra of Sb$_2$S$_3$ based solar cells.

<table>
<thead>
<tr>
<th>DC Bias</th>
<th>$R_S$</th>
<th>$R_{Sb_2S_3}$</th>
<th>QPE$_{Sb_2S_3}$</th>
<th>$R_{HTM}$</th>
<th>QPE$_{HTM}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.2</td>
<td>9.26(2)</td>
<td>12.1(4)</td>
<td>2.83(6)·$10^{-7}$</td>
<td>9818(7)</td>
<td>5.15(2)·$10^{-8}$</td>
</tr>
<tr>
<td>0</td>
<td>9.14(2)</td>
<td>11.1(4)</td>
<td>3.5(1)·$10^{-7}$</td>
<td>5647(4)</td>
<td>5.24(3)·$10^{-8}$</td>
</tr>
<tr>
<td>0.2</td>
<td>9.03(2)</td>
<td>6.5(3)</td>
<td>5.6(2)·$10^{-7}$</td>
<td>2714(2)</td>
<td>4.84(3)·$10^{-8}$</td>
</tr>
</tbody>
</table>

Table 5.2: Parameter of fitted impedance spectra of P3HT:PCBM based solar cells. As length of the model $L = 0.1$ was chosen.

<table>
<thead>
<tr>
<th>DC Bias</th>
<th>$R_S$</th>
<th>$R_i$</th>
<th>$R_{\zeta,i}$</th>
<th>CPE$_{\zeta,i}$</th>
<th>$R_{rec}$</th>
<th>QPE$_{\mu}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>-0.2</td>
<td>10.7(7)</td>
<td>1978(42)</td>
<td>89(6)</td>
<td>6.4(14)·$10^{-6}$</td>
<td>3501(53)</td>
<td>2.57(3)·$10^{-8}$</td>
</tr>
<tr>
<td>0</td>
<td>16.05(7)</td>
<td>1287(2)</td>
<td>57.7(5)</td>
<td>2.45(6)·$10^{-6}$</td>
<td>596(4)</td>
<td>1.24(1)·$10^{-7}$</td>
</tr>
<tr>
<td>0.2</td>
<td>21.13(5)</td>
<td>382(13)</td>
<td>33.97(2)</td>
<td>9.14(3)·$10^{-7}$</td>
<td>23.4(3)</td>
<td>1.42(5)·$10^{-8}$</td>
</tr>
</tbody>
</table>

In addition, impedance spectra are acquired with various bias voltages. Figure 5.8 shows Nyquist plots and their corresponding fits for applied DC voltages of $-0.2$, $0$ and $0.2$ V.
Comparison Of Optimized flat Sb$_2$S$_3$-P3HT and P3HT:PCBM BHJ Solar Cells

Figure 5.8: Impedance spectra measured at applied DC voltages of −0.2, 0 and 0.2 V. The inset shows the zoomed in area at high frequencies.

In all cases, P3HT:PCBM cells exhibit lower absolute values of total resistance compared to Sb$_2$S$_3$ based cells. Moreover, in P3HT:PCBM cells a nonlinear voltage dependency of total resistance is observed. The former indicates higher recombination resistances of Sb$_2$S$_3$ based cells and is in accordance with smaller recombination rates of Sb$_2$S$_3$ determined by PVD.

However, the total resistance obtained by IS corresponds to the reciprocal slope of the I-V curve at the applied bias, which is not in line with shown I-V measurements of Figure 5.2. Furthermore, recombination resistance of P3HT:PCBM cells decreases nonlinear with increasing bias, which is also contrary to observed I-V curves and corresponding FF. This indicates that impedance spectra and derived characteristics of different types of solar cells are not directly comparable and the corresponding recombination processes have to be considered in order to explain made observations.

Thus, keeping in mind that monomolecular recombination is the dominant loss mechanism in Sb$_2$S$_3$ and charge separation is dependent on potential, an applied positive bias should mainly result in a slower extraction of already separated charge carriers and a decreased dissociation rate of new excitons. In contrast, a reverse bias should do the opposite and improve both, extraction and separation. Compared to measured IS data and fits, this assumption is confirmed by the nearly linear behavior of the total recombination resistance.

---

6 Broadly speaking, the point of intersection with the Z'-axis rightmost. A more detailed description of the composition can be found in [85].
In contrast, excitons in the P3HT:PCBM blend are quickly separated into free charge carriers due to a typically short distance to the next interface. However, the large interface area still leads to a high bimolecular recombination rate, despite the applied voltage.

Nevertheless, further investigations on the intrinsic properties of Sb$_2$S$_3$ ETA solar cells have to be done in order to determine the contribution of the individual layers.
6 The Role of The Hole Transporter in Sb$_2$S$_3$ ETA Solar Cells

6.1 Introduction

So far, P3HT was used as HTM for optimization and characterization of Sb$_2$S$_3$ ETA solar cells. However, the optimization process of Chapter 4 made it clear that a decreasing P3HT layer thickness improves performance until fabricated cells become unstable. Moreover, Figure 4.6 shows a high absorption of Sb$_2$S$_3$ up to 750 nm, which overlaps the absorption of P3HT (Figure 6.4). EQE spectra of optimized solar cells shown in Figure 5.1 even reveal a negative impact of a rapidly decreasing EQE for wavelengths above 500 nm, thus, limiting maximal achievable $I_{SC}$ roughly by a factor of two$^1$. The total decrease in EQE can not be assigned exclusively to the HTM. However, the shape of the absorption edge can be addressed clearly.

Different HTMs have been investigated in order to clarify the role of the HTM and to improve charge generation and extraction. Energy band alignment of investigated HTMs, Sb$_2$S$_3$, the electrodes as well as electron and hole blocking layers are shown in Figure 6.1.

Figure 6.1: Energy band diagram of used materials: ITO$^{[39]}$, TiO$_2$$^{[15, 113]}$, Sb$_2$S$_3$$^{[71]}$, P3HT$^{[35, 54]}$, PCPDTBT$^{[35, 114]}$, PBDTTT-C-T$^{[37, 38]}$, MDMO-PPV$^{[36, 115]}$, spiro-OMeTAD$^{[29, 116]}$, CuSCN$^{[71, 117]}$, PEDOT:PSS$^{[118]}$, WO$_3$$^{[15]}$, Ag$^{[15, 41]}$. Energy bands without HOMO or LUMO indication either behave like metals or are representing the HOMO level of the material.

$^1$Estimated by Equation 2.7 with 80% absorption, 750 nm absorption onset and the AM1.5G spectra.
6.2 Experimental Methods

This chapter covers experimental results of solar cell devices with various preparation parameters and can be divided into three parts: concentration dependency of layer thickness, comparison of different layer thicknesses through I-V measurements, and analysis of the HTM contribution to EQE. Parameters of these three parts are summarized in Table 6.1, 6.2 and 6.3, respectively. All Sb$_2$S$_3$ layers are annealed at 325 °C for 35 minutes in N$_2$ after CBD, and HTM solutions are spin-coated at 2000 rpm for 60 s with an acceleration set to 10. For solar cells, WO$_3$ (8 nm) was thermally evaporated as electron blocking layer.

CBZ was used as solvent of organic materials/P3HT, PCPDTBT, MDMO-PPV, PBDTTT-C-T, and spiro-OMeTAD, whereas CuSCN was dissolved in dipropyl sulfid. For the latter two solutions were prepared using two different recipes. The first solution was prepared by solving $\sim$ 110 mg CuSCN in 3 ml dipropyl sulfide resulting in a heavily oversaturated solution.$^{[45]}$ For the second solution only $\sim$ 40 mg of CuSCN are dissolved in 2 ml of dipropyl sulfide, which is slightly greater than the soluble concentration of the second recipe.$^{[47]}$ Both recipes mention different soluble concentrations of 40 mg/ml and < 20 mg/ml of CuSCN in dipropyl sulfide, respectively. Due to the more recent publication date of the second recipe, 20 mg/ml were assumed as soluble amount. However, in both cases the excess material dropped to the bottom and formed needle-shaped crystals after a few days. Therefore, both solutions should have adjusted to the same concentration.

Table 6.1: Preparation parameters for layer thickness measurement. Microscope slides were used as substrates, which were cleaned prior to the deposition of the HTM by oxygen plasma.

<table>
<thead>
<tr>
<th>HTM</th>
<th>concentration (mg/ml)</th>
<th>HTM</th>
<th>concentration (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>10, 20 and 30</td>
<td>PBDTTT-T-C-T</td>
<td>10, 20 and 30</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>10, 20 and 30</td>
<td>spiro-OMeTAD</td>
<td>10, 20 and 30</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>5, 10 and 15</td>
<td>CuSCN</td>
<td>20</td>
</tr>
</tbody>
</table>

Table 6.2: Preparation parameters for comparison of layer thickness by I-V measurements. CBD time was 105 minutes. Silver (100 nm) was thermally evaporated as top contact.

<table>
<thead>
<tr>
<th>HTM</th>
<th>concentration (mg/ml)</th>
<th>annealing conditions</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>10 and 20</td>
<td>120 °C, 60 s</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>10 and 15</td>
<td>120 °C, 10 min in N$_2$</td>
</tr>
<tr>
<td>spiro-OMeTAD</td>
<td>20 and 40</td>
<td>-</td>
</tr>
</tbody>
</table>
Table 6.3: Preparation parameters for experiments of HTM contribution to EQE. CBD time was 85 minutes. 15 and 125 nm Ag were thermally evaporated as semi- and nontransparent top contacts, respectively. Additionally, 100 nm Ag were deposited on the outer part of semitransparent contacts to improve the connection to the measuring Au pin.

<table>
<thead>
<tr>
<th>HTM</th>
<th>concentration (mg/ml)</th>
<th>annealing</th>
<th>HTM</th>
<th>concentration (mg/ml)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3HT</td>
<td>6.6, 10 and 20</td>
<td>120 °C, 60 s</td>
<td>PBDTTT-C-T</td>
<td>20</td>
</tr>
<tr>
<td>PCPDTBT</td>
<td>15</td>
<td>-</td>
<td>spiro-OMeTAD</td>
<td>40</td>
</tr>
<tr>
<td>MDMO-PPV</td>
<td>12</td>
<td>-</td>
<td>CuSCN</td>
<td>20</td>
</tr>
</tbody>
</table>

Furthermore, squaraine dye sensitized solar cells with P3HT as HTM were fabricated for comparison of EQE spectra. Therefore, flat TiO$_2$ substrates were immersed in a dye bath for 20 minutes. Subsequently, substrates were rinsed in isopropanol and dried in N$_2$. Different concentrations of P3HT were spin-coated at 2000 rpm and annealed at 120 °C. WO$_3$ and Ag were thermally evaporated with thicknesses of 8 and 15 nm, respectively. Additionally, 100 nm Ag were evaporated on the outer part of the electrode in order to establish a better connection to the measuring Au pin.

Characterization of fabricated cells was done by I-V and EQE measurements, whereas the AFM was used to determine layer thicknesses of used HTMs.

### 6.3 Results and Discussion

Initially, HTM layer thicknesses were determined by AFM in order to produce comparable solar cells for I-V and EQE measurements. The results of the AFM measurements are illustrated in Figure 6.2 indicating a mainly linear increase of layer thickness with increased concentration of all materials in the examined range. Using this data, concentrations of 20 mg/ml (P3HT and PBDTTT-CT), 15 mg/ml (PCPDTBT), 12 mg/ml (MDMO-PPV) and 40 mg/ml (spiro-OMeTAD) were estimated in order to prepare layer thicknesses of approximately 80 nm for all HTMs.

In case of CuSCN, no reliable preparation process was found to produce competing efficiencies or at least stable cells. Also MDMO-PPV did not result in competing efficiencies. Therefore, no further experiments have been performed on this materials, although several groups achieved highly promising results for CuSCN as HTM in combination with Sb$_2$S$_3$ (see Table 1.1). Nevertheless, CuSCN shows equal layer thicknesses for both recipes, as was expected in the experimental part due to the recrystallization of the excess material.
Figure 6.2: Layer thicknesses of different HTMs including corresponding linear fits as guide to the eye. One data point of CuSCN was shifted to the right for better comparison.

I-V characteristics of solar cells with P3HT, PCPDTBT and sprio-OMeTAD and layer thicknesses of approximately 40 and 80 nm are shown in Figure 6.3. As found for P3HT in Chapter 4.3, these characteristics indicate the same layer thickness dependency of solar cell efficiency. Specifically, overall efficiency increases with decreasing layer thickness mainly due to a 20 – 30 \% higher \textit{I}_\text{SC} and FF but only slightly increased \textit{V}_\text{OC}.

Figure 6.3: PCE, \textit{I}_\text{SC}, \textit{V}_\text{OC}, and FF of P3HT, PCPDTBT and sprio-OMeTAD with comparable layer thicknesses of 40 and 80 nm for lower and higher concentration, respectively.

EQE spectra were recorded in order to clarify the contribution of the HTM. Therefore, samples are either illuminated through the glass/TCO (front illumination) as usual or through the semitransparent Ag contact (back illumination). In the latter case, the influence of the HTM was believed to increase proportionally with the light absorbed in
this layer. In addition, it is worth mentioning that the absolute EQE of back illuminated samples is lower due to the reflection of light at the semitransparent Ag back contacts.

For comparison, a squaraine dye sensitized solar cell with P3HT as HTM was fabricated, wherein I-V measurements were already presented in Figure 4.12. Corresponding EQE and absorption curves are shown in Figure 6.4 and reveal a main contribution of P3HT ((1) and (2)) to current generation. Since only a monolayer of dye on a flat surface was used as sensitizer, the dye absorption is relatively low and photocurrent is mainly generated upon photon absorption in the HTM. However, one of the main absorption peaks of the squaraine dye is at 675 nm and can be determined in the EQE spectrum (3) which is monitored while the sample is illuminated through the TCO substrate.\cite{119, 120}

![Figure 6.4: EQE spectra of a flat TiO$_2$-squarain dye-P3HT solar cell illuminated as normal through the TCO (front) and through the semitransparent Ag contacts (back). In addition, the absorption of P3HT is shown in the lower part.](image)

Although TiO$_2$ absorbs up to 400 nm\cite{121}, it does not contribute to current generation in a significant way (4) since most excitons are generated at the TiO$_2$-TCO interface, which does not allow an inefficient dissociation. If the samples are illuminated through the semitransparent Ag contacts the contribution of the dye vanishes completely and P3HT is heavily suppressed. This indicates that no significant exciton dissociation occurs at the P3HT-WO$_3$ interface and due to the P3HT layer thickness of $\sim$ 80 nm most excitons recombine before they reach the P3HT-dye interface. The leftmost peak (5) coincides with the absorption peak of WO$_3$\cite{122} and can be assigned to exciton dissociation at the WO$_3$-Ag interface. However, since this WO$_3$ layer is only 8 nm thick, it is more likely that the contribution of TiO$_2$ is increased due to the exciton generation at the right interface (TiO$_2$-P3HT).

\footnote{The second is at about 625 nm and completely superposed by P3HT.}

\textit{Eugen Zimmermann}
In combination with Sb$_2$S$_3$, front and back illuminated EQE measurements of solar cells with P3HT, PBDTTT-C-T, PCPDTBT, and spiro-OMeTAD as HTM have been investigated. Additionally, absorption spectra of all these materials are recorded. All resulting EQE and absorption spectra are summarized in Figure 6.5.

Figure 6.5: EQE spectra of a) P3HT, b) PBDTTT-C-T, c) PCPDTBT and d) spiro-OMeTAD illuminated as normal through the TCO (front) and through the semitransparent Ag contacts (back). Lower part illustrates absorption Sb$_2$S$_3$ and the HTM, respectively.

Front illuminated solar cells with P3HT exhibit the same characteristic EQE shape as could be seen for optimized solar cells in Figure 5.1 b) including the rapid decrease of EQE at wavelengths larger than 500 nm. In addition, contribution of TiO$_2$ at $\sim 325$ and 375 nm can be identified, which is also visible in EQE spectra of all other investigated HTMs. Nevertheless, compared to the absorption spectra of P3HT this rapid decrease in EQE on the right coincides with the maximum absorption of P3HT at about 550 nm and its absorption onset at $\sim 650$ nm. Similar behavior is also seen for PCPDTBT in the region of $\sim 400$ nm.
However, in case of PBDTTT-C-T and the main absorption region of PCPDTBT this can only be guessed since no EQE spectrum was measured which shows pure contribution by Sb$_2$S$_3$. The latter was assumed for spiro-OMeTAD, which absorbs mainly at wavelengths below 400 nm. However, it shows a highly suppressed EQE spectrum between 500 and 650 nm compared to literature and can not be explained.\textsuperscript{[55]} In back illuminated EQE spectra all HTMs are showing the same light filtering effect as described for flat squaraine dye sensitized cell and lead to high exciton recombination rates and strongly decreased EQE at wavelengths which coincides with the absorption of the HTM.

In summary, none of the investigated HTM shows any significant contribution to charge generation. Moreover, the absorption of light by the HTM is not just unnecessary but even decreases efficiency of fabricated solar cells. This can be addressed either to a filtering of light by the HTM, an increased recombination due to charge transfer problems at the Sb$_2$S$_3$-HTM interface, or both. In the former case, the HTM is decreasing the amount of photo-current due to the absorption of light that otherwise would be reflected by the back contact and probably absorbed by Sb$_2$S$_3$. This could be solved by increasing the surface area of the cell and therefore maximizing the amount of light that is absorbed by Sb$_2$S$_3$. Alternatively, incomplete charge carrier transport at the Sb$_2$S$_3$ interface to the HTM can lead to highly increased recombination rates and reduce the FF and consequently PCE of Sb$_2$S$_3$ based solar cells as found in \textsuperscript{[35]}. Specifically, the chemical interaction at the interface of Sb$_2$S$_3$ and the used HTM determines how efficient charge transfer occurs. This chemical interaction was found to be improved for P3HT and PCPDTBT as HTM due to good binding of their thiophene moieties to Sb$_2$S$_3$.\textsuperscript{[35]} Additionally, own measurements on spiro-OMeTAD and PBDTTT-C-T as HTM, which do not exhibit such a good binding, revealed a highly increased FF and PCE if the solar cells were kept for at least 10 minutes in light prior to the measurement. In this case, it is assumed that interface trap states are filled due to the illumination, which in case of P3HT and PCPDTBT are already decreased due to the reported chemical interaction.

Nevertheless, the characteristic EQE shape of Sb$_2$S$_3$ based solar cells with P3HT as HTM is even visible for an improved contact of P3HT to Sb$_2$S$_3$ and a highly increased surface area by using an interface modifier and mesoporous TiO$_2$, respectively.\textsuperscript{[62]} Such optimized cells exhibit a FF of nearly 70 % FF and indicate that both mechanisms are involved.

In order to investigate the particular contribution of these mechanisms, EQE measurements of solar cells with different P3HT layer thicknesses were performed. In addition, the Ag back contact was fabricated as nontransparent and semitransparent type in order to measure the EQE response of fabricated configurations to different illumination directions and electrode transparencies. Figure 6.6 a), b) and c) illustrate measured EQE spectra of nontransparent as well as front and back illuminated samples, respectively, and reveal three interesting wavelength regions, which will be discussed in more detail.
6.3 Results and Discussion

Figure 6.6: EQE spectra of Sb$_2$S$_3$ based solar cells with different P3HT layer thicknesses as HTM. a) Non transparent and semitransparent Ag back contact, where b) is illuminated through the glass/TCO and c) through the back contact.

As previously stated and can be seen in the absorption spectra of P3HT, at wavelengths between 300 and 450 nm (1) the Sb$_2$S$_3$ is responsible for the EQE with some contribution from the TiO$_2$. EQE in this region is mainly independent of the P3HT layer thickness, when illuminated through the front, but restricted to wavelengths above 350 nm due to the absorption by the TiO$_2$ at the wrong interface. This indicates that in a) and b) most of this light is already absorbed by the TiO$_2$ and Sb$_2$S$_3$ and does not affect P3HT anymore. However, if the samples are illuminated through the back contact, the contribution of wavelengths below 350 nm drastically increases but simultaneously became more dependent to layer thickness of the P3HT. The latter can be expected since P3HT slightly absorbs light of these wavelengths.

In contrast, at wavelengths between 450 and 600 nm (2) both Sb$_2$S$_3$ and P3HT exhibit a high extinction coefficient. But even the combination of both layers in flat bilayer arrangement is still too thin to absorb 100% of the incident photons, leading to a P3HT layer thickness dependency in a) and c) but not in b). This is clear in c) and can be explained exactly as in the case of the squaraine dye sensitized cell where the excitons are mainly generated at the wrong side of the P3HT layer and recombine before they reach the dissociating interface.

In a) the thickness of the Ag back contact makes the difference to b). In the former case, the back contact is nontransparent and reflects all of the not yet absorbed light. Therefore, in order to probably contribute to the EQE these photons have to pass the P3HT layer twice and result in a just slight increase of EQE. In the latter case, the back contact reflects only a negligible fraction of light and, therefore, no additional contribution to the EQE occurs. In addition, this indicates that there is no significant charge transport limitation of separated charge carriers due to the increased layer thickness of P3HT.
At wavelengths above 650 nm (3), the absorption of P3HT almost vanishes completely, which is indicated by the layer thickness independent EQE in c). However, in a) the thickness still plays an important role and is assumed to be a result of a standing wave of light, where the HTM is acting as optical spacer and leads to a maximum of intensity exactly in Sb$_2$S$_3$.\textsuperscript{123} This can also be assumed in b) where the semitransparent back contact is reflecting at least a fraction of the incident light.
7 Conclusion and Outlook

This work presents a summarized compilation of the fabrication, optimization, and characterization of Sb$_2$S$_3$ coatings and Sb$_2$S$_3$ based extremely thin absorber cells.

First, deposition conditions and parameters of the chemical bath have been investigated in order to achieve homogeneous and reproducible Sb$_2$S$_3$ coatings of flat and nanostructured TiO$_2$ surfaces. For this purpose, deposition temperature, positioning of the substrates, immersion time, and pre- and post-treatments have been examined. Additionally, surface modifications and their influence on film growth and cell performance were tested. As a result, a detailed instruction could be described on how to produce high quality Sb$_2$S$_3$ coatings.

As a next step, layer thickness and crystallization conditions of previously fabricated coatings in combination with a well-studied hole transport material have been explored. This resulted in optimized flat Sb$_2$S$_3$ based heterojunction solar cells with as compared to literature record efficiencies of over 3.2%.

However, internal recombination processes limit further efficiency improvements and even optimized cells exhibit relatively low FF. In order to identify and probably overcome these limitations, comparative measurements with a solar cell typically free of charge transport or recombination limitations have been performed. As a result, limitations by space charges were excluded and high exciton diffusion lengths confirmed. However, as main loss mechanisms monomolecular recombination of excitons and long charge carrier pathways have been revealed. Furthermore, a potential dependency of charge separation was found to further decrease the FF.

Finally, several hole transport materials have been compared in order to determine the influence on charge transport and charge generation. In addition, a flat dye sensitized solar cell was used as reference. However, none of the investigated materials showed any significant contribution to charge generation. Instead, absorption by the HTM was observed to reduce the efficiency in at least one kind, whereas the second was shortly discussed with the help of literature.

In summary, some of the found limitations possibly can be addressed through the use of nanostructured metal oxides. These include the strong monomolecular recombination,
long and inefficient pathways of the charge carriers, and the potential dependency of charge separation. Nevertheless, additional investigations have to be done on nonabsorbent, or to charge generation contributing HTMs which include a good interface connection to Sb$_2$S$_3$.

Still, this work demonstrates flat Sb$_2$S$_3$ based heterojunction solar cells with relatively high performances. Moreover, Sb$_2$S$_3$ layers are produced in a low cost manufacturing process, which except of the nitrogen atmosphere for annealing, only requires clean H$_2$O, a uniform cooling, and relatively cheap precursor chemicals. Thus, optimizing the morphology and resolving the found limitations possibly results in solar cells which can compete with amorphous silicon or other thin film solar cells.
List of Figures

1.1 Global direct normal irradiance of sunlight. [3] ................................. 1
1.2 a) Generation, movement and b) recombination processes of Frenkel and charge-transfer (CT) excitons. (1) Frenkel excitons are generated throughout the absorbing layer and are moving by diffusive hopping transport (2). At interfaces or impurities they can relax into CT excitons (3) or completely dissociate into free charge carriers (4), which subsequently move towards the electrodes (5). Meanwhile recombination can occur at several steps, e.g., if the mean free path length of Frenkel excitons is shorter than their distance to the interface (6), when the separation time of CT excitons is sufficiently larger or they meet a surface defect (7) or when charge carriers of different excitons meet by chance at an interface (8). In nanostructured solar cells recombination additionally occurs in unconnected islands filled with one type of charge carriers (9). ........................................ 3
1.3 a) Schematic of a flat bilayer heterojunction solar cell and b) corresponding energy diagram, with two active layers (acceptor and donor), two blocking layers, a transparent conductive oxide (TCO) layer, and metallic back- and front contacts. 4
1.4 Schematic illustration of a dye-sensitized solar cell, utilizing mesoporous TiO$_2$ to produce a high surface area, which is coated with a monolayer of strong absorbing dye. A liquid electrolyte is used for transportation of holes to the electrode. . . . 5
1.5 Schematic illustration of different nanostructured morphologies. a) Nanowires, b) Nanotubes and c) inverse opal structure. ................................. 6
1.6 Schematic illustration of an organic bulk heterojunction solar cell. ........... 7
1.7 Same impedance at all frequencies possible in a) Voight-, b) Maxwell- and c) Ladder-representation of equivalent circuit, if values of the components are matching$^{[84, p.92]}$ ................................. 13
1.8 Simulation of different RC series combinations (R in $\Omega$ and C in F). .......... 14
1.9 3D illustration of a simulated RC parallel ($R_1$ and $C_1$) combination with preceding series resistor $R_s$ by plotting Frequency vs. $Z'$ vs. $Z''$. ................................. 16
1.10 Simulation of a RC parallel ($R_1$ and $C_1$) combination with preceding series resistor $R_s$. a) Impedance plane and b) bode plot for fixed capacitance $C_1 = 10^{-8}$ F and different series and parallel resistors (values in $\Omega$). ................................. 16
1.11 Simulation of a RC parallel (R₁ and C₁) combination with preceding series resistor Rₛ. a) Impedance plane plot and b) bode plot for fixed resistances Rₛ = 500 Ω and R₁ = 5000 Ω and varying values of the capacitor (in F). For better comparison, each curve is shifted to the previous by 1000 upwards. 

1.12 Simulation of resistor-constant phase element parallel (R₁ and CPE/QPQ) combination with an additional preceding resistor Rₛ. a) Impedance plane plot and b) bode plot for fixed values of Rₛ = 500 Ω, R₁ = 5000 Ω. In addition, values Q = T = 10⁻⁸ F of the constant phase elements CPE and QPE are fixed and only n = p (see Table 1.2) is changing. Each curve is shifted by 1000 for a better comparison.

1.13 Simulation of two RC parallel (R₁, C₁, R₂ and C₂) combinations with an additional preceding resistor Rₛ. a) Impedance plane plot and b) bode plot for fixed values of Rₛ = 500 Ω, R₁ = 1000 Ω and R₂ = 5000 Ω and varying values of ratio c = \frac{C₁}{C₂}.

1.14 a) Impedance plane plot and b) bode plot of a simulated transmission line for ordinary (p = 1) and anomalous (p < 1) diffusion (N repetitions of R₁ (in Ω) and ζ₁ = CPE (in F)).

1.15 Simulated behavior of an inductor L in a RC parallel (R₁ and C₁) combination. Fixed values for Rₛ = 500 Ω, R₁ = 5000 Ω, R₂ = 10000 Ω and C₁ = 10⁻⁸ F. Varying values for L (in H).

2.1 CBD of antimony sulfide in an ice bath after a) 13 and b) 103 minutes of mixing precursors.

2.2 a) Teflon sample holder with as usually for deposition tilted and for comparison straight sample placement. b) Color gradient of the bath in two minute steps after Sb₂S₃ concentration is high enough for visual recognizability. Numbers represent minutes after pouring precursors into the water beaker.

2.3 Schematic of standard solar cell configuration. a) Side view with detailed stacking of layers. b) Top view of three independent solar cells/pixels. The dimensions are illustrating the predefined active areas of 12.5 mm² each, when illuminated through the shadow mask.

2.4 Simulated I-V curves under illumination and in dark as described by ideal diode model of Equation 2.3. Most important characteristics are short circuit current I_{SC} and open circuit voltage V_{OC} of the theoretical maximum power point (P_t) as well as current I_{MPP} and voltage V_{MPP} of the maximum power point (P_{max}). Furthermore series resistance Rₛ and shunt resistance R_{sh} can be determined by analysis of the data.

2.5 DC equivalent circuit of an ideal diode model, containing illumination induced photocurrent I_{light}, thermal induced saturation current I_{s}, series resistance Rₛ and shunt resistance R_{sh}. 

X

LS Schmidt-Mende, Uni Konstanz
2.6 Schematic of the used 8453 UV-Vis by Agilent Technologies. Cuvette was replaced by a self-made sample holder. With changes adopted from [94].

2.7 AM 1.5G spectrum\cite{95} as well as absorption and EQE spectrum of a typically fabricated solar cell. Colored areas correspond to the calculated values of $I_{SC}$, using Equation 2.5 and 2.7, respectively.

2.8 Schematic of the PVD/PCD setup.

2.9 Schematic of the experimental setup for IS-measurements with a Metrohm Autolab PGSTAT302N and the cage containing a white light diode and the sample.

3.1 Comparison of different immersion times, sample positions and drying positions. Immersion time: direct immersion after mixing solutions a)-f) (105 minutes in bath) vs. immersion after Sb$_2$S$_3$-formation becomes visible e)-h) (55 minutes in bath). Sample position: tilted a), b), e), f) vs. upright c), d), g), h). Drying position: lying on a clean base a), d), e) h) vs. upright in the sample holder b), c), f) g).

3.2 AFM picture of as prepared Sb$_2$S$_3$ films. Surface roughness/mean hight across the image is about $\sim 21 \pm 3 \text{nm}$ on profile 1 and $\sim 19 \pm 3 \text{nm}$ on profile 2.

3.3 a) SEM top view on a typically produced TiO$_2$-nanowire array as well as SEM cross sections of a complete Sb$_2$S$_3$ based solar (ITO/TiO$_2$/145 minutes CBD Sb$_2$S$_3$/P3HT/PEDOT:PSS/Ag) cell b) broken by hand and c) cut by a focused ion beam.

3.4 Power conversion efficiencies of three surface modifier experiments on (a, b and c) flat and one experiment on (d) nanostructured samples. Data is acquired by I-V measurements, where each point represents a working pixel on a fabricated solar cell.

3.5 I-V measurements of experiments on surface modified flat (left) and nanostructured (right) substrates, fabricated and measured on the same day and stored under same conditions until the next measurement. For each group the I-V curve of the best and simultaneously stable cell is shown.

4.1 Compilation of Sb$_2$S$_3$ deposition time experiments, showing summarized efficiencies of fabricated flat bilayer solar cells. Each data point represents one pixel.

4.2 Mean absorption of (annealed) Sb$_2$S$_3$ films at different wavelengths in respect to deposition time.

4.3 SEM cross sections of finished solar cells with the structure ITO/flat TiO$_2$/Sb$_2$S$_3$/P3HT/PEDOT:PSS/Ag, including annealing of Sb$_2$S$_3$. a) Sb$_2$S$_3$ CBD of 100 minute from experiment 2 and b) 85 minutes from experiment 3. c) another view on b) with estimated layer thicknesses of ITO, TiO$_2$, Sb$_2$S$_3$ + P3HT and PEDOT:PSS.
4.4 AFM picture and corresponding height profile of Sb$_2$S$_3$ on silicon. The edge for determining the height of the Sb$_2$S$_3$ layer was formed by a strip, which has been masked prior to deposition. .................................................. 48
4.5 I-V curves (a) and summarized power conversion efficiencies (b) of solar cells, fabricated on TiO$_2$ nanowires. ................................................................. 49
4.6 Absorption of amorphous (dashed lines 1-4) and polycrystalline (solid line 1'-4') Sb$_2$S$_3$ with increasing film thickness from $\sim 33$ nm (1 and 1') to $\sim 132$ nm (4 and 4').[73] ........................................................................ 49
4.7 I-V curves of best pixels of (a) annealing temperature and (b) annealing duration experiment. a) Constant duration of 35 minutes. b) Constant temperature of 325 $^\circ$C. 50
4.8 Characteristics $I_{SC}$, $V_{OC}$, and PCE of annealing temperature experiment. ..... 51
4.9 Characteristics $I_{SC}$, $V_{OC}$, and PCE of annealing temperature experiment. ..... 51
4.10 Summarized PCE values of several experiments performed in order to find optimum layer thickness of P3HT. ................................................................. 53
4.11 P3HT layer thickness measurement using AFM, whereas the linear fit acts as a guide to the eye. ................................................................. 54
4.12 I-V curves (a) and PCE values (b) of fabricated flat TiO$_2$-dye-P3HT solar cells. 54
4.13 a) Nyquist plot of impedance spectra recorded for solar cells with different P3HT layer thickness under illumination. b) Equivalent circuit used for data fitting. 55
4.14 I-V curves of solar cells with best so far optimized layer thicknesses of Sb$_2$S$_3$ and P3HT. ................................................................. 56
5.1 a) Calculated amount of global irradiance contributing to the b) EQE spectra of highest quality Sb$_2$S$_3$ ETA and a reference P3HT:PCBM BHJ solar cell. 58
5.2 I-V curves and characteristics of Sb$_2$S$_3$ and P3HT:PCBM solar cells. 59
5.3 a) Short circuit current density and b) open circuit voltage in respect to light intensity. .................................................................................. 60
5.4 Visualized charge collection probabilities of a) Sb$_2$S$_3$ and b) P3HT:PCBM based solar cells by normalizing light intensity dependent I-V curves (inset) to an I-V curve measured in dark. .................................................. 61
5.5 Photovoltage and photocurrent decay rates of Sb$_2$S$_3$ and P3HT:PCBM solar cells. 62
5.6 a) Nyquist and b) bode plots of impedance spectra of Sb$_2$S$_3$ and P3HT:PCBM cells. Inset in a) shows an enlarged region of high frequencies. 63
5.7 Equivalent circuits used for fitting acquired impedance spectra of a) Sb$_2$S$_3$ and b) P3HT:PCBM solar cells. 64
5.8 Impedance spectra measured at applied DC voltages of $-0.2$, $0$ and $0.2$ V. The inset shows the zoomed in area at high frequencies. 65
List of Figures

6.1 Energy band diagram of used materials: ITO[39], TiO$_2$[15, 113], Sb$_2$S$_3$[71], P3HT[35, 54], PCPDTBT[35, 114], PBDTTT-C-T[37, 38], MDMO-PPV[36, 115], spiro-OMeTAD[29, 116], CuSCN[71, 117], PEDOT:PSS[118], WO$_3$[15], Ag[15, 41]. Energy bands without HOMO or LUMO indication either behave like metals or are representing the HOMO level of the material. 67

6.2 Layer thicknesses of different HTMs including corresponding linear fits as guide to the eye. One data point of CuSCN was shifted to the right for better comparison. 70

6.3 PCE, $I_{SC}$, $V_{OC}$, and FF of P3HT, PCPDTBT and spiro-OMeTAD with comparable layer thicknesses of 40 and 80 nm for lower and higher concentration, respectively. 70

6.4 EQE spectra of a flat TiO$_2$-squarain dye-P3HT solar cell illuminated as normal through the TCO (front) and through the semitransparent Ag contacts (back). In addition, the absorption of P3HT is shown in the lower part. 71

6.5 EQE spectra of a) P3HT, b) PBDTTT-C-T, c) PCPDTBT and d) spiro-OMeTAD illuminated as normal through the TCO (front) and through the semitransparent Ag contacts (back). Lower part illustrates absorption Sb$_2$S$_3$ and the HTM, respectively. 72

6.6 EQE spectra of Sb$_2$S$_3$ based solar cells with different P3HT layer thicknesses as HTM. a) Non transparent and semitransparent Ag back contact, where b) is illuminated through the glass/TCO and c) through the back contact. 74
List of Tables

1.1 Summarized overview of research on Sb\textsubscript{2}S\textsubscript{3} based solar cells of recent years.

1.2 Common electrical circuit elements used in IS,\cite[p.15]{ref1} Formulas for impedance containing imaginary number i, angular frequency \( \omega = 2\pi f \) and the symbols for corresponding circuit elements. For ideal resistors \( R \), capacitors \( C \) and inductors \( L \) and non-ideal capacities \( T \) and \( Q \) in constant phase elements.

1.3 Different representations and corresponding functions of impedance,\cite[p.15]{ref1}, wherein \( L \) and \( A \) are the length and area of the sample.

1.4 List of common diffusion processes and their corresponding generic components \( \zeta \) used in equivalent circuits.\cite[p.58]{ref1}

3.1 Summarized overview of investigated parameters.

4.1 Preparation parameters of time study experiments. For better filling of nanowires a spin-coating process with two steps was used.

5.1 Parameter of fitted impedance spectra of Sb\textsubscript{2}S\textsubscript{3} based solar cells.

5.2 Parameter of fitted impedance spectra of P3HT:PCBM based solar cells. As length of the model \( L = 0.1 \) was chosen.

6.1 Preparation parameters for layer thickness measurement. Microscope slides were used as substrates, which were cleaned prior to the deposition of the HTM by oxygen plasma.

6.2 Preparation parameters for comparison of layer thickness by I-V measurements. CBD time was 105 minutes. Silver (100 nm) was thermally evaporated as top contact.

6.3 Preparation parameters for experiments of HTM contribution to EQE. CBD time was 85 minutes. 15 and 125 nm Ag were thermally evaporated as semi- and non-transparent top contacts, respectively. Additionally, 100 nm Ag were deposited on the outer part of semitransparent contacts to improve the connection to the measuring Au pin.
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Eugen Zimmermann


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\(^1\) and Lego
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\(^3\) most (sometimes I did not believe, but in the end you were right)
\(^4\) Even if I do not know for what reason
Final Statement

Ich versichere hiermit, dass ich die anliegende Arbeit mit dem Thema:

Nanostructured Extremely Thin Absorber Solar Cells

selbstständig verfasst und keine anderen Hilfsmittel als die angegebenen benutzt habe. Die Stellen, die anderen Werken dem Wortlauf oder dem Sinne nach entnommen sind, habe ich in jedem einzelnen Falle durch Angabe der Quelle, auch der benutzten Sekundärliteratur, als Entlehnung kenntlich gemacht.

Konstanz, den 03.06.2013

(Eugen Zimmermann)