CIS/CIGS BASED THIN-FILM SOLAR CELLS

Mark-Daniel Gerngroß, Julia Reverey
Faculty of Engineering
University of Kiel

ABSTRACT: The compound semiconductor copper-indium-gallium-diselenide (CIGS) as the basis material satisfies the requirements of thin film solar cells. CIGS is a direct gap semiconductor with high absorptivity. Therefore CIGS-based solar cells can be produced monolithically in large area thin film technique on cheap substrates. The band-gap structure is a complex heterojunction system. These solar cells show high efficiency and very good stability in outdoor tests.
Keywords: CIGS, CIS, thin film solar cell

1 MATERIAL PROPERTIES

1.1 General material properties

The crystal structure of CIS/CIGS is a tetragonal chalcopyrite structure, which is derived from the zinc blende structure. [1]
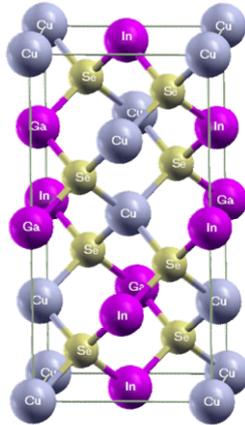
Figure 1: Crystal structure of chalcopyrite CIGS [4]

Figure 1 shows the tetrahedral coordination of lattice elements - Se atoms have two bonds to In/Ga and two bonds to Cu atoms. Each Cu and In/Ga atom has four bonds to Se atoms. [1]

The band-gap of CIGS is continuously adjustable from 1.04eV for pure CIS to 1.68eV for pure $CuGaSe_2$.

A characteristic property of CIGS is the high absorptivity. About 99% of the incoming light will be absorbed within the first micrometer of the material. [1]

The Minority-carrier lifetime, electron diffusion length and charge-carrier mobilities are properties that depend very much on the preparation conditions of the thin films. Therefore only approximated values can be provided. The minority-carrier lifetime amounts to several ns, the electron diffusion length is in the order of a few µm and the electron mobility in single crystal adds up to 1000 cm²/Vs. [1]

1.2 Phase diagram of CIS

The most relevant phase for application in solar cells is the α-phase. At RT the range of the α-phase is from 24-24.5 at% Cu. The optimal region for high efficient thin film solar cells is in the range of 22-24 at% Cu. [1]

The phase diagram in figure 2 shows this range lying within the α-phase at growth temperatures of 500-550°C, but outside at RT, which causes phase separation at RT.
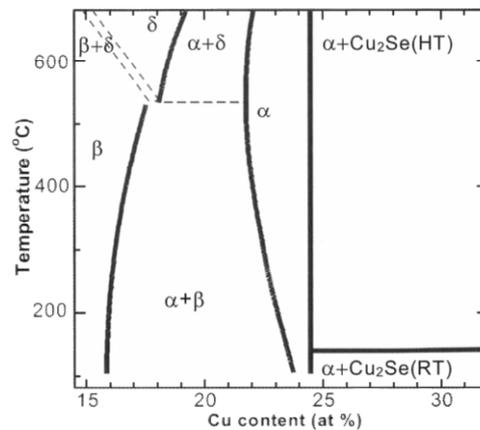
Figure 2: Pseudobinary cut Cu_2Se-In_2Se_3 of ternary phase diagram [1]

The β-phase ($CuIn_3Se_5$) is a defect phase built by ordered arrays of defect pairs (Cu vacancies V_{Cu} & In_{Cu} anti sites). [1]

The δ-phase is the high temperature phase. It is constructed by disordering the cation sub-lattice (Cu, In), which leads to the zinc blende structure. [1]

The Cu_2Se phase is similar to the β-phase, being constructed from the chalcopyrite structure by using Cu interstitials and Cu_{In} anti sites. [1]

2 IMPURITIES AND DEFECTS

2.1 Impurities

The α-phase is highly narrowed by the α+β and the α+Cu_2Se region at RT. By substitution of 20-30% of In by Ga, the α-phase region is widened and the band-gap of the CIGS layer is adjusted. The ratio of Ga/(Ga+In) is important for the cell performance. The optimal ratio is approximately 0.3. [1]

0.1at% of Na are incorporated into the film by precursors such as Na_2Se. Because of the incorporation intermediate compounds of $NaSe_y$ are formed, causing a better film morphology with enlarged grains, a passivation of grain-boundaries, improving the p-type conductivity of the film and reducing the defect concentration within the CIGS film. [1]

2.2 Defects

Defects in CIS/CIGS loom large because of the huge number of possible intrinsic defects playing an important

role for the photovoltaic performance. [1]

CIS/CIGS is doped with native defects. P-type conductivity is reached, if the material is Cu-poor and annealed under high Se-vapor pressure. But under Se saturation, Se atoms reevaporate from the film, producing Se vacancies, which act as compensating donors. [1]

N-type conductivity is reached, if the material is Cu-rich with a Se deficiency. The dominant donor for n-type conduction is the Se vacancy. [1]

CIS/CIGS is electrically tolerant to large off-stoichiometries because the nonstoichiometry accommodates in a secondary phase that is harmless for the photovoltaic quality of the material. Defects related to the off-stoichiometry are electronically inactive. [1]

Structural defects in CIS/CIGS are electrically neutral because defect complexes have lower formation energies than the corresponding isolated defects. Thus defect complexes are formed such as $\langle 2V_{Cu}, In_{Cu}\rangle$, $\langle Cu_{In}, In_{Cu}\rangle$ and $\langle 2Cu_i, In_{Cu}\rangle$. Due to the formation of defect complexes no energy levels lie within the band-gap, in contrast to the isolated In_{Cu} antisite that is a deep recombination center. Ordered arrays of these complexes serve as building blocks for the β-phase in Cu-poor region. [1]

3 GROWTH METHODS FOR THIN-FILMS

3.1 Coevaporation process

The thin film is produced by evaporating Cu, In, Ga and Se from elemental sources. The setup is shown in figure 3. [1]
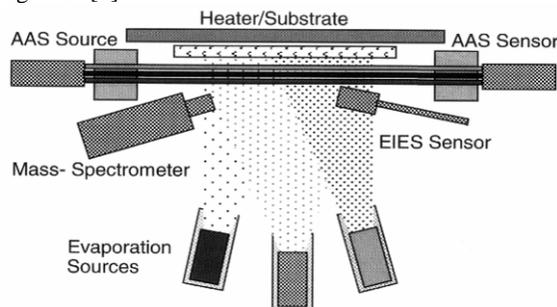
Figure 3: Setup including process control units [1]

To achieve the favored film composition, a precise control of the particular evaporation rates is necessary. Therefore an electron impact emission spectrometer (EIES) and an atom absorption spectrometer (AAS) or a mass spectrometer is used. The process requires a substrate temperature between 300°C and 550°C for a certain time during film growth. [1]

The inverted three-stage process is most favored coevaporation process. At first In, Ga and Se are evaporated with different rates and deposited as $(In,Ga)_2Se_3$ at 300°C on the substrate. Afterwards Cu and Se are evaporated and deposited on the substrate at elevated temperatures. At last In, Ga, and Se are evaporated again. The inverted three-stage process leads to smoother film morphology and high efficiency solar cells.[1]

3.2 Sequential process

There are two different techniques according to the selenization of the film.

3.2.1 Selenization from Se vapor

The substrate is a soda lime glass coated with a thin film of Mo as the back contact of the solar cell. Cu and In,Ga layers are sequentially deposited on the substrate by sputtering. The different layers are selenized in an H_2Se atmosphere and converted into a CIGS thin film by a thermal process. [1]

The advantage of this process compared with the coevaporation process is that large-area depositions of CIGS films are commercially producible. The main disadvantage is that H_2Se is toxic. [1]

3.2.2 Anealing of stacked elemental layers

The substrate and deposition technique of Cu and In, Ga are identical to the selenization from vapour process. The deposition of Se is done by evaporation and the rapid thermal process takes place in an inert atmosphere. With this technique large-area deposition of CIGS films are commercially producible. The main advantage is the avoidance of the H_2Se atmosphere. [1]

3.2.3 Roll to roll deposition

Polyimides or stainless steel foils are used as flexible substrates coated with a thin film of Mo. [5]

If stainless steel foil is used as substrate an insulator between the steel foil and the Mo layer is necessary for interconnection. Polyimides provide high electric strength and high dimensional stability under heat. Cu, In, Ga and Se are deposited by an ion beam supported low temperature deposition technique. [5]

The low cost production and available flexible modules with high power per weight ratio are huge advantages, but actually the efficiency is still lower compared to the other processes. [5]

4 DEVELOPMENT OF CIGS SOLAR CELLS

4.1 Structure of CIGS-based thin film solar cell

Figure 4 shows a cross section of a CIGS thin film solar cell built on 2 mm soda lime glass substrate. [3]
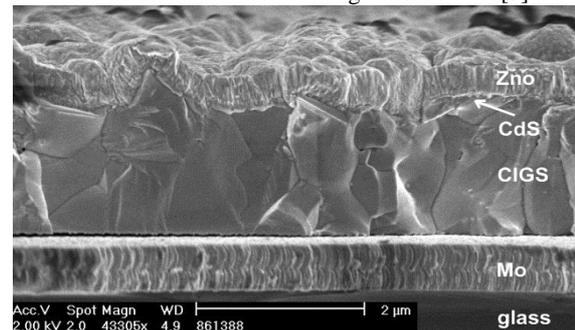
Figure 4: SEM picture of a cross section of a CIGS thin film solar cell structure [3]

The substrate is coated with a layer of Mo of about 1μm thickness to prevent an uncontrolled diffusion of Na from the substrate into the absorber material. The Mo layer also serves as the back contact of the solar cell. [3]

Upon the Mo layer, the p-type CIGS absorber layer of about 1.6μm thickness is situated. [3]

The CdS layer is placed on top of the CIGS layer with a thickness of only 50nm. [3]

Upon the buffer layer the ZnO layer is located with a thickness of approximately 1μm. [3]

4.2 Buffer layer: cadmium sulfide

The CdS layer is deposited by chemical bath deposition (CBD) with a layer thickness of 50nm. The band-gap energy of CdS is 2.5eV. CdS is n-type conducting and has a high specific resistance. [1]

The Cd $^{2+}$ ions diffuse from the aqueous solution into the CIGS absorber material during CBD. The concentration of Cd ions is the highest at the CIGS surface and decreases to the background level within the first 20 nm. At the CdS/CIGS interface Cu atoms are substituted by Cd ions causing Cd_{Cu} anti-sites, which act as donors and provide positive space charges near to the CdS/CIGS interface. Thus recombination at the interface is decreased. In order to achieve these features it is very important to deposit the CdS layer very uniformly - otherwise the solar cell will be less efficient. [1]

The CdS layer is used to reduce the lattice misfit between the CIGS and the ZnO layer and to protect the absorber layer from further processing steps. [1]

4.3 Window layer: zinc oxide

The ZnO bilayer is deposited by radio frequency (RF) sputtering or by atomic layer deposition (ALD). [1]

The band-gap energy of ZnO is 3.3eV. The resistivity of the ZnO layer depends on the deposition rate (RF sputtering) respectively on the flow rate (ALD). [1]

The high resistivity layer has a thickness of about 0.5µm and is intrinsic conducting. [1]

The low resistivity layer is highly doped with Al of about $10^{20}cm^{-3}$. Due to the doping this layer is n-type conducting.[1]

The bilayer of ZnO is used as the transparent front contact of the solar cell. The heterojunction is formed by the CIGS and the ZnO layer. [1]

4.3 Band-gap structure of ZnO/CdS/CIGS solar cell

Figure 5 shows the band structure of a CIGS-based solar cell. The i-ZnO already lies within the space-charge region. A discontinuity of about 0.4eV is found in the conduction band close to the interface of i-ZnO/CdS. The discontinuity in the conduction band in transition from CdS to CIGS varies from -0.4eV for CIS to +0.3eV for $CuGaSe_2$ depending on the concentration of Ga. [2]
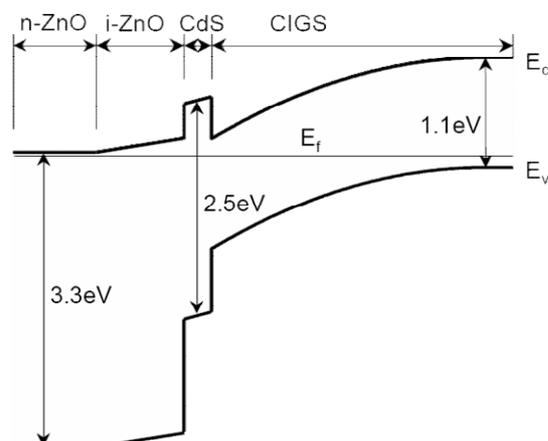
Figure 5: Band-gap structure of ZnO/CdS/CIGS module

The lion's share of the positive space charge in the n-type conducting ZnO area is already situated at the CdS/CIGS interface. [2]

As a result of the huge band discontinuities of the valence-band edge the minority charge carriers exclusively overcome the heterojunction. [2]

The heterojunction can rather be described as a n+ip contact than a Schottky contact. [2]

5 FABRICATION TECHNOLOGIES

5.1 Cell processing

This description of the cell processing is just schematically and does not include all steps in detail.

It is started with cleaning the substrate. The deposition of the metal base electrode is followed by the first patterning done by a laser. [1]

Afterwards the p-type CIGS-based absorber is superimposed and covered by a buffer layer consisting of CdS. Subsequently the existing structure is patterned by a CNC machine. After that the n-type window layer is deposited on top of the whole structure and patterned by a CNC machine. This process step is followed by the metallization and the deposition of the antireflection coating consisting of MgF_2. [1]

5.2 Module processing

The module processing is nearly identical to the packaging technology of crystalline Si solar cells. [1]

The CIGS-based circuit is embedded in ethylene vinyl acetate (EVA) superimposed at 150°C to protect the circuit from environmental influences. After cooling, the EVA becomes crystal clear and is cross-linked three-dimensionally forming an enduring compound. [1]

To protect the cell against mechanical stress tempered glass is used as cover glass. Following the junction box including the leads is connected to the module. The module is framed by an Al frame with joint sealant. [1]

6 CONCLUSION AND PROSPECTS

6.1 Conclusion
- High reliability [3]
- Highest efficiency among thin film solar cells [3]
- Less consumption of materials and energy [3]
- Monolithical integration [3]
- High level of automation [3]

6.2 Prospects
- Increasing appliance (solar parks, aerospace etc.) [3]
- Optimization of fabrication processes [3]
- Gain in efficiency for large area solar cells [3]
- Possible short run of In and Ga resources [3]

7 REFERENCES

[1] Y. Hamakawa, Thin Film Solar Cells, 28-31, 163-209 2004.

[2] T. Meyer, Relaxationsphänomene im elektrischen Transport von Cu(In,Ga)Se$_2$, 1999. 5-19

[3] B. Dimmler,CIS-Dünnschicht-Solarzellen, 2006.

[4] S. Chen, X. G. Gong: Physical Review B **75**, 205-209, 2007.

[5] M.E.Beck,Tolerance of Three-Stage CIGS Deposition to Variations Imposed by Roll-to-Roll Processing,2003.