Chapter 1
Introduction – Physics and Technology of Amorphous-Crystalline Heterostructure Silicon Solar Cells

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1.1 General Introduction

Although photovoltaic solar energy technology (PV) is not the sole answer to the challenges posed by the ever-growing energy consumption worldwide, this renewable energy option can make an important contribution to the economy of each country. According to the *New Policies Scenario* of the "World Energy Outlook 2010" published in November 2010 by the International Energy Agency (IEA) [1], it is to be expected that the share of renewable energies in global energy production increases threefold over the period 2008-2035, and that almost one third of global electricity production will come from renewables by 2035, thus catching up with coal. The "Solar Generation 6" report of the European Photovoltaic Industry association published in October 2010 [2] predicts in its *Solar Generation Paradigm Shift* Scenario that by 2050, PV could generate enough solar electricity to satisfy 21% of the world electricity needs, i.e. a total of up to 6750 TWh of solar PV electricity in 2050, coming from an installed capacity of 4670 GW in 2050. This is to be compared with 40 GW installed in the world at the end of 2010 [3].

After the first solar cell was demonstrated in silicon 55 years ago [4] the cost has declined by a factor of nearly 200, and high-throughput mass-production compatible processes are omnipresent all over the globe. More than 90% of the current production uses first generation PV wafer based crystalline Silicon (c-Si), a technology with the ability to continue to reduce its cost at its historic rate [5,6]. The direct production costs for crystalline silicon modules are expected to be around 1 €/Wp in 2013, below 0.75 €/Wp in 2020 and lower in the long term, as stated in the Strategic Research Agenda of the European Photovoltaic Technology Platform [7].

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However the challenge of developing photovoltaic technology to a cost-competitive alternative for established fossil-fuel based energy sources remains enormous and new cell concepts based on thin films of various types of organic and inorganic materials are entering the market. Thin film silicon (TFS), cadmium telluride (CdTe), copper indium selenide (CIS) generally are denoted as the second generation of PV technologies and are currently considered a very interesting market alternative to crystalline silicon. Advanced thin film approaches such as dye-sensitized titanium oxide (TiO_2) and blends of polythiophene and C_{60} (P3HT:PCBM) [8] are showing fast progress. World-record solar cell efficiencies are regularly updated, see e.g. [9], and some interesting initiatives related to their industrialization and commercialization have recently been undertaken.

For large scale PV deployment in large power plants or in building integrated applications it is a prerequisite that the performance of solar energy systems is enhanced by assuring low cost in production and long term reliability (>25 years). This requires the following issues to be addressed: 1) increase of the efficiency of solar irradiation conversion; 2) decrease of the amount of materials that are used, while these materials should be durable, stable, and abundant on earth; and 3) reduction of the manufacturing and installation cost.

The fantastic boom of thin film technology in recent years can suggest further development on the medium to long term due to the application of innovative concepts to conventional materials and developments of new classes of thin film materials stemming from nanotechnologies, photonics, optical metamaterials, plasmonics and new semiconducting organic and inorganic sciences, most of them recognized as next (third) generation approaches.

On the other hand the growth of the PV industry is also requesting well proven technology in order to sustain the emerging market; here, crystalline silicon has a long history of ‘pulling rabbits out of the hat’ [5].

Today, the industry has reached a new level of scale that is mobilizing vast new resources, enthusiasm, skills, and energy in order to reduce wafer thickness, enhance efficiency and improve processes related to substrate cleaning, junction realization, surface passivation, contact realization. We see that PV’s historic price reduction is a result from the combined effects of step-by-step evolutionary improvements in a wide variety of areas rather than one or two huge breakthroughs [5,6]. For example, processes such as dry texturing, spray-on phosphorus doping sources or impurity gettering have become standard, while last but not least actions related to increase the factory size and automation further lead to cost reductions (“economies of scale”).

In contrast, larger values of the conversion efficiency of PV technology have been reached with the realization of sophisticated crystalline silicon (c-Si) cell structures, involving numerous and very complicated steps. This approach inevitably implies an increase of costs, which is not compatible with industrial production requirements that demand simple, high-throughput and reproducible processes.

In order to realize reliable devices characterized by high efficiency and low cost, an approach has been developed on the basis of amorphous/crystalline silicon heterojunction solar cells (SHJ), which combines wafer and thin film technologies. In this area impressive results were achieved by Sanyo Electric with the so called a-Si/c-Si Heterojunction with Intrinsic Thin layer (HIT) solar cell [10,11]. This technology showed excellent surface passivation (open circuit voltage (V_{oc}) values of around 730 mV) and the highest power conversion efficiency to date for a cell size of 100.4 cm^2: 23.0% was obtained [11].

1.2 Amorphous Crystalline Heterojunction Solar Cells

The design of the silicon hetero-junction solar cell is based on an emitter and back surface field (BSF) that are produced by low temperature growth of ultra-thin layers of amorphous silicon (*a*-Si:H) on both sides of a thin crystalline silicon wafer-base, less than 200 µm in thickness, where electrons and holes are photogenerated. The low temperature *a*-Si:H deposition lowers the thermal budget in the production of the cell (see Fig. 1.1), and at the same time will allow for high-throughput production machinery. Taken together, this can lead to a considerable lowering of manufacturing costs thus opening opportunities for the production of GWp/year manufacturing plants to sustain the booming PV market.

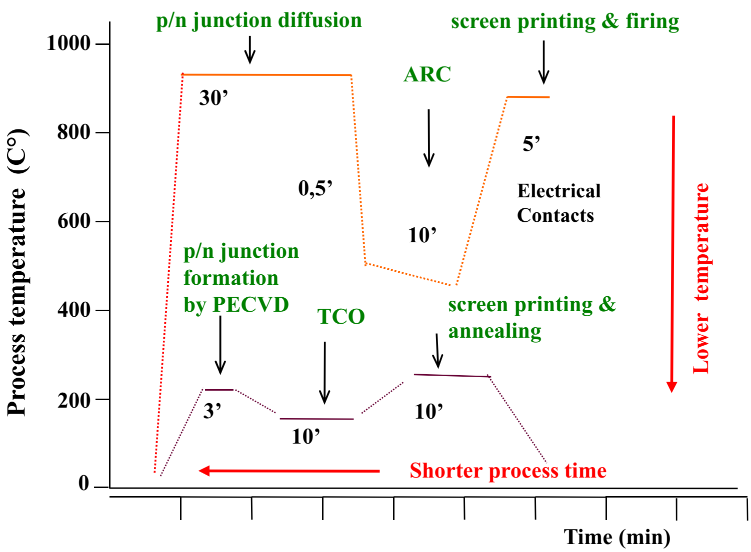

Fig. 1.1 Authors’ estimated thermal budget and process time for the conventional c-Si technology (top curve) and SHJ technology (bottom curve).

The idea of making solar cells from silicon heterojunctions is a rather old one: It was first published in 1974 by Walther Fuhs and coworkers from the University of Marburg (Germany) [12]. However, it turned out that to realize the V_{oc} potential > 700 mV inherent to the heterojunction concept, it is mandatory to include additional, very thin (of the order of 10 nm) undoped – so called intrinsic – *a*-Si:H buffer layers between the wafer and the doped (emitter or BSF) *a*-Si:H layers. Briefly, the reason is that the defect density in *a*-Si:H increases strongly with doping, and this leads to an increase in interface defect density at the *a*-Si:H/*c*-Si junction, thus to enhanced recombination and a lower V_{oc}. This finding is the essence of a patent filed by Sanyo in 1991, which can be seen as the “core patent”

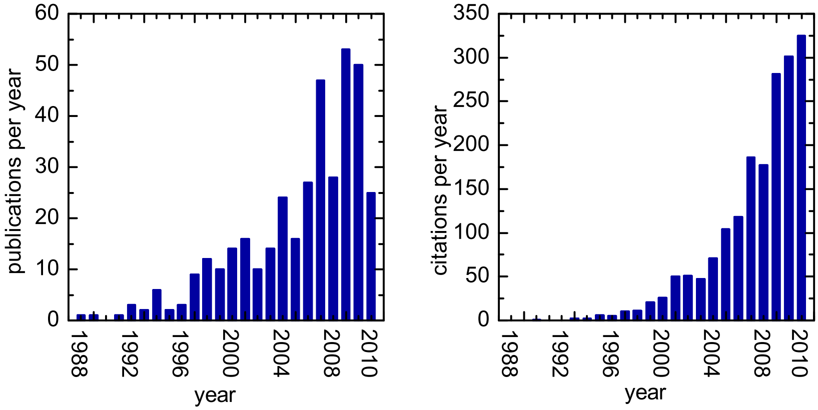

Fig. 1.2 Development of the number of both publications and citations related to silicon heterojunction solar cells over time [14].

for the subsequent successful commercialization of their so-called "HIT" concept. This patent has expired in 2010. A more in-depth discussion of the intellectual property aspect can be found in [13].

As a consequence, over the last decade, there have been many encouraging results on developing alternative concepts making use of *a*-Si:H/*c*-Si heterojunctions for high efficiency cells, such as omitting the undoped buffer and lowering the doping levels in the emitter and BSF, working on p-type *c*-Si substrates (the HIT cell is produced on n-type material), or on modifications to the *a*-Si:H layers like using *a*-Si:H/*μc*-Si stacks, *a*-SiC:H etc. This is reflected in the steadily increasing number of publications and citations related to *a*-Si:H/*c*-Si heterojunction solar cells, cf. Fig. 1.2[1]. Still, it appears that among other factors, the expiry of the mentioned "core patent(s)" has contributed significantly to the strongly increased interest in HIT-type cells seen in the last few years.

Today, many research groups and industries are pursuing intense R&D to further develop the a-Si:H/c-Si heterojunction technology. One such consortium has received funding from the European Commission in the framework of the 7th Research Framework Programme to develop a knowledge base and optimized device structure based on new insights in the physics and technology of wafer-based silicon heterojunction devices, within the project "*Heterojunction Solar Cells based on a-Si c-Si"* (HETSI) [15] [2].

[1] The database used for this analysis does not contain the proceedings of the European photovoltaic conferences prior to ~ 2008.

[2] The partners (acronym, country) are Institut National de l'Energie Solaire (INES, FR), Centre National de la Recherche Scientifique (CNRS, FR), Energieonderzoek Centrum Nederland (ECN, NL), Utrecht University (UU, NL), Agenzia Nazionale per le Nuove Tecnologie, l'Energia e lo Sviluppo Economicamente Sostenibile (ENEA, IT), Interuniversity MicroElectronics Centrum (IMEC, BE), Institut de Microtechnologie - Ecole Polytechnique Fédérale de Lausanne (EPFL, CH), Helmholtz-Zentrum Berlin für Materialien und Energie (HZB, DE), SOLON SE (DE), Photowatt SAS (FR), Q-Cells SE (DE), and ALMA Consulting Group SAS (FR).

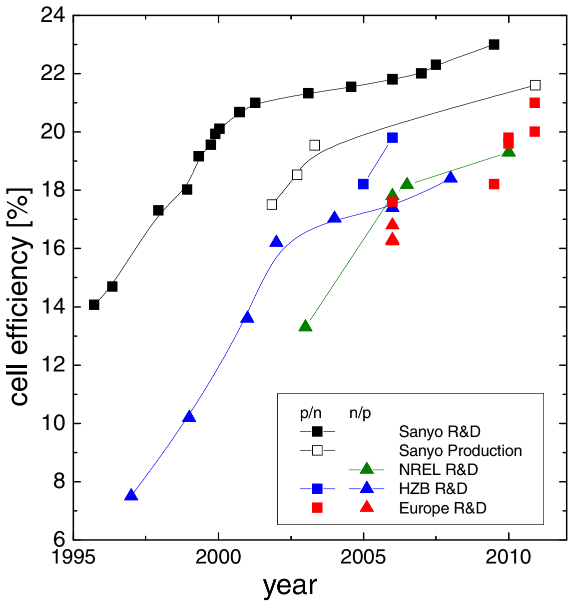

Fig. 1.3 Development of *a*-Si:H/*c*-Si heterojunction cell efficiency vs. time. Both (n)*a*-Si:H/(p)*c*-Si and (p)*a*-Si:H/(n)*c*-Si cell structures are shown.

The reported cell efficiencies have developed accordingly: Fig. 1.3 gives a (non-exhaustive) overview on the progress over time, where the distinction is made between (n)*a*-Si:H/(p)*c*-Si type cells and the "canonical" (p)*a*-Si:H/(n)*c*-Si structure as used by Sanyo. There is evidence for the gap in cell efficiencies between the two doping sequences being due to differences in fundamental device physics (carrier mobilities, band offsets), cf. Chapter 6 in this book. Furthermore, it is apparent that the Sanyo HIT cell has a significant lead on the reported cell efficiencies, by ~2% absolute at the time of writing. Nevertheless, others are covering lost ground at a fast pace: The latest reported cell efficiencies from NREL (US) are 18.2% on n-type and, interestingly, 19.3% (V_{oc} of 678 mV) on p-type wafers [16]. In Europe, the highest efficiencies reported so far are 21.0% obtained at Roth & Rau Switzerland in cooperation with EPFL Neuchâtel [17] and up to 19.6 % (20 % on 100 cm²) with a V_{oc} up to 718 mV on industrially relevant surfaces, i.e. large area 148 cm² pseudo-square n-type *c*-Si industrial wafers [18]. Recently Sanyo reported on opportunities to reach impressive efficiencies over 23% based on the utilization of very thin wafers (<100 µm) [19].

The realization of high quality a-Si:H/c-Si heterojunctions is not a trivial process requiring a very deep knowledge of several chemical and physical aspects on which the interface formation and the doped layers growth is based. Surface cleaning and/or preparation are critical, and chemistry and physics of the gas phase interaction during plasma deposition or treatment is another key issue [20]. Different process schemes affect structural quality of deposited films, surface morphology, roughness, surface reactivity and surface composition. The kinetics of impinging plasma particles and the formation of chains and islands of radicals on the surface dramatically change electrical and optical properties of the deposited films including the optical gap, activation energy, band offset, band bending, gap state and interface state density.

After formation of the a-Si:H/c-Si heterojunction, the cell is contacted using a ~80 nm thin transparent conductive oxide (TCO) layer and a metal grid on the front. The TCO is typically InO doped with Sn (ITO) or ZnO doped with Al. Often, a TCO is also used to form a dielectric mirror on the back side of the cell. Thus, to understand and optimize the whole a-Si:H/c-Si solar cell, also the influence of the TCOs on the optoelectronic properties of the cell has to be considered: Due to its high doping, the TCO behaves electronically like a metal with rather poor charge carrier mobility, and the electronic behavior of the TCO/a-Si:H junction is usually assumed as similar to a metal-semiconductor junction. The TCO work function plays an important role for the band alignment in the TCO/a-Si:H/c-Si structure and for charge carrier transport across the heterojunctions. Furthermore, TCO deposition on the about 10 nm thin a-Si:H is usually done using sputter processes; here, the possibility of damaging the delicate a-Si:H/c-Si interface during this sputter process should be taken into consideration and has to be accounted for during process optimization.

1.3 HETSI Workshop

A workshop has been organized at Utrecht University in February 2010 by the HETSI Consortium, at which many experts in the field presented an overview of the state-of-the-art in physics and technology of amorphous-crystalline heterostructure silicon solar cells, including a hands-on training session on computer modeling of cells. Over 80 attendees coming from different organizations and countries around the globe experienced an informal atmosphere with ample interaction possibilities.

In this book, the contributors to this workshop have written on their expertise, and we believe that as a whole, the book contains a broad overview of amorphous-crystalline heterostructure silicon solar cells, from the fundamental physical principles to the experimental and modeling details. It is intended to serve the strongly growing scientific and industrial PV community, not limited to silicon heterojunctions.

1.4 Guide to the Reader

The content of this book is organized as follows: Chapter 2 (Miro Zeman and Dong Zhang) introduces the heterojunction concept: The best wafer-based homojunction and heterojunction crystalline silicon solar cells are compared, and the advantages of heterojunction silicon solar cells related to the processing of the junction and solar cell operation are explained. The current status of SHJ R&D is outlined, summarizing the different approaches by institutes world-wide and comparing to Sanyo's HIT cell concept. This sets the stage for the subsequent Chapters 3-10 that follow loosely the processing steps of an actual silicon heterojunction cell. Chapters 11-14 then deal with characterization and modelling of SHJ cells, followed by two chapters on modelling and realization of interdigitated back contact silicon heterojunction (IBC-SHJ) cells. The final chapter 17 closes this book by arguing that silicon heterojunction cells are a smart choice for the high efficiency cell of the future.

Chapter 3 (Heike Angermann and Jörg Rappich) discusses the wet-chemical pre-treatment of c-Si wafers. This is a mandatory processing step to achieve a low density D_{it} of surface states on the wafer, which influences strongly the passivation quality at the a-Si:H/c-Si interface. The influence of these treatments on surface morphology and electronic interface properties is discussed for a wide scope of materials comprising not only a-Si:H, but also Si oxides (SiO_x), Si nitride (a-SiN_x:H) and Si carbide (a-SiC:H), which are frequently applied in Si heterostructure solar cells. An important aspect is the stability of wet-chemical surface passivation during storage in ambient air, which is found to be strongly influenced by the preparation-induced surface morphology. As shown for various heterojunction structures, the effect of optimized wet-chemical pre-treatments can be preserved during the subsequent soft PECVD growth of a-Si:H, a-SiN_x:H or a-SiC:H.

Chapter 4 (Jörg Rappich) is also devoted to c-Si surface preparation, but focuses on advanced concepts of using electrochemistry approaches for c-Si surface passivation, such as electropolishing in the current oscillating regime in diluted HF solutions. In addition, the use of *in-situ* photoluminescence and surface photovoltage is put forth as non-destructive technique to monitor the electronic surface properties during electrochemical oxidation, hydrogenation, and grafting of organic molecules and ultra-thin polymeric layers.

Chapter 5 (Pere Roca i Cabarrocas) provides an overview of the many deposition processes presently in use for the deposition or growth of amorphous and microcrystalline silicon. It is pointed out that the choice of the deposition technique may help to favour a particular type of film precursor, in particular SiH_3 which is often considered as the most suitable to obtain device grade material. The growth process and film properties are mainly controlled by the surface and subsurface reactions: a growth zone exists close to the film surface, where cross-linking reactions leading to bulk-like formation take place. It is suggested that film properties are governed neither by the film precursor, nor by the deposition technique. The chapter closes with the issue of substrate dependence of the growth process, which is of special importance in the case of heterojunction solar cells.

Chapter 6 (Lars Korte) discusses the electronic properties of the ultrathin a-Si:H layers used in SHJ cells and their interface to the c-Si wafer. The well-known properties of thick (several 10–100 nm) a-Si:H layers such as those used in a-Si:H *pin* cells are briefly summarized. Subsequently, it is shown how for ultrathin a-Si:H on c-Si substrates the density of occupied valence band and defect states $N_{occ}(E)$ and the position of the Fermi level in the band gap can be measured. The measured *a*-Si:H properties are correlated to the band bending in the *c*-Si absorber, to charge carrier recombination at the *a*-Si:H/*c*-Si interface and to solar cell open circuit voltage V_{oc}. The current state-of-the-art of *c*-Si surface passivation by (i)*a*-Si:H is reviewed. Furthermore, the use of temperature-dependent current-voltage measurements on complete *a*-Si:H/*c*-Si solar cells to extract information on recombination and transport is discussed. The chapter also shows how an important parameter of the *a*-Si:H/*c*-Si junction, the band offset in the valence and conduction band edges, can be determined using a special variant of photoelectron spectroscopy.

Chapter 7 (Stefaan De Wolf) takes a closer look at the a-Si:H/c-Si interface passivation and its correlation to the a-Si:H properties: The relevant literature on *c*-Si surfaces is briefly reviewed, including the effect of hydrogenation of surface states. The physical passivation mechanism of intrinsic *a*-Si:H is elucidated, and it is concluded that it stems from chemical surface state passivation, i.e. saturation of Si dangling bonds by hydrogen, similar to defect passivation in the *a*-Si:H bulk. For these films, it is also argued how epitaxial growth may detrimentally influence the passivation quality. The effect of doping on the amorphous films is discussed, and an explanation is proposed for the experimental fact that *a*-Si:H/*c*-Si interface passivation decreases when (p)*a*-Si:H or stacks of (*p*/*i*)*a*-Si:H are deposited, as compared to passivation by (i)*a*-Si:H alone. The HIT cell concept is thus understood as providing a compromise between doping and surface-passivation by employing an intrinsic buffer layer, between the doped film and the wafer.

Still within the context of interface recombination, Chapter 8 (Rudolph Brüggemann) discusses how photoluminescence (PL) and electroluminescence (EL) from amorphous/crystalline silicon heterostructures can be used for the characterisation of precursor structures for solar cell optimisation and for the study of related physical aspects. It is shown that the luminescence yield, or more precisely the deduced quasi-Fermi level splitting, is directly related to the open-circuit voltage of the device which itself is limited by factors like the interface recombination rate. The usefulness of contactless PL and EL techniques for investigations of the SHJ physics as well as for process control are thus highlighted.

Chapter 9 (Florian Ruske) deals with the next step of fabricating a typical SHJ cell, namely the deposition of transparent conductive oxides (TCOs) – typically ITO or ZnO:Al – on top of the *a*-Si:H in order to provide light trapping and a sufficient lateral conductivity towards the metal of the grid fingers. The optical properties of these films strongly depend on the electrical transport properties, especially the carrier concentration. The details of this mutual dependency are discussed using models for optical absorption, and it is shown that it is advantageous to use materials with moderate carrier concentrations. Non-vacuum and vacuum deposition techniques for TCOs are discussed, with a focus on magnetron sputtering, a process belonging to the latter class. It is shown how the additional challenges posed by the use of sputtered TCOs in SHJ, i.e. the low thickness of the films and the low deposition temperature, can be handled.

The final step of cell fabrication, the deposition of metal contacts, is discussed in Chapter 10 (Mario Tucci, Luca Serenelli, Simona De Iuliis, Massimo Izzi). Here, the doping of amorphous films is discussed together with the possibility to enhance the amorphous film conductivity by using chromium silicide formation on top of doped films. A finite difference numerical model is used to describe the a-Si:H/c-Si heterojunction solar cell in which both contacts are made by amorphous films, and a detailed investigation is presented comparing experimental current voltage characteristics of heterojunction contacts with the numerical models. TCOs and the formation of contacts by screen printing are discussed, and three examples of heterojunction solar cells are proposed using different approaches to form the contacts.

The following five chapters deal with characterization and modelling of SHJ cells: Chapter 11 (Jatin Rath) describes the standard electrical characterization techniques of SHJ solar cells which should elucidate the link between improvements in cell parameters obtained via process development and the microscopic nature of the functioning of the SHJ device. Although the SHJ cell is a bulk device, the parts of the SHJ cell that control the charge transport are limited to very thin regions. Characterization of such thin layers, in particular defect densities, conductivity, carrier recombination, is a complex issue. The chapter discusses the origin of the so-called S-type character in the I-V characteristics. Also, experimental methods to determine the band offset and the tunneling behavior at the spikes in the bands are described. Determining interface states is difficult to perform, however, electrically detected magnetic resonance (EDMR) or spin dependent photoconductivity (SDPC) is described as a potentially powerful technique to measure these states.

In Chapter 12 (Jean-Paul Kleider), a technique to determine the band offsets in *a*-Si:H/*c*-Si heterojunctions from electrical measurements is discussed. The chapter starts by recalling the principal models for band lineup at interfaces, with particular emphasis on Anderson's electron affinity rule and Tersoff's branching point alignment theory. The principal electrical characterization tools based on capacitance and admittance measurements are presented, and the main potential problems and sources of uncertainty when applying the C-V technique to the *a*-Si:H/*c*-Si system are addressed. Finally, a simple technique based on the measurement of the planar conductance of *a*-Si:H/*c*-Si structures is presented, and the determination of band offsets from such measurements and related modeling on both (p)*a*-Si:H/(n)*c*-Si and (n)*a*-Si:H/(p)*c*-Si structures is discussed. Note that the results obtained here compare favourably with those in Chapter 6, obtained with a completely different technique.

Chapter 13 (Rolf Stangl and Caspar Leendertz) discuss the approaches for numerical modelling of SHJ cells, and Chapter 14 (Caspar Leendertz and Rolf Stangl) gives a "hands-on" introduction to using a concrete simulation software, AFORS-HET (Automat for Simulation of Heterostructures), for this purpose: Chapter 13 outlines the basic equations for the optical and electrical calculations used in AFORS-HET, then focuses on the detailed description of the equations needed to calculate the recombination via defects in the semiconductor layers. Then, Chapter 14 describes the physical models and material parameters needed to simulate an *a*-Si:H/*c*-Si solar cell with AFORS-HET, and a simulation study showing the dependence of solar cell characteristics on emitter doping, i-layer thickness and interface quality is presented. The AFORS-HET user interface is introduced and a step-by-step explanation of how to define a structure and how to simulate a solar cell under different external conditions is given, so that the interested reader can repeat the simulation study.

While AFORS-HET is limited to simulations in one spatial dimension (1D), the simulation issue is taken one step further by discussing 2D simulations in Chapter 15 (Djicknoum Diouf, Jean Paul Kleider, Christophe Longeaud). These are carried out to investigate interdigitated back contact silicon heterojunction (IBC-SHJ) solar cells. A comparative study between the IBC-SHJ structure based on *n*-type and *p*-type *c*-Si is discussed. Similar to the 1D case (front and rear contacted cells), the results on IBC indicate that the key parameters to achieve high efficiency are a high *c*-Si substrate quality, low surface recombination velocity especially at the front surface, and *a*-Si:H/*c*-Si interfaces with low recombination velocity.

The properties of actual IBC-SHJ cells realized in different labs world-wide are discussed in Chapter 16 (Niels Posthuma, Barry O'Sullivan, Ivan Gordon): The advantages of such cells are outlined, e.g. the high current density since no metal contacts are present at the front of the cell and easier series interconnection between various cells at module level. After a discussion of conventional homojunction IBC concepts, which have shown 21 to 23% energy conversion efficiency on large area industrially produced cells, SHJ-IBC cells are introduced, and the research on implementing the heterojunction emitter at the rear of the wafer, which has a rather short history of only about five years, is presented. It is concluded that the current SHJ-IBC cells, with cell structures and processing that are not optimized and are typically fabricated on small area, are just the start of a new development.

The book closes with Chapter 17 (Delfina Muñoz, Thibaut Desrues, Pierre-Jean Ribeyron) that takes a look at the big picture: First, it outlines the current state of the photovoltaics market and discusses how the market share of high efficiency cell concepts such as the SHJ can be expected to develop in the future. Then, all process steps discussed in detail in the previous chapters are briefly reviewed and put into context. Finally, the question is answered whether the SHJ is a good choice with respect to other, competing high efficiency concepts. It is concluded that the advantages of the SHJ, i.e. high efficiency with comparably simple, low temperature processing steps, easy module integration, cost reduction potential in conjunction with thin wafers etc., make silicon heterojunction cells indeed a smart choice for the high efficiency cell of the future.

We trust that with the contents laid out in this book, it will find widespread use in the photovoltaics community, both industrial and academic because it covers a broad range of scientific and technical aspects related to silicon heterojunction technology. Particularly, parts of the book are well-suited for use in (under)graduate courses, thus we hope that this publication can serve as a means to train students in those skills that are in high demand to sustain the growth in the photovoltaic industry. In fact the SHJ is among the more effective concepts used to tackle reduction of material consumption (g/Wp), for which new manufacturing technologies are in development that carefully consider costs, high throughput and yield, and integrated industrial processing. It is expected that within a few years these developments will lead to costs that are competitive with traditional technologies that generate electricity. All of these concepts are needed for the challenge to reach a carbon neutral society by the middle of this century.

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