## ET3034TUx - 5.2.1 - Thin film silicon PV technology 1

Last week we have discussed the dominant PV technology in the current market, the PV technology based on c-Si wafers.

Now we will discuss a different silicon technology, the thin-film silicon PV technology, which belongs to the so-called second generation PV technology.

As discussed in week 1 these PV technologies are focused on reducing the cost price of the PV module to a level where the cost price per Wp drops below that of crystalline silicon technology.

An advantage of thin-film silicon solar cells is that they can be deposited on glass substrates and flexible substrates.

So, the first question we have to answer is which type of silicon alloys are being used as an absorber layer.

The typical lattice structure is either amorphous or nanocrystalline.

Nanocrystalline is also called microcrystalline in the literature.

In a moment I come back how these lattices really look like.

"a-" is the abbreviation of amorphous, "nc-" is the abbreviation for nanocrystalline silicon.

First I want to focus on the composition of the various alloys.

First we have hydrogenated amorphous silicon and nanocrystalline silicon.

It means that we have a lattice of silicon in which some of the valence electrons are passivated by hydrogen.

The ":H" in the abbreviation corresponds to the incorporated hydrogen.

The hydrogen content for these types of silicon alloys typically ranges from 5 up to 15%.

The second alloy is silicon mixed with the next element in the periodic table with four valence electrons: germanium.

Both hydrogenated amorphous and nanocrystalline silicon germanium alloys are being used in thin-film silicon solar cells.

Silicon is also mixed using the four valence electron material, carbon, leading to hydrogenated amorphous silicon carbide.

Another interesting silicon based alloy, is that in which the 6-valence electron atom, oxygen, is incorporated in the lattice.



This nanocrystalline silicon oxide is being used in thin-film silicon solar cells as well.

All these alloys can be doped.

Even the nanocrystalline silicon oxide can be doped p-type adding boron or n-type by adding phosphorous.

How does an amorphous lattice look like?

Last week we have discussed crystalline silicon.

Cyrstalline silicon has an ordered lattice in which the orientation and structure is repeated in all directions.

For amorphous silicon this is not the case.

The lattice is disordered as you can see in this animation.

The animation shows the growth of a so-called continuous random network.

On atomic length scales, or also called short-range order, the atoms still have a tetrahedrally coordination structure.

The silicon bond angles and silicon-silicon bond lengths are slightly distorted in reference to a crystalline silicon network.

On short-range order the lattice still might look very crystalline like.

However, at larger length scales, or also referred to as long-range, the lattice does not look crystalline anymore.

Here you only see a disordered network which is only built up out of silicon atoms.

In a real amorphous network you will have volume deficiencies in the lattice.

Examples of volume deficiencies are vacancies, multivacancies or nanosized voids.

The surfaces of these volume deficiencies are passivated with hydrogen.

Another phase of hydrogenated silicon alloys is the nanocrystalline lattice.

This is a heterogeneous material.

It consists of small grains with a crystalline lattice.

These grains are embedded into a tissue of hydrogenated amorphous silicon.

Typical grain sizes are in the order of a few tens of nanometers.



This illustration made by the Forschungszentrum in Jülich Germany, nicely shows the various phases of thin-film silicon going from left to right.

At the right hand side, the phase represents the amorphous lattice.

At the left hand side, a fully crystalline phase is shown, which is close to that of polycrystalline silicon, except that it has much more cracks and pores in it.

Note, that the nanocrystalline and microcrystalline silicon refers to the same phase.

Going from right to left, the amorphous phase is changing into a mixed phase with a few small crystalline grains to a phase which is dominated by large crystalline grains and a small fraction of amorphous tissue.

The best nanocrystalline silicon bulk materials used in solar cells has a network close to the so-called amorphous to nanocrystalline silicon transition and its crystalline volume fraction is in the order of 60%.

The band gap of nanocrystalline silicon is close to that of crystalline silicon due to the crystalline network in the grains.

The band gap of amorphous silicon is larger in reference to crystalline silicon.

It is out of the scope of this course to discuss this in great detail, but the distortions in bond angles and bond lengths make the band gap larger in reference to crystalline silicon lattice.

An important consequence of a disordered lattice is that the electron moment is poorly defined in contrast to crystalline silicon.

In crystalline silicon, the electronic band diagram versus lattice momentum looks like this.

Both energy and momentum transfer is needed to excite an electron from the valence band to the conduction band.

Crystalline silicon is an indirect band gap material.

This band gap does not hold anymore for an amorphous lattice.

Therefore, the amorphous silicon does not act like an indirect band gap material but a direct band gap material.

This has a positive effect on the absorption of the hydrogenated amorphous silicon.

It is more likely that a photon can be absorbed to excite an electron from valence to conduction band.

This is demonstrated in the next graph.

Here the absorption coefficient is plotted versus the photon energy expressed in eV.



The black line represents crystalline silicon.

The green line represents amorphous silicon.

The absorption coefficient for amorphous silicon is in the visible spectrum much larger in reference to crystalline silicon.

It can be 2 orders of magnitude larger, which means that much thinner silicon films can be used in reference to the typical wafers in crystalline silicon solar cells.

The red line respresent amorphous silicon germanium which has lower band gaps and much higher absorption coefficient in the visible.

Hydrogenated amorphous silicon has a band gap in the order of 1.6 up to 1.9 eV, which can be tuned by the amount of hydrogen incorporated into the silicon network.

Nanocrystalline silicon has a band gap in the range of 1.1-1.3 eV.

The band gap of the silicon alloy can be tuned by inclusion of the other elements as well.

The hydrogenated amorphous silicon germanium alloys, can have band gaps in the range of 1.4 up to 1.6 eV.

Silicon mixed with carbon, the so-called a-SiC:H can have band gaps of 1.9 eV and larger.

Nanocrystalline silicon oxides have band gaps larger than 2 eV.

The hydrogenated amorphous and nanocrystalline silicon films have a relatively high defect density in reference to crystalline silicon.

Due to the disordered structure not all valence electrons are able to make bonds with the neighboring atoms.

The so-called dangling bonds can act as defects.

This means that the lifetime of the light excited charge carriers is limited by the Shockley-Read-Hall recombination, which controls the diffusion length.

The recombination is so high that the diffusion length of the charge carriers in hydrogenated amorphous silicon is only 100 up to 300 nm.

This means that the transport of charge carriers in a thick absorber layer cannot rely on diffusion.

A typical amorphous silicon solar cell is therefore not based on a p-n junction like the wafer based crystalline silicon solar cells.

The amorphous silicon solar cell is based on a p-i-n junction.



What is a p-i-n junction?

The absorber layer is based on an intrinsic amorphous silicon absorber film which is sandwiched between thin layers of p-doped and n-doped amorphous silicon.

The red layer indicates the p-doped amorphous silicon and yellow indicates the amorphous n-layer in this illustration of a single junction amorphous silicon solar cell.

The p- and n-doped layers create an built-in electric field over the intrinsic absorber layer.

This can be illustrated by an electronic band diagram of the amorphous silicon solar cell.

The solar cell consists of a thin p-layer, with typical thickness of only 10 nm.

Note, that the Fermi level of a p-layer is closer to the valence band than to the conduction band.

The intrinsic film has a typical thickness of 100 up to 300 nm, and its Fermi level is positioned in the middle of the band gap.

The n-type layer is in the order of 20 nm and its Fermi level is closer to the conduction band than to the valence band.

If these layers are connected together, we know that the Fermi level equals out in the dark and thermal equilibrium.

This creates a slope over the electronic band in the intrinsic film as you can see in this illustration.

This reflects the built-in electric field.

The light-excited charge carrier will move due to the electric field.

The holes move up the slope in the valence band to the p-layer and the electrons move down the slope in the conduction band to the n-layer.

Note, that as the absorber layer is intrinsic, the charge carriers neither belong to the minority or majority charge carriers, the hole and electron density is in the same order of magnitude.

In the p-layer the holes are the majority charge carriers and the dominant transport mechanism is diffusion.

In the n-layer the electrons are the majority charge carriers and diffusion is the dominant transport mechanism.

Due to the relative low diffusion length, both the p- and n-layers cannot be too thick.



A wafer based crystalline silicon solar cell, discussed last week, can be considered as a diffusion solar cell.

Diffusion is the dominant transport mechanism for the charge carriers in the absorber layer.

An amorphous silicon solar cell is a drift device, the dominant transport mechanism in the absorber layer is drift.

Typical solar cells look like this.

This is a solar cell in the superstrate configuration.

If people talk about p-i-n junctions they refer to the sequence in which the silicon layers were deposited, so first the p-layer, then the i-layer and then the n-layer.

The front contact is a transparent conductive oxide abbreviated with TCO.

Typical TCO layers are fluor-doped tin oxide, aluminum-doped zinc oxide, boron-doped zinc oxide, hydrogen-doped indium oxide, ITO which is tin-doped indium oxide.

These films are processed using either sputtering, low-pressure chemical vapor deposition, metal-organic chemical vapor deposition and atmospheric pressure chemical vapor deposition.

P-doped layers are boron-doped amorphous silicon, but also the higher band gap materials as boron-doped silicon carbide and silicon oxide layers are used to enhance the transmission of the blue-ish light into the absorber layer.

As back reflector usually a TCO/metal back reflector is integrated into the device.

Metals are either aluminum or the more expensive silver, which has a higher back reflection compared to aluminum.

As the band gap of hydrogenated amorphous silicon is relatively high in the order of 1.75 eV, it only has a spectral response below wavelengths of 700 nm.

The best current density achieved in single junction amorphous silicon solar cells are 17 up to 18 mA/cm^2 whereas the theoretical current available in the spectrum is in the order of 23 mA/cm^2 which means that the spectrally average EQE is in the order of 74 up to 77%.

The best open-circuit voltages are in the order of 1.0 eV.

With respect to a band gap of 1.75 eV the band gap utilization is relatively low due to the high levels of SRH recombination and the relative broad valence and conduction band tails.

The best stabilized efficiencies of a single junction solar cell is 10.1% obtained by the research labs of Oerlikon Solar, currently part of Tokyo Electron.

Nanocrystalline silicon films are used as intrinsic absorber layer as well in a p-i-n solar cell.



Challenge the future

The spectral utilization of the nanocrystalline silicon p-i-n junction is better in reference to amorphous silicon due to the lower band gap of the nanocrystalline silicon.

However, to utilize the spectral part from 700 up to 950 nm, thicker films are required.

Typical intrinsic film thicknesses are 1 up to 3 microns for nanocrystalline silicon.

The maximum short-circuit current densities obtained are 30 to 31 mA/cm<sup>2</sup> as demonstrated by United Solar in the United States.

The highest open-circuit voltages are in the order of 600 mV.

The record conversion efficiency for a single junction nanocrystalline silicon solar cell is 10.7% as achieved by the EPFL in Neuchâtel Switzerland.

Both the single junction amorphous and nanocrystalline silicon solar cell, do not have an optimum spectral utilization.

For that reason multi-junction concepts are being used in the thin-film silicon field as well.

One of the most studied concepts is the so-called micromorph concept, which is a double junction that consists of one amorphous silicon p-i-n junction and a nanocrystalline silicon p-i-n junction.

How does such double junction solar cell work?

First, the amorphous junction has the highest band gap of both materials and will act as top cell.

The top cell is the p-i-n junction that is facing to the front and where the incident light is passing first.

The cell with the highest band gap acts like the top cell as the spectral part with the most energetic photons has the smallest penetration depth in materials.

The bottom cell is the cell with the lowest band gap.

This cell has to harvest the photons from spectral parts with the lower energetic photons.

