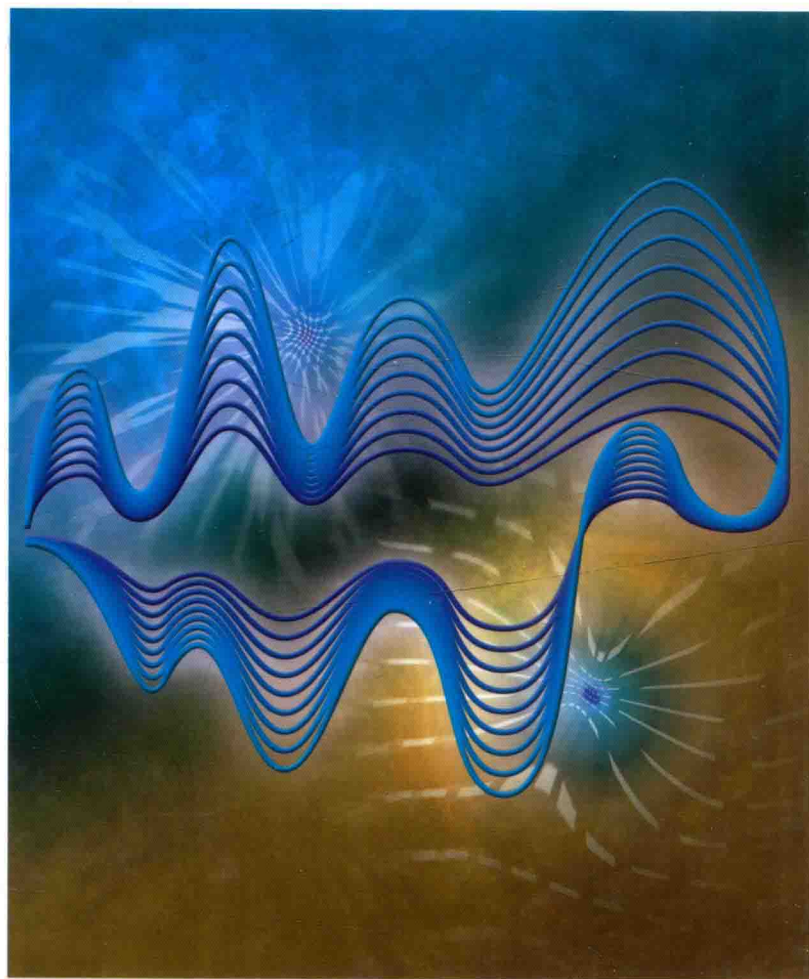


Alkire, Kolb, Lipkowski, Ross (Eds.)

WILEY-VCH

Photoelectrochemical Materials and Energy Conversion Processes

Volume 12



Advances in Electrochemical Science and Engineering

Volume 12

*Photoelectrochemical Materials and
Energy Conversion Processes*

Edited by

*Richard C. Alkire, Dieter M. Kolb, Jacek Lipkowski,
and Philip N. Ross*



WILEY-
VCH

WILEY-VCH Verlag GmbH & Co. KGaA

The Editors

Prof. Richard C. Alkire

University of Illinois
600 South Mathews Avenue
Urbana, IL 61801
USA

Prof. Dieter M. Kolb

University of Ulm
Institute of Electrochemistry
Albert-Einstein-Allee 47
89081 Ulm
Germany

Prof. Jacek Lipkowski

University of Guelph
Department of Chemistry
N1G 2W1 Guelph, Ontario
Canada

Prof. Philip N. Ross

Lawrence Berkeley National
Laboratory
Materials Science Department
1 Cyclotron Road MS 2-100
Berkeley, CA 94720-0001
USA

All books published by Wiley-VCH are carefully produced. Nevertheless, authors, editors, and publisher do not warrant the information contained in these books, including this book, to be free of errors. Readers are advised to keep in mind that statements, data, illustrations, procedural details or other items may inadvertently be inaccurate.

Library of Congress Card No.: applied for

British Library Cataloguing-in-Publication Data

A catalogue record for this book is available from the British Library.

Bibliographic information published by the Deutsche Nationalbibliothek

The Deutsche Nationalbibliothek lists this publication in the Deutsche Nationalbibliografie; detailed bibliographic data are available on the Internet at <http://dnb.d-nb.de>.

© 2010 WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim Germany

All rights reserved (including those of translation into other languages). No part of this book may be reproduced in any form – by photoprinting, microfilm, or any other means – nor transmitted or translated into a machine language without written permission from the publishers. Registered names, trademarks, etc. used in this book, even when not specifically marked as such, are not to be considered unprotected by law.

Typesetting Toppan Best-set Premedia Limited, Hong Kong

Printing and Binding betz-druck GmbH, Darmstadt

Cover Design Grafik-Design Schulz, Fußgöheim

Printed in the Federal Republic of Germany
Printed on acid-free paper

ISBN: 978-3-527-32859-8

ISSN: 0938-5193

**Advances in
Electrochemical Science
and Engineering**

Volume 12
Photoelectrochemical
Materials and Energy
Conversion Processes

Advances in Electrochemical Science and Engineering

Advisory Board

Prof. Elton Cairns, University of California, Berkeley, California, USA

Prof. Adam Heller, University of Texas, Austin, Texas, USA

Prof. Dieter Landolt, Ecole Polytechnique Fédérale, Lausanne, Switzerland

Prof. Roger Parsons, University of Southampton, Southampton, UK

Prof. Laurie Peter, University of Bath, Bath, UK

Prof. Sergio Trasatti, Università di Milano, Milano, Italy

Prof. Lubomyr Romankiw, IBM Watson Research Center, Yorktown Heights, USA

*In collaboration with the International
Society of Electrochemistry*



Preface

The purpose of this series is to provide high-quality advanced reviews of topics of both fundamental and practical importance for the experienced reader. This volume focuses on photovoltaic materials for energy conversion processes with emphasis on electrochemical science aspects associated with phenomena, reactions, and materials; and engineering fundamentals associated with fabrication processes and functional capabilities. The chapters of this volume, along with more than 1100 references therein, illustrate the considerable potential of electrochemistry as a tool that can be used for the preparation and characterization of materials for solar cells. Electrochemical processes may soon take a central position as an enabling technology that will have an impact on the large-scale deployment of photovoltaic devices.

Lewerenz reviews the basic principles of the operation of photoelectrochemical devices, along with the physics of the underlying phenomena that occur. Experimental methods for the investigation of fundamental phenomena are described, along with results for major classes of materials including silicon, indium phosphide, and copper indium dichalcogenides. The role of these fundamentals in the operation of photovoltaic photoelectrochemical devices is discussed with emphasis on ternary chalcopyrites, indium phosphide solar cells, and nanostructured silicon. In addition, the role of photocatalysis in tandem structures to capture the broad spectral range of photonic energy is discussed for p-Si nanoemitter configurations, as well as thin epitaxial p-InP films.

Dale and Peter review material requirements for inorganic thin-film solar cells, the development of new and sustainable materials, and prospects for fabrication technologies based on the direct synthesis of solar cells by electrochemical processing routes. The electrodeposition of cadmium telluride is reported with special emphasis on reaction mechanisms as well as the resulting structural properties that are critically important for solar cell applications. Various methods for preparing of copper–indium–gallium–selenium (CIGS) compounds are described along with experience in achieving high-efficiency performance. Extensive coverage is devoted to the preparation of copper–zinc–tin–sulfur compounds, which offer the attractive benefit of sustainability owing to the widespread occurrence of these elements. Also discussed are the advantages offered by room-temperature ionic liquids. Issues associated with the semiconductor–electrolyte junction are presented in the context of characterizing solar cell device components.

Schlettwein, Yoshida, and Lincot provide a critical review of the research literature on porous zinc oxide sensitized by organic dyes, and the potential use of these materials for the development of large-scale photovoltaic solar cells. An introduction is provided to the electrodeposition of zinc oxide thin films, their means of sensitization by a variety of organic molecules, and their preparation by one-step deposition from solutions containing water-soluble dyes to produce hybrid materials suitable for solar cell. The advantages of various substrates for large-scale cells are discussed for plastic and textile materials.

Miyasaka reviews the photoelectrochemistry of dye-sensitized mesoporous semiconductor electrodes with emphasis on application to the fabrication of thin, flexible photovoltaic cells. The discussion focuses on low-temperature preparation methods for electrode materials and the use of these methods in rapid, printable processes that enable manufacture of low-cost, lightweight integrated modules on plastic substrates. A wide variety of novel procedures are described for achieving high levels of light-harvesting performance, as well as bifacial photovoltaic capability. The complex interplay between various system components is discussed in the content of optimizing spectral sensitizers and developing printable materials for catalyzed electrochemical processes on the counterelectrode.

Savadogo presents the fundamental thermodynamic and kinetic considerations for fabricating inorganic thin-film materials with special emphasis on chemical deposition from mixed solutions, electrodeposition, and sol-gel methods. The exceptional range of materials that have been prepared by these methods is noteworthy, as is the low cost of the processing methods. Treated in detail are the syntheses of the component chemicals, as well as the mechanistic and synergistic role of the components including the important role played by additives.

The field of semiconductor electrochemistry cannot be discussed without recognizing the central contributions of Prof. H. Gerischer, who also served as co-editor of this monograph series from 1977 to 1994. Stimulated by work in the mid-1950s on the germanium-electrolyte interface by Brattain and Garrett at the Bell Telephone Laboratories, Prof. Gerischer soon contributed a series of pioneering publications that clarified many of the underlying principles on which the field rests today. These include establishing criteria for the stability of semiconductor electrodes under illumination, developing experimental techniques for study of photosensitization, elucidating the principles behind electrochemical photo and solar cells, and photoassisted oxidation of organic molecules on semiconductor particles. He continued to publish on semiconductor electrochemistry for the remainder of his life. This body of literature has, in turn, served to inspire others throughout the world to contribute to the field of semiconductor electrochemistry and engineering.



Prof. H. Gerischer, 1919–1994

Urbana, Illinois, March 2010

Richard Alkire

List of Contributors

Phillip Dale

Université du Luxembourg
Laboratoire Photovoltaïque
41 rue du Brill
4422 Belvaux
Luxembourg

Hans Joachim Lewerenz

Institute of Solar Fuels and Energy
Storage Materials
Division of Solar Energy
Helmholtz Center Berlin for
Materials and Energy
Lise-Meitner-Campus,
Hahn-Meitner-Platz 1
14109 Berlin
Germany

Daniel Lincot

IRDEP, Institut de Recherche et
Développement sur l'Energie
Photovoltaïque
UMR 7174, EDF-CNRS-ENSCP, 6
quai Watier
78401 Chatou Cedex
France

Tsutomu Miyasaka

Toin University of Yokohama
Graduate School of Engineering
1614 Kurogane-cho, Aoba-ku, Yokohama
Kanagawa 225-8502
Japan

Laurence Peter

University of Bath
Department of Chemistry
Bath BA27AY
UK

Oumarou Savadogo

École Polytechnique de Montréal
Laboratory of New Materials for
Electrochemistry and Energy
(LaNoMat)
CP 6079 Succ. Centre-ville
Montréal, Qc, H3C 3A7
Canada

Derck Schlettwein

Justus-Liebig-Universität Gießen
Institut für Angewandte Physik
35394 Gießen
Germany

Tsukasa Yoshida

Gifu University
Graduate School of Engineering
Environmental and Renewable Energy
Systems (ERES) Division
Yanagido 1-1
Gifu 501-1193
Japan

Contents

Preface IX

List of Contributors XIII

1	Applications of Electrochemistry in the Fabrication and Characterization of Thin-Film Solar Cells	1
	<i>Phillip Dale and Laurence Peter</i>	
1.1	Introduction	1
1.2	Electrochemical Routes to Thin-Film Solar Cells	3
1.2.1	Basic Cell Configurations	3
1.2.2	Material Requirements for PV Applications	4
1.2.2.1	Implications of Materials Requirements for the Direct Synthesis of Absorber Layers by Electrodeposition	5
1.2.2.2	Synthetic Routes Involving Deposition and Annealing (EDA)	7
1.2.2.3	Summary of EDA Routes	11
1.2.3	EDA route to p-Type Semiconductors for Thin-Film Photovoltaics	13
1.2.3.1	Electrodeposition of CdTe for CdS/CdTe Solar Cells	13
1.2.3.2	Electrodeposition of CIGS for CIGS/CdS/ZnO Solar Cells	19
1.2.3.3	CZTS	30
1.2.4	Future	39
1.3	Characterization of Solar Cell Materials using Electrolyte Contacts	40
1.3.1	Overview	40
1.3.2	The Semiconductor–Electrolyte Junction	41
1.3.3	Photovoltammetry	42
1.3.4	External Quantum Efficiency (EQE) Spectra	43
1.3.5	Electrolyte Electroreflectance/Absorbance: EER/EEA	50
1.4	Conclusions	54
	Acknowledgments	55
	References	55

2	Tailoring of Interfaces for the Photoelectrochemical Conversion of Solar Energy	61
	<i>Hans Joachim Lewerenz</i>	
2.1	Introduction	61
2.2	Operation Principles of Photoelectrochemical Devices	62
2.2.1	Currents, Excess Carrier Profiles, and Quasi-Fermi Levels	62
2.2.1.1	Dark Current and Photocurrent	62
2.2.1.2	Excess Minority Carrier Profiles	65
2.2.1.3	Quasi-Fermi Levels	69
2.2.2	Photovoltages and Stability Criteria	71
2.2.3	Photovoltaic and Photoelectrocatalytic Mode of Operation	77
2.2.3.1	Photovoltaic Photoelectrochemical Solar Cells	77
2.2.3.2	Photoelectrocatalytic Systems	78
2.2.4	Separation of Charge Transfer and Surface Recombination Rate	81
2.3	Surface and Interface Analysis Methods	83
2.3.1	<i>In Situ</i> Methods: I. Brewster Angle Analysis	84
2.3.2	<i>In Situ</i> Methods: II. Stationary Microwave Reflectivity	87
2.3.3	X-ray Emission and (Photo)Electron Spectroscopies	90
2.3.3.1	Selected X-ray Surface/Interface Analysis Methods	90
2.3.3.2	In-System Synchrotron Radiation Photoelectron Spectroscopy	94
2.3.3.3	High-Resolution Electron Energy Loss Spectroscopy	99
2.3.4	Tapping-Mode AFM and Scanning Tunneling Spectroscopy	99
2.3.4.1	Tapping-Mode AFM	100
2.3.4.2	Scanning Tunneling Spectroscopy	101
2.4	Case Studies: Interface Conditioning	104
2.4.1	Silicon Nanotopographies	107
2.4.1.1	Nanostructures by Divalent Dissolution	107
2.4.1.2	Step Bunched Surfaces	111
2.4.1.3	Oxide-Related Nanotopographies	121
2.4.2	Indium Phosphide	130
2.4.2.1	The InP(111) A-face	131
2.4.2.2	The In-Rich InP(100) (2×4) Surface	136
2.4.3	Copper Indium Dichalcogenides	137
2.4.3.1	CuInSe ₂	138
2.4.3.2	CuInS ₂	140
2.5	Photovoltaic, Photoelectrochemical Devices	143
2.5.1	Ternary Chalcopyrites	145
2.5.2	InP Solar Cells	146
2.5.3	Nanoemitter Structures with Silicon	147
2.5.3.1	Device Development	147
2.5.3.2	Surface Chemical Analysis of the Electrodeposition Process	154
2.6	Photoelectrocatalytic Devices	162
2.6.1	Nanoemitter Structures with p-Si	162
2.6.2	Thin-Film InP Metal–Interphase–Semiconductor Structure	165
2.6.2.1	Basic Considerations	165

2.6.2.2	Device Preparation and Properties	166
2.7	Synopsis	170
2.7.1	Summary	170
2.7.2	Reflections on Future Development Routes	171
	Acknowledgments	172
	Appendix 2.A	172
	Appendix 2.B	172
	Appendix 2.C	173
	References	173
3	Printable Materials and Technologies for Dye-Sensitized Photovoltaic Cells with Flexible Substrates	183
	<i>Tsutomu Miyasaka</i>	
3.1	Introduction: Historical Background	183
3.2	Low-Temperature Coating of Semiconductor Films	184
3.3	Photoelectric Performance of Plastic Dye-Sensitized Photocells	186
3.4	Polymer-Based Counter Electrodes with Printable Materials	190
3.5	Investigation of High-Extinction Sensitizers and Co-adsorbents	197
3.6	Durability Development for Plastic DSSCs	208
3.7	Fabrication of Large-Area Plastic DSSC Modules	212
3.8	Concluding Remarks	218
	References	218
4	Electrodeposited Porous ZnO Sensitized by Organic Dyes—Promising Materials for Dye-Sensitized Solar Cells with Potential Application in Large-Scale Photovoltaics	221
	<i>Derck Schlettwein, Tsukasa Yoshida, and Daniel Lincot</i>	
4.1	Introduction	221
4.2	Electrodeposition—A Well-Established Technology	225
4.3	Electrodeposition of ZnO Thin Films	226
4.4	Sensitization of ZnO	227
4.5	Alternative Sensitizer Molecules	228
4.5.1	Porphyrins and Phthalocyanines as Alternative Metal Complexes	230
4.5.1.1	Frontier Orbital Positions	231
4.5.1.2	Photosensitization by Porphyrins and Phthalocyanines	235
4.5.2	Purely Organic Dyes	244
4.6	Electrodeposition of Hybrid ZnO/Organic Thin Films	244
4.7	Porous Crystalline Networks of ZnO as Starting Material for Dye-Sensitized Solar Cells	249
4.8	Adaptation of Electrodeposition Towards Specific Demands of Alternative Substrate Materials	252
4.8.1	Plastic Solar Cells	252
4.8.2	Textile-Based Solar Cells	253
4.9	State of the Art and Outlook	256
	References	259

5 Thin-Film Semiconductors Deposited in Nanometric Scales by Electrochemical and Wet Chemical Methods for Photovoltaic Solar Cell Applications 277

Oumarou Savadogo

- 5.1 Introduction 277
- 5.2 Materials and Composite Materials Fabrication 279
 - 5.2.1 Fundamental Considerations 279
 - 5.2.1.1 Chemical Bath Deposition 279
 - 5.2.1.2 Electrodeposition 289
 - 5.2.1.3 Sol-Gel Method 295
 - 5.2.1.4 Other Wet Methods 299
 - 5.2.2 Preparation of Active Materials 307
 - 5.2.2.1 Preparation by Chemical Deposition 307
 - 5.2.2.2 Preparation by Electrochemical Deposition 325
 - 5.2.2.3 Preparation by the Sol-Gel Method 329
 - 5.2.2.4 Thin Films Deposited with Heteropolycompounds 330
- 5.3 Systems Development 336
 - 5.3.1 State-of-the-Art Thin-Film Solar Technology using Chemical, Electrochemical, and/or Sol-Gel Fabrication Methods 336
 - 5.3.2 Toxicity and Sustainability Issues 338
- 5.4 Conclusions and Perspectives 339
- References 340

Index 351

1

Applications of Electrochemistry in the Fabrication and Characterization of Thin-Film Solar Cells

Phillip Dale and Laurence Peter

1.1

Introduction

Tackling climate change has become a priority for the scientific as well as the political community. The European Union has set a target for photovoltaic (PV)-generated electricity to become competitive with conventional electricity generation by 2020–2030, and the Council of the European Union aims to reduce greenhouse gas emission by 60–80% by 2050. The UK's Stern Review [1], which deals with the economic impact of global climate change, states that “the benefits of strong, early action on climate change outweigh the costs” and goes on to identify “development of a range of low-carbon and high-efficiency technologies on an urgent timescale” as essential to any strategy that aims to address the problems of climate change. These targets have implications for the science and technology of PV. If PV is to make a major contribution to a low-carbon energy economy, issues of materials and manufacturing costs [2] as well as materials sustainability need to be considered. Current non-silicon PV technologies are based on cadmium telluride and the chalcopyrite materials $\text{Cu}(\text{In,Ga})\text{Se}_2$ (CIGS) and CuInS_2 . Both of these materials are unlikely to be sustainable in the long term for terawatt deployment [3] of terrestrial PV, so that a search for alternative materials has assumed considerable importance.

Figure 1.1 illustrates the nature of the problem by summarizing the natural abundance and raw elemental costs for materials that are used in thin-film solar cells. It is important to note that a logarithmic scale has been used for both the abundance and the raw materials cost. The most expensive material by far is indium, and the availability and cost of indium have become geopolitical issues in recent months since it is used in the manufacture of liquid crystal displays and touch screens.

The rarest element shown in Figure 1.1 is tellurium, and it is reasonable to suppose that this has implications for the long-term sustainability of cadmium telluride solar cell technology. Sustainability issues of this kind provide the rationale for expansion of the range materials that deserve study for PV applications. A promising new candidate for sustainable PV is $\text{Cu}_2\text{ZnSnS}_4$.

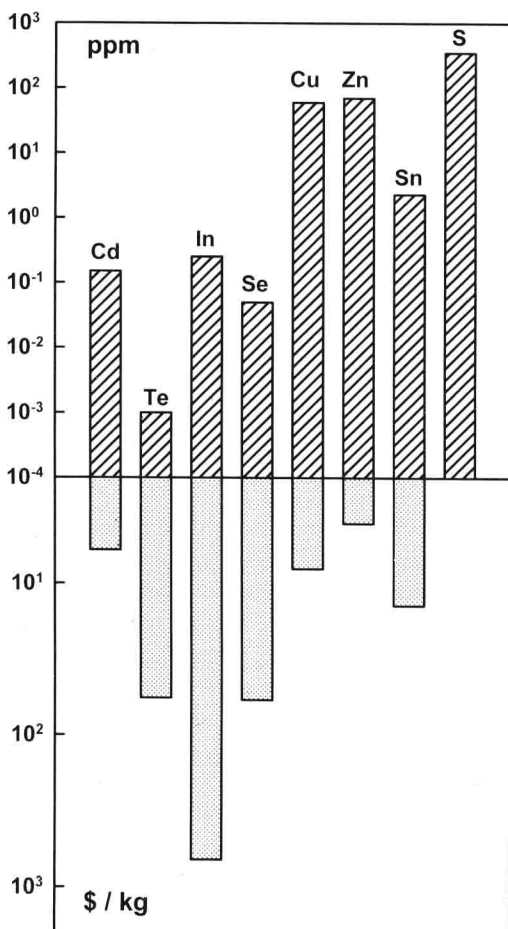


Figure 1.1 Comparison of availability and costs of elements used for the fabrication of solar cells. Note the logarithmic scales.

(CZTS), a compound with electronic properties similar to those of CIGS that contains cheap and plentiful non-toxic elements. However, remarkably little work has been carried out to characterize the potential of this material for PV applications.

Sustainability and environmental issues are also associated with the fabrication processes used in PV. The authors of this chapter believe that electrochemical methods have the potential for large-scale low-cost preparation of PV materials [4], and, in addition, electrochemical methods are powerful tools for the characterization of PV materials and device components [5]. These two topics are explored in the present chapter.

1.2

Electrochemical Routes to Thin-Film Solar Cells

1.2.1

Basic Cell Configurations

Examples of thin-film PV devices based on compound semiconductor absorber films are shown in Figure 1.2. The n-CdS/p-CdTe solar cell (Figure 1.2a) is an example of a superstrate cell. The thin CdS layer is grown on glass coated with a transparent conducting layer (e.g., fluorine-doped tin oxide, FTO). CdTe is then deposited onto the CdS layer and, following thermal treatment, the device is completed by the addition of ohmic contacts to the CdTe. CIGS solar cells are mostly made in the substrate configuration (Figure 1.2b) where the CIGS is deposited onto a metallic back contact, for example Mo-coated glass (although efficient CIGS superstrate cells have also been fabricated). The CIGS is coated with a thin CdS layer followed by a layer of intrinsic ZnO and a layer of Al-doped ZnO, which acts as a conducting transparent top contact. An Al grid is used to collect the current.

CdTe devices have achieved 16.7% efficiency in the laboratory [6], whereas CIGS cells have reached 20.0% [7]. The most efficient CIGS devices contain around 30% Ga distributed non-uniformly through the film, with higher concentrations preferred at the front and back of the layer. Kesterites are emerging as suitable In-free materials for absorber layers, but current understanding of the factors that

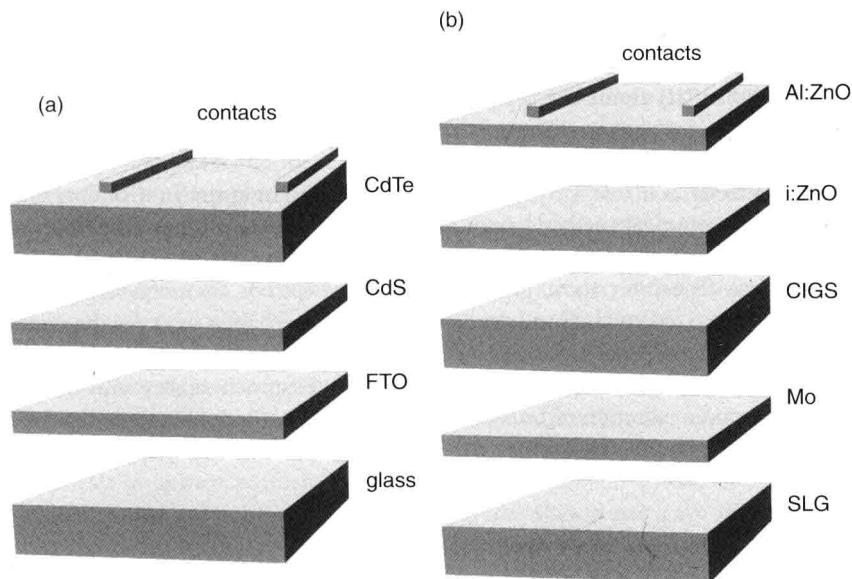


Figure 1.2 Comparison of superstrate and substrate solar cell configurations. (a) Superstrate configuration used for CdS/CdTe solar cells. (b) Substrate configuration commonly used for CIGS solar cells.

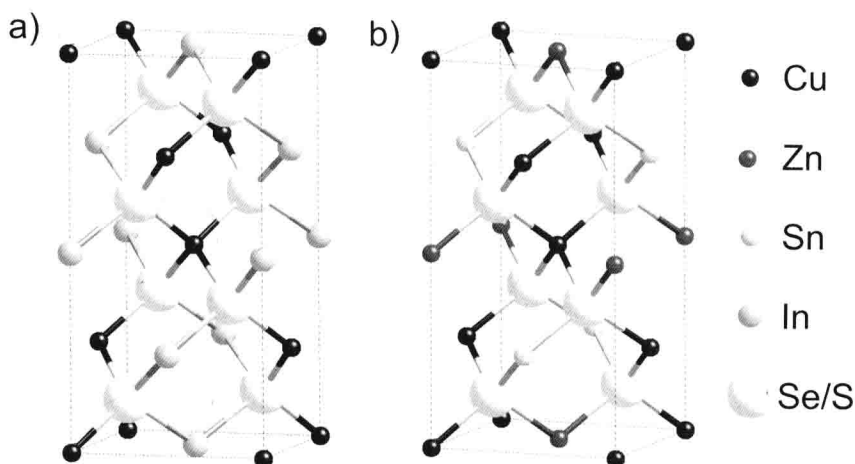


Figure 1.3 Crystal structures of (a) chalcopyrite and (b) kesterite [12].

determine the optoelectronic properties of these materials is limited. The best kesterite-based devices, like CIGS devices, have absorber layers that are Cu deficient [8, 9]. The best published efficiency of 6.7% has been reported by Katagiri *et al.* [10] for a device that is Zn rich and Sn deficient. Our research has shown that CZTS device performance improves if the surface of the absorber layer is etched in KCN which is known to remove CuS phases [11].

The kesterite structure $\text{Cu}_2\text{ZnSnS}_4$ is isoelectronic with chalcopyrite CuInS_2 . Half of the In(III) atoms are replaced with Zn(II) atoms, and the other half are replaced with Sn(IV) atoms. The crystal structures of the chalcopyrite and kesterite are shown in Figure 1.3.

The methods available for preparation of the different layers in thin-film solar cells include physical methods such as vacuum sputtering, vapor-phase deposition, and molecular beam epitaxy as well as chemical methods such as chemical vapor-phase deposition, metal organic vapor-phase epitaxy, chemical bath deposition (CBD), and electrochemical deposition (ED). This chapter explores the potential of electrodeposition as a route to the fabrication of absorber layers such as CdTe, CIGS, and CZTS for thin-film solar cells. Electrochemistry may also be useful for the preparation of transparent layers such as ZnO; this topic has been reviewed by Pauporte and Lincot [13].

1.2.2

Material Requirements for PV Applications

In this section we discuss first the general materials requirements for an absorber layer. Specific issues for particular materials are then considered in subsequent sections. The specific optoelectronic properties of each absorber layer will not be