I. M. Dharmadasa

Advances in Thin-Film Solar Cells

Second Edition

Advances in

Thin-Film Solar Cells

Second Edition

Advances in Thin-Film Solar Cells

Second Edition

I. M. Dharmadasa

Pan Stanford Publishing

Published by

Pan Stanford Publishing Pte. Ltd.
Penthouse Level, Suntec Tower 3
8 Temasek Boulevard
Singapore 038988

Email: editorial@panstanford.com
Web: www.panstanford.com

British Library Cataloguing-in-Publication Data
A catalogue record for this book is available from the British Library.

Advances in Thin-Film Solar Cells (Second Edition)

ISBN 978-981-4800-12-9 (Hardcover)
ISBN 978-0-429-02084-1 (eBook)

Contents

Preface to the Second Edition xiii
List of Symbols and Abbreviations xvii

1 Photovoltaic Solar Energy Conversion 1
1.1 Introduction 1
1.2 Photovoltaic Effect 3
1.3 Solar Energy Materials 3
1.4 Electronic Devices Used for Solar Energy Conversion 5
1.4.1 p–n Junctions 5
1.4.2 p–i–n Junctions 7
1.4.3 Hetero-junctions 8
1.4.4 n–n and p–p Junctions 9
1.4.5 Metal/Semiconductor (or Schottky) Contacts 10
1.4.6 Metal/Insulator/Semiconductor Interfaces 12
1.5 Characteristics of a Solar Cell 14
1.5.1 I–V Characteristics of a Solar Cell Under Dark Conditions 14
1.5.2 I–V Characteristics of a Solar Cell Under Illuminated Conditions 18
1.5.3 How to Maximise V_{oc} 20
1.5.4 How to Maximise J_{sc} 21
1.5.5 How to Maximise FF 22
1.6 Summary 22
Exercises 24

2 Status Report on Solar Energy Technologies 27
2.1 Introduction 27
2.2 Si Solar Cell Technology 28
2.3 PV Manufacturing Cost Based on Si Technology 32

2.4 PV Technology Based on III–V Compounds 34
2.5 Disruptive Technology for PV Development 35
2.6 Emerging Low-Cost Thin-Film Technologies 36
2.7 Next-Generation Solar Cells 37
2.8 Summary 39
Exercise 41

3 Electrochemical Deposition of Solar Energy Materials 43
3.1 Introduction 43
3.2 Electrodeposition of Semiconductors 44
3.3 Strengths and Advantages of Electrodeposition 45
3.3.1 Simplicity, Low-Cost, Scalability, and Manufacturability 45
3.3.2 Self-Purification and Built-In Hydrogen Passivation 47
3.3.3 Extrinsic and Intrinsic Doping 48
3.3.4 Ability in Bandgap Engineering 49
3.3.5 Other Advantages of Electrodeposition 49
3.4 Experimental Evidence 50
3.4.1 Observations in XRD 50
3.4.2 Observations in XRF 50
3.4.3 Observations in PEC Cell Measurements 52
3.4.4 Observations in Optical Absorption Measurements 56
3.4.5 Observations in Photoluminescence 57
3.4.6 Impurity Control in Semiconductors 59
3.5 Issues in Electrodeposition of Semiconductors 60
3.6 Summary of Electroplated Materials to Date 63
3.7 Applications in PV Devices 63
3.8 Summary 66
Exercises 69

4 Background of the CdTe Solar Cell and the New Device Concept 71
4.1 Introduction 71
4.2 The Previous Model for a Glass/Conducting Glass/CdS/CdTe/Metal Solar Cell 73

4.3 Key Observations That Led to the Formulation of a New Model 76
4.3.1 Surface Modification of CdTe 76
4.3.2 Effects of Surface Modification on Defect Levels 76
4.3.3 Effects of Defect Levels on Electronic Devices 77
4.3.4 Similar Observations on Thin-Film CdS/CdTe Solar Cells 79
4.4 New Concept for CdS/CdTe Solar Cell 80
4.5 Description of Experimental Results Using the Two Models 85
4.5.1 Current–Voltage (I–V) Characteristics 85
4.5.2 Capacitance–Voltage (C–V) Characteristics 86
4.5.3 Electron Beam–Induced Current Measurements 87
4.5.4 Observation of Discrete Barrier Heights and V_{oc} Values 87
4.5.5 A Thin-Film CdTe Solar Cell Device Without a CdS Layer 88
4.5.6 Results from Electrical Contacting Work 89
4.5.7 Doping of CdS and CdTe Layers 90
4.5.8 Further Experimental Evidence to Confirm the True Structure of the Device 91
4.6 Predictions for the Further Development of CdS/CdTe Solar Cells and Latest Observations 94
4.6.1 Doping of Window and Absorber Materials with n-Dopants 94
4.6.2 Improvements to Back Contact Using MIS-Type Structures 99
4.6.3 A Multi-layer Graded Bandgap Approach 102
4.6.4 Dealing with Defects 103
4.6.5 Progress during the Period 2011–2016 105
4.7 Summary 107
Exercises 111

5 Extension of the New Model to CIGS Thin-Film Solar Cells 115
5.1 Introduction 115
5.2 Summary of Accumulated Knowledge on CIGS-Based Materials 116

5.2.1 Different Growth Techniques 116
5.2.2 Structural, Optical, and Electrical Properties 116
5.2.3 Ordered Defect Compound Layer 117
5.2.4 Latest Developments in Materials Growth 117
5.3 Summary of Accumulated Knowledge on CIGS-Based Solar Cells 118
5.3.1 Conventional Device Structure 118
5.3.2 Frequently Used Energy Band Diagram 119
5.4 Current Views of the Physics Behind CIGS Solar Cells 121
5.4.1 p-CIGS/n-CdS Hetero-junction 121
5.4.2 p-CIGS/n-CIGS Homo-junction 121
5.4.3 p-CIGS/n-ODC Hetero-junction 122
5.5 Reported Device Performance 122
5.6 Recent Work on Metal/p-CIGS Interfaces 124
5.7 Deeper Understanding of Mo/CIGS/CdS/i-ZnO/n-ZnO:Al/Metal-Grid Solar Cells 126
5.7.1 Type I CIGS-Based Solar Cell 126
5.7.2 Type II CIGS-Based Solar Cell 130
5.8 Discussion on Further Improvements of CIGS Solar Cells 132
5.8.1 Optimisation of Growth, Doping, and Bandgap Engineering 133
5.8.2 Defect Level Identification and Engineering 133
5.8.3 Growth of CIGS with Controlled Orientation 134
5.8.4 Replacement of Mo Using TCO for Tandem and Double-Faced Solar Cells 134
5.8.5 Further Improvements of the Device Structure 135
5.9 Conclusions 136
5.10 Summary 138

6 Effective Harvesting of Photons 143
6.1 Introduction 143
6.2 Tandem Solar Cells 144
6.2.1 Connection in Series 145
6.2.2 Connection in Parallel 146
6.3 Comparison of the Two Connecting Methods 148
6.3.1 Disadvantages of Series Connections 148
6.3.2 Advantages of Parallel Connections 149

6.4 Conclusions 151
6.5 Summary 152
Exercise 154

7 Multi-layer Graded Bandgap Solar Cells 155
7.1 Introduction 155
7.1.1 Incorporation of the Impurity PV Effect 156
7.1.2 Incorporation of Impact Ionisation 157
7.2 Summary of Growth and Process Details of the Device Structure 157
7.3 Experimental Results of Fully Processed Devices 158
7.3.1 Electrical Properties Under Dark Conditions 159
7.3.2 Electrical Properties Under AM1.5 Illumination 161
7.3.3 IPCE Measurements 163
7.3.4 EBIC Measurements 164
7.3.5 SIMS Profiling 166
7.3.6 Optimisation of Si Doping Concentration 167
7.4 Discussions 171
7.5 Summary 173
Exercise 175

8 Solar Cells Active in Complete Darkness 177
8.1 Introduction 177
8.2 Summary of Experimental Results 177
8.3 Search for Experimental Evidence of the Impurity PV Effect 179
8.4 Responsivity Measurements 180
8.5 *I–V* Measurements Under Dark Conditions 181
8.5.1 *I–V* as a Function of Light Intensity 181
8.5.2 *I–V* Measurements Under Complete Darkness 182
8.6 Discussion 184
8.7 Conclusions 186
8.8 Summary 186
Exercise 188

9 Effects of Defects on Photovoltaic Solar Cell Characteristics 189
9.1 Introduction 189
9.2 Variations of *I–V* Characteristics of Metal/n-CdTe Interfaces 190

9.3 Effects on the Performance of CdS/CdTe Solar Cells 193
9.4 Variations in GaAs/AlGaAs Solar Cells 195
9.4.1 Device Structures Used 196
9.4.2 Instability of *I–V* Characteristics 197
9.4.3 Application of Electrical Stresses to the Device 197
9.4.4 Discussion and Possible Explanations 199
9.5 Variations in CIGS Solar Cells 205
9.6 Summary 208

10 Progress in Development of Graded Bandgap Thin-Film Solar Cells with Electroplated Materials 211
10.1 Introduction 211
10.2 The Concept and Experimental Validation 213
10.3 Multi-layer Graded Bandgap Device Structure Utilising Electroplated Materials 214
10.3.1 Stage 1: Preliminary Work on Glass/FTO/n-ZnS/n-CdS/n-CdTe/Au 215
10.3.2 Stage 2: Optimisation of Materials and Device Structures 216
10.3.3 Stage 3: CdTe Multi-layer Configuration 219
10.4 Summary 222

11 A Future Dominated by Solar Energy 227
11.1 Introduction 227
11.2 Early Applications with Low Power Requirements 228
11.3 Early Applications with Moderate Power Requirements 229
11.4 Applications in Solar Home Systems (~50 W Range) 229
11.5 Applications in Drip Irrigation Systems (~100 W Range) 231
11.6 Applications in Powering Computers (500–1,000 W Range) 232
11.7 Applications in Large-Scale Water Pumping (~1,000 W and Above) 233
11.8 Solar Power Applications on Roads 238
11.9 Solar Power Applications on Buildings (~3 kW Range) 239

11.10 Energy from Solar Farms and Deserts (MW Range) 242
11.11 Recommendations for Developing Countries 243
11.12 Recommendations for Developed Countries 244
11.13 Summary 245

12 Is Fermi-Level Pinning Affecting GaAs-Based Solar Cells? 247
12.1 Introduction 247
12.2 Observation of Discrete Sets of I–V Characteristics 247
12.3 Observation of Discrete Sets of V_{oc} Values 248
12.4 Discussion of New Observations 249

13 Thoughts on Future Directions of Thin-Film Solar Cell Research and Development 251
13.1 Introduction 251
13.2 Areas for Research and Development Efforts 251
13.2.1 Dealing with Defects in Thin-Film Device Structures 251
13.2.2 Is Impact Ionisation and Impurity PV Effect Contributing to the PV Effect? 252
13.2.3 Are Intermittent Observations of High J_{sc} Values Genuine? 253
13.2.4 Graded Bandgap Multi-layer Structures for Next-Generation Solar Cells 255
13.3 Conclusions 256

Solutions 257

Index 277

Preface to the Second Edition

Light energy was first converted into electricity by Edmund Becquerel in 1839, but until the 1950s, no considerable development had taken place. However, during the two decades of the 1950s and the 1960s, Si-based solar cells were developed, manufactured, and applied in applications such as satellites and remote communication stations. The first oil crisis, in the early 1970s, gave a huge push to the search for alternative energy conversion methods, and researchers actively searched for new materials and low-cost device structures. As a result, thin-film solar cells based on III–V compounds (GaAs and InP), amorphous Si, CdTe, and $CuInGaSe_2$ (CIGS) were introduced to mainstream solar energy conversion. In the early 1990s, dye-sensitised solar cells were introduced by Michael Grätzel, and organic solar cells were introduced in the early 2000s. With the renewed interest in nanomaterials, researchers worldwide are exploring the ways of using new materials such as perovskites in solar cell devices. At present, all these photovoltaic (PV) fronts are moving toward producing low-cost and high-efficiency solar cells to convert sunlight into electricity.

The main hurdle in the rapid market penetration of solar energy applications is their high cost. Although there are active research programmes to reduce manufacturing costs and increase conversion efficiencies, the progress is painfully slow for various reasons—one reason being the lack of deeper understanding of material issues and physics behind solar cell devices. This book does not deal with well-documented semiconductor properties and device principles but presents the latest developments and advances in thin-film solar cells, with an introduction to the most required background knowledge. The targeted audience will be undergraduate and postgraduate students in science and engineering; electronic device researchers in chemistry, material science, physics, mathematics, and engineering; and PV module developers and technologists in the industry. This book concentrates mainly on advances in thin-film solar cells based on CdTe-, CIGS-, and GaAs-based devices, but the ideas are equally applicable to all thin-film solar cells.

Chapter 1 introduces solar energy conversion to all readers in a simple manner with the aid of diagrams, references, and animations placed on the author's website. The next chapter provides a brief status report on PV technology. The main barrier in the PV sector is the high manufacturing cost due to the use of expensive materials (Si and III–V compounds) and the high energy consumption during materials growth and device processing. The initial high capital cost of equipment also exacerbates this situation. As a solution to this, a low-cost and scalable materials growth technique (electro-chemical deposition) for II–VI and alloy compounds will be described in Chapter 3. This growth method is also a suitable low-cost technique for growing nanomaterials for various other applications in nanotechnology. In all solar cells, two electrical contacts are needed to extract the photo-generated charge carriers from the device and, hence, these metal/semiconductor (MS) interfaces play a very important role in the overall performance. Chapter 4 summarises the most striking recent breakthroughs which improved the understanding of PV action in thin-film solar cells. This chapter describes the history of the CdTe solar cell, the application of new ideas to this device, the formation of a new concept to describe the solar energy conversion process, and the way forward for the development of the device. Chapter 5 extends the applicability of the Fermi-level pinning concept to CIGS-based solar cells. The next three chapters are devoted to revisiting the current practice in tandem solar cells based on tunnel junctions and the use of multi-layer graded bandgap device structures in solar energy conversion. The latter device design has been tested with a well-researched GaAs/AlGaAs system and experimentally observed the highest reported 1,175 mV open circuit voltage with the highest achievable fill factor of $\sim$0.86 for a single device. The new device concept is mainly based on a set of defects within these devices, and Chapter 9 describes the effects of defects on the performance of solar cells. It also describes the way forward for dealing with defects in order to achieve higher performance in devices. Chapter 10 is new in the second edition. It summarises the progress of graded bandgap devices fabricated using electroplated materials during the two years (2014–2016), achieving 15.3% efficiency. Chapter 11 is for the general public and describes the scenario of a future dominated by solar energy. This is based on author's 27 years of public understanding of science activities and real projects carried out on the ground. The solar village project designed and piloted successfully by the author is described, and the replication programme is indicated in this chapter. There are two short chapters included at the end of this book—Chapter 12 presents the evidence collated to date for Fermi-level pinning in GaAs-based solar cells, and Chapter 13 indicates some thoughts on future directions of thin-film solar cell research. In this second edition, relevant exercises and their solutions have been included, and these will be really useful for academics teaching in this field.

I am grateful to all the people who have supported me to develop and progress in this sector. My PhD supervisors, late Sir Professor Gareth Roberts and Professor Mike Petty at Durham University, put me on the right track at the very beginning, in the late 1970s. Working with active scientists in the field, Professors R. H. Williams and E. H. Rhoderick, enabled me to be well established in this field during my four-year postdoctoral research in University College Cardiff, in early 1980s. Since then, I have worked on and learned the subject from numerous colleagues from chemistry, physics, mathematics, and engineering disciplines, both in academia and in the industry (BP Research, Sunbury). During the last 28 years of my academic career at Sheffield Hallam University, many postdoctoral researchers, 28 PhD students, and numerous visiting researchers contributed to this work in order to understand the chemistry and physics behind these complex materials and devices. University lecturing on relevant subjects like electricity and magnetism, thermodynamics, solid-state physics, quantum mechanics, high-specification materials, device design and manufacture, optical fibre communication, engineering product analysis and design and Si processing in clean room environment for over three decades helped me in understanding these complex devices. This accumulated

knowledge, new breakthroughs and recent advances are presented in this book to share with the present and future scientists, engineers, and the general public. I am grateful to my immediate family for their help and support during this journey. In particular, I thank Dahiru Diso, Gavin Tolan, Jayne Wellings, Gafar Muftah, Osama Elsherif, Ajith Weerasinghe, Kingsley Obi Echendu, Fijay Bin Fauzi, Azlian Abdul-Manaf, Olusola Olajide, Mohammed Madugu, Salim Hussein, Ojo Ayotunde, Ruvini Dharmadasa, and Asela Dharmadasa for their contributions during the preparation of this book. I also thank Sidath Kalyanaratne, Nishith Patel, and Ashfaque Alam for preparing some of the diagrams used in this book.

Finally, this book is dedicated to my beloved parents, who worked hard to support me during my childhood with limited resources while living in the sun-rich environment of Sri Lanka. I am hopeful that this book will contribute to reverse this situation for future generations by bringing prosperity to all the people who live wherever the sun is shining.

I. M. Dharmadasa
Senior Staff Grade Professor and Head of Electronic Materials & Sensors Group
Materials & Engineering Research Institute
Sheffield Hallam University, United Kingdom
March 2018

List of Symbols and Abbreviations

h	Planck constant
f	frequency in Hz
e	electronic charge
k	Boltzmann constant
χ	electron affinity
ε_0	dielectric permittivity of free space
ε_s	dielectric permittivity of semiconductor
ε_r	relative permittivity of semiconductor
σ	electrical conductivity
T	temperature in Kelvin
φ_b	potential barrier height
φ_m	metal work function
E_g	energy bandgap of a semiconductor
A^*	Richardson constant for thermionic emission
S	area of a solar cell
n	ideality factor of a diode
V_oc	open circuit voltage of solar cells
I_sc	short circuit current of solar cells
J_sc	short circuit current density of solar cells
FF	fill factor, or curve factor, of solar cells
η	solar to electric power conversion efficiency
CdTe	cadmium telluride
CIGS	copper indium gallium diselenide
GaAs	gallium arsenide
AlAs	aluminium arsenide