

ET3034TUx - 6.1 - Third generation PV technologies

The last two weeks we have discussed the first and second generation photovoltaic technology.

This week we will discuss some third generation PV concepts.

In addition, we will look at alternative technologies to convert the energy in the sunlight into heat, solar fuels and again electricity.

First, we will start with third generation PV technology.

As discussed in week 1, third generation technology is technology based on concepts, which are able to surpass the so-called Shockley-Queisser limit of a single junction solar cell.

The Shockley-Queisser limit as discussed in week 3, is a kind of thermodynamic approach to estimate the maximum performance of a single junction solar cell.

The AM1.5 spectrum is incident on a solar cell.

We don't allow the solar cell to increase in temperature.

This means that all energy in the incoming AM1.5 spectrum can escape the system of the solar cell by either the current density generated or by the radiative recombination of charge carriers.

As a result the maximum efficiency which can be achieved is around 33% in the band gap range from 1.0 eV up to 1.8 eV as indicated by the black area in the shown graph.

Now we are going to look at a very fundamental limitation of the photovoltaic effect as we have discussed it so far.

What physical principles are limiting the extent of photogeneration?

First, one problem is, that in a single junction only one band gap material is used.

A large fraction of the energy in the most energetic photons is lost as heat as illustrated here.

The arrows represent photons with different energies.

The arrows on the right indicate how much energy is wasted as heat.

Secondly, most solar cells concepts are based on irradiance incidence of 1 sun.

Higher irradiance means more current generation.

Thirdly, every photon only excites one electron in the conduction band creating only one electron-hole pair.

The energy of high energetic photons could be utilized better if they would create more than one excited electron in the conduction band.

Fourthly, the photons below the band gap are not used.

They do not result in charge carrier excitation.

Finally, the charge carriers populate single energy levels.

Light absorption excites electrons and holes up into the conduction or down into the valence band.

However, the charge carriers relax very fast, the electron to the bottom of the conduction band and the hole to the top of the valence band.

The potential difference between the charge carriers right after the excitation is not utilized.

In addition, in the band are no states, so the light below the band gap does not excite any charge carriers.

Tackling these fundamental limitations means that we can develop PV concepts with conversion efficiencies that can surpass the Shockley-Queisser limit.

Tackling the first problem has been discussed last week.

Both the III-V semiconductor PV technology and the thin-film silicon technology use the concept of multi-junctions - several solar cell junctions stacked upon each other with a response to different parts of the solar spectrum.

The second problem, that concepts are based on 1-sun irradiance, is tackled using concentrator solar cells.

As discussed last week, the concentrator technology is applied on multi-junctions based on III-V semiconductor materials.

As a result, the highest conversion efficiencies of 44% have been achieved.

This exceeds the Shockley-Queisser limit by more than 10%.

The fact that every photon can only generate at maximum one collected electron can in theory be tackled by two approaches.

The first one is down-conversion, which is a spectral conversion approach.

The high energetic photons are split in two or even more low energetic photons, before being absorbed in the PV active part.

As a result high energetic photons can result in more than one electron being collected.

The second approach to enhance the charge carrier excitation by a single energetic photon is called multiple exciton generation (MEG).

Here nanostructure semiconductor materials might be able to convert the energy of a photon in two or more excited electron-hole pairs.

The problem of the non-use of the photon below the band gap can be tackled with a spectral conversion approach as well.

Here the same low energetic photons, which are transmitted through the solar cell, are converted into one photon with an energy above that of the band gap of the semiconductor material.

If this photon is reflected back in the material it can be absorbed.

The last problem in the list is that of a single population of each charge carrier.

In theory, this can be tackled by hot carrier solar cells.

Here the charge carriers are collected, just after light excitation, before they are relaxed back to the edges of the electronic bands.

This improves the band gap energy utilization.

Another, theoretical solution is the concept of intermediate band solar cells.

This is the concept in which intentionally an electronic band within the band gap is engineered to enable photons below the band gap to help additional electrons to be excited as well.

Note, that besides multi-junction and the concentrator approach, none of these concepts have resulted in high-efficiency solar cells or even been demonstrated yet.

These other concepts are still in a fundamental research phase.

Here I will give you a quick introduction to down-conversion, multiple exciton generation, up-conversion, hot carrier solar cells and intermediate band solar cells.

Let's start with spectral conversion, which results in splitting one photon in multiple lower energetic photons.

It might tackle the problem that per photon only one electron is excited.

A down converter is a magic material that absorbs a high energetic photon and converts this photon in at least two lower energetic photons.

If the energy of both photons is still larger than that of the band gap of the photovoltaic material, both photons can be absorbed and used for exciting charge carriers.

As a result, a high energetic photon, like a photon in the blue visible part, can result in two excited electrons in the blue part.

In other words, the maximum theoretical EQE of 100% at the wavelength of the blue photon can be increased to 200%.

If the photon has enough energy to be split into three photons with an energy higher than the band gap, a theoretical EQE of 300% could be obtained.

So spectral down-conversions first convert photons into lower energetic photons, and these photons are used in photovoltaic devices.

Multiple exciton generation, abbreviated with MEG, is another approach, which can accomplish the excitation of more than one electron-hole pair per photon.

The difference with spectral down-conversion is that all fundamental energy conversion steps occur in the PV active layer.

In a normal semiconductor material, a high energetic photon has some rest energy, which is not used to excite the electron.

This excess energy is usually lost as heat.

In down-conversion approach this rest energy is transferred as a quantized energy package within the material, where it can excite a second electron into the conduction band.

It means that the energy in one photon, results in two excited electrons.

The requirement of course is that the energy in the initial photon is at least two times that of the band gap energy.

In this way, theoretical EQE of 200% can be achieved as well.

If we would have a photon with an energy larger than three times the band gap, a theoretical EQE of 300% could be achieved.

Both for down-conversion and multiple exciton generation, nanostructured semiconductors are studied and developed.

These structures are based on so-called quantum dots.

Quantum dots are small spherical nanoparticles made of semiconductor materials with typical diameters of a few nanometers.

These semiconductor particles still behave like a semiconductor material; however, due to quantum mechanical effects the band gap can be larger of the semiconductor quantum dots in reference to the band gap of the semiconductor material in large bulk materials.

The band gap can be tuned by the size of the nanoparticles.

The smaller the particles, the larger the band gap.

This enables interesting band gap engineering possibilities, such as a multi-junction solar cell, based on junctions with different quantum dot sizes in every junction.

To use QDs for down-conversion or multiple exciton generation, an ensemble of nanoparticles is embedded in a host material.

How can the properties of an ensemble of nanoparticles be used for down-conversion?

Here we see the electronic band gap diagram of two nanoparticles.

The particles are at a very close distance from each other, in the order of a nanometer.

In one particle an electron is excited into the conduction band.

It appears that in such nanoparticle systems the quantized rest energy is not necessarily lost as heat to the lattice, but can be transferred as a quantized energy package to a neighboring quantum dot.

Here a second electron is excited into conduction band of the second quantum dot.

Now we have generated two electron-hole pairs out of one photon.

If other recombination loss mechanisms like Auger recombination and SRH recombination can be suppressed, these electron-hole pairs in both quantum dots can radiatively recombine.

It means they send out two red-ish photons.

As a result, one blue-ish photon is converted into two red-ish photons, which can be absorbed by a PV material.

Multiple exciton generation in an ensemble of quantum dots is quite similar.

Again, in one particle an electron is excited into the conduction band.

This quantized energy package is transferred to a neighboring quantum dot.

Here a second electron is excited into the conduction band of the second quantum dot.

If the charge carriers are separated and collected before they recombine, the result is that one photon is able to produce more than one collected electron.

Here you see some experimental results on down-conversion based on silicon quantum dots in a narrow spectral range from a paper of Jursberg et al.

The horizontal axis represents the photon emission wavelength.

At around 790 nm a down-conversion efficiency of 60% is achieved.

Here we see the results out of paper of Semonin demonstrating that EQE above 100% can be achieved.

The absorber layer contains PbSe quantum dots and in the blue region, from 3.1 up to 3.4 eV, the quantum dots realize an EQE above 100%.

The challenge is to move this spectral response to lower photon energies as the solar spectrum contains far more photons in this spectral range.

Spectral up-conversion is the process in which two or more low energetic photons excite electrons many steps from the ground state up to higher excited states.

If the electrons occupy the higher excited states they can fall directly back to the ground state by sending out higher energetic photons.

As a result many low energetic photons result in one high energetic photon.

This photon can be absorbed in the PV active material.

So many low energetic photons can excite charge carriers as well.

Studies have been performed on materials containing rare-Earth ions, like erbium.

They can pump up electrons by infrared photons to an excited level, which emits in the visible light.

However, the problem is that these systems have low efficiencies and only have a response in a very narrow spectral range.

Next we look at the intermediate band solar cell.

This concept tries to tackle the problem that each charge carrier only has a single population state.

Here we see a semiconductor material with valence band and conduction band.

An intermediate band material contains a narrow electronic band in the band gap as well.

Such structure is believed to increase the spectral utilization.

The high energetic photons can excite an electron from the valence band into the conduction band, just like in a normal semiconductor material.

The difference is, that photons below the band gap can excite an electron from the valence band into the intermediate band.

A second photon is required to excite the electron from the intermediate band into the conduction band.

Various ideas exist how these charge carriers are excited, transported and collected in those devices.

I won't go into detail, but in this slide you see some of the ideas.

Most important is that the photons below the band gap also result in an excited charge carrier.

In addition, the two photons with energy smaller than the band gap can effectively result in quasi-Fermi level splittings larger than the energy of one of the low energetic photons.

The last concept we will discuss is the hot carrier solar cell.

It basically improves the band gap energy utilization.

Here we see the light-excited charge carriers in a semiconductor material.

The population of the charge carrier levels reflects the situation just after the excitation by the absorption of a photon.

This distribution is not in thermal equilibrium.

The electrons are excited into a position higher in the conduction band.

The holes are excited down to a lower level in the valence band.

Such charge carriers are called hot electrons and hot holes.

It takes only a few picoseconds for the hot charge carriers to relax back to the edges of the electronic bands.

A hot carrier solar cell is based on the collection of charge carriers when they are still hot.

It means that the energy larger than the band gap energy could be utilized per excited charge carrier.

The fundamental challenge is to collect the hot carriers before they relax back to the edge of the electronic bands.

Such a concept would require selective contacts.

These are contacts which only select electrons above a particular energy level in the conduction band and contacts that selectively collect holes below a certain energy level in the valence band.

In theory, the band gap utilization could be higher than the band gap itself.

At the moment the main challenge is to increase the lifetime of the hot charge carriers, such that they have the time to move from the absorber layer to the selective contacts.

With the third generation PV concepts we finish our introduction into the various PV technologies.

Now we are going to focus on harvesting the heat out of the solar light.

In the next block we will discuss solar thermal technology.

See you in the next block.