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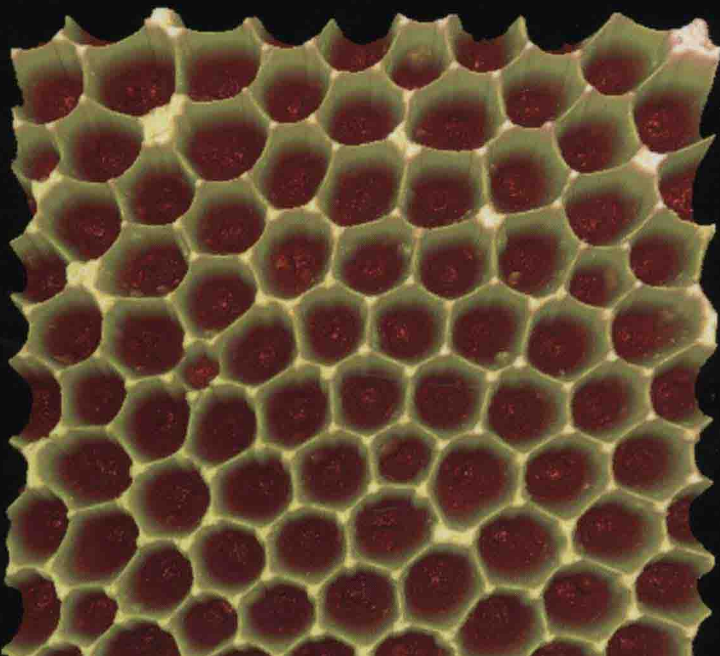
Lukas Schmidt-Mende, Jonas Weickert

ORGANIC AND HYBRID SOLAR CELLS

AN INTRODUCTION



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Organic and Hybrid Solar Cells

An Introduction

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The **cover image** shows an AFM topographic height profile of an anodized aluminum oxid (AAO) membrane electrochemically processed in phosphoric acid used in the Schmidt-Mende group for the preparation of nanostructured organic and hybrid solar cells. The shown AFM image of a self-organized AAO membrane was recorded by Dr. Thomas Pfadler with a Bruker Multimode8 AFM in tapping mode, equipped with a Nanotools MC60 high precision probe. The authors thank Nanotools Munich GmbH for access to their laboratories.

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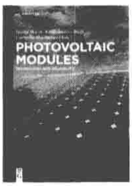

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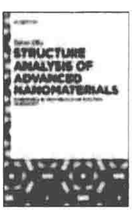

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Preface

Over the past years the field of organic and hybrid solar cells has attracted many researchers and the progress has been tremendous. Whereas the organic electronics with organic light-emitting diodes and organic field-effect transistors has been seen as a promising technology with market readiness, the organic and hybrid solar cells have remained for a long time a niche field of research due to their low efficiencies and short lifetimes. However, over the past few years the efficiencies have increased drastically and also research on the lifetime of organic and hybrid solar cells has shown promising results. Until 2012 organic bulk heterojunction and dye-sensitized solar cells have been the focus of research. Since first reports of 10% efficient perovskite solar cells came out, many researchers have started to work on these exciting solar cell materials. As perovskite solar cells have been achieved with efficiencies of >20%, in terms of efficiency these cells are already competitive to inorganic semiconductors, even though reproducibility and lifetime issues need to be solved. Indeed, with these perovskite solar cells, the field of organic and inorganic solar cells seems to merge somehow with the field of inorganic solar cells as these cells are solution processed like the organic solar cells but in many aspects resemble the inorganic solar cells in their behavior. It remains exciting whether other new materials with similar properties will be found in future.

This book is based on a lecture given at the University of Konstanz for master's students with background in solid-state physics. We have not yet found such an introductional textbook on organic and hybrid photovoltaics and hope that this book will close that gap and be the starting point for everyone who is interested in this topic. We kept it short to focus only on the general ideas and methods. The reader is advised to consult the literature for deeper insights into the topics. The book is designed to give the interested reader an overview and to discuss the most relevant topics. It will be very helpful as a starting point when working on organic and hybrid solar cells. We also hope that the more advanced researcher finds it useful when consulting it for different aspects in this field of research and hopefully as a source of inspiration. The reader should have some basic background in solid-state physics, even though the most important aspects concerning semiconductor physics are briefly introduced. The book is divided into six chapters. It starts with a short general introduction giving a brief historical overview. In Chapter 2 we describe semiconductors and junctions, including an introduction to inorganic semiconductors, before discussing organic semiconductors. Chapter 3 is devoted to the working mechanisms in organic and hybrid solar cells. In this chapter the basic principles of solar cells are described and then the different organic and hybrid solar cell architectures and their working mechanisms are discussed in more detail, including bulk heterojunction, dye-sensitized, hybrid, and perovskite solar cells. In Chapter 4 we discuss the most relevant characterization techniques to investigate organic and hybrid solar cells, which includes steady-state as well as time-resolved characterization techniques. Finally in Chapter 5 we discuss some issues concerning fabrication and device lifetime, the important factors for commercialization of organic and hybrid solar cells. We finish the book with a brief conclusion and outlook.

Certainly the book focuses on many important and interesting aspects. It is a very opinionated selection of topics. There are many exciting topics that could have additionally been included. However, that would have extended the book considerably and might be less appropriate for an introduction into the field.

We realized that writing a book is far more time consuming than writing a research or review article, thesis, or book chapter as it is much longer and contains a variety of aspects. Not in all of them we are experts or do research on, which means that we had to collect a lot of information and summarize the most important aspects in a concise way. The book is certainly not perfect and we are very happy to get inputs from the readers on what could or even should be added or improved in future.

Finally we thank everyone who contributed to this book in one or another way by supporting us, especially all members of the "Hybrid Nanostructures" group at the University of Konstanz for their fruitful discussion on various topics. We also thank the students who listened to our lecture, gave us important feedback, and helped us correct the script. Finally we thank our families for their continuous support and encouragement.

Lukas Schmidt-Mende & Jonas Weickert
Konstanz, 2016

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1 Introduction

1.1 General Introduction

Currently the main source of our energy supply is delivered through not only fossil fuels, such as oil, gas, and coal, but also nuclear power using ^{235}U. As it becomes more and more apparent that these sources are limited and environmentally problematic due to the large CO_2 emission or the danger of radioactive pollution, there is a strong need for alternative sources to deliver the needed energy.

A combination of increasing energy demands and thereby the increasing CO_2 emission, which is a consequence of combustion of fuels, leads to global warming. In Figure 1.1 the temperature anomalies and CO_2 emissions over the years are plotted and a strong correlation between the emissions and the global warming is found.

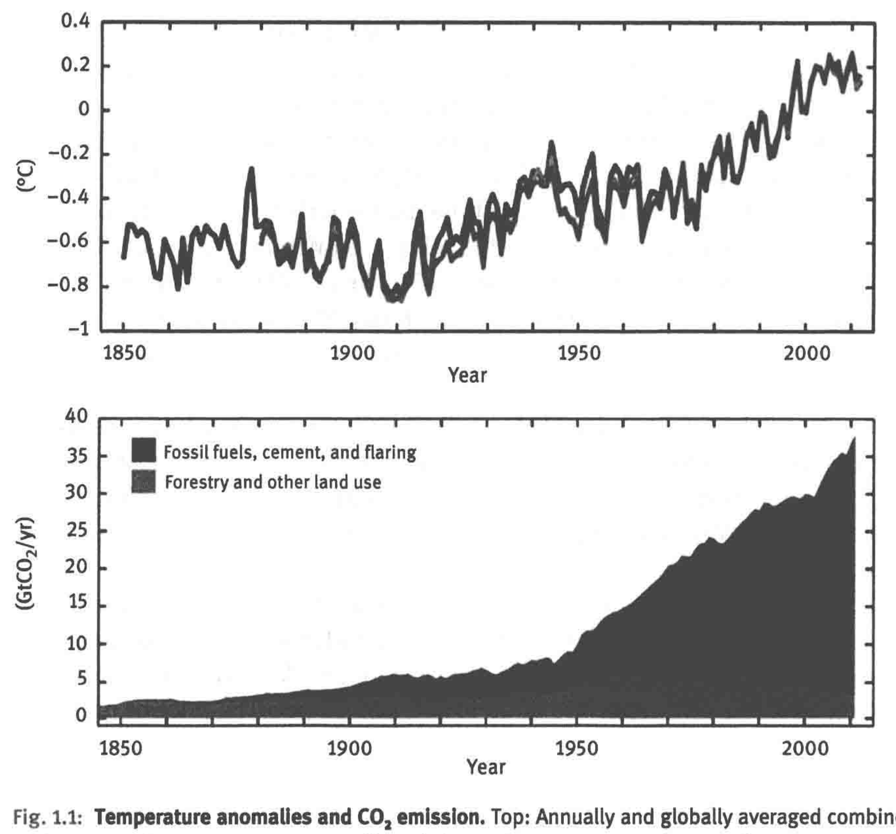

Fig. 1.1: **Temperature anomalies and CO_2 emission.** Top: Annually and globally averaged combined land and ocean surface temperature anomalies relative to the average over the period 1986 to 2005 with different data sets indicated by colors. Bottom: Global anthropogenic CO_2 emission. Quantitative information of CH_4 and N_2O emission time series from 1850 to 1970 is limited Figure adapted from [1].

In addition to these environmental issues we see a limitation of fossil fuels, which will make them more and more expensive. If we want to avoid these effects, we need to save energy and simultaneously find alternative energy sources that are renewable. Currently the largest renewable energy source are hydropower stations. Other renewable energy sources are wind power, biomass energy, geothermal power, biofuel production, tidal power, and solar power. A finding by the International Energy Agency states that renewable power could increase from just over a fifth of global electricity generation today to nearly a third by 2030. This would be a bigger share when compared to coal, gas, or nuclear power. Photovoltaics are expected to have the largest potential to grow significantly.

Renewable energy sources will be successful only if they are delivered at a competitive price compared to conventional energy sources based on fossil fuels. As the price of fossil fuels will rise due to larger demands, it will make renewable energy sources more attractive.

Conversion of the solar energy is especially interesting as the sun delivers a constant energy of around 1,360 Wm^{-2} above earth's atmosphere. Therefore, the total energy is several 1,000 times higher than the energy need of the world population.

An easy calculation allows us to give a rough estimate of the power of photovoltaics. Assuming an average solar constant of 1,360 Wm^{-2} falling on earth with a surface area of $A = 4\pi R^2$, only half of this area exposed to the sun $A = 4\pi R^2/2$ gives a irradiation of 680 Wm^{-2}. Thirty percent of the light is reflected by the atmosphere, and 6–12 hrs daylight yields an average of roughly 3–6 kWh $day^{-1}m^{-2}$. The electrical energy need is around 2×10^{16} Wh $year^{-1}$ (= 365 days) = 20.000 TWh $year^{-1}$. Ten percent efficient solar cells let us convert 450 Wh $day^{-1}m^{-2}$, resulting in an area of 1.2×10^5 km^2. Therefore "only" an area of 350×350 km^2 covered with solar cells with efficiencies of 10% would generate the 2×10^4 TWh yearly electricity demand. As solar cells can reach efficiencies considerably larger than 10%, this area can be even smaller.

The energy of the sun can also be used in other processes, such as solar thermal energy and photocatalysis. Plants make use of the sun's energy in the photosynthesis process. Photovoltaics are especially interesting where the energy is needed in the form of electricity.

Photovoltaics is one of the fastest growing technologies in the world with growth rates of 35–40% per year. Currently over 80% of the global photovoltaic market is based on crystalline silicon solar cells. Major photovoltaic plants have been installed or are being installed with capacities of up to 500 MW output. The price of photovoltaic installations has dropped dramatically over the past years. However, the energy costs of inorganic photovoltaics are still higher than those of conventional fossil-based energy sources. Organic solar cells allow a simple and cheap fabrication technique as they usually can be processed from a solution and at low temperatures. Even a roll-to-roll fabrication on plastic substrates seems to be feasible. It is expected that this can lower the cost considerably, if efficiency and lifetime become comparable to inorganic solar cells.

1.2 Brief History

In this chapter we briefly describe the history of inorganic, organic, and hybrid solar cells, listing only the most important milestones that have been achieved so far with respect to photovoltaics. It is interesting that some findings have been made by different groups in the same year, indicating that in these cases the research development promoted such findings or in other words the time was just ripe.

1.2.1 Inorganic Solar Cells

The word *photovoltaics* is a combination of the Greek word for light *φως* and the name of the Italian physicist and chemist Alessandro Volta, the inventor of the battery. The photovoltaic effect was first recognized in 1839 by the French physicist Alexandre Edmond Becquerel (the father of Antoine Henry Becquerel, known for winning the Nobel Prize for the radioactivity). While working in his father's lab at age 19, he experimented with silver chloride in an acidic solution and illuminated it while keeping it connected to platinum electrodes, which generated a voltage and current. Over 30 years later, in 1873, Willoughby Smith and Joseph May discovered that selenium changes its electrical resistance under illumination, which triggered research on this effect and in 1877 led to the observation of the photovoltaic effect in solid-state selenium by Williams G. Adams and Richard E. Day [2]. In 1883, the first photovoltaic device was developed by Charles Fritts. He coated selenium with a thin layer of gold to form a junction, which gave a solar cell performance of ~1%. Only few years later, in 1887, Edward Weston received the first patents (US389124 and US389125) on solar cells.

Many years later, in 1946, Russell Ohl from Bell Labs received the first patent on modern junction semiconductor solar cells (US2402662, "Light-sensitive device"). This can be seen as the starting point of the modern solar cell. At Bell Labs, Chapin, Fuller, and Pearson further developed this into a diffused p–n junction solar cells by diffusing dopants, which had an efficiency of 6% with a remarkable stability [3]. The cell was remeasured in 2005 – almost 50 years later – and still it showed an efficiency of 5.1%. Hoffman Electronics Corporation pioneered the fabrication of solar cells and improved its efficiency. Still the costs of these cells were about $250 per Watt, a multiple of the cost of the energy delivered by a coal plant. These high costs have always been the major hurdle to purchase photovoltaics onto the mass market. The breakthrough of solar technology came with the advent of satellites, where solar cells could deliver the energy required to power them. The processing had been further improved, which allowed to cut down the production costs considerably. With the growing silicon industry, silicon from feedstock became largely available and silicon even with minor imperfections could still be used for solar cells, although useless for the silicon electronics. Today crystalline silicon is the main material and gives highest efficiencies of over 25%. GaAs solar cells are close to 30% efficiency, and the most efficient multijunction solar cells now reach values of over 45%. However, these high efficiencies also come with a high production cost, making the price exorbitant and uninteresting for day-to-day applications.

1.2.2 Organic and Hybrid Solar Cells

In this subsection we now focus on the development of organic and hybrid solar cells. It gives an overview over the most important device architectures that have been developed up to now, which will be discussed in detail in chapter 3.

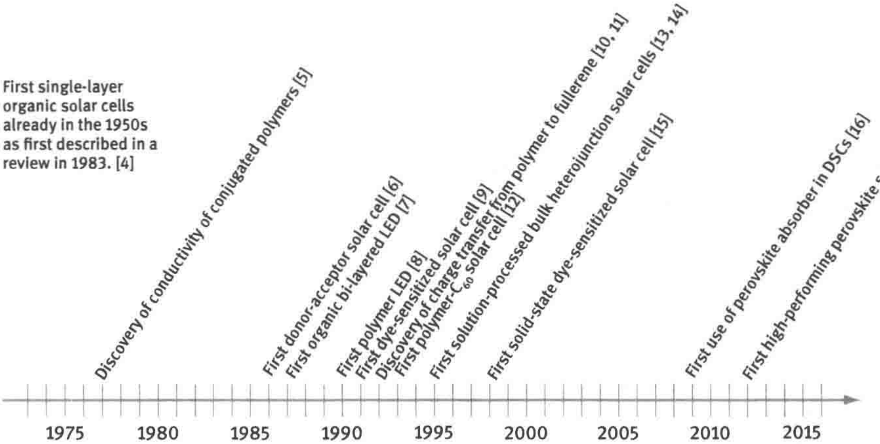

Fig. 1.2: **Milestones in organic and hybrid solar cell research.** In this timeline we have added the most important discoveries that have led to the state-of-the art organic and hybrid solar cells over the last few decades.

In Figure 1.2, we have plotted the most important milestones that have been achieved Interestingly, research on organic solar cells started very early sometime in the 1950s as described by a review on organic solar cells from 1983 written by Chamberlain [4]. Here single-layer organic solar cells have been investigated. An important milestone was the discovery of conductivity of conjugated polymers by Heeger, MacDiarmid, and Shirakawa in 1977 [5]. In 2000, they have been awarded the Nobel Prize in Chemistry for their discovery. The first modern donor–acceptor solar cell was then introduced by Tang in 1986 using a copper–phthalocyanine in combination with a perylene derivative – materials that are still under investigation. The solar cell exhibited an impressive efficiency of about 1% under AM2 illumination [6]. A tear later, the same author discovered the organic LED [7]. This was followed in 1990, by the discovery of polymer LEDs [8]. In the 1990s, the field developed rapidly. In 1991 O'Regan and Grätzel reported about the first dye-sensitized solar cell based on mesoporous TiO_2 [9]. In 1992, the groups of Yoshino and Wudl reported about electron transfer from polymer to fullerene, which is the basic working mechanism for organic donor–acceptor solar cells [10, 11]. This was followed by the first polymer–C_{60} solar cells in 1993 [12] and the first solution-processed bulk heterojunction solar cells in 1995 [13, 14]. In 1998, the first solid-state dye-sensitized solar cells were reported by Bach et al. [15]. This has triggered a lot of research in hybrid solar cells. All these cell types have been improved considerably since their first discovery. The newest milestone is the use of methylammonium lead iodide perovskite, which was first introduced as a sensitizer in a liquid electrolyte dye-sensitized solar cell architecture [16]. The real breakthrough of perovskite solar cells came in 2012 when the groups of Snaith and Grätzel/Park reported perovskite solar cells with efficiencies around 10% [17, 18]. Now this type of solar cell has further developed in terms of efficiency reaching more than 20%. Also we find a variety of different solar cell architectures leading to high-efficiency perovskite solar cells. The device physics is quite different from organic and dye-sensitized solar cells. Therefore, we see perovskite solar cells as a new additional branch of hybrid solar cells, which show remarkable properties resembling in many aspects the properties of inorganic solar cells.

Even though in the described timeline (Figure 1.2) only some important milestones are reported, it can be clearly seen that they cover the full range with the newest important results only a few years back. We expect that this timeline will need updating in future as more – not yet been discovered – milestones will add to it. This is a very vibrant field of research, and we expect many exciting further developments and achievements over the next decade.

2 Semiconductors and Junctions

To understand the function of a solar cell, a device with a complicated multilayer structure, it is imperative to take a closer look at the properties of the constitutive parts. For organic and conventional inorganic solar cells, there are semiconductors that absorb and convert light and transport charge carriers to external metal electrodes.

This chapter gives a brief overview of inorganic semiconductors and introduces the concept of doped semiconductors. We will then move on to a more general introduction to organic semiconductors. The final section of the chapter discusses semiconductor–semiconductor and semiconductor–metal junctions, which play a central role in the working mechanisms of photovoltaic devices.

For further reading on inorganic semiconductors, see, e.g. Hunklinger [19], Seeger [20], Kittel [21], Grundmann [22], and many others. Fundamentals of organic semiconductors are discussed in more detail, e.g. in Pope and Swenberg [23], Brütting [24], and Köhler and Bässler [25]. A more comprehensive overview of different electronic junctions can be found in Milnes [26] and Mönch [27].

2.1 Introduction to Inorganic Semiconductors

A semiconductor is an ensemble of atoms. It therefore exhibits properties like mass density, melting point, and stiffness, which arise from a collective behavior of the constituent elements. For a photovoltaic device, which converts photon energy into electric energy, mainly the optoelectronic properties are of interest.

2.1.1 Electronic States in Inorganic Semiconductors

2.1.1.1 Energy Bands in Solids

Within an atom, electrons can occupy only discrete electronic states (orbitals) as schematically depicted in Figure 2.1. For two atoms in close proximity the electronic states combine and form molecular orbitals. These molecular energy levels lie slightly below and above the original energy level of a single atom and effectively every energy level is split into two new levels. For every atom that is added to the solid the energy levels split accordingly, so that for N atoms every orbital splits into N states. For large numbers of atoms the energy splitting between two adjacent levels becomes very small, which can be separated by quantum mechanically forbidden energy regions where no states are located.

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