Investigation and development of CIGS solar cells on flexible substrates and with alternative electrical back contacts

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Investigation and Development of CIGS Solar Cells on Flexible Substrates and with Alternative Electrical Back Contacts

A dissertation submitted to
ETH ZURICH

for the degree of
DOCTOR OF SCIENCES

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Zurich, 2009
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Summary

Photovoltaic is a very promising field among various renewable energies. But solar cells can only establish themselves durable on the market, if they are also economically profitable. R&D is not only focusing on enhancing the conversion efficiency and the stability of the solar cells, but is also trying to find processes and technologies to reduce the costs. Flexible Cu(In,Ga)Se₂ (CIGS) solar cells are therefore very attractive because of their high conversion efficiencies, their low cost potential and the many application possibilities. The focus of the thesis was to apply innovation for development of next generation CIGS solar cells based on flexible foils and also novel devices for better utilization of solar spectrum to yield higher efficiency and performance stability.

In the first part of this work the development of CIGS solar cells on flexible substrates like polyimide and aluminum foils is described. The biggest challenge was to develop a deposition process for CIGS layers of suitable structural and opto-electronic properties at lower substrate temperature due to the thermophysical properties of layers and substrates. Additionally, a new method for controlled incorporation of an optimum amount of Na in CIGS was implemented for high-efficiency cells since there is no diffusion of Na from polyimides or metal foils unlike from the usual soda lime glass substrates. On polyimide a record conversion efficiency of 14.1% has been achieved, which is the highest efficiency ever reported for any kind of solar cell grown on polymer. For the first time CIGS solar cells have been successfully grown on aluminum substrates and the influence of aluminum substrates on different process steps and layers of the cell has been investigated.

The second part of the thesis deals with the research and development of alternative electrical back contacts. The application of alternative materials than the commonly used Mo can not only bring advantages like enhancement of the long term performance stability, better thermal expansion match, or reduction of
material and processing costs, but can also offer multifunctionality, e.g. mirror or diffusion barrier properties. Transparent conducting back contacts also are a requirement for the development of multijunction (tandem) solar cells, in order to get better solar spectrum utilization.

CIGS solar cells on metal nitride and ITO based contacts have been grown and investigated. To facilitate a quasi-ohmic electrical contact a very thin MoSe$_2$ interface layer has been applied between the back contact and the CIGS layer in order to obtain carrier transport through tunneling. Similar efficiencies than on Mo back contacts could be achieved. The results suggest that the determining part is not the back contact material by itself, but the interface between back contact and absorber.

The concept of multijunction solar cells is demonstrated by the combination of CIGS with dye sensitized solar cells to tandem cells. Not only the proof of concept could be achieved, but also a record efficiency of 15.1%, which is the highest efficiency for dye sensitized solar cells including tandem devices.
Zusammenfassung


Der Hauptfokus dieser Arbeit war, die nächste Generation von CIGS-Solarzellen auf biegsamen und leichten Folien zu entwickeln und vor allem neue elektrische Rückkontakte zu finden und zu charakterisieren, um eine noch optimalere Ausnützung des Sonnenspektrum zu erreichen und die Stabilität der Solarzelle weiter zu verbessern.

Zusammenfassung


1 Introduction: Flexible Cu(In,Ga)Se$_2$ Solar Cells and Technologies


Abstract

Flexible Cu(In,Ga)Se$_2$ (CIGS) solar cells are very attractive because of their high conversion efficiencies, their low cost potential and the many application possibilities. They can be grown on metal or polymer substrates with a variety of deposition methods. The conversion efficiency depends on the choice of the substrates and of the processing technology. Higher efficiencies are achieved on metal foils than on polymer and by using vacuum evaporation methods. Solution based methods for CIGS deposition yield lower efficiencies, but offer other advantages. For industrial application roll-to-roll deposition and interconnected modules are required. Monolithic interconnection technologies for flexible CIGS modules are not yet fully developed on industrial scale. And cost effective encapsulation facilitating stable outdoor performance for more than 20 years is still a challenge. In this chapter an overview of the state of the art of flexible CIGS solar cells and their issues is presented.
1 Introduction: Flexible Cu(In,Ga)Se$_2$ Solar Cells and Technologies

1.1 Introduction

Cu(In,Ga)Se$_2$ (CIGS) solar cells on flexible substrates offer several advantages for their manufacturing as well as applications compared to solar cells on rigid glass substrates. They are lightweight, can be applied on uneven surfaces and can be rolled-up when not in use. Flexible and lightweight CIGS modules open-up new applications possibilities for terrestrial and space applications. From the industrial production point of view, manufacturing of flexible solar modules with roll-to-roll deposition process offers considerable potential for cost effective solar modules. Not only the mass production of flexible CIGS modules will improve with inline roll-to-roll machines, but also other issues like shipments, installations will be easier thanks to the light weight of the modules. However, roll-to-roll manufacturing equipments for CIGS deposition are neither well developed nor easily available. Different types of flexible substrates can be used, e.g. polymer or metal foils and the choice of substrates is critical for the processing methods and configuration of the solar modules, since the substrate determines what type of deposition processes and conditions can be tolerated and how much conversion efficiency can be expected.

More than 20 institutions worldwide are involved in R&D and in establishing pilot production-lines with diverse objectives. Several companies are in early stage of industrial development based on different vacuum or non-vacuum CIGS technologies; the methods include evaporation, sputtering, electro deposition, paste printing, layer-transfer etc.

Modules aspects, i.e. interconnection and encapsulation, are also crucial for a successful development of flexible solar modules. Two types of interconnections are possible: either monolithic or serial connections of individual solar cells with metal grids. Both have issues and advantages and a lot of progress have been made in the last few years, especially with the emergence of advanced laser for laser scribing techniques. Some progress has been made for encapsulation as well, but reliable and transparent encapsulation suitable for building applications still remains a challenge in terms of long term stability and cost effectiveness.

A comparison of different technologies of layer deposition and module fabrication is presented in this chapter and the technical results available in public domain are summarized.
1 Introduction: Flexible Cu(In,Ga)Se₂ Solar Cells and Technologies

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE  [10⁻⁶ K⁻¹]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Substrates</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SLG</td>
<td>9</td>
<td>2.5</td>
</tr>
<tr>
<td>Steel</td>
<td>11 - 16</td>
<td>7.8</td>
</tr>
<tr>
<td>Ti</td>
<td>8.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Al</td>
<td>23.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Polyimide</td>
<td>12 - 24</td>
<td>1.5</td>
</tr>
<tr>
<td><strong>Insulating layers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SiOₓ</td>
<td>1 - 9</td>
<td>2.2 - 2.7</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>6 - 8</td>
<td>3.9</td>
</tr>
<tr>
<td><strong>Solar cell layers</strong></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mo</td>
<td>4.8</td>
<td>10.2</td>
</tr>
<tr>
<td>CIGS</td>
<td>8 - 11</td>
<td>5.9</td>
</tr>
<tr>
<td>CdS</td>
<td>4.5</td>
<td>4.8</td>
</tr>
<tr>
<td>ZnO</td>
<td>4.75 / 2.9</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 1.1: Properties of substrate and solar cells materials. Coefficient of thermal expansion (CTE) mostly from [31], density from [44].

1.2 Issues and state of the art

1.2.1 Substrates

The choice of the substrate is very important since it dictates several processing steps. The substrate should be vacuum compatible, i.e. it should not degas or degrade during the various deposition steps, and should be chemically inert. This means it should not corrode or decompose during processing or use, not react with Se or S, and not release impurities into the absorber. Additionally it should also be thermally stable, since most of deposition methods require high temperatures in the range of 400-600°C. Anyway, in order to not encounter delamination and adhesion problems, the substrate material should be chosen so,
that the coefficient of thermal expansion (CTE) lies in the range of the CTE of CIGS (see Table 1.1), since the sample has to go through big changes in temperature during deposition. Due to its comparably low CTE, some cracking in the Mo back contact layer can appear as well, if the CTE of the substrate is too high. To a certain extent stress related problems can be overcome with appropriate Mo deposition process and application of buffer layers.

In principle we differentiate between two categories of flexible substrates: polymers and metal foils. The used polymers are usually special heat resistant polyimides (PI), like Upilex or Kapton. Nevertheless the highest temperatures, they can withstand, are around 450° - 500°C, which is still ~100 K lower than usual deposition temperatures on glass. The metal foils (stainless steel, Ti, Cu, Mo, etc.) on the other hand can be used at higher temperatures without any deterioration of the substrate, but have to deal with other problems. One is the diffusion of impurities from the substrate into the absorber layer, which have negative effects on the photovoltaic properties of the solar cells [1]. This means
that an additional barrier layer between the substrate and the back contact is needed to eliminate or reduce it to such low impurities diffusion, so that it does not harm the solar cell properties anymore. Additionally the diffusion barrier can be used, if the layer is not conductive, for a second purpose at the same time. It can make an electrical isolation of the devices from the substrate in order to perform monolithical integration for modules. But all those buffer/barrier layers should withstand high temperature processing. Any cracking in these layers can be detrimental.

For the barrier layers as well as for all other layers of a solar cell the roughness of the substrate is fundamental. In order to have a homogenous cover and to avoid pinholes and shunts, the surface of the substrate should be very smooth. Figure 1.1 shows atomic force microscope (AFM) images of the surface of different flexible substrates. In the case of polyimides the roughness is thanks to its properties very low without any treatment (roughness average of 1.3 nm for 12.5μm thick Upilex, Fig. 1.1e). Unpolished metal foils on the other hand have a high roughness (47.2 nm for Ti, Fig. 1.1a; 20.0 nm for SS, Fig. 1.1d) and need special treatment before deposition of additional layer on it. Figure 1.1b and 1.1c show as example the influence of mechanical and electro-polishing on Ti-foil. The average roughness reduces from 47.2 nm to 4.6 nm for mechanical and to 1.9 nm for electro polished Ti-foils. So far higher conversion efficiencies have been achieved on metal foils with 17.5% on SS [2] and 16.7% on Ti [3] than on polymer, 14.1% [4]. But since the polymer substrates require less preparation steps, have well defined surface, have no metallic impurities, are insulating and lighter, their use for mass production may be advantageous, especially for monolithic interconnected modules.

1.2.2 CIGS absorber

In the last few years many new companies and institutes have got engaged in the R&D of CIGS solar cells on flexible substrates and a lot of progress has been made in this field. With the increasing number of groups, the number of deposition methods has also increased. While some groups focus on vacuum based deposition methods for higher cell efficiencies, others are attempting solution based methods, which yield lower efficiencies, but offer the advantage
Introduction: Flexible Cu(In,Ga)Se₂ Solar Cells and Technologies

Figure 1.2: CIGS solar cells on a polyimide substrate. The inset shows a scanning electron microscope image of the cross-section.

of lower investment cost of CIGS equipment and higher material utilization during growth. Table 1.2 gives an overview of companies/institutes using different processes and substrates. Also best achieved conversion efficiencies on small (laboratory scale) solar cells are given.

In principle we can classify the deposition methods in following categories: The first one is the co-evaporation of elemental Cu, In, Ga, and Se in ultra high vacuum (UHV). This is the most used deposition technique and the one, which leads to the best results so far. Various companies (like Ascent Solar, Daystar, Flisom, Global Solar, Matsushita, Solarion) and institutes (ETH Zurich, HMI, IEC, NREL, ZSW) use co-evaporation (see Table 1.2). The deposition sequence of the elements can vary from simultaneous evaporation, bilayer or 3-stage static processes [31] to in-line processes, where the evaporation sources are placed successively in such order to achieve the best composition and band gap grading. The substrate is heated to temperatures of 400 - 600°C, depending on the choice of the substrate, to permit the growth of appropriate CIGS layer with desired structure and electronic properties. The second approach is to first deposit elemental layers on the back contact by sputtering and then to selenize
### Table 1.2: Overview of companies and institutes working on CIGS solar cells on flexible substrates.

<table>
<thead>
<tr>
<th>Group</th>
<th>CIGS Deposition method</th>
<th>Substrate*</th>
<th>Best reported η</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Companies</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ascent Solar (ITN)</td>
<td>co-evaporation</td>
<td>PI</td>
<td>11.3%</td>
<td>[5]</td>
</tr>
<tr>
<td>Avancis (ex Shell)</td>
<td>sputtered stacked elemental layer &amp; rapid thermal processing</td>
<td>PI, Ti</td>
<td>13.9%</td>
<td>[6]</td>
</tr>
<tr>
<td>CIS Solartechnik GmbH</td>
<td>electrodeposited stacked elemental layer &amp; rapid thermal processing</td>
<td>Cu, SS</td>
<td>9.0% 10.4%</td>
<td>[7] [8]</td>
</tr>
<tr>
<td>Daystar</td>
<td>co-evaporation (at NREL) rapid activation process</td>
<td>SS, metal</td>
<td>16.9% 15.2%</td>
<td>[2] [9]</td>
</tr>
<tr>
<td>Fisom</td>
<td>co-evaporation</td>
<td>PI</td>
<td>14.1%</td>
<td>[10]</td>
</tr>
<tr>
<td>Global Solar Energy</td>
<td>co-evaporation</td>
<td>PI, metal</td>
<td>11.3% 13.2%</td>
<td>[11] [12]</td>
</tr>
<tr>
<td>Heliovolt</td>
<td>Layer transfer method (FASST™)</td>
<td>?</td>
<td></td>
<td>[13]</td>
</tr>
<tr>
<td>International Solar Electric Technology Inc. (ISET)</td>
<td>coatings of nano-particles precursor layer (non vacuum) &amp; selenization with H₂Se</td>
<td>PI, Mo</td>
<td>8.9% 11.7%</td>
<td>[14] [14]</td>
</tr>
<tr>
<td>Matsushita</td>
<td>co-evaporation</td>
<td>SS</td>
<td>17.0%</td>
<td>[15]</td>
</tr>
<tr>
<td>Miasole</td>
<td>magnetron sputtering in Se-atmosphere</td>
<td>SS</td>
<td>9.3%</td>
<td>[16]</td>
</tr>
<tr>
<td>Nanosolar</td>
<td>screen printing of nanoparticles &amp; rapid thermal processing</td>
<td>PI</td>
<td></td>
<td>[17]</td>
</tr>
<tr>
<td>Odersun</td>
<td>Cu-tape, galvanic deposition of In &amp; sulfuration (CISCuT)</td>
<td>Cu</td>
<td>9.1%</td>
<td>[18]</td>
</tr>
<tr>
<td>Solarion</td>
<td>ion-beam assisted co-evaporation</td>
<td>PI</td>
<td></td>
<td>[19]</td>
</tr>
<tr>
<td>Solopower</td>
<td>electrodeposition</td>
<td>?</td>
<td></td>
<td>[20]</td>
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<tr>
<td><strong>Institutes</strong></td>
<td></td>
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<td></td>
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<tr>
<td>National Institute of Advanced Industrial Science and Technology (AIST)</td>
<td>co-evaporation</td>
<td>PI? metal?</td>
<td></td>
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<td>Aoyama Gakuin University</td>
<td>co-evaporation</td>
<td>PI</td>
<td></td>
<td></td>
</tr>
<tr>
<td>ETH Zurich</td>
<td>co-evaporation</td>
<td>PI, AI</td>
<td>14.1% 6.6%</td>
<td>[4] [21]</td>
</tr>
<tr>
<td>Florida Solar Energy Center (FSEC)</td>
<td>sputtered stacked elemental layer &amp; sulfuration with H₂S</td>
<td>SS</td>
<td>10.4%</td>
<td>[23]</td>
</tr>
<tr>
<td>Hahn-Meitner Institut (HMI)</td>
<td>co-evaporation</td>
<td>PI, Ti</td>
<td>10.8% 16.7%</td>
<td>[24] [3]</td>
</tr>
<tr>
<td>Institut für Solar Technologien (IST)</td>
<td>Cu-tape, galvanic deposition of In &amp; sulfuration (CISCuT)</td>
<td>Cu</td>
<td>9.1%</td>
<td>[18]</td>
</tr>
<tr>
<td>Institute of Energy Conversion (IEC)</td>
<td>co-evaporation</td>
<td>PI</td>
<td>12.1%</td>
<td>[25]</td>
</tr>
<tr>
<td>Korea Advanced Institute of Science and Technology</td>
<td>co-evaporation</td>
<td>SS</td>
<td>10.6%</td>
<td>[26]</td>
</tr>
<tr>
<td>National University of Kaohsiung (Taiwan)</td>
<td>electrodeposition</td>
<td>plastic</td>
<td>-</td>
<td>[27]</td>
</tr>
<tr>
<td>National Renewable Energy Laboratory (NREL)</td>
<td>co-evaporation</td>
<td>SS</td>
<td>17.5%</td>
<td>[2]</td>
</tr>
<tr>
<td>Zentrum fuer Sonnenenergie- und Wasserstoff-Forschung (ZSW)</td>
<td>co-evaporation</td>
<td>PI, Ti, SS, FS</td>
<td>11.2% 14.2% 12.3% 13.8%</td>
<td>[28] [28] [29] [30]</td>
</tr>
</tbody>
</table>

* Al = aluminum foils, Cu = copper-tape, FS = ferritic steel, Mo = Mo foils, PI = polyimide, SS = stainless steel, Ti = Ti foils
or sulfurize those layers. Different methods are employed for selenization/sulfurization: While Avancis evaporates a Se-layer on the stacked elemental layers and then performs a simultaneous selenization and sulfurization by rapid thermal processing (RTP) [6], FSEC let the Cu-In-Ga layers react in the H$_2$S:Ar gas environment [23]. Miasole instead does the selenization already during the sputtering step by using a Se-atmosphere [16].

Alternatively, in order to avoid vacuum processes, the deposition of Cu, In, and Ga can be done by applying some precursor layers of pastes containing nanoparticles. Those pastes can be applied by doctor blade, by screen printing, or by spraying. Then, as for the sputter method, the selenization can be done by RTP (Nanosolar) or in a mixed-gas atmosphere of H$_2$Se and N$_2$ gases (ISET) [14].

Finally the last reported method is the electro deposition. There is again the approach to deposit precursor layer of Cu, In, and Ga and then selenize it by RTP (CIS Solartechnik) or sulfurize in N$_2$/S$_x$ atmosphere (Odersun, IST) [18]. Some groups (Solopower, University of Kaohsiung) are also trying to make directly CuInSe$_2$ (CIS) or CIGS by electro deposition without any selenization/sulfurization step. The use of metal foils offers in the case of the electro deposition a big advantage compared to non-conductive substrate since the metal foil could work as electrode by itself.

1.2.3 Na supply

It is well known that a small amount of Na (typically of the order of 0.1 at%) in the polycrystalline CIGS absorber layers is necessary for high efficiency cells. The fact, that neither metal nor polymer foils contain Na, requires additional Na incorporation. On glass, Na would diffuse from the substrate through the Mo back contact during CIGS growth, but metal and PI foils need alternative Na incorporation methods to obtain highest cell efficiencies. The common alternatives are deposition of a Na-containing precursor layer (e.g. NaF, Na$_2$S, or Na$_2$Se) onto the Mo back contact prior to CIGS growth or in the case of co-evaporation method simultaneous evaporation of a Na compound during CIGS growth. Alternatively the in-diffusion of Na into as-grown, Na-free CIGS layers leads to an improvement in cell performance, which works especially good for
CIGS evaporated at low temperatures (400°C - 500°C) and is therefore optimal for solar cells on polyimide [32].

1.2.4 Module aspects

1.2.4.1 Cells interconnection

The possibility to deposit CIGS on large surface, like all other thin film PV technologies, offers new approaches in interconnection of single cells to modules. The monolithic cell integration is interesting also for roll-to-roll manufacturing. The cells are connected in series, whereas the front contact of the previous solar cell makes contact with the back contact of the following cell (Fig 1.3). Therefore three consecutive steps are needed: the patterning of the back contact (P1), the removal of the CIGS (P2), and the separation of individual cells after deposition of front contact (P3). A selective removing of the different layers is therefore needed. As opposite to glass substrates with hard surface, where mechanical scribing can be used, polymer or metal foils require a non-contact method in order to not damage the polymer surface or the insulating layer. Techniques, like photolithography or screen printing, are possible, but should avoid to be used with masks or screens since the positioning of the P2 and P3 in relation to P1 is complicated [33]. Laser scribing on the other hand fulfill all requirements for in-line processing. The challenges here are to find the right parameters (wavelength, power, etc) to remove just the desired layer without damaging the others and the imaging for having the scribes at the right position. While scribing/patterning technologies for glass substrates are well established, the methods for flexible substrates are not yet fully developed on industrial scale.

Another way of making modules is to cut single solar cells, often larger and with a grid, and assemble them by shingling. In that case it is advantageous to use metal foils without insulating layer, so that the substrate, which is at the same time back contact, may be connected to the front contact of the following solar cell [18]. An advantage of this method is that one can select/short good/poor cells, but the disadvantage is that one does not exploit the full potential of thin film technologies.
1.2.4.2 Contacts

To connect the solar modules to external electrical circuit, the front and back contacts must be bonded to conductive wires or tapes. The connection should show good adhesion, low specific contact resistance ($< 1 \, \Omega \, \text{cm}^2$), long term stability, and still remain flexible.

Different connection technologies are possible, although only few are really suitable for flexible CIGS solar module. Soldering, the common used method for silicon solar cells, can only be used with In or In-alloys, since alternative solders require temperatures higher than 200°C, which would deteriorate the CIGS modules [34]. But even the In based solders, despite the fact that they are expensive, have the disadvantage to induce high mechanical stress. Completely stress-free approaches on the other hand, like mechanical clamping, are problematic in term of stability [35].

With flexible substrates two methods seems to give promising results: ultrasonic welding and conductive adhesives. In the case of ultrasonic welding, metals are
fused together by simultaneous action of static and dynamic forces. The advantages are short welding times (< 1 s), no need of filler material, and application at room temperature [36]. But this also means that direct contacting to the front contact is not possible and some Al undercoating has to be evaporated on the front contact. Conductive adhesive tapes, usually consisting of a silver- and resin-based adhesive and a coated Cu or Al tape [34, 35, 37], offer more flexibility and better long term stability than welding, but have lower adhesion and require curing temperatures of 150°C [37]. Even if some new methods and concepts, e.g. inkjet printed direct write contacts [38] or transparent polymers [39], have appeared, ultrasonic welding and adhesive tapes are the only two techniques used for flexible CIGS modules reported so far.

1.2.4.3 Encapsulation

To ensure long term performance and stability of solar modules, some encapsulation is required to prevent penetration of water and oxygen into the devices. Without any protection the solar modules would degrade rapidly, mostly because of conductivity losses in front contacts and interconnections, since the electronic properties of ZnO:Al are sensitive to moisture and Mo, like any other metal contact, can corrode [40].

Flexible encapsulants consist of multi-layer combinations of polymer and inorganic dielectric layers, like SiOₓ or AlOₓ. Typically used polymers are ethylene vinyl acetate (EVA) or polyethylenenterephthalat (PET). However nowadays no cost effective, flexible transparent encapsulation products fulfill the requirements. The water-vapor transmission rate (WVTR) of present products is in the range of 10⁻¹ g/m²/day, while it should not be higher than 10⁻⁴ g/m²/day to assure life-times of 20 years and more [41-43]. Several companies are currently working on this topic and have announced suitable products for soon (e.g. Barrix from Vitex), but they still have difficulties to adapt them to roll-to-roll. The only cost-effective encapsulation possibility for long term stability at the moment for companies is to use rigid glass, where all benefits of flexibility and lightweight disappear.
1.3 Conclusion

A lot of progress has been made in the field of CIGS on flexible substrates. The choice and preparation of the substrate, polymer or metal foils, dictates the processing steps and determines the achievable efficiencies. The deposition of the CIGS absorber layer is mostly done either by co-evaporation or by deposition of precursor layer, followed by selenization. Thought high efficiency cells have been developed in several laboratories, pilot scale productions are still in early stage of development, with the exception of Global Solar, who has already brought flexible modules on steel foils on the market.

In view of industrial production, module aspects need more attention: Techniques for cells interconnection, monolithical integration and shingling, and contacting methods, like ultrasonic welding and conducting adhesive taps, start to establish themselves, but more work is needed. In term of encapsulation no cost effective, transparent, flexible foils are available, which fulfill the diffusion requirements for 20 years of stable outdoor performance. However recent R&D and industrial trends suggest that solutions should appear in the market in the next few years.

1.4 References

Introduction: Flexible Cu(In,Ga)Se₂ Solar Cells and Technologies


1 Introduction: Flexible Cu(In,Ga)Se₂ Solar Cells and Technologies


2 Aim of the Thesis

The aim of this thesis is to search for innovations in processing, materials and design to develop the next generation of flexible solar cells based on Cu(In,Ga)Se$_2$ semiconductor material for better utilization of the solar spectrum to yield higher efficiency and performance stability.
3 Flexible Cu(In,Ga)Se$_2$ Solar Cells on Polymer Films


Abstract

Flexible and lightweight Cu(In,Ga)Se$_2$ (CIGS) solar cells are interesting for terrestrial and space applications. Development of high efficiency CIGS solar cells on polymers is challenging because of the thermo-physical properties of layers and substrates. CIGS layers of suitable structural and opto-electronic properties should be grown at low temperature (< 500°C) as polyimides tend to degrade at higher deposition temperatures. Additionally, a method for controlled incorporation of an optimum amount of Na in CIGS is needed for high-efficiency cells since polyimides do not contain Na. High-efficiency CIGS solar cells were developed on commercially available Upilex foils. CIGS layers were grown by evaporation of elemental Cu, In, Ga and Se at different substrate temperatures. Na from a NaF film was incorporated into evaporated CIGS layers with a post-deposition diffusion method that is suitable for in-line production of solar cells. Properties of CIGS absorbers and solar cells were characterized. Independent measurements performed at Fraunhofer ISE Freiburg, Germany have confirmed 14.1% efficiency ($V_{oc} = 649$ mV, $J_{sc} = 31.5$ mA·cm$^{-2}$, FF = 69.1%, total area = 0.595 cm$^2$, no anti-reflection coating) under simulated AM1.5 standard test conditions. This is the highest efficiency reported to date for any kind of solar cell grown on polymer films. An average reflectance loss of about 13% was measured for these solar cells.
3.1 Introduction

Thin-film solar cells based on Cu(In,Ga)Se₂ (CIGS) absorber layers on flexible substrates have a lot of advantages compared to CIGS cells prepared on (rigid) soda-lime glass (SLG): They are lightweight, they can be applied on uneven surfaces and they can be rolled up when not in use. So flexible CIGS modules open new applications possibilities for terrestrial use. Their excellent radiation tolerance and their high ratio of delivered power to module weight also make them ideal candidates for space use. From the industrial point of view, flexible cells offer the considerable advantage to allow manufacturing with a roll-to-roll deposition process, which would reduce production costs significantly.

Typical substrates for the processing of flexible cells are metal or polyimide foils. On stainless steel substrates, conversion efficiencies up to 17.5% have been reported, while with Ti substrates, efficiencies up to 16.7% were achieved so far (see chapter 1). Deposition on metallic substrates allows CIGS growth at substrate temperatures in the range of 520-600 °C, similar to cells on standard SLG substrates. Nevertheless, also low-temperature CIGS growth processes may be interesting for them, since the demands on diffusion barriers and insulation layers are less stringent [1].

Polymer substrates offer advantages for monolithically interconnected module development and for providing high specific power (kW/kg). However the thermal stability of polyimide (PI) films is limited, therefore solar cells on PI substrates have to be processed at substrate temperatures below 500 °C. Low-temperature CIGS growth processes to date resulted in efficiencies below 15% on any substrate [2]. The highest previously reported conversion efficiencies achieved with CIGS cells on commercial PI foils are 13.2% (without anti-reflection coating) [3] and 12.1% (with anti-reflection coating) [4], while 12.8% (without anti-reflection coating) were achieved on a non-commercial PI film [5].

The fact that neither metal nor polymer foils contain Na requires additional Na incorporation, since a small amount of Na (typically of the order of 0.1 at%) in the polycrystalline CIGS absorber layers is well known to increase cell efficiencies significantly. On SLG, Na would diffuse from the substrate through the Mo back contact during CIGS growth, but metal and PI foils need alternative
Na incorporation methods to obtain highest cell efficiencies. The common alternatives are deposition of a Na-containing precursor layer (e.g. NaF, Na₂S, or Na₂Se) onto the Mo back contact prior to CIGS growth or co-evaporation of a Na compound during CIGS growth. Also in-diffusion of Na into as-grown, Na-free CIGS layers leads to an improvement in cell performance [6]. In this chapter the development of flexible CIGS solar cells on polymer foils with the highest efficiencies reported to date is described.

3.2 Experimental

We have grown CIGS solar cells on different commercially available polyimide (PI) foils. We found that for our processes Upilex-S (trade mark name) is the most suitable; different thicknesses were evaluated but most of the work was done on 12.5 μm thick Upilex-S foils. The samples were carefully cleaned in isopropanol-aceton ultrasonic bath and rinsed with de-ionized water to remove electrostatic charges. The solar cells were grown on 5 x 5 cm² foils. For better handling during different deposition processes the Upilex foils were mounted in specially designed frames. An approximately 1 μm-thick Mo back contact was directly deposited by dc sputtering without application of any additional intermediate layer. CIGS absorber layers were grown by evaporation of elemental Cu, In, Ga and Se and using the "3-stage" process [7]. During the 1st stage of the absorber growth the substrate temperature was kept at 400 °C, while during 2nd and 3rd stages the substrate temperature (in the following called T_{sub,max}) was kept at 400 °C or increased up to 500 °C. Na in CIGS was incorporated in-situ by a post-deposition treatment (PDT) method. This consists of evaporation of about 30 nm NaF on CIGS, without substrate heating, and then annealing the sample at 400 °C for 20 minutes. More details of the CIGS deposition process and PDT method can be found in [8].

The solar cells were finished by deposition of a CdS buffer layer by chemical bath deposition, rf sputtering of i-ZnO/ZnO:Al front contacts (~300 nm thick) and electron beam evaporation of Ni-Al contact grids for better current collection. No anti-reflection (AR) coating was applied. Current density - voltage (J-V) characteristics of solar cells were measured under simulated AM1.5 conditions at room temperature.
3.3 Results and discussion

First experiments were performed to ensure the improvements in cell efficiencies on PI films with PDT method. The results have shown that the indiffusion of Na significantly improves the efficiencies. Typical consequence of the presence of Na during CIGS growth on the cell parameters, as reported in the literature [9-11] are substantial improvements in $V_{OC}$ and FF, but hardly in $J_{SC}$. Since PDT Na incorporation gives rise to corresponding changes in the cell parameters, it is likely that the dominating Na mechanisms responsible for the improvements are the same, although CIGS growth kinetics, grain size and crystallographic orientation are not affected with PDT Na incorporation.

The presence of Na during CIGS growth leads to structurally and electronically modified absorber material, resulting for example in different grain sizes, smoother surfaces and increased net carrier concentration. The wealth of effects attributed to sodium has led to numerous suggestions of mechanisms that may be responsible for Na-induced cell efficiency improvements. However, although the importance of Na was realized more than a decade ago [12], no mechanism for the action of Na is commonly accepted. Experiments suggest that interaction of Na with grain boundaries in CIGS is the dominant mechanism responsible for improvements in layer and cell properties [13].

**Figure 3.1:** Cell efficiencies vs. substrate temperature. Best cells are obtained at deposition temperature of 450-460°C.
Absorber depositions at different $T_{\text{sub, max}}$ have shown that best efficiencies are obtained at $T_{\text{sub, max}} = 450$-$460$ °C (Fig. 3.1). At higher temperature the efficiency of PDT processed cells are lower as also reported for cells grown on Al$_2$O$_3$ coated soda-lime glass [13].

The cross-section scanning electron microscope (SEM) images of solar cells with CIGS absorbers grown at $T_{\text{sub, max}} = 450$ °C (Fig. 3.2a) and 500 °C (Fig. 3.2b) show small grains of CIGS near the Mo back contact, but larger grains of dimensions approaching 1 μm are observed in the upper half of the CIGS layers. The CIGS film surface is rather smooth, which is typical also for CIGS films grown with the 3-stage process at high substrate temperatures [14]. SEM images were taken at a certain angle, therefore the layer thicknesses appear smaller than they really are. The actual thickness of the absorber layer is 1.7 μm and the ZnO-layer is 300 nm.

The structural difference between the two samples (Fig. 3.2) is small; the one grown at $T_{\text{sub, max}} = 500$ °C seems to have slightly larger grains. Although solar cell component layers and substrate have different thermal expansion coefficients (Upilex: 12-24·10$^{-6}$ K$^{-1}$, Mo: 4.8-5.9·10$^{-6}$ K$^{-1}$, CIGS: 7.9-11.4·10$^{-6}$ K$^{-1}$) [2], no cracks have appeared on the samples, even after high temperature deposition and/or after CBD-CdS and ZnO/ZnO:Al depositions. This required optimization of Mo sputtering and CIGS deposition processes.
Secondary ion mass spectrometry (SIMS) measurements (Fig. 3.3) do not show carbon contamination from the substrate into the absorber layer, which suggests that no intermediate diffusion barrier is needed between the PI-substrate and Mo back contact. Na diffuses, as expected, through the whole absorber layer and can be observed even in the Mo layer and in the polyimide. Due to the low interdiffusion of Ga and In at low substrate temperature a Ga dip and In peak in composition profiles appear near the absorber surface, which results in a band-gap grading in the absorber layer. It should be clarified that the Cu dip is a matrix effect as cross-checked with several samples of different types. The band-gap grading (or composition profiles) depends on CIGS deposition temperature and the results are consistent with previous results on SLG [13].

The CIGS deposition process was optimized for efficiency improvement. Figure 3.4 shows the current-voltage characteristics of a 14.1%-efficiency cell on PI ($V_{oc} = 649.4$ mV, $FF = 69.1 \%$, $J_{sc} = 31.48$ mA/cm², total area = 0.595 cm², no anti-reflection coating) measured under AM1.5 standard test conditions at the Fraunhofer Institute for Solar Energy Systems, Freiburg, Germany. This is the highest reported efficiency for any solar cell grown on a polymer substrate to date.

The efficiency improvement with respect to the previous record cell of our group [5] ($\eta = 12.8 \%$, non commercial PI, and Na incorporation during growth by
Figure 3.4: Current-voltage characteristics of a CIGS solar cell on a polyimide foil under AM1.5 standard test conditions. The efficiency of 14.1% presents a world record for solar cells on polymer substrates. The measurement was certified by the Fraunhofer Institute for Solar Energy Systems in Freiburg, Germany. Na in the CIGS absorber layer was incorporated with a post-deposition treatment.

Figure 3.5: External quantum efficiency characteristics of a CIGS solar cell on polyimide and the corresponding reflection from front contact (ZnO:Al) surface. An average reflectance loss of about 13% was measured in the visible-near IR spectral region.
diffusion from a NaCl buffer layer through the PI) is attributed to two main factors. The first is that Na incorporated with the PDT cannot have a detrimental influence on CIGS phase formation (the presence of Na during growth slows down In–Ga interdiffusion as well as Cu in-diffusion [8]), while the beneficial influence of Na incorporation, probably passivation of defects, can still be exploited. However the detrimental influence of Na on low-temperature phase formation of CIGS may be less pronounced when a bilayer process (as for the previous record cell) or a single-stage process are used instead of the 3-stage process, because less interdiffusion of the elements is required for the formation of a homogeneous phase with these processes. The second factor is the bandgap grading; with the 3-stage process and low substrate temperatures, a spontaneous, pronounced band-gap grading through the film occurs, as discussed above. The band-gap profile contains a back and a front grading, where the back grading is considered beneficial and the front grading may or may not have an influence on device performance [15].

As mentioned above, no anti-reflection coating was applied to the solar cells. Therefore the external quantum efficiency (EQE) does not exceed 80-85 % (Fig. 3.5). The low EQE between 400 nm and 550 nm wavelength comes from the photon absorption loss in the CdS buffer layer. Absorption at wavelength until 1200 nm confirms the presence of a band-gap grading of Ga and grains with low Ga content. The oscillation of EQE, most pronounced around 1000 nm, comes from the interferences in the reflectance. An average reflectance loss of about 13 % was measured in the visible-near IR spectral region for these solar cells. Therefore application of a commonly used anti-reflection coating would minimize the reflection loss to 2-4% [16] and a further gain of about 10% (relative) in efficiency would enable more than 15 % efficiency flexible CIGS solar cells on polyimide films.

3.4 Conclusion

A low temperature (450 °C) CIGS deposition process and a reliable method for controlled incorporation of Na into CIGS with a PDT method has been applied to develop high-efficiency flexible CIGS solar cells on commercially available polyimide films. Independent measurements at Fraunhofer ISE Freiburg,
Germany have confirmed an efficiency of 14.1 % without anti-reflection coating. Measurements of quantum efficiency and reflection loss suggest that application of a commonly used anti-reflection coating would enable more than 15 %-efficiency flexible CIGS solar cells on polyimide films. This process can also be used for high-efficiency cells on metal foils, since low deposition temperature will be effective in reducing metal impurity diffusion in CIGS, especially from stainless steel foils.

3.5 References


4 Cu(In,Ga)Se$_2$ Solar Cells on Al-Foils


Abstract

Cu(In,Ga)Se$_2$ (CIGS) solar cells on aluminum foils offer the advantage to be flexible, lightweight and, because of the low cost substrate, can be used for several applications, especially in buildings, where aluminum is already commonly used. There are reports of a-Si solar cells on Al foil, but development of CIGS solar cells on Al foils has not been reported. We have developed CIGS solar cells on coated Al-foil samples. When using Al as substrate, CIGS layers of suitable structural and opto-electronic properties should be grown at low (< 450°C) deposition temperatures, because of the difference in the thermo-physical properties of layers and substrates. We have grown CIGS layers by evaporation of elemental Cu, In, Ga, and Se at different substrate temperatures and investigated the properties of these CIGS layers by different methods. The photovoltaic properties of small area solar cells were characterized with I-V and quantum efficiency measurements. An efficiency of 6.6% has been achieved, which is the highest efficiency reported to date for CIGS solar cells on Al foils. We have also observed that some Al from the foil dissolves during Chemical Bath Deposition (CBD) of CdS. The presence of Al in the bath seems, in some cases, to be beneficial for the electrical properties of the CIGS solar cells. Thinner and more homogenous CdS-layers are obtained. Elastic Recoil Detection Analysis (ERDA) and SIMS measurements have shown incorporation of Al in the CdS.
4 Cu(In,Ga)Se₂ Solar Cells on Al-Foils

4.1 Introduction

Cu(In,Ga)Se₂ (CIGS) solar cells on flexible substrates offer a lot of advantages compared to cells on rigid substrates, i.e. soda lime glass (SLG): They can be applied on uneven surfaces, rolled for storage and, because of thinner substrate-thickness, they are very lightweight. This is not only offering new possibilities for terrestrial applications, like building integration or mobile use, but is also very interesting for space applications due to cost reduction for satellite launch. Flexible CIGS modules have an excellent radiation tolerance and a high ratio of delivered power to module weight. From the industrial point of view, the capability to manufacture modules with a roll-to-roll deposition process will reduce production costs significantly.

The two different kind of substrates for the processing of flexible cells are metal and polyimide (PI) foils. Polymer substrates offer advantages for monolithically interconnected module development and for providing high specific power (kW/kg). However the thermal stability of PI films is limited, therefore solar cells on PI substrates have to be processed at substrate temperatures below 500°C. The best achieved efficiency so far for solar cells on PI is 14.1% [1]. On metal substrates, conversion efficiencies up to 17.5% on stainless steel [2] and 16.7% on titanium [3], have been reported. Deposition on metallic substrates allows CIGS growth at similar substrate temperature (520-600°C) as on standard SLG substrates. Nevertheless, efficiencies of CIGS solar cells on SLG are to date still higher: 19.5% [4].

One reason for the lower efficiencies of the flexible substrates is the “natural” diffusion of Na from the SLG into the absorber. Na is well known to increase cell efficiencies and neither metal nor polymer foils contain it. Therefore an alternative incorporation method for Na is needed for metal and PI foils. A second handicap for metal substrates is the requirement of diffusion barriers to prevent impurities to diffuse from the substrate into the absorber, especially at higher substrate temperatures. A low-temperature CIGS growth process may therefore also be interesting for them, since the demands on diffusion barriers and insulating layers (for monolithical interconnection) are less stringent [5].

Development of CIGS solar cells on aluminum (Al) foils has to our knowledge not been reported by any other group so far. Al is an interesting material because
4.2 Experimental

We have grown CIGS solar cells on 100 μm thick Al foils as well as coated Al foils, which are also used for a-Si solar cells. On one side of the substrate a SnO$_2$:F layer has been deposited at 450°C. The samples of 5 x 5 cm$^2$ were carefully cleaned in isopropanol-aceton in an ultrasonic bath, rinsed with de-ionized water, and mounted in a specially designed frame for easier handling.

The Mo back contact was deposited by dc sputtering either directly on the Al-foil, in which case the SnO$_2$:F protects the rear of the sample, or on the SnO$_2$:F, which then acts as diffusion barrier layer between Al and Mo. We have used different thicknesses for the Mo layer (0.5 – 2 μm) to investigate the barrier and thermo-physical mismatch buffer properties of the back contact.

CIGS absorber layers were grown by evaporation of elemental Cu, In, Ga and Se and using the “3-stage” process [6-8]. During the 1$^{\text{st}}$ stage of absorber growth the substrate temperature was kept at 400°C, while during the 2$^{\text{nd}}$ and 3$^{\text{rd}}$ stages the substrate temperature (T$_{\text{sub, max}}$) was kept either at 400°C or increased up to 550°C. There was no addition of Na before, during or after the growth of the absorber layer. It should be mentioned that these temperatures are measured by a thermocouple between sample and heater and are suspected to be 50-100°C lower than the true substrate temperatures.

The CdS buffer layer is deposited by chemical bath deposition (CBD), for detailed process description see [9]. When the rear of the sample was not protected by the SnO$_2$:F, a chemical reaction between Al and OH$^-$ was observed, which results in the presence of aluminum ions in the bath. In order to investigate the effects on the properties of solar cells, CdS has been deposited on CIGS solar cells grown on SLG by standard CBD and by CBD with addition of
Cu(In,Ga)Se₂ Solar Cells on Al-Foils

<table>
<thead>
<tr>
<th>Material</th>
<th>CTE [$10^{-6}$ K⁻¹]</th>
<th>Density [g/cm³]</th>
</tr>
</thead>
<tbody>
<tr>
<td>SLG</td>
<td>9 (20-300°C)</td>
<td>2.5</td>
</tr>
<tr>
<td>Steel</td>
<td>11-16</td>
<td>7.8</td>
</tr>
<tr>
<td>Ti</td>
<td>8.6</td>
<td>4.5</td>
</tr>
<tr>
<td>Al</td>
<td>23.1</td>
<td>2.7</td>
</tr>
<tr>
<td>Polyimide</td>
<td>12-24 (20-400°C)</td>
<td>1.5</td>
</tr>
<tr>
<td>Mo</td>
<td>4.8-5.9 (20-600°C)</td>
<td>10.2</td>
</tr>
<tr>
<td>CuInSe₂</td>
<td>11.2-11.4/7.9-8.6 (20°C)</td>
<td>5.9</td>
</tr>
<tr>
<td>ZnO</td>
<td>4.75 / 2.9</td>
<td>5.6</td>
</tr>
</tbody>
</table>

Table 4.1: Properties of substrate and solar cells materials. Coefficient of thermal expansion (CTE) from [13], density from [14].

Al₂(SO₄)₃ or Al-foil. CdS-layers with identical deposition times and similar layer thicknesses have been compared.

The solar cells were then finished by rf sputtering of i-ZnO/ZnO:Al front contacts (200 nm thick) and electron beam evaporation of Ni-Al contact grids for better current collection. No anti-reflection (AR) coating was applied. Current – voltage (I-V) characteristics of the solar cells were measured under simulated AM1.5G conditions at room temperature.

4.3 Results and discussion

4.3.1 Absorber properties

One of the biggest challenges in depositing CIGS absorber on Al-foil is the large mismatch between the thermal expansion coefficient (CTE) of CIGS and Al (Table 4.1). The mismatch causes stress between the different layers, which can create cracks in the absorber and consequently shunt the cell. In the worst case, the CIGS delaminates. The stress between the layers depends on the growth temperature. The higher the temperature the more stress is created during cooling down, therefore lower growth temperatures result in better adhesion. On the other hand a minimum growth temperature of about 350-400°C is needed to obtain “device quality” CIGS layers and working solar cell devices.
Figure 4.1: Scanning electron microscope (SEM) images of CIGS solar cells grown on Al foils at (a) $T_{\text{sub,max}} = 400^\circ\text{C}$ and (b) $T_{\text{sub,max}} = 550^\circ\text{C}$ showing the cross-sections of the Mo back contact, the CIGS absorber and the i-ZnO/ZnO:Al window layers.

We have used different thicknesses of Mo back contact as a thermo-physical mismatch buffer to decrease the stress. As expected the stress between substrate and absorber seems to decrease with increasing Mo thickness. Some tests with intermediate layers like ITO or SnO$_2$ led to contradictory results and will need further investigations. ITO and SnO$_2$-layers have also been applied on the rear of the sample to protect the Al foil from the ammonium hydroxide solution and to prevent reaction of the foil during the CBD process (cf section 4.3.3). A thickness of a few hundred nanometers seems to fulfill this purpose.

As mentioned above, the growth temperature has the most important impact on the structure and the quality of the absorber. Solar cells grown at $T_{\text{sub,max}} = 400^\circ\text{C}$ do not show significant photovoltaic conversion properties. As it can be seen in Fig. 4.1a, the temperature was not high enough to permit the interdiffusion of the elements and inadequate for CIGS phase formation. Three distinct regions in the CIGS layer are visible due to the insufficient temperature for a proper Cu-In-Ga interdiffusion. The top part of the absorber shows CIGS with relatively small grains, whereas the bottom has a typical structure of Cu-poor CIGS. A micro crack in the left upper part of CIGS and the separation between Mo and CIGS is due to the sample preparation for SEM measurement.

For an absorber grown at $T_{\text{sub,max}} = 550^\circ\text{C}$ we can observe two different regions (Fig. 4.1b), which can be observed for the 3-stage process at low tempera-
Figure 4.2: SIMS depth profiles of CIGS/Mo layers in solar cells grown on Al foils at (a) 450°C, (b) 500°C, and (c) 550°C. The Ga-dip/In-hill around 800 nm is due to the 3-stage process. The Cu-dip below 1200nm shows that temperature of (a) and (b) is not high enough to ensure a proper interdiffusion and correct formation of CIGS.
Figure 4.3: SIMS depth profile of CIGS/Mo layers in solar cells grown on Al foils at 550°C without barrier layer. Diffusion of Al through the Mo back contact and contamination of CIGS can be observed.

At the top we can find large grains with sizes up to a few μm. At the bottom the grain size is much smaller. The small crack near the surface in a big grain is most probably due to stress relaxation during cool down step in the layer. In this case, unlike in Fig. 4.1a, the crack is not a result of sample preparation as can be seen by the intact ZnO layer. Also interesting are the small holes in different crystal grains, especially at the bottom. We assume, that they are correlated to the recrystallization of the grains.

Secondary ion mass spectrometry (SIMS) depth profiles (Fig. 4.2 & 4.3) confirm the compositional changes suspected from SEM images for the different process temperature and the better intermixing at higher temperature. At all temperature the Ga signal shows clearly a dip, while an In peak appears near the absorber surface. This results in a band-gap grading in the absorber layer. As it can be seen at the lower Cu-concentration at sputter depth between 1500 nm and 2000 nm (Fig. 4.2a & 4.2b), a minimum temperature is needed to ensure a proper interdiffusion. It should be noted, that the Cu dip at sputter depth above 1000 nm is a matrix effect as cross-checked with several samples of different types. The band-gap grading (or composition profiles) depends on CIGS deposition temperature and the results are consistent with previous results on SLG and PI [1, 7].
4 Cu(In,Ga)Se$_2$ Solar Cells on Al-Foils

**Figure 4.4:** Current-voltage characteristics of a CIGS solar cell on Al foil under AM1.5 standard test conditions. No Na was incorporated and no AR coating applied.

**Figure 4.5:** Normalized external quantum efficiency (EQE) characteristics of a CIGS solar cell on Al foil. Absorption until 1250 nm confirms the presence of a band-gap grading and grains with low Ga content.

If no barrier is applied between substrate and back contact, an aluminum contamination of the absorber is observed (Fig. 4.3). Al diffuses from the substrate through the Mo back contact into the absorber. To prevent those contaminations the application of an intermediate barrier layer or a lower deposition temperature is needed. The Al-signal at the top comes from the Al-doped ZnO front contact and has no relation to the substrate.

### 4.3.2 Electrical characteristics

Fig. 4.4 shows the current-voltage characteristics of the best solar cell achieved so far. A conversion efficiency of 6.6 % (V$_{oc}$ = 434 mV, J$_{sc}$ = 30.7 mA/cm$^2$, FF = 49.3 %, total area = 0.3 cm$^2$; no AR coating) was measured under AM1.5G standard test conditions. While the short circuit current is reasonable, the open current voltage and the fill factor need to be improved, e.g. by incorporating Na in the absorber. Substantial improvements of V$_{oc}$ and FF are typical consequences Na incorporation into CIGS growth [8,10-12]. Application of an anti-reflection coating would additionally contribute to raise the efficiency.

The external quantum efficiency (EQE) of the solar cell is shown in Fig. 4.5. The low EQE between 450 nm and 550 nm wavelength comes from the photon
absorption loss in the CdS buffer layer. Absorption at wavelength until approximately 1250 nm confirms the presence of a band-gap grading of Ga and grains with low Ga content.

4.3.3 Effects of Al presence during CBD

Observing a reaction of the Al foil with the ammonium hydroxide solution, when the rear of the foil was not coated by a protecting layer, we investigated the influence of Al presence during the CBD process. Al has been added to the bath by using Al$_2$(SO$_4$)$_3$ or by putting a piece of Al foil into the bath. With Al, the CdS deposition process is slower, but the CdS layers are more homogenous. Therefore we compared samples with identical deposition time as well as samples with similar CdS thicknesses (Table 4.2). For similar thickness the electrical properties of the solar cells were similar for all parameters. For identical deposition time the efficiency of the solar cells with Al in the CBD were slightly higher ($\Delta \eta \approx 0.5\%$), due to higher FF and $V_{oc}$.

The reason of the improvement is not yet completely understood. Several factors could play a role. One is that the etching of the CIGS may be different, because Al reacts with OH$^-$ and acts as a buffer, and therefore the induction-time of CdS growth is longer. The fact that similar CdS thicknesses show same results, seems to contradict this explanation. Elastic Recoil Detection Analysis (ERDA) and SIMS measured a small amount of Al in the CdS-layer (Fig. 4.6). But again the thickness comparison leads us to assume that this has no influence on the cells.

| Table 4.2: Photovoltaic properties (average of 12 cells) of CIGS solar cells with Al addition in CdS-CBD process. |
|-----------------|-----------------|-------------|----------|----------|----------|
| CBD             | deposition time | $V_{oc}$ [mV] | $J_{sc}$ [mA] | FF [%]  | $\eta$ [%] |
| identical       | standard        | 17'          | 533       | 27.2     | 66.3     | 9.6     |
| deposition time | Al-foil         | 17'          | 611       | 26.6     | 66.5     | 10.8    |
|                  | standard        | 17'          | 516       | 27.6     | 65.5     | 9.3     |
|                  | Al$_2$(SO$_4$)$_3$ | 17'       | 533       | 28.5     | 63.8     | 9.7     |
| similar          | standard        | 14'          | 628       | 27.8     | 67.6     | 11.8    |
| thickness        | Al-foil         | 20'          | 606       | 28.2     | 67.6     | 11.5    |
Figure 4.6: Elastic Recoil Detection Analysis (ERDA) showing the presence of Al in the CdS buffer layer.

Also the presence of Al at the CIGS/CdS interface seems not to be relevant, since ERDA shows concentration increase away from interface. The most probable reason for an enhancement of photovoltaic properties should be, the slower deposition process itself. The CdS-layer can be deposited more homogenous, therefore thinner layers are possible without risk of having uncovered parts.

4.4 Conclusion

CIGS solar cells have been deposited on aluminum foil substrates and investigated. A low temperature process is needed to avoid impurities diffusion and stress between substrate and absorber, which can result in cracks or even in the delamination of the absorber. Due to the 3-stage process and low substrate temperature a strong band-gap grading in CIGS was observed. A conversion efficiency of 6.6% has been achieved under AM1.5G standard test conditions. The dissolving of Al from the foil into the solution during CBD of CdS influences the deposition conditions and photovoltaic properties of the solar cells. The deposition process is slowed down and, therefore, thinner and more homogenous CdS-layers are obtained.
4.5 References


5 Alternative Back Contacts for Cu(In,Ga)Se₂ Solar Cells

Abstract

In Cu(In,Ga)Se₂ (CIGS) solar cells the conventionally used electrical back contact (BC) layer consists of molybdenum (Mo), since it shows the best results so far. But the application of alternative BCs could offer several advantages: enhancement of the device stability, better thermal expansion match of the different layers, reduction of material and processing costs. Additionally an alternative material can also offer multifunctionality, like higher reflection for thickness reduction of absorber or transparent conducting BC can be useful for multijunction (tandem) solar cells for better solar spectrum utilization. Therefore CIGS solar cells have been developed on ITO, ZrN and TiN back contacts. To facilitate a quasi-ohmic electrical contact a very thin MoSe₂ interface layer has been applied between the back contact and the CIGS layer in order to obtain carrier transport through tunneling. Thanks to this interface layer efficiencies similar to on Mo could be achieved for the cells on alternative BC. The results suggest that the determinating part is not the BC material by itself, but the interface between BC and absorber. Best conversion efficiencies up to almost 14% could be achieved. First experiments on the application of ITO as alternative BC on polymer substrates by using ITO were also successful and resulted in a best efficiency of 11.9%.
5.1 Introduction

Thin film solar cells based on Cu(In,Ga)Se₂ (CIGS) absorber layers have already shown their high potential with efficiencies up to 19.5% [1]. But because of the multilayer structure of the CIGS solar cells and the different thermal expansion coefficients of the involved materials and the substrates (especially flexible ones), the search for ideal materials and processes for stress reduction and adhesion improvements remains very crucial. The conventionally used electrical back contact (BC) consists of a molybdenum (Mo) layer, since it has shown the best results so far. However there are several motivations to replace the Mo back contact with alternative materials. One important motivation is surely to find a material that resolve the disadvantages of Mo, like its expensive price or its inadequate thermal expansion coefficient for CIGS and most of the substrates, which would increase the adhesion of the absorber onto the back contact. Mo can also contribute to reduced performance stability due to easy oxidation in air, which is especially a troublesome matter for monolithically interconnected solar modules, due to corrosion of exposed Mo after the P2 scribing step [2].

In addition to improve the adhesion and corrosion properties, an alternative material can also offer multifunctionality. A back contact layer with a high reflectivity in the red or near infra-red spectrum would enable multiple light scattering for thickness reduction of CIGS layer without losses in conversion efficiency. The advantage of having thinner absorber layers would result in saving material, time and eventually costs. At the same time that BC layer can act as a diffusion barrier against impurities during CIGS deposition and moisture during the lifetime of the solar cells. Transparent and conducting back contacts, like transparent conductive oxides (TCO), would make back illumination possible in addition to front illumination and are indispensable for the development of multijunction solar cell. Those are needed to further improve the photovoltaic conversion efficiencies to very high values by better utilization of the solar spectrum in stacked solar cells based on different absorbers.

A large number of metals or semi-metals can be considered as an alternative to Mo [3], and the selection of prospective materials could be narrowed down by considering the following criteria:

\[ \Phi_m > E_g + \chi \]
for p-type semiconductors, where $\Phi_m$ is the BC work function, $E_g$ the bandgap and $\chi$ the electron affinity of the absorber. However, unfortunately none of those alternative back contact forms ohmic contact with the CIGS absorber layer because of incompatibility of work-function and/or interface related problems. In previous work our group has shown that a very thin MoSe$_2$-layer (Fig. 5.1), which forms automatically on Mo BCs during CIGS growth, is responsible for forming quasi-ohmic contact at the interface of the heterojunction [4], suggesting that MoSe$_2$ may be used as an interface layer between CIGS and other metals/semimetals as long as the layers remain chemically compatible and electrically stable. The crystal structure and orientation, and therefore the growing and diffusion properties, of the MoSe$_2$ layer depends on the substrate temperature and is significantly influenced by Na concentration [5].

In this chapter we investigated different alternative materials (metal nitrides and TCOs) for the electrical back contact layer and introduced very thin MoSe$_2$ interface layers between CIGS absorbers and the alternative back contact to facilitate the ohmic contact and to obtain solar cell efficiencies comparable to those on conventional Mo back contacts.

**Figure 5.1:** High resolution transmission electron microscopy image (TEM) of a Mo back contact showing the formation MoSe$_2$. 
Alternative Back Contacts for Cu(In,Ga)Se$_2$ Solar Cells

<table>
<thead>
<tr>
<th></th>
<th>R$_\square$ [Ω/$\square$]</th>
<th>d [nm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mo (reference)</td>
<td>0.2</td>
<td>1000</td>
</tr>
<tr>
<td>TiN</td>
<td>3.1</td>
<td>500</td>
</tr>
<tr>
<td>ZrN</td>
<td>5.5</td>
<td>500</td>
</tr>
<tr>
<td>ITO</td>
<td>11.0</td>
<td>250</td>
</tr>
</tbody>
</table>

Table 5.1: Sheet resistance (R$_\square$) and approx. thickness of used back contacts.

5.2 Experimental

We have deposited all back contact materials by sputtering on soda lime glass (SLG). The nitride back contacts (i.e. ZrN, TiN) were deposited by reactive sputtering; first a metallic layer (Zr, Ti) directly on SLG to ensure a good adhesion and conductivity, then the nitride layer. The total thickness of the back contact was ca. 500 nm for ZrN with a sheet resistance of 5.5 $\Omega$/□ and 500 nm for TiN with 3.1 $\Omega$/□ sheet resistance. For transparent back contacts 250 nm thick tin doped indium oxide (ITO) layers were deposited by rf sputtering resulting in 11.0 $\Omega$/□ sheet resistance. On some samples Mo layers of 1 μm ($R_\square = 0.2 \ \Omega$/□) or 10 nm thickness were dc sputtered on the alternative back contact (Table 5.1). Prior to the deposition of the CIGS absorber layer some of the samples with 10 nm Mo were separately selenized in order to convert the Mo layer into a MoSe$_2$ layer. These experiments were aimed towards the understanding of the role of Mo or MoSe$_2$ in facilitating quasi-ohmic contact.

The CIGS absorber layers were grown by evaporation of elemental Cu, In, Ga and Se and using the “3-stage” process [6-8]. During the 1$^{st}$ stage of absorber growth the substrate temperature was kept at 400°C, while during 2$^{nd}$ and 3$^{rd}$ stages the substrate temperature (in the following called $T_{sub,max}$) was increased to 450°C. The low deposition temperature was chosen in order to have no degradation in the conductive properties of the ITO and for the other samples the same temperature was used to make direct comparison possible. Furthermore the application of flexible substrate like polyimide is possible at those temperatures.

Since all these used alternative back contacts act also as impurity diffusion barrier and inhibit the Na diffusion from the glass substrates during CIGS
5 Alternative Back Contacts for Cu(In,Ga)Se2 Solar Cells

growth, we have added Na separately using an in-situ post deposition treatment (PDT) developed in our group [9], which consist of evaporation of 30 nm NaF on CIGS after the growth and annealing the sample at 400 °C. More details of the CIGS deposition process and PDT method can be found in [9].

The solar cells were finished by deposition of a CdS buffer layer by chemical bath deposition, rf sputtering of i-ZnO/ZnO:Al front contacts (300nm thick) and electron beam evaporation of Ni-Al contact grids for better current collection. No anti-reflection (AR) coating was applied. Current density – voltage (J-V) characteristics of the solar cells were measured under simulated AM1.5 standard condition.

5.3 Results

5.3.1 Reflection and transmission of alternative back contacts

One of the advantages, which are expected from alternative BC, is either an enhanced reflectivity compared to Mo or a good transmission in the case of transparent BCs. In Figure 5.2 the transmission is shown for an ITO layer on soda lime glass (SLG) with and without an additional thin Mo-layer. While the ITO/SLG has good transmittance over 80% for almost all wavelengths, a 10nm thick Mo-layer (Mo/ITO/SLG) reduce it to 40% in the red and near IR part. The transmission can be improved a little in the longer wavelength part by selenization and conversion of the Mo into MoSe2, which has a band-gap of ~1.4 eV [10], but it still remains below 50%. The thickness of the Mo layer should therefore be reduced as much as possible to ensure high transparency. For TiN and ZrN the reflectivity was measured in the wavelength range of 300nm to 1500nm and compared to Mo (Fig. 5.3). For ZrN the reflection is significantly higher compared to Mo. TiN on the other hand seems to have similar reflection values in the relevant range of 800-1200nm. But one should take into account that the measurements were done in air with a refraction index of 1. If we consider the refraction index of CIGS the reflectivity of TiN compared to Mo will increase and surpass the reflectivity of Mo [11]. The application of the thin Mo-layer reduces the reflection as well. The effect is smaller than for transmission, but still important. The selenization of the Mo even reduce the
Figure 5.2: Transmission of light through transparent conductive oxide (ITO) back contact and coated with Mo and MoSe$_2$.

Figure 5.3: Reflection (to air) for different back contacts with and without thin Mo-layer.
### Table 5.2: Photovoltaic properties of CIGS solar cells on alternative back contacts. (PDT: post-deposition treatment)

<table>
<thead>
<tr>
<th>Back Contact</th>
<th>Na</th>
<th>$V_{oc}$ [mV]</th>
<th>$J_{sc}$ [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>TiN</td>
<td>-</td>
<td>487</td>
<td>27.8</td>
<td>40.6</td>
<td>5.5</td>
</tr>
<tr>
<td>Mo (1μm) / TiN</td>
<td>-</td>
<td>546</td>
<td>31.0</td>
<td>64.3</td>
<td>10.9</td>
</tr>
<tr>
<td>Mo (10 nm) / TiN</td>
<td>-</td>
<td>585</td>
<td>29.9</td>
<td>62.8</td>
<td>11.0</td>
</tr>
<tr>
<td>MoSe₂ (10 nm) / TiN</td>
<td>-</td>
<td>592</td>
<td>30.9</td>
<td>67.1</td>
<td>12.3</td>
</tr>
<tr>
<td>Mo (10 nm) / TiN PDT</td>
<td>655</td>
<td>30.3</td>
<td>69.7</td>
<td>13.8</td>
<td></td>
</tr>
<tr>
<td>MoSe₂ (10 nm) / TiN PDT</td>
<td>626</td>
<td>30.5</td>
<td>65.6</td>
<td>12.5</td>
<td></td>
</tr>
<tr>
<td>ZrN</td>
<td>-</td>
<td>423</td>
<td>28.3</td>
<td>42.8</td>
<td>5.2</td>
</tr>
<tr>
<td>Mo (1μm) / ZrN</td>
<td>-</td>
<td>529</td>
<td>28.5</td>
<td>66.0</td>
<td>10.0</td>
</tr>
<tr>
<td>Mo (10 nm) / ZrN</td>
<td>-</td>
<td>528</td>
<td>30.6</td>
<td>61.5</td>
<td>9.9</td>
</tr>
<tr>
<td>MoSe₂ (10 nm) / ZrN</td>
<td>-</td>
<td>529</td>
<td>28.4</td>
<td>57.6</td>
<td>8.7</td>
</tr>
<tr>
<td>ZrN PDT</td>
<td>-</td>
<td>599</td>
<td>27.9</td>
<td>57.4</td>
<td>9.4</td>
</tr>
<tr>
<td>Mo (10 nm) / ZrN PDT</td>
<td>649</td>
<td>29.3</td>
<td>72.5</td>
<td>13.9</td>
<td></td>
</tr>
<tr>
<td>MoSe₂ (10 nm) / ZrN PDT</td>
<td>635</td>
<td>29.9</td>
<td>68.2</td>
<td>13.0</td>
<td></td>
</tr>
<tr>
<td>ITO</td>
<td>-</td>
<td>503</td>
<td>28.4</td>
<td>53.9</td>
<td>7.7</td>
</tr>
<tr>
<td>Mo (1μm) / ITO</td>
<td>-</td>
<td>528</td>
<td>28.4</td>
<td>66.7</td>
<td>10.0</td>
</tr>
<tr>
<td>Mo (10 nm) / ITO</td>
<td>-</td>
<td>516</td>
<td>29.1</td>
<td>65.2</td>
<td>9.7</td>
</tr>
<tr>
<td>MoSe₂ (10 nm) / ITO</td>
<td>-</td>
<td>548</td>
<td>30.2</td>
<td>67.7</td>
<td>11.2</td>
</tr>
<tr>
<td>Mo (10 nm) / ITO PDT</td>
<td>621</td>
<td>30.2</td>
<td>71.0</td>
<td>13.3</td>
<td></td>
</tr>
<tr>
<td>MoSe₂ (10 nm) / ITO PDT</td>
<td>573</td>
<td>29.6</td>
<td>67.1</td>
<td>11.4</td>
<td></td>
</tr>
</tbody>
</table>

reflectivity significantly more. So here again the thickness of the Mo-layer should be reduced as much as possible. It should be mentioned, that those tests and measurements were done without growing CIGS layer on the Mo layers.

### 5.3.2 Photovoltaic characteristics

The photovoltaic properties of the CIGS solar cells with different alternative BCs are shown in table 5.2. From the analysis of the results it is clear that growing the CIGS layers directly on the alternative BC results in reduced efficiencies due to lower $V_{oc}$ and FF. The reason is obviously a barrier effect at the absorber/BC interface as can be seen by plotting the current density – voltage curve (Fig. 5.4). The double diode behavior is clear indication of lack of ohmic contact at the absorber/BC interface, since a diode, resulting in a certain
Figure 5.4: J-V curve of CIGS solar cells grown on ITO BC with and without intermediate Mo-layer. The double diode for cells grown directly on ITO indicates a barrier effect at the interface.

Figure 5.5: J-V-curves of CIGS solar cells with ZrN back contacts and intermediate Mo layers.

Figure 5.6: J-V-curves of CIGS solar cells with TiN back contacts and intermediate Mo layers.
MoSe₂ helps in narrowing down the depletion layer width of the blocking barrier, which allows tunneling of carrier giving quasi-ohmic contact.

The function of electric conduction is then done by the other conductive layer, since the 10nm of Mo are not sufficient to carry the current. However it seems that not the complete 10nm Mo are converted into MoSe₂ for the "Mo (10 nm) / BC" samples due to the low processing temperature, which only permits the MoSe₂ formation parallel to the surface, hence limiting the conversion [4]. For the "MoSe₂ (10 nm) / BC" samples the Mo layer was
Figure 5.8: SIMS Na-profile in the CIGS layer on TiN back contact. Due to the selenization process, for the "MoSe/TiN" samples, Na diffuses through pinholes into the CIGS layer and the cells reach similar values than for Na-PDT CIGS cells.

Figure 5.9: SIMS measurements of CIGS on TiN back contacts with 10nm intermediate Mo layer show typical composition profiles for 3-stage process CIGS at low temperature.
previously completely converted. The thicker resulting MoSe$_2$-layers (compared to "Mo (10 nm) / BC") lead to slightly lower $V_{oc}$ and FF (Table 5.2), excepted for the cells on TiN and ITO without Na-PDT. This leads to the conclusion that as thin as possible MoSe$_2$ layer are needed to obtain highest conversion efficiencies, which would confirm the carrier transport through tunneling.

TiN, ZrN, or ITO-layers act as Na diffusion barrier but any pinholes, formed during sputtering process or due to unclean substrates, may provide leakage path for Na-diffusion. The better efficiencies of the "MoSe$_2$ (10 nm) / TiN" and "MoSe$_2$ (10 nm) / ITO" samples is due to a diffusion of the Na through pinholes during the selenization phase, as can clearly be seen by secondary ions mass spectroscopy (SIMS) measurements (Fig. 5.8) and therefore should not be compared with the "Mo (10 nm) / BC" samples, but with the ones where Na-PDT was used.

The SIMS measurements (Fig. 5.9) also show the typical composition profile for 3-stage processed CIGS at low temperatures. Due to the low interdiffusion of Ga and In at low substrate temperatures, a band-gap grading in the absorber layer forms, identifiable at the Ga dip and In peak in composition profiles near the absorber surface. The Na distribution shows an Na increase towards the bottom of the absorber layer and higher concentration near the interfaces, which can be correlated to the microstructure of the CIGS layer [9]. As expected the addition of Na also improves significantly the $V_{oc}$ as well as the FF, leading to high conversion efficiencies (see chapter 3 or [9]). The best conversion efficiencies were 13.3 % on ITO, a 13.8 % on TiN, and 13.9 % on ZrN. Comparison with literature shows that those values are very near to the best efficiencies ever reached on Mo back contacts at a processing temperature of 450°C: Kessler et al. reached 14.1% using NaF precursor [12], Rudmann et al. 14.4 % by using Na-PDT [9] and Wada et al. 14.8 % with diffusion from SLG [13]. Nakada et al. achieved even 15.2 % on ITO BCs, but with a processing temperature of 520°C and an ITO layer, which let Na diffusion during CIGS growth [14].
Table 5.3: Photovoltaic properties of CIGS solar cells on flexible polyimide substrates with ITO back contacts.

<table>
<thead>
<tr>
<th>area</th>
<th>Voc [mV]</th>
<th>Jsc [mA/cm²]</th>
<th>FF [%]</th>
<th>η [%]</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.582</td>
<td>593</td>
<td>28.1</td>
<td>61.3</td>
<td>10.2</td>
</tr>
<tr>
<td>0.307</td>
<td>626</td>
<td>28.9</td>
<td>64.8</td>
<td>11.7</td>
</tr>
<tr>
<td>0.187</td>
<td>629</td>
<td>28.0</td>
<td>67.2</td>
<td>11.9</td>
</tr>
</tbody>
</table>

5.3.3 ITO back contacts on polyimide substrates

Since the deposition process has been developed for low temperature, preliminary experiments were also tried on flexible polyimide (PI) substrates using ITO as back contacts. Even if the process still needs a lot of optimization, especially for the scribing of the cells, conversion efficiencies up to 11.9% could be achieved (Table 5.3, Fig. 5.10).

5.4 Conclusion

The obtained results and solar cells show that high efficiency CIGS solar cells are possible with alternative BCs. As long as the BC does not react during or after CIGS deposition and has a good conductivity, it seems that the choice of the material for the BC does not really matter, but an interface layer between BC
and absorber is needed to ensure highest performance. In order to create a (quasi-) ohmic contact the presence of MoSe\(_2\) is necessary. This layer should be as thin as possible, not only to improve transmission or reflection, but also to favor the tunneling effect. However the supply of Na should be taken into account, since alternative BCs often work as Na barrier. By using 10nm of Mo as interface layer and the Na-PDT, the achieved conversion efficiencies were similar to those on Mo-BC at same deposition temperature. First experiments have also result in a successful application of transparent ITO BC on polyimide foils.

### 5.5 References


5 Alternative Back Contacts for Cu(In,Ga)Se$_2$ Solar Cells


6 Nanocrystalline Dye-Sensitized / Cu(In,Ga)Se₂ Tandem Solar Cells


Abstract

The opto-electronic properties of Cu(In,Ga)Se₂ (CIGS) absorbers, especially the high photon absorption even at longer wavelengths (> 900 nm) and the possibility to adapt the band gap of the semiconductor from 1.04 eV to 1.67 eV, makes them highly attractive candidates for the bottom cell in a tandem configuration. Different combinations like CuGaSe₂/CuInSe₂ or CdTe/CIGS have already been tried by different groups. In a novel approach nanocrystalline dye sensitized solar cells (DSC) are used as a top cell for the conversion of the high energy photons in wavelengths of 350 - 700 nm and applied on a CIGS solar cell as the bottom cell for the remaining unabsorbed photons of wavelengths > 700 nm. The resulting tandem solar cell shows a conversion of 15.1 % under AM1.5 illumination and further potential for efficiency improvement.
6 Nanocrystalline Dye-Sensitized / Cu(In,Ga)Se₂ Tandem Solar Cells

6.1 Introduction

Silicon based photovoltaics has almost reached its maturity and lower limits of production cost which is still too high to compete with conventional power sources. Thin film photovoltaics could provide a solution to the high cost through large area and large volume (terawatt) capacity production levels [1,2] and providing a step jump in efficiency with the use of multi-junction or tandem solar cells by employing the concept of maximum spectrum utilization with a combination of different band gap absorbers [3].

Currently, III-V materials based tandem cells have shown highest efficiency > 30% and show great promise [4]. These are however limited to specific space applications due to cost issues. On the other hand, high performance thin film solar cells have initiated a significant interest globally for viable terrestrial applications. It is estimated and efforts are continuing to attain ~ 25% efficiency by the end of this decade [5]. The NREL polycrystalline thin film group recently demonstrated a 4-terminal polycrystalline thin-film tandem cell consisting of a CdTe-based top cell and a CuInSe₂-based bottom cell with an efficiency of 15.3% [6]. Some of the other potential technologies being pursued for next generation cells are amorphous silicon (a-Si), dye-sensitized nanocrystalline solar cells (DSC), molecular or organic photovoltaic cells (OPV). The market share for thin film solar cells is presently 5% but it is expected to grow significantly over the next decade. Most of the annual 50-70 MW thin film market is presently served by amorphous silicon (a-Si) solar cells.

Alloys based on the compound chalcopyrite semiconductor CuInSe₂ allow a wide range of bandgaps to be attained, from 1.0 eV for CuInSe₂ to 1.5 eV for CuInS₂ to 1.7 eV for CuGaSe₂ to 2.7 eV for CuAlSe₂. Widening the bandgap with Ga (or Al or S) has several advantages: providing a better match to the AM1.5 spectrum, reducing the losses at higher operating temperatures, reducing the cell current density hence allowing improved module design (due to lower resistance losses and area related isolation scribe losses) and ability to produce a wider-bandgap top cell. Cu(In,Ga)Se₂ (CIGS) cells with efficiency of 19.5% [7] and modules over 10% have been achieved. CIGS alloys have produced the highest efficiency thin film solar cell devices and are today the only ones that
can be expected to compete with c-Si efficiencies, already matching multicrystalline Si.

DSC on the other hand for tandem cell application can be designed by appropriate choice of the sensitizer to absorb incident photons in selective spectral regions of the solar emission, while maintaining high transparency in the remaining wavelength range [8-11]. A further advantage of DSCs is that their optical transmission and short circuit photocurrent can be readily adjusted by changing the film thickness, pore size and the dye loading. This, along with the ease of forming layered structure e.g. by producing the mesoscopic oxide films using screen printing or doctor blading methods renders the DSC particularly well suited for the fabrication of tandem cell structures. Several previous publications have dealt with the use of stacked DSC configurations where two dyes absorbing different parts of the solar spectrum were employed as sensitizers [12-15]. The record conversion efficiency of a single junction DSC stands currently at 11.3 % [16].

This chapter describes the development of a high efficiency mechanical tandem solar cell over 15%, combining state of art CIGS and DSC technologies. This is achieved by using nanocrystalline dye sensitized solar cells as a top cell for the conversion of the high energy photons in wavelengths of 350 - 700 nm and applied a CIGS solar cell as bottom cell for the remaining unabsorbed photons of wavelengths 700 - 1200 nm.

### 6.2 Experimental

The CIGS cell was fabricated by depositing a stack of polycrystalline layers of ZnO:Al/ZnO/CdS/CIGS/Mo on soda-lime glass substrates. About 1 µm thick Mo back electrical contact layer was deposited by dc sputtering, followed by the CIGS absorber layer that was grown by evaporation of Cu, In, Ga and Se elements by using a “3-stage” evaporation process. During the 1st stage of the absorber growth substrate temperature was kept at ~400 °C, while during the 2nd and 3rd stages the substrate temperature was raised to a maximum temperature of 580°C. Detailed description of the “3-stage” and solar cell processing can be found elsewhere [17,18]. The solar cells were finished by a chemical bath
Figure 6.1: A schematic configuration of the mechanical stack of top nanocrystalline dye and bottom CIGS tandem solar cell showing various device layers.

deposition of a CdS buffer layer followed by rf sputtering of i-ZnO/ZnO:Al front contacts (300 nm thick) and electron beam evaporation of Ni-Al contact grids for better current collection. No anti-reflection (AR) coating was applied.

The DSC was produced according to a previously published procedure using the N-719 dye as a sensitizer [19]. A 12 µm thick film consisting of 20 nm sized TiO₂ particles was screen printed on float glass covered with a conducting fluorine doped tin dioxide (FTO) layer rendering the film highly transparent. Prior to this a transparent single layer consisting of 20 nm sized TiO₂ particles (dense layer) was employed using spray pyrolysis. The dye derivatized
nanocrystalline TiO$_2$ film shows negligible light absorption or scattering above 1.65 eV which corresponds to the highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO - LUMO) gap of the sensitizer. The counter electrode was made on tin doped indium oxide (ITO) glass which entails much smaller optical losses as compared to FTO as described later. Figure 6.1 shows the mechanical stack of the resulting DSC/CIGS tandem solar cell.

### 6.3 Results

Figure 6.2 gives a comparison of the transmission data for FTO and ITO glass along with the fabricated DSC. FTO does absorb in the near IR wavelength region above 1000 nm, thereby reducing significantly the photocurrent drawn by the bottom cell. The diffuse transmission spectra for a DSC using FTO glass both as front and back contacts were employed, along with the individual spectra for FTO and ITO glass, for the purpose. Clearly the ITO has a much larger window in the near IR extending to 1600 nm, while the FTO absorbs light of wavelength > 800 nm. In order to reduce these optical losses, the DSCs described below employed FTO only for the front contact, and the counter electrode is made of ITO glass.

Figure 6.3 shows a typical photocurrent action spectra measured separately for a DSC and a CIGS cell. The external quantum efficiency (incident photon to current conversion efficiency) is plotted as a function of wavelength of the light. The spectral response of the two systems is complementary. The DSC shows a strong response in the UV, blue and green wavelength domain where the performance of the CIGS cell as expected is limited due to absorption from the CdS buffer layer. By contrast the CIGS cell exhibits high external quantum efficiencies in the red and near IR part of the spectrum extending from 700 - 1150 nm where the DSC is insensitive to light.

By combining the two cells with optimized spectral response (strong response in UV, blue and green for DSC, red and IR for CIGS) the total conversion efficiency of the single cells have been increased in tandem configuration described as follows. Superposition of the two cells produced a four contact stack whose photovoltaic performance was tested under AM 1.5 sunlight. CIGS
Figure 6.2: Optical transmission spectra including the diffuse part measured with an Ulbricht sphere, of ITO glass (c), FTO glass (b), and the DSC with mesoporous TiO$_2$ sensitized by a N-719 analogue dye (a). The front and back contacts of this cell are made of FTO glass.

Figure 6.3: Spectral response curves of the photocurrent for a DSC top cell (bold line) and a red and near IR sensitive bottom cell (dotted line). The external quantum efficiency (incident photon to current conversion efficiency) is plotted as a function of wavelength of the incident light.
bottom cell yielded $J_{sc} = 15.7 \text{ mA/cm}^2$, $V_{oc} = 0.689 \text{ V}$, $FF = 75 \%$, and $\eta = 8.2 \%$ (with the remaining light after passing top cell), while the corresponding parameters for the DSC top cell are $J_{sc} = 12.2 \text{ mA/cm}^2$, $V_{oc} = 0.858 \text{ V}$, $FF = 72 \%$, and $\eta = 7.6 \%$ under AM1.5 illumination. The combined conversion efficiency of 15.8 \% was higher than that of the individual cells even though the FTO glass causes significant transmission losses in the near IR range, as discussed above.

An attempt was also made to realize a two-wire tandem cell by adapting the film thickness of the top cell in order to match the photocurrent of the CIGS bottom device. Results are shown in Figure 6.4. Figure 6.4a gives the J-V curve for the DSC top cell in the stack yielding $J_{sc} = 13.7 \text{ mA/cm}^2$; $V_{oc} = 0.798 \text{ V}$; $FF = 75 \%$ and $\eta = 8.2 \%$, while the Figure 6.4b shows the J-V curve for the CIGS bottom cell in the stack producing $J_{sc} = 14.3 \text{ mA/cm}^2$; $V_{oc} = 0.65 \text{ V}$; $FF = 77 \%$, and $\eta = 7.3 \%$. These nearly current matched cells were connected in series to produce a two terminal DSC/CIGS tandem cell with the photovoltaic parameters of $J_{sc} = 14.1 \text{ mA/cm}^2$, $V_{oc} = 1.45 \text{ V}$, $FF = 74 \%$, and $\eta = 15.1 \%$.

The initial parameters of CIGS bottom cell, without the light absorption losses due to the top cell, were $J_{sc} = 26.8 \text{ mA/cm}^2$, $V_{oc} = 0.699 \text{ V}$, $FF = 74 \%$, and $\eta = 13.9 \%$, which shows that the efficiency has been increased even with significant transmission losses in the near IR caused by the DSC.

It is remarkable that such a high efficiency is obtained even though the photocurrents of the two cells were not perfectly matched, producing the hump in the J-V curve in Figure 6.4c, and there are significant optical losses in the stack. Therefore room for further improvement of this tandem system exists, which appears to be a promising configuration for realizing high conversion efficiencies.
Figure 6.4: Photocurrent density-voltage characteristics under AM 1.5 full sunlight (100 mW/cm²) for a two-wire tandem DSC/CIGS cell. (a) J-V curve for the DSC top cell in the stack producing $J_{sc} = 13.66$ mA/cm²; $V_{oc} = 0.798$ V; FF = 0.75 and $\eta = 8.18\%$; b) J-V curve for the CIGS bottom cell in the stack producing $J_{sc} = 14.3$ mA/cm²; $V_{oc} = 0.65$ V; FF = 0.77 and $\eta = 7.28\%$; (c) Two terminal DSC/CIGS tandem cell producing $J_{sc} = 14.05$ mA/cm²; $V_{oc} = 1.45$ V; FF = 0.74; $\eta = 15.09\%$. 
6.4 Conclusion

An efficient 4-terminal DSC / CIGS tandem solar cell has been realized for the first time, employing the favorable spectral response of DSC in 400-650 nm wavelength range and of CIGS absorber for 600-1200 nm. It has been successfully demonstrated that the resulting combination produced an efficiency of 15.1% (current matched) which was more than the efficiencies of the individual cells. With further optimization of the DSC and CIGS and minimization of optical losses, high efficiency cells can be achieved.

6.5 References


7 Conclusion & Outlook

The work presented in this thesis describes the progress that has been achieved in advancement of performance and processing of CIGS solar cells on flexible substrates. The developed low temperature process is suitable not only for polyimide but also for aluminum foils and other substrates. For CIGS solar cells on laboratory scale the 14.1% conversion efficiency is the best ever reported and the deposition method shows very good reproducibility. For further improvements of the efficiency different approaches could be used: the reduction of losses in the short wavelength part (< 600 nm), e.g. by an improvement of the transmission properties of the buffer layer, or in the long wavelength part (> 850 nm), by reducing the electron-hole recombination; application of anti-reflection coatings would enhance the number of photons reaching the absorber layer and therefore increase the current; the development of new type of high temperature stable polyimides could make deposition at higher temperatures possible and enable a better crystallization of the CIGS. The adaptation of the low temperature process for metal foils, which are more stable than polyimide, may also result in better results. Anyway, in my opinion this technology is quite matured and the next developments should focus on up scaling for industrial application. Especially an in-line and roll-to-roll process should be developed to bring the technology nearer to manufacturing and a final product.

On the topic of alternative back contacts it has been demonstrated that, as long as the back contact has a good conductivity and does not react during or after CIGS deposition, several materials can be used. The application of a MoSe₂ interface layer is essential to ensure quasi-ohmic contact between absorber and back contact. But a few questions are still open for this interface layer: What is the optimal thickness of the MoSe₂-layer? Which is the best deposition method? Are other materials than MoSe₂ possible for the interface layer? To answer those
questions a deeper understanding of the physical processes happening at the interface is needed and therefore more investigations necessary.

For the tandem solar cells a proof of concept of stacked dye-sensitized/CIGS tandem have been given. Since this work was just preliminary investigation and should give hints for future developments and collaborations, a lot of improvements by optimization are expected. The transmission of the top cells has to be improved and the current of the two cells should be optimized to have a better match. Alternatively other photovoltaic technology, like CdTe with alloy for wider bandgap, amorphous silicon, polymer or organic solar cells, can be substitute to the top or bottom cell and/or added to form multijunction solar cells with optimal spectrum utilization.

Of course the different topics discussed in this thesis can be combined to enhance the performance and stability. For example the use of adequate alternative back contacts on flexible substrates may result in a better match of the expansion coefficient of the different layer. Or the use of transparent back contacts opens the possibility to use CIGS solar cells as top cell in multijunction devices.

Anyway a lot of interesting topics and research fields still remain open and I am sure that amazing progress and discoveries will happen in photovoltaics in the future.
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Abbreviations and Symbols

AFM Atomic force microscope
AM1.5 Air mass 1.5
AR Anti-reflection
ARC Anti-reflection coating
BC (electrical) Back contact
CBD Chemical bath deposition
CIGS Compound formed from Cu, In, Ga, Se; usually Cu(In,Ga)Se$_2$
CIS Compound formed from Cu, In, Se; usually CuInSe$_2$
CTE Coefficient of thermal expansion
dc Direct current
DSC Dye sensitized solar cells
$E_F$ Fermi energy
$E_g$ Bandgap energy
EQE External quantum efficiency
ERDA Elastic recoil detection analysis
EVA Ethylene vinyl acetate
FF Fill factor
FTO Fluorine doped tin dioxide
HOMO Highest occupied molecular orbital
I-V Current - voltage
IR Infrared
ITO Indium tin oxide
## Abbreviations and Symbols

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<tr>
<th>Abbreviation</th>
<th>Description</th>
</tr>
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<tbody>
<tr>
<td>J-V</td>
<td>Current density - voltage</td>
</tr>
<tr>
<td>J_{sc}</td>
<td>Short-circuit current</td>
</tr>
<tr>
<td>LUMO</td>
<td>Lowest unoccupied molecular orbital</td>
</tr>
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<td>PDT</td>
<td>Post-deposition treatment</td>
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<td>PET</td>
<td>Polyethylenterephthalat</td>
</tr>
<tr>
<td>PI</td>
<td>Polyimide</td>
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<tr>
<td>PV</td>
<td>Photovoltaics</td>
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<tr>
<td>P1</td>
<td>Patterning of back contact</td>
</tr>
<tr>
<td>P2</td>
<td>Patterning of the absorber (CIGS)</td>
</tr>
<tr>
<td>P3</td>
<td>Patterning of front contact</td>
</tr>
<tr>
<td>rf</td>
<td>Radio frequency</td>
</tr>
<tr>
<td>RTP</td>
<td>Rapid thermal processing</td>
</tr>
<tr>
<td>R□</td>
<td>Sheet resistance</td>
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<tr>
<td>SEM</td>
<td>Scanning electron microscope</td>
</tr>
<tr>
<td>SIMS</td>
<td>Secondary ion mass spectrometry</td>
</tr>
<tr>
<td>SLG</td>
<td>Soda-lime glass</td>
</tr>
<tr>
<td>SS</td>
<td>Stainless steel</td>
</tr>
<tr>
<td>TCO</td>
<td>Transparent conducting oxide</td>
</tr>
<tr>
<td>TEM</td>
<td>Transmission electron microscopy</td>
</tr>
<tr>
<td>T_{sub}</td>
<td>Substrate temperature</td>
</tr>
<tr>
<td>T_{sub,max}</td>
<td>Highest used substrate temperature</td>
</tr>
<tr>
<td>UHV</td>
<td>Ultra high vacuum</td>
</tr>
<tr>
<td>V_{oc}</td>
<td>Open-circuit voltage</td>
</tr>
<tr>
<td>WVTR</td>
<td>Water-vapor transmission rate</td>
</tr>
<tr>
<td>η</td>
<td>Solar cells conversion efficiency</td>
</tr>
<tr>
<td>Φ_m</td>
<td>Work function</td>
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<tr>
<td>χ</td>
<td>Electron affinity</td>
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