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TABLE OF CONTENTS

VOLUME I

Cherry Award

Chairs: M. Yamaguchi
J. Schmid

Willian Cherry Address

Fabrication of a New Type of Synthetic Semiconductor in Space 1
Y. Hamakawa

Highlights EUPSEC

Chair: R. Hill

European Strategies in Photovoltaics 9
W. Palz

European PV Industry—The Future Beckons 12
D.J. Shah

Thin Film Photovoltaics—Strategy of Eurec Agency 15
W.H. Bloss

Switzerland's Approach to Photovoltaic Applications 22
T. Nordmann

Highlights PVSEC

Chair: M. Yamaguchi

Present Status and Future Prospects of Electro-Magnetic Casting for Silicon Solar Cells 30
K. Kaneko, R. Kawamura and T. Misawa

Recent Advances of Thin Film Solar Cells and Their Technologies 34
Y. Hamakawa

Japanese Space Solar Cell Activities—GaAs and Si— 42
S. Matsuda, Y. Yamamoto and O. Kawasaki

Japanese Activities for Introducing Residential PV Systems as a National Energy Supply 48
K. Kurokawa

P2 Plenary Session
CIGS and CdTe Solar Cells

Chairs: T. Nakada
B. Basol

Polycrystalline Thin-Film Technologies: Status and Prospects 52
A. Catalano

Sequential Deposition of Cu(In,Ga)(S,Se)$_2$ 60
S. Zweigart, T. Walter, C. Köble, S.M. Sun, U. Rühle and H.W. Schock

High Efficiency Cu(In,Ga)Se$_2$-Based Solar Cells: Processing of Novel Absorber Structures 68
M.A. Contreras, J. Tuttle, A. Gabor, A Tennant, K. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang and R. Noufi

201 CIS and CIGS Films and Devices

Chairs: L. Stolt
H.S. Ullal

Processing Issues for Thin-Film CdTe Cells and Modules 76
R.W. Birkmire and P.V. Meyers

Band-Gap Engineering in Cu(In,Ga)Se$_2$ Thin Films Grown from (In,Ga)$_2$Se$_3$ Precursors 83
A.M. Gabor, J.R. Tuttle, A. Schwartzlander, A.L. Tennant, M.A. Contreras and R. Noufi

Development of High-Efficiency CuIn$_x$Ga$_{1-x}$Se$_2$ Thin-Film Solar Cells by Selenization with Elemental Se Vapor in Vacuum 87
K. Kushiya, A. Shimizu, K. Saito, A. Yamada and M. Konagai

A Novel Cadmium Free Buffer Layer for Cu(In,Ga)Se$_2$ Based Solar Cells 91
D. Hariskos, M. Ruckh, U. Rühle, T. Walter and H.W. Schock

202 CdTe Film and Device Processing Issues

Chairs: A.H. Fahrenbruch
R.W. Birkmire

Superstrate-Type CuInSe$_2$ Solar Cells with Chemically Deposited CdS Window Layers 95
T. Nakada, N. Okano, Y. Tanaka, H. Fukuda and A. Kunioka

The Effects of CdS Processing and Glass Substrates on the Performance of CdTe Solar Cells 99
C.S. Ferekides, K. Dugan, V. Ceekala, J. Killian, D. Oman, R. Swaminathan and D.L. Morel

Vapor Chloride Treatment of Polycrystalline CdTe/CdS Films 103
T.X. Zhou, N. Reiter, R.C. Powell, R. Sasala and P.V. Meyers

A Treatment to Allow Contacting CdTe with Different Conductors 107
B.E. McCandless, Y. Qu and R.W. Birkmire

RF Sputtered CdS/CdTe Solar Cells: Effects of Magnetic Field, RF Power, Target Morphology and Substrate Temperature 111
A.D. Compaan, M. Shao, C.N. Tabory, Z. Feng, A. Fischer, I. Matulionis and R.G. Bohn

203 CdTe and CIS Film Characterization and Device Modelling

Chairs: H.W. Schock
K. Sato

Health and Environmental Hazards of CdTe Photovoltaic Module Production, Use and Decommissioning 115
P.D. Moskowitz, H. Steinberger and W. Thumm

Six-Year Efficiency Gains for CdTe and $CuIn_{1-X}Ga_XSe_2$ Solar Cells: What Has Changed? 119
J.R. Sites and X. Liu

Numerical Modeling of Graded Band GAP CIGS Solar Cells 123
J.L. Gray and Y.J. Lee

Micro Through Nanostructure Investigations of Polycrystalline CdTe: Correlations with Processing and Electronic Structures 127
D.H. Levi, H.R. Moutinho, F.A. Hasoon, B.M. Keyes, R.K. Ahrenkiel, M. Al-Jassim, L.L. Kazmerski and R.W. Birkmire

Optical Characterization of $CuInSe_2$ Grown by Molecular Beam Epitaxy 132
S. Niki, Y. Makita, A. Yamada, H. Shibata, P.J. Fons, A. Obara, T. Kurafuji, S. Chichibu and H. Nakanishi

Tailoring the Electronic Properties of One Step Electrodeposited $CuInSe_2$ Films by Annealing in Se Vapor Under Controlled Activity Conditions. Elaboration of Efficient CIS/ZnO Solar Cells 136
D. Lincot, J.-F. Guillemoles, P. Cowache, S. Massaccesi, L. Thouin, K. Fezzaa, F. Boisivon and J. Vedel,

204 CIS Process and Substrate Effects

Chairs: J.R. Sites
V.K. Kapur

Process Development for $CuInSe_2$-Based Power Modules 140
J. Britt, A. Delahoy, G. Butler, F. Faras, A. Muthaiah, A. Sizemore, F. Ziobro and Z. Kiss

The Impact of Controlled Sodium Incorporation on Rapid Thermal Processed $Cu(InGa)Se_2$-Thin Films and Devices 144
V. Probst, J. Rimmasch, W. Riedl, W. Stetter, J. Holz, H. Harms, F. Karg and H.W. Schock

Studies on Substrates and Contacts for CIS Films and Devices 148
B.M. Başol, V.K. Kapur, C.R. Leidholm, A. Minnick and A. Halani

Substrate Influences on CIS Device Performance 152
D.F. Dawson-Elli, C.B. Moore, R.R. Gay and C.L. Jensen

Influence of Substrates on the Electrical Properties of $Cu(In,Ga)Se_2$ Thin Films 156
M. Ruckh, D. Schmid, M. Kaiser, R. Schäffler, T. Walter and H.W. Schock

2P1 CIS and Related Alloys

Chair: S. Niki

Binary Phase Segregation in $CuInS_2$ Thin Films for Efficient Solar Energy Conversion 160
R. Scheer, I. Luck, S. Hessler, H. Sehnert and H.J. Lewerenz

Sodium Diffusion, Selenization and Microstructural Effects Associated with Various Molybdenum Back Contact Layers for CIS-Based Solar Cells 164
J.H. Scofield, S. Asher, D. Albin, J. Tuttle, M. Contreras, D. Niles, R. Reedy, A. Tennant and R. Noufi

Preparation of $CuIn_xGa_{1-x}Se_2$ Thin Films on Si Substrates 168
Y. Yamamoto, T. Yamaguchi, M. Suzuki, Y. Demizu and A. Yoshida

Structure and Optoelectronic Properties of Single Crystal Epitaxial $Cu(In_{1-x}Ga_x)Se_2$ and Ordered Defect Compounds 172
A. Rockett, G. Berry, D. Schroeder, H.-Z. Xiao and L.C. Yang

Oscillating Temperature Selenization of Cu, Ga, In Elemental Layers in a Se Vapour 176
N. Romeo, A. Bosio, V. Canevari and R. Tedeschi

The Low Temperature Deposition of ICB-Grown $CuInSe_2$ Thin Films 179
H. Sano, S. Nakamura, K. Kondo and K. Sato

Development of Manufacturable CIS Processing 182
G. Attar, A. Muthaiah, H. Natarajan, D. Nierman, S. Karthikeyan, S. Zafar, C.S. Ferekides and D.L. Morel

A Novel Method of Synthesizing P-$CuInSe_2$ Thin Films from the Stacked Elemental Layers Using a Closed Graphite Box 186
F.O. Adurodija, M.J. Carter and R. Hill

Polycrystalline $CuIn_{1-x}Ga_xSe_2$ Thin Film PV Solar Cells Prepared by Two-Stage Selenization Process Using Se Vapor 190
N.G. Dhere, S. Kuttath, K.W. Lynn, R.W. Birkmire and W.N. Shafarman

Non-Cadmium ZnO/CIS and ZnSe/CIS Solar Cells 194
L.C. Olsen, F.W. Addis, D. Greer, W. Lei and F. Abulfotah

A Comprehensive Characterization of the Interfaces in Mo/CIS/CdS/ZnO Solar Cell Structures 198
D. Schmid, M. Ruckh and H.W. Schock

Preparation of $CuInSe_2$ Thin Films Using Electrodeposited In/Cu Metallic Layer 202
Y.H. Kim, Y.E. Lee, H.J. Kim and J. Song

Progress in $Cu(In,Ga)Se_2$ Solar Cells and Submodules 206
J. Kessler, S. Wideman, L. Russell, T. Lommasson, S. Skibo, J. Fogleboch, T. Kloss and R.R. Arya

Photovoltaic Cells with Efficiency Exceeding 10% Using Monocrystalline $CuInSe_2$ Substrates 210
L.S. Yip and I. Shih

Recent Developments in ZnO/CdS/$CuGaSe_2$ Single Crystal Solar Cells 214
M. Saad, H. Riazi-Nejad, E. Bucher and M.C. Lux-Steiner

Development of ZnO/ZnSe/$CuIn_{1-x}Ga_xSe_2$ Thin-Film Solar Cells with Band Gap of 1.3 to 1.5 eV 218
Y. Ohtake, K. Kushiya, A. Yamada, M. Konagai

Photovoltaic Properties of $Cu(In,Ga)Se_2$ Thin Film Solar Cell Fabricated by Coevaporation Process 222
M. Nishitani, T. Negami, M. Ikeda, N. Kohara, M. Terauchi, T. Wada and T. Hirao

The Effect of SE Content on Defect Levels in $CuInSe_2$ Single Crystals Detected by Photoacoustic Spectrometry 226
A. Zegadi, M.V. Yakushev, E. Ahmed, M.A. Slifkin, A.E. Hill and R.D. Tomlinson

Growth Studies of $CuInSe_2$ Using Cu-Se Fluxes 230
M. Casteleyn, M. Burgelman, B. Depuydt, A. Niemegeers and I. Clemminck

Characterization of Cu-In-Ga Precursors Used to Form $Cu(In,Ga)Se_2$ Films 234
M. Marudachalam, R. Birkmire, J.M. Schultz and T. Yokimcus

A Chemical Kinetic Analysis of the Formation of $CuInSe_2$ at Different Temperatures 238
T.W.F. Russell, N. Orbey and R.W. Birkmire

Heteroepitaxy of $CuIn_xSe_y$ on Si and PbSe/CaF_2/Si Substrates 242
S. Blunier, A.N. Tiwari, K. Kessler, H. Zogg, M. Döbeli and M. Filzmoser

Fabrication and Characterization of Thin Films of $CuIn(S,Se)_2$ Quaternary Compounds Obtained by Close-Spaced Vapor Transport 246
F. Guastavino A. Zouaoui, C. Llinarès, K. Djessas and G. Massé

CIS Solar Cells with ZnO Windows Deposited by ALE 250
L. Stolt, J. Hedström and J. Skarp

Effects of Cd-Free Buffer Layer for $CuInSe_2$ Thin-Film Solar Cells 254
T. Nii, I. Sugiyama, T. Kase, M. Sato, Y. Kaniyama, S. Kuriyagawa, K. Kushiya and H. Takeshita

Thermal Oxidation of $CuInSe_2$: Experiment and Physico-Chemical Model 258
M.E. Boiko and G.A. Medvedkin

Environmental and Health Aspects of CIS-Module Production, Use and Disposal 262
W. Thumm, A. Finke, B. Neumeier, B. Beck, A. Kettrup, H. Steinberger and P.D. Moskowitz

2P2 Polycrystalline Thin Film Materials and Devices

Chair: N. Romeo

Overview of the U.S. DOE/NREL Polycrystalline Thin-Film Photovoltaic Technologies 266
H.S. Ullal, K. Zweibel, B.G. von Roedern, R. Noufi and P. Sheldon

Effect of Thin Film Module Geometry on Solar Cell Current-Voltage Analysis 271
I.L. Eisgruber and J.R. Sites

Room-Temperature FT-Luminescence Analysis of $Cu(In,Ga)Se_2$ Films and Devices 275
J.D. Webb, M. Contreras and R. Noufi

Study on the Interfacial Structure and Junction Depth of Polycrystalline $Cu(In,Ga)Se_2$ Devices 279
A.J. Nelson, A.M. Gabor, M.A. Contreras, J.R. Tuttle, R. Noufi, P. Asoka-Kumar and K.G. Lynn

Interpretation of Laser Scans From Thin-Film Polycrystalline Photovoltaic Modules 283
I.L. Eisgruber, R.J. Matson, J.R. Sites and K.A. Emery

The Effects of the Band Bending Caused by Interface States in CdTe/CIS Solar Cells 287
Y.J. Lee and J.L. Gray

Admittance Measurements on $Cu(In,Ga)Se_2$ Polycrystalline Thin-Film Solar Cells 291
J.H. Scofield, M. Contreras, A.M. Gabor, R. Noufi and J.R. Sites

Electronic Properties of Intimate Mo and CdS Junctions In-Situ Formed on $CuInSe_2$ (011) Cleavage Planes 295
T. Löher, C. Pettenkofer and W. Jaegermann

Surface Energy Band Gap of Polycrystalline $CuInSe_2$ Thin-Films in Tunneling Spectroscopy 299
Z. Zhang, P. Heuell, M. Kulakov and B. Bullemer

Evidence for Amorphous Like Behavior in Small Grain Thin Film Polycrystalline Solar Cells 303
J.E. Phillips, W.N. Shafarman and E. Shan

Preparation and Characterization of CdTe Thin Films Deposited by CSS 307
G. Gordillo, J.M. Florez, L.C. Hernandez and P. Teherán

Environmentally Responsible Production, Use and Disposition of Cd-Bearing PV Modules 311
R.A. Sasala, T. Zhou and W.M. Kocher

Photovoltaic Properties of Sintered CdS/CdTe Solar Cells with TCO Electrodes 315
H.D. Kim, D.S. Kim, J.S. Song and B.T. Ahn

Surface Cleaning of the Screen Printed CdS Film 319
T. Aramoto, H. Higuchi, T. Arita, T. Nishio, H. Ohyama, A. Hanafusa, S. Kumazawa, H. Takada, K. Omura, N. Nakayama, H. Takakura and M. Murozono

Growth of Epitaxial CdTe/CdS Heterostructures for Single Crystal Thin Film Solar Cell Applications 323
K. Kessler, A.N. Tiwari, S. Blunier and H. Zogg

Optical and Electrical Characterization of Chemically Deposited Cadmium Sulfide Thin Films 327
M.E. Özsan, D.R. Johnson, M. Sadeghi, D. Sivapathasundaram, L.M. Peter, M.J. Furlong, G. Goodlet, A. Shingleton, D. Lincot, B. Mokili and J. Vedel

A Comparative Study of Compositional and Structural Properties of CdTe Thin Films Prepared by Different Electroplating Techniques 331
P.D. Paulson, V. Dutta and C. Singh

Polycrystalline Thin Film CdTe Solar Cells Fabricated by Electrodeposition 334
D. Kim, S. Pozder, Y. Zhu and J.U. Trefny

Effect of Annealing on Microstructure, Residual Stress and Photovoltaic Characteristics of Electrodeposited CdTe Films 338
D. Kim, B. Qi, D.L. Williamson and J.U. Trefny

High Conductivity CdS Thin Films Formed by Gas Assisted Chemical Vapor Transport (CVTG) 342
P.J. Sebastian and A. Sanchez

Optimization and Characterization of Reactively Sputtered ZNO 346
S. Zafar, C.S. Ferekides and D.L. Morel

In Situ Interference Measurements of Glass Substrate Temperature 350
Z. Feng, C.N. Tabory and A.D. Compaan

RF Sputtered Films of Cu-Doped and N-Doped ZnTe 354
R.G. Bohn, C.N. Tabory, C. Deak, M. Shao, A.D. Compaan and N. Reiter

Thin Film Solar Cells Based on Layered Chalcogenides: Fundamentals and Perspectives of van der Waals Epitaxy 357
W. Jaegermann, C. Pettenkofer, O. Lang, R. Schlaf, S. Tiefenbacher and Y. Tomm

A Thin Film Solar Cell Based on the $CuIn_3Se_5$ Ordered Vacancy Compound 361
S. Menezes, J. Kessler, D. Schmid, H.W. Schock, A. Nelson and R.J. Matson

Investigation on SnS Film by RF Sputtering for Photovoltaic Application 365
W. Guang-Pu, Z. Zhi-Lin, Z. Wei-Ming, G. Xiang-Hong, C. Wei-Qun, H. Tanamura, M. Yamaguchi, H. Noguchi, T. Nagatomo and O. Omoto

Study of CdS_XTe_{1-X} Solid Solutions Obtained by Screen Printing 369
O. de Melo, M. Melendez-Lira, I. Hernandez-Calderon, L. Baños and A. Morales-Acevedo

Amorphous Silicon Technology: Coming of Age 373
C.R. Wronski

P4 Plenary Session
Amorphous Silicon Technology

Chairs: M. Konagai and C. Wronski

Progress in Triple-Junction Amorphous Silicon-Based Alloy Solar Cells and Modules Using Hydrogen Dilution 380
J. Yang, A. Banerjee, T. Glatfelter, K. Hoffman, X. Xu and S. Guha

Approaches for Stable Multi-Junction a-Si Solar Cells 386
Y. Hishikawa, K. Ninomiya, E. Maruyama, S. Kuroda, A. Terakawa, K. Sayama, H. Tarui, M. Sasaki, S. Tsuda and S. Nakano

Progress in Amorphous Silicon Based Multijunction Modules 394
R.R. Arya, R.S. Oswald, Y.M. Li, N. Maley, K. Jansen, L. Yang, L.F. Chen, F. Willing, M.S. Bennett, J. Morris and D.E. Carlson

401 Amorphous Silicon Cells and Modules-I

Chairs: H. Okamoto
J. Yang

Large Area Module Performance and Identification and Control of P-I Interface-Correlated Device Degradation and Further Improvement in Stabilized Efficiencies of Single-Junction a-Si Solar Cells 401
J. Xi, D. Shugar and H. Volltrauer

Application of P-Type Microcrystalline Silicon to a-Si Alloy Solar Cells 405
H. Sannomiya, K. Nomoto, A. Chida, Y. Nakata and Y. Yamamoto

Intrinsic Microcrystalline Silicon (μc-Si:H)— A Promising New Thin Film Solar Cell Material 409
J. Meier, S. Dubail, R. Flückiger, D. Fischer, H. Keppner and A. Shah

High Efficiency a-Si Solar Cells with ZnO Films 413
W.W. Wenas, K. Dairiki, A. Yamada, M. Konagai, K. Takahashi, J.H. Jang and K.S. Lim

The Utilization of Microcrystalline Si and SiC for the Efficiency Improvement in a-Si Solar Cells 417
W. Ma, T. Saida, C.C. Lim, S. Aoyama, H. Okamoto and Y. Hamakawa

402 Amorphous Silicon Materials-I

Chairs: J.M. Ruiz
V.L. Dalal

Real Time Characterization of the Preparation of Amorphous Silicon-Based Solar Cells 421
Y. Lu, S. Kim, I.-S. Chen, Y. Lee, C.M. Fortmann, C.R. Wronski and R.W. Collins

Atomic Force Microscopy of Ultra Thin Amorphous Silicon Films Deposited on Various Substrate Surfaces 425
M. Matsuse, M. Kawasaki and H. Koinuma

Correlation Between Improved Stability and Microstructural Properties of a-Si:H and a-Ge:H 429
T. Haage, S. Bauer, B. Schröder and H. Oechsner

H_2 Diluted Low Temperature Deposited a-Si:H, Initial Degradation and Modeling 433
A. Rothwarf, Y. Lubianiker, I. Balberg, R.R. Arya and J. Keane

Precise Investigation of the Light-Saturated Defect Density in Amorphous Silicon Very Thin Films and Solar Cells 437
J. Kočka, M. Vaněček, P. Macháček, A. Fejfar, E. Šípek, Ho-The-Ha, I. Pelant, J. Fric, J. Rosa, Z. Remeš, A. Poruba, M. Konagai and W. Kusian

403 Amorphous Silicon Cells and Modules-II

Chairs: S. Tsuda
R. Arya

A New Structure a-Si Solar Cell With Plastic Film Substrate 441
Y. Ichikawa, K. Tabuchi, S. Kato, A. Takano, T. Sasaki, M. Tanda, S. Saito, H. Sato, S. Fujikake, T. Yoshida and H. Sakai

Diagnosing Tandem Cells 445
J. Hou, S.J. Fonash, M. Ghosh, J. Xi, T. Liu and F. Kampas

Metastable Shunt Paths in a-Si Solar Cells 449
T.J. McMahon and M.S. Bennett

Preparation of High Quality Widegap a-Si:H Films and Its Applications to a-Si Solar Cells 453
Y. Ashida, N. Ishiguro, K. Saitoh, T. Miyashita, N. Yanagawa, H. Tanaka, M. Sadamoto and N. Fukuda

Considerations for Light Soaking of Amorphous Silicon Photovoltaic Modules 457
W. Luft and B. von Roedern

A Critical Review of the Growth and Properties of A- (Si,Ge):H 464
V.L. Dalal, S. Kaushal, J. Xu and K. Han

Mobility and Optical Gaps in Different a-Si:H Based Materials and Their Impact on Cell Performance 468
I.-S. Chen, T. Jamali-beh, Y. Lee, C.-Y. Li and C.R. Wronski

Improvement in Stabilized Efficiency of a-Si:H Solar Cells Through Optimized p/i-Interface Layers 472
B. Rech, C. Beneking and H. Wagner

Determination of the Quality of a-Si:H Films: "True" Transport Parameters 476
N. Beck, A. Shah and N. Wyrsch

The Roles of Atomic Hydrogen Played in "The Chemical Annealing" For Fabrication of a-Si:H 480
K. Nakamura, K. Yoshino and I. Shimizu

Examination of Optimized Structures for a-Si:H Based Triple Junction Solar Cells 484
S. Bae and S.J. Fonash

The Role of Interfaces in the End-Of-Life Performance of a-Si:H Solar Cells 488
K. Vasanth, S. Wagner, D. Caputo and M. Bennett

Improvement of a-Si Solar Cells Fabricated by Mercury-Sensitized Photo-CVD Using H_2 Dilution Method 492
P. Siamchai, A. Yamada, M. Konagai, J.H. Jang and K.S. Lim

Correlation Between TCO/p and p/i Heterojunction and Effect of n/TCO Heterojunction on a-Si:H Solar Cell Performance 496
F. Smole, M. Topič and J. Furlan

Solution of the ZnO/p Contact Problem in a-Si:H Solar Cells 500
M. Kubon, E. Boehmer, M. Gastel, F. Siebke, W. Beyer, C. Beneking and H. Wagner

Lessons Learned from a Hydrogen Explosion at a Photovoltaic Research Facility 504
P. Moskowitz, W. Buchanan and W. Shafarman

Transport Properties of Doped Silicon Oxycarbide Microcrystalline Films Produced by Spatial Separation Techniques 508
R. Martins, M. Vieira, I. Ferreira, E. Fortunato and L. Guimarães

Direct Correlations of Bulk Charged and Neutral Defect Densities of States in a-Si:H Films with Characteristics of Schottky Barrier Solar Cell Structures 512
M. Güneş, H. Liu, C.M. Fortmann and C.R. Wronski

Investigation of TCO/p-Interface and Surface Morphology of a-Si:H Solar Cells by In-Situ Ellipsometry 516
H.N. Wanka, M.B. Schubert and E. Lotter

Characterization of Amorphous Silicon Pin Solar Cells by Transient Measurement Techniques 520
G. Schmid, M.B. Schubert, H. Brummack and N. Bernhard

Induced Defects in a-Si:H and a-Ge:H Calculated by Molecular Orbital Theory 524
A. Yoshida, Y. Matsuda, K. Nakanose and H. Ogawa

Outdoor Performance Stability and Controlled Light-Soak Testing of Amorphous Silicon Multijunction Modules at NREL 528
L. Mrig, J. Burdick, W. Luft and B. Kroposki

Monitoring Outdoor Performance and Photodegradation of a-Si:H Modules by Evaluation of Continuously Measured I-V Curves 531
G. Kleiss, K. Bücher, P. Ragot and M. Chantant

New Type of Large-Area a-Si Module Produced Using a Polymer Encapsulation Method 535
K. Hayashi, A. Ishikawa, T. Endho and H. Yamagishi

Back Reflector Texture and Stability Issues in High Efficiency Multijunction Amorphous Silicon Alloy Solar Cells 539
A. Banerjee, K. Hoffman, X. Xu, J. Yang and S. Guha

Charged and Neutral Defect States in a-Si:H Determined from Improved Analysis of the Constant Photocurrent Method 543
F. Siebke, H. Stiebig, A. Abo-Arais and H. Wagner

Improvement of Film Stability of a-Si:H Deposited by RPCVD Using SiH_2Cl_2 547
M.K. Chu, J.S. Byun, H.B. Jeon, K.H. Lee, M. Park, K.C. Park, J. Jang, H.R. Park, D.W. Kim and K.S. Yoon

Low Bandgap a-Si:H Film with Better Stability Prepared by RF PECVD Method Using Helium Dilution 551
S. Ray, S. Hazra, A.R. Middya and A.K. Barua

New Evaluation Technique for Thin-Film Solar Cell Back-Reflector Using Photothermal Deflection Spectroscopy 555
X. Deng and K.L. Narasimhan

High Electron and Hole Drift Mobility in a-Si:H 559
G. Ganguly and A. Matsuda

In situ Characterization of Growing Hydrogenated Amorphous Silicon Thin Films by P-Polarized Laser Light Reflection Measurement 563
N. Naito, M. Sumiya, M. Kawasaki and H. Koinuma

Optimization of Multijunction a-Si:H Solar Cells Using an Integrated Optical/Electrical Model 567
R.E. Rocheleau and M. Vierthaler

a-Si:H Optical Speed Detector Based on the Flying Spot Technique 571
M. Vieira, A. Fantoni, A. Maçarico, F. Soares and R. Martins

Comparison of Diffusion Length Measureaments from the Flying Spot Technique and the Photocarrier Grating Method in Amorphous Thin Films 575
M. Vieira, A. Fantoni, R. Martins, V. Chu, S. Koynov, F. Wang, S. Grebner and R. Schwarz

Effect of "Soft Start" i-Layer Deposition on the Performance and Stability of a-Si:H p-i-n Solar Cells 579
W. Herbst, U.I. Schmidt, H. Schade, B. Schröder and H. Oechsner

Degradation of a-Si:H Solar Cells: New Evidence for a Bulk Effect 583
N. Wyrsch and A. Shah

Role of the Lateral Leakage Current on Amorphous Silicon Solar Cells 587
R. Martins, E. Fortunato, A. Bicho and G. Lavareda

4P2 Amorphous Silicon-II

Chair: J. Kocka

Recombination in a-Si:H: Results from the Standard and Defect Pool Models 591
E. Morgado

Effect of a Wide Band Gap Emitter Layer and Its Patterning on the Performance of a-Si:H Based Heterojunction Solar Cells 595
P. Chatterjee

Computer Modeling of Amorphous Silicon Tandem Cells 599
J.A. Willemen, M. Zeman and J.W. Metselaar

Spectral Response Modelling of a-Si:H Solar Cells Using Accurate Light Absorption Profiles 603
H. Stiebig, A. Kreisel, K. Winz, N. Schultz, C. Beneking, T. Eickhoff, H. Wagner and M. Meer

Quantum Efficiencies Exceeding Unity in Amorphous Silicon Solar Cells 607
D. Vanmaekelbergh, J. van de Lagemaat and R.E.I. Schropp

Monitoring a-Si:H Solar Cells Degradation by Two Sides Blue Light Collection 610
G. Masini, D. Fischer, J. Hubin, F. Palma and A. Shah

Investigation of Current Mechanisms in a-Si:H Alloy Solar Cells 614
K.R. Lord II, F.U. Syed, M.R. Walters and J.R. Woodyard

The P/I Interface Layer in Amorphous Silicon Solar Cells; A Numerical Modeling Study 618
V. Suntharalingam, C.M. Fortmann, S.J. Fonash and F.A. Rubinelli

Quantum Efficiency of a-Si:H P-I-N Solar Cells in the 250 to 375 K Range—Insights from Defect Pool Modelling 622
T. Eickhoff, C. Ulrichs, H. Stiebig, W. Grünen, W. Reetz and H. Wagner

Progress in Inexpensive a-Si:H/a-Si:H Tandem Module Technology 626
R.E.I. Schropp, M.B. von der Linden, J. Wallinga, D. Knoesen, J. Hyvärinen, J. Skarp, T. Suntola, J.A. Willemen, M. Zeman, J.W. Metselaar, W. Loyer, D. Guillardeau and E. Fabre

Properties of ZnO:Al Thin Films for Solar Cells by Pyrosol Method 630
J. Song, W.-Y. Cho, K.-S. Lim, K.-H. Yoon and G.-J. Yu

Charged and Neutral Defects in Light-Soaked a-Si:H 634
M. Kumeda, J.-H. Zhou and T. Shimizu

Optimum Technique of Depositing High-Rate Films by Normal PCVD Method 638
X. Lin, K. Lin, Y. Yu, Y.W. Lam, Y.C. Chan, S. Lin and Y.M. Chan

Degradation and Failure Mechanisms of a-Si:H Solar Cells with Aluminum Contacts 642
M.S. Haque, H.A. Naseem and W.D. Brown

Effect of Different TCO Interfaces on the Performances Presented by Hydrogenated Amorphous Silicon P-I-N Solar Cells 646
E. Fortunato, C.N. Carvalho, A. Bicho and R. Martins

Improving the Stability of Amorphous Silicon Tandem Cells 650
J. Daey Ouwens and R.E.I. Schropp

Parametric Analysis of a-SI Solar Cells from Current Voltage Measurements 654
S.S. Hegedus and J.E. Phillips

Internal Opto-Electric Properties of p-i-n a-Si:H Solar Cell on Grooved TCO Texture 658
J. Furlan, S. Amon, P. Popović and F. Smole

Generation Lifetime in Amorphous Silicon as Determined by MOS Admittance Measurements 662
W.R. Fahrner, H.C. Neitzert and E. Klausmann

Optical Modeling of a-Si:H Based Solar Cells on Textured Substrates 666
G. Tao, M. Zeman and J.W. Metselaar

Applications of Amorphous Silicon Photovoltaics: Myths and Facts 670
D.S. Shugar

ZnO/Ag Sputtering Deposition on a-Si Solar Cells 674
K. Hayashi, M. Kondo, A. Ishikawa and H. Yamagishi

Dependence of a-Si Solar Cell V_{OC} on Deposition Temperature 678
X. Deng, K.L. Narasimhan, J. Evans, M. Izu and S.R. Ovshinsky

Fabrication and Properties of the Flexible a-Si:H Solar Cells on Plastic Films Using Roll-to-Roll Method 682
H. Shinohara and M. Abe

Light-Induced Changes in Hydrogenated Amorphous Silicon: Anomalous Recombination Behaviour at Low Temperatures 686
J.C.L. Cornish, Subaer, P. Jennings and G.T. Hefter

Metalized Polymer Substrate for Flexible Amorphous Silicon Solar Cell 690
L.-C. Kuo, Y.-T. Tsai, W.-Y. Hsu and N.-H. Lu

International Photovoltaic Markets, Developments and Trends Forecast to 2010 694
P.D. Maycock

P5 Plenary Session
Terrestrial Photovoltaics

Chairs: A. Geotzberger
C. Jennings

Non-Technical Barriers to the Commercialisation of PV in Developing Countries 700
J.A. Gregory and B. McNelis

A Photovoltaic-Diesel Hybrid Generation System for Small Islands 708
T. Tadokoro, K. Taira and M. Asaoka

Sunplicity: from Complex System Design to Standard Product Level 716
M.G. Real, U. Bühler, P. Toggweiler, G. Roth and E. Bolliger

501 Module and BOS Component Evaluation and Performance

Chairs: K. Sakuta
J. Bigger

Research and Development of Evaluation Technology of Photovoltaic Power Systems 722
H. Mine, H. Yokouchi, T. Oshiro, M. Yukawa and K. Kurokawa

Data Sampling Speed Versus Energetic Measurement Errors in Photovoltaic System Monitoring 726
K. Kurokawa

Effect of Installation Conditions on the Output Characteristics of Photovoltaic Modules 730
K. Akhmad, F. Belley, A. Kitamura, F. Yamamoto, S. Akita, H. Takakura, H. Okamoto and Y. Hamakawa

Actual Optical and Thermal Performance of PV-Modules 734
S. Krauter and R. Hanitsch

DC Fluorescent Lamp for OV Home Power System 738
A. Wang, D. Zhang and Y. Wang

502 Off Grid Systems

Chairs: J. Schmid
W. Bowe

One Year Evaluation of the PV-Wind-Diesel Hybrid Project in X-Calak, Mexico 740
J.M. Huacuz, J. Agredano, G. Munguia, M.A. Borja, S. Durand, R. Foster and R. Pate

Living on PV Power in Comfort and Style 743
A. Mizany

Remote Power—Integrated, Customer Oriented Solutions 747
D. Jordan, M. Twidell, J. Patel, F. Teofilo and R. Soin

503 Utility and Grid-Connected Systems

Chairs: S. Corsi
K. Kurokawa

The 3.3 MW-Peak Photovoltaic Power Sation at Serre 750
A. Previ, A. Iliceto, G. Belli, V. Arcidiacono, S. Corsi and L. Lambri

PVUSA Utility-Scale System Capital and Maintenance Costs 754
C. Jennings, A.B. Reyes and K.P. O'Brien

Islanding Phenomenon Elimination Study at Rokko Test Center 759
A. Kitamura, M. Okamoto, F. Yamamoto, K. Nakaji, H. Matsuda and K. Hotta

Developing, Managing and Assessing a Utility Sponsored, Industry Supported PV Off-Grid Program 763
W.R. Gould

Motorway Sound Barriers: Recent Results and New Concepts for Advancement of Technology 766
T. Nordmann and A. Goetzberger

504 PV On Buildings

Chairs: T. Nordmann
A. Rohatgi

Building Integration of an Amorphous Silicon Photovoltaic Facade 770
H.A. Ossenbrink, L. Rigolini, O. Chehab and O. van der Venne

High Efficiency Photovoltaic Roof Tiles with Static Concentrators 774
S. Bowden, S.R. Wenham, M.R. Dickinson and M.A. Green

R&D of Photovoltaic Modules Integrated with Construction Materials 778
F. Shinjo

Building Opportunities in the U.S. for PV (PV:Bonus) a Progress Report 781
R.W. Taylor

Multifunctional Solar Facades—A New Challenge for Photovoltaic 784
J. Benemann

505 System Economics, Market Trends and Issues

Chairs: K.M. Hynes and P.D. Maycock

Photovoltaics in the Light of Sustainable Development and Qualitative Growth 788
J. Moesslein

Measuring the Value of Distributed Photovoltaic Generation: Final Results of the Kerman Grid-Support Project 792
H.J. Wenger, T.E. Hoff and B.K. Farmer

Pollution Mitigation and Photovoltaic Demand-Side Results from the U.S. Environmental Protection Agency Photovoltaic Demonstrations 797
E.C. Kern, Jr. and D.S. Greenberg

Distributed Photovoltaic Demand-Side Generation: An Economic Evaluation for Electric Utilities 801
G.J. Leng and J. Martín

Solar Energy Mapping by Using Cloud Images Received from GMS 805
K. Otani, T. Saitoh, I. Tsuda and K. Kurokawa

506 Module and BOS Component Design and Manufacturing

Chairs: A. Kitamura and C.E. Witt

Analysis of Grounded and Ungrounded Photovoltaic Systems 809
W.I. Bower and J.C. Wiles

Single Cell Converter System (SCCS) 813
M. Wuest, P. Toggweiler and J. Riatsch

Fourth-Generation Concentrator System: From the Lab to the Factory to the Field 816
M.J. O'Neill and A.J. McDanal

Continuous Roll-to-Roll Serpentine Deposition for High Throughput a-Si PV Manufacturing 820
M. Izu, H.C. Ovshinsky, X. Deng, A.J. Krisko, K.L. Narasimhan, R. Crucet, T. Laarman, A. Myatt and S.R. Ovshinsky

Photovoltaic Cz Silicon Manufacturing Technology Improvements 824
T.L. Jester, K.W. Mitchell, R. Probst, D. Tanner and S. Vasquez

5P1 Module and BOS Component Evaluation and Performance

Chair: S. Krauter

Advanced Automation Techniques for Interconnecting Thin Silicon Solar Cells 828
M.J. Nowlan, S.J. Hogan, G. Darkazalli, S.F. Sutherland, W.F. Breen, J.M. Murach and J.S. Patterson

Solarex Crystalline PVMaT Program 832
J.H. Wohlgemuth, D. Whitehouse, T. Koval, J. Creager, F. Artigliere and M. Conway

Development of CdTe Module Manufacturing 836
D.W. Sandwisch

Simulation Calculation of Solar Array Output Connecting Two Sub-Arrays with Different Azimuth Angles 840
H. Takakura, K. Koujitani, K. Akhmad, F. Belley, A. Kitamura, Y. Hamakawa

Calculated Effect of Central DC/AC Power Conversion from PV Generators with Different Orientations 844
T.C.J. van der Weiden and A.J. Kil

Fault Finding in a 1 MW Photovoltaic Plant by Reflectometry 846
L. Schirone, F.P. Califano, U. Moschella and U. Rocca

Technical Evaluation of a Dual-Junction Same-Band-Gap Amorphous Silicon Photovoltaic System at NREL 850
T. Strand, L. Mrig, R. Hansen and K. Emery

Performance of a 268Wp Stand-Alone PV System Test Facility 854
K.G. Adanu

A Comparison of Photovoltaic Module Performance Evaluation Methodologies for Energy Ratings 858
B. Kroposki, K. Emery, D. Myers and L. Mrig

Measurement Techniques for the 3RD Pep Round Robin 863
R.F.M. Roes, W.J. Zaaiman and H.A. Ossenbrink

Wide-View-Angle Absolute Cavity Radiometer for Solar Simulator Use 867
F. Nagamine, R. Shimokawa, T. Abe, M. Suzuki, H. Ikeda and Y. Miyake

Ultimate Transistor Electronic Load for Electrical Performance Measurement of Photovoltaic Devices Using Pulsed Solar Simulators 871
E.G. Mantingh, W. Zaaiman and H.A. Ossenbrink

Spectral Response Calibration Facility for Photovoltaic Cells 874
R. Budde, W. Zaaiman and H.A. Ossenbrink

Spectracube: A Fast Spectroradiometer for Pulsed Simulator Spectral Mismatch Corrections 877
W.J. Zaaiman, H.A. Ossenbrink and M. Mertens

Qualification Testing of Thin-Film and Crystalline Photovoltaic Modules 880
J. Burdick, J. Pruett and E. Beck

Photovoltaic Module Certification and Laboratory Accreditation Criteria Development 885
C.R. Osterwald, R. Hammond, G. Zerlaut and R. D'Aiello

Reliability Testing of PV Modules 889
J.H. Wohlgemuth

Investigation into the Causes of Browning in EVA Encapsulated Flat Plate PV Modules 893
W.H. Holley, Jr., S.C. Agro, J.P. Galica, L.A. Thoma, R.S. Yorgensen, M. Ezrin, P. Klemchuk, G. Lavigne and H. Thomas

Factors that Affect the EVA Encapsulant Discoloration Rate Upon Accelerated Exposure 897
F.J. Pern

A More Elemental Examination of Factors Governing PV Module Environmental Stability 901
T.L. Jester, D. Aldrich, J. Hummel, R.D. Wieting, J.P. Galica and L. Thoma

The Effect of Annealing and Oxidation on APCVD TiO_x Film and its Impact on the Process of Silicon Solar Cells 905
D.C. Wong, A. Waugh, B. Yui and P. Sharrock

Recent Test Results of 6 Commercial Inverters for Grid Connected PV Systems 909
E.J. Wildenbeest, S.W.H. de Haan and N.C. van der Borg

High-Performance Inverters for Grid-Connected PV Applications 913
F.J. ter Heide and J. Wanner

A Lightweight Inverter for Off-Grid and Grid-Connected Systems 917
F. Barone

Characteristics and Performance of a PV-System Consisting of 20 AC-Modules 921
L.E. de Graaf and T.C.J. van der Weiden

Test Results of a 130W AC Module; A Modular Solar AC Power Station 925
S.W.H. de Haan, H. Oldenkamp and E.J. Wildenbeest

Module Orientated Photovoltaic Inverters a Comparison of Different Circuits 929
G. Keller, T. Kreiger, M. Viotto and U. Krengel

Evaluation of the Batteries and Charge Controllers in Small Stand-Alone Photovoltaic Systems 933
J.R. Woodworth, M.G. Thomas, J.W. Stevens, S.R. Harrington, J.P. Dunlop and M.R. Swamy

Development of Intermittent Redox Flow Battery for PV System 946
I. Tsuda, K. Kurokawa and K. Nozaki

Development of Vanadium Redox Flow Battery for Photovoltaic Generation System 950
A. Shibata, K. Sato and M. Nakajima

Material and Environmental Implications of Ultra High Efficiency Solar Cells 954
A.E. Baumann, K.M. Hynes and R. Hill

An Assessment of the Environmental Impacts of Thin Film Cadmium Telluride Modules Based on Life Cycle Analysis 958
K.M. Hynes, A.E. Baumann and R. Hill

Strategies for Recycling CdTe Photovoltaic Modules 962
C. Eberspacher, C.F. Gay and P.D. Moskowitz

5P2 PV on Buildings

Chair: R.W. Taylor

Amorphous Silicon Alloy-Based Roof Integrated Photovoltaic Systems 966
P. Nath, C. Vogeli, A. Singh and J. Call

Photovoltaic Modules Integrated with a Metal Curtain Wall 969
M. Yoshino, N. Nakada, T. Mori, K. Yamagishi, S. Yoshida, Y. Hagshi and K. Shirasawa

Development of Photovoltaic Modules Integrated with Roofing Materials (Heat Insulated Roof Panel) 973
Y. Nitta, T. Hatukaiwa, T. Yamawaki, Y. Matumura and S. Mizukami

PV Modules, Using Color Solar Cells, Designed for Building 977
N. Ishikawa, H. Yamashita, S. Goda, I. Hide, T. Yoshida, K. Iwai, N. Sagara, K. Tazawa, M. Komiyama, H. Nishi and T. Harada

Siting, Installation and Performance Issues for Commercial Roof-Mounted PV Systems 981
J. Berdner, C. Whitaker, H. Wenger, C. Jennings, E. Kern and M. Russell

A New Flexible a-Si PV Module and Its Application to Rooftop PV Systems 986
Y. Ichikawa, T. Ihara, T. Hama, Y. Watanuki, S. Kato, H. Ota, H. Sakai, N. Sakai, J. Kurihara and O. Ishikawa

Lightweight Flexible Rooftop PV Module 990
M. Izu, H.C. Ovshinsky, K. Whelan, L. Fatalski, S.R. Ovshinsky, T. Glatfelter, K. Younan, K. Hoffman, A. Banerjee, J. Yang and S. Guha

Effects of Inhomogeneous Irradiation Distribution of a PV Array in an Urban Environment 994
A. Kovach

The Importance of Hybrid PV-Building Integration 998
M. Posnansky, S. Gnos and S. Coonen

Optimizing Roof-Integrated Photovoltaics: A Case Study of the PowerGuard$tm Roofing Tile 1004
T.L. Dinwoodie and D.S. Shugar

A New Type of Photovoltaic Shingle 1008
N. Okuda, T. Yagiura, M. Morizane, N. Nakamura, M. Ohnishi, S. Nakano, T. Ito, S. Omoto, Y. Yamashita, H. Ito and T. Fujiwara

"Capthel," a 66% Efficient Hybrid Solar Module and the "Ecothel" Co-Generation Solar System 1012
A. Ricaud and P. Roubeau

PV-Modules at the Facade of an Inner Courtyard—Measurements and Simulation 1016
H.G. Groehn and H. Barthels

Development, Testing and First Installations of an Integrated Solar Roof System 1020
B.M. Cross

Test Facilities and Safety Regulations for Rooftop Mounted and Gridconnected PV Systems 1024
J.H. Boumans, A.J.N. Schoen and S.A.M. Verhoeven

Performance of Modular Grid Connected PV Systems with Undersized Inverters in Portugal and the Netherlands 1028
A.J. Kil and T.C.J. van der Weiden

A PV-House Experience in Japan 1032
K. Sato, H. Ida and O. Ishikawa

5P3 Utility and Grid Connected Systems

Chair: S. Corsi

A New Performance Index for PV System Analysis 1036
T. Townsend, C. Whitaker, B. Farmer and H. Wenger

Grid-Tied PV System Modelling: How and Why 1040
M.C. Russell

Photovoltaics for Demand-Side Management Utility Markets: A Utility/Customer Partnership Approach 1044
J. Byrne, S. Letendre, R. Nigro, C. Govindarajalu, W. Wallace and Y.-D. Wang

Avoided Cost Benefits of PV on Diesel-Electric Grids 1048
E. Usher and S. Martel

A New Expert System Based Control Tool for Power Systems with Large Integration of PVs and Wind Power Plants 1052
E. Nogaret, G. Stavrakakis, J.C. Bonin, G. Kariniotakis, M. Papadoupoulos, N. Hatziargyriou, S. Papathanassiou, J. Gatopoulos, E. Karagounis, J. Halliday, G. Dutton, J. Pecas-Lopes, A. Androutsos and P. Pligoropoulos

Dynamic Stability Analysis of PV-Injected Power into a Parallel AC-DC Power System 1056
F.M.A. Ghali, H.A. El-Khashab and M.S. Abel-Motaleb

A Novel High-Concentration PV Technology For Cost Competitive Utility Bulk Power Generation 1060
V. Garboushian, S. Yoon, G. Turner, A. Gunn and D. Fair

A Utility-Connected Residential PV System Adapted a Novel Single-Phase Composite PWM Voltage Source Inverter 1064
S. Nonaka

Analysis of Bidirectional PWM Converter for Application of Residential Solar Air Conditioning System 1069
H.-S. Kim, G.-H. Choe, G.-J. Yu and J.S. Song

Design, Development and Installation of 100KW Utility and Grid Connected Solar PV Power Plants for Rural Applications-An Indian Experience 1073
B.M.R. Narayanan, D.V. Gupta, R.C. Gupta and R.S. Gupta

Anti-Islanding Protection Using a Twin-Peak Band-Pass Filter in Interconnected PV Systems and Substantiating Evaluations 1077
T. Ishida, R. Hagihara, M. Yugo, Y. Makino, M. Maekawa, A. Takeoka, R. Suzuki and S. Nakano

A Development of Compact and Reliable Protective Control Unit for Grid Connected Small Residential PV Systems 1081
K. Takigawa and H. Kobayashi

Statistical Evaluation of Optimum Islanding Preventing Method for Utility Interactive Small Scale Dispersed PV Systems 1085
H. Kobayashi and K. Takigawa

The Control System of Enel's 3.3 MWp PV Plant 1089
V. Arcidiacono, S. Corsi and L. Lambri

Optimization of Setting Arrays Considering the Influence of Front Array's Shadow 1094
Y. Ishisaka, K. Harada, Y. Ishihara, T. Todaka, H. Yokouchi and M. Yukawa

A Matrix for Indexing Knowledge About Utility Photovoltaic Projects 1098
W.P. McNaughton and J.E. Bigger

Silicon and GaAs/Ge Concentrator Power Plants: A Comparison of Cost of Energy Produced 1103
R.A. Whisnant, J.A. Hutchby, M.L. Timmons, R. Venkatasubramanian and J.S. Hills

Design and Cost Optimization of Utility-Grade Off-Grid Power Systems 1107
J. Berdner, C. Whitaker, H. Wenger and C. Jennings

Integrating Photovoltaics into Utility Distribution Systems 1111
H.W. Zaininger and P.R. Barnes

Luminescent Concentrator Module of a Practical Size 1115
K. Sakuta, S. Sawata and M. Tanimoto

An Optimum Design and Properties of a Static Concentrator with a Non-Imaging Lens 1119
K. Yoshioka, M. Kobayashi, A. Suzuki, K. Endoh, N. Ohe and T. Saitoh

Flat High Concentration Devices 1123
J.C. Miñano, J.C. González and I. Zanesco

Design and Drawing Support System for Photovoltaic Array Structure 1127
T. Hirasawa, K. Iida, S. Yamaguchi, N. Asayama and Y. Naito

Testing the New Solar Tracker with Shape Memory Alloy Actors 1131
V. Poulek

5P4 Off Grid System Applications and Models

Chair: S.J. Durand

Los Sabinos PV Rural Electrification Project: Results After 30 Months of Operation 1134
J.M. Huacuz, J. Agredano, G. Munguia and R. Flores

Field Experience and Comparison of Photovoltaic Off-Grid Power Systems and Reticulated Supply 1137
I.F. MacGill, M.E. Watt and R.J. Kaye

PV Based Systems, With Wind, Diesel or LPG Genset Backup, Supplying Small TV Rebroadcast Stations in Portugal 1141
H.F. Ramos

Development and Operation of a Photovoltaic Power System for Use at Remote Antarctic Sites 1145
M.F. Piszczor, L.L. Kohout, M. Manzo and A.J. Colozza

Analysis of Market Development for Photovoltaics 1149
J.A. Gregory, A.S. Bahaj and R.S. Stainton

Photovoltaic Power Without Batteries for Continuous Cathodic Protection and an Alternate Photovoltaic/Ultracapacitor Combined Power Source 1153
W.W. Muehl, Sr.

Monitoring Results of PV for Electric Propulsion in Recreational Boating 1157
G. Loois, F.P.H. Wouters, G.M. Koerts and T.C.J. van der Weiden

Transportable Stand-Alone Solar Immission Measuring Station with Optimised Photovoltaic Energy Supply 1161
R. Rudischer and Günter Ulbrich

Optimisation of Photovoltaic Water Pumps Coupled with an Interfacing Pulse Width Modulated DC/AC Inverter Power Conditioning Device 1165
N. Argaw

Field and Armature Control for Separately Excited DC Motors Powered by Photovoltaic Cells 1169
K.H. Hussein, I. Muta, T. Hoshino and M. Osakada

Optimizing the Number of a-Si Solar Cells in a Module for Load Matching 1173
P.K. Koner and H. Ossenbrink

Effects of Advantageous Placing of PV Cells and Modules in Generating Units 1176
K. Reiche, R. Preu, G. Kleiss and K. Bücher

Trimode Power Converter Optimizes PV, Diesel and Battery Energy Sources 1180
G. O'Sullivan

Calculating Method of the Capacity of Photovoltaic Array and Battery Considering Power Failure Probability in Stand-Alone PV Systems 1184
A. Ueda, K. Harada, Y. Ishihara, T. Todaka, M. Yukawa and H. Yokouchi

A New Method for Optimising the Operation of Stand-Alone PV Hybrid Power Systems 1188
M. Hancock, H.R. Outhred and R.J. Kaye

A New Approach to Optimal Sizing of Components in Stand-Alone Photovoltaic Power Systems 1192
R.J. Kaye

Sizing Procedure for Photovoltaic Systems 1196
E. Endo and K. Kurokawa

Deployment of a Dispatchable Photovoltaic System: Technical and Economic Results 1200
J. Byrne, Y.-D. Wang, S. Letendre, C. Govindarajalu, R. Nigro and W. Bottenberg

Building-Integrated PV—Analysis and US Market Potential 1204
L. Frantzis, S. Hill, P. Teagan and D. Friedman

Holographic Solar Concentrator for Terrestrial Photovoltaics 1208
J. Ludman, J. Riccobono, N. Reinhand, I. Semenova, J. Martin, W. Tai, X.-L. Li and G. Syphers

Development of a Residential Use, Utility Interactive PV Inverter with Isolation Transformer-less Circuit—Development Aspects 1216
H. Shinohara, K. Kimoto, T. Itami, T. Ambou, C. Okado, K. Nakajima, S. Hojo, K. Owada, M. Kuniyoshi and Y. Sato

High-Efficiency a-Si/c-Si Heterojunction Solar Cell 1219
T. Sawada, N. Terada, S. Tsuge, T. Baba, T. Takahama, K. Wakisaka, S. Tsuda and S. Nakano

VOLUME II

P1 Plenary Session Silicon Cells and Materials

Chairs: W. Wettling
T. Ciszek

Production of Low Cost Silicon Wafers by Continuous Casting Method—Development of Drip-Controlled Method 1227
S. Goda T. Moritani, Y. Hatanaka, H. Shimizu and I. Hide

Limits to the Efficiency of Silicon Multilayer Thin Film Solar Cells 1234
S.R. Wenham, M.A. Green, S. Edmiston, P. Campbell, L. Koschier, C.B. Honsberg, A.B. Sproul, D. Thorpe, Z. Shi and G. Heiser

Latest Efficiency Results with the Screenprinting Technology and Comparison with the Buried Contact Structure 1242
J. Nijs, E. Demesmaeker, J. Szlufcik, J. Poortmans, L. Frisson, K. De Clercq, M. Ghannam, R. Mertens and R. Van Overstraeten

Silicon Material Growth and Characterization

Chairs: A. Ayer
J.P. Kalejs

Growth Kinetics Studies of Silicon LPE from Metal Solutions 1250
T.H. Wang and T.F. Ciszek

Growth of High Quality c-SiGe p-n Double Layers for High-Efficiency Solar Cells 1254
P.O. Hansson, M. Konuma, I. Silier, E. Bauser, M. Albrecht, W. Dorsch and H.P. Strunk

Preparation and Properties of High Quality Crystalline Silicon Films Grown by ECR Plasma Deposition 1258
S. DeBoer and V. Dalal

Silicon on Graphite Cloth 1262
J.A. Rand, J.E. Cotter, C.J. Thomas, A.E. Ingram, Y.B. Bai, T.R. Ruffins and A.M. Barnett

The Reformation of Cz Si Photovoltaics 1266
K.W. Mitchell, R.R. King, T.L. Jester and M. McGraw

102 Silicon Device and Process Modelling

Chairs: T. Warabisako
P.A. Basore

A Virtual Crystallization Furnace for Solar Silicon 1270
I. Steinbach, D. Franke, W. Krumbe and J. Liebermann

Reflectance Control for Multicrystalline-Silicon Photovoltaic Modules Using Textured-Dielectric Coatings 1274
J.M. Gee, H.L. Tardy, T.D. Hund, R. Gordon and H. Liang

Rear Surface Effects in High Efficiency Silicon Solar Cells 1278
S.R. Wenham, S.J. Robinson, X. Dai, J. Zhao, A. Wang, Y.H. Tang, A. Ebong, C.B. Honsberg and M.A. Green

Progress on the Power Silicon Solar Cell Concept 1283
G. Willeke, P. Fath and E. Bucher

Prospect of the High Efficiency for the VEST (Via-hole Etching for the Separation of Thin Films) Cell 1287
M. Deguchi, Y. Kawama, Y. Matsuno, Y. Nishimoto, H. Morikawa, S. Arimoto, H. Kumabe and T. Murotani

103 Single Crystal and High Efficiency Silicon Devices

Chairs: M.A. Green
J. Nijs

Back Surface Cell Structures for Reducing Recombination in CZ Silicon Solar Cells 1291
R.R. King, K.W. Mitchell and J.M. Gee

Low-High Heterojunction of C-Si Substrate and μC-Si:H Film Under Rear Contact for Improvement of Efficiency 1295
S. Okamoto, M. Nishida, I. Yamasaki, Y. Komatsu, M. Kaneiwa and T. Nammori

Rapid Thermal Processing of High-Efficiency Silicon Solar Cells with Controlled In-Situ Annealing 1299
P. Doshi, A. Rohatgi, M. Ropp, Z. Chen, D. Ruby and D.L. Meier

High Efficiency (>22%) Si-Solar Cells with Optimized Emitter 1303
S. Sterk, S.W. Glunz, J. Knobloch and W. Wettling

High-Flux Solar Furnace Processing of Silicon Solar Cells 1307
Y.S. Tsuo, J.R. Pitts, M.D. Landry, C.E. Bingham, A. Lewandowski and T.F. Ciszek

104 Multicrystalline and Thin-Layer Silicon Devices

Chairs: L.A. Verhoef
A. Blakers

Characterization of Thickness Dependence on Defect Density and Hydrogen Passivation for Thin Film Polycrystalline Silicon Solar Cells 1311
S. Arimoto, H. Morikawa, M. Deguchi, Y. Kawama, Y. Matsuno, T. Ishihara, K. Kumabe and T. Murotani

Polycrystalline Silicon Thin-Film Solar Cell Prepared by the Solid Phase Crystallization (SPC) Method 1315
T. Baba, T. Matsuyama, T. Sawada, T. Takahama, K. Wakisaka, S. Tsuda and S. Nakano

Process Improvements for Large Area Polycrystalline Silicon Buried Contact Solar Cell Sequence 1319
S. Narayanan, J. Creager, S. Roncin, A. Rohatgi and Z. Chen

Optimal Surface and Bulk Passivation of High Efficiency Multicrystalline Silicon Solar Cells 1323
H.E. Elgamel, A. Rohatgi, Z. Chen, C. Vinckier, J. Nijs and R. Mertens

A Simple Single-Photomask Process for Fabrication of High-Efficiency Multicrystalline-Silicon Solar Cells 1327
W.K. Schubert, D.S. Ruby, P.A. Basore, J.M. Gee, M.E. Buck and H.L. Tardy

105 Silicon Defect and Impurity Effects in Growth and Processing

Chairs: K. Kaneko
S. Narayanan

Silicon Surface and Bulk Defect Passivation by Low Temperature PECVD Oxides and Nitrides 1331
Z. Chen, A. Rohatgi and D. Ruby

A Statistical Analysis of the Effect of PECVD Deposition Parameters on Surface and Bulk Recombination in Silicon Solar Cells 1335
D.S. Ruby, W.L. Wilbanks and C.B. Fleddermann

The Effects of Solvent and Dopant Impurities on the Performance of LPE Silicon Solar Cells 1339
Z. Shi, W. Zhang, G.F. Zheng, V.L. Chin, A. Stephens, M.A. Green and R. Bergmann

Effect of Nitrogen Doping on Microdefects and Minority Charge Carrier Lifetime of High-Purity, Dislocation-Free and Multicrystalline Silicon 1343
T.F. Ciszek, T.H. Wang, R.W. Burrows, T. Bekkedahl, M.I. Symko and J.D. Webb

Mechanical Wafer Engineering for High Efficiency Solar Cells: An Investigation of the Induced Surface Damage 1347
P. Fath, G. Willeke, E. Bucher, J. Szlufcik, R.M. Murti, K. De Clercq, J. Nijs and R. Mertens

1P1 Silicon Crystal Growth Silicon Device Modeling

Chair: K.W. Mitchel

High-Efficiency Solar Cells Using HEM Silicon 1351
C.P. Khattak, F. Schmid and W.K. Schubert

Material Electronic Quality Specification Factors for Polycrystalline Silicon Wafers 1356
J. Bailey, J.P. Kalejs and C. Keaveny

Photoelectrochemical Diffusion Length Measurements on P-Type Multicrystalline Silicon for Industrial Quality Control 1360
D. Sarti, B. Chareyron, Q.N. Le, S. Bastide and D. Lincot

Characterization of Silicon Spheres for Spheral Solar Cells 1364
J.K. Arch, J.S. Reynolds, M.D. Hammerbacher, R.K. Ahrenkiel, S. Asher, K.M. Jones and M. Al-Jassim

Minority-Carrier Lifetime Studies of Silicon Spheres 1368
R.K. Ahrenkiel, D.H. Levi and J. Arch

The Growth of Si_xGe_{1-x}-Crystals for Infrared Solar Cell Applications 1372
J. Wollweber, D. Schulz, W. Schröder and N.V. Abrosimov

Physical Properties of RT-LPCVD and LPCVD Polysilicon Thin Films: Application to Emitter Solar Cell 1375
M. Lemiti, B. Semmache, Q.N. Lê, D. Barbier and A. Laugier

Thin Film Polycrystalline Si by a Novel Solution Growth Technique 1379
R.L. Wallace, W.A. Anderson and K.M. Jones

Preferentially-Oriented Polycrystalline Si Growth for Thin Film Solar Cells Using SiH_2Cl_2 Decomposed in Plasma 1383
T. Fuyuki, H. Yoshida and H. Matsunami

A New Fabrication Method for Multicrystalline Silicon Layers on Graphite Substrates Suited for Low-Cost Thin Film Solar Cells 1387
M. Pauli, T. Reindl, W. Krühler, F. Homberg and J. Müller

17% Efficient Thin Film Silicon Solar Cell by Liquid Phase Epitaxy 1391
K.J. Weber, A.W. Blakers, M.J. Stocks, M.J. Stuckings, A. Cuevas, A.J. Carr, T. Brammer and G. Matlakowski

Thickness Dependence of Defect Density in Thin Film Polycrystalline Silicon Formed on Insulator by Zone-Melting Recrystallization 1394
A. Takami, S. Arimoto, H. Naomoto, S. Hamamoto, T. Ishihara, H. Kumabe and T. Murotani

Polycrystalline Silicon for Thin Film Solar Cells 1398
R. Bergmann, J. Kühnie, J.H. Werner, S. Oelting, M. Albrecht, H.P. Strunk, K. Herz and M. Powalla

Fabrication of High Quality Polysilicon Thin Film on Glass and Its in situ Real-Time Monitoring by Spectroscopic Ellipsometry 1402
T. Akasaka, Y. Tanaka and I. Shimizu

Electrical and Structural Properties of the Si/C Interface in Poly-Si Thin Films on Graphite Substrates 1406
T. Reindl, W. Kreühler, M. Pauli and J. Müller

Characterization and Analysis of Multilayer Solar Cells 1410
A.B. Sproul, Z. Shi, J. Zhao, A. Wang, Y.H. Tang, F. Yun, T. Young, Y. Huang, S. Edmiston, S.R. Wenham and M.A. Green

Capitalizing on Two Dimensional Minority Carrier Injection in Silicon Solar Cell Design 1413
C.B. Honsberg, S. Edmiston, L. Koschier, S.R. Wenham, A.B. Sproul and M.A. Green

A Performance Simulation for the n^+pp^+ BSF and the Bifacial Silicon Solar Cells with Additional Irradiation from the Backside of the Cells 1417
K. Matsukuma, K. Morita, K. Tsukuda and H. Shigeta

Modelling of the Electronic Transport in Multijunction Solar Cells 1421
U. Rau and M. Goldbach

Why Li's Solar Cell Concept Cannot Work 1425
Z.T. Kuznicki

Identifying the Recombination Losses that Limit V_{oc} in Thin Silicon Solar Cells by Bifacial Spectral Response Measurements 1429
Y.B. Bai, J.E. Phillips and A.M. Barnett

Extended Infrared Response of Silicon Solar Cells and the Impurity Photovoltaic Effect 1433
M.J. Keevers and M.A. Green

Numerical Analysis of Silicon-on-Insulator Thin-Film Solar Cells 1437
H. Iwata, T. Ohzone and H. Takakura

Modeling of Power Reflection in Microwave Detected Photoconductance Decay 1441
M.Y. Ghannam, S.F. Mahmoud and J.F. Nijs

Extraction of the Surface Recombination Velocity of Passivated Phosphorus-Doped Silicon Emitters 1446
A. Cuevas, G. Giroult-Matlakowski, P.A. Basore, C. DuBois and R.R. King

Evaluating the Effectiveness of Optical Coupling Techniques 1450
J.H. Wohlgemuth, T. Koval, D. Whitehouse and J. Creager

Quantum Efficiency of Thin Film Silicon Solar Cells on a Highly Doped Substrate 1454
M. Hirsch, R. Brendel, J.H. Werner and U. Rau

Calculation of Thermal Stresses During the Soldering of Solar Cell Strings 1458
D. Franke and I. Steinbach

1P2 Crystalline Silicon Devices

Chair: R.A. Sinton

The Waffle: A New Photovoltaic Diode Geometry Having High Efficiency and Backside Contacts 1462
O. Leistiko

A New High Efficiency Solar Cell Concept Based on Truncated Pyramids 1466
R. Hezel

The JCT Buried BSF Silicon Solar Cell a Model of Simplicity and High Efficiency 1470
J. Mandelkorn, J. Broder, L. Kreinin, N. Bordin and N.P. Eisenberg

High Efficiency, Low Cost Buried Contact Silicon Solar Cells 1473
C.B. Honsberg, S.R. Wenham, A. Ebong, M. Taouk, Y-H. Tang, S. Ghozati, F. Yun, A. Grados, M.A. Green and W. Warta

24% Efficient Silicon Solar Cells 1477
J. Zhao, A. Wang P.P. Altermatt, S.R. Wenham and M.A. Green

High Efficiency Silicon Solar Cells 1481
Z. Yuwen, L. Zhongming, M. Chundong, L. Kun and L. Zhiming

Efficiency (17.2%) All-Implanted Single Crystalline Silicon Solar Cells with Screen Printed Contacts 1485
M. Ružinský, V. Šály, D. Ružinská and P. Redi

Series Resistance in Polysilicon Contacted Solar Cells 1489
L. Castañer, J. Carter, S. Silvestre, P. Ashburn, R. Alcubilla, A. Luque, J. Alonso, J. Pons and T. Markvart

New Approach to Obtain Boron Selective Emitters 1492
A. Moehlecke and A. Luque

Novel Buried Contact Technology for Advanced Silicon Solar Cells 1496
C.N. Dheasuna, A. Mathewson, L. Hecking and G.T. Wrixon

Reduced Temperature Dependence of High-Concentration Photovoltaic Solar Cell Open-Circuit Voltage (Voc) at High Concentration Levels 1500
S. Yoon and V. Garboushian

Towards Realization of a δ-BSF Solar Cell 1505
Z.T. Kuznicki, L. Wu, J.-J. Grob and J.-C. Muller

High-Quality Surface Passivation by Corona-Charged Oxides for Semiconductor Surface Characterization 1509
M. Schöfthaler, R. Brendel, G. Langguth and J.H. Werner

The Effect of Hydrogen-Radical Annealing for SiO_2 Passivation 1513
H. Nagayoshi, M. Yamaguchi, Y. Yamamoto, M. Ikeda, T. Saitoh, K. Kamisako and T. Uematsu

Passivation Properties of a-$Si_{1-x}N_x$:/H/SiO_2 Double-Layer Structures 1515
M. Yamaguchi H. Nagayoshi, Y. Yamamoto, M. Ikeda, T. Uematsu, T. Saitoh and K. Kamisako

Low Temperature Formation of Emitter and BSF by Rapid Thermal Co-Diffusion of P, Al or B 1519
B. Hartiti, S. Sivoththaman, R. Schindler, J. Nijs, J.C. Muller and P. Siffert

Novel Coatings for Solar Cells with the Capability of Controlled Charge Storage 1523
P. Günther and A. Mathewson

Simultaneous Formation of Emitter and Passivation Layer in a Single Rapid Thermal Cycle 1527
J. Kopp, A. Lachiq, A. Slaoui, L. Ventura, H. Lautenschlager, J.C. Muller and P. Siffert

The Behavior of Silicon Materials in Various Production Processes 1531
R.O. Bell, M. Prince, F.V. Wald, W. Schmidt and K.D. Rasch

Rapid Thermal Sintering of the Metallizations of Silicon Solar Cells 1535
A. Laugier, H. El Omari, J.P. Boyeaux, B. Hartiti, J.C. Muller, L.Q. Nam and D. Sarti

Contacts Realization by Rapid Thermal Annealing in Multicrystalline Silicon Solar Cells with Special Emphasis on Metal Influence 1539
H. El Omari, J.P. Boyeaux and A. Laugier

A Comparative Study of Buried Contact and Screen Printed Polycrystalline Silicon Solar Cells with a Mechanically V-Grooved Surface Texturization 1543
P. Fath, E. Bucher, G. Willeke, J. Szlufcik, J. Horzel, J. Nijs and R. Mertens

Low-Cost Multicrystalline Silicon Solar Modules with 16% Encapsulated Cell Efficiency 1547
L.A. Verhoef, P.-P. Michiels, R.J.C. van Zolingen, H.H.C. de Moor, A.R. Burgers, R.A. Steeman and W.C. Sinke

Texturing of Polycrystalline Silicon 1551
M.J. Stocks, A.J. Carr and A.W. Blakers

The Effect of Encapsulation on the Reflectance of Photovoltaic Modules Using Textured Multicrystalline-Silicon Solar Cells 1555
J.M. Gee, W.K. Schubert, H.L. Tardy, T.D. Hund and G. Robison

1P3 Impurities and Defects in Crystalline Silicon and Thin Layer Devices

Chair: R.B. Hall

2.8 Watt, Large-Area Silicon-Film$tm Solar Cells 1559
D.H. Ford, A.M. Barnett, J.C. Checchi, S.R. Collins, R.B. Hall, C.L. Kendall, S.M. Lampo, J.A. Rand and A.M. Trabant

Innovative Structures for Thin Film Crystalline Silicon Solar Cells to Give High Efficiencies from Low Quality Silicon 1563
A.B. Sproul, S. Edmiston, S.R. Wenham, G.H. Heiser and M.A. Green

The Study of the Influence of the Layer Resistivity of Thin Epitaxial Si Cells 1567
O. Evrard, T. Vermeulen, J. Poortmans, M. Caymax, P. Laermans, J. Nijs and R. Mertens

An Analysis of Thin Film Silicon for Photovoltaic Applications 1571
Y. Yi, R. Wallace, B. Jaganathan, X. Gu, K. Etemadi and W.A. Anderson

Thin-Film Polycrystalline Si Solar Cell on Glass Substrate Fabricated by a Novel Low Temperature Process 1575
K. Yamamoto, A. Nakajima, T. Suzuki, M. Yoshimi, H. Nishio and M. Izumina

Solution Growth of Polycrystalline Silicon on Glass at Low Temperatures 1579
Z. Shi, T.L. Young and M.A. Green

High Performance Porous Silicon Solar Cell Development 1583
S.M. Vernon, N.M. Kalkhoran, H.P. Maruska and W.D. Halverson

Defects in Crystalline Silicon for Solar Cells (DIXSI): A Co-Operative German Research Project 1587
A. Eyer and I. Reis

Impurity and Defect Engineering Approaches for Realization of 18% Commercial Silicon Solar Cells 1591
J.P. Benner and B.L. Sopori

Gettering in Multicrystalline Silicon— A Design-of-Experiments Approach 1595
W.K. Schubert

Photoluminescence Characterization of Phosphorus Diffusion Gettering in Silicon Substrates for Solar Cells 1599
M. Tajima, M. Warashina, T. Hisamatsu, A. Suzuki and S. Ibuka

The Effect of Silicon Purity on Spheral Solar® Cell Processing and Performance 1603
R.R. Schmit, J.S. Reynolds, J.K. Arch and G.D. Stevens

Efficiency-Limiting Defects in Polycrystalline Silicon 1607
S.A. McHugo, J. Bailey, H. Hieslmair and E.R. Weber

Investigation of Lifetime Limiting Microdefects in Polycrystalline Silicon for Photovoltaic Applications 1611
M. Werner, E.R. Weber, S. McHugo and J. Bailey

Hydrogen in Silicon: Current Understanding of Diffusion and Passivation Mechanisms 1615
B.L. Sopori, X. Deng, J.P. Benner, A. Rohatgi, P. Sana, S.K. Estreicher, Y.K. Park and M.A. Roberson

A Study on the Microscopical and Macroscopical Effects of Hydrogenation on the Performance of Multicrystalline Solar Cells 1621
M. Rosmeulen, H.E. Elgamel, J. Poortmans, M.-A. Trauwaert, J. Vanhellemont and J. Nijs

Comparison of Spatially Resolved Carrier Lifetimes in mc-Si with Solar Cell and Material Characteristics 1625
S.W. Glunz, Ch. Hebling, W. Warta and W. Wettling

Contamination and Gettering Evaluation by Lifetime Measurements During Single Crystal Cell Processing 1629
R. Lagos, A. Moehlecke, J. Alonso, I. Tobías and A. Luque

Imaging the Local Forward Current Density of Solar Cells by Dynamical Precision Contact Thermography 1633
O. Breitenstein, W. Eberhardt and K. Iwig

Efficiency Improvements of Silicon Solar Cells by Absorption Enhancement with Germanium 1637
E. Borne, J.P. Boyeaux and A. Laugier

Enhanced Optoelectronic Conduction in Polycrystalline Silicon Films Deposited by a Layer-by-Layer Technique Using SiF_4/H_2 1640
D. He, N. Okada and I. Shimizu

New Direct Spectroscopic Method for Determination of the Energy Distribution of Interface States 1644
H. Kobayashi, Y. Yamashita, Y. Nakato, M. Koshizuka and Y. Nishioka

Evaluation of Microroughness at SiO_2/Si Interfaces for High-Efficiency Crystalline Si Solar Cells 1648
T. Saitoh and K. Mori

Operation and Crystalline Properties of Electro-Magnetic Casting 1652
R. Kawamura, K. Sasatani, T. Onizuka and K. Kaneko

Microwave Reflections for Carrier Lifetime Measurements: A Comprehensive Study on Sensitivity and Transient Response 1656
M. Schöfthaler and R. Brendel

World's First 15%-Efficient Multicrystalline Silicon Modules 1660
D.L. King, W.K. Schubert and T.D. Hund

Practical High Efficiency Bifacial Solar Cells 1663
A. Moehlecke, I. Zanesco and A. Luque

Multilayer Solar Cell with Thin Polycrystalline Silicon Layers 1667
S. Wagner and T. Otto

P3 Plenary Session
III–V and Multijunction Cells

Chairs: R.G. Little
M.L. Timmons

High-Efficiency GaInP/GaAs Tandem Solar Cells for Space and Terrestrial Applications 1671
K.A. Bertness, S.R. Kurtz, D.J. Friedman, A.E. Kibbler, C. Krammer and J.M. Olson

High Efficiency AlGaAs/Si Tandem Solar Cell Over 20% 1679
M. Umeno, T. Kato, M. Yang, Y. Azuma, T. Soga and T. Jimbo

$Ga_xIn_{1-x}As$ Thermophotovoltaic Converters 1685
M.W. Wanlass, J.S. Ward, K.A. Emery and T.J. Coutts

Material and Device Characterization Toward High-Efficiency GaAs Solar Cells on Optical-Grade Polycrystalline Ge Substrates 1692
R. Venkatasubramanian, D.P. Malta, M.L. Timmons, J.B. Posthill, J.A. Hutchby, R. Ahrenkiel, B. Keyes and T. Wangensteen

301 III–V Multijunction Devices

Chairs: Y.C.M. Yeh
K.A. Bertness

GaAs One-Sun and Concentrator Solar Cells Based on LPE-ER Grown Structures 1697
A. Baldus, A.W. Bett, U. Blieske, T. Duong, F. Lutz, C. Schetter, W. Wettling and O.V. Sulima

Growth of GaAs and AlGaAs on Si Substrates by Atomic Hydrogen-Assisted MBE (H-MBE) for Solar Cell Applications 1701
Y. Okada, A. Kawabata, M. Kawabe, N. Yui and H. Kawanami

Development of InP Solar Cells on Inexpensive Si Wafers 1705
S.J. Wojtczuk, N.H. Karam, P. Gouker, P. Colter, S.M. Vernon, G.P. Summers, R.L. Walters and R. Statler

Minority-Carrier Lifetime in InP as a Function of Light Bias 1709
J.A. Yater, I. Weinberg, P.P. Jenkins and G.A. Landis

A Thermophotovoltaic Electric Generator Using GaSb Cells with a Hydrocarbon Burner 1713
L. Fraas, R. Ballantyne, J. Samaras and M. Seal

302 III–V Cell Growth and Characterization

Chairs: K. Bogus
J.A. Hutchby

Improved Large-Area, Two-Terminal $InP/Ga_{0.47}In_{0.53}As$ Tandem Solar Cells 1717
M.W. Wanlass, J.S. Ward, K.A. Emery, A. Duda and T.J. Coutts

Concentrator Tandem Solar Cells Based on AlGaAs/GaAs-InP/InGaAs (or GaSb) Structures 1721
V.M. Andreev, L.B. Karlina, A.B. Kazantsev, V.P. Khvostikov, V.D. Rumyantsev, S.V. Sorokina and M.Z. Shvarts

Development of P-on-N $GaInP_2/GaAs$ Tandem Cells 1725
P.R. Sharps, M.L. Timmons, Y.C.M. Yeh and C.L. Chu

High Efficiency InGaP Solar Cells for InGaP/GaAs Tandem Cell Application 1729
T. Takamoto, E. Ikeda, H. Kurita and M. Ohmori

Methods for Analysis of Two-Junction, Two-Terminal Photovoltaic Devices 1733
S.R. Kurtz, K. Emery and J.M. Olson

3P1 III–V Single and Multijunction Cells-I

Chair: D. Friedman

Lattice Mismatched InGaAs Photovoltaic Devices for Thermophotovoltaic Power Systems 1738
D.M. Wilt, D.J. Brinker, N.S. Fatemi, R.W. Hoffman, Jr., P.P. Jenkins and R. Lowe

New Upper Efficiency Limits for Semiconductor Solar Cells 1742
J.H. Werner, R. Brendel and H.J. Queisser

Considerations for Modeling Heterojunction Transport in Solar Cells 1746
S.M. Durbin and J.L. Gray

Design and Fabrication of Thermophotovoltaic Cells 1750
P.A. Iles and C.L. Chu

Experimental Analysis of GaAs-InGaAs MQW Solar Cells 1754
F.W. Ragay, J.H. Wolter, A. Martí and G.L. Araújo

Photoellipsometry Characterization of AlGaAs/GaAs Heterojunctions for Solar Cells 1759
Y.-M. Xiong, C.C. Wong and T. Saitoh

Development of a TPV Converter for Co-Generation of Electricity and Heat from Combustion of Wood Powder 1764
L. Broman and J. Marks

Bias-Dependent Photoluminescence Intensity for the Estimation of Surface Recombination Velocity in Compound-Semiconductor Solar Cell 1767
A. Yamamoto, M. Ohkubo, Y. Tashiro and A. Hashimoto

Recombination Mechanisms at Window/Emitter Interface in InP and Other III-V Semiconductor Based Solar Cells 1771
J. Lammasniemi, K. Tappura and K. Smekalin

Electrochemical Characterization of InP and GaAs Based Structures for Space Solar Cell Applications 1775
M. Faur, M. Faur, D.J. Flood, P.P. Jenkins, M. Goradia and D.M. Wilt

Nanocrystalline Electrochemical Solar Cells 1779
A.J. McEvoy, M. Grätzel, H. Wittkopf, D. Jestel and J. Benemann

Voltage Performance of Quantum Well Solar Cells in the $Al_xGa_{1-x}As/GaAs$ and the $GaAs/In_yGa_{1-y}As$ Material Systems 1783
G. Haarpaintner, J. Barnes, K.W.J. Barnham, J.P. Connolly, S.S. Dosanjh, J. Nelson, C. Roberts, C. Button, G. Hill, M.A. Pate and J.S. Roberts

Modeling p-i(Multi Quantum Well)-n Solar Cells: A Contribution for a Near Optimum Design 1787
P. Renaud, M.F. Vilela, A. Freundlich, A. Bensaoula and N. Medelci

The Effect of Chromatic Aberrations on Two-Junction, Two-Terminal Devices in a Concentrator System 1791
S.R. Kurtz, D.J. Friedman and J.M. Olson

Photoluminescence-Based Measurement Technique of Surface Recombination Velocity for High Efficiency Silicon and Compound Semiconductor Solar Cells 1795
T. Saitoh, T. Nakagawa, K. Yoh and H. Hasegawa

Effects of Concentrator Chromatic Aberration on Multi-Junction Cells 1799
L.W. James

Raman Scattering Controlled Free-Carrier and Composition Distribution in Solar Cell Structures 1803
A.M. Mintairov, V.P. Khvostikov, V.R. Larionov, E.V. Paleeva, S.V. Sorokina and A.F. Ioffe

Schottky Barrier Enhancement on N-INP— Solar Cell Applications 1807
T. Clausen and O. Leistiko

Photovoltaic Conversion in a Common Solar Concentrating and Spectrally Splitting System 1811
N. Yehezkel, J. Appelbaum and A. Yogev

AC-Photoconductivity of Amorphous Gallium Phosphide (a-GaP) Formed by Nitrogen Ion Beam Assisted Deposition 1814
H. Kubota, T. Tashiro, T. Hiyayu, T. Chikushima, T. Fujiyoshi, R. Miyagawa and M. Onuki

InP Solar Cell Improvement by Inverse Delta-Doping 1818
J. Piprek and K.W. Böer

Near Infrared Inelastic Light Scattering Spectroscopy of High Efficiency Solar Cells Device Structures Based on III-V Compounds 1822
B.H. Bairamov, I.P. Ipatova, V.K. Negoduyko, V.A. Voitenko, V.V. Toporov, G. Irmer and J. Monecke

A Simple Model of a Graded Band-GAP pn-Heterojunction Cell 1826
J. Sinkkonen

3P2 III–V Single and Multijunction Cells-II

Chair: R.L. Statler

GaInP/GaAs Monolithic Tandem Concentrator Cells 1829
D.J. Friedman, S.R. Kurtz, K.A. Bertness, A.E. Kibbler, C. Kramer, J.M. Olson, D.L. King, B.R. Hansen and J.K. Snyder

Artificial Enhancements and Reductions in the PV Efficiency 1833
K. Emery and H. Field

GaAs and $Al_{0.2}Ga_{0.8}As$ Solar Cells with an Indirect-Bandgap $Al_{0.8}Ga_{0.2}As$ Emitter—Heterojunction Cells 1839
4xR. Venkatasubramanian, M.L. Timmons, J.A. Hutchby, H. Field and K. Emery

GaAsSb-Based Heterojunction Tunnel Diodes for Tandem Solar Cell Interconnects 1843
J.C. Zolper, J.F. Klem, T.A. Plut and C.P. Tigges

High Efficiency Monolithic GaAs/Si Tandem Solar Cells Grown by MOCVD 1847
M. Yang, T. Soga, T. Jimbo and M. Umeno

The Effect of Temperature on the Radiative Performance of Ho-Yag Thin Film Selective Emitters 1851
R.A. Lowe, D.L. Chubb and B.S. Good

Improvement of AlGaAs Solar Cell Grown on Si Substrate 1855
T. Soga, M. Yang, Y. Azuma, H. Uchida, T. Jimbo and M. Umeno

Tunnel Junction Interconnects in GaAs-Based Multijunction Solar Cells 1859
K.A. Bertness, D.J. Friedman and J.M. Olson

Thermophotovoltaic System Parametric Modelling 1863
D.R. Burger and R.L. Mueller

Efficient ZnO/CdS/InP Heterojunction Solar Cell 1867
S. Saito, Y. Hashimoto and K. Ito

GaAs Solar Cell with GaInP Window Grown by All Metalorganic Source MOVPE 1871
H. Matsubara, T. Tanabe, A. Saegusa, S. Takagishi and T. Shirakawa

Transient Response of Gallium Arsenide and Silicon Solar Cells Under Laser Pulse 1874
R.K. Jain and G.A. Landis

Carrier Generation and Transport in InGaAs/GaAs Multiple Quantum Well Solar Cells 1878
Y. Yazawa, T. Kitatani, J. Minemura, K. Tamura and T. Warabisako

High Efficiency InP Solar Cells from Low Toxicity Tertiarybutylphosphine and Trimethylindium by OMVPE 1882
R.W. Hoffman, Jr., N.S. Fatemi, D.M. Wilt, P.P. Jenkins, D.J. Brinker and D.A. Scheiman

InP-Based Quantum Well Solar Cells Grown by Chemical Beam Epitaxy 1886
A. Freundlich, V. Rossignol, M.F. Vilela, R. Renaud, A. Bensaoula and N. Medelci

MOCVD Growth of GaAsP on Si for Tandem Solar Cell Application 1890
K. Hayashi, T. Soga, H. Nishikawa, T. Jimbo and M. Umeno

High-Efficiency AlGaAs-GaAs Solar Cells with Internal Bragg Reflector 1894
V.M. Andreev, V.V. Komin, I.V. Kochnev, V.M. Lantratov and M.Z. Shvarts

Epitaxial Lift-Off in Photovoltaics: Ultra Thin $Al_{0.2}Ga_{0.8}As$ Cell in a Mechanically Stacked (Al,Ga)As/Si Tandem 1898
K. Zahraman, J.C. Guillaume, G. Nataf, B. Beaumont, M. Leroux, P. Gibart and J.P. Faurie

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M.F. Vilela, N. Medelci, A. Bensaoula, A. Freundlich and P. Renaud

P6 Plenary Session
Space Systems

Chairs: M. Tajima
P.M. Stella

The FAST Solar Array: Challenging Requirements, Novel Design 1949
M. Kruer and J. Lyons

Technology Challenges for Space Solar Cells 1957
P.A. Iles and F. Ho

A Solar Module Fabrication Process for HALE Solar Electric UAVs 1963
P.G. Carey, R.C. Aceves, N.J. Colella, K.A. Williams, R.A. Sinton and G.S. Glenn

Solar Panels for Microsatellites: GaAs, GaAs/Ge and Beyond 1970
T.A. Cross, R. Kimber and C. Goodbody

601 Space Systems

Chairs: M. Tajima
Lee Goldhammer

Spacecraft Level Impacts of Integrating Concentrator Solar Arrays 1978
D.M. Allen and M.F. Piszczor, Jr.

Results from the Goddard Space Flight Center's Long Duration Exposure Facility Solar Array Component Test 1982
E.M. Gaddy

The Hubble Space Telescope Solar Array Blanket: Post Flight Technology Verification—Recent R&D Results for the Assessment of Weld Joints 1986
H. Bebermeier

Flight Performance of the Magellan Solar Array 1990
O. Short, K. Sharmit and W. Adams

6P1 Space Systems

Chair: T. Cross

In-Orbit Performance Characteristics of Intelsat-V Solar Arrays 1994
A. Ozkul, D. Cooper and A. Dunnet

High Efficiency Solar Cell Arrays System Trade-Offs 1998
E.L. Ralph

Use of Advanced Solar Cells for Commercial Communication Satellites 2002
S.G. Bailey and G.A. Landis

Design of a GaAs/Ge Solar Array for Unmanned Aerial Vehicles 2006
D.A. Scheiman, D.J. Brinker, D.J. Bents and A.J. Colozza

On-Sun Test Results of McDonnell Douglas' Prototype Solar Thermophotovoltaic Power System 2010
K.W. Stone, E.F. Leingang, S.M. Kusek, R.E. Drubka, T.D. Fay

The GaAs Deployable Solar Array for SAC-B 2014
A. Caon, L. Brambilla, R. Contini, G. D'Accolti, E. Rossi, G. Verzeni, C. Flores, F. Paletta, G. Pedrazzoli, M. Grattarola, F. Svelto and R. Ibba

Development of the Astro Edge Solar Array 2018
B.R. Spence and G.W. Marks

Development of a Line-Focus Refractive Concentrator Array for Space Applications 2022
M.F. Piszczor, M.J. O'Neill and L.M. Fraas

Evaluation of Welded Interconnects on Thermally Cycled Silicon Solar Cells 2026
P.C. Brennan, R.A. Jamieson, A. Garcia III, P.A. Malachesky and E.J. Simburger

Dust-Induced Degradation of Solar Arrays on Mars 2030
G.A. Landis

Scaling Nominal Solar Cell Impedances for Array Design 2034
R.L. Mueller, M.T. Wallace and P. Iles

Simulation and Real-Time Modelling of Space Photovoltaic Systems 2038
K. Khouzam, C. Ly, C.K. Koh and P.Y. Ng

Minimization of Solar Cell Hot-Spots on GPS Solar Arrays Using Saber™ Modeling 2042
A. Garcia III, E. Simburger, T. Lam and P. Malachesky

Thermo-Optical Design Analysis of Space Satellite Solar Arrays 2045
C.C. Vaz, L.C.M. Miranda and L.F. Perondi

The Effects of Radiation and Annealing on Amorphous Silicon Solar Cell Space Arrays 2049
G.J. Vendura, Jr., M.A. Kruer, R.M. Kurland and J. Newton

The Infra Red Reflecting Coverglass for Silicon & GaAs Solar Cells Used in Near Earth & Geostationary Orbits 2054
G. Jones, K. Mullaney, C. Kitchen and J.C. Larue

Teflon Bonding of Solar Cell Assemblies Using Pilkington CMZ & CMG Coverglasses—Now a Production Process 2058
C.A. Kitchen, A.A. Dollery, K. Mullaney and K. Bogus

Qualification Test Results for Blue-Red Reflecting Solar Cell Covers and Other New Products for the Solar Power Market 2062
W.T. Beauchamp, B. McLean and M. Larro

An Analysis of Eight-Year Operation of GaAs Solar Array at Space Station "MIR" 2066
M. Kagan, V. Nadorov and V. Rjevsky

P7 Plenary Session
Space Solar Cells

Chairs: S. Matsuda
G.A. Landis

A New Approach to Damage Prediction for Solar Cells Exposed to Different Radiations 2068
G.P. Summers, R.J. Walters, M.A. Xapsos, E.A. Burke, S.R. Messenger, P. Shapiro and R.L. Statler

Post-Flight Investigation of the ASGA Solar Cell Experiment on Eureca 2076
C. Flores, R. Campesato, F. Paletta, G.L. Timò and F. Svelto

PV Technology for Low Intensity, Low Temperature (LILT) Applications 2082
P.M. Stella, F.S. Pool, M.A. Nicolet and P.A. Iles

Performance of Proton- and Electron-Irradiated, Two-terminal, Monolithic InP/$Ga_{0.47}In_{0.53}As$ Tandem Solar Cells 2088
H.L. Cotal, R.J. Walters, S.R. Messenger and G.P. Summers

701 Space Solar Cells-I

Chairs: C.R. Lewis
C. Flores

High-Efficiency (24.6%, AM 0) LPE Grown AlGaAs/GaAs Concentrator Solar Cells and Modules 2096
V.M. Andreev, A.B. Kazantsev, V.P. Khvostikov, E.V. Paleeva, V.D. Rumyantsev and M.Z. Shvarts

Study of Solar Simulator Calibration Method and Round Robin Calibration Plan of Primary Standard Solar Cell for Space Use 2100
O. Kawasaki, S. Matsuda, Y. Yamamoto, Y. Kiyota and Y. Uchida

Final Results of the Advanced Photovoltaic Experiment Flight Test 2104
D.J. Brinker and J.R. Hickey

19.6% Electron-Irradiated GaInP/GaAs Cells 2108
S.R. Kurtz, K.A. Bertness, D.J. Friedman, A.E. Kibbler, C. Kramer and J.M. Olson

Electron and Proton Damage Coefficients for Heteroepitaxial InP Solar Cells 2112
R.K. Jain, I. Weinberg, D.J. Brinker, D.A. Scheiman, C. Vargas-Aburto and C.K. Swartz

702 Space Solar Cells-II

Chairs: N.M. Pearsall
G. Summers

Designing Cascade Cells with Specified Radiation Tolerance 2116
C.L. Chu and P.A. Iles

Large Area $GaInP_2$/GaAs/Ge Multijunction Solar Cells for Space Applications 2120
P.K. Chiang, D.D. Krut, B.T. Cavicchi, K.A. Bertness, S.R. Kurtz and J.M. Olson

Silicon and Gallium Arsenide Solar Cells for Low Intensity, Low Temperature Operation 2124
G. Strobl, P. Uebele, R. Kern, K. Roy, C. Flores, R. Campesato, C. Signorini and K. Bogus

A Simple, Low Resistance Contact System for Shallow Junction p^+nn^+ InP Solar Cells that Preserves Emitter Integrity During Sintering 2129
N.S. Fatemi, V.G. Weizer, D.M. Wilt and R.W. Hoffman

Development of High Efficiency Silicon Space Solar Cells 2133
T. Katsu, K. Shimada, H. Washio, Y. Tonomura, T. Hisamatsu, K. Kamimura, T. Saga, T. Matsutani, A. Suzuki, O. Kawasaki, Y. Yamamoto and S. Matsuda

7P1 Space Solar Cells

Chair: D.C. Marvin

Flight Performance of InP Solar Cells 2137
N.M. Pearsall, M.F. Piszczor, Jr. and C. Goodbody

A New High Volume MOVPE Reactor for III-V Solar Cells 2141
J. Ermer, P.S. Vijaykumar, K.I. Chang, D.R. Lillington, B.T. Cavicchi, E. Woelk, G. Strauch, D. Schmitz and H. Jurgensen

The Radiation Response of Heteroepitaxial p^+n InP/Si Solar Cells 2145
R.J. Walters, S.R. Messenger, M. Panunto, G.P. Summers, S.J. Wojtczuk and P. Gouker

A Unified Model for Radiation-Resistance of Advanced Space Solar Cells 2149
M. Yamaguchi, S. Katsumoto and C. Amano

Co^{60} Gamma Ray Irradiations of Solar Cells: A New Way to Predict Space Radiation Damage 2153
S.R. Messenger, M.A. Xapsos, G.P. Summers and E.A. Burke

Radiation Degradation Modeling of High Efficiency GaAs/Ge Solar Cells 2157
L.C. Kilmer

Production Experience and Performance of Large Area GaAs/Ge Solar Cells 2161
S. Khemthong, M. Yang, T. Ou and G. Jara

The Design of a More Accurate, Higher Fidelity Dual Source Air Mass Zero Solar Simulator 2165
L.C. Kilmer

Early Results From the PASP Plus Flight Experiment 2169
H. Curtis, M. Piszczor, P. Severance, D. Guidice and D. Olson

Performance of $Ga_{0.47}In_{0.53}As$ Cells Over a Range of Proton Energies 2173
I. Weinberg, R.K. Jain, C. Vargas-Aburto, D.M. Wilt and D.A. Scheiman

Pulsed Laser Illumination of Photovoltaic Cells 2177
J.A. Yater, R.A. Lowe, P.P. Jenkins and G.A. Landis

P-N and N-P GaInAsP Solar Cells: Technology and Material Analysis 2181
C. Hardingham, T.A. Cross, J. Burrage and C. Goodbody

Thermal Annealing of Radiation-Induced Defect Centers During Recovery of Diffused Junction and Epitaxial InP Solar Cells 2185
R.J. Walters, S.R. Messenger and G.P. Summers

Space Environmental Testing of Blue Red Reflecting Coverglasses for Gallium Arsenide and High Efficiency Silicon Solar Cells 2189
R. Herschitz and A. Bogorad

The Growth and Radiation Response of n^+p Deep Homojunction InP Solar Cells 2192
M.J. Panunto, R.J. Walters, S.R. Messenger, G.P. Summers, M.L. Timmons, R. Venkatasubramanian, J.A. Hancock and J.S. Hills

Gold Interconnectors for Solar Generators in Low Earth Orbits 2196
G.J. La Roche, C. Oxynos-Lauschke and K.-H. Wehner

Interference Effects on Room-Temperature Photoluminescence Spectra of GaAs/Ge Space Solar Cells 2200
G.L. Timò and C. Flores

Material Quality and Dislocation Trapping in Hydrogen Passivated Heteroepitaxial InP/GaAs and InP/Ge Solar Cells 2204
S.A. Ringel, B. Chatterjee, R.M. Sieg, E.V. Schnetzer and R. Hoffman

Amorphous Diamondlike Carbon Films—A Hard Optical Material for Silicon Solar Cells 2208
M. Alaluf, J. Appelbaum, L. Klibanov, D. Brinker, D. Scheiman and N. Croitoru

Status of Diffused Junction p^+n InP Solar Cells for Space Power Applications 2211
M. Faur, M. Faur, D.J. Flood, C. Goradia, D.J. Brinker, M. Goradia, J. Moulot, S. Bailey, N.S. Fatemi, P.P. Jenkins and D.M. Wilt

Direct Glassed and Ultrathin GaAs Cells 2217
C. Hardingham, A. Hayward, T.A. Cross and C. Goodbody

New Silicon Space Solar Cells with IBF (Integrated Bypass Function) 2220
T. Hisamatsu, H. Washio, H. Yoshioka, T. Saga, T. Matsutani, A. Suzuki, O. Kawasaki, Y. Yamamoto and S. Matsuda

NASDA's Space Solar Cell -Ground Test Data and Flight Data 2224
O. Kawasaki, Y. Yamamoto and S. Matsuda

Predicting Short Circuit Current of Single Junction and Multi-Junction Solar Cells at Low Temperature for Planetary Missions 2228
P. Jenkins, D. Scheiman and D. Brinker

The Solar Cell Experiment of the First Brazilian Satellite: 500 Days of Data Analysis 2232
P. Nubile, N. Veissid and A.F. Beloto

Solar Cells on the Base of Monocrystalline GaAs with Higher Radiation and Temperature Stability 2236
M. Kagan, G. Grigoryeva and T. Nuller

100 CM^2 Biface-Sensitive Silicon Solar Cells for Space and Terrestrial Application 2238
M. Kagan, V. Letin, V. Rjevsky and V. Unishkov

P8 Plenary Session National Programs

Chairs: A. Zervos
J.L. Stone

New Technology Developments of Solar Cell Fabrication by NEDO 2240
H. Katsumata, T. Ihara and F. Tatekura

The IEA Photovoltaic Power Systems Cooperative Programme 2247
R. Vigotti and A. Claverie

The Role of Development of Photovoltaics for Mongolia 2251
N. Enebish, D. Agchbayar, M. Baatarkhuu and D. Nachin

801 National Programs Economics and Technology

Chairs: H. Aulich
D.M. Allen

Crystalline-Silicon Photovoltaics: Necessary and Sufficient 2254
P.A. Basore and J.M. Gee

Analysis of Financial Support for Photovoltaic System Installation with the Economic Simulation Model 2258
E. Imamura and Y. Uchiyama

Recent Progress in the Photovoltaic Manufacturing Technology Project (PVMaT) 2262
C.E. Witt, L.O. Herwig, R.L. Mitchell, H. Thomas, R. Sellers and D.S. Ruby

Testing Experience of Photovoltaic Modules for a Multimegawatt Power Plant 2271
A. Iliceto, A. Previ, S. Fleres and M. Scuto

Measurement and Analysis Programme within the Thousand Roofs Programme 2275
G. Heilscher, K. Kiefer and V.U. Hoffmann

801 National Programs Status and Prospects

Chairs: C. Lee
C. Vargas-Aburto

PV in the Netherlands, Learning While Growing 2279
J.T.N. Kimman, E.W. ter Horst and E.H. Lysen

Photovoltaic Rural Electrification in France 2283
A. Claverie, P. Courtiade and P. Vezin

The United States Department of Defense Terrestrial Photovoltaic Program—A 1994 Status Report 2287
G.D. Smith, C. Combs, R. Ducey, L.W. Strother, R.N. Chapman and J.F. Hoelscher

Status of PV Application in Mexico 2291
Y. Matsumoto, J.A. Urbano and R. Asomoza

The CILSS-Project: A Large-Scale Application of Photovoltaics in Africa 2295
S. Makukatin, E. Cunow, M. Theißen and H.A. Aulich

8P1 National Programs

Chair: R.R. Hill

The Significance of Photovoltaics for a Climatically Benign Energy Supply in Baden-Wuerttemberg, A State in Southern Germany 2299
J. Moesslein

Danish National Photovoltaic Program 2302
I. Katic, B. Sørensen and J. Windeleff

Photovoltaic Development in Argentina 2306
E.M. Godfrin, J.C. Durán, A. Frigerio and J.A. Moragues

Photovoltaics for Household Energy in Mongolia: Experience and Potential 2309
B. Chadraa, A. Derrick and G. Purevdorge

Impact of Photovoltaic Demand-Side Management System on Summer Peaking Utility 2313
G.J. Leng, M. Lesser and T.T. Rooney

U.S. Department of Energy Directions in Photovoltaic Power Conditioner Development Using Smart Power/Power Integrated Circuit Technologies 2317
A. Bulawka, S. Krauthamer and R. Das

Dissemination of Photovoltaics in the Developing World: The Role of International Centers of Excellence 2321
I. Chambouleyron

Overcoming Political, Social and Economic Barriers to Promote Solar Photovoltaic Technology in a Developing Country 2325
P. Wijesooriya and H. Hande

Antitrust Implications of Utility Participation in the Market for Remote Photovoltaic Systems 2329
T.J. Starrs

Performance Evaluation of a 2-Mode PV Grid Connected System in Thailand-Case Study 2333
C. Jivacate, S. Mongconvorawan, E. Sinratanapukdee and W. Limsawatt

Implementation of the U.S. Utility Industry's Team-Up Commercialization Initiative 2341
M. Bergman, J. Bigger, S. Hester, J. Serfass and J. Hoffner

Assessment of PV Device Performance: The FHG-ISE PV-Charts 2345
K. Bücher and S. Kunzelmann

Technical Development of Equipment for Rural Electrification Resulting from the Lessons Drawn from the Polynesian Programmes of the Eighties 2349
P. Jourde

Best Practices for PV Solar Home System Projects 2352
M. Cosgrove-Davies and A. Cabraal

A New Path to Self-Sustaining Markets for PV 2356
Solarenergie-Förderverein

Arranging Social Circumstances for Spreading Photovoltaic Power Generation Systems 2360
K. Nakagawa and H. Katsumata

Low-Cost Approach to High-Volume Production and Practical Considerations to Improving Efficiency of Single Crystalline Silicon Solar Cells for Developing Countries 2364
D.T. Barki, E.S. Ramamurthy, R. Srivatsan and R.S. Rani

An Assessment of the Successes and Shortcomings of Government Sponsored Stand-Alone Photovoltaic Projects in Massachusetts 2367
W. Berg and N. Bolgen

Prospects for PV Generation and Market in China 2371
Y. Peinuo, G. Ningke and W. Xin

Power Plants Development in Romania 2374
F.T. Tanasescu and N. Olariu

Fifty Mega Watt Peak (50 MWp) Photovoltaic Rural Electrification in Indonesia 2378
A.S. Dasuki and M. Djamin

Joint U.S./Brazilian Renewable Energy Rural Electrification Project 2382
R.W. Taylor, C. Leboeuf, M. Moszkowicz and L.G. Valente

Least Cost Analysis of Renewable Energy Projects 2386
M. Cosgrove-Davies and A. Cabraal

Solar Energy and Job Creation Benefits of Photovoltaics in Times of High Unemployment 2390
O.H. Hohmeyer

Photovoltaic Research and Development in Slovakia 2394
M. Ružinský, V. Šály and D. Ružinská

A Study of Utilization of Photovoltaics for Rural Electrification in the Republic of Kiribati 2398
T. Tani, S. Kamiyacho M. Takahashi, H. Semba, K. Hashizaki, T. Inoue and H. Wade

LOW TEMPERATURE FORMATION OF EMITTER AND BSF BY RAPID THERMAL CO-DIFFUSION OF P, Al or B

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ABSTRACT

Rapid thermal processing (RTP) is now emerging as a promising simplified process for manufacturing of terrestrial solar cells in a continuous way. In earlier works, we have shown that RTP can advantageously replace classical furnace for performing emitter, BSF and surface passivation in addition to an efficient gettering of metallic impurities during these steps.

In this work, we present results about co-diffusion of two dopant elements in a single rapid thermal cycle at low temperature in order to form emitter and BSF simultaneously. We have, in particular, found that the diffusion kinetics of dopant elements are enhanced during rapid thermal co-diffusion of P, Al or B and lead to the optimal dopant activity and profile for high efficiency silicon solar cells at low temperature. Additionally, the gettering effect induced by the co-diffusion of P and Al is more efficient than can be achieved by a single diffusion of these two elements. Finally, test solar cells were performed on these structures and gave, for a low processing temperature (800°C/60 s), an efficiency of 11 % on polished FZ mono-crystalline substrates without antireflecting coating.

INTRODUCTION

Rapid thermal processing (RTP) based on incoherent sources of light is seen for more than ten years as a very promising candidate to replace conventional furnace annealing. These optical heating techniques have many advantages as being rapid, dry and clean. The energy is directly transfered to the sample without significant heating of the reactor. Moreover, it has been shown that all the kinetics of diffusion, gettering, oxidation and annealing are enhanced as compared to classical thermal processing [1, 2].

RTP also offers many other technical advantages over classical thermal steps since in such closed reactor the lamps (used as heating source) are turned on only during the short duration of the thermal cycle. The major benefit of this kind of process is a reduction in the thermal budget and potentially of the pay-back time. On the other hand, due its safety in handling, the spin-on coating from liquid source can easily be associated to RTP for the preparation of low-cost silicon solar cells in a continuous way.

In previous works, we have shown that the use of RTP for specific thermal steps in the solar cell manufacturing may lead to relatively high efficiency. As a first example, rapid thermal annealing in oxygen atmosphere has been performed on structures with a conventional diffused emitter and Al evaporation on the back. Using this procedure, a 16.6 % efficiency [3] has been obtained on single silicon substrates. On the other hand, rapid thermal co-diffusion into Polix material of phosphorus and boron from doped oxide layers followed by a conventional thermal oxidation leads to the formation of solar cells with a 15.1 % efficiency [4]. In a near future, we expect that all the thermal steps including surface passivation, AR coating and contact sintering can be performed by RTP with a minimum number of cycles. This will contribute to simplify the production lines of large scale manufacturing processes.

In this work, we will show that rapid thermal co-diffusion of P, Al or B is very efficient to perform emitter and BSF for silicon solar cells at a lower temperature compared to those used during a single diffusion. The explanation of this phenomena is probably due to the mutual influence of one doping element on the another though injection of point defects during their co-diffusion in silicon. This enhancement of the diffusion kinetics leads to lower sheet resistance of the diffused layer and deeper profiles of the dopant elements.

EXPERIMENTAL PROCEDURE

1 Ωcm p-type float-zone (FZ) single silicon wafers and Polix multicrystalline material from Photowatt have been processed. Two different dopant sources have been used : phosphorus doped glass films deposited by the spin-on technique from liquid solution or AP-CVD oxides in order to form the emitter and Al evaporation or boron doped AP-CVD oxides for the formation of the BSF.

The RTP unit used here was model FAV4 of Jipelec (Grenoble, France), which is characterized by "cold walls" (< 250°C for a wafer processed at 1100°C) and programmable temperatures, ramps and steps. The temperature was measured by an infrared pyrometer. The characteristic features of the temperature profile are a heating rate of 250°Cs^{-1}, then a plateau at a temperature T with time duration Δt (from 5 to 120 s), followed by a rapid cool-down with a rate typically around 80°Cs^{-1}, which will inherently include a "quenching step". The total time taken to reach room temperature was less than 1 min. The RTP cycles were generally done under a pure argon flow and the plateau temperatures ranged between 800 and 1100°C.

JUNCTION FORMATION AT A LOWER TEMPERATURE

Shallow junctions can be formed in silicon by diffusion using RTP in a few tens of seconds compared to the classical furnace diffusions for relatively longer time. There are different propositions to explain the acceleration of diffusion kinetics of metallic elements. Two of them are : (i) the effect of temperature gradients [5] and (ii) the effect of light especially the near UV [6]. According to the first proposition, too large temperature gradients imply the generation of constraints in the material and that these constraints are accompanied by the injection of large concentration of point defects (vacancies, auto-interstitials). The dopants and the

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metallic elements diffuse by the intermediary of these defects, resulting in an accelerated diffusion of the elements. According to the second proposition, the energetic light (from UV to visible) of the lamps (whose filaments are at much higher temperatures than the substrate, unlike the case in classical furnaces) can cause certain chemical processes (i.e. bond braking) having higher activation energies allowing the creation of point defects and facilitating pairing just as the creation of electron-hole pairs which influence the state of charge of chemical species and accelerate their diffusion.

Mutual enhancement of the dopant diffusion kinetics in a co-diffusion processing step

In Fig.1 we report Secondary Ion Mass Spectroscopy (SIMS) profiles of phosphorus diffused or co-diffused with aluminium for different time-temperature cycles in a rapid thermal furnace. They show an enhancement of the phosphorus diffusion in the case of RTP co-diffusion of P and Al. This result can be probably explained by a mutual influence of Al on P (P on Al) through the injection of point defects during their diffusion in silicon. We have probably the same phenomena as the "pull" [7] effect in microelectronics in which the diffusion kinetics of one dopant is accelerated by the other. This enhancement is also present in the case of a co-diffusion of boron and phosphorus, as shown on Fig. 2. The same phenomena can also be observed when the co-diffusion of the P and B are performed from AP-CVD silicate sources.

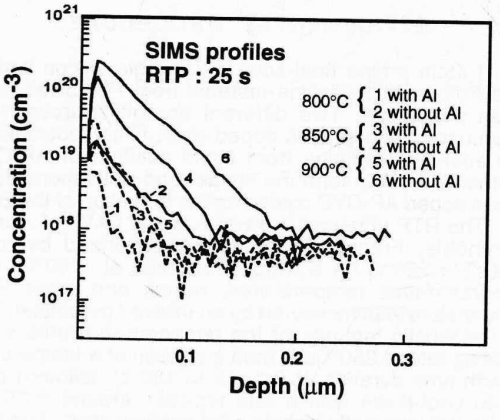


Fig. 1. Phosphorus diffusion enhancement during co-diffusion with Al.

Dopant activity enhancement due to co-diffusion

Figure 3 shows the evolution of the sheet resistance ($R_\square$)values of phosphorus diffused or co-diffused samples with aluminium on the back for various time-temperature cycles in the lamp furnace.

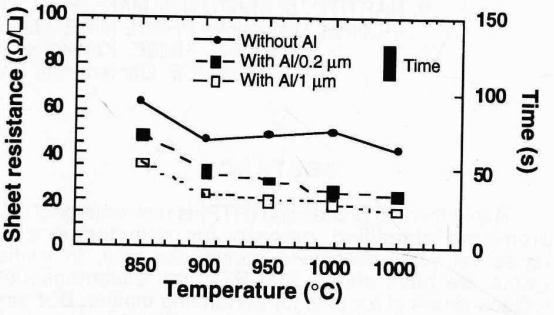


Fig. 3. Evolution of the sheet resistance of phosphorus doped layers after a single diffusion and after co-diffusion of P and Al for two different thicknesses.

We can observe a systematic decrease of the $R_\square$ with increasing diffusion temperatures. The values after co-diffusion were systematically lower than those achieved by single diffusion. This is probably due to a higher phosphorus activity and, as reported before, to a deeper profile of phosphorus after co-diffusion.

To summarize this section, we can point out that co-diffusion processing by RTP can offer the possibility to lower the temperature of the thermal cycle if it is necessary (as we will show it in the case of the use of a multicrystalline substrate) or at the same time to avoid too shallow junctions by keeping the temperature at a higher level. Althrough shallow junctions with high surface dopant concentrations can be a good way for homogeneous emitter of laboratory solar cells as the metallization procedure can be adapted, too shallow junctions can result more generally in shunting and fill factor losses in an industrial processing using screen printed contacts.

EFFECTS ON THE BULK

A major obstacle for the use of RTP in photovoltaics is the generation of electrically active defects which degrade the minority carrier lifetime in silicon so that processing conditions which induce a gettering are of atmost importance in order to counterpart this negative effect.

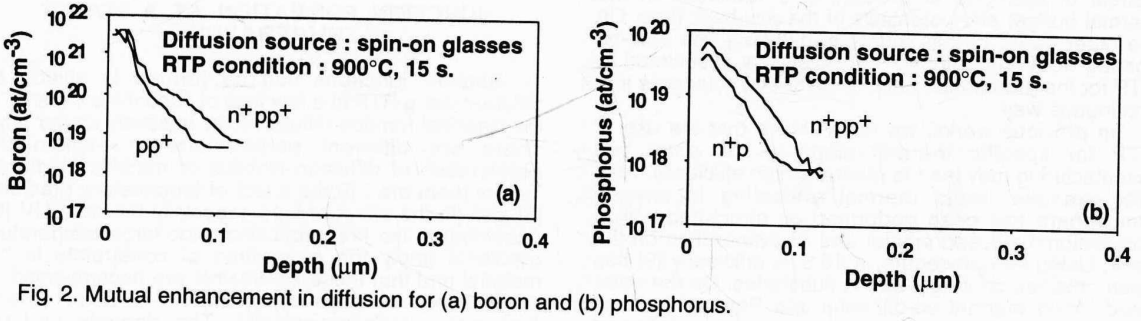


Fig. 2. Mutual enhancement in diffusion for (a) boron and (b) phosphorus.

Petitioner Canadian Solar Inc. - Ex. 1012, p. 1520

Diffusion length enhancement due to P/Al co-diffusion

Figure 4 shows the evolution of the minority carrier diffusion length (L_D) values in P and P/Al co-diffused samples at different temperatures during 25 s. One can see the beneficial effects of the co-diffusion in the improvement of the diffusion length in the material. It results in part from the gettering of metallic impurities during the RTP co-diffusion and secondly by a reflector effect due to the presence of the rear BSF performed by Al alloying.

The evolution of the L_D values for a multicrystalline substrate as Polix is similar, with also an important improvement of the L_D values starting at the lowest temperature range with a maximum at 850°C. However, for higher annealing temperatures, we observe a gradual degradation of the L_D values which could be due to the activation of metallic impurities present in the starting material as we will discuss later on.

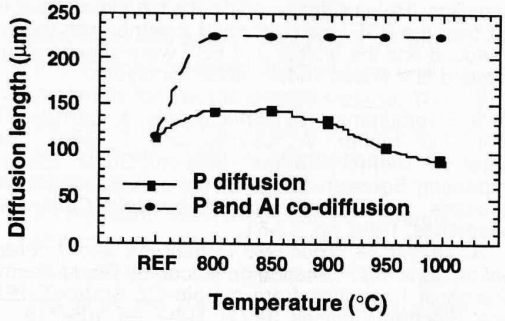


Fig. 4 : Surface PhotoVoltage (SPV) measurements of L_D on monocrystalline silicon after an RTP co-diffusion of P and Al at different temperatures showing the spectacular improvement of L_D up to the sample thickness.

Necessity of a subsequent classical anneal in the case of a P/B co-diffusion

In Fig. 5, one can note a large degradation in L_D (from an initial value of > 200 µm down to 45 µm) at very high RTP temperature.

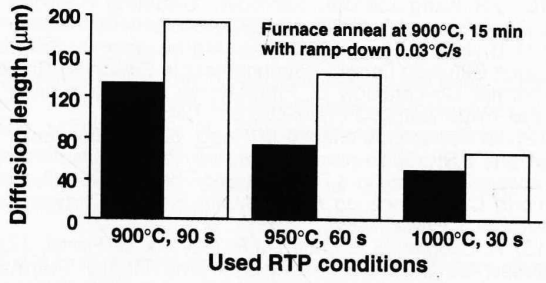


Fig. 5 : SPV measured diffusion length on Polix material after an RTP treatment (in black) and following a subsequent furnace anneal (in white).

This could be due to the reactivation of metallic impurities present into the Polix material, and also due to the activation of grain boundaries after this thermal treatment [8]. At higher temperatures, supersaturated interstitital (metallic) impurity concentration also would be high [9]. The diffusion of dopants such as P and B is accompanied by the dissolution of metallic precipitates, which, once in solution, remain frozen in active sites after the rapid cooling. The partial restoration of L_D observed after the subsequent furnace anneal with slow ramp-down notably in the RTP temperature range 900-950°C (Fig. 5) is mainly due to the precipitation of most of the metallic impurities and defects in electrically inactive form during the slow cooling process (0.03°C/s).

The first conclusion emerging from these measurements is the necessity to keep the processing temperature as low as possible in order to avoid a second thermal treatment in a classical furnace.

The second interesting result to point out is the difference between the two kinds of co-diffusion processes (P-Al, P-B), not in terms of mutual enhancement of the diffusion kinetics, but in terms of effects on the bulk diffusion length, especially in the case of a multicrystalline substrate in which the gettering is more in competition with the activation of residual metallic impurities.

It is well known that boron is less efficient that phosphorus in terms of gettering [10] and has not the additional reflector effect of Al [11]. Moreover, as we have, in the case of Al, on the backside an Al-Si eutectic which is molten during the RTP process, the diffusion of silicon self-interstitial (Si_I) coming from the front surface will be enhanced in order to fill up the lack of Si_I on the backside induced by the formation of the Al-Si eutectic. This excess of interstitial can simultaneously enhance the P diffusion and transform by the kick-out mechanism the substitutional metal into an interstitial one so that the gettering effect overcomes easier the activation procedure.

SOLAR CELL TESTING

Our preliminary solar cell evaluation concerns only FZ monocrystalline substrates and in a first run we have only compared structures having roughly the same emitter profile after the RTP cycle.

RTP cycle	Structure	V_{OC} (mV)	I_{SC} (mA/cm^2)	FF (%)	η (%)
800°C/60 s	n^+pp^+	605	23.38	78	11
950°C/60 s	n^+p	578	22.43	77	10

Table I : Performance of 4 cm^2 polished FZ silicon solar cells without antireflecting coating fabricated by RTP co-diffusion of P and Al or by simple P diffusion.

In Table I, we have reported photovoltaic parameter values obtained on polished FZ monocrystalline substrates by rapid thermal P diffusion or P and Al co-diffusion. We can notice that the performance of the co-diffused cells at low temperatures are higher than those achieved after a high processing temperature or after a single diffusion process. The highest efficiency value is 11 % without AR coating for a cell P and Al co-diffused at 800°C/60 s.

This preliminary result is encouraging and an invitation to continue in this way of reduction of the processing temperature, especially for multicrystalline substrates which are more sensitive to the activation of residual impurities during the quenching step induced by the RTP cycle.

On the other hand, if the cell manufacturing procedure at the present time includes a subsequent

Petitioner Canadian Solar Inc. - Ex. 1012, p. 1521

classical oxidation step in the same temperature range that was used for the restoration of L_D in the previous sub-section, we can use higher RTP temperatures for the Polix material as well as P/B doping sources as it is illustrated on Table II.

Moreover, if Al is used as BSF, the classical oxidation step can be replaced by a rapid thermal oxidation which can be performed during the drive-in of the Al as illustrated on Table II for a FZ monocrystalline sample with a classical P diffused emitter.

Anyway, if up to now not all steps are optimized, these conversion efficiencies of RTP cells are very promising and represent the highest values for mono- and multicrystalline cells of this category. Moreover, the future integration of other RTP steps as the surface passivation, which can be combined with the dopant diffusion in a single thermal cycle [12] and of the contact sintering [13] will contribute to reduce the number of manufacturing steps. This simplification of the cell processing together with a reduction of the duration and temperature of the thermal cycles will make this technology more cost-effective.

In summary, these results contribute to the emerging of RTP as an attractive alternative to the classical thermal processes for silicon solar cell manufacturing.

RTP cycle	Substrate	Structure n^+pp^+	Passivation SiO_2	V_{OC} (mV)	I_{SC} (mA/cm^2)	FF (%)	η (%)	Ref.
1000°C/20 s	mono	P/Al	RTO	616	34.1	79	16.6	[3]
950°C/45 s	multi	P/B	CTO	591	32.6	78.6	15.1	[4]

Table II : Best performance of 4 cm^2 mono (FZ) and multicrystalline (Polix) silicon solar cells having at least two classical thermal steps replaced by a single RTP cycle. For the first one, the BSF was performed together with the front oxide by introducing oxygen in the RTP furnace (RTO) and for the second one the emitter and BSF were simultaneously diffused from AP-CVD deposited layers. Both cells have been AR coated and tested under AM1.5 conditions.

CONCLUSION

This study of RTP silicon solar cells on the way of the replacement of all classical thermal steps by a minimum of short duration cycles in a lamp furnace has up to now demonstrated that the emitter and BSF can be performed simultaneously on mono as well as on multicrystalline substrates. Moreover, a significant enhancement of the diffusion kinetics is observed during the co-diffusion of the two dopants which allow us to reduce the processing temperature. For multicrystalline substrates, which are more sensitive to the activation of residual impurities or defects, it is up to now preferable to use Al on the back-side instead B due to its greater gettering efficiency. The future integration of other RTP steps as the surface passivation and contact sintering, which simplify the cell processing and lower the time and power consumption will bring this technology close to its industriability.

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