

## 8.3 Making Thin Film Solar Cells

### 8.3.1 Types of Thin Film Solar Cells

#### General Remarks

The **bulk-Si solar cell** was called "**bulk**" because its thickness of  $> 200 \mu\text{m}$  is far larger than the thickness of the space charge region in the necessary junction.

There are two reasons why we make these bulk-**Si** solar cells:

1. Infrared and even red light may penetrate **Si** to a depth of many  $\mu\text{m}$ . In fact, **Si** membranes with a thickness of just a few  $\mu\text{m}$  are somewhat transparent even in visible light as shown. If we want to absorb as much light as possible we must use "bulk" **Si**.
2. If we use a thickness of  $> 200 \mu\text{m}$ , the solar cell is self-supporting (even so it breaks easily) and we do not need a substrate.

The catch is that we need a lot of expensive Silicon.

**Class Exercise:** *How much area in  $\text{m}^2$  and how many kg of **Si** do you need for a 1 GW power plant. Assume an efficiency  $\lambda=15\%$  and that the average power delivered is 12 % of peak power.*

This gives us some (connected) major conditions for making **thin film solar cells**.

1. The semiconductor should have a suitable direct band gap  $E_g \approx 1.5 \text{ eV}$  since this ensures high absorption coefficients for all light with  $h\nu > E_g$  and high efficiencies.
2. There must be a process-compatible and cheap substrate on which we can deposit the thin layers.
3. Since perfect single crystalline layers are impossible under the circumstances, "defects" in the layer and its interfaces must be harmless with respect to recombination.
4. There must be some efficient (and cheap) way to produce a junction and decent ohmic contacts.

Those are tough requirements. While some (which ones?) are valid for *all* solar cells, they might be considered very special for a given thin film system.

We certainly have enough semiconductors to choose from - remember this [link](#)? So far, however, only a few semiconductors have made it - in the sense that you can find them in the form of solar modules on roofs. A few more can be found in laboratories, but all in all the list is rather short.

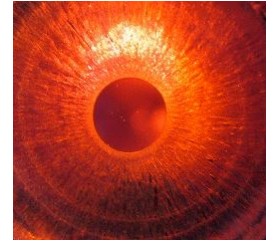
Major **thin film** solar cells belong to one of the groups given below:

1. Amorphous **Si**.
2. Nanocrystalline thin film **Si**.
3. Polycrystalline thin film **Si**.
4. The **CuIn<sub>x</sub>Ga<sub>1-x</sub>Se<sub>2</sub>** or "**CIGS**" family.
5. The **CdTe** solar cell.
6. The **TiO<sub>2</sub>** - dye based family.
7. Multi-layer based **tandem cells** or multi-junction cells.
8. Exotica.

If you feel that points **1 - 8** could be seen as the table of contents for a complete lecture course - you are right. Indeed, there would be a lot of ground to cover if we just were to look at the basic research, development and - where already applicable - production of the thin film solar cells enumerated above. To give just one example of the complexity encountered:

Why is "**CIGS**" better than just "**CIS**" (=CuInGaSe<sub>2</sub>)? Why are traces of **Na** important for making good **CIGS** solar cells? Why is **Mo** the best metal for the backside contact? Will there be enough **In** available for making **CIGS** cells in a big way? Why are properly made **CIGS** solar cells quite immune to radiation (as encountered by satellites in space)? Why are the recombination properties of the **CIGS** layer rather insensitive to its production method (sputtering, **CVD** in many variants, galvanic deposition, sintering, ...; everything seems to work)? What are the major limits to the efficiency? How stable is the combination of the many materials found in a **CIGS** cell over decades?

All we can do here is to give a short summary of what is meant with the catch words in the list, and to look at a few essentials of production methods for thin film solar cells in the next sub-chapter. In time, advanced modules may spring into existence with additional information to each type of thin film solar cell.



Backlit polycrystalline **Si** with a thickness around  $5 \mu\text{m}$  shows some transparency in the red.

## Amorphous Si Solar Cells

Amorphous **Si** or **a-Si** solar cells are almost as old as crystalline (or **c-Si**) solar cells. It is rather easy to produce thin film amorphous **Si** - just sputter from a **Si** target, or use **Si-CVD** at temperature  $< \approx 400 \text{ }^\circ\text{C}$ . A layer thickness of  $1 \text{ } \mu\text{m}$  or less is enough to absorb all light and thus we are truly talking "thin film" here.

However, pure amorphous **Si** is a good insulator and rather useless because it contains by necessity many "**dangling bonds**" that introduce electronic states in the band gap in a high density. Only if we "**passivate**" these dangling bonds with **hydrogen (H)** do we become a halfway decent semiconductor that behaves like a *direct* semiconductor with a band gap of about **1.7 eV**.

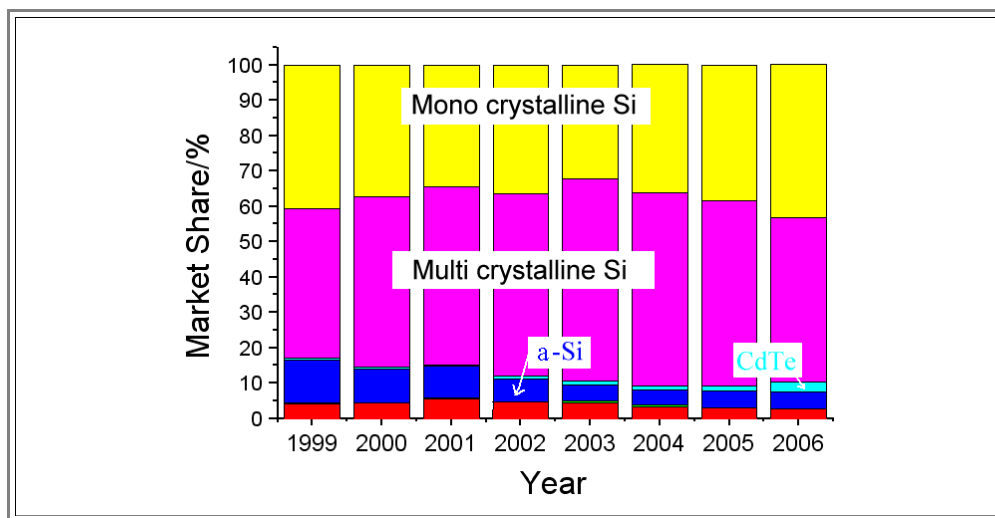
Now we have the first mystery about "amorphous **Si**". While the density of dangling bonds is large but still well below **1 %** of all bonds, we need to put **5 % - 30 %** hydrogen into the material to achieve decent semiconducting properties, i.e. far more than we would need for just compensating the dangling bonds. In fact, what all and sundry calls "amorphous **Si**" is actually an amorphous **Si-hydride**; the abbreviation **a-Si:H** is often used.

**Eschewing** these "details", we are left with a material that behaves in many respects roughly like **Si**, can be doped **n**-type and **p**-type, comes relatively cheap, and can be handled to a large extent by existing **Si** technology. It also can be deposited on large-area substrates.

We thus can produce solar cells, e.g. on a glass substrate. Contacts are a problem, but neglecting that for a moment, **a-Si:H** solar cells have been plagued from the very beginning by some specific problems that have not gone away even after decades of **R&D**:

- The efficiency  $\eta$  is rather low ( $< \approx 10 \%$  to give a number) for various reasons, and not easily (=cheaply) raised. For serious power application this is bad - being cheap at some point does no longer compensate for low efficiencies.
- **a-Si:H** solar cells are prone to show the so-called **Staebler-Wronski effect**, i.e. their efficiency  $\eta$  degrades by up to **30 %** if the solar cell is exposed to light for some time!
- The efficiency recovers upon heating the solar cell, but that is of little use. What exactly causes the Staebler-Wronski effect is a matter that has been intensively investigated for **> 20** years, but the final word is not yet in.

Nevertheless, **a-Si:H** solar cells do have a noticeable market share as shown below:



Note that a *constant* market share still means substantial growth in absolute numbers if there is substantial market *growth* - which we do have! Also note that beside **a-Si:H** solar cells, and lately **CdTe** solar cells, all other thin film cells hold only a miniscule market share (**CIGS** cells are shown in green; the red part denotes "**RGS**" - ribbon growth on substrate, a variant of **Si** solar cell technology).

You probably own **a-Si:H** solar cells - in your pocket calculator, your watch, or in other small electronic devices where the efficiency (and durability) is not critical, but size, weight, price and easy production compatibility are important.

While there are also some large scale applications, it is not clear at present if **a-Si:H** solar cells will play a big role in the future.

## Nanocrystalline Thin Film Si Solar Cell

While nowadays everything either just small or complex goes as "nano this-or-that", solar cells made from truly nanocrystalline thin film **Si** is actually called "**micro-crystalline Si**" or **μc-Si:H** in most publications.

- Be that as it may, the fact is that it became clear some **6** years ago that thin layers of **Si** that actually consist of **Si** nanocrystals (diameters in the **10 nm** region) embedded in a **α-Si:H** matrix (still containing plenty of hydrogen), if made exactly right, could be used to make solar cells with efficiencies of up to **14 %** and with practically no Staebler-Wronski effect.
- That gave a big boost to the many researchers engaged with **a-Si:H** solar cells since it offered a new outlook to the future of these solar cells.
- What exactly makes the **μc-Si:H** thin films so much better than just **a-Si:H**, and how far this can be carried, is not all that clear at present.

To the best of my knowledge, there are no nanocrystalline thin film **Si** solar cells up on roofs in a major way at present. If this kind of thin film solar cell will make it into large scale production, is an open question at present, but it is seen as a major future contender for the presently firmly entrenched bulk **Si** solar cell.

## Multi-crystalline "Thin" Film Si Solar Cell

Make a bulk **mc-Si** solar cell with just about **(2 - 5) μm** thick multi-crystalline **Si**. It will not absorb all the light, so add a "mirror" at the back and other measures to keep the light inside the **Si**.

- This would work quite well - except that you can neither make **5 μm** thin slices, nor handle them without fracturing them rather quickly.
- So put your **5 μm**, or even just **2 μm**, of large-grained or "multi-crystalline (**mc**)**Si**" on a mechanically (and thermally) stable substrate. This is the concept of the "**thin film Si**" solar cell as it is usually called.

There is no uncertainty about possible high efficiencies, long life times without degradation, etc. - it's good old and well-known **Si** technology after all. The problem, alluded to many times by now is: money.

- In other words, you are competing against good, old, and well-known bulk **Si** technologies - and you must be just as good and considerably cheaper before you are being noticed. So you must solve the following problems:
  - Deposit rather thick layers of rather good **Si** (pure, large-grained, ...) **quickly** (at least **1 m<sup>2</sup>/min**). Normal **Si CVD** processes are not that fast, and tend to produce small-grained films.
  - Find a cheap and process-compatible substrate.
  - Think about the temperature budget. While the **Si** part would be easier at high temperatures (deposition rates go up, grains grow larger, ...), you better stay at low temperatures all the time - or you will be very restricted in the choice of your substrate (heating also costs money).
  - What about the backside contact if that cannot be your substrate (because you picked glass)?
  - And what about the backside "mirror"?
  - And so on and so forth.
- Impressive progress has been made with the thin film **Si** solar cell. If it will become competitive in the near future remains to be seen.

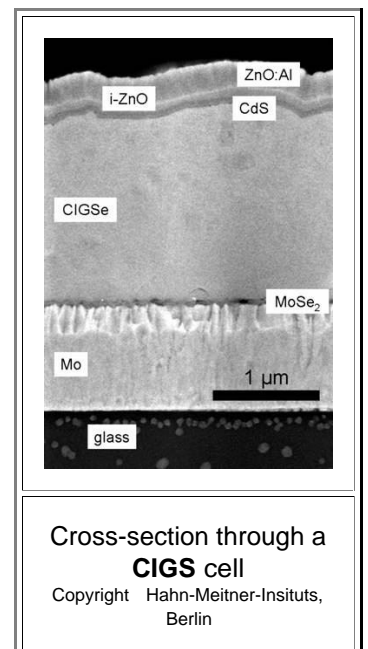
## The CIGS Solar Cell

Solar cells from the **CIGS** family have an "old" history - it goes back more than **20** years to the times around the first oil crisis (**1975**), when semiconductors of the metal1-metal2-chalcogenide family were studied with some effort..

- One of the first promising materials contained mercury (**Hg**), and since mercury acquired a really bad name in those days, there were reservations about these materials, too. This might be about as smart as having reservations about **NaCl** because both **Na** and **Cl** do belong to the terrorist group in the periodic table.
- Anyway, with lots of research it became clear that the "**CIGS**" family showed real promise. Serious production started around **2005**, and by now the first [large factories](#) are up and running.

Some topics around **CIGS** solar cells have already been [raised above](#). Here we note that having an (always **p**-doped) **CIGS** layer of about **(1 - 2) μm** in thickness is not enough, we also need a **pn**-junction and (low resistivity) contacts.

- The **pn**-junction is actually a **hetero junction**; the **n**-part is supplied by a very thin layer of **CdS** and intrinsic (=high resistivity) **ZnO**. The backside metal is **Mo**, possibly reacting with the **CIGS** upon deposition to a thin intermediate layer of **MoSe<sub>2</sub>** as shown above.



- Heavily **p**-doped (with **Al**) **ZnO** forms the transparent contact layer on top. The not-so-great resistivity of the top layers causes problems that will be dealt with in the [next sub-chapter](#). Just take it for granted at that point that the simple technique of [screen printing](#) some metal contacts, as known from bulk **Si** solar cells, does not work here.

Anyway, after many years of **R&D**, we have almost **20 %** efficiency **CIGS** cells in the laboratory and around **13 %** in mass production.

- Also, after many years of **R&D**, we still have some "**black art**" involved in making **CIGS** solar cells. In the words of the Hahn-Meitner-Institut in Berlin, one of the leading **CIGS R&D** places:

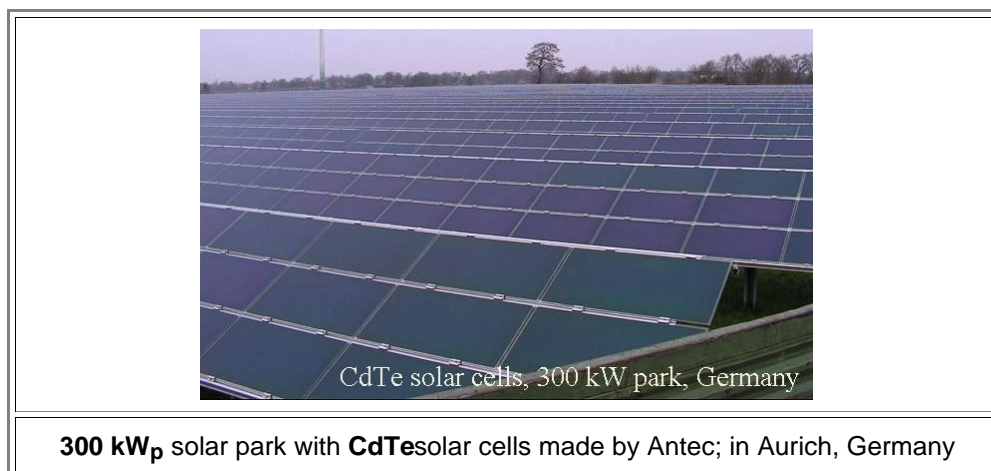
*"Despite the large CIGS progress made in the last 10 years, the material science (of CIGS) is still behind that of established semiconductors like, e.g., Si. Progress in increasing the efficiency by semi-empirical optimization of the physical and chemical processing steps was essential for success. In other words: 'It worked first and was explained later'"*

Since **CIGS** solar cells have the potential for good efficiencies around **20 %** and could be potentially cheap, they are seen as the major competitor to the **Si** bulk cell right now. Time will tell.

## The CdTe Solar Cell

● **CdTe** solar cells have a bad image right now (around **2007**) because they use **Cd**, one of the more *despicable* elements in present mythology (possibly belonging to the terrorist group of the periodic table).

- However, **CdTe** solar cells are relatively easy to make, not too bad, and rather cheap. The real problem comes from the fact that all of the solar cell industry must consider how to recycle their products eventually - and that might be not so cheap with **Cd** containing waste.
- Beside image problems, a real problem might be that the efficiency of **CdTe** solar cells might be limited to values not competitive in future markets. There are, however, already large-scale installations as shown below. Again, time shall tell if **CdTe** solar cells are here to stay.

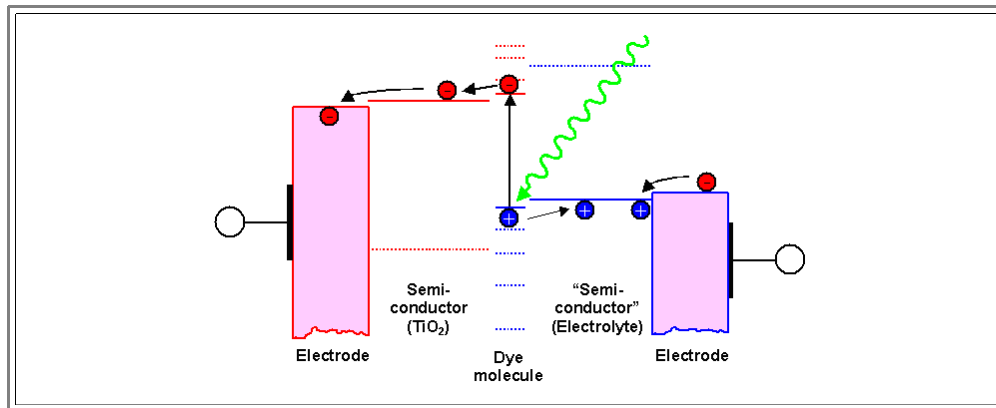


● **Feb. 2010:** Time did tell. First Solar, making exclusively **CdTe** solar cells, is now the biggest solar cell company on the planet.

- Thin film **CdTe** solar cells enjoyed a tremendous success story in just a few years. The concern now is rather if there is enough **Te** around to allow many **GW** of installations.

## The TiO<sub>2</sub> - Dye Based Family

The basic idea behind this solar cell concept is best illustrated in a schematic band diagram



- We use an optimized **dye** molecule that absorbs light extremely efficiently, and in doing so kicks an electron up from the **highest occupied molecular orbital (HOMO-level)**; shown as solid blue line) to the **lowest unoccupied molecular orbital (LUMO-level)**. In semiconductor terms an electron-hole pair is generated; in more general terms we have an exciton (=electron-hole pair at close range, feeling some interaction).
- The trick is to separate the two carriers. If we find suitable semiconductors that have their conduction band just right below the **LUMO** level (so the electron can jump over with some energy gain) or their valence band right above the **HOMO** level (so the hole can jump over with some energy gain), respectively, and some metal electrodes with suitable Fermi levels - we have a solar cell.
- Well, not quite, because at least one side needs to be transparent to light. In this case it will be the hole side, where Indium-Tin-Oxide commonly known as "**ITO**" works well enough. On the electron side we can use **TiO<sub>2</sub>** and some metal with a lot of advantages as we will see.
- The problem is the blue "hole" semiconductor. It must also be transparent to light - and presently there is no good candidate. The so-called "**Graetzel**" cell, the paradigm of this kind of cell, therefore uses a "redox" **electrolyte** that can transport the electrons from right to left (akin to transporting a hole from left to right) at the proper energy levels.
  - The big advantage of the **Graetzel** cell (and its many variants) is that the **TiO<sub>2</sub>** + dye side is very simple and dirt cheap: Take **TiO<sub>2</sub>** nanoparticles, sinter them lightly onto a metal substrate, and coat the resulting nano-sponge with the dye. **TiO<sub>2</sub>** nanoparticles dispersed in some solvent, in case you don't know, is what you buy as "white paint" in building supply stores - it is truly cheap.
  - The dye might be a problem, but organic chemistry will solve it for you. It may not be dirt cheap but you only need tiny amounts.
- The real problem, of course, is the electrolyte side, in particular if it is supposed to work for **> 20** years without a problem.
  - The Graetzel cell holds a lot of attraction for many **R&D** oriented people and organisations. It doesn't require expensive semiconductor equipment to start experiments, and it offers a chance for researchers from various disciplines other than semiconductor materials science to try their hand at solar energy. It is therefore small wonder that some "Graetzel cell" concept has been touted as the solution to the problems plaguing solar energy every few years since the eighties.
  - However, the few efforts at large-area semi-commercial Graetzel cells invariably did not result in industrial production. One problem is that efficiencies are well below **10 %** at present - and that is just not good enough. Another problem is the required massive series connection, which is just not that easy if liquids are involved.
  - Nevertheless, given the large number of researchers and institutions working on some variant of this cell concept, the final word is: Time will tell.



## Tandem or Multi Junction Cells

It was emphasized many times that with a given band gap the efficiency of a solar cell is limited, and that the "best" bandgap for sunlight would be about **1.5 eV**, giving a maximum efficiency of about **30 %**.

- How about using solar cells made from semiconductors with different bandgaps, stacked on top of each other? The first one, facing the light should have a wide bandgap, taking out just the ultraviolet part of the spectrum. It will generate a relatively high voltage and some current.
- Below the first layer then sits a medium bandgap solar cell, responding, let's say, to yellow and beyond. It would generate a medium voltage and some current.
- Finally, in the **triple junction** solar cell we are generating, we have a small bandgap semiconductor absorbing the left-over red and infrared radiation; generating a small voltage and some current.

We see the first problem of our **high-efficiency multi-junction** solar cell: we need **current matching**! The current generated in the individual cells must flow through all three cells since they are switched in series. If the three cells do not generate the same amount of current, we will have problems.

- **Current matching** can be achieved if the thickness of the individual layers, the bandgaps, and so on, are matched to the solar spectrum. Tedious, but possible.

**Class Exercise:** *What would happen if there is no current matching? It is sufficient to consider a tandem cell with two junctions.*

- If we made sure that we have current matching, the individual cell voltages will add up and we may have an efficiency exceeding the maximal **30 %** for single junction cells. For example, with **Ge** as the "bottom cell", and plenty of other cells on top ( $\infty$  many with incrementally increasing bandgap for "easy" theory), the theoretical limit is **> 50 %**.

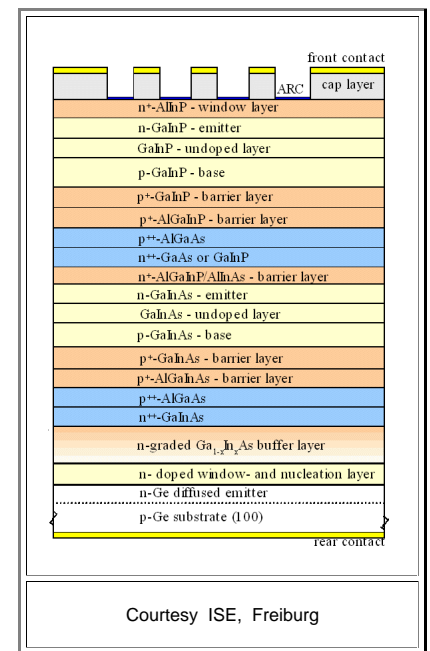
However, besides current matching, we must solve another problem. If we pile many different semiconductors on top of each other, the interfaces should better be "good" in the sense of not recombining carriers. In other words: no **misfit dislocations**.

- That narrows down the possible combinations but we still can do quite a bit - as shown in the figure. The band gap goes up in steps from the **0.66 eV** of **Ge** to about **1.8 eV** of the **GaInP**.
- The misfit is kept small, and experimental efficiencies in excess of **40 %** have been obtained

The catch is obvious: Multi-junction solar cells will not come very cheaply! There is no way to make **m<sup>2</sup>** of this structure in an inexpensive and fast way. This leaves two escape routes:

1. Make far simpler structures - e.g. a simple variant of a tandem cell, e.g. by just using **a-Si:H** on top of **a-Si/Ge:H**. Instead of using amorphous **p-Si** as absorber, alloy some **Ge** into this layer, lowering the band gap. On top put regular **n-type** amorphous **Si** with a larger band gap. This will not give you "high efficiency", but possibly more than just a simple **a-Si:H** solar cell. Or use **n-type a-Si:H** with its relatively wide band gap on top of crystalline bulk **p-type Si**. Or --- you get the idea.
2. Make the best multi-junction solar cell you can, and put it in the focus of some parabolic mirror, or any other cheap focussing device like Fresnel lenses. In other words, concentrate the sun light collected from a large area on a small area solar cell - which then can be expensive. This is the principle of the **concentrator solar cell** with the obvious catch that it will only work in direct sun light (i.e. not in my home state of Schleswig-Holstein, where we might not see the sun for weeks on end) **and and** if some mechanical contraption follows the sun.

There is definitely a market for concentrator cells; how large it is remains to be seen.



## Exotica

- ▶ Even the most stupid American (G.W. Bush?) realized by now (2007) that it is time to worry about the climate *and* about the finite resources of cheap energy carriers like oil. This means that the **USA** are just now (re)discovering solar energy. Since they almost completely missed the big economical boom of solar energy after the year **2000**, they are lacking behind in solar cell production but have now taking the lead in solar cell *hyperbole*.
  - Check the Internet. Tip: Start with "nanosolar". You will find all kinds of new concepts for making cheap and very good solar cells. However, as the saying goes: "the proof of the pudding is in the eating" - or time will tell.
- ▶ There are, however, many more serious "exotic" solar cells concepts in the sense that they are either considered or actually used for very special applications (like supplying power to satellites), or objects of intensive **R&D**.
  - In the first category we have all kinds of **GaAs** based solar cells - optimal band gap for best efficiencies of single junction cells; used whenever price doesn't matter (in space).
- ▶ In the second category we have, for example, solar cells based on **organic semiconductors**.
  - Light emitting diodes (electric power in; light out) made from organic semiconductors are already on the market; so the inverse device (Light in; electric power out=solar cell) should be possible too as seen from a somewhat naive point of view.
  - Yes, organic solar cells are possible. Right now, however, they are subject to a host of problems. If those problems could be solved, leading to a potentially extremely cheap technology ("paint on your solar cell"), only time will tell.

## Famous Last Words

- ▶ In the text above, we have a lot of "*remains to be seen*" or "*time will tell*". This is true enough - provided somebody does the work required.
  - This somebody will have to be someone like *you!* The matter is complex, transcending the ken of classical physicists or chemists. It is right at the heart of Materials Science and Engineering.