

Contents

Preface	<i>XVII</i>
List of Contributors	<i>XXI</i>
Acknowledgments	<i>XXVII</i>
Abbreviations	<i>XXXI</i>

Part one Introduction 1

1	Introduction to Thin-Film Photovoltaics	3
	<i>Thomas Kirchartz and Uwe Rau</i>	
1.1	Introduction	3
1.2	The Photovoltaic Principle	5
1.2.1	The Shockley–Queisser Theory	5
1.2.2	From the Ideal Solar Cell to Real Solar Cells	9
1.2.3	Light Absorption and Light Trapping	10
1.2.4	Charge Extraction	12
1.2.5	Nonradiative Recombination	16
1.3	Functional Layers in Thin-Film Solar Cells	18
1.4	Comparison of Various Thin-Film Solar-Cell Types	20
1.4.1	Cu(In,Ga)Se ₂	20
1.4.1.1	Basic Properties and Technology	20
1.4.1.2	Layer-Stacking Sequence and Band Diagram of the Heterostructure	22
1.4.2	CdTe	23
1.4.2.1	Basic Properties and Technology	23
1.4.2.2	Layer-Stacking Sequence and Band Diagram of the Heterostructure	24
1.4.3	Thin-Film Silicon Solar Cells	25
1.4.3.1	Hydrogenated Amorphous Si (a-Si:H)	25
1.4.3.2	Metastability in a-Si:H: The Staebler–Wronski Effect	27
1.4.3.3	Hydrogenated Microcrystalline Silicon (μc-Si:H)	27

1.4.3.4	Micromorph Tandem Solar Cells	27
1.5	Conclusions	28
	References	28

Part Two Device Characterization 33

2	Fundamental Electrical Characterization of Thin-Film Solar Cells	35
	<i>Thomas Kirchartz, Kaining Ding, and Uwe Rau</i>	
2.1	Introduction	35
2.2	Current/Voltage Curves	36
2.2.1	Shape of Current/Voltage Curves and their Description with Equivalent Circuit Models	36
2.2.2	Measurement of Current/Voltage Curves	41
2.2.3	Determination of Ideality Factors and Series Resistances	42
2.2.4	Temperature-Dependent Current/Voltage Measurements	44
2.3	Quantum Efficiency Measurements	47
2.3.1	Definition	47
2.3.2	Measurement Principle and Calibration	49
2.3.3	Quantum Efficiency Measurements of Tandem Solar Cells	51
2.3.4	Differential Spectral Response (DSR) Measurements	52
2.3.5	Interpretation of Quantum Efficiency Measurements in Thin-Film Silicon Solar Cells	53
	References	58
3	Electroluminescence Analysis of Solar Cells and Solar Modules	61
	<i>Thomas Kirchartz, Anke Helbig, Bart E. Pieters, and Uwe Rau</i>	
3.1	Introduction	61
3.2	Basics	62
3.3	Spectrally Resolved Electroluminescence	65
3.4	Spatially Resolved Electroluminescence of c-Si Solar Cells	68
3.5	Electroluminescence Imaging of Cu(In,Ga)Se ₂ Thin-Film Modules	71
3.6	Modeling of Spatially Resolved Electroluminescence	75
	References	77
4	Capacitance Spectroscopy of Thin-Film Solar Cells	81
	<i>Jennifer Heath and Pawel Zabierowski</i>	
4.1	Introduction	81
4.2	Admittance Basics	82
4.3	Sample Requirements	83
4.4	Instrumentation	84
4.5	Capacitance–Voltage Profiling and the Depletion Approximation	85
4.6	Admittance Response of Deep States	86
4.7	The Influence of Deep States on CV Profiles	90
4.8	DLTS	91

4.8.1	DLTS of Thin-Film PV Devices	94
4.9	Admittance Spectroscopy	95
4.10	Drive Level Capacitance Profiling	97
4.11	Photocapacitance	98
4.12	The Meyer–Neldel Rule	99
4.13	Spatial Inhomogeneities and Interface States	100
4.14	Metastability	102
	References	102

Part Three Materials Characterization 107

5 Characterizing the Light-Trapping Properties of Textured Surfaces with Scanning Near-Field Optical Microscopy 109

Karsten Bittkau

5.1	Introduction	109
5.2	How Does a Scanning Near-Field Optical Microscope Work?	110
5.3	Light Scattering in the Wave Picture	112
5.4	The Role of Evanescent Modes for Light Trapping	113
5.5	Analysis of Scanning Near-Field Optical Microscopy Images by Fast Fourier Transformation	116
5.6	How to Extract Far-Field Scattering Properties by Scanning Near-Field Optical Microscopy?	120
5.7	Conclusion	122
	References	122

6 Spectroscopic Ellipsometry 125

Sylvain Marsillac, Michelle N. Sestak, Jian Li, and Robert W. Collins

6.1	Introduction	125
6.2	Theory	127
6.2.1	Polarized Light	127
6.2.2	Reflection from a Single Interface	128
6.3	Ellipsometry Instrumentation	129
6.3.1	Rotating Analyzer SE for <i>Ex-Situ</i> Applications	130
6.3.2	Rotating Compensator SE for Real-Time Applications	131
6.4	Data Analysis	133
6.4.1	Exact Numerical Inversion	133
6.4.2	Least-Squares Regression	134
6.4.3	Virtual Interface Analysis	134
6.5	RTSE of Thin Film Photovoltaics	134
6.5.1	Thin Si:H	135
6.5.2	CdTe	139
6.5.3	CuInSe ₂	141
6.6	Summary and Future	145
6.7	Definition of Variables	145
	References	146

7	Photoluminescence Analysis of Thin-Film Solar Cells	151
	<i>Thomas Unold and Levent Gütaý</i>	
7.1	Introduction	151
7.2	Experimental Issues	154
7.2.1	Design of the Optical System	154
7.2.2	Calibration	156
7.2.3	Cryostat	156
7.3	Basic Transitions	157
7.3.1	Excitons	158
7.3.2	Free-Bound Transitions	159
7.3.3	Donor–Acceptor Pair Recombination	160
7.3.4	Potential Fluctuations	162
7.3.5	Band–Band Transitions	163
7.4	Case Studies	164
7.4.1	Low-Temperature Photoluminescence Analysis	164
7.4.2	Room-Temperature Measurements: Estimation of V_{oc} from PL Yield	168
7.4.3	Spatially Resolved Photoluminescence: Absorber Inhomogeneities	170
	References	173
8	Steady-State Photocurrent Grating Method	177
	<i>Rudolf Brüggemann</i>	
8.1	Introduction	177
8.2	Basic Analysis of SSPG and Photocurrent Response	178
8.2.1	Optical Model	178
8.2.2	Semiconductor Equations	180
8.2.3	Diffusion Length: Ritter–Zeldov–Weiser Analysis	181
8.2.3.1	Evaluation Schemes	183
8.2.4	More Detailed Analyses	184
8.2.4.1	Influence of the Dark Conductivity	184
8.2.4.2	Influence of Traps	184
8.2.4.3	Minority-Carrier and Majority-Carrier Mobility-Lifetime Products	186
8.3	Experimental Setup	187
8.4	Data Analysis	189
8.5	Results	192
8.5.1	Hydrogenated Amorphous Silicon	192
8.5.1.1	Temperature and Generation Rate Dependence	192
8.5.1.2	Surface Recombination	193
8.5.1.3	Electric-Field Influence	193
8.5.1.4	Fermi-Level Position	194
8.5.1.5	Defects and Light-Induced Degradation	194
8.5.1.6	Thin-Film Characterization and Deposition Methods	195
8.5.2	Hydrogenated Amorphous Silicon Alloys	196

8.5.3	Hydrogenated Microcrystalline Silicon	196
8.5.4	Hydrogenated Microcrystalline Germanium	197
8.5.5	Other Thin-Film Semiconductors	197
8.6	Density-of-States Determination	198
8.7	Summary	198
	References	198
9	Time-of-Flight Analysis	203
	<i>Torsten Bronger</i>	
9.1	Introduction	203
9.2	Fundamentals of TOF Measurements	204
9.2.1	Anomalous Dispersion	205
9.2.2	Basic Electronic Properties of Thin-Film Semiconductors	207
9.3	Experimental Details	208
9.3.1	Accompanying Measurements	210
9.3.1.1	Capacitance	210
9.3.1.2	Collection	212
9.3.1.3	Built-in Field	212
9.3.2	Current Decay	212
9.3.3	Charge Transient	215
9.3.4	Possible Problems	217
9.3.4.1	Dielectric Relaxation	217
9.3.5	Inhomogeneous Field	218
9.4	Analysis of TOF Results	219
9.4.1	Multiple Trapping	219
9.4.1.1	Overview of the Processes	219
9.4.1.2	Energetic Distribution of Carriers	220
9.4.1.3	Time Dependence of Electrical Current	223
9.4.2	Spatial Charge Distribution	223
9.4.2.1	Temperature Dependence	223
9.4.3	Density of States	225
9.4.3.1	Widths of Band Tails	225
9.4.3.2	Probing of Deep States	226
	References	228
10	Electron-Spin Resonance (ESR) in Hydrogenated Amorphous Silicon (a-Si:H)	231
	<i>Klaus Lips, Matthias Fehr, and Jan Behrends</i>	
10.1	Introduction	231
10.2	Basics of ESR	232
10.3	How to Measure ESR	235
10.3.1	ESR Setup and Measurement Procedure	235
10.3.2	Pulse ESR	238
10.3.3	Sample Preparation	239
10.4	The g Tensor and Hyperfine Interaction in Disordered Solids	240

10.4.1	Zeeman Energy and g Tensor	240
10.4.2	Hyperfine Interaction	243
10.4.3	Line-Broadening Mechanisms	245
10.5	Discussion of Selected Results	248
10.5.1	ESR on Undoped a-Si:H	248
10.5.2	LESR on Undoped a-Si:H	252
10.5.3	ESR on Doped a-Si:H	253
10.5.4	Light-Induced Degradation in a-Si:H	257
10.5.4.1	Excess Charge-Carrier Recombination and Weak Si-Si Bond Breaking	258
10.5.4.2	Si-H Bond Dissociation and Hydrogen Collision Model	260
10.5.4.3	Transformation of Existing Nonparamagnetic Charged Dangling-Bond Defects	260
10.6	Alternative ESR Detection	263
10.6.1	History of EDMR	264
10.6.2	EDMR on a-Si:H Solar Cells	265
10.7	Concluding Remarks	268
	References	269
11	Scanning Probe Microscopy on Inorganic Thin Films for Solar Cells	275
	<i>Sascha Sadewasser and Iris Visoly-Fisher</i>	
11.1	Introduction	275
11.2	Experimental Background	276
11.2.1	Atomic Force Microscopy	276
11.2.1.1	Contact Mode	277
11.2.1.2	Noncontact Mode	278
11.2.2	Conductive Atomic Force Microscopy	279
11.2.3	Scanning Capacitance Microscopy	280
11.2.4	Kelvin Probe Force Microscopy	282
11.2.5	Scanning Tunneling Microscopy	284
11.2.6	Issues of Sample Preparation	285
11.3	Selected Applications	286
11.3.1	Surface Homogeneity	286
11.3.2	Grain Boundaries	288
11.3.3	Cross-Sectional Studies	291
11.4	Summary	294
	References	294
12	Electron Microscopy on Thin Films for Solar Cells	299
	<i>Daniel Abou-Ras, Melanie Nichterwitz, Manuel J. Romero, and Sebastian S. Schmidt</i>	
12.1	Introduction	299
12.2	Scanning Electron Microscopy	299
12.2.1	Imaging Techniques	301
12.2.2	Electron Backscatter Diffraction	302

12.2.3	Energy-Dispersive and Wavelength-Dispersive X-Ray Spectrometry	305
12.2.4	Electron-Beam-Induced Current Measurements	307
12.2.4.1	Electron-Beam Generation	308
12.2.4.2	Charge-Carrier Collection in a Solar Cell	309
12.2.4.3	Experimental Setups	310
12.2.4.4	Critical Issues	311
12.2.5	Cathodoluminescence	312
12.2.5.1	Example: Spectrum Imaging of CdTe Thin Films	315
12.2.6	Scanning Probe and Scanning-Probe Microscopy Integrated Platform	318
12.2.7	Combination of Various Scanning Electron Microscopy Techniques	322
12.3	Transmission Electron Microscopy	323
12.3.1	Imaging Techniques	324
12.3.1.1	Bright-Field and Dark-Field Imaging in the Conventional Mode	324
12.3.1.2	High-Resolution Imaging in the Conventional Mode	325
12.3.1.3	Imaging in the Scanning Mode Using an Annular Dark-Field Detector	327
12.3.2	Electron Diffraction	327
12.3.2.1	Selected-Area Electron Diffraction in the Conventional Mode	327
12.3.2.2	Convergent-Beam Electron Diffraction in the Scanning Mode	328
12.3.3	Electron Energy-Loss Spectrometry and Energy-Filtered Transmission Electron Microscopy	329
12.3.3.1	Scattering Theory	329
12.3.3.2	Experiment and Setup	330
12.3.3.3	The Energy-Loss Spectrum	331
12.3.3.4	Applications and Comparison with EDX Spectroscopy	334
12.3.4	Off-Axis and In-Line Electron Holography	335
12.4	Sample Preparation Techniques	338
12.4.1	Preparation for Scanning Electron Microscopy	338
12.4.2	Preparation for Transmission Electron Microscopy	339
	References	341
13	X-Ray and Neutron Diffraction on Materials for Thin-Film Solar Cells	347
	<i>Susan Schorr, Christiane Stephan, Tobias Törndahl, and Roland Mainz</i>	
13.1	Introduction	347
13.2	Diffraction of X-Rays and Neutron by Matter	347
13.3	Neutron Powder Diffraction of Absorber Materials for Thin-Film Solar Cells	351
13.3.1	Example: Investigation of Intrinsic Point Defects in Nonstoichiometric CuInSe ₂ by Neutron Diffraction	351
13.4	Grazing Incidence X-Ray Diffraction (GIXRD)	354

13.5	Energy Dispersive X-Ray Diffraction (EDXRD)	357
	References	362
14	Raman Spectroscopy on Thin Films for Solar Cells	365
	<i>Jacobo Álvarez-García, Víctor Izquierdo-Roca, and Alejandro Pérez-Rodríguez</i>	
14.1	Introduction	365
14.2	Fundamentals of Raman Spectroscopy	366
14.3	Vibrational Modes in Crystalline Materials	368
14.4	Experimental Considerations	370
14.4.1	Laser Source	370
14.4.2	Light Collection and Focusing Optics	372
14.4.3	Spectroscopic Module	372
14.5	Characterization of Thin-Film Photovoltaic Materials	373
14.5.1	Identification of Crystalline Structures	373
14.5.2	Evaluation of Film Crystallinity	377
14.5.3	Chemical Analysis of Semiconducting Alloys	378
14.5.4	Nanocrystalline and Amorphous Materials	380
14.5.5	Evaluation of Stress	382
14.6	Conclusions	383
	References	384
15	Soft X-Ray and Electron Spectroscopy: A Unique “Tool Chest” to Characterize the Chemical and Electronic Properties of Surfaces and Interfaces	387
	<i>Marcus Bär, Lothar Weinhardt, and Clemens Heske</i>	
15.1	Introduction	387
15.2	Characterization Techniques	388
15.3	Probing the Chemical Surface Structure: Impact of Wet Chemical Treatments on Thin-Film Solar Cell Absorbers	394
15.4	Probing the Electronic Surface and Interface Structure: Band Alignment in Thin-Film Solar Cells	399
15.5	Summary	405
	References	405
16	Elemental Distribution Profiling of Thin Films for Solar Cells	411
	<i>Volker Hoffmann, Denis Klemm, Varvara Efimova, Cornel Venzago, Angus A. Rockett, Thomas Wirth, Tim Nunney, Christian A. Kaufmann, and Raquel Caballero</i>	
16.1	Introduction	411
16.2	Glow Discharge-Optical Emission (GD-OES) and Glow Discharge-Mass Spectroscopy (GD-MS)	413
16.2.1	Principles	413
16.2.2	Instrumentation	413
16.2.2.1	Plasma Sources	413

16.2.2.2	Plasma Conditions	415
16.2.2.3	Detection of Optical Emission	415
16.2.2.4	Mass Spectroscopy	416
16.2.3	Quantification	416
16.2.3.1	Glow Discharge-Optical Emission Spectroscopy	416
16.2.3.2	Glow Discharge-Mass Spectroscopy	417
16.2.4	Applications	418
16.2.4.1	Glow Discharge-Optical Emission Spectroscopy	418
16.2.4.2	Glow Discharge-Mass Spectroscopy	418
16.3	Secondary Ion Mass Spectrometry (SIMS)	420
16.3.1	Principle of the Method	420
16.3.2	Data Analysis	423
16.3.3	Quantification	425
16.3.4	Applications for Solar Cells	426
16.4	Auger Electron Spectroscopy (AES)	427
16.4.1	Introduction	427
16.4.2	The Auger Process	427
16.4.3	Auger Electron Signals	428
16.4.4	Instrumentation	429
16.4.5	Auger Electron Signal Intensities and Quantification	431
16.4.6	Quantification	432
16.4.7	Application	433
16.5	X-Ray Photoelectron Spectroscopy (XPS)	435
16.5.1	Theoretical Principles	435
16.5.2	Instrumentation	437
16.5.3	Application to Thin Film Solar Cells	438
16.6	Energy-Dispersive X-Ray Analysis on Fractured Cross Sections	440
16.6.1	Basics on Energy-Dispersive X-Ray Spectrometry in a Scanning Electron Microscope	440
16.6.2	Spatial Resolutions	442
16.6.3	Applications	442
16.6.3.1	Sample Preparation	445
	References	445
17	Hydrogen Effusion Experiments	449
	<i>Wolfhard Beyer and Florian Einsele</i>	
17.1	Introduction	449
17.2	Experimental Setup	450
17.3	Data Analysis	454
17.3.1	Identification of Rate-Limiting Process	455
17.3.2	Analysis of Diffusing Hydrogen Species from Hydrogen Effusion Measurements	458
17.3.3	Analysis of H ₂ Surface Desorption	459
17.3.4	Analysis of Diffusion-Limited Effusion	460

17.3.5	Analysis of Effusion Spectra in Terms of Hydrogen Density of States	462
17.3.6	Analysis of Film Microstructure by Effusion of Implanted Rare Gases	463
17.4	Discussion of Selected Results	467
17.4.1	Amorphous Silicon and Germanium Films	467
17.4.1.1	Material Density versus Annealing and Hydrogen Content	467
17.4.1.2	Effect of Doping on H Effusion	468
17.4.2	Amorphous Silicon Alloys: Si-C	469
17.4.3	Microcrystalline Silicon	470
17.4.4	Zinc Oxide Films	471
17.5	Comparison with Other Experiments	471
17.6	Concluding Remarks	472
	References	473

Part Four Materials and Device Modeling 477

18 *Ab-Initio* Modeling of Defects in Semiconductors 479

Karsten Albe, Péter Ágoston, and Johan Pohl

18.1	Introduction	479
18.2	Density Functional Theory and Methods	480
18.2.1	Basis Sets	480
18.2.2	Functionals for Exchange and Correlation	481
18.2.2.1	Local Approximations	481
18.2.2.2	Functionals Beyond LDA/GGA	481
18.3	Methods Beyond DFT	483
18.4	From Total Energies to Materials' Properties	485
18.5	<i>Ab-initio</i> Characterization of Point Defects	486
18.5.1	Thermodynamics of Point Defects	488
18.5.2	Formation Energies from <i>Ab-Initio</i> Calculations	493
18.5.3	Case study: Point Defects in ZnO	494
18.6	Conclusions	497
	References	497

19 One-Dimensional Electro-Optical Simulations of Thin-Film Solar Cells 501

Bart E. Pieters, Koen Decock, Marc Burgelman, Rolf Stangl, and Thomas Kirchartz

19.1	Introduction	501
19.2	Fundamentals	501
19.3	Modeling Hydrogenated Amorphous and Microcrystalline Silicon	503
19.3.1	Density of States and Transport Hydrogenated Amorphous Silicon	503
19.3.2	Density of States and Transport Hydrogenated Microcrystalline Silicon	507

19.3.3	Modeling Recombination in a-Si:H and $\mu\text{-Si:H}$	508
19.3.3.1	Recombination Statistics for Single-Electron States: Shockley–Read–Hall Recombination	508
19.3.3.2	Recombination Statistics for Amphoteric States	510
19.3.4	Modeling Cu(In,Ga)Se ₂ Solar Cells	512
19.3.4.1	Graded Band-Gap Devices	512
19.3.4.2	Issues when Modeling Graded Band-Gap Devices	513
19.3.4.3	Example	514
19.3.5	Modeling of CdTe Solar Cells	514
19.3.5.1	Baseline	516
19.3.5.2	The $\Phi_b - N_{Ac}$ (Barrier–Doping) Trade-Off	516
19.3.5.3	C–V Analysis as an Interpretation Aid of I – V Curves	518
19.4	Optical Modeling of Thin Solar Cells	519
19.4.1	Coherent Modeling of Flat Interfaces	519
19.4.2	Modeling of Rough Interfaces	519
19.5	Tools	521
19.5.1	AFORS-HET	521
19.5.2	AMPS-1D	522
19.5.3	ASA	523
19.5.4	PC1D	523
19.5.5	SCAPS	523
19.5.6	SC-SIMUL	524
	References	524
20	Two- and Three-Dimensional Electronic Modeling of Thin-Film Solar Cells	529
	<i>Ana Kanevce and Wyatt K. Metzger</i>	
20.1	Introduction	529
20.2	Applications	529
20.3	Methods	531
20.3.1	Equivalent-Circuit Modeling	531
20.3.2	Solving Semiconductor Equations	532
20.3.2.1	Creating a Semiconductor Model	533
20.4	Examples	534
20.4.1	Equivalent-Circuit Modeling Examples	534
20.4.2	Semiconductor Modeling Examples	535
20.5	Summary	539
	References	539
	Index	541