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Mini project
-
Solar cells other than Si

FY 3114 – Functional Materials

NTNU

Summary

Introduction

Nowadays, only two methods are used to generate significant electric power. The first and common one is the dynamo effect, which is produced by the movement of a magnetic field and a conductor. Thus, all the turbines, moved by steam (like in nuclear power), water (hydro power) or whatever, are all based on the same physical effect to generate electric power.

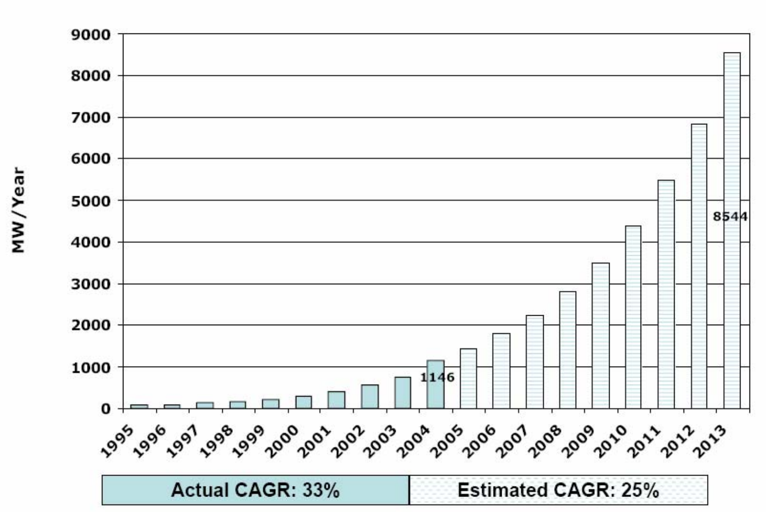
The second is the photovoltaic effect, generates by solar cells. The principle is here to produce electricity directly from an electromagnetic radiation-usually light coming from the sun-without any moving part. This effect was discovered by Becquerel in 1839, but we have to wait until 1954 for its development as a power source, when Chapin, Fuller and Pearson used doped semiconductor silicon.

Even though solar cells are a relative new technology, the photovoltaic power has been one of the fastest growing renewable energy : between 1990 and 2003, the production of solar cells grew tenfold, and the growth keeps increasing ! This fact is also driven by the growing will for renewable energies' development. Indeed, such technology is interesting to develop, due to the fact that it does not emit pollution (at least not directly, but the process to build solar cells surely emits some) and needs only sun's light to work properly.

The solar cells we are currently using are made of Silicon, but it is also (as we will see) possible to construct different types of solar cells. A few questions have here to be asked :

- Why do not we use more other types of solar cells ?
- In which case would it be interesting to develop other types ?

In order to give some answers to these legitimate questions, we need to see at first how works a solar cell. We will have also a look to the sun's radiative emission, captured by a solar cell. Then we will see some examples of solar cells other than Si and what do they bring new.



Source: Photon International, PV News, REC estimates

The growth of solar cells' s economic importance

I. Solar cell's principle

Photovoltaic's power generation is caused by electromagnetic radiation separating positive and negative charge carriers while absorbed by the solar cell. If an electric field is present, these charges can move and produce a current, which could be used in an external circuit.

A. *Recall of semi-conductor physics*

In order to go further in the explanations, we need to recall some knowledge in electronic properties of materials, and one very important concept is the energy band of a material. The energy band model is crucial to any detailed treatment of semiconductor devices, as it provides the framework needed to understand the concept of an energy bandgap and that of conduction in an almost filled band as described by the empty states.

Energy bands consisting of a large number of closely spaced energy levels existing in crystalline materials. The bands can be thought of as the collection of the individual energy levels of electrons surrounding each atom. The wavefunctions of the individual electrons, however, overlap with those of electrons confined to neighboring atoms. The Pauli exclusion principle does not allow the electron energy levels to be the same so that one obtains a set of closely spaced energy levels, forming an energy band.

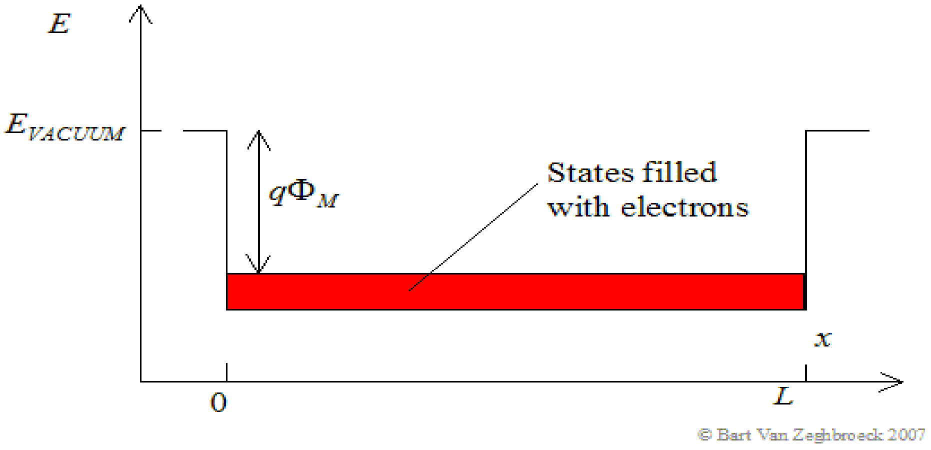
1. Free electron model

The free electron model of metals has been used to explain the photo-electric effect. This model assumes that electrons are free to move within the metal but are confined to the metal by potential barriers as illustrated by the figure below. The minimum energy needed to extract an electron from the metal equals $q\Phi_M$, where Φ_M is the workfunction.

The density of states, defined by $Z(E) = \frac{\Delta N}{\Delta E}$ is the number of incremental state per incremental energy. For this model, we have $Z(E) = \frac{\pi}{2\varepsilon_0}\sqrt{\frac{E}{E_0}}$ and so we have an energetic dependence in square root form.

This model is frequently used when analyzing metals. However, this model does not work well for semiconductors since the effect of the periodic potential due to the atoms in the crystal has been ignored.

We will therefore continue directly to the next model, which take in count the periodicity of a crystal (semi-conductor have namely a crystalloid structure).

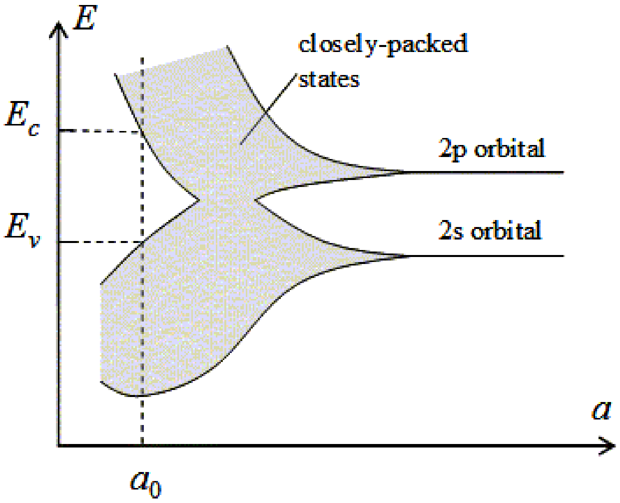


The free electron model of a metal.

2. Periodic potentials

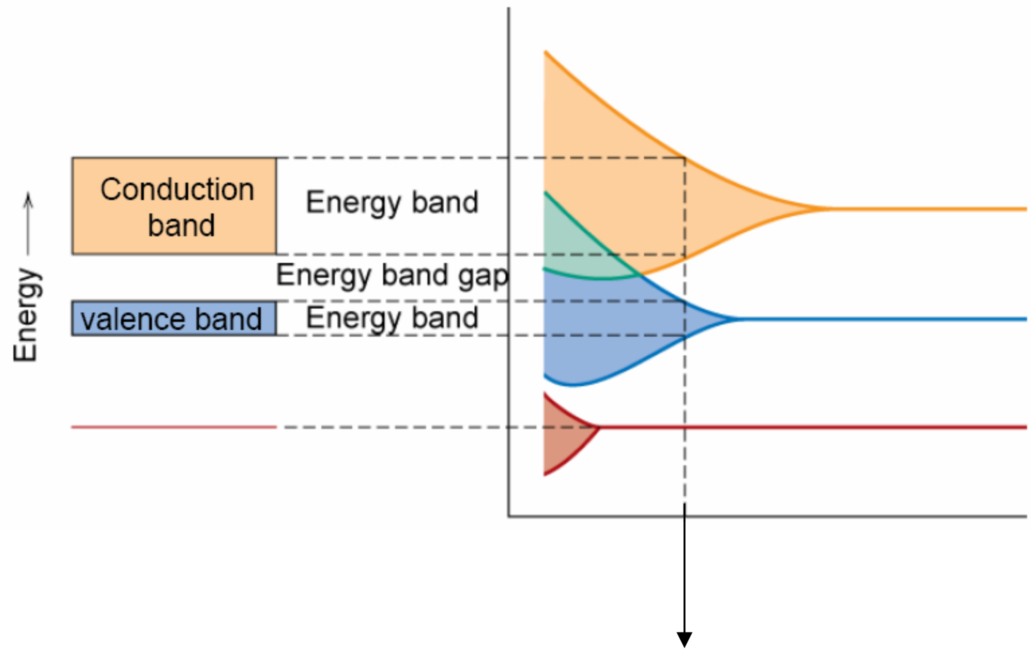
The analysis of periodic potentials is required to find the energy levels in a semiconductor. This requires the use of periodic wave functions, called Bloch functions which are studied by quantum physics. The result of this analysis is that the energy levels are grouped in bands, separated by energy band gaps. The behavior of electrons at the bottom of such a band is similar to that of a free electron. However, the electrons are affected by the presence of the periodic potential. The combined effect of the periodic potential is included by adjusting the value of the electron mass. This mass is referred to as the effective mass.

The effect of a periodic arrangement on the electron energy levels is illustrated by the figure below. Shown are the energy levels of electrons in a carbon crystal with the atoms arranged in a diamond lattice. These energy levels are plotted as a function of the lattice constant, a.

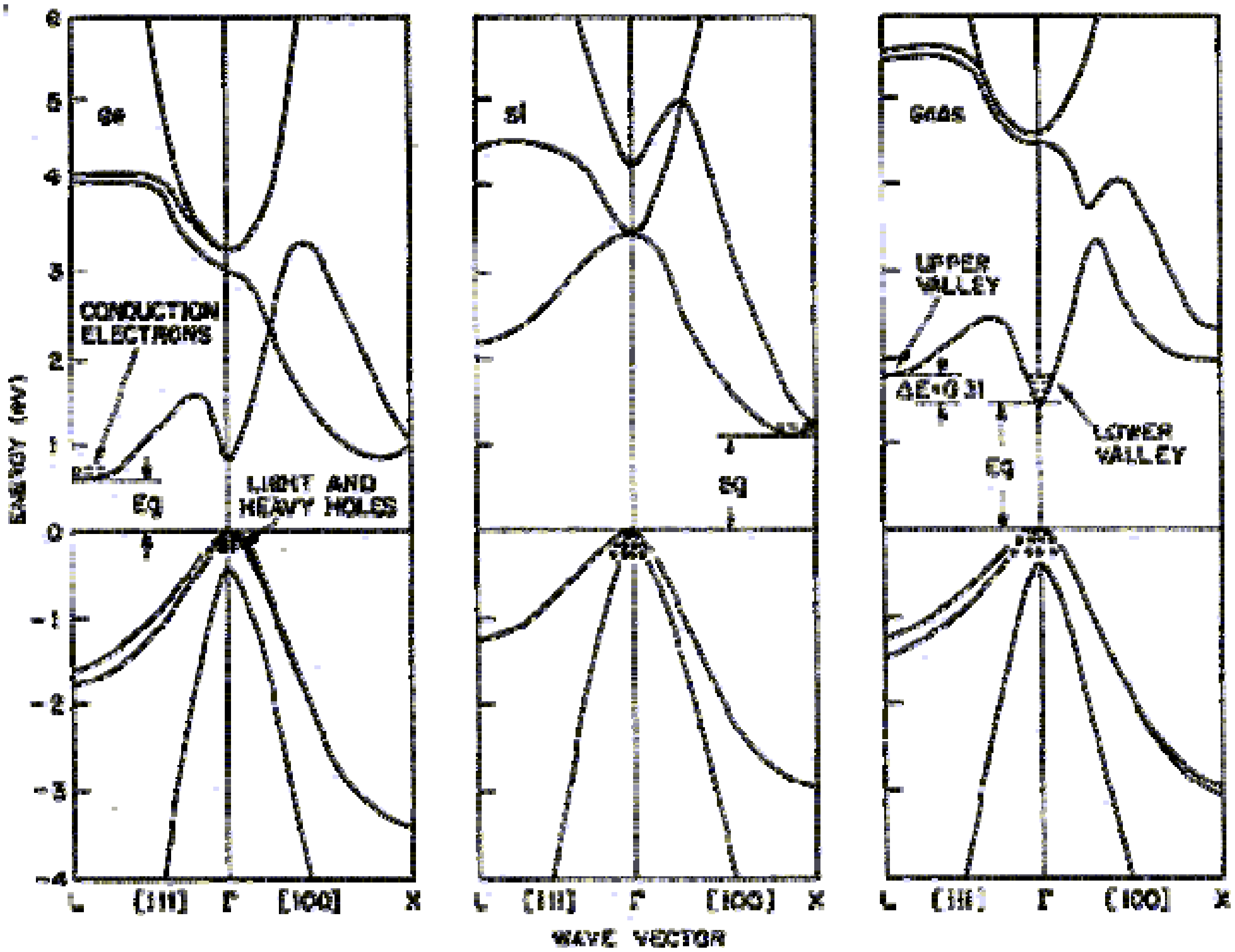


Energy bands for diamond versus lattice constant.

As the lattice constant is reduced, there is an overlap of the electron wavefunctions occupying adjacent atoms. This leads to a splitting of the energy levels consistent with the Pauli exclusion principle. The splitting results in an energy band containing 2N states in the 2s band and 6N states in the 2p band, where N is the number of atoms in the crystal. A further reduction of the lattice constant causes the 2s and 2p energy bands to merge and split again into two bands containing 4N states each. At zero Kelvin, the lower band is completely filled with electrons and labeled as the valence band. The upper band is empty and labeled as the conduction band. See scheme below :



The visualization of the conduction and the valence band is quite useful to explicit the electric properties of a material. But we have to keep in mine that the shape of the band structures are more complex than the one usually show in the previous scheme. Indeed, in order to analyze precisely and hence better understand the electric properties of a semi-conductor, the energy is plot as a function of the wavenumber k. This $E(k)$ curve is known as the dispersion relation. This energetic dependence is due to the fact that, as we can expect, the electric properties of a material are often anisotropic, which means they depends of the direction chosen. Moreover, the representation of a semi-conductor's band gap is often noted in 2 dimensions, but of course the real band gap is 3 dimensions.



Band structure of common semi-conductors : Ge, Si and GaAs

With this band structures we get informations of the band gap of the semi-conductor considered : its width and its nature, i.e. direct or indirect.
A band gap is called “direct” if the bottom of the band conduction is in front of the top of the valence band. This nature will result exploited in different applications. As an example we can state the Si, which has an indirect band gap and therefore will be a bad photodiode (bad light emitter), but a good photon receptor. This is due to the fact that for both absorption and emission of photons, phonons (vibrations of the crystal, relied to the transport of heat into a material) are involved.

To end the explanation of the band gap’s notion, we can confront the difference of the band gap between metals, semi-conductors and insulators. It is simply a difference width : the more the band gap is wide, the more the material isolates (in general, a material is considered insulator if the band gap is > 4-5 eV). The other point we can underline, is that semi-conductors differs from metals and insulators by their almost-full valence band and their almost-empty conduction band. For an insulator, the conduction band is totally empty of electrons to the profit of a totally full valence band. At last, for the case of metals, 2 configurations could be possible. An half full valence band, which contains only one valence e^- per atom, this is the case of most highly conductive metals, such as silver or copper. The other possibility is an overlap of the conduction and the valence band, with atoms containing 2 valence e^- or more.

3. Electric conduction in a Semiconductor

As we stated before, semi-conductors have the particularity to have their valence band almost filled and their conduction band almost depleted. This will result in an ability to have transport of carriers in both bands.

In the conduction band, the charge carrier is the e^-, whereas in the valence band, the electric conduction is carried out by the holes. Holes are rather a concept than a pure physical reality : it has a positive charge and is a missing e^-. This concept is quite useful when too much e^- are involved : rather than see a mobility of a lot of e^-, we see a mobility of few holes instead. To get an image of this concept, it is like bubbles (holes) in a soda. Rather than see the soda falling, we assimilate bubbles going up. Thus, we simplify a lot the analysis by considering less particles. The positive charge of the hole resides in the fact that an atom missed a valence e^-, and thus, locally we have a positive charge.

Thus the resulting conduction in the semi-conductor will depends on the density of holes/e^- available. But before knowing this density of carriers, we need to know first the density of states Z(E), in order to know the number of “places” (states) available for them, from an energetically point of view.

Thus, the number of real states N(E) is the product of the density of states times the probability of each state, F(E) :

$N(E) = 2Z(E) \times F(E)$ where the factor 2 comes from the Pauli principle

The probabilistic function F(E), called Fermi-Dirac function (used for fermions description, such as e^-) is expressed as

$F(E) = \frac{1}{e^{\frac{(E-E_F)}{kT}} + 1}$ where E_F, the Fermi level, is the last level occupied by the e^- at 0 Kelvins. This Fermi level is often given as a reference level of energy and takes all its importance when discussing on intrinsic or doped semi-conductors. This energy level is a reference because it always indicates that we have 50% of chance to have an e^- on it, if the temperature is higher than 0K.

As a result, we obtain the global conductivity of the semi-conductor :
$\sigma = |e|(N_e\mu_e + N_h\mu_h)$ with μ_e and μ_h the mobility of e^- an holes respectively

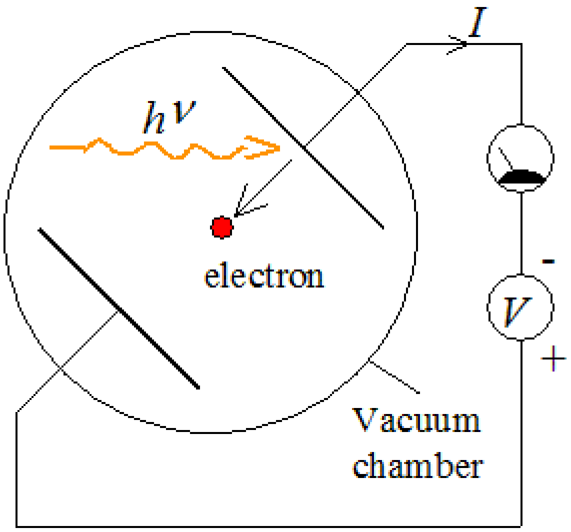
In an intrinsic semi-conductor (non-doped : all the free carriers result from thermal excitation), $N_e = N_h$. This is easily understandable : when enough thermal energy give the opportunity for an e^- to pass trough the potential barrier of the band gap, it will result a e^- in the conduction band and simultaneously a hole (left by the e^-) in the valence band. Thus, we have the same amount of e^- and holes.

In an extrinsic semi-conductor, impurities have been added with a different valence band than the host. Two types are possible : n-type ($N_e > N_h$) or p-types ($N_e < N_h$). As a consequence, the Fermi level is moved more closed to the conduction band, or to the valence band (respectively).

B. From the semiconductor to the solar cell

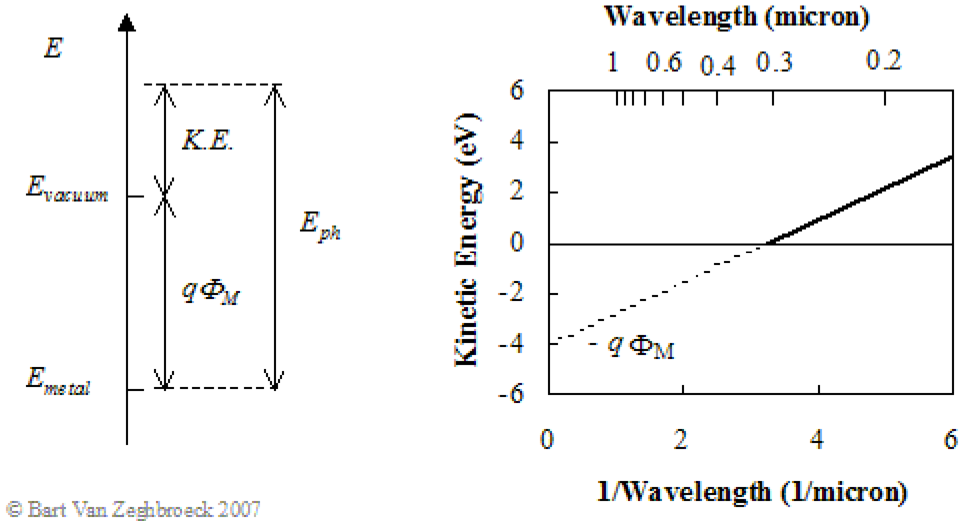
1. The photo-electric effect

The photoelectric effect is by now the "classic" experiment, which demonstrates the quantized nature of light: when applying monochromatic light to a metal in vacuum one finds that electrons are released from the metal. This experiment confirms the notion that electrons are confined to the metal, but can escape when provided sufficient energy, for instance in the form of light. However, the surprising fact is that when illuminating with long wavelengths (typically larger than 400 nm) no electrons are emitted from the metal even if the light intensity is increased. On the other hand, one easily observes electron emission at ultra-violet wavelengths for which the number of electrons emitted does vary with the light intensity. A more detailed analysis reveals that the maximum kinetic energy of the emitted electrons varies linearly with the inverse of the wavelength, for wavelengths shorter than the maximum wavelength.



Experimental set-up to measure the photoelectric effect.

The experimental apparatus consists of two metal electrodes within a vacuum chamber. Light is incident on one of two electrodes to which an external voltage is applied. The external voltage is adjusted so that the current due to the photo-emitted electrons becomes zero. This voltage corresponds to the maximum kinetic energy, K.E., of the electrons in units of electron volt. That voltage is measured for different wavelengths and is plotted versus the inverse of the wavelength as shown in figure below. The resulting graph is a straight line.



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Albert Einstein explained this experiment by postulating that the energy of light is quantized. He assumed that light consists of individual particles called *photons*, so that the kinetic energy of the electrons, $K.E= p^2/2mn$ equals the energy of the photons, E_{ph}, minus the energy, $q\Phi_M$, required to extract the electrons from the metal. The workfunction, Φ_M,therefore quantifies the potential, which the electrons have to overcome to leave the metal. The slope of the curve was measured to be 1.24 eV/micron, which yielded the following relation for the photon energy, E_{ph} :

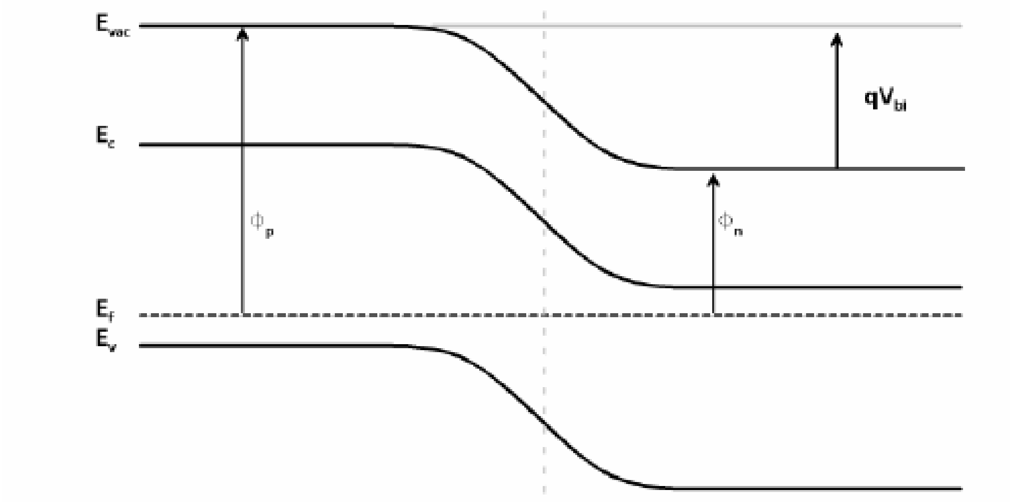
$$E_{ph} = h\nu = \frac{hc}{\lambda}$$

Next, the same process occurs for a semiconductor : the photon absorbed should have an energy superior to the band gap. The incoming photon with the good wavelength is absorbed and provides enough energy to an electron of the valence band to reach the conduction band, which left by the way a hole in it. We say that the incoming photon has generate an electron/hole pair.

2. Structure of a solar cell

Solar cells are composed of various semiconducting materials.

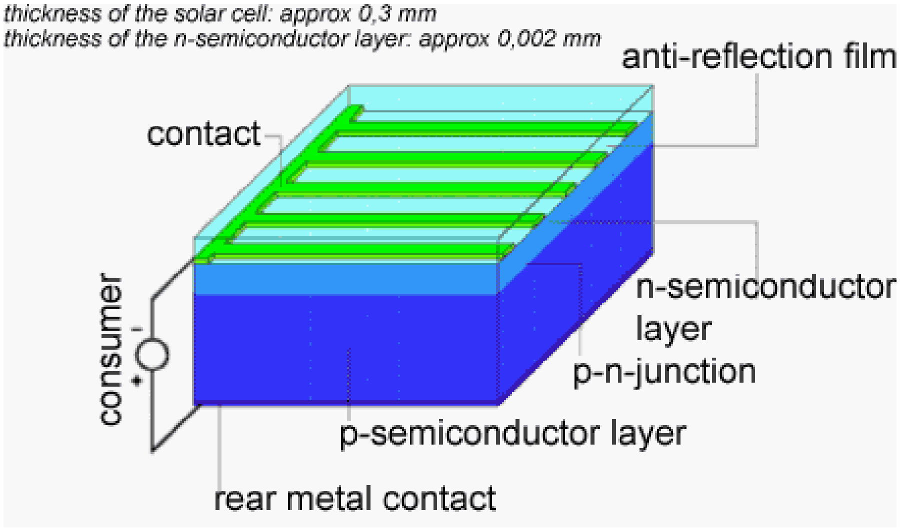
To produce a solar cell, the semiconductor is contaminated or doped. Then, two differently contaminated semiconductor layers are combined, in order to form a P/N junction. The band gap has thus the shape shown as the scheme below :



P/N junction : P region to the left/N region to the right

Without any light, an equilibrium occurs. Indeed, the normal trend consists of a migration of the holes from the p region to the n region, whereas for the e^- from the n-region it is the opposite. On the other hand, as these charge carriers transit, an electric field is created (due to the immobile charges from the P and N regions), which is opposed to the migration of holes/e^-. It will grow until this migration stops and an equilibrium is achieved. Thus, in the dark, the P/N junction is assimilated as a diode, because it facilitates the movement of carriers in one direction.

Under light, on the other hand, a P/N junction could be assimilated as a current generator in parallel with as diode. This is due to the fact that under light electron/hole pairs are generated, and under the pre-existing electric field, holes generated in N junction are moved to the P junction and electrons from P are moved to the N-junction. This carrier migration generates a generation current, which will be used to provide the electricity wanted.



Model of a crystalline solar cell

At this junction, an interior electric field is built up which leads to the separation of the charge carriers that are released by light. Through metal contacts, an electric charge can be tapped. If the outer circuit is closed, meaning a consumer is connected, then direct current flows.

Silicon cells are approximately 10 cm by 10 cm large (recently also 15 cm by 15 cm). A transparent anti-reflection film protects the cell and decreases reflective loss on the cell surface.

One can distinguish three cell types according to the type of crystal: monocrystalline, polycrystalline and amorphous. To produce a monocrystalline silicon cell, absolutely pure semiconducting material is necessary. Monocrystalline rods are extracted from melted silicon and then sawed into thin plates. This production process guarantees a relatively high level of efficiency.

The production of polycrystalline cells is more cost-efficient. In this process, liquid silicon is poured into blocks that are subsequently sawed into plates. During solidification of the material, crystal structures of varying sizes are formed, at whose borders defects emerge. As a result of this crystal defect, the solar cell is less efficient.

If a silicon film is deposited on glass or another substrate material, this is a so-called amorphous or thin layer cell. The layer thickness amounts to less than 1µm (thickness of a human hair: 50-100 µm), so the production costs are lower due to the low material costs. However, the efficiency of amorphous cells is much lower than that of the other two cell types. Because of this, they are primarily used in low power equipment (watches, pocket calculators) or as facade elements.

Material	**Level of efficiency in % Lab**	**Level of efficiency in % Production**
Monocrystalline Silicon	approx. 24	14 to17
Polycrystalline Silicon	approx. 18	13 to15
Amorphous Silicon	approx. 13	5 to7

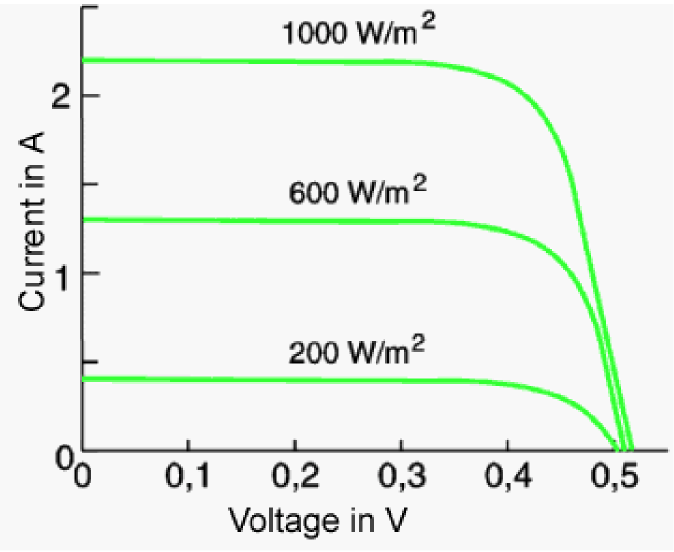
From the Cell to the Module

In order to make the appropriate voltages and outputs available for different applications, single solar cells are interconnected to form larger units. Cells connected in series have a higher voltage, while those connected in parallel produce more electric current. The interconnected solar cells are usually embedded in transparent Ethyl-Vinyl-Acetate, fitted with an aluminum or stainless steel frame and covered with transparent glass on the front side.

The typical power ratings of such solar modules are between 10 Wpeak and 100 Wpeak. The characteristic data refer to the standard test conditions of 1000 W/m² solar radiation at a cell temperature of 25° Celsius. The manufacturer's standard warranty of ten or more years is quite long and shows the high quality standards and life expectancy of today's products.

3. Characteristics of a Solar Cell

The usable voltage from solar cells depends on the semiconductor material. In silicon it amounts to approximately 0.5 V. Terminal voltage is only weakly dependent on light radiation, while the current intensity increases with higher luminosity. A 100 cm² silicon cell, for example, reaches a maximum current intensity of approximately 2 A when radiated by 1000 W/m².



Current-voltage line of a Si-solar cell

The power generated by a solar cell, $P = IV = I_{SC}V - I_0V(e^{\frac{|e|V}{kT}} - 1)$ where I_{SC} is the short circuitt current (I when V=0). It is represented, regarding the scheme, by the area under the curve until I is still constant.

Another important characteristic of a solar cell, is its efficiency $\eta = \frac{I_{\max}V_{\max}}{P_{in}}$

The level of efficiency indicates how much of the radiated quantity of light is converted into usable electrical energy.

The output (product of electricity and voltage) of a solar cell is temperature dependent. Indeed, because the band gap of a semiconductor decrease slightly with the temperature, higher cell temperatures lead to lower output, and hence to lower efficiency.

II. Solar radiation dependence

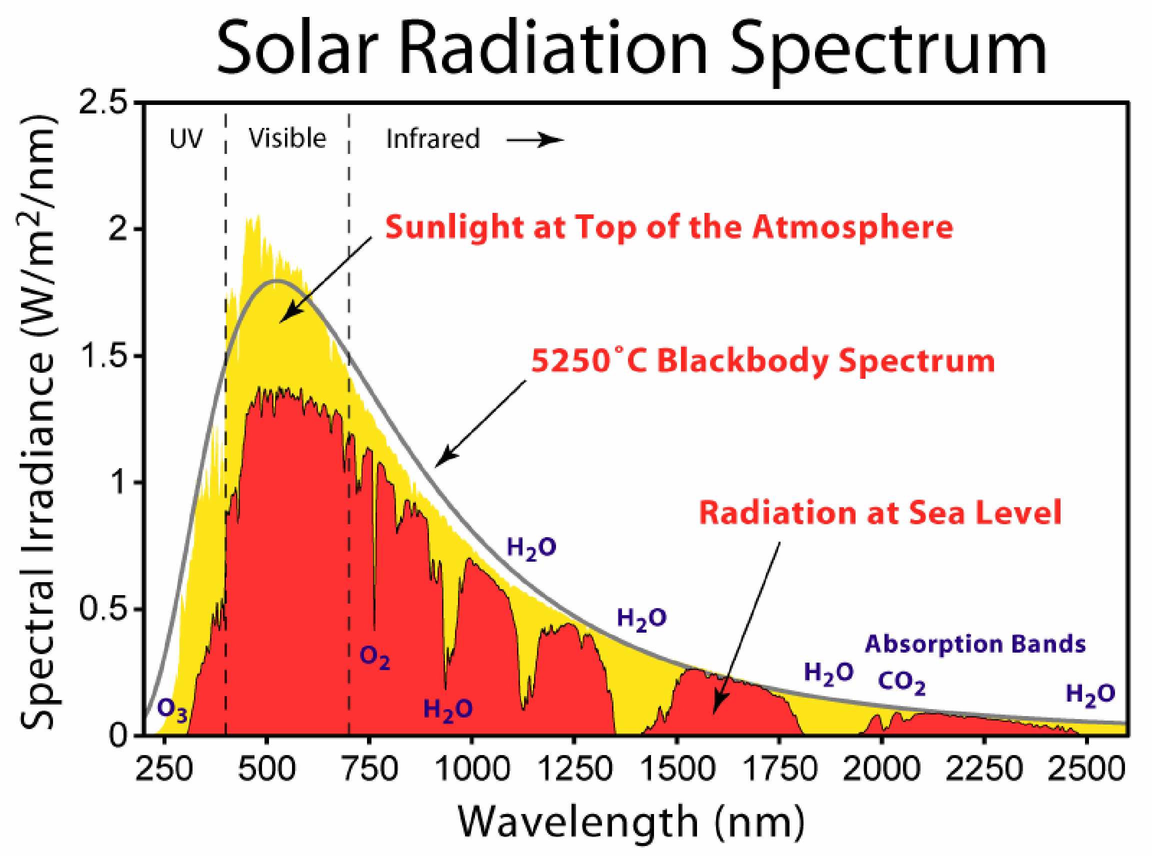
Solar radiation is radiant energy emitted by the sun from a nuclear fusion reaction that creates electromagnetic energy. The spectrum of solar radiation is close to that of a black body with a temperature of about 5800 K. About half of the radiation is in the visible short-wave part of the electromagnetic spectrum. The other half is mostly in the near-infrared part, with some in the ultraviolet part of the spectrum.

The solar constant is the amount of incoming solar electromagnetic radiation per unit area, measured on the outer surface of Earth's atmosphere, in a plane perpendicular to the rays. The solar constant includes all types of solar radiation, not just the visible light. It is measured by satellite to be roughly 1366 watts per square meter, though it fluctuates by about 6.9% during a year - from 1412 W/m2 in early January to 1321 W/m2 in early July, due to the earth's varying distance from the sun, and by a few parts per thousand from day to day. Thus, for the whole Earth, with a cross section of 127,400,000 km^2, the power is 1.740×1017 W, plus or minus 3.5%. The solar constant is not quite constant over long time periods either; see solar variation. The value 1366 W/m2 is equivalent to 1.96 calories per minute per square centimeter.

The Earth receives a total amount of radiation determined by its cross section (π R2), but as the planet rotates this energy is distributed across the entire surface area (4 π R2). Hence, the average incoming solar radiation (or irradiance), taking into account the half of the planet not receiving any solar radiation at all, is one fourth the solar constant or ~342 W/m^2. At any given location and time, the amount received at the surface depends on the state of the atmosphere and the latitude. Thus, a solar cell will have different efficiency regarding its position on Earth.

Between 1902 and 1957, measurements by Charles Greeley Abbot and others at various high-altitude sites found values between 1322 and 1465 W/m2.

Note : The angular diameter of Earth seen from the sun is ca. 1/11,000 radian, so the solid angle of Earth seen from the sun is ca. 1/140,000,000 steradian. Thus, the sun emits about 2 billion times the amount of radiation that is caught by Earth, or about 3.86×1026 watts



The solar constant includes all wavelengths of solar electromagnetic radiation, not just the visible light.

Because of this sun dependence, one important aspect of a solar cell is its absorption factor, and this explains why studies are done on light capture layers or other Concentrator cells. A higher light intensity focused on the solar cells using mirror and lens systems provides more power. Other systems such as tracking sun system, thus always using direct radiation, are also studied.

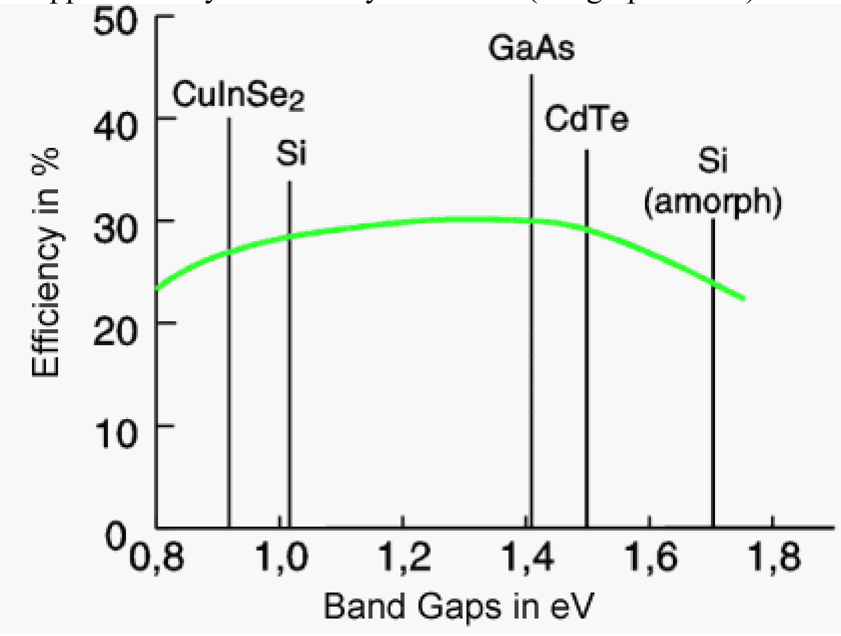
Solar concentrators

III. Exemples of solar cells other than Si

At a first glance, why Si is widely used for solar cells ?
Over 95% of all the solar cells produced worldwide are composed of the semiconductor material Silicon (Si). As the second most abundant element in earth`s crust, silicon has the advantage, of being available in sufficient quantities, and additionally processing the material does not burden the environment.

Natural Limits of Efficiency

In addition to optimizing the production processes, work is also being done to increase the level of efficiency, in order to lower the costs of solar cells. However, different loss mechanisms are setting limits on these plans. Basically, the different semiconductor materials or combinations are suited only for specific spectral ranges. Therefore a specific portion of the radiant energy cannot be used, because the photons do not have enough energy to "activate" the charge carriers. On the other hand, a certain amount of surplus photon energy is transformed into heat rather than into electrical energy. In addition to that, there are optical losses, such as the shadowing of the cell surface through contact with the glass surface or reflection of incoming rays on the cell surface. Other loss mechanisms are electrical resistance losses in the semiconductor and the connecting cable. The disrupting influence of material contamination, surface effects and crystal defects, however, are also significant.
Single loss mechanisms (photons with too little energy are not absorbed, surplus photon energy is transformed into heat) cannot be further improved because of inherent physical limits imposed by the materials themselves. This leads to a theoretical maximum level of efficiency, i.e. approximately 28% for crystal silicon (see graph below).



The GaAs solar cell has got efficiency greater than that of the Si solar cell in normal working conditions or under concentration. The studies on this type of solar cell obtained encouraging results. Further studies, for more complex structures such as the solar tendencies with three junctions in order to increase the efficiency is still in work-in-progress, but sound promissing.

Another interesting aspect, is that with higher bandgap than Si, the power generated is higher, but moreover, we get closer to the maximum of sun's irradiance (see solar radiation spectrum in previous chapter). Si absorbed radiations around 1,1 μm, whereas a bandgap of 2,25eV for instance, will absorbed radiations around 550nm, which is the sun's irradiance power peak. A solar cell with such a bandgap will have its efficiency drastically improved, as it both capture more power from the sun and it produces more power (due to bigger bandgap).

New Directions

Surface structuring to reduce reflection loss: for example, construction of the cell surface in a pyramid structure, so that incoming light hits the surface several times. New material: for example, gallium arsenide (GaAs), cadmium telluride (CdTe) or copper indium selenide ($CuInSe^2$).

Tandem or stacked cells: in order to be able to use a wide spectrum of radiation, different semiconductor materials, which are suited for different spectral ranges, will be arranged one on top of the other.

MIS Inversion Layer cells: the inner electrical field are not produced by a p-n junction, but by the junction of a thin oxide layer to a semiconductor.

Grätzel cells: Electrochemical liquid cells with titanium dioxide as electrolytes and dye to improve light absorption.

An exemple from Berkeley …

A new generation of solar cells that combines nanotechnology with plastic electronics has been launched with the development of a semiconductor-polymer photovoltaic device by researchers with the U.S. Department of Energy's Lawrence Berkeley National Laboratory (Berkeley Lab) and the University of California at Berkeley (UCB). Such hybrid solar cells will be cheaper and easier to make than their semiconductor counterparts, and could be made in the same nearly infinite variety of shapes as pure polymers.

The use of solar, or photovoltaic, cells — devices that can absorb and convert light into electrical power — has been limited to date because production costs are so high. Even the fabrication of the simplest semiconductor cell is a complex process that has to take place under exactly controlled conditions, such as high vacuum and temperatures between 400 and 1,400 degrees Celsius.

Ever since the discovery in 1977 of conducting plastics (polymers which feature conjugated double chemical bonds, that enable electrons to move through them), there has been interest in using these materials in the fabrication of solar cells. Plastic solar cells can be made in bulk quantities for a few cents each; however, the efficiency with which they convert light into electricity has been quite poor compared to the power-conversion efficiencies of semiconductor cells.

“Inorganic semiconductors offer excellent, well established electronic properties, and they are very well suited as solar cell materials. Polymers offer the advantage of solution processing at room temperature, which is cheaper and allows for using fully flexible substrates, such as plastics." say the researchers.

At the heart of all photovoltaic devices are two separate layers of materials, one with an abundance of electrons that functions as a "negative pole," and one with an abundance of electron holes (vacant, positively-charged energy spaces) that functions as a "positive pole." When photons from the sun or some other light source are absorbed, their energy is transferred to the extra electrons in the negative pole, causing them to flow to the positive pole and creating new holes that start flowing to the negative pole. This electrical current can then be used to power other devices such as a pocket calculator.

In a typical semiconductor solar cell, the two poles are made from n-type and p-type semiconductors. In a plastic solar cell, they're made from hole-acceptor and electron-acceptor polymers. In their new hybrid solar cell, Alivisatos, Huynh, and Dittmer used the semicrystalline polymer known as poly(3-hexylthiophene), or P3HT, for the hole acceptor or negative pole, and nanometer-sized cadmium selenide (CdSe) rods as the positive pole.

With CdSe rods measuring 7 nanometers by 60 nanometers, hybrid solar cells achieved a monochromatic power conversion efficiency of 6.9 percent, one of the highest ever reported for a plastic photovoltaic device.

The most important step is here to increase the amount of sunlight absorbed in the red part of the spectrum, which they can do by going to other semiconductor materials such as cadmium telluride.

Conclusion

Many types of solar cells are possible, and the flourishing development of solar cells is in a good way to multiply the variety of them. The point is, the more we develop new types of solar cells, the better we can answer to our needs.

As an exemple in the space industry, GaAs based solar cells are preferred for powering space satellites. The use of Ga substrates reduces weight significantly; more over the conversion efficiency, further increased by using GaInP/GaAs tandem solar cells. These types of solar cells are superior to Si cells due to their lower weight and their higher resistance to the cosmic radiation. Mechanical, electrical, optical properties of a material have to be analyzed and exploited to obtain the most fitted solar cell for a precise purpose. Installing solar cells panels for a dwelling has a different aspect than panels for industry. That is to say, from an economical point of view, undoubtedly the most efficient future solar cells will be costly and it is good to work on both efficient but also priceless solar cells. By studying and developing other solar cells than Si, we can find out some clues to create interesting solar cells, regarding efficiency and price.

Nowadays, the technologic processes are insufficient to make them really competitive from an economical aspect. In this field, good knowledge of material physics is relevant to tackle these problems and understand in which ways orient the research. The development of technologies will of course support this enhancement. In the future, many engineering tricks can be applied to make the cells more efficient, as the answer are not always complex.