## ET3034TUx - 5.3 - CIGS PV Technology

The next thin-film PV technology we will discuss today is based on CIGS.

CIGS stands for copper indium gallium selenide sulfide.

The typical CIGS alloys are heterogeneous materials.

The physical properties of CIGS are rather complex and many different views exist on these properties among scientists.

Some important compounds in the material are CuInSe2 with a band gap of 1.0 eV, CuInS2, having a band gap of 1.5 eV and CuGaSe2, having a band gap of 1.7 eV.

These materials cover a wide range of both band gaps and lattice constants.

The CIGS material is a direct band gap semiconductor material therefore it has a large absorption coefficient.

It requires only a thickness of 1-2 microns to absorb a large fraction of the light above the band gap.

Typical electron diffusion lengths are in the same order of a few microns.

A variety of CIGS alloys exist, but the best performing layers have something in common - they contain a polycrystalline alpha-phase.

The lattice atoms are tetrahedrally bonded.

Such a lattice structure is a so-called chalsopyrite structure as you can see in this illustration.

The heterogeneous material consists of a phase of copper indium selenide, often indicated by CIS, and copper indium gallium selenide.

x=0 means it is a CuGaSe2 material and x=1 means it is a CuInSe2 material.

It means using the Cu/Ga ratio x, the band gap can be tuned from the CuGaSe2 at 1.7 eV at x=0 down to 1.0 eV for x=1.0.

The CIGS absorber layer is a p-doped layer.

The doping is a result of intrinsic defects in the material, related to Cu deficiencies.

These vacancies efficiently act as an acceptor, it means electrons excited from the valence band can get easily trapped.

As a result the holes become the majority charge carrier density.

Let's look at a typical CIGS solar cell structure.



The substrate is glass.

On top of the glass a molybdenum layer with typical thickness of 1 micron is deposited, which acts as the back contact.

On that the p-type CIGS absorber layer is deposited with thickness ranging from 2 up to 4 microns.

The p-n junction is formed by a thin n-layer of around 15 nm on top of p-type CIGS that is based on CdS.

This layer is referred to as the buffer layer.

The n-type region is extended with an n-type TCO.

First an intrinsic ZnO is placed followed by an Al-doped ZnO.

The Al-doping makes the ZnO n-type.

Similar to some concepts of the thin-film silicon technology, the aluminum-doped ZnO acts like a transparent front contact for the solar cell.

On top of this transparent conductive oxide, anti-reflective coatings can be placed as discussed for the c-Si technology.

Here we see the electronic band diagram of a CIGS solar cell.

The light enters the cell from the left, at the ZnO side.

The p-type CIGS absorber layers used in industrial modules have a typical band gap of 1.1-1.2 eV.

This band gap is accomplished by a ratio of Ga to In of around 0.3.

The n-type CdS buffer layer has a band gap of 2.5 eV.

Since the band gap of the n- and p-type junction materials are different, this CIGS cell can be considered as a heterojunction.

The light-excited minority electrons in the CIGS layers have to diffuse to the CdS/CIGS interface to be separated.

The holes diffuse to the molybdenum back contact to be collected.

Here, the holes recombine with the electrons supplied from this molybdenum back contact.

ZnO acts like the front contact.

The band gap of the ZnO is very large, minimizing the parasitic absorption losses in this device.



The electrons have to be separated at the CIGS/CdS interface.

As with every interface, this interface has more defects and could act as a loss mechanism to the minority electrons.

This can be prevented by placing an n-type CIGS type of layer between the p-type CIGS and the CdS interface, which screens the CdS/CIGS interface from the holes.

The n-type CIGS is an indium rich alloy, like Cu(In,Ga)3Se5.

In Cu deficient p-type CIGS materials, the dominant recombination mechanism is Shockley-Read-Hall recombination in the bulk.

In contrast, in Cu rich CIGS films the SRH recombination at the CIGS/CdS interface becomes dominant.

One of the important aspects of CIGS solar cells is the role of sodium.

Low contamination of sodium appears to increase the conductivity in the p-type CIGS materials, it leads to a welcome texture and an increase in the average grain size.

Similar to multicrystalline silicon as discussed last week, the larger the grain size, the less grain boundaries and less recombination are present in the material.

This results in higher band gap ultilization and higher open-circuit voltages.

Typical optimum concentration of sodium in the CIGS layers is 0.1%.

The sodium source in the growth mechanism can be the soda-lime glass used as substrate.

In CIGS solar cell concepts, were this soda-lime glass is missing, the sodium has to be intentionally added during the deposition process.

In the CIGS field the exact reason why sodium improves several properties of the CIGS is still under debate.

In contrast to the thin-film silicon technology discussed earlier, CIGS films can be deposited using a variety of deposition technologies.

As many of these activities are developed within companies, not much detailed information is available on many of these processing techniques.

One of the processing techniques is co-evaporation or co-sputtering under vacuum conditions.

Using various targets of copper, gallium and indium, the precursors in various steps are coevaporated onto a substrate.

Two approaches can be used.



First is the sputtering and co-evaporation on a substrate at high temperatures.

During the process there is an additional selenium source.

During deposition a CIGS film is formed.

The second approach is sputtering and co-evaporation on a substrate at room temperature.

The deposited films on the cold substrate are thermally annealed in presence of a selenide vapor to form the final CIGS structure.

Another option is to deposit a selenium-rich layer on top of the initial deposited alloy and this is annealed.

Because of the variety and complexity of the reactions taking place during such 'selenization' process, the properties of CIGS are difficult to control.

Companies that use or have used the co-evaporation process are Würth Solar, Global Solar and Ascent solar.

Among CIGS companies using sputter approaches are Showa Shell, Solar Frontier, Avancis, Miasole and Honda Soltec.

An alternative approach is based on a kind of wafer bonding technique.

Two different films are deposited on a substrate and superstrate.

The films are pressed together under high pressure.

When heated the film is released from the superstrate and a CIGS film remains on a substrate.

This processing technique is used by the company Heliovolt.

Non-vacuum techniques are based on depositing nanoparticles of the precursor materials on a substrate after which the film is sintered.

Sintering is a process in which films are made out of powder.

The powder is heated up to a temperature below the melting point.

Atoms in the particles can diffuse across the boundaries of the particles.

As a result the particles fuse together, forming one big solid.

An important advantage of the CIGS PV technology is that on lab-scale it has achieved the highest conversion efficiencies among the thin-film solar cells.

Lab-scale CIGS solar cells processed on glass have a record efficiency of 19.9% as achieved by National Renewable Energy Lab in the US.



Typical open-circuit voltages are close to 700 mV, FF of 81% and short-circuit current density between 35 and 36 mA/cm^2 have been achieved.

The world record on flexible substrates has been obtained at the Swiss Federal Laboratories of Materials Science and Technology.

The CIGS cell on a flexible polymer foil resulted in an impressive conversion efficiency of 20.4%.

CIGS cells in a module are similarly interconnected as we have seen for thin-film silicon cells discussed earlier.

First the molybdenum back contact is deposited on top of the glass substrate and the cell areas are defined by laser scribes.

Then the CIGS p-layer and CdS n-layer are deposited including a laser scribe step.

Finally the intrinsic and p-doped ZnO is deposited, followed by a final laser scribe step.

Now the front TCO electrode is connected with the molybdenum back contact of the next solar cell.

The record efficiencies of modules are significantly lower than that for the lab-scale cells.

Defining conversion efficiencies we have to make a distinction between two types of numbers.

The aperture area, which means that only the area of the PV active part is considered when the conversion efficiency is considered.

Total area means that the entire module area is considered when calculating the conversion efficiency.

This area includes the dead area created by interconnection and the edges of the module.

The record efficiencies of 1 m<sup>2</sup> modules are in the order of 13%, whereas the aperture area efficiencies are just above 14% as confirmed by NREL.

The German manufacturer Manz AG has presented a 15.9% aperture area efficiency and a total area efficiency of 14.6%.

Solar Frontier in Japan claims a 17.8% aperture area efficiency on a very small module of 900 cm<sup>2</sup>.

With these results, CIGS has the highest conversion efficiency achieved among the thin-film PV technologies.



However, as CIGS is a rather complex material with complex deposition processes over large areas, an important challenge for the CIGS PV industry is to achieve a high production yield of CIGS modules.

Another challenge is that this technology includes the element indium.

Here we see an illustration that shows the abundance of the various elements in the Earth's crust.

The red line is an indication for the critical abundance of a source material to be used for a large-scale production.

As you can see, indium is not a very abundant element as it lies below the red line.

Therefore indium might be the limiting step to upscale the CIGS PV technology to future terawatt scales.

In addition, the current display industry depends on indium as well, as ITO is integrated in many display screens.

Consequently, the interest in copper zinc tin sulfide, referred to as CZTS, is increasing, to replace the CIGS absorber layer.

CZTS is based on non-toxic and abundantly available elements.

The current record efficiencies of CZTS solar cells on lab-scale is around 11% as achieved by IBM.

In the next block we will discuss the thin-film CdTe PV technology, this is a PV technology, which has currently the lowest demonstrated cost price per Wp.

See you in the next block!

