# 1
Introduction

The subject of this book is sketched in Figure 1.1. It is a heterostructure solar cell based on polycrystalline thin films comprising a metallic back contact, a semiconducting absorber layer, and some kind of emitter which is transparent for most of the solar spectrum. Typical film thicknesses are around $1-3\ \mu m$ – enough to gather most of the photons incident from the sun. The film thickness of the absorber layer is in the size range of the polycrystalline grain and the absorption length of sunlight. All films are deposited by astonishingly simple methods, given that chalcogenide based cells today have the highest efficiency among the thin film solar cells. In the following, we give a historical digest on solar cell development. We try to label some milestones of progression and understanding. Certainly, the prospect of these cells is more difficult. Hence, we only outline some facts and useful estimations.
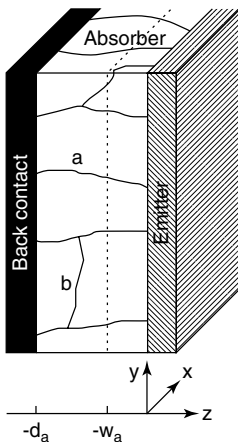

Figure 1.1 Sketch of a polycrystalline thin film cell with window layer and absorber layer. The boundaries of the large grains of the absorber layer are outlined. The thickness of the window and absorber layers are d_w and d_a. w_a is the width of the space charge layer within the absorber layer. The letters (a) and (b) indicate perpendicular (a) and parallel (b) grain boundaries with respect to the space charge layer.

1.1
History of Cu(In,Ga)(S,Se)$_2$ Solar Cells

The history of Cu(In,Ga)Se$_2$ (CIGSe)-based solar cells began in 1975 when Bell laboratory scientists achieved 12% solar energy conversion efficiency with a cell where a layer of CdS was evaporated onto a CuInSe$_2$ single crystal [1]. Stimulated by this

result, the development of CuInSe$_2$ thin films started. At the University of Maine (see Figure 1.2), thin films were deposited by dual source evaporation of CuInSe$_2$ and Se [2]. Small area devices in the substrate configuration were built with an efficiency in the range of 5%. In the early 1980s, companies started developing CIGSe solar cells (see Figure 1.2). At this stage, two different preparation concepts for CIGSe were pursued. Boeing used a co-evaporation process where Cu, In, and Se were deposited from separate evaporation sources. The Boeing group was the first to demonstrate a more than 10% efficient thin film device [3]. Arco Solar, in contrast, developed a deposition–reaction process using Cu and In metallic precursors, with H$_2$Se as the reacting chalcogen source. Surprisingly, for a period of time the deposition–reaction technology gave better device efficiencies than the co-evaporation approach (see Figure 1.2). The reason was that, during the reaction step, the absorber layer was doped with Na – a fact that was overlooked by the rest of the research community. In 1995, Na-containing glasses became standard and both technologies – co-evaporation and deposition–reaction – gave almost similar efficiencies of around 14% on the cell level. The deposition–reaction technology, however, was much easier to scale up: sputtering of metal films was well established in the glass industry. The limitation was rather in the width of available quartz tubes for the selenization reactor. Accordingly, the first modules developed by Arco Solar were only 1 ft (305 mm) wide. Parallel selenization of up to 20 substrates was a batch process with around 6 h process time.
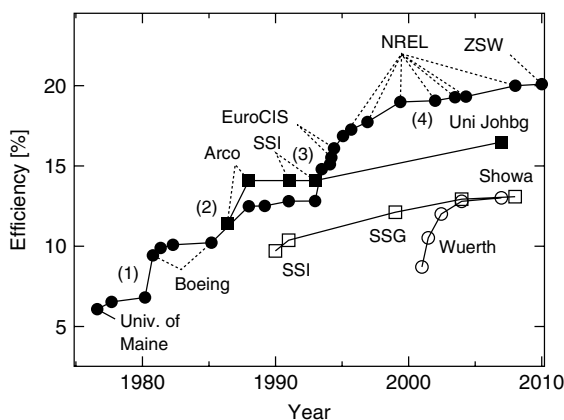
Figure 1.2 Solar energy conversion efficiency of thin film cells and modules based on Cu(In,Ga)(S,Se)$_2$ (CIGSSe). Full circles – cells by co-evaporation, open circles – full modules by co-evaporation, full squares – cells from deposition–reaction technology, open squares – full modules from deposition–reaction. Abbreviations: Arco – Arco Solar, SSI – Siemens Solar Industries (USA), EuroCIS – University Stuttgart and University Uppsala, SSG – Siemens Solar AG (Germany), Wuerth – Wuerth Solar (Germany), Showa – Showa Shell (Japan), Uni Johbg – University of Johannisburg (South Africa), NREL – National Renewable Energy Laboratories (USA), ZSW (Germany). Labels (1) to (4) refer to milestones of (CIGSSe) development which are discussed in the text.
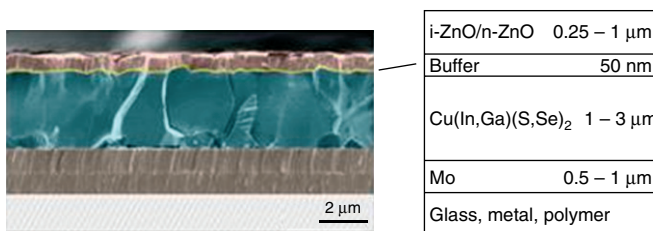
The headstart achieved by co-evaporated solar cells (not modules) began with employing more complicated evaporation processes. The so-called three-stage process invented in 1994 by the National Renewable Energy Laboratories (NREL) group [4] provided the basis for an efficiency of 20%. Around 2000, an effort was made at Wuerth Solar to bring the co-evaporation technology into production. Wuerth Solar designed line-evaporation sources that were able to deposit on substrates 2 ft wide. As depicted in Figure 1.2, co-evaporated module efficiency could rapidly compete with modules from the deposition–reaction technology. In 2008, several laboratories around the world had the experience to prepare a CIGSe solar cell with an efficiency above 19%. Concerning large area modules (>0.4 m^2), both co-evaporation and deposition–reaction technologies reached above 12% efficiency. While writing these lines, submodules of Cu(In,Ga)(S,Se)$_2$ formed by the deposition–reaction process have been reported with module efficiencies approaching 16% [5]. Both process schemes are still in competition and may further be pursued in parallel. Today, a large number of subvariants of these process schemes are being investigated by research laboratories and companies. They all have the medium-term goal of a thin film module with more than 15% efficiency produced with costs below 0.5 €/W$_p$.

1.1.1
Milestones of Cu(In,Ga)(S,Se)$_2$ Development

As the first evaporated CuInSe$_2$ films (from CuInSe$_2$ and Se evaporation sources) suffered from poor control of the ratio of copper to group III element, Cu/In (in early days the group III element was only indium), the first milestone, labeled (1) in Figure 1.2, was to apply a triple-source evaporation geometry in which the copper and indium rates during deposition and thus the Cu/In ratio in the film could deliberately be adjusted. Soon it was recognized that the best cell efficiencies were achieved by a copper-poor composition, that is, Cu/In < 1.

Around 1988, two innovations, summarized under milestone (2), led to devices with ∼12% efficiency. The first innovation was the use of a thin CdS layer prepared in a chemical bath. This thin buffer layer (see Figure 1.3) rendered a reduction of the optical absorption and a better coverage of the polycrystalline CuInSe$_2$ surface. Due to the complete coverage of the absorber by a CdS layer ∼50 nm thick, shunting

i-ZnO/n-ZnO	0.25 – 1 μm
Buffer	50 nm
Cu(In,Ga)(S,Se)$_2$	1 – 3 μm
Mo	0.5 – 1 μm
Glass, metal, polymer	

2 μm

Figure 1.3 Schematic outline of a substrate-type solar cell based on Cu(In,Ga)(S,Se)$_2$ (CIGSSe).

paths could be eliminated. Chemical bath deposition of the buffer at that time became standard, and today turnkey equipment for this process step is available. The second innovation was the employment of a Cu-rich growth period during CuInSe$_2$ film formation. Although CuInSe$_2$ films require a Cu-poor composition in the end, their morphology and electronic properties are superior if they are partly grown under an excess of Cu. CIGSe films grown by the deposition–reaction process pass the Cu-rich growth regime automatically.

In the beginning of the 1990s, it became clear that CuInSe$_2$ solar cells perform better if the cells are prepared on sodium (Na)-containing glass and if part of the indium is replaced by gallium (Ga). (As a speciality of the deposition–reaction process, also a part of the selenium was replaced by sulfur.) Thus, the absorber became a multinary compound semiconductor. This established milestone (3) which allowed demonstrating efficiencies of around 14%. Today, Na and Ga doping is an issue for all types of CIGSe preparation. With the introduction of Ga (and S), the CuInSe$_2$ cell became a CIGSSe cell with a material stack as shown in Figure 1.3 – a molybdenum back contact, a Cu(In,Ga)(S,Se)$_2$ absorber layer, a CdS buffer layer, and ZnO formed by two separate layers. We note, however, that the principle outline of the cell (Mo/absorber/CdS/ZnO) was invented in 1987 by the ARCO Company [6].

Although in the mid-1990s there was still room for improvement for all types of CIGSe preparation techniques, it was a very particular innovation which yielded around 18% devices and brought up milestone (4) at the end of the 1990s. The use of a complicated three-stage co-evaporation process which until then had only been realized in the laboratory. The principle of this process is explained in Section 5.2.3. Subtle parameter variations and the optimization of the contact scheme for single 0.5 cm^2 cells brought up a cell of 20% air mass (AM) 1.5 efficiency [7]. Figure 1.4 shows the current–voltage curve of such a highly efficient CIGSe solar cell (redrawn from [8]). This laboratory cell shows the enormous potential of CIGSe
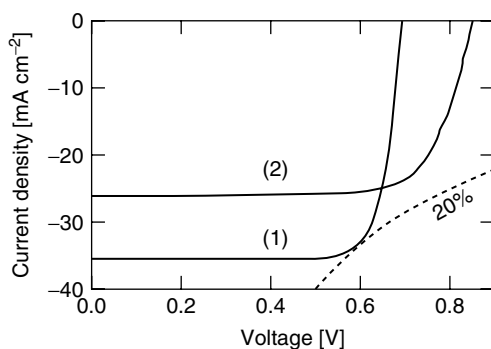

Figure 1.4 Current density versus voltage curve of (1) a high efficiency Mo/Cu(In,Ga)Se$_2$/CdS/ZnO solar cell and (2) a high efficiency BC/CdTe/CdS/Zn$_2$SnO$_4$/Cd$_2$SnO$_4$ solar cell (redrawn after Ref. [8]).

solar cells. Also, cells made by the deposition reaction process have been improved in the past decade due to parameter optimizations (Figure 1.2).

1.2
History of CdTe Solar Cells

The development of CdTe solar cells was initially motivated by their potential space application in communication satellites. In 1963, the first thin film solar cell of the type n-CdTe/p-Cu$_2$Te was demonstrated by a General Electric Research Laboratory [9]. The cell had an efficiency of 6%, but device instability (caused by Cu diffusion) led to the quest for an alternative heteropartner for CdTe. In 1972, Bonnet and Rabenhorst presented a p-CdTe/n-CdS heterojunction solar cell which also had 6% efficiency [10]. The CdTe layer was deposited by vapor transport deposition (cf. Section 5.1.4), a method that today is used in mass production. These cells were of the substrate type, having a Mo back contact and a CdTe thickness of more than 10 µm [10]. Ten years later, Tyan *et al.* [11] presented a superstrate thin film cell with more than 10% efficiency (Figure 1.5). This cell was grown by closed-space sublimation – the leading method of later champion devices. Encouraged by this achievement, several companies started inhouse developments. The goal was to find the best low-cost deposition method that allowed high throughput and that could deliver more than 10% efficient modules. Surprisingly, this goal was reached using very diverse deposition methods such as vapor transport deposition, electrodeposition, spray pyrolysis, and screen printing (cf. Table 5.2). CdTe was
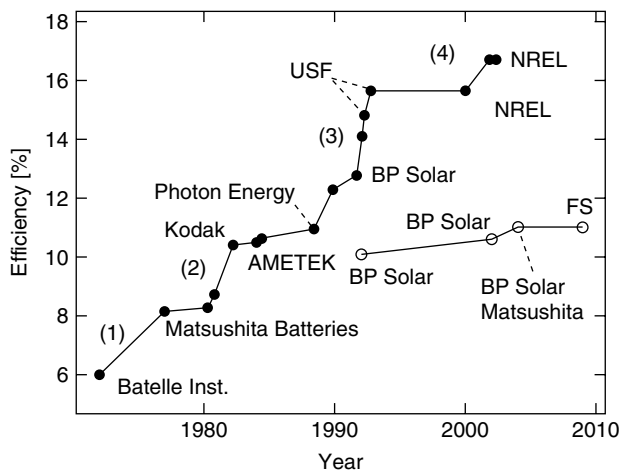
Figure 1.5 Solar energy conversion efficiencies of thin film cells (full marker) and modules (open markers) based on CdTe. Abbreviations: USF – University of South Florida, NREL – National Renewable Energy Laboratories (USA), FS – First Solar.

considered as an extraordinary forgiving material. Nevertheless, it was not earlier than 2002 that CdTe modules became a mass product on basis of vapor transport deposition while the so-called low-cost methods such as spray pyrolysis and screen printing have been ruled out – at least for the time being. Reasons for the stepback of early industrial players were probably rather in strategic decisions than in technological obstacles. On the cell level, the NREL (USA) in 2001 achieved the long-standing record of 16.5% efficiency [8]. They used close-space sublimation for the absorber preparation. Nowadays, CdTe modules are produced on the GW_p/year level and currently are the cost leader in the photovoltaic industry. In a sense, the CdTe technology exemplifies the cost advantage of thin film photovoltaics over wafer-based technologies – an advantage that has been claimed for quite some time.

1.2.1
Milestones of CdTe Development

Soon after realization of the first CdS/CdTe device it was recognized that this type of cell is more efficient if formed in the superstrate configuration. Use of this configuration (Figure 1.6) was the first milestone, as shown in Figure 1.5. Interdiffusion between CdS and CdTe which can easily happen in the process sequence was believed to be a reason for the superior performance of the superstrate configuration. The second milestone in 1982 was the incorporation of oxygen during film deposition. Several effects of oxygen on film properties are discussed in Section 5.1.6.

Use of chlorine may have been implicit for several preparation techniques such as screen printing and electrodeposition. But it was the third milestone when researchers after 1990 became aware that the activation of the CdTe by chlorine treatment substantially increases the device efficiency. Since that time, chlorine activation using specific and critical process parameters has always been part of the process. The result of such parameter optimization were laboratory-scale solar cells with efficiencies exceeding 15% – first demonstrated by Ferekides *et al.* [12]. It took almost 10 years before the fourth milestone led to a 16.5% device. We identify this

Glass	
TCO	0.5 – 1 µm
CdS	100 nm
CdTe	2 – 8 µm
Back contact	

1 µm
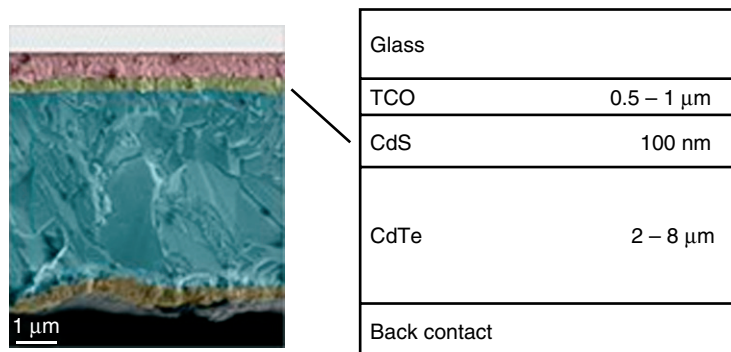
Figure 1.6 Schematic outline of a superstrate-type solar cell based on CdTe with a ZnTe:Cu/Ti back contact.

milestone with the insertion of a high mobility window layer of Cd-stannate. The current–voltage (JV) curve of such a highly efficient device is shown in Figure 1.4. Highest module efficiencies are around 11% since the champion cell technology has not yet been completely transferred to production.

1.3
Prospects of Chalcogenide Photovoltaics

If chalcogenide photovoltaics are to substantially contribute to future energy supply, we speak of some terawatts of installed capacity. Currently, chalcogenide module production is in the gigawatts/year range, mostly driven by one CdTe module producer (First Solar). We want to address the question about possible hurdles for future expansion. Zweibel assessed future cost reduction potentials of thin film photovoltaics [13]. Table 1.1 condenses this work and reveals that both technologies [CdTe and $Cu(In,Ga)(S,Se)_2$] have about the same cost perspective for large scale production of around 0.5 $/W_p$. Already today (2009) CdTe module production is reported with costs of 0.85 $/W_p$ at an efficiency of 11%. Thus, it appears realistic that future cost reduction and efficiency increase will lead to the figures in Table 1.1. With an anticipated module lifespan of 30 years and the listed costs for ground-mounted and rooftop installations, these numbers translate into about 0.06–0.09 $/kWh AC electricity costs in sunny climates with around 1800 kWh m^{-2} year^{-1} [13]. Even lower-cost figures are derived in a study by Keshner and Arya (Hewlett Packard) [14]. In the climate referenced above, the energy payback time of today's CdTe modules is around 1.1 years [15]. Thus, we see no hurdles for CdTe and $Cu(In,Ga)(S,Se)_2$ technology expansions in terms of costs and energy payback time.

A chalcogenide thin film module contains, depending on the chalcogenide film thickness, some grams per square meter of metals and chalcogens (see Table 1.2). Among the materials listed in Table 1.2, indium and tellurium are considered most critical in terms of availability. In order to estimate the maximum installation possible based on each material, two different approaches are pursued: (i) use of published material reserves and (ii) extrapolation of current annual material

Table 1.1 Cost projections of CdTe and $Cu(In,Ga)(S,Se)_2$ module production according to Ref. [13] assuming gigawatts/year production level.

	Projected efficiency (%)	Module costs ($/W_p$)	Systems costs for large ground mounted systems ($/W_p$)	Systems costs for large commercial roof top systems ($/W_p$)
CdTe/glass	14	0.47	1.12	1.61
CIGSSe/glass	15.5	0.51	1.18	1.67

Table 1.2 Material consumption for chalcogenide modules with absorber thickness 1 μm and material resources after United States Geological Survey data for 2008. Maximum possible installations of CdTe and $CuIn_{0.7}Ga_{0.3}(S,Se)_2$ single junction solar cells assuming efficiencies of 14 and 15.5%, respectively, a module lifespan of 30 years, and complete use of the resource.

	g/m^2	Reserves $(10^6 \, kg)$	Reserve base $(10^6 \, kg)$	Maximum installation (TW_P) according to Anderson [16]	Maximum installation (TW_P) according to Schubert *et al.* [17]	Maximum installation (TW_P) according to Zweibel [13]
Cd	3.2	490	1200	12.5	–	–
Te	3.3	22	48	1.51	–	15
In	1.5	11	16	3.8	1.29	8.5
Ga	0.27	No data	>1000	No data	–	–
Se	2.4	86	172	12.5	–	150

extraction. Both approaches are reflected in Table 1.2. Anderson [16] uses reported reserves for indium and tellurium and derives 1.51 and 3.8 TW_p maximum installation for CdTe and Cu(In,Ga)(S,Se)$_2$, respectively. About half this number for Cu(In,Ga)(S,Se)$_2$ is obtained by Schubert *et al.* [17] but there only about 50% use of indium for PV is assumed. The original figures of Anderson need correction because indium reserve estimations increased by a factor of ~2.5 (!) between 2007 and 2008. Interestingly, for 2009 no data are given by the U.S. Geological Survey, reflecting the fact that the reserves data for indium contain large uncertainties. This is why Zweibel [13] uses a different approach. Today, indium is exploited from Zn ore (although also contained in copper, lead, tin, and tungsten ores). Extrapolating the Zinc mining capacity with 1% annual growth gives an alternative estimation for indium reserves. This approach (and the corresponding one for tellurium) is used by Zweibel in Ref. [13] and in the respective column of Table 1.2. After correction to 1 μm absorber thickness (for the sake of comparability) we arrive at around 10 TW_p for each technology. Thinning the chalcogenide absorber to 0.5 μm simply doubles these values. (Today, the world average power demand is around 10 TW.) We may conclude that – based on the current estimates – chalcogenide thin film solar cells based on CdTe and Cu(In,Ga)(S,Se)$_2$ can substantially add to the world power supply. However, it is questionable whether the reserves are sufficient to make them the only photovoltaic technologies of the future.