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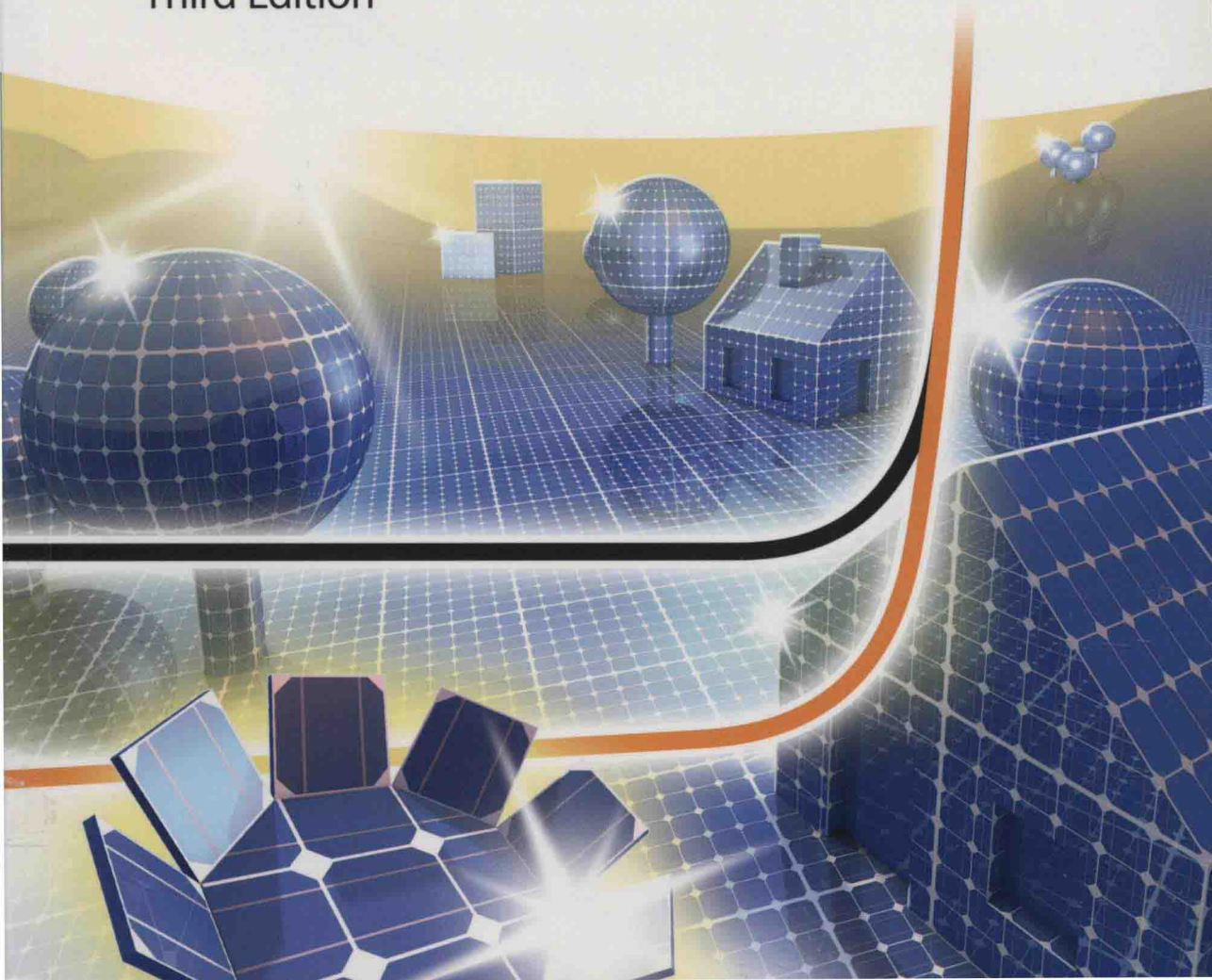
Peter Würfel and Uli Würfel

Physics of Solar Cells

From Basic Principles to Advanced Concepts

Third Edition



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From Basic Principles to Advanced Concepts

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Peter Würfel and Uli Würfel

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List of Symbols

h, $\hbar = h/(2\pi)$	Planck's constant	eVs
$\hbar\omega$	photon energy	eV
$a(\hbar\omega)$	absorptance	
$r(\hbar\omega)$	reflectance	
$t(\hbar\omega)$	transmittance	
$\varepsilon(\hbar\omega) = a(\hbar\omega)$	emittance	
$\alpha(\hbar\omega)$	absorption coefficient	cm^{-1}
k	Boltzmann's constant	$\mathrm{eV\,K}^{-1}$
σ	Stefan–Boltzmann constant	$\mathrm{W\,m}^{-2}\mathrm{K}^{-4}$
T	temperature	K
n_j	concentration of particle type j	cm^{-3}
e	electron	
h	hole	
γ	photon	
Γ	phonon	
n_e, n_h	concentration of electrons, holes	cm^{-3}
n_i	intrinsic concentration of electrons and holes	cm^{-3}
N_C, N_V	effective density of states in conduction band, valence band	cm^{-3}
ε_e, ε_h	energy of an electron, hole	eV
ε_C	energy of an electron at the conduction band minimum	eV
ε_V	energy of an electron at the valence band maximum	eV
μ_j	chemical potential of particle type j	eV
η_j	electrochemical potential of particle type j	eV
χ_e	electron affinity	eV
φ	electrical potential	V
e	elementary charge	As
ϵ_0	dielectric permittivity of free space	$\mathrm{As\,(V\,m)}^{-1}$
ϵ	relative dielectric permittivity	
V	voltage $= [\eta_\mathrm{e}(x_1) - \eta_\mathrm{e}(x_2)]/\mathrm{e}$	V

ε_{FC}	Fermi energy for electron distribution in conduction band	eV
ε_{FV}	Fermi energy for electron distribution in valence band	eV
m_e^*, m_h^*	effective mass of electrons, holes	g
b_e, b_h	mobility of electrons, holes	$cm^2\,(Vs)^{-1}$
D_e, D_h	diffusion coefficient of electrons, holes	$cm^2\,s^{-1}$
τ_e, τ_h	recombination life time of electrons, holes	s
R_e, R_h	recombination rate of electrons, holes	$cm^{-3}s^{-1}$
G_e, G_h	generation rate of electrons, holes	$cm^{-3}s^{-1}$
σ_e, σ_h	cross-section for the capture of an electron, hole by an impurity	cm^2
j_j	current density of particles of type j	$(cm^2s)^{-1}$
j_Q	charge current density	$A\,cm^{-2}$

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 nonphysicists particularly with the background for a thorough understanding.

Emphasis is placed on a thermodynamic approach that 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)]

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 that is transported by the current is defined by its index, as in j_Q for the density of a charge current or j_e for the density of a current of electrons. In adhering to this principle, all particle concentrations are given the symbol n, with n_e representing the concentration of electrons, n_h the concentration of holes and n_γ 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 and *Uli Würfel*

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

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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 ^{235}U. Two problems arise when we use our reserves to satisfy our energy needs. A source of energy can continue only until it is depleted. Well before this time, that is, right now at the latest, 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 composed not only of fossil energy carriers but also of the oxygen in the air that burns with them. In addition, we 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 and 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 that 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 3.6×10^6 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 nonscience press such as kilowatt per hour for power, because most people

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mistake kilowatt to be the unit 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 equiv.).

The following relations apply:

$1\,\text{kWh} = 3.6 \times 10^6\,\text{J} = 1\,\text{kWh}$
$1\,\text{t coal equiv.} = 29 \times 10^9\,\text{J} = 8200\,\text{kWh}$
$1\,\text{kg oil} = 1.4\,\text{kg coal equiv.} = 12.0\,\text{kWh}$
$1\,\text{m}^3\,\text{gas} = 1.1\,\text{kg coal equiv.} = 9.0\,\text{kWh}$
$1\,\text{barrel oil} = 195\,\text{kg coal equiv.} = 1670\,\text{kWh}$

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

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

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

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

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

Table 1.2 shows the consumption of primary energy in the world in 2002, with a population of 6×10^9. This energy consumption is supplied from the available reserves of energy with the exception of hydro, wind, and biomass. The current 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 current prices. The actual reserves may be up to 10 times as large, about 10×10^{12} t coal equiv.

Table 1.1 Primary Energy Consumption in Germany in 2002.

Type	Consumption (10^6 t coal equiv./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 in 2002.

Type	Consumption (10^9 t coal equiv./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

Table 1.3 The World's Remaining Energy Reserves.

Type	Reserves in 10^9 t coal equiv.
Oil	210
Gas	170
Coal	660
Total	1040

The global energy consumption of 13.2×10^9 t coal equiv. per year appears to be very small when compared with the continuous energy current from the Sun of

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

that radiates toward the Earth.

In densely populated regions such as Germany, however, the balance is not so favorable if we restrict ourselves to the natural processes of photosynthesis for the conversion of solar energy into other useful forms of energy. The mean annual energy current that the Sun radiates onto Germany, with an area of $0.36 \times 10^6\ \text{km}^2$, is about $3.6 \times 10^{14}\ \text{kWh/a} = 4.3 \times 10^{10}$ t coal equiv./a. Photosynthesis, when averaged over all plants, has an efficiency of about 1% and produces around 400×10^6 t coal equiv./a from the energy of the Sun. This is insufficient to cover the requirements of primary energy of 494×10^6 t coal equiv./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, by photosynthesis, the oxygen that is consumed in the combustion of gas, oil and coal. And this does not even take into consideration that the biomass 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 we run out of oxygen 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 there are elementary metals on the surface of the Earth even today, although 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 a lower limit to the size of the carbon reserves stored in the products of photosynthesis under the assumption that all oxygen produced by photosythesis is still present as free oxygen.

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

$$n \times (H_2O + CO_2) \Longrightarrow n \times CH_2O + n \times O_2$$

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

$$1\ \text{mol}\ O_2 \Longrightarrow 1\ \text{mol}\ C \quad \text{or}$$
$$32\ \text{g}\ O_2 \Longrightarrow 12\ \text{g}\ C$$

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

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

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