Peter Würfel

# Physics of Solar Cells

*From Principles to New Concepts*

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*Physics of Solar Cells: From Principles to New Concepts*. Peter Würfel

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# List of symbols

| | | |
|---|---|---|
| $h, \hbar = h/(2\pi)$ | Planck's constant | eVs |
| $\hbar\omega$ | photon energy | eV |
| $a(\hbar\omega)$ | absorptivity | |
| $r(\hbar\omega)$ | reflectivity | |
| $t(\hbar\omega)$ | transmission | |
| $\varepsilon(\hbar\omega) = a(\hbar\omega)$ | emissivity | |
| $\alpha(\hbar\omega)$ | absorption coefficient | 1/cm |
| $k$ | Boltzmann's constant | eV/K |
| $\sigma$ | Stefan-Boltzmann constant | W/(m$^2$K$^4$) |
| $T$ | temperature | K |
| $n_j$ | concentration of particle type $j$ | 1/cm$^3$ |
| e | electron | |
| h | hole | |
| $\gamma$ | photon | |
| $\Gamma$ | phonon | |
| $n_\mathrm{e}, n_\mathrm{h}$ | concentration of electrons, holes | 1/cm$^3$ |
| $n_\mathrm{i}$ | intrinsic concentration of electrons and holes | 1/cm$^3$ |
| $N_\mathrm{C}, N_\mathrm{V}$ | effective density of states in conduction band, valence band | 1/cm$^3$ |
| $\varepsilon_\mathrm{e}, \varepsilon_\mathrm{h}$ | energy of an electron, hole | eV |
| $\varepsilon_\mathrm{C}$ | energy of an electron at the conduction band minimum | eV |
| $\varepsilon_\mathrm{V}$ | energy of an electron at the valence band maximum | eV |
| $\mu_j$ | chemical potential of particle type $j$ | eV |
| $\eta_j$ | electro-chemical potential of particle type $j$ | eV |
| $\chi_\mathrm{e}$ | electron affinity | eV |
| $\varphi$ | electrical potential | V |
| e | elementary charge | As |
| $V$ | voltage = $[\eta_\mathrm{e}(x_1) - \eta_\mathrm{e}(x_2)]/\mathrm{e}$ | V |
| $\varepsilon_\mathrm{FC}$ | Fermi energy for electron distribution in conduction band | eV |
| $\varepsilon_\mathrm{FV}$ | Fermi energy for electron distribution in valence band | eV |
| $m_\mathrm{e}^*, m_\mathrm{h}^*$ | effective mass of electrons, holes | g |

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| | | |
|---|---|---|
| $b_{\mathrm{e}}, b_{\mathrm{h}}$ | mobility of electrons, holes | $\mathrm{cm}^2/(\mathrm{Vs})$ |
| $D_{\mathrm{e}}, D_{\mathrm{h}}$ | diffusion coefficient of electrons, holes | $\mathrm{cm}^2/\mathrm{s}$ |
| $\tau_{\mathrm{e}}, \tau_{\mathrm{h}}$ | recombination life time of electrons, holes | s |
| $R_{\mathrm{e}}, R_{\mathrm{h}}$ | recombination rate of electrons, holes | $1/(\mathrm{cm}^3\mathrm{s})$ |
| $G_{\mathrm{e}}, G_{\mathrm{h}}$ | generation rate of electrons, holes | $1/(\mathrm{cm}^3\mathrm{s})$ |
| $\sigma_{\mathrm{e}}, \sigma_{\mathrm{h}}$ | cross-section for the capture of an electron, hole by an impurity | $\mathrm{cm}^2$ |
| $j_j$ | current density of particles of type $j$ | $1/\mathrm{cm}^2$ |
| $j_Q$ | charge current density | $\mathrm{A}/\mathrm{cm}^2$ |

# Preface

Mankind needs energy for a living. Besides the energy in our food necessary to sustain our body and its functions (100 W), 30 times more energy is used on average to make our life more comfortable. Electrical energy is one of the most useful forms of energy, since it can be used for almost everything. All life on earth is based on solar energy following the invention of photosynthesis by the algae. Producing electrical energy through photovoltaic energy conversion by solar cells is the human counterpart. For the first time in history, mankind is able to produce a high quality energy form from solar energy directly, without the need of the plants. Since any sustainable, i. e. long term energy supply must be based on solar energy, photovoltaic energy conversion will become indispensable in the future.

This book provides a fundamental understanding of the functioning of solar cells. The discussion of the principles is as general as possible to provide the basis for present technology and future developments as well. Energy conversion in solar cells is shown to consist of two steps. The first is the absorption of solar radiation and the production of chemical energy. This process takes place in every semiconductor. The second step is the transformation into electrical energy by generating current and voltage. This requires structures and forces to drive the electrons and holes, produced by the incident light, through the solar cell as an electric current. These forces and the structures which enable a directional charge transport are derived in detail. In the process it is shown that the electric field present in a pn junction in the dark, usually considered a prerequisite for the operation of a solar cell, is in fact more an accompanying phenomenon of a structure required for other reasons and not an essential property of a solar cell. The structure of a solar cell is much better represented by a semiconducting absorber in which the conversion of solar heat into chemical energy takes place and by two semi-permeable membranes which at one terminal transmit electrons and block holes and at the second terminal transmit holes and block electrons. The book attempts to develop the physical principles underlying the function of a solar cell as understandably and at the same time as completely as possible. With very few exceptions, all physical relationships are derived and explained in examples. This will provide the non-physicists particularly with the background for a thorough understanding.

Emphasis is placed on a thermodynamic approach which is largely independent of existing solar cell structures. This allows a general determination of the efficiency limits for the conversion of solar heat radiation into electrical energy and also demonstrates the potential and the limits for improvement for present-day solar cells. We follow a route first taken by W. Shockley and H. J. Queisser.[1]

[1] W. Shockley, H. J. Queisser, *J. Appl. Phys.* **32**, (1961), 510.

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This book is the result of a series of lectures dealing with the physics of solar cells. I am grateful to the many students who called my attention to errors and suggested improvements. The material presented here, which differs from the usual treatment of solar cells relying on an electric field for a driving force, is the result of several years of collaboration with my teacher, W. Ruppel.

In some respects this book is more rigorous than is customary in semiconductor device physics and in solar cell physics in particular. The most obvious is that identical physical quantities will be represented by identical symbols. Current densities will be represented by $j$ and the quantity which is transported by the current is defined by its index, as in $j_Q$ for the density of a charge current or $j_\mathrm{e}$ for the density of a current of electrons. In adhering to this principle, all particle concentrations are given the symbol $n$, with $n_\mathrm{e}$ representing the concentration of electrons, $n_\mathrm{h}$ the concentration of holes and $n_\gamma$ the concentration of photons. I hope that those who are used to $n$ and $p$ for electron and hole concentrations do not find it too difficult to adapt to a more logical notation.

The driving force for a transition from exhausting energy reserves, as we presently do, to using renewable energies, is not the exhaustion of the reserves themselves, although oil and gas reserves will not last for more than one hundred years. The exhaustion does not bother most of us, since it will occur well beyond our own lifetime. We would certainly care a lot more, if we were to live for 500 years and would have to face the consequences of our present energy use ourselves. The driving force for the transition to renewable energies is rather the harmful effect which the byproducts of using fossil and nuclear energy have on our environment. Since this is the most effective incentive for using solar energy, we start by discussing the consequences of our present energy economy and its effect on the climate. The potential of a solar energy economy to eliminate these problems fully justifies the most intensive efforts to develop and improve the photovoltaic technology for which this book tries to provide the foundation.

*Peter Würfel*

# 1 Problems of the Energy Economy

The energy economy of nearly all and in particular, of the industrialized countries is based on the use of stored energy, mainly fossil energy in the form of coal, oil and natural gas, as well as nuclear energy in the form of the uranium isotope U235. Satisfying our energy needs from reserves, introduces two problems. A source of energy can continue only until it is depleted. Well before this time, that is, at the latest right now, we have to consider how life will continue after this source of energy is gone and we must begin to develop alternatives. Furthermore, unpleasant side effects accompany the consumption of the energy source. Materials long buried under the surface of the earth are released and find their way into air, water and into our food. Up to now, the disadvantages are hardly perceptible, but they will lead to difficulties for future generations. In this chapter we estimate the size of the fossil energy resources, which, to be precise, are comprised not only of fossil energy carriers, but also of the oxygen in the air which is burned together with them. In addition, we will examine the cause of the greenhouse effect, which is a practically unavoidable consequence of burning fossil fuels.

## 1.1 Energy economy

The amount of chemical energy stored in fossil energy carriers is measured in energy units, some more, some less practical. The most fundamental unit is the Joule, abbreviated J, which is, however, a rather small unit representing the amount of energy needed to heat 1 g of water by a quarter of a degree, or the amount of energy which a hair drier with a power of 1 kW consumes in 1 ms. A more practical unit is the **k**ilo **W**att **h**our (kWh), which is $3.6 \times 10^6$ J. 1 kWh is the energy contained in 100 g of chocolate. The only problem with this unit is that it is derived from the Watt, the unit for power, which is energy per time. This makes energy equal to power times time. This awkwardness leads to a lot of mistakes in the non-science press like kW per hour for power, since most people mistake kW for energy which they perceive as the more basic quantity. The energy of fossil fuels is often given in barrels of oil equivalents or in (metric) tons of coal equivalents (t coal equ.).

The following relations apply:

| | | | | |
|---|---|---|---|---|
| 1 kWh | = | $3.6 \times 10^6$ J | = | 1 kWh |
| 1 t coal equ. | = | $29 \times 10^9$ J | = | 8200 kWh |
| 1 kg oil | = | 1.4 kg coal equ. | = | 12.0 kWh |
| 1 $m^3$ gas | = | 1.1 kg coal equ. | = | 9.0 kWh |
| 1 barrel oil | = | 195 kg coal equ. | = | 1670 kWh |

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**Table 1.1:** Primary energy consumption in Germany in 2002.

| Type | Consumption ($10^6$ t coal equ./a) | Per capita consumption (kW/person) |
|---|---|---|
| Oil | 185 | 2.24 |
| Gas | 107 | 1.30 |
| Coal | 122 | 1.48 |
| Nuclear energy | 62 | 0.75 |
| Others | 17 | 0.21 |
| Total | 494 | 5.98 |

**Table 1.2:** World primary energy consumption 2002.

| Type | Consumption ($10^9$ t coal equ./a) | Per capita consumption (kW/person) |
|---|---|---|
| Oil | 4.93 | 0.82 |
| Gas | 3.19 | 0.53 |
| Coal | 3.36 | 0.56 |
| Nuclear energy | 0.86 | 0.14 |
| Others | 0.86 | 0.14 |
| Total | 13.2 | 2.19 |

The consumption of chemical energy per time is an energy current (power) taken from the energy reserves. Thus, the consumption of one ton of coal per year, averaged over one year amounts to an energy current of

$$1\,\text{t coal equ.}/\text{a} = 8200\,\text{kWh}/\text{a} = 0.94\,\text{kW} .$$

We look at Germany, as an example of a densely populated industrialized country. Table 1.1 shows the 2002 consumption of primary energy in Germany, with a population of $82.5 \times 10^6$. These figures contain a consumption of electrical energy per year of

$$570\,\text{TWh}/\text{a} = 65\,\text{GW} \Rightarrow 0.79\,\text{kW}/\text{person} .$$

The energy consumption per capita in Germany of 5.98 kW is very high compared with the energy current of $2000\,\text{kcal}/\text{d} = 100\,\text{W} = 0.1\,\text{kW}$ taken up by human beings in the form of food, representing the minimum requirement for sustaining life.

Table 1.2 shows the 2002 consumption of primary energy in the world, with a population of $6 \times 10^9$. This energy consumption is supplied from the available reserves of energy with the exception of hydro, wind and biomass. The presently remaining reserves of energy are shown in Table 1.3. This is the amount of energy that is estimated to be recoverable economically with present-day techniques at present prices. The actual reserves may be up to 10 times as large, of about $10 \times 10^{12}$ t coal equ.

The global energy consumption of $13.2 \times 10^9$ t coal equ. per year appears to be very small when compared with the continuous energy current from the sun of

$$1.7 \times 10^{17}\,\text{W} = 1.5 \times 10^{18}\,\text{kWh}/\text{a} = 1.8 \times 10^{14}\,\text{t coal equ.}/\text{a}$$

which radiates towards the earth.

**Table 1.3:** The world's remaining energy reserves.

| Type | Reserves in $10^9$ t coal equ. |
|---|---|
| Oil | 210 |
| Gas | 170 |
| Coal | 660 |
| Total | 1040 |

In densely populated regions such as Germany, however, the balance is not so favourable if we restrict ourselves to the natural processes of photosynthesis for the conversion of solar energy to other useful forms of energy. The mean annual energy current which the sun radiates onto Germany, with an area of $0.36 \times 10^6\,\mathrm{km}^2$, is about $3.6 \times 10^{14}\,\mathrm{kWh/a} = 4.3 \times 10^{10}$ t coal equ./a. Photosynthesis, when averaged over all plants, has an efficiency of about 1% and produces around $400 \times 10^6$ t coal equ./a from the energy of the sun. This is insufficient to cover the requirements of primary energy of $494 \times 10^6$ t coal equ./a for Germany. What is even more important, is that it also shows that over the entire area of Germany, plants are not able to reproduce the oxygen by photosynthesis which is consumed in the combustion of gas, oil and coal. And this does not even take into consideration that the bio-mass produced in the process is not stored, but decays, which again consumes the oxygen produced by photosynthesis. This estimate also shows that solar energy can cover the energy requirements of Germany over its area only if a substantially higher efficiency for the conversion process than that of photosynthesis can be achieved. The fact that no shortage in the supply of oxygen will result in the foreseeable future is owed to the wind, which brings oxygen from areas with lower consumption. Nevertheless, well before oxygen is in short supply we will be made aware of an increase in the combustion product $CO_2$.

## 1.2 Estimate of the maximum reserves of fossil energy

For this estimate[1] we assume that neither free carbon nor free oxygen was present on the earth before the beginning of organic life. The fact that carbon and oxygen react quickly at the high temperatures prevailing during this stage of the earth's history, both with each other to form $CO_2$ and also with a number of other elements to form carbides and oxides, is a strong argument in support of this assumption. Since today there are still elementary metals on the surface of the earth, even though only in small amounts, it must be assumed that neither free carbon nor free oxygen was available to react.

The free oxygen found in the atmosphere today can therefore only be the result of photosynthesis occurring at a later time. The present-day amount of oxygen in the atmosphere thus allows us to estimate the size of the carbon reserves stored in the products of photosynthesis.

During photosynthesis, water and carbon dioxide combine to form carbohydrates, which build up according to the reaction

$$n \times (H_2O + CO_2) \Rightarrow n \times CH_2O + n \times O_2.$$

[1] G. Falk, W. Ruppel, *Energie und Entropie*, Springer-Verlag, Berlin 1976.

A typical product of photosynthesis is glucose: $C_6H_{12}O_6 \equiv 6\times\ CH_2O$. For this compound and also for most other carbohydrates, the ratio of free oxygen produced by photosynthesis to carbon stored in the carbohydrates is:

$$1\,\text{mol}\ O_2 \Rightarrow 1\,\text{mol}\ C \quad \text{or}$$

$$32\,\text{g}\ O_2 \Rightarrow 12\,\text{g}\ C$$

The mass of the stored carbon $m_C$ can therefore be found from the mass of free oxygen $m_{O_2}$:

$$m_C = \frac{12}{32}\, m_{O_2}.$$

The greatest proportion of the oxygen resulting from photosynthesis is found in the atmosphere and, to a lesser extent, dissolved in the water of the oceans. The fraction in the atmosphere is sufficiently large to be taken as the basis for an estimate.

From the pressure $p_E$ = 1 bar = 10 N/cm$^2$ on the surface of the earth resulting from the air surrounding our planet, we can calculate the mass of air from the relationship $m_{Air} \times g = p_E \times$ area:

$$m_{Air}/\text{area} = p_E/g = \frac{10\,\text{N/cm}^2}{10\,\text{m/s}^2} = 1\,\text{kg/cm}^2.$$

Multiplying by the surface of the earth gives the total mass of air

$$m_{Air} = 1\,\text{kg/cm}^2 \times 4\pi R_{earth}^2 = 5\times 10^{15}\ \text{tons of air.}$$

Since air consists of 80% $N_2$ and 20% $O_2$ (making no distinction between volume percent and weight percent), the mass of oxygen is: $m_{O_2} = 10^{15}\,\text{t}\ O_2$. The maximum amount of carbon produced in photosynthesis and now present in deposits on the earth is therefore:

$$m_C = \frac{12}{32}\, m_{O_2} = 400\times 10^{12}\ \text{tons of carbon.}$$

Up to now $10.4\times 10^{12}$ t coal equ. have been found.

Thus, there is reason to hope that the reserves of fossil energy will continue to grow as a result of continued exploration. In fact, in recent years the known reserves have grown continuously because more has been found than was consumed. There are rumours that very large reserves of methane hydrate can be found in moderate depths on the ocean floor. This compound dissociates into methane and water when it is warmed up or is taken out of the ocean. The prospects of possibly large reserves, however, must not distract our attention from the urgency of restricting the mining of these reserves. If we actually use up the entire reserves of carbon for our energy requirements, we will in fact reverse the photosynthesis of millions of years and in doing so eliminate all our oxygen. Even if more than the estimated $400\times 10^{12}$ tons of carbon should exist, we cannot burn more than $400\times 10^{12}$ tons of carbon because of the limited amount of oxygen.

If we examine oil and gas consumption as an example for the consumption of fossil energy reserves over a long period of time, e. g., since the birth of Christ, Figure 1.1 gives a frightening picture. Up to the beginning of the twentieth century, the consumption of reserves was practically negligible. From this time on, it then rises exponentially up to a maximum value which will be reached in one or two decades. Consumption will then fall off again, as

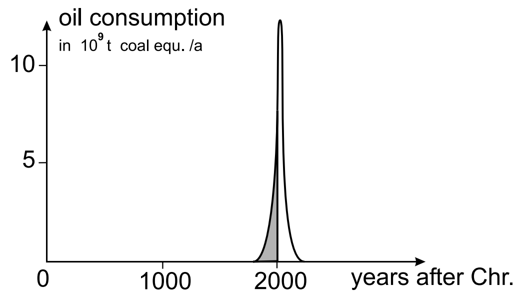


**Figure 1.1:** Annual consumption of oil. The area under the curve gives the estimated total oil reserves.

the reserves are gradually used up. The maximum consumption is expected when the reserves have fallen off to one half of their original levels. The reserves which have accumulated over millions of years will then literally go up in smoke over a time of only about one hundred years. Here, the elimination of energy reserves is the lesser problem. Much worse will be the alteration of the atmosphere as a result of the products of combustion. These effects will last for a long time. Even if later generations have changed over to supplying energy from regenerative sources, they will still suffer from the heritage which we have left them.

## 1.3 The greenhouse effect

$CO_2$ is produced in the combustion of fossil energy carriers. The increase in the concentration of carbon dioxide in our atmosphere will have serious consequences for our climate. At the present time the atmosphere contains a fraction of 0.03 % of $CO_2$. This corresponds to $2.3 \times 10^{12}$ t of $CO_2$.

### 1.3.1 Combustion

Pure carbon is consumed according to the reaction $C + O_2 \Rightarrow CO_2$. Accordingly 12 g C + 32 g $O_2 \Rightarrow$ 44 g $CO_2$. The mass of $CO_2$ produced by combustion is given by the mass of carbon consumed according to $m_{CO_2} = 44/12\, m_C$. The combustion of 1 t of carbon thus results in 3.7 t of $CO_2$.

For different compounds of carbon other relationships apply:

– Carbohydrates:

$$30\,\text{g}\ CH_2O + 32\,\text{g}\ O_2 \Rightarrow 18\,\text{g}\ H_2O + 44\,\text{g}\ CO_2$$

resulting in $m_{CO_2} = 1.47\, m_{CH_2O}$. This is the chemical reaction for the combustion of food in the human body.

– Methane (main component of natural gas):

$$16\,\text{g}\ CH_4 + 64\,\text{g}\ O_2 \Rightarrow 36\,\text{g}\ H_2O + 44\,\text{g}\ CO_2$$

resulting in $m_{CO_2} = 2.75\, m_{CH_4}$.

The present global consumption of the $10^{10}$ t coal equ./a produces globally $\Rightarrow 2.2 \times 10^{10}$ t of $CO_2$ per year. Half of this is dissolved in the water of the oceans, and half remains in the atmosphere. If the annual energy consumption does *not* continue to rise, the amount of $CO_2$ in the atmosphere will double only after about 200 years. However, it is necessary to take into account that energy consumption continues to increase. At the present time the growth of one percent per year is relatively low. In the developing countries, energy consumption even decreased in 1999, because of the inability of these countries to pay for more energy. If global energy consumption continues to increase at about one percent per year, the $CO_2$ concentration in the atmosphere will have doubled already after about 100 years. This increase is less the result of a per capita increase in energy consumption than a result of the increasing global population. The increasing $CO_2$ concentration in the atmosphere will have consequences for the temperature of the earth.

### 1.3.2 The temperature of the earth

The temperature of the earth is stationary, i. e., constant in time if the energy current absorbed from the sun and the energy current emitted by the earth are in balance. We want to estimate the temperature of the earth in this steady state condition. For this purpose we will make use of radiation laws not derived until the following chapter.

The energy current density from the sun at the position of the earth (but outside the earth's atmosphere) is

$$j_{E,\text{sun}} = 1.3\,\text{kW/m}^2 \,.$$

For the case of complete absorption, the energy current absorbed by the entire earth is the energy current incident on the projected area of the earth:

$$I_{E,\text{abs}} = \pi R_e^2\, j_{E,\text{sun}} \qquad \text{with} \qquad R_e = 6370\,\text{km} \quad \text{(radius of the earth)}\,.$$

According to the Stefan–Boltzmann radiation law, the energy current density emitted by the earth into space is given by

$$j_{E,\text{earth}} = \sigma T_e^4 \qquad \text{where} \qquad \sigma = 5.67 \times 10^{-8}\,\text{W}/(\text{m}^2\text{K}^4)\,,$$

is the Stefan–Boltzmann constant. The energy current emitted by the entire earth is

$$I_{E,\text{emit}} = 4\pi R_e^2 \sigma T_e^4 .$$

From the steady state condition $I_{E,\text{abs}} = I_{E,\text{emit}}$ it follows that the estimated mean temperature of the earth is $T_e = 275\,\text{K}$.

The mean temperature of the earth is in fact around 288 K. The approximate agreement is, however, only coincidental. Taking into account that about 30% of the incident solar radiation is reflected back into space by the atmosphere of the earth and thus only about 70% ($1\,\text{kW/m}^2$) reaches the surface of the earth, a temperature of 258 K then results. The actual temperature of the earth is in fact greater, because the radiation emitted by the earth is partly absorbed in the atmosphere. The atmosphere then becomes warmer and emits heat back to the earth. The same effect occurs in greenhouses, where the glass covering absorbs the thermal radiation emitted by the greenhouse and emits some of it back into the greenhouse.

We can understand the greenhouse effect of the atmosphere using a simple model. Due to a temperature of 6000 K of the sun, the solar radiation spectrum (expressed as energy current