"Silicon Solar Cells"

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1 Introduction

The energy consumption in the world today has reached $4.4 \cdot 10^{20}$ J and is still getting higher due to increasing standard of living and world population [1]. The major contributors to the population growth are the developing countries. Taking into account that the economic growth also is strongest in these regions, the future energy demand is expected to be considerable.

The energy consumption in the world today mainly relies on fossil energy, which cover about 80 % of the energy demand. Only about 13 % comes from renewable energy sources [1]. If we consider the fact that fossil fuels are major contributors to air pollution and global heating, and also the limited amount of fossil fuels available, it is clear that other options to energy supply have to be investigated for the future.

One source of energy is the electromagnetic waves from the sun. The sun supply the earth with $1.2 \cdot 10^{17}$ W, which is enough to cover the yearly energy demand for human activities in less than an hour [2]. One way of exploiting this energy is through solar cells. Solar cells convert the energy of light into electrical energy using the photovoltaic effect.

There are several advantages connected to solar cells compared to other means of electric energy production. Solar cells do not have any emission of pollutants. They are quiet and there is no need for power lines, since the energy can be produced where it is needed. This fact makes solar cells a good option for supply of electric energy in areas without power lines, like in developing countries, at a cabin or in space. The downside is that commercial solar cells convert the solar energy with only about 15 % efficiency. In addition the production of solar cells is both costly and time consuming. A lot of research is being done to improve these things in order to make solar cells economically competitive with other means of electric energy production.

The basis for all solar cells is a semi conducting material, and silicon is the semiconductor most frequently used for solar cell applications. This it due to the fact that silicon has an almost optimal band gap and because of the practically endless supply of silicon. In addition the technology for producing pure silicon and silicon crystals is well developed.

In this paper we have tried to give an overview of the physical principles behind the "traditional" silicon solar cell, also known as first generation cell. This involves description of semiconductors, doping, pn-junctions and IV-characteristics. We have then taken a look at the most important reasons for efficiency losses in solar cells. Furthermore, a short description of standard processing of silicon solar cells is given, with the main focus on the doping processes. The last chapter gives a taste of next generation cells.

2   Silicon

2.1   Why silicon is a semiconductor

In order to understand why silicon has the properties of a semiconductor, one needs to understand how electrons arrange in a material with a given crystal structure. The first step is to simplify the crystal-lattice-model by assuming that the atoms and their belonging electrons don't interact. Furthermore, looking at the electrons separately, one can say that they are all exposed to a periodic potential as shown in figure 1;

$$V(x + a) = V(x) \tag{1}$$

where **a** is the lattice-constant in the given material. The area of size **a**, can then be designated to be a unit cell.
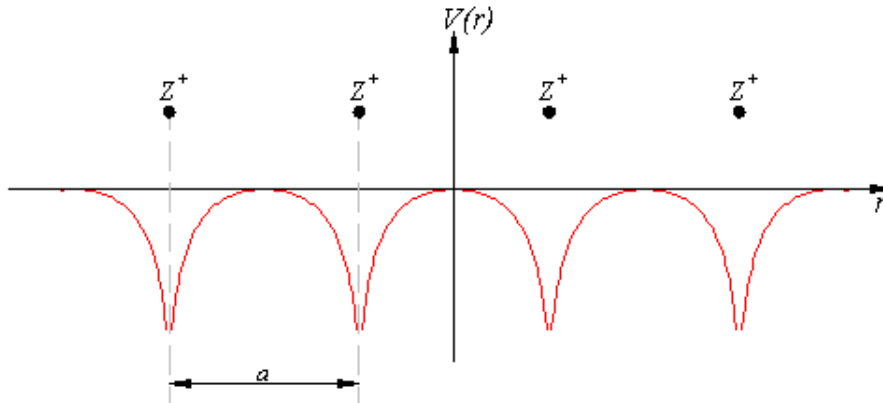

Figure 1: Periodic potential with lattice constant a

Because the potential is periodic, the same must be accounted for the physical state of the electron. Its quantum-state must then fulfill;

$$|\Psi(x + a)|^2 = |\Psi(x)|^2 \tag{2}$$

where $\Psi(x)$ is the eigenfunction of an electron.

If the Schrödinger-equation is solved for a periodic potential, one will end up with equations of states and their belonging energy eigenvalues which turns out to distribute in a special way. The spectrum of the energies is continuous piece by piece. That means, with alternating energy bands and gaps. The energies in the gaps don't fulfill the Schrödinger-equation, and can therefore not be allocated by the electrons.

In the ground states at T=0 K, the electrons will prefer a configuration which leads to a minimum total energy in the material. This means that they will start to fill the energy bands in the lowest part of the spectrum, and will do so until all have found their respective positions.

The upper band which is totally or partly filled, is called the valence band. The electrons located here connect the atoms and hold them together. The band above is called the conduction band, and can be filled by electrons which have managed to tear themselves away from their valence positions. This makes the material conducting and able to transport electricity and thermal energy.

The size of the gap between the valence- and conduction band is what actually separates the metals from insulators and semiconductors. For the ground state of an insulator the gap is relatively large, and a large amount of energy(more than $\approx 3eV$) is needed to excite an electron to the conduction band. In a semiconductor the gap is smaller, and thermal energies are sufficient for excitation. In metals on the other hand, one has overlapping valence- and conduction bands, something which makes them conducting in all cases. See figure 2.
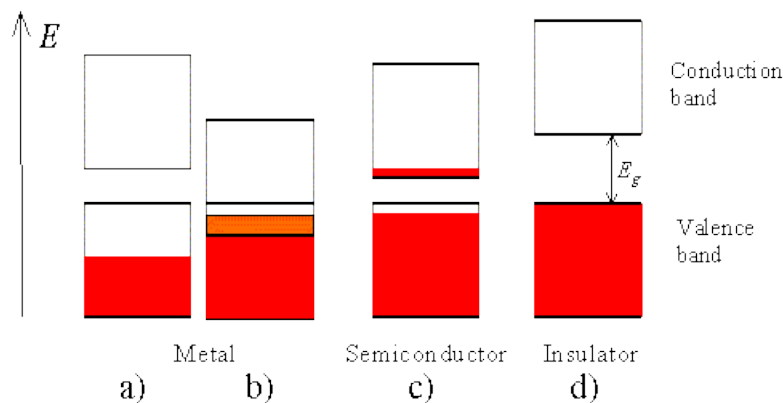

Figure 2: Valence- and conduction-bands in metals, semiconductors and insulators. The gap in-between the bands is what prevents conduction

In the model with a periodic potential, it turns out that each energy band contains N different spatial states, where N is the number of unit cells i the material structure. Because we are looking at electrons with spins of -1/2 and 1/2, the Pauli-principle says that each state can only hold two electrons. The total number of states will therefore be $2 \cdot N$. Furthermore, if each unit cell contains an even number of electrons, the number of filled energy bands will be;

$$\frac{N \cdot (\text{even number of electrons})}{2 \cdot N} = \text{an even number} \tag{3}$$

This means that all bands containing electrons will be totally filled, and the material will be a semiconductor or an insulator. On the other hand, if each unit cell has an

odd number of electrons, the number of filled energy bands will be;

$$\frac{N \cdot (\text{odd number of electrons})}{2 \cdot N} = \frac{\text{odd number}}{2} \tag{4}$$

In other words, the outer band is only half-filled, and we have got an overlap between the valence and conduction band. The material is then a metal.

2.2   Extrinsic silicon

Until now we have only looked at pure materials made up of one kind of atoms. By adding impurities to the original material, it is also possible to change the conducting ability of the structure. Looking at silicon, one knows that the four valence electrons will form covalent bonds creating a diamond lattice. If now small amounts of arsenic is added, which is located in group 15 in the periodic table, only four of its five valence electrons will be able to bond covalently to silicon. The one which is left over is more loosely bound, and makes the new material about 1000 times more conducting than the original, intrinsic one. A material of such excess electrons are said to be of "n-type".

Also atoms from group 13, e.g gallium with only three valence electrons, can be added to silicon. The situation now is that we are missing one electron per gallium atom for the octet rule to be fulfilled. The "holes" can be thought of having the same functions as a positive charge because it can be filled by electrons. This causes a current-direction opposite to the one caused by electrons. Materials with this kind of doping, is said to be of "p-type".

2.3   The pn-junction

What is really interesting, and being an essential part in solar cells, is what happens when extrinsic semiconductiors of n- and p-type are joined together in on piece. The loosely bound electrons in the n-type will diffuse into the holes in the p-type area and create a diffusion current, I_r. An area free from excess charge carriers is created; a junction which is called "the depletion zone". One side of the junction will be slightly negative and the other slightly positive, resulting in an electric field which in silicon is approximately 0.6 V. See figure 3. What is created is paractically a semiconductor diode.
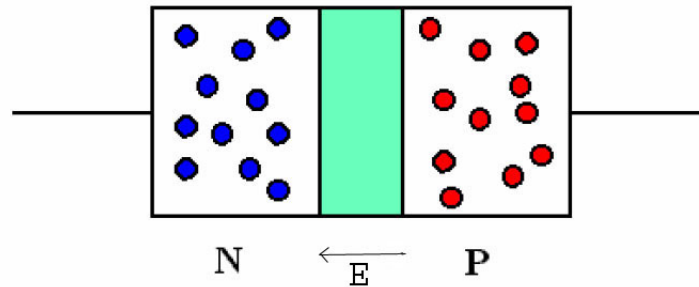
Figure 3: Junction between n- and p-type semiconductor. Blue dots indicate electrons, red dots indicate holes. The green area in-between is the depletion zone with the electric field

The electric field will try to counteract the diffusion process, creating a barrier at the pn-junction. The size of the barrier has of course a direct impact on the diffusion current I_r. In addition to I_r, there will also excist a certain current resulting from minority carriers. These carriers are created when electrons are thermally exited to the conduction band, on the p- and n-side respectively. If not recombined, they will diffuse to the depletion zone and be swept rapidly over to the other side of the junction. This current; I_g, is called the "drift current" and is temperature-dependent. In an open circut one has no net current through the depletion zone, something which means that $I_r = I_g$ has to be fullfilled.

Biased pn-junction

When an external potential V_y is connected to the pn-junction, with the positive pole at the n-side and negative pole at the p-side, the diode is said to be "reverse biased". What happends is that the potential on the n-side is lowered with V_y, leading to a increment of the difference between energy levels on the n- and p-side. See figure 4(a). Because the junction-barrier increases, the diffusion current will be reduced. It can be shown that the diffusion flux varies exponentially and is given by[3];

$$J_e^r \propto exp(qV_y/kT) \tag{5}$$

where q is the carrier charge, V_y is the external potential, k is Boltzman's constant and T is the temperature.

If now the poles connected to the p- and n-side are switched, the junction is said to be "forward biased". Because of the change in potential on each side (see figure 4(b)), the size of the depletion zone is reduced, leading to increasing diffusion current.

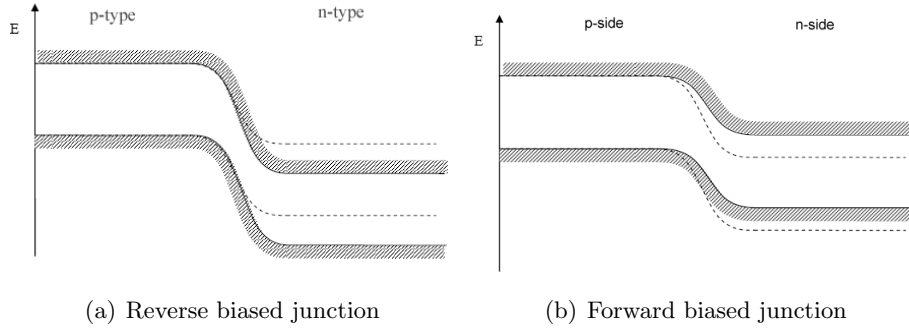(a) Reverse biased junction   (b) Forward biased junction

Figure 4: Band-structure with external potential. Dotted line indicates original structure[3]

To describe the total current, both the drift- and diffusion-current need to be included, resulting in (6);

$$I_{tot} = I_r - I_g \qquad (6)$$

The drift-current I_g is independent of the external potential, whereas the diffusion-current is given by (7).

$$I_r = I_r^0 e^{\frac{qV_y}{kT}} \qquad (7)$$

Making sure that I_{tot}=0 for V_y=0, gives $I_r^0 = I_g$, and the final expression for I_{tot} reads;

$$I_{tot} = I_s(e^{\frac{qV_y}{kT}} - 1) \qquad (8)$$

where $I_s = I_r^0$.

As shown in figure 5, for large negative potentials the total current approches a saturation current I_s. For solar cells it is important that this current is as small as possible to achieve a high power efficiency.
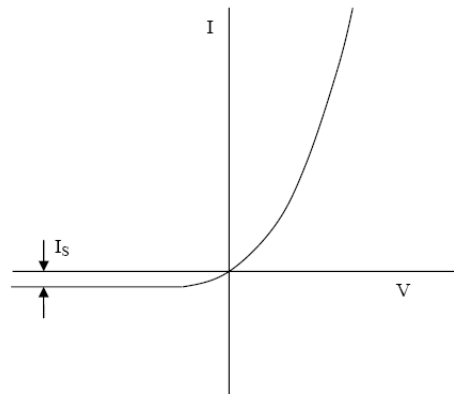
Figure 5: Total current in pn-junction as a function of external potential.[3]

2.4 Illuminated pn-junction

The functionality of solar cells is based on the process which is taking place when it is illuminated by light. If the incoming photons have enough energy, they may be able to excite an electron from the valence band to the conduction band. This creates an electron-hole pair, creating minority carriers on the p- or n-side. The minority charges are electrons on the p-side and holes on the n-side. If the pair-generation occurs in the depletion zone, or closer than one diffusion-length from it, the probability is high for creating a light-generated current I_L, directed opposite to the diffusion current, I_r. Like the drifting current I_g, I_L is independent of the bias V_y. Compared to figure 5, the total current vil be shiftet by I_L, as indicated in figure 6.
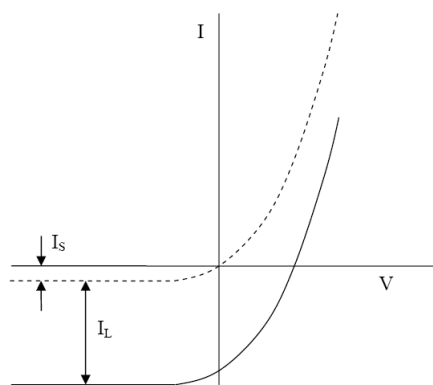

Figure 6: Current-shifting caused by illumination.[3]

It is more common though, to define the current in solar cells as positive, as shown in figure 7.

Figure 7: Positive current characterization.[3]
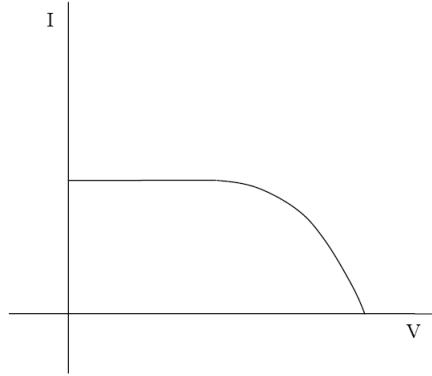
The total current is now characterized as follows;

$$I_{tot} = I_L - I_S(e^{\frac{qV}{kT}} - 1) \tag{9}$$

If the circuit is short-cutted, $V_y = 0$. From (9) this gives;

$$I_{tot} \equiv I_{SC} = I_L \tag{10}$$

For an open circuit, $I_{tot} = 0$, resulting in the following voltage characterization;

$$V_{open} = \frac{kT}{q} ln \left(\frac{I_L}{I_S} + 1 \right) \tag{11}$$

3 Efficiency limits

The power produced reaches its maximum when the product of I and V is maximum. This is indicated in Figure 8 below.
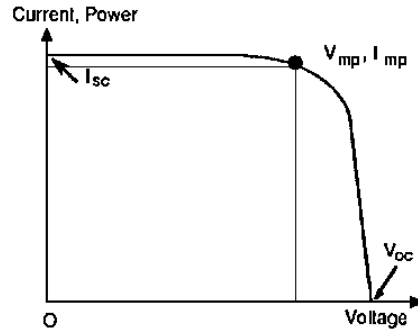

Figure 8: The I-V characteristic of a solar cell with the maximum power point [4].

The maximum power P_{max} is given as:

$$P_{max} = V_{mp}I_{mp} = \text{FF}V_{open}I_{SC} \tag{12}$$

where the short circuit current, I_{SC}, is simply the light generated current I_L, and V_{open} is the open circuit voltage. The fill factor FF is defined as:

$$\text{FF} = \frac{V_{mp}I_{mp}}{V_{open}I_{SC}} \tag{13}$$

and defines how 'square' the graph in Figure 8 is. FF is usually in the range 0.75 to 0.85 [5]. The performance of the solar cell is characterized by the tree factors FF, V_{open} and I_{SC}.

3.1 Different loss mechanisms

3.1.1 Short circuit current losses

There are four different types of losses in solar cells which contributes to a reduced short circuit current:

- Top-surface reflection

- Top contact shading

- Incomplete absorption

- Recombination of electrons and holes before they enter the outer circuit

3.1.2   Open circuit voltage losses

The fundamental loss mechanism that reduces the open circuit voltage V_{open} is recombination.

Figure 9 below shows how both the open circuit voltage losses and the short circuit current losses reduce the maximum power output for the solar cell.

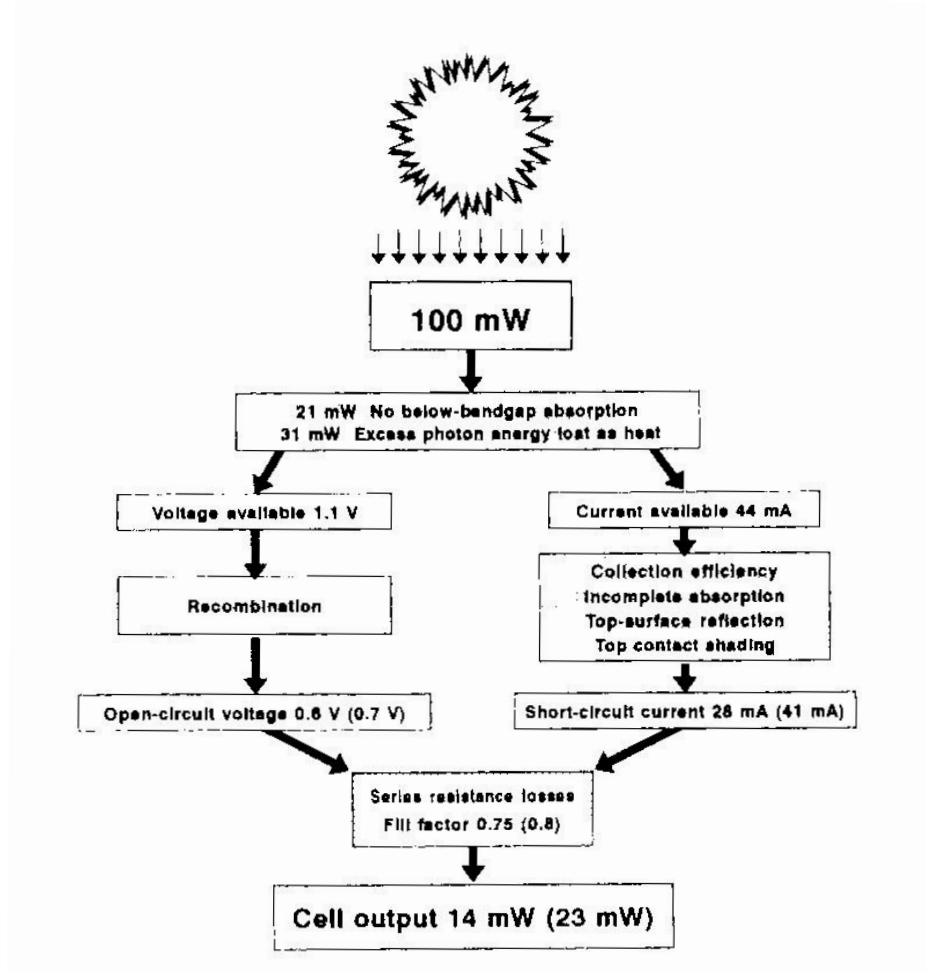Figure 9: The power losses in silicon solar cells. The figures are per square centimeter for production cells and (in brackets) for laboratory cells [2]

The different loss mechanisms are described below.

3.1.3   Top-surface reflection

As the light hits the solar cell a certain fraction of the incident photons, R, will be reflected and the rest is transmitted into the semiconductor. The transmitted photons

can be absorbed in the semiconductor by exciting electrons from low-energy states to higher-energy states if the photon energy is larger than the band gap. The index of refraction for an absorbing material can be written as $\hat{n}_c = \hat{n} - i\hat{k}$, where $\hat{k}$ is the extinction coefficient. If assuming normal incidence, the fraction of light that is reflected is given by [6] and [7] as

$$R = \frac{(\hat{n} - 1)^2 + \hat{k}^2}{(\hat{n} + 1)^2 + \hat{k}^2} \tag{14}$$

By inserting values for silicon it is found that over 30 % [8] of the light with appropriate wavelengths is reflected. With antireflection coating this reflection loss can be reduced to about 10 %.

3.1.4   Metal grid

It is necessary to make electrical contacts on both the p- and n-type regions of the solar cell. This results in a metal grid contact on the top-surface of the cell. This blocks for 5 to 15 % [8] of the incoming light.

3.1.5   Incomplete absorption

Direct band gap semiconductors are good light absorbers and they absorb all photons with energy higher than the band gap in a few micrometer thick layer. For indirect gap semiconductors, as silicon, absorption is not that efficient. The minimum energy in the conduction band and the maximum energy in the valence band occur at different values of crystal momentum. In order to conserve momentum it is required that lattice vibrations (phonons) must participate in the conversion of a photon into an electron-hole pair. Due to this the the probability of light being absorbed by this process is much less than in the direct band gap case. Hence the absorption coefficient is low and the light can pass a larger distance in the material without being absorbed. For silicon hundreds of micrometers are necessary to absorb all the above-bandgap photons [2].

3.1.6   Recombination

Electron-hole pairs are created when photons with high enough energy hit the solar cell. This increases the concentration of carries. However these carriers can loose their excess energy and the concentration of carriers then decreases. This recombination process can happen in different ways as described below. The net recombination rate is the sum of the different processes since they are independent of each other. In Figure 9 recombination loss is the same as the losses due to collection efficiency.

Radiative recombination

When an electron from the conduction band falls down to the valence band, the energy difference between the energy levels will be sent out as a photon. This process is only possible if there are both electrons and holes available. The total radiative recombination rate R_{rad} for this process is therefore proportional to the concentration of electrons in the conduction band and the concentration of holes in the valence band:

$$R_{rad} = C_{rad}np \tag{15}$$

where C_{rad} is a material dependent constant. When the light source is turned off the net recombination rate U_{rad} is given by the total recombination rate minus the equilibrium generation rate:

$$U_{rad} = C_{rad}\left(np - n_i^2\right) \tag{16}$$

In thermal equilibrium ($np = n_i^2$) the total radiative recombination rate R_{rad} is balanced by the generation rate. When it is assumed that $n = \Delta n$ and $p = N_A + \Delta n$, and that the equilibrium electron concentration in the conduction band, n_i, can be neglected, the expression for the radiative band-to-band recombination rate for a p-type semiconductor is given by:

$$U_{rad} = C_{rad}\Delta n \left(N_A + \Delta n\right) \tag{17}$$

where N_A is the density of acceptor dopants and Δn is the excess carrier density. Radiative recombination is a really important recombination process for direct-band-gap semiconductors, such as GaAs, but for Si (indirect-band-gap) other processes are much more important.

Auger recombination

Auger recombination occurs when the electron recombining with a hole gives away the excess energy to a second electron in the conduction band. This second electron then falls back to its original position and then gives away the additional energy as a phonon. This is referred to as eeh (electron-electron-hole) recombination. When the similar process occurs in the valence band it is referred to as ehh (electron-hole-hole) recombination. Figure 10 illustartes these two processes:

The net Auger recombination rate is given by:

$$U_A = (C_{p0}p + C_{n0}n)\left(np - n_i^2\right) \tag{18}$$

where n_i^2 is the intrinsic carrier density and C_{p0} and C_{n0} are the Auger recombination constants for the ehh and eeh processes respectively. In heavily doped material upon low injection (defined as $\Delta n \ll n_0 + p_0$, where n_0 and p_0 are the concentrations of electrons and holes in thermal equilibrium), the type of doping will determine which of these processes becoming the dominant one. In heavily doped p-type materials ehh will
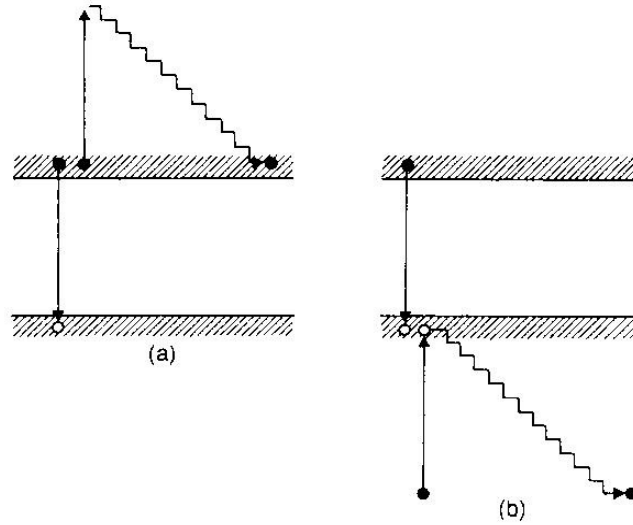
Figure 10: Auger recombination: (a) in the conduction band; (b) in the valence band [5]

be the dominant. For a heavily doped p-type semiconductor the Auger recombination rate at low injections then can be written as

$$U_{ehh} = C_{p0}\Delta n N_A^2 \tag{19}$$

where N_A is the acceptor doping level and Δn is the density of electrons injected to the conduction band. For heavily doped n-type semiconductors the Auger recombination rate, U_{eeh}, is found by changing N_A with the donor doping level N_D. At higher injection levels both processes has to be taken into account when calculating the Auger recombination rate. At $T = 300\,\text{K}$ the Auger recombination constants C_{p0} and C_{n0} are found to be $2.8 \cdot 10^{-31}$ cm^6/s and $9.9 \cdot 10^{-32}$ cm^6/s respectively [9].

Auger recombination is much more important in indirect than direct band gap materials, and is the dominant loss mechanism in very pure silicon and germanium.

Shockley Read Hall recombination
Impurities or crystallographic defects in silicon give rise to allowed energy levels in the otherwise forbidden gap. These levels are called traps and can capture both electrons and holes, causing carrier recombination if both of these processes occur. The different ways of capturing and emitting electrons and holes are shown in Figure 11.

It is usefull to define the electron and hole capture time constants, τ_{n0} and τ_{p0}, as:

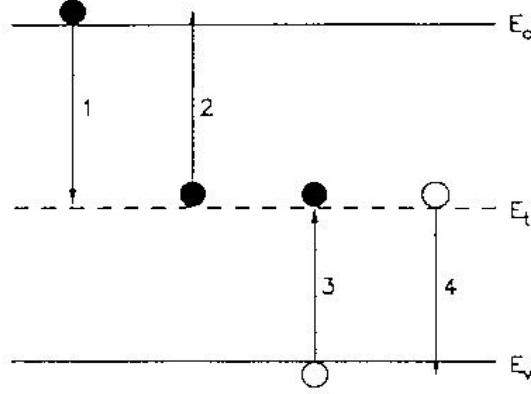$$\tau_{n0} = \frac{1}{N_t\sigma_n v_{th}} \tag{20}$$

Figure 11: Recombination through traps: (1) electron capture; (2) electron emission; (3) hole capture; (4) hole emission [5]

$$\tau_{p0} = \frac{1}{N_t \sigma_p v_{th}} \qquad (21)$$

where N_t is the density of traps, σ_n and σ_p is the capture cross section of the trap for electrons or holes respectively. v_{th} is the carrier thermal velocity. The rate for electrons in the conduction band falling down to an empty trap is then:

$$R_{nc} = \frac{n f_{tp}}{\tau_{n0}} \qquad (22)$$

where f_{tp} is the fraction unoccupied traps. Electrons captured in a trap can be released with the emission rate:

$$R_{ne} = \frac{n_t f_t}{\tau_{n0}} \qquad (23)$$

where $f_t = 1 - f_{tp}$ is the fraction of occupied traps and n_t is he electron density when the electron Fermi level is equal to the trap level.

This leads to the net capture rate for electrons:

$$U_{nc} = \left(n f_{tp} - n_t f_t \right) / \tau_{n0} \qquad (24)$$

Similarly the net capture rate for holes is given by:

$$U_{pc} = \left(p f_t - p_t t f_{tp} \right) / \tau_{p0} \qquad (25)$$

To obtain steady-state conditions it is required that the net capture rate for electrons must be equal to that of holes. Setting $U_{nc} = U_{pc}$ and solving for f_t gives:

$$f_t = \frac{B_n n - B_p p_t}{B_n \left(n + n_t \right) + B_p \left(p + p_t \right)} \qquad (26)$$

where $B_n = 1/\tau_{n0}N_t$ and $B_p = 1/\tau_{p0}N_t$. Inserting the values for f_{tp} and f_t into the net rate expressions finally gives the steady-state recombination rate for electrons and holes:

$$U_{SRH} = \frac{np - n_i^2}{\tau_{p0}(n + n_t) + \tau_{n0}(p + p_t)} \tag{27}$$

This expression for the recombination rate through traps was first derived by Shockley and Read [10], and independently by Hall [11]. This recombination process is therefore commonly referred to as Shockley-Read-Hall (SRH) recombination. Trapping levels lying near the middle of the band gap are the most effective recombination centers.

Surface Recombination
The SRH recombination rate (27) depends on varying carrier concentrations n and p, and on the number of traps N_t. A higher density of traps will shorten the time before electrons and holes are captured. At the surface of the material defects are likely to occur and this gives many allowed states in the forbidden energy gap. Recombination at the surface therefore happens very effectively by the SRH mechanism. The net recombination rate per unit area U_{surf} is given as:

$$U_{surf} = \frac{S_{n0}S_{p0}\left(n_s p_s - n_i^2\right)}{S_{n0}\left(n_s + n_t\right) + S_{p0}\left(p_s + p_t\right)} \tag{28}$$

where n_s and p_s are the electron and hole densities at the surface. S_{n0} and S_{p0} are the surface recombination velocities for electrons and holes given by:

$$S_{n0} = B_n N_s \tag{29}$$

$$S_{n0} = B_p N_s \tag{30}$$

N_s is the density of traps per unit area on the surface. As for the SRH recombination, trapping levels lying near the middle of the band gap are the most effective recombination centers.

3.1.7   Fill factor losses

Series resistance
The series resistance, R_s, consists of the bulk resistance of the semiconductor material making up the cell, the bulk resistance of the metallic contacts and interconnections, and the contact resistance between the metallic contacts and the semiconductor.
neline

Shunt resistance
The Shunt resistance, R_{sh}, is caused by leakage across the p-n junction around the

edge of the cell. During the diffusion of the n emitter, impurity particles can hinder diffusion at certain points. This gives to point defects in the p-n junction and leads to low parallel resistance.
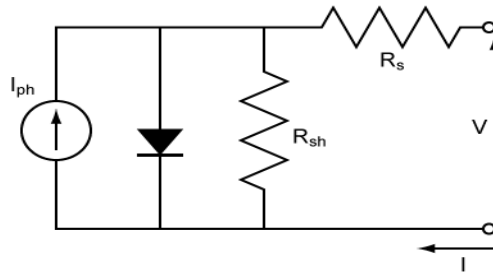

Figure 12: Equivalent circuit of a solar cell [12]

Both series resistance and shunt resistance reduces the fill factor. This is indicated in Figure 12 above.

Due to the different loss mechanisms described in this section, together with the fact that below-band gap photons are not absorbed and that the photon energy excessing the band gap is lost as heat, the efficiency of todays solar cells are about 23 %. The typical production silicon solar cell has an efficiency of about 14 %, but devices with efficiency approaching 18 % are beginning to appear on the market.

4   Processing

When the first solar cells were produced in the 1950s, they were mainly used in space technology. These were solar cells made from semiconductor grade silicon and single crystalline silicon solar cells. The efficiency of these cells is high, but so is the cost, so after the manufacturing of solar cells for terrestrial use started in the 1970s, there was a demanding wish to reduce the cost. Today the commercial silicon solar cells are made from something in between the metallurgical grade silicon (MG-Si) and the semiconductor grade silicon; the so-called solar-grade silicon. It contains about ten times more impurities than semiconductor grade silicon, but it still permits reasonably efficient cells. An additional reduction of the cost is made by using multi crystalline solar cells instead of mono crystalline solar cells. Today half of the solar cells are made from multi crystalline silicon wafers [2, p55].

The standard technology for processing solar cells can be divided into the following stages:

1. From sand to metallurgical grade silicon

2. Purification of the metallurgical grade silicon

3. Producing crystalline silicon wafers

4. From wafers to solar cells

5. From solar cells to solar cell modules

A short description of the different processing steps are given below. Step 3 and 4 involve doping of the wafers. Since the doping concentrations are of major importance for the efficiency of the solar cell, these steps are described in greater detail.

4.1   From Sand to Metallurgical Grade Silicon

As mentioned in the introduction, silicon is the major constituent of sand, which makes out about 60 % of the earth's crust. Silicon comes in the form of silicon dioxide, and the source for extraction of silicon is the crystalline from of SiO_2; quartzite. It is reduced to silicon in a large arc furnance together with carbon according to the reaction

$$SiO_2 + 2C \rightarrow Si + 2CO \tag{31}$$

The silicon is removed from the furnace and further purified by blowing it with oxygen/chlorine. At the end the molten silicon is poured into shallow troughs where it is solidified and broken into chunks. The MG-Si has a purity of 98 to 99 % where aluminum and iron are the two major impurities. This process is neither very energy consuming nor costly.

4.2   Purification of the Metallurgical Grade Silicon

The silicon has to be further purified in order to be used for solar cells. The Siemens-process is the standard approach for doing this. With the presence of a Cu catalyst, MG-Si is transformed into a fluid according to the reaction

$$Si + 3HCl \rightarrow SiHCl_3 + H_2 \qquad (32)$$

The fluid is run through a condenser and the desired purity is reached by multiple distillations

$$SiHCl_3 + H_2 \rightarrow Si + 3HCl \qquad (33)$$
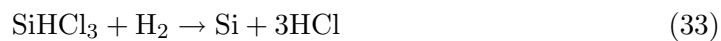
The resulting semiconductor grade silicon is a solid material with a silicon concentration of 99,99999 % [2]. The Siemens process is highly energy consuming with a low yield (37 %), and this processing step is therefore a prime target for improvement.

4.3   Producing crystalline silicon wafers

The silicon produced from the Siemens-process consists of billions of tiny micro-crystals and is called poly-crystalline silicon. The major part of solar celles produced today are made of crystalline silicon, and therefore a method for crystallizing silicon is needed. The most common crystalization method used for silicon is the Czochralski (CZ) method, which produces single crystaline silicon. Silicon is mixed with either an n- or a p-type impurity in a crucible giving an uniformly doped wafer at the end of this processing step. A small seed of crystalline silicon is brought in contact with the melt and then pulled out very slowly. By carefully controlling the temperature, the molten silicon in contact with the seed will solidify and arrange themselves according to the seed. This prosedure is repeated until a 1 metre long single crystallline sylinder with a diameter of about 20 cm^2 is obtained. The sylinder is then cut into wafers with a thickness of about 150 µm. These are often referred to as substrates. The Czochralski method is illustrated in figure 13.

The CZ method is both time and energy consuming, and as much as 30 % of the silicon is wasted as kerf loss during the cutting of the wafers [2]. In addition a considerable ammount of silicon is lost in cutting the wafers into squares. In order to reduce cost and improve production rates, new technologies have been developed. One of the most sucessful alterantives produce multicrystalline parllelpipeds. This process is faster than the CZ method and less silicon is lost in making the wafers square. In addition methods for growing the silicon crystals directly into sheet form has been investigated. Most of these methods have showed a high production rate and a good efficiency.
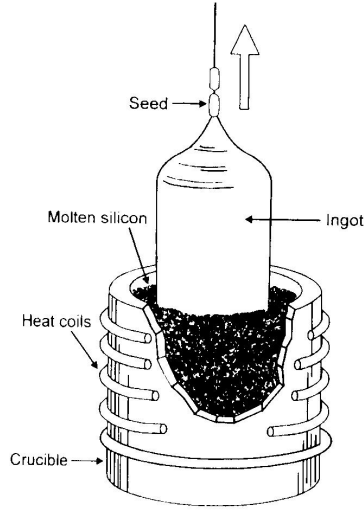
Figure 13: Single crystal silicon ingot growth by the Czochralski method [2].

Doping level of the substrate

Most wafers are doped with p-type impurities, also called acceptor doping since the doping atoms accept electrons. The concentration of acceptors, N_A, affect the short circuit current and the open circuit voltage. To maximize the efficiency of the cell, we want both to be as big as possible.

In order to get as high current output as possible, a large amount of minority charge carriers have to cross the depletion region per unit time. For the generated charge carriers to flow across the depletion region, they first have to diffuse into this area. The probability for reaching the depletion region is dependent of the lifetime, τ, of the charges, which is the average time before the charges recombine. The larger τ is, the more charge carriers diffuse into the depletion region and contribute to I_{SC}.

Each of the different recombination mechanisms comes with a corresponding lifetime. The total recombination rate is a sum of the different recombination rates, and is given by

$$\frac{1}{\tau_{\mathrm{e}}} = \frac{1}{\tau_{\mathrm{eRad}}} + \frac{1}{\tau_{\mathrm{eAug}}} + \frac{1}{\tau_{\mathrm{eSRH}}} + \frac{1}{\tau_{\mathrm{eSurf}}} \tag{34}$$

Each of the different recombination lifetimes, except the surface recombination lifetime, depends on N_A. τ_{eRad} and τ_{eSRH} is proportional with $\frac{1}{N_A}$, while τ_{eAug} has an even stronger dependence, being proportional with $\frac{1}{N_A^2}$ [8, section 8.3]. From this we can conclude that increasing N_A will tend to decrease I_{SC}.

If we take a look at V_{open} at the other hand, N_A will have the opposite effect. Referring

to equation 11, we see that the smaller saturation current, I_S, the larger V_{open}. I_S is given by [8, p 76]

$$I_S = qA(\frac{D_e n_i^2}{L_e N_A} + \frac{D_h n_i^2}{L_h N_D})$$ (35)

where A is the cross sectional area of the cell, N_D is the doping concentration of the n-dopants, D_e and D_h are the diffusion coefficients and L_e and L_h are the diffusion lengths for the electrones and holes respectivily. In order to make I_S as small as possible, and thereby maximize V_{open}, the doping concentrations should be big.

Because of the opposite dependencies of I_{SC} and V_{open} upon N_A, there exists an optimum acceptor concentration for maximum efficiency. This is illustrated in figure 14.
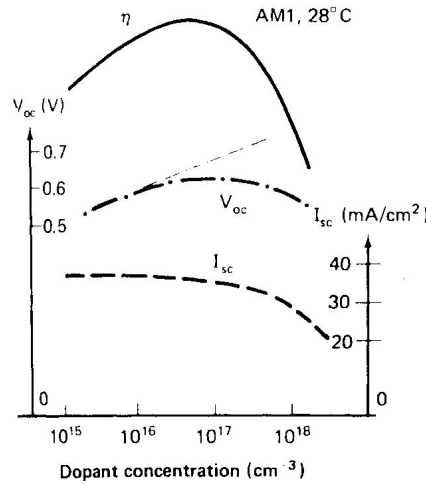

Figure 14: The open circuit voltage and the short circuit current as a function of doping concentration of the substrate [8, p 149].

4.4   From wafers to solar cells

At this point we have uniformly n-doped or p-doped wafers. Most wafers are doped with boron, making them p-doped. In order to make a pn-junction, an n-type impurity has to be introduced. Phosphorus is the most frequently used impurity for n-doping. The dopant is typically done by ion implantation or diffusion. In standard solar cell technology, the phosphorus impurities are made available at the sufrace of the wafer and diffused into the wafer at high temperatures. The pn-junction is formed at the distance into the wafer where the concentration of the p and the n-type impurities are equal. The typical way of doing this is by having a carrier gas bubbled through liquid $POCl_3$ along with O_2 and H_2 into a quartz tube with furnace containing the wafers. This is illustrated in figure 15.
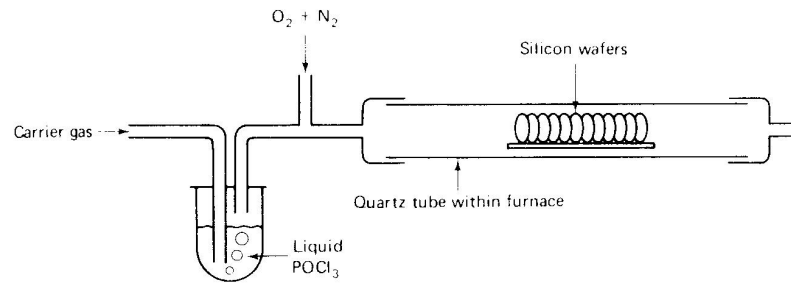
Figure 15: Phosphorus diffusion process [8, p 109].

At temperatures of about 800 °C the phosphorus is diffused into the wafers over a time period of about 20 minutes. After the diffusion, the phosphorus concentration is very high at the surface and decreases into the wafer. At a distance of 0.5 μm or less [8], the p-impurities override the n-impurities, making a pn-junction.

In standard solar cell technology the metal contacts are then attached to both sides of the cell by vacuum evaporation. The back surface is covered completely by a metal layer, while the contacts on the top layer has the form of a grid. Finally an anti-reflection coating is usually deposited on the surface of the solar cell. The material used for this has to have the right refractive index and the right thickness in order to minimize the reflected sunlight. Titanium oxide is typically used for this. The finished solar cell is shown in figure 16.
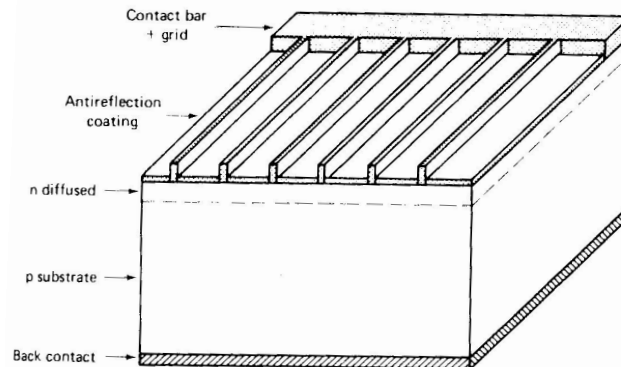

Figure 16: Cross section of a solar cell.

Junction depth

The depth of the junction is of major importance for the efficiency of the solar cell. As will be explained below, the probability for a generated charge carrier to contribute to the short circuit current decreases as the junction depth increases, thereby decreasing the efficiency of the solar cell.

When a free charge carrier is generated, it will be transported by diffusion until it either recombines or reaches the depletion region. If it reaches the depletion region, it will be swept away by the electric field, and thereby contributing to the short circuit current. The diffusion length of the minority charge, L, says something about the average distance a minority charge will diffuse before it recombines. It is therefore clear that the further away from the depletion region the charge is generated, the bigger is the probability that it will recombine before it reaches this region. In order to illustrate this, we define a collection efficiency, f_c. This is the probability that a generated minority charge carrier will reach the depletion region and contribute to the short circuit current. The collection probability can be expressed as [8]

$$f_c = \mathrm{e}^{-x/L} \tag{36}$$

where x is the distance from the depletion region. L depends on the type of minority charge carrier. The collection probability is illustrated in figure 17, where we can see that the probability for contributing to I_{SC} is largest close to the depletion region.
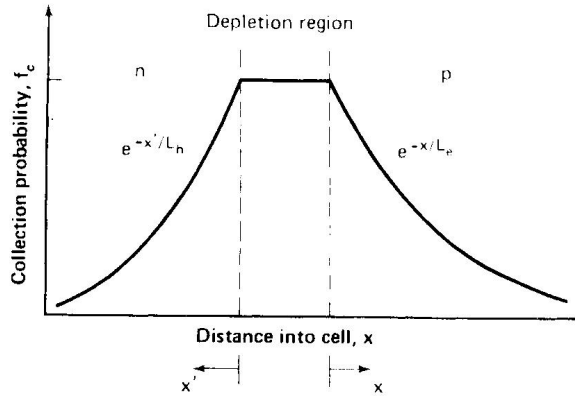

Figure 17: The collection probability as a function of the distance from the depletion region [8, p 142].

The next thing to consider, is where the probability of generating charge carriers is largest. When the cell is illuminated by monochromatic light, the generation rate as a function of the distance into the cell, x, is given by [8]

$$G = (1 - R)\alpha N e^{-\alpha x} \tag{37}$$

Here N is the incoming photon flux, R is the fraction which is reflected and α is the absorption coefficient. As illustrated in figure 18, the generation rate is large at the surface but decreases fast into the solar cell. This means that the generation rate is biggest at the surface where the collection probability is smallest. In order to maximize the amount of minority charges crossing the depletion region, the junction

should therefore be as close to the surface as possible. A typical junction depth of commercial solar cells is approximately 0.2 μm.
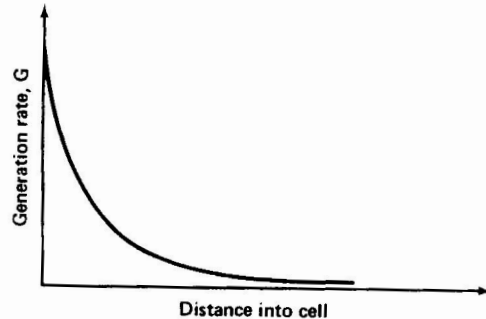

Figure 18: The generation rate as a function of the depth into the wafer [8, p 144].

4.5 From solar cells to solar cell modules

At the end single solar cells are interconnected to form a module. Typically 36 cells are connected in series and encapsulated to form a module. There are several things to consider during the construction of modules. For example the encapsulation needs to reduce the transmission of uv-light, have a tolerance to temperature extremes, keep the temperatures as low as possible to minimize power loss and have a self-cleaning ability.

How the solar cells are interconnected to form a module is of major importance for the electrical performance of the cell. If the cells put together have a mismatch in their operating characteristics, the total power output of the module be lower than the sum of the voltage output from the individual cells. This difference is called a mismatch loss, and is largest for series connected cells.

Another source of losses which is even more significant than the mismatch losses, is the potential for overheating in the poorest cell in a series string. An increase in the cell temperature will lower the open circuit voltage and thereby lower the voltage output for the entire module. If a large temperature increase occurs in a localized area of a module, severe damage can be done to the cells and the module encapsulation. The same effect is caused by a shadowing of some cells in the module or cracked cells.

In order to minimize these losses, the cells are sorted by their operation characteristics to create modules consisting of similar cells. The arrangement of cells in the module is also of great importance. Two frequently used techniques are series paralleling and the use of bypass diodes across one or more series blocks in the diode [8, section 6.6.4].

5   The three generations

When talking about photovoltaics, its technology is often divided into three different generations. The first generation is the traditional one formerly described in the report, and the one people often refer to when talking about solar cells. Compared to this, the second generation represent a stage where the goal is to make the wafers as thin as possible. The effeciency may be poorer than in a "thick" wafer, but the production cost per watt produced is significantly better. The third kind of solar cells is a more sophisticated one. Here one tries to manipulate the band structure of the material to improve efficiency. The relation between cost and efficiency for the three is as shown in figure 19.
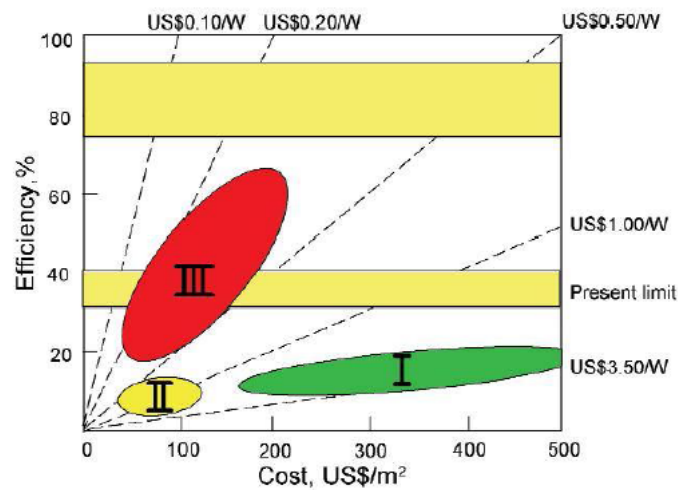

Figure 19: Efficiency vs. cost for the three generations.[13]

5.1   Second generation

The main difference between the first and second generation solar cells, is the amount of material which is used to produce it. For a 300 - 400 μm thick wafer, 90 % of its energy is generated in the top 15-20 μm. The potential of a material cost reduction, without significant efficiency-loss, is therefore huge.

Amorphous Silicon (a-Si) modules were the first thin film solar cells to be commercialized, and today it's the only thin film technology which have managed to capture a significant share of the total PV-market with its 4 %. a-Si as a pure material is of litte use for photovoltaics because of high dangling-bond[1] density and intragap state density in the material. By alloying it with hydrogen, these properties of a-Si can to a large extent be improved.

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[1]A dangling bond occurs when an atom is missing a neighbor to which it would be able to bind. Such dangling bonds are defects that disrupt the flow of electrons and that are able to collect the electrons. -Wikipedia-

In its simplest form, these devices have the structure of a single p-i-n layer. Multi junction structures are used to improve stability and efficiency even more. See figure 20 The disadvantage of amorphous material though, is that the material tends to degrade when exposed to sunlight so that efficiency is reduced. It turns out that the stabilized module may have an output power 15-35 % lower than the initial one. This effect is better known as the Staebler-Wronski Effect.
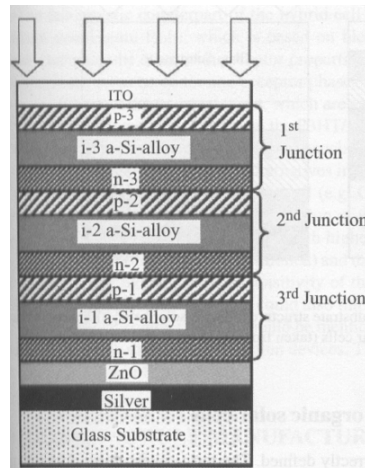

Figure 20: Multijunction thin film a-Si:H solar cell.[14]

An alternative to the a-Si technology, is to use polycrystalline silicon instead, which has grain sizes between 1 μm and 1 mm. Still, the question is rised upon whether this is the right grain size to be used or not. When it comes to the structure of the cell, this is in fact similar to the one used in standard bulk crystalline solar cells, but with efficiencies of about 10 %.

5.2 Third generation

As the size of the band gap in silicon is of approximately 1.166 eV, it's clear that not all photon energy in a broadbanded solar spectrum can be utilized to excite electrons. First of all, some photons have energies below the band gap value and cannot contribute to excitation at all. Next, a portion of energy is lost in radiation. Finally, for photons with energies above the band gap, their excess energy after excitation is lost in the form of thermal energy. For the standard solar spectrum AM1.5g, the maximum cell efficiency as a function of energy gap is given in figure 21(a). This is found by drawing a rectangle intersecting the inner curve. One way of covering a larger portion of the spectrum, is to make "**tandem-cells**". This means that junctions with decreasing energy gaps are placed in series. The result is shown in figure 21(b). The disadvantage of this technique is that the total current is determined by the cell with lowest efficiency.
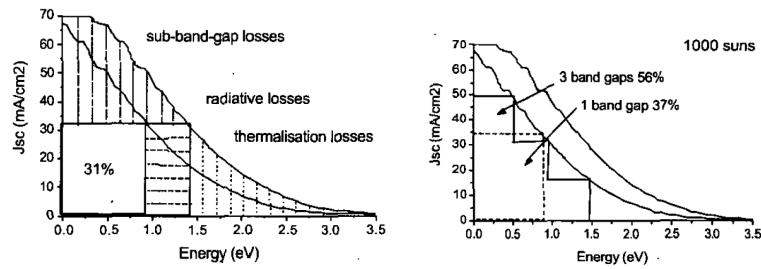
(a) Cell efficiency for single junction.   (b) Efficiency for tandem cell.

Figure 21: Maximum cell efficiency as a function of energy gap. [15]

For "**Hot carrier cells**" the goal is to collect the photo generated carriers before it thermalized, and their excess energy is transfered to lattice phonons. The thermalisation process can be allowed, but is slowed down if the lattice is held at high temperatures. Ideally at 4000 K.

Another approach for improving efficiency is to add certain impurities to the given solar cell material, so that new bands are added to the original ones. As illustrated in figure 22, this opens up for additional electron excitations in gap 2 and 3 so that more photons can be converted to electricity. Even though this reduces the bandwidth of the conduction band, the net effect is positive.
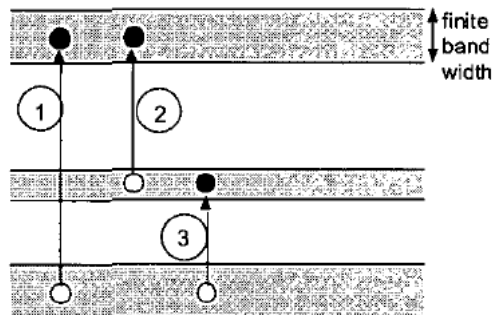

Figure 22: Band structure after impurities are added.[15]

Normally only one electron-hole-pair is generated per absorbed photon. To increase this generation, a photon energy of more than twice the energy gap can be split in two or more quantums. A limunescence converter makes this possible, and the photon is said to be down-converted. Should the photon have a sub-band-gap-energy, a frequency converter can be used to combine energy quantums into a larger one. An up-conversion has taken place, and excitation of electrons can now be achieved.

In the concept of "**thermo photovoltaics**", the source of energy for the solar cell is an emitter (figure 23).
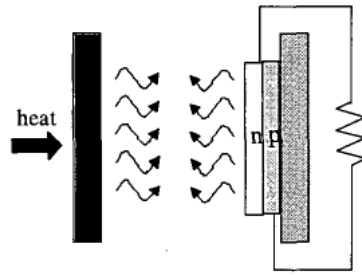
Figure 23: Principle of thermo photovoltaics.[15]

This is heated by e.g. sunlight. The idea of this technique is to recycle photons not having a sufficient energy to be absorbed by the receiver. After having arrived at the cell, the energy of the photon can be radiated back to the original emitter and later "collect" enough energy to break the band gap limit.

References

[1] T. W. Reenaas, "B and G, Chapter 4, part 1." Lecture notes in TFY4300 Energy and Enviromantal physics, NTNU, 2007.

[2] T. Markvart, *Solar Electricity*. Wiley, second ed., 2000.

[3] S. Sunde, "Supplement to solar part.." Lecture notes in TMT4285 Hydrogen technology,solar cell and fuel cells, NTNU, 2005.

[4] The Australian National University, "Photovoltaic panel simulation user's guide." `http://solar.anu.edu.au/level_1/Sun/help/PVguide.html`.

[5] J. K. A. Goetzberger and B. Voss, *Crystalline Silicon Solar Cells*. John Wiley and Sons Ltd., West Sussex, 1998. ISBN 0-471-97144-8.

[6] O. S. Heavens, *Optical Properties of Thin Solid Films*. Butterworths, London, 1955.

[7] J. I. Pankove, *Optical Processes in Semiconductors*. Prentice-Hall, Englewood Cliffs, 1971.

[8] M. A. Green, *Solar Cells - Operation Principles, Technology and System Applications*. The University og New South Wales, Kensington, 1998. ISBN 0-85823-580-3.

[9] M. A. Green, *Silicon Solar Cells - Advanced Principles and Practice*. Centre for Photovoltaic Devices and Systems, Sydney, 1995. ISBN 0-7334-0994-6.

[10] W. Shockley and W. T. Read, "Statistics of the recombination of holes and electrons," *Physical Review*, 1952.

[11] R. N. Hall, "Electron-hole recombination in germanium," *Physical Review*, 1952.

[12] Wikipedia, "Solar Cell Equivalent Circuit 3." `http://commons.wikimedia.org/wiki/Image:SolarCell-EquivalentCircuit3.PNG`.

[13] J. Nelson, "Third generation solar cells." `http://www.jointsolarpanel.nl/nelsonzc04.pdf`.

[14] J. Poortmans and V. Arkhipov, *Thin film solar cells*. Wiley, 2006.

[15] K. R. Catchpole and M. A. Green, "Third generation photovoltaics," *Conference on Optoelectronic and Microelectronic Materials and Devices*, 2002.