SUMMARY OF PATENTS & PATENT APPLICATIONS:

A6. "Hydrokinetic Turbine and Array Performance Optimization by Dynamic Tuning", **John R. Tuttle**, # 63/168,748

A5. "Low Hydrogen Photovoltaic Cell'", Robert F. Zwaap, Troy Berens, **John R. Tuttle**, #20070116893, May 24, 2007.

A4. "Vertical production of photovoltaic devices," **John R. Tuttle**, #20060219547, October 5, 2006.

A3. "Process and photovoltaic device using an akali-containing layer," **John R. Tuttle**, #20060219288, October 5, 2006.

A2. "Pallet based system for forming thin-film solar cells," **John R. Tuttle**, #20060096635, May 11, 2006.

A1. "Pressure control system in a photovoltaic substrate deposition apparatus," **John R. Tuttle**, #20060096536, May 11, 2006.

1) "Method and apparatus for forming a thin-film solar cell using a continuous process," **John R. Tuttle**, 7,576,017, August 18, 2009.

2) "Thermal process for creation of an in-situ junction layer in CIGS," **John R. Tuttle**, 7,319,190, January 15, 2008.

3) "Methods and apparatus for treating a work piece with a vaporous element," Robert F. Zwaap, Troy Berens, **John R. Tuttle**, 7,442,413, October 28, 2008.

4) "Thin-film solar cell fabricated on a flexible metallic substrate," **John R. Tuttle**, Rommel Noufi, and Fallah S. Hasoon, #7,053,294, May 30, 2006.

5) "Preparation of Copper Indium Gallium Diselenide Films for Solar Cells", R. Bhattacharya, M.A. Contreras, J. Keane, A. Tennant, **J.R. Tuttle**, K. Ramanathan, and R. Noufi, USPTO patent # 5,804,054, Sept. 8, 1998.

6) "Preparation of $Cu_xIn_yGa_zSe_n$ (x=0-2, y=0-2, z=0-2, n=0-3) Precursor Films by Electrodeposition for Fabricating High-Efficiency Solar Cells," R. Bhattacharya, M.A. Contreras, J. Keane, A. Tennant, **J.R. Tuttle,** K. Ramanathan, and R. Noufi, USPTO patent # 5,730,852, March 24, 1998.

7) "Recrystallization Method to Selenization of Thin-Film Cu(In,Ga)Se2 for Semiconductor Device Applications," D.S. Albin, J.J. Carapella, **J.R. Tuttle**, M.A. Contreras, A.M. Gabor, R. Noufi, A.L. Tennant, USPTO patent # 5,436,204, Jul. 25, 1995.

8) "Method of Fabricating High-Efficiency $Cu(In,Ga)(Se,S)_2$ Thin Film Solar Cells," R. Noufi, A.M. Gabor, **J.R. Tuttle**, A.L. Tennant, M.A. Contreras, D.S. Albin, J.J. Carapella, USPTO patent # 5,441,897, Aug. 15, 1995.

9) "Enhanced Quality Thin-Film $CuInSe_2$ for Solar Cell Applications by Vapor-Phase Recrystallization," **John R. Tuttle**, Miguel Contreras, Rommel Noufi, and David S. Albin, #5,356,839, Oct. 18, 1994.

SUMMARY OF PUBLICATIONS:

1. "Clean Energy Technologies: A Potential Way Forward to Finance Disruptive Innovation", J**.R. Tuttle**, M.E. deSa, K. Brown, and D. Chambers, Whitepaper, Advanced Research Projects Agency – Energy, 2017, *Under Review*.

2. "PROGRESS TOWARD IMPROVED DEVICE PERFORMANCE IN LARGE-AREA Cu(In,Ga)Se2 THIN FILM SOLAR CELLS," J. Abushama, J. Wax, T. Berens, and **J.R. Tuttle**, *Proceedings of the 4th World Conference on Photovoltaic Energy Conversion*, Waikoloa, HI, May 2006.

3. "Solar Energy Cost Breakthrough Ahead – Photovoltaic Industry Pushes the Limits", **J.R. Tuttle**, *Solar Today*, Jan/Feb 2006, pp. 20-23.

4. "The Terawatt Challenge", **J.R. Tuttle**, *Power Engineering International*, Dec. 2005.

5. "Design Considerations and Implementation of Very-Large Scale Manufacturing of CIGS Solar Cells and Related Products", **J.R. Tuttle**, T. Schuyler, E. Choi, and J. Freer, *To be Published in the Proceedings of the 20th European Photovoltaic Solar Energy Conference and Exhibition – Barcelona, Spain – June 2005.*

6. "Gigawatt-Scale Manufacturing of Discrete Flexible CIGS Solar Cells as a Near-Term Catalyst for the Transition to a 'Solar Economy'", **J.R. Tuttle** and T. Schuyler, *To be Published in the Conference Proceedings of the International Solar Energy Society 2005 Solar World Congress – Orlando, Fl – August 6-12, 2005.*

7. "A 15.2% AM0 / 1433 W/kg Thin-Film Cu(In,Ga)Se2 Solar Cell For Space Applications", **J. R. Tuttle**, Aaron Szalaj and James Keane, *Proceedings of the 28th IEEE Photovoltaics Specialists Conference*, Anchorage, AK September 15-22, 2000.

8. "Progress Towards Commercialization of a 4.5-Sun, Flat-Plate Concentrating PV Module and System", **J. R. Tuttle**, Aaron Szalaj, and Kelly Beninga, *Proceedings of the 28th IEEE Photovoltaics Specialists Conference*, Anchorage, AK September 15-22, 2000.

9. "A novel "flat-plate'" PV concentrator package", J.R. Tuttle, E.D. Cole, T.A. Berens, A. Szalaj, J. Keane, and J. Alleman, *AIP Conference Proceedings* 462, 315 (1999); https://doi.org/10.1063/1.57906

10. "Ternary Semiconductors", Noufi, R. and **Tuttle, J.,** *Wiley Encyclopedia of Electrical and Electronics Engineering*, 1999.

11. "A Crystalline and Thin-Film Cell PV Concentrator Package", **J.R. Tuttle**, E.D. Cole, T. Berens, *J. Alleman, and *J. Keane, *Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, Vienna, Austria, 6-10 July 1998, (in press).

12. "Progress Towards Commercialization of a Thin-Film Based Photovoltaic Filament Cell and Module Technology", **J.R. Tuttle**, E.D. Cole, T. Berens, *J. Alleman, and *J. Keane, *Proceedings of the 14th European Photovoltaic Solar Energy Conference and Exhibition*, Barcelona, Spain June 30 - July 4, 1997, pp. 1365-1368.

13. "Investigations Into Alternative Substrate, Absorber, and Buffer Layer Processing for Cu(In,Ga)Se_2-Based Solar Cells", **J.R. Tuttle**, T.A. Berens, J. Keane, K.R. Ramanathan, J. Granata, R.N. Bhattacharya, H. Wiesner, M.A. Contreras, and R. Noufi, *Proceedings of the 25th IEEE Photovoltaic Specialists Conference*, Washington, D.C., 13-17 May, 1996, (IEEE, New Jersey) pp. 797-800.

14. "Effects of the Concentration of Ga on Junction Formation in Thin-film ZnO/CdS/$CuIn_xGa_{1-x}Se_2$ /Mo Photovoltaic Devices", Matson, R., Contreras, M., **Tuttle, J.**, Swartzlander, A., Parilla, P., & Noufi, R. (1996). *MRS Proceedings, 426*. doi:10.1557/PROC-426-183

15. "Defect Chalcopyrite $Cu(In_{1-x}, Ga_x)_3Se_5$ Polycrystalline Thin-Film Materials", Contreras, M., Wiesner, H., Matson, R., **Tuttle, J.**, Ramanathan, K., & Noufi, R. (1996). *MRS Proceedings, 426*. doi:10.1557/PROC-426-243

16. "The Performance of Cu(In,Ga)Se_2-Based Solar Cells in Conventional and Concentrator Applications", **J.R. Tuttle**, J.S. Ward, A. Duda, T.A. Berens, M.A. Contreras, K.R. Ramanathan, A.L. Tennant, J. Keane, E.D. Cole, K. Emery, and R. Noufi, *Proceedings of the 1996 Spring MRS Meeting*, Symposium J, San Fran., CA, 8-12 April, 1996, pp. 143-151.

17. "Prescriptions for the Fabrication of High-Efficiency Cu(In,Ga)Se_2-Based Thin Films and Devices," **J.R. Tuttle**, M.A. Contreras, K.R. Ramanathan, A.L. Tennant, S.A. Asher, D. Niles, R. Matson, J. Keane, and R. Noufi, *Proceedings of the 13th European Photovoltaic Solar Energy Conference*, Nice, FRANCE, 23-27 Oct., 1995, p.2131.

18. "The Influence of Ga in Trace Quantities on the Properties and Performance of CuIn(Ga)Se_2-Based Thin Films and Devices", B. Keyes, **J.R. Tuttle**, A.L. Tennant, S.A. Asher, M.A. Contreras, K.R. Ramanathan, A.M. Gabor, J. Webb, and R. Noufi, *Proceedings of the 10th International Conference on Ternary and Multinary Compounds*, Stuttgart, GERMANY, Sept. 19-22, 1995 (in press).

19. "Absorber Processing Issues in High-Efficiency Thin-Film Cu(In,Ga)Se_2-Based Solar Cells", **J.R. Tuttle**, *Proceedings of the 13th NREL Photovoltaic Program Review,* Lakewood, CO, May 17-19, 1995, p.47.

20. "Thin-film Cu(In,Ga)Se_2 materials and devices: A versatile material for flat-plate and concentrator photovoltaic applications," **J.R. Tuttle**, M.A. Contreras, J.S. Ward, A.L. Tennant, K.R. Ramanathan, J. Keane, and R. Noufi, *Proceedings of the SPIE 40th Annual Meeting,* 9-14 July, 1995, SPIE Vol. 2531, p194.

21. "A Perspective on High-Efficiency Cu(In,Ga)Se_2-Based Thin-Film Solar Cells Fabricated by Simple, Scalable Processes," **J.R. Tuttle**, M.A. Contreras, A.M. Gabor, K.R. Ramanathan, A.L. Tennant, D.S. Albin, J. Keane, and R. Noufi, *Prog. in Photovoltaics*, Nov.-Dec., 1995 (in press).

22. "A 17.1%-Efficient Cu(In,Ga)Se_2-Based Thin-Film Solar Cell," **J.R. Tuttle**, M.A. Contreras, T.J. Gillespie, K.R. Ramanathan, A.L. Tennant, J. Keane, A.M. Gabor, and R. Noufi, *Prog. in Photovoltaics*, July-August, Vol. 3, 235-238, 1995.

23. "The Formation of Large-Grain $CuInSe_2$ Films by Selenization by High-Rate Se Transport Under Moderate Vacuum Conditions", D.S. Albin, **J.R. Tuttle**, R. Noufi, J.Elec.Materials, **24**(4), 1995, p. 1.

24. "High-Efficiency Cu(In,Ga)Se_2-Based Thin-Film Solar Cells : 16.8% Total-Area 1-Sun and 17.2% Total-Area 22-Sun Device Performance", **J.R. Tuttle**, M.A. Contreras, J.S. Ward, A.M Gabor, K.R. Ramanathan, A.L. Tennant, L. Wang, J. Keane, and R. Noufi, *Proceedings of the 1st World Conference on Photovoltaic Energy Conversion*, 5-9 Dec., 1994, Waikoloa, HI, p. 1942.

25. "Band-Gap Engineering In Cu(In,Ga)Se_2 Thin Films Grown From $(In,Ga)_2Se_3$ Precursors", A.M. Gabor, **J.R. Tuttle**, A. Schwartzlander, A.L. Tennant, M.A. Contreras, and R. Noufi,

Proceedings of the 1st World Conference on Photovoltaic Energy Conversion, 5-9 Dec., 1994, Waikoloa, HI, p. 83.

26. "High-Efficiency Cu(In,Ga)Se_2-Based Solar Cells : Processing of Novel Absorber Structures", M.A. Contreras, **J.R. Tuttle**, A.M. Gabor, A.L. Tennant, K.R. Ramanathan, S. Asher, A. Franz, J. Keane, L. Wang, and R. Noufi, *Proceedings of the 1st World Conference on Photovoltaic Energy Conversion*, 5-9 Dec., 1994, Waikoloa, HI, p. 68.

27. "Sodium Diffusion, Selenization, and Microstructural Effects Associated with Various Molybdenum Back Contact Layers for CIS-Based Solar Cells", J.H. Scofield, S. Asher, D.S. Albin, **J.R. Tuttle**, M. Contreras, D. Niles, R. Reedy, A. Tennant, and R. Noufi, *Proceedings of the 1st World Conference on Photovoltaic Energy Conversion*, 5-9 Dec., 1994, Waikoloa, HI, p. 164.

28. "Study on the Interfacial Structure and Junction Depth of Polycrystalline Cu(In,Ga)Se_2 Devices," A.J. Nelson, A.M. Gabor, M.A. Contreras, **J.R. Tuttle**, and R. Noufi, *Proceedings of the 1st World Conference on Photovoltaic Energy Conversion*, 5-9 Dec., 1994, Waikoloa, HI, p. 279.

29. "The Structure, Chemistry, and Growth Mechanisms of Thin-Film $CuInSe_2$ Grown From a Mixed-Phase Precursor", **J.R. Tuttle**, M. Contreras, M.H. Bode, D. Niles, D.S. Albin, R. Matson, A.M. Gabor, A. Tennant, and R. Noufi, *J. Appl. Phys.*, **77** (1), 1995, pp. 1-9.

30. "16.4% Total-Area Conversion Efficiency Thin-Film Polycrystalline MgF_2/ZnO/CdS/Cu(In,Ga)Se_2/Mo Solar Cell," M.A. Contreras, A.M. Gabor, A.L. Tennant, S. Asher, **J.R. Tuttle**, and R. Noufi, *Prog. in PV*, **2**, 1994, pp. 287-292.

31. "Characterization and Modeling of Cu(In,Ga)$(S,Se)_2$-Based Photovoltaic Devices: A Laboratory and Industrial Perspective," **J.R. Tuttle** *et. al., Prog. in Photovoltaics,* **3**, pp.89-104, 1995.

32. "High-Efficiency $CuIn_xGa_{1-x}Se_2$ Solar Cells Made From $(In_x,Ga_{1-x})_2Se_3$ Precursor Films," A.M. Gabor, **J.R. Tuttle**, D.S. Albin, M.A. Contreras, and R. Noufi, *Appl. Phys. Lett.* **65** (2) 1994, pp. 198-200.

33. "A Microstructural Comparison of Cu(In,Ga)Se_2 Thin Films Grown From Cu_xSe and $(In,Ga)_2Se_3$ Precursors," A.M. Gabor, **J.R. Tuttle**, D.S. Albin, R. Matson, A. Franz, D.W. Niles, M.A. Contreras, A.M. Hermann, and R. Noufi, (to be published in the *Proceedings of the MRS 1994 Spring Meeting, Symposium H*, 4-94).

34. "High-Efficiency Thin-Film Cu(In,Ga)Se_2 Solar Cells: Achievement of a Confirmed World-Record 16.4% Total-Area Efficiency," A.M. Gabor, **J.R. Tuttle**, M.A. Contreras, D.S. Albin, A. Franz, D.W. Niles, and R. Noufi, *Proceedings of the 12th European Photovoltaic Solar Energy Conference,* 11-15 April, 1994, The Netherlands (H.S. Stephens & Associates, U.K., 1994) pp. 939-943.

35. "High-Efficiency Cu(In,Ga)Se_2-Based Thin-Film Solar Cells Fabricated by Simple, Scalable Processes", **J.R. Tuttle**, A.M. Gabor, D.S. Albin, A. Tennant, M. Contreras, and R. Noufi, *Technical Digest of the 7th Sunshine Workshop,* Shinjuku, Tokyo, Japan, Nov. 1993, p. 109.

36. "Characterization of Variable-Band-Gap Thin-Film Cu(In,Ga)Se_2: A Simple Model For The Interdiffusion of In and Ga In Alloy Structures", **J.R. Tuttle**, D.S. Albin, A. Tennant, A.M. Gabor, M. Contreras, J.J. Carapella, Y. Qu, D. Du and R. Noufi, Proceedings of the 7th Photovoltaic Science and Engineering Conference, Nagoya, Japan, Nov. 1993, *Sol. Energy Mats. and Sol. Cells*, **35** (1-4) 1994, pp. 193-202.

37. "High-Efficiency Polycrystalline CuInGaSe$_2$-Based Solar Cells", A.M. Gabor, **J.R. Tuttle**, M.A. Contreras, D.S. Albin, A. Tennant, A.M. Hermann, and R. Noufi, AIP Conference Proceedings 306, *Proceedings of the 12th NREL Photovoltaic Program Review ,* Denver, CO, Oct. 13-15, 1993 p.59.

38. "TEM Investigations of Ordered Phases in CuInSe$_2$", M. Bode, **J.R. Tuttle**, M.M. Al-Jassim, AIP Conference Proceedings 306, *Proceedings of the 12th NREL Photovoltaic Program Review,* Denver, CO, Oct. 13-15, 1993 p.421.

39. "Photoemission Investigation of the Electronic Structure at Polycrystalline CuInSe$_2$ Thin-Film Interfaces", A.J. Nelson, A.B. Swartzlander, **J.R. Tuttle**, and R. Noufi, R. Patel, and H. Höchst, J.Appl. Phys., **74** (9), 1993, pp. 5757-5760.

40. "The Meyer-Neldel Rule in Emission Rates From Defects in Copper Indium Diselenide", F.R. Shapiro, **J.R. Tuttle**, Solid State Communications, **87** (3), 1993, pp. 199-202.

41. "Graded Band-Gap Cu(In,Ga)Se$_2$ Thin-Film Solar Cell Absorber with Enhanced Open-Circuit Voltage", M.A. Contreras, **J.R. Tuttle**. D. Du, Y. Qu, A. Swartzlander, A. Tennant, and R. Noufi, Appl. Phys. Lett., **63** (13), 1993, pp. 1824-1826.

42. "High-Efficiency Thin-Film Cu(In,Ga)Se$_2$-Based Photovoltaic Devices: Progress Towards a Universal Approach To Absorber Fabrication", **J.R. Tuttle**, M. Contreras, A. Tennant, D.S. Albin, and R. Noufi, *Proceedings 23rd IEEE Photovoltaic Specialists Conference*, Louisville, KY, 1993, pp. 415-421.

43. "Validation of an In-Line Evaporation Process For Large-Scale Production of CuInSe$_2$-Based Solar Cells", M.A. Contreras, **J.R. Tuttle**, D.S. Albin, A. Tennant, and R. Noufi, *Proceedings 23rd IEEE Photovoltaic Specialists Conference*, Louisville, KY, 1993, pp. 486-490.

44. "Novel Processing and Device Structures in Thin-Film CuInSe$_2$-Based Solar Cells," **J.R Tuttle**, M. Contreras, A. Tennant, R. Matson, A. Duda, J. Carapella, D.S. Albin, and R. Noufi, *AIP Proceedings of the NREL Photovoltaic Advanced Research and Development 11th Review Meeting,* May 13-15, 1992, Denver, CO, **268**, p178.

45. "Fundamental Thermodynamics and Experiments in Fabricating High Efficiency CuInSe$_2$ Solar Cells by Selenization Without the Use of H_2Se," D. Albin, J Carapella, A. Gabor, A. Tennant, **J.R Tuttle**, A. Duda, R. Matson, M. Contreras, and R. Noufi, *AIP Proceedings of the NREL Photovoltaic Advanced Research and Development 11th Review Meeting,* May 13-15, 1992, Denver, CO, **268**, p108.

46. "CuInSe$_2$ Thin-Film Formation by Rapid Annealing off the Elemental Precursor," A. Gabor, A. Hermann, **J.R Tuttle**, D.S. Albin, A. Franz, and R. Noufi, *Proceedings of the NREL Photovoltaic Advanced Research and Development 11th Review Meeting,* May 13-15, 1992, Denver, CO, **268**, p236.

47. "The Design and Fabrication of Polycrystalline Thin-Film CuInSe$_2$ and Cu(In,Ga)Se$_2$-Based Photovoltaic Materials and Devices," **J.R Tuttle**, D.S. Albin, R. Noufi, and S.K Deb, *Proceedings of the 6th International Photovoltaic Science and Engineering Conference*, Febuary 10-14, 1992, New Delhi, India p.849.

48. "The Effect of Copper Vacancies on the Optical Bowing of Chalcopyrite Cu(In,Ga)Se2 Alloys" Albin, D., Carapella, J., **Tuttle, J.**, & Noufi, R. (1992). *MRS Proceedings, 228*. doi:10.1557/PROC-228-267

49. "Microcharacterization of CuInSe2 Grown by Coevaporation and Selenization ", Bode, M., Al-Jassim, M., Tuttle, J., & Albin, D. (1992). *MRS Proceedings, 283*. doi:10.1557/PROC-283-927

50. "Physical, Chemical, and Structural Modifications to Thin-Film $CuInSe_2$-Based Photovoltaic Devices", **J.R. Tuttle**, M. Contreras, D.S. Albin, and R. Noufi, *Proceedings of the 22nd IEEE Photovoltaics Specialists Conference*, Las Vegas, NV (IEEE, New York, 1991) p. 1062.

51. "Optical Band Gap and Lattice Constant of $Cd_xZn_{1-x}Se_yS_{1-y}$ Thin-Film Alloys for Heterojunction Photovoltaic Cells", R. Noufi, **J.R. Tuttle**, D.S Albin, M. Contreras, J. Carapella, A. Mason, and A. Tennant, *Proceedings of the 22nd IEEE Photovoltaics Specialists Conference*, Las Vegas, NV (IEEE, New York, 1991) p. 1105.

52. "The Effect of Microstructure and Strain in In/Cu/Mo/Glass Precursors on CdS/$CuInSe_2$ Photovoltaic Device Fabrication by Selenization", D. Albin, J. Carapella, A. Duda, **J. Tuttle**, A. Tennant, and R. Noufi, *Proceedings of the 22nd IEEE Photovoltaics Specialists Conference*, Las Vegas, NV (IEEE, New York, 1991) p. 907.

53. "Modifications to the Interfacial and Bulk Region of $CuInSe_2$-Based Photovoltaic Devices: Alloys, Windows, and Grain-Size Enhancement", **J.R. Tuttle**, M. Contreras, J. Carapella, D.S. Albin, and R. Noufi, *Proceedings of the 26th Intersociety Energy Conversion Engineering Conference*, Boston, MA, (American Nuclear Society, La Grange Park, IL, 1991) Vol. 5, p.106.

54. "Issues Concerning the Design and Fabrication of Polycrystalline Thin-Film $Cu(In,Ga)Se_2$-Based Photovoltaic Materials and Devices", **J.R. Tuttle**, D.S. Albin, and R. Noufi, *Proceedings of the ISES 1991 Solar World Congress,* Denver, CO,(Pergamon Press, New York, 1991) Vol. 1, p.21.

55. "Thoughts on the Microstructure of Polycrystalline Thin Film $CuInSe_2$ and its Impact on Material and Device Performance", **J.R. Tuttle**, D.S. Albin, and R. Noufi, *Solar Cells*, **30**, 21(1991).

56. "The Phase Behavior of Evaporated Copper and Indium Precursors for Selenization," D.S. Albin, G.D. Mooney, J. Carapella, A. Duda, **J.R. Tuttle**, R. Matson, and R. Noufi, *Solar Cells*, **30**, 41(1991).

57. "Enhanced Grain Growth in Polycrystalline $CuInSe_2$ Using Rapid Thermal Processing," D.S. Albin, G.D. Mooney, A. Duda, **J.R. Tuttle**, R. Matson, and R. Noufi, *Solar Cells*, **30**, 47(1991).

58. "Formation of $CuInSe_2$ Thin Films by Rapid Thermal Recrystallization," G.D. Mooney, A.M. Hermann, **J.R. Tuttle**, D.S. Albin, and R. Noufi, *Appl. Phys. Lett.*, **58**(23), p. 2678(1991).

59. "Novel Approaches to the Design and Fabrication of $CuInSe_2$ Based Thin Film Photovoltaic Devices", **J.R. Tuttle**, M. Contreras, J.J. Carapella, D.S. Albin, A.L. Tennant, and R. Noufi, Extended Abstracts of the 179th Meeting of the Electrochemical Society, (in press).

60. "The Effect of Copper Vacancies on the Optical Bowing of Chalcopyrite $Cu(In,Ga)Se_2$ Alloys," D.S. Albin, J.J. Carapella, **J.R. Tuttle**, and R. Noufi, *Proceedings of the 1991 MRS Spring Meeting, "Materials for Optical Information Processing*",.

61. "Microstructural Characterization of Polycrystalline Thin Film $CuInSe_2$: A Promising Yet Complex Material for Photovoltaic Applications", **J.R. Tuttle**, D.S. Albin, J.J. Carapella, and

R. Noufi, *Proceedings of the 25th Intersociety Energy Conversion Engineering Conference*, Reno, NV (AIChE, New York, 1990) Vol. 5, p.31.

62. "Secondary and Polymorphic Phase Behavior of Thin Film $CuInSe_2$: Ramifications on the Device Performance", **J.R. Tuttle**, D.S. Albin, J.P. Goral, and R. Noufi, *Proceedings of the 21st IEEE Photovoltaics Specialists Conference*, Kissimee, FL (IEEE, New York, 1990) p. 748.

63. "A Study on the Optical and Microstructural Characteristics of Quaternary $Cu(In,Ga)Se_2$ Polycrystalline Thin Films", D.S. Albin, **J.R. Tuttle**, G.D. Mooney, J.J. Carapella, A. Duda, A. Mason, and R. Noufi, *Proceedings of the 21st IEEE Photovoltaics Specialists Conference*, Kissimee, FL (IEEE, New York, 1990) p. 562.

64. TEM Identification of Secondary Phases in Non-Stoichiometric Polycrystalline $CuInSe_2$ Thin Films," J.P. Goral, M.M. Al-Jassim, D.S. Albin, **J.R. Tuttle**, and R. Noufi, *Proceedings of the XIIth International Congress for Electron Microscopy*, p. 604(1990).

65. "An Optical and Microstructural Characterization Study and Microstructural Model of Co-Evaporated Polycrystalline Thin Film $CuInSe_2$ for Photovoltaic Applications", **J.R. Tuttle**, Ph.D. Dissertation, May 1990.

66. "Characterization of Thin-Film $CuInSe_2$ and $CuGaSe_2$: The Existence and Identification of Secondary Phases," **J.R. Tuttle**, D.S. Albin, and R. Noufi, *Solar Cells*, **27**, 231(1989).

67. "A Comprehensive Study of the Optical Properties of Thin-Film CuInSe2 as a Function of Composition and Substrate Temperature," **J.R. Tuttle**, D.S. Albin, R.J. Matson, and R. Noufi, *J. Appl. Phys.*, **66**(9), 4408(1989).

68. "Experiments of the Modification of the Bi-Layer Structure in $CdS/CuInSe_2$ Devices," **J.R. Tuttle**, M. Ruth, D.S. Albin, A. Mason, and R. Noufi, *Proceedings of the 20th IEEE Photovoltaics Specialists Conference*, Las Vegas, NV (IEEE, New York, 1989) p. 1525.

69. "Physical and Chemical Modifications of the Bi-Layer Structure in $CdS/CuInSe_2$ Devices," R. Noufi, **J.R. Tuttle**, M. Ruth, D.S. Albin, and A. Mason, *Proceedings of the 9th E.C. Photovoltaic Solar Energy Conference*, Freiburg, Fed. Rep. of Germany (Kluwer Academic Publishers, Dordrecht 1989)p. 283.

70. "Effects of Composition and Substrate Temperature on the Electro-Optical Properties of Thin-Film $CuInSe_2$ and $CuGaSe_2$," **J.R. Tuttle**, D.S. Albin, J. Goral, C. Kennedy, and R. Noufi, *Solar Cells*, **24**, 67(1988).

71. "The Optical and Structural Properties of $CuGaSe_2$ Polycrystalline Thin Films," D.S. Albin, **J.R. Tuttle**, J. Goral, A. Mason, R. Noufi, and S.H. Risbud, *Proceedings of the 20th IEEE Photovoltaics Specialists Conference*, Las Vegas, NV (IEEE, New York, 1989) p. 1495.

72. "Composition-Structure Relationships for Multi-Source Evaporated $CuGaSe_2$ Thin Films," D.S. Albin, R. Noufi, **J.R. Tuttle**, J. Goral, and S.H. Risbud, *J. Appl. Phys.*, **64**(10), 4903(1988).

73. "Microstructural Characterization of $CuGaSe_2$ Thin Films by X-Ray Diffraction," D.S. Albin, R. Noufi, **J.R. Tuttle**, and S.H. Risbud, *ACS-MRS Proceedings of the 41st West Coast Regional Meeting of the American Ceramic Society (Ceramic Transactions)*, **5**, p.141(1988) .

74. "Aluminum Doped Zinc Oxide Thin Films Deposited by Ion Beam Sputtering," M. Ruth, **J.R. Tuttle**, J. Goral, and R. Noufi, *J. Crys. Growth*, **96**, p. 363(1989).

75. "The Effect of Composition on the Optical Properties of $CuInSe_2$ Thin Films," **J.R. Tuttle**, R. Noufi, and R.H. Dhere, *Proceedings of the 19th IEEE Photovoltaics Specialists Conference*, New Orleans, LA (IEEE, New York, 1988) p. 1494.

76. "Sample Preparation and Characterization Study of $CdSnP_2$," **J.R. Tuttle**, M.S. Thesis, Colorado School of Mines, 1984.

77. "Photoelectrochemical Characterization of $CdSnP_2$ Crystals," J.C.W. Folmer, **J.R. Tuttle**, J.A. Turner, and B.A. Parkinson, *Journal of the Electrochemical Society*, **132**(7), 1985.

78. "II-VI-V_2 Chalcopyrite-Type Photoelectrodes: The $CdSnP_2$ Aqueous Polysulfide System," J.C.W. Folmer, **J.R. Tuttle**, D.L. Williamson, J.A Turner, B.A. Parkinson, S.K. Deb, and D. Cahen, *Progress in Crystal Growth and Characterization*, **10** (1985).

SUMMARY OF PRESENTATIONS

Business / Technical / Investment (2003-2010)

Dr. Tuttle has conducted well over 250 presentations to Investor, business, and technical audiences on various subject matters including Energy, Photovoltaics (PV), Business Start-up, PV Industry, PV markets, Technology Competitiveness, Business and Technology Strategy, Innovation, Technology Transfer, and Manufacturing.

Technical (1990 - 2000)

1) "A 15.2% AM0 / 1433 W/kg Thin-Film Cu(In,Ga)Se2 Solar Cell For Space Applications", John R. Tuttle, Aaron Szalaj and James Keane, *Proceedings of the 28th IEEE Photovoltaics Specialists Conference*, Anchorage, AK September 15-22, 2000 (*oral*).

2) "Progress Towards Commercialization of a 4.5-Sun, Flat-Plate Concentrating PV Module and System", John R. Tuttle, Aaron Szalaj, and Kelly Beninga, *Proceedings of the 28th IEEE Photovoltaics Specialists Conference*, Anchorage, AK September 15-22, 2000 (*poster*).

3) "A Crystalline and Thin-Film Cell PV Concentrator Package", **J.R. Tuttle**, E.D. Cole, T. Berens, *J. Alleman, and *J. Keane, *Proceedings of the 2nd World Conference and Exhibition on Photovoltaic Solar Energy Conversion*, Vienna, Austria, 6-10 July 1998, (poster).

4) "Progress Towards Commercialization of a Thin-Film Based Potovoltaic Filament Cell and Module Technology", **J.R. Tuttle**, E.D. Cole, T. Berens, *J. Alleman, and *J. Keane, 14th European Photovoltaic Solar Energy Conference and Exhibition, Barcelona, Spain June 30 - July 4, 1997, (oral).

5) "A Cu(In,Ga)Se_2-Based Solar Cell, Module, and Manufacturing Project: The Fast Track to PV Power Commercialization", Tenth Sunshine Workshop on Thin-Film Solar Cells, Shinjuku, Tokyo, JAPAN, 8-9 November, 1996, (Invited).

6) "Investigations Into Alternative Substrate, Absorber, and Buffer Layer Processing for Cu(In,Ga)Se_2-Based Solar Cells", 25th IEEE Photovoltaic Specialists Conference, Washington, D.C., 13-17 May, 1996, (oral).

7) "The Performance of Cu(In,Ga)Se_2-Based Solar Cells in Conventional and Concentrator Applications", 1996 Spring MRS Meeting, Symposium J, San Fran., CA, 8-12 April, 1996, (Invited).

8) "Absorber Processing Issues in High-Efficiency Cu(In,Ga)Se2-Based Solar Cells," 1995 Fall Meeting of the Materials Research Society, Boston, MA, Nov. 27 - Dec. 1, 1995 (oral).

9) "Prescriptions for the Fabrication of High-Efficiency Cu(In,Ga)Se_2-Based Thin Films and Devices," 13th European Photovoltaic Solar Energy Conference, Nice, FRANCE, 23-27 Oct., 1995 (oral).

10) "Thin-film Cu(In,Ga)Se_2 materials and devices: A versatile material for flat-plate and concentrator photovoltaic applications," The SPIE 40th Annual Meeting, 9-14 July, 1995 (oral).

11) "Absorber Processing Issues in High-Efficiency Thin-Film Cu(In,Ga)Se_2-Based Solar Cells", 13th NREL Photovoltaic Program Review, Lakewood, CO, May 17-19, 1995 (oral).

12) "High-Efficiency Cu(In,Ga)Se_2-Based Thin-Film Solar Cells : 16.8% Total-Area 1-Sun and 17.2% Total-Area 22-Sun Device Performance", 1st World Conference on Photovoltaic Energy Conversion, 5-9 Dec., 1994, Waikoloa, HI (Poster).

13) "High-Efficiency Thin-Film Cu(In,Ga)Se_2-Based Photovoltaic Devices: Progress Towards A Universal Approach To Absorber Fabrication", 1994 OPA/OER Review, Nov. 16, 1994 (Oral).

14) "High-Efficiency Cu(In,Ga)Se_2-Based Thin-FIlm Solar Cells Fabricated by Simple, Scalable Processes", 7th Sunshine Workshop on Thin-Film Solar Cells, Shinjuku, Tokyo, Japan, Nov. 29-30, 1993 (oral).

15) "High-Efficiency Cu(In,Ga)Se_2-Based Thin-Film Solar Cells: 15% Device Efficiencies and Beyond by Simple Fabrication Processes", 7th Photovoltaic Science and Enginering Conference, Nagoya, Japan, Nov. 22-26, 1993 (oral).

16) "High-Efficiency Thin-Film Cu(In,Ga)Se_2-Based Photovoltaic Devices: Progress Towards A Universal Approach To Absorber Fabrication", 23rd IEEE Photovoltaics Specialists Conference, Louisville, KY, May 10-14, 1993 (oral).

17) "Growth Mechanisms, Characterization, and Device Performance of Thin-Film Cu(In,Ga)Se_2 Solar Cells", 1993 Spring Meeting of the Materials Research Society, San Francisco, CA, April 1993 (oral).

18) "Novel Processing and Device Structures in Thin-Film $CuInSe_2$-Based Solar Cells," NREL Photovoltaic Advanced Research and Development 11th Review Meeting, Denver, CO May 13-15, 1992 (oral).

19) "Physical, Chemical, and Structural Modifications to Thin-Film $CuInSe_2$-Based Photovoltaic Devices", 22nd IEEE Photovoltaics Specialists Conference, Las Vegas, NV, October 1991 (poster, Polycrystalline Solar Cells Poster Award)

20) "Modifications to the Interfacial and Bulk Region of $CuInSe_2$-Based Photovoltaic Devices: Alloys, Windows, and Grain-Size Enhancement," 26th IECEC, Boston, MA, August 1991 (oral).

21) "Issues Concerning the Design and Fabrication of Polycrystalline Thin-Film Cu(In,Ga)Se_2-Based Photovoltaic Materials and Devices," ISES 1991 Solar World Congress, Denver, CO, August 1991 (oral, honors paper).

22) "The Microstructure of Non-Stoichiometric Polycrystalline Thin-Film $CuInSe_2$," Twelfth Conference on Crystal Growth, Fallen Leaf Lake, CA, May 1991 (oral).

23) "Characterization of $CuInSe_2$ Thin Film Materials and Devices", 10th Photovoltaic Advanced Research and Development Conference, Denver, CO, October 1990 (Oral).

24) "Issues Concerning the Design and Fabrication of Polycrystalline Thin Film Cu(In,Ga)Se_2 Based Photovoltaic Materials and Devices", Purdue University, Lafayette IN, and University of North Carolina, Chapel Hill NC, September 1990 (Oral).

25) "An Overview of Thin Film Photovoltaic Research at the Solar Energy Research Institute", 25th IECEC, Reno NV, August 1990 (Oral).

26) "Secondary and Polymorphic Phase Behavior of Thin Film $CuInSe_2$: Ramifications on the Device Performance", 21st IEEE PVSC, Kissimmee FL, May 1990 (Poster).

27) "Microstructural Characterization of Polycrystalline Thin Film $CuInSe_2$: A Promising Yet Complex Material for Photovoltaic Applications", University of Colorado, Boulder CO, February 1990 (Oral).

US005356839A

United States Patent [19]

Tuttle et al.

[11] Patent Number: 5,356,839

[45] Date of Patent: Oct. 18, 1994

[54] **ENHANCED QUALITY THIN FILM CU(IN,GA)SE_2 FOR SEMICONDUCTOR DEVICE APPLICATIONS BY VAPOR-PHASE RECRYSTALLIZATION**

[75] Inventors: **John R. Tuttle**, Denver; **Miguel A. Contreras; Rommel Noufi**, both of Golden; **David S. Albin**, Denver, all of Colo.

[73] Assignee: **Midwest Research Institute**, Kansas City, Mo.

[21] Appl. No.: **45,860**

[22] Filed: **Apr. 12, 1993**

[51] **Int. Cl.**[5] **H01L 21/302**

[52] **U.S. Cl.** **437/225**; 437/5; 437/234; 136/260; 136/265; 136/258

[58] **Field of Search** ..... 437/225, 5, 103, 106, 437/234; 136/258 PC, 260, 265, 264

[56] **References Cited**

U.S. PATENT DOCUMENTS

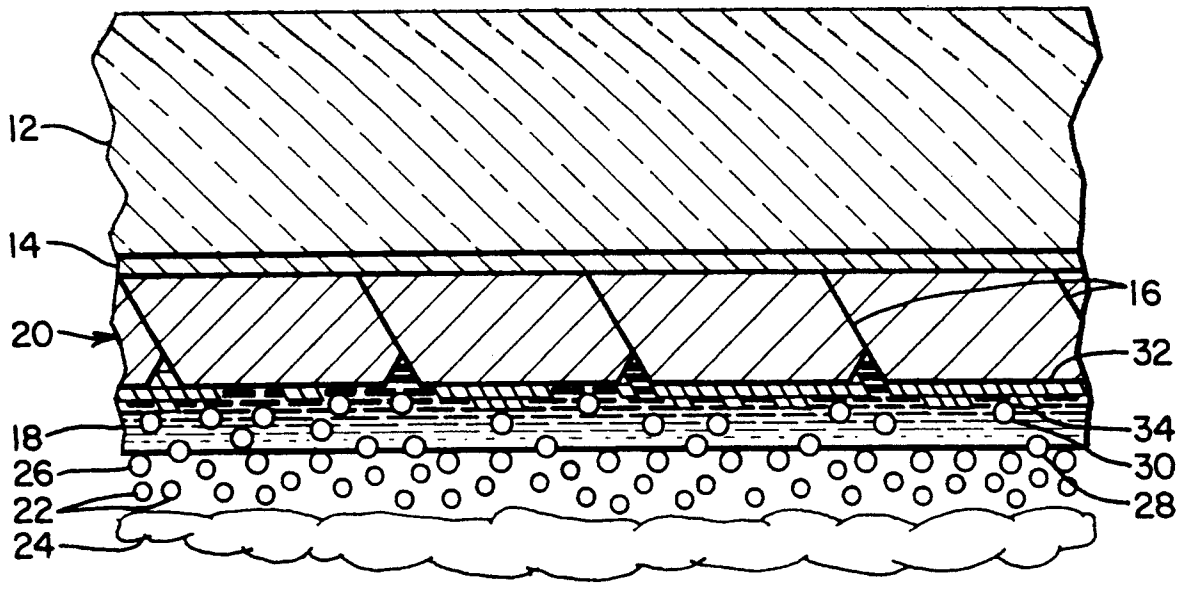
4,465,575	8/1984	Love et al.	136/260
4,581,108	4/1986	Kapur et al.	136/260
4,703,131	10/1987	Dursch	136/258
4,915,745	4/1990	Pollock et al.	136/260
5,078,804	1/1992	Chen et al.	437/5

Primary Examiner—Tom Thomas
Assistant Examiner—Tuan Nguyen
Attorney, Agent, or Firm—Ken Richardson

[57] **ABSTRACT**

Enhanced quality thin films of $Cu_w(In,Ga_y)Se_z$ for semiconductor device applications are fabricated by initially forming a Cu-rich, phase-separated compound mixture comprising $Cu(In,Ga):Cu_xSe$ on a substrate to form a large-grain precursor and then converting the excess Cu_xSe to $Cu(In,Ga)Se_2$ by exposing it to an activity of In and/or Ga, either in vapor In and/or Ga form or in solid $(In,Ga)_ySe_z$. Alternatively, the conversion can be made by sequential deposition of In and/or Ga and Se onto the phase-separated precursor. The conversion process is preferably performed in the temperature range of about 300°–600° C., where the $Cu(In,Ga)Se_2$ remains solid, while the excess Cu_xSe is in a liquid flux. The characteristic of the resulting $Cu_w(In,Ga)_ySe_z$ can be controlled by the temperature. Higher temperatures, such as 500°–600° C., result in a nearly stoichiometric $Cu(In,Ga)Se_2$, whereas lower temperatures, such as 300°–400° C., result in a more Cu-poor compound, such as the $Cu_z(In,Ga)_4Se_7$ phase.

26 Claims, 3 Drawing Sheets



US007053294B2

(12) **United States Patent**
Tuttle et al.

(10) **Patent No.: US 7,053,294 B2**
(45) **Date of Patent: May 30, 2006**

(54) **THIN-FILM SOLAR CELL FABRICATED ON A FLEXIBLE METALLIC SUBSTRATE**

(75) Inventors: **John R. Tuttle**, Frisco, CO (US); **Rommel Noufi**, Golden, CO (US); **Falah S. Hasoon**, Arvada, CO (US)

(73) Assignee: **Midwest Research Institute**, Kansas City, MO (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 0 days.

(21) Appl. No.: **10/480,880**

(22) PCT Filed: **Jul. 13, 2001**

(86) PCT No.: **PCT/US01/22192**

§ 371 (c)(1),
(2), (4) Date: **Dec. 12, 2003**

(87) PCT Pub. No.: **WO03/007386**

PCT Pub. Date: **Jan. 23, 2003**

(65) **Prior Publication Data**

US 2005/0074915 A1 Apr. 7, 2005

(51) **Int. Cl.**
H01L 31/336 (2006.01)
H01L 31/392 (2006.01)

(52) **U.S. Cl.** **136/265**; 136/256; 136/252; 136/264; 136/245; 136/244; 438/94; 438/95; 438/98; 257/431; 257/461; 257/464

(58) **Field of Classification Search** 136/256, 136/262, 265, 264, 245, 252, 244; 438/94, 438/95, 98; 257/431, 461, 464
See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

3,586,541 A * 6/1971 Chamberlin 136/206
4,191,794 A * 3/1980 Shirland et al. 438/80

(Continued)

FOREIGN PATENT DOCUMENTS

DE 2741954 A1 * 3/1979

(Continued)

OTHER PUBLICATIONS

Gabor et al, "Band-gap engineering in Cu(In,Ga)Se2 thin films grown from (InGa)2Se3 precursors," Solar Energy Materials and Solar Cells, vol. 41/42, pp. 247-260, (1996).*

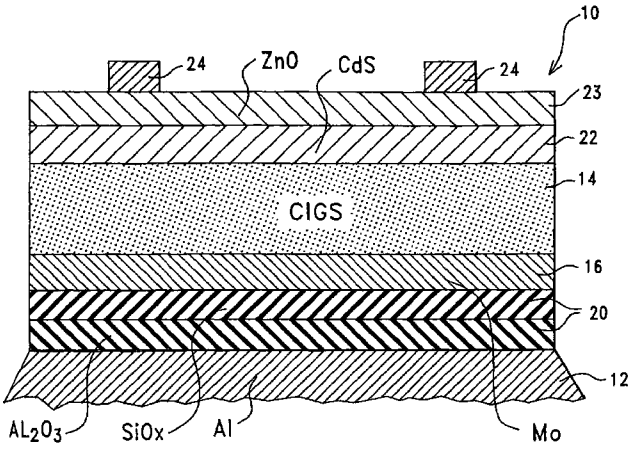
(Continued)

Primary Examiner—Alan Diamond
(74) *Attorney, Agent, or Firm*—Paul J. White

(57) **ABSTRACT**

A thin-film solar cell (**10**) is provided. The thin-film solar cell (**10**) comprises a flexible metallic substrate (**12**) having a first surface and a second surface. A back metal contact layer (**16**) is deposited on the first surface of the flexible metallic substrate (**12**). A semiconductor absorber layer (**14**) is deposited on the back metal contact. A photoactive film deposited on the semiconductor absorber layer (**14**) forms a heterojunction structure and a grid contact (**24**) deposited on the heterjunction structure. The flexible metal substrate (**12**) can be constructed of either aluminium or stainless steel. Furthermore, a method of constructing a solar cell is provided. The method comprises providing an aluminum substrate (**12**), depositing a semiconductor absorber layer (**14**) on the aluminum substrate (**12**), and insulating the aluminum substrate (**12**) from the semiconductor absorber layer (**14**) to inhibit reaction between the aluminum substrate (**12**) and the semiconductor absorber layer (**14**).

33 Claims, 3 Drawing Sheets



US007319190B2

(12) **United States Patent**
Tuttle

(10) **Patent No.: US 7,319,190 B2**
(45) **Date of Patent: Jan. 15, 2008**

(54) **THERMAL PROCESS FOR CREATION OF AN IN-SITU JUNCTION LAYER IN CIGS**

(75) Inventor: **John R. Tuttle**, Mechanicville, NY (US)

(73) Assignee: **Daystar Technologies, Inc.**, Halfmoon, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 81 days.

(21) Appl. No.: **11/272,386**

(22) Filed: **Nov. 10, 2005**

(65) **Prior Publication Data**

US 2006/0102230 A1 May 18, 2006

Related U.S. Application Data

(60) Provisional application No. 60/626,843, filed on Nov. 10, 2004.

(51) **Int. Cl.**
H01L 31/00 (2006.01)

(52) **U.S. Cl.** **136/264**; 136/262; 136/265

(58) **Field of Classification Search** 136/262, 136/264, 265

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,392,451	A	7/1983	Mickelsen et al.
4,576,830	A	3/1986	Kiss
4,663,829	A	5/1987	Hartman et al.
4,851,095	A	7/1989	Scobey
5,343,012	A	8/1994	Hardy
5,411,592	A	5/1995	Ovshinsky et al.
5,470,784	A	11/1995	Coleman
5,849,162	A	12/1998	Bartolomei
6,270,861	B1	8/2001	Mashburn
6,288,325	B1	9/2001	Jansen et al.
6,323,417	B1	11/2001	Gillespie et al.
6,554,950	B2	4/2003	van Mast
6,881,647	B2	4/2005	Stanbery
2004/0063320	A1	4/2004	Hollars
2005/0056863	A1	3/2005	Negami et al.

OTHER PUBLICATIONS

Tuttle, J.R. et al, "Investigations Into Alternative Substrate, Absorber, and Buffer Layer Processing for Cu(In,Ga)Se2-Based Solar Cells", 25th PVSC; May 13-17, 1996. pp. 797-800.*

Nakada, T. et al, "Superstrate-Type CuInSe2 Thin Fllm Solar Cells with Selenide Buffer Layers", 25th PVSC; May 13-17, 1996. pp. 893-896.*

Kampmann, A. et al, "A Cadmium-free CuInSe2 Superstrate Solar Cell Fabricated by Electrodeposition Using a ITO/In2Se3/CuInSe2/Au Structure", Prog. Photovolt: Res. Appl. 7, 129-135. (1999).*

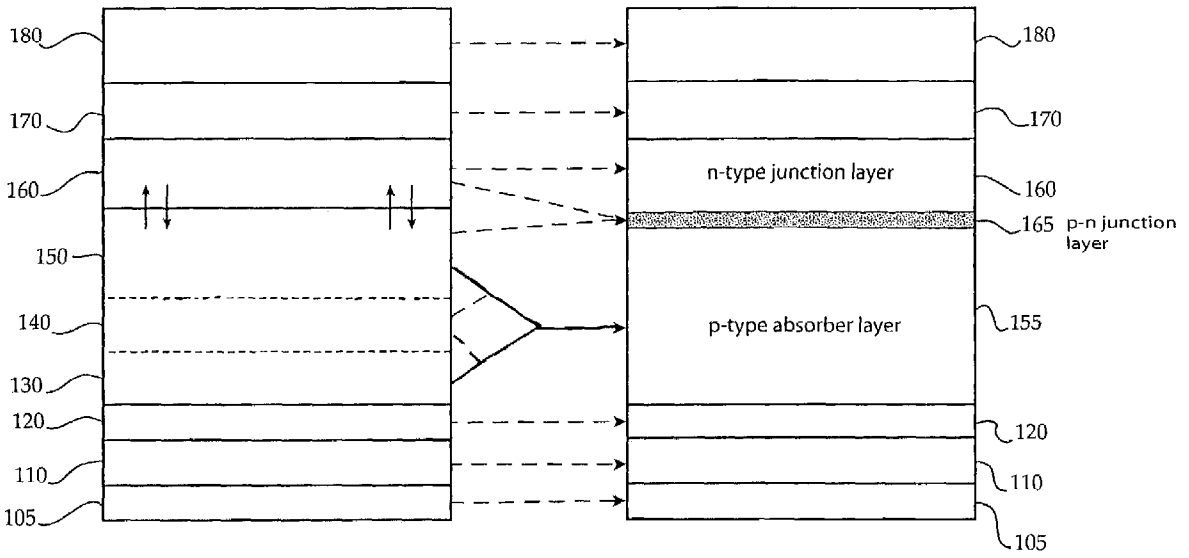
(Continued)

Primary Examiner—Nam Nguyen
Assistant Examiner—Jeffrey Barton
(74) *Attorney, Agent, or Firm*—Hiscock & Barclay, LLP.; Thomas R. FitzGerald, Esq.

(57) **ABSTRACT**

The present invention relates generally to the field of photovoltaics and more specifically to manufacturing thin-film solar cells using a thermal process. Specifically, a method is disclosed to manufacture a CIGS solar cell by an in-situ junction formation process.

10 Claims, 1 Drawing Sheet



US007576017B2

(12) **United States Patent**
Tuttle

(10) **Patent No.: US 7,576,017 B2**
(45) **Date of Patent: Aug. 18, 2009**

(54) **METHOD AND APPARATUS FOR FORMING A THIN-FILM SOLAR CELL USING A CONTINUOUS PROCESS**

(75) Inventor: **John R. Tuttle**, Mechanicville, NY (US)

(73) Assignee: **DayStar Technologies, Inc.**, Halfmoon, NY (US)

(*) Notice: Subject to any disclaimer, the term of this patent is extended or adjusted under 35 U.S.C. 154(b) by 251 days.

(21) Appl. No.: **11/271,583**

(22) Filed: **Nov. 10, 2005**

(65) **Prior Publication Data**

US 2006/0096537 A1 May 11, 2006

Related U.S. Application Data

(60) Provisional application No. 60/626,843, filed on Nov. 10, 2004.

(51) **Int. Cl.**
H01L 21/00 (2006.01)
C23C 16/00 (2006.01)

(52) **U.S. Cl.** ..... **438/800**; 118/719; 118/723 VE

(58) **Field of Classification Search** ..... 118/723 VE; 438/800

See application file for complete search history.

(56) **References Cited**

U.S. PATENT DOCUMENTS

4,392,451	A *	7/1983	Mickelsen et al.	118/690
4,576,830	A	3/1986	Kiss	
4,663,829	A	5/1987	Hartman et al.	
4,851,095	A	7/1989	Scobey	
5,258,075	A *	11/1993	Kurokawa	118/719
5,343,012	A	8/1994	Hardy	
5,366,554	A *	11/1994	Kanai et al.	118/719
5,411,592	A	5/1995	Ovshinsky et al.	
5,470,784	A	11/1995	Coleman	
5,474,611	A *	12/1995	Murayama et al.	118/723 VE
5,849,162	A	12/1998	Bartolomei	
6,270,861	B1	8/2001	Mashburn	
6,288,325	B1	9/2001	Jansen et al.	
6,323,417	B1	11/2001	Gillespie et al.	
6,554,950	B2	4/2003	van Mast	
6,881,647	B2	4/2005	Stanbery	
2004/0063320	A1	4/2004	Hollars	
2005/0056863	A1	3/2005	Negami et al.	

OTHER PUBLICATIONS

K. Ramanathan, F.S. Hasoon, S. Smith, D.L. Young and M.A. Contreras, P.K. Johnson, A.O. Pudov and J.R. Sites, "Surface Treatment of $CuInGaSe_2$ Thin Films and its Effect on the Photovoltaic Properties of Solar Cells", Presented at the 13th ICTMC, held Oct. 14-18, 2002.

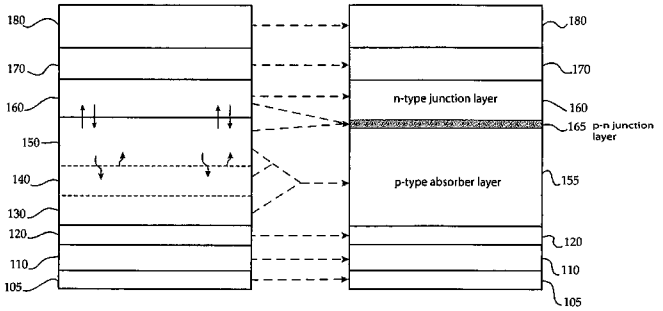
(Continued)

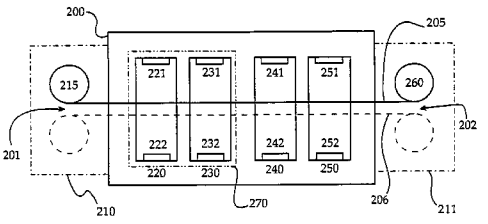
Primary Examiner—Lex Malsawma
(74) *Attorney, Agent, or Firm*—Hiscock & Barclay, LLP

(57) **ABSTRACT**

The present invention relates to new methods for manufacturing photovoltaic devices and an apparatus for practicing those methods of manufacture. The present invention employs a transfer-through system for advancing work piece substrates through an integrated apparatus of multiple treatment chambers that control each of the manufacturing processes.

44 Claims, 6 Drawing Sheets





Clean Energy Technologies:
A Potential Way Forward to Finance Disruptive Innovation

John R. Tuttle [1]*, Michael E. deSa [1,#a], Kristen Brown [1,#b], and Don Chambers [2]

ABSTRACT

Funding of early-stage clean-energy technologies exhibits exacting challenges resulting from capital intensity in a regulated industry. ARPA-E conducted a one-year research study with investors, innovators and intermediaries in which we categorize technologies as additive or disruptive and investors as real-money[3] or conventional. Conventional investors such as angels, private and corporate venture capital invest in additive technologies due to lower risk and clearer exits into existing supply chains. Real-Money Investors, which include philanthropic, sovereign wealth and other institutional capital, currently invest into disruptive hard technologies for duration and a potential hedge against exposure to incumbent energy infrastructure obsolescence. We propose a potential way to close the investment risk 'relay' gap that prevails among real-money investors, with an innovative financial mechanism that needs empirical validation and application to prove its efficacy. (129 words).

INTRODUCTION

The U.S. Department of Energy's Advanced Research Projects Agency – Energy (ARPA-E or the "Agency") funds high-risk, high-reward early-stage energy technology research with a focus towards (i) reducing energy imports, (ii) reducing energy-related emissions and greenhouse gases, and (iii) improving energy efficiency in all sectors of the U.S. economy.

ARPA-E is charged with overcoming the long-term and high-risk technological barriers in the development of energy technologies. ARPA-E has two primary funding modalities: 1) Focused programs targeting a specific technology or problem; and 2) OPEN solicitations that seek innovative solutions that address the Agency's broad mission. To date, efforts have resulted in the distribution of ~$1.5B in research funding to both corporate (small and large companies) and non-corporate (federal labs and academic institutions) entities developing technologies requiring significant development of "hard" technology

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* Corresponding Author: john.tuttle@hq.doe.gov, jtuttle59@mac.com

[3] *Capital from investors who have not borrowed.* http://www.financepractitioner.com/dictionary/real-money

("hardtech"). In fact, approximately 90% of projects clearly require hardware, biological systems, or materials advancements, all of which are fields well known to require high capital investment and long development cycles. The remaining 10% of programs support predominately software-based innovations in electrical grid controls, energy efficient mobility, and vehicle automation. Realizing the impact of these programs relies on continued engagement with ARPA-E personnel after awards are made around aggressively set technical milestones.

In addition to the technical guidance given to selected projects, a critical component of the funding structure is providing guidance on a strategy for growth after ARPA-E funding subsides. The Agency contains dedicated resources with the specific mandate of providing such guidance on how to transition energy innovations into a market to realize energy or emissions impact. Understandably, optimizing the growth strategy for each unique project requires a detailed understanding of the commercialization ecosystem, which engages entrepreneurs, small and large businesses, and the private capital community to identify appropriate partners for financing, manufacturing, and customer acquisition.

One challenge often highlighted as being exceptionally difficult for early-stage energy technologies requiring long development cycles and comprising substantial hardware risk is the acquisition of private capital. In an effort to deepen the understanding of challenges associated with financing early-stage technologies, and to highlight opportunities for innovation in financing, ARPA-E engaged in a multi-part research study. The elements of this research effort include: 1) a thorough literature review to ascertain the state-of-the-art of understanding of early stage technology development financing; 2) draft and release of a request for information (RFI) seeking input from Innovators and capital providers; 3) analysis of both written responses and follow-up oral interviews; 4) the utilization of the RFI data to design a workshop to explore the issues; and 5) convening of the workshop attended by 60+ innovators, capital providers, and various types of intermediaries, to present the data and explore future opportunities. Our study synthesized all stages of the qualitative and focus study with cross validation.

Here, we provide background for the work, summarize the research methodology and findings and conclude with a discussion on how this work supports the existing knowledge base, offers new observations and insights on present investment trends and suggests future areas of research and practical experimentation that could lead to enhanced financing of clean energy 'disruptive' technology and its commercialization.

BACKGROUND

Funding Challenges

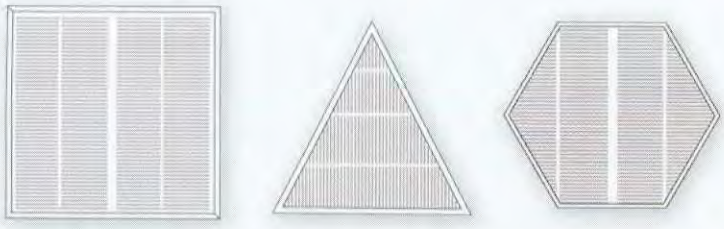
The process of moving a technology from invention through development to implementation has been of interest in a myriad of disciplines (Van de Ven 2013). The figure below, we provide two example illustrations of the sequential innovation process, beginning with ideation and ending with commercial success. The intermediate stages between initial conception and final commercialization range from three to five, and, in some cases, more (Branscomb & Auerswald 2002, Jenkins & Mansur 2011, Ford, Koutsky & Spiwak 2007, Zindler & Locklin 2010).

Solar Energy Cost Breakthrough Ahead?

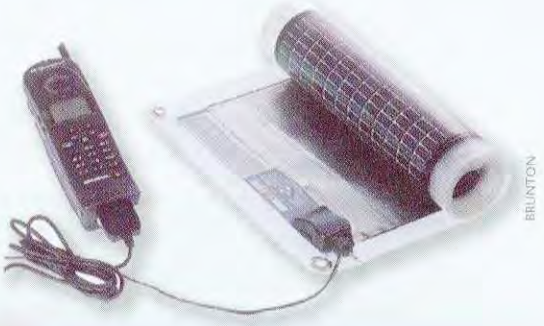
Photovoltaic Industry Pushes

One company looks to thin-film production efficiencies as the path to widespread adoption.

By John R. Tuttle, Ph.D.



Thin-film cell technologies are a promising alternative to break through the barriers related to silicon cell cost, scaling and feedstock. Thin-film technology used in consumer products enables them to be flexible, portable and lightweight. Below, from left, the Juice Bag daypack from Reluminati LLC, Power Shade field shelter from PowerFilm Solar, and the SolarRoll from Brunton.



BRUNTON

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POWERFILM SOLAR

Right, DayStar's solar cell manufacturing equipment is derived from commodity computer component industries.

To be Published in the Conference Proceedings of the
International Solar Energy Society 2005 Solar World Congress – Orlando, Fl – August 6-12, 2005

GIGAWATT-SCALE MANUFACTURING OF DISCRETE FLEXIBLE CIGS SOLAR CELLS AS A NEAR-TERM CATALYST FOR THE TRANSITIION TO A "SOLAR ECONOMY"

John R. Tuttle, Ph.D., Terence Schuyler
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ABSTRACT

Meeting the challenges of future worldwide electricity demand will eventually require a shift to the real-time use of today's most abundant source of energy – the Sun. Sustainability will likewise require the foundation of our economy to shift as well. A "solar economy" will only result from a technology approach that allows healthy near-term and sustainable return on investment (ROI) for the capital markets.

This contribution explores a unique approach to producing high-quality CIGS PV solar cells, with a low capital to capacity ratio that will enable high ROI gigawatt scale manufacturing. Through this pathway, the PV technology described herein could become the necessary catalyst towards the transition to a solar economy.

INTRODUCTION

Worldwide demand for energy is growing rapidly. One estimate is that this increase will be 75% by 2015, or 3 Terawatts (TW) of new generation capacity (1 TW = 10^{12} Watts). Other estimates say that to raise the standard of living of the developing world to that of the developed world (2-3 kW/person) will require 16-20 TW of new electricity generation. In either case, the world is heading toward an irreconcilable future where energy demand and the present form of energy supply irreversibly diverge.

Concerns about global environmental health and changing economies in the electricity market are encouraging a look at new energy technology choices. But, significant and sustainable change will only occur when those with the "power" to change (i.e. access to capital) conclude there are near-term opportunities in the solar market that justify their attention and risk of investment.

Our Sun (our "Day Star") is the "Sol" source from which all present forms of useable energy originates. Rather than the economic and environmental constraints posed by our present reliance on conventional fossil fuels – our "Ancient Sunlight" - we are obliged to develop an energy economy that exploits our most abundant source of real-time energy. Renewable solar energy generation technologies must transition from "alternative" status to that of a viable energy option. To achieve this transition requires a shift from a carbon-based economy (primarily Oil) to a Solar Economy. The timeframe, rate and magnitude of this shift will be fundamentally dependant on the perceived ROI that will result from making the change.

In order to achieve these goals, the PV industry must begin to focus efforts on material technologies, factory design, economics and financing methods that will enable a healthy ROI. When the investment community achieves healthy returns, further investment is stimulated, and an economic foundation is laid that will contribute to the GNP and resulting tax basis. This sets in motion a cycle of associated government subsidies that are supported by the investment community, benefit middle class job growth, and set in motion positive changes that affect global economic growth with minimal environmental impact.

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DESIGN CONSIDERATIONS AND IMPLEMENTATION OF VERY-LARGE SCALE MANUFACTURING OF CIGS SOLAR CELLS AND RELATED PRODUCTS

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ABSTRACT: Discrete CIGS solar cells on flexible metal substrates offer an alternative to wafer-Si based cells. The manufacture of this cell technology additionally offers capital cost, throughput and yield advantages over the manufacture of either wafer-Si or traditional monolithically integrated thin-film modules. Economies of scale and volume can be achieved with the implementation of gigawatt-scale manufacturing. Likewise, vertical integration within the production line to include In refinement, steel substrate finishing, source material synthesis and formation, as well as module packaging materials (either glass and Al or plastic) provide for optimization of cost and supply-chain issues.
Keywords: CIGS, Photovoltaic, Solar City, Solar Cell, Solar Panel, Learning Curve

1. INTRODUCTION

Electricity demand is predicted to grow at an annual rate of 2.3 - 3.4% in the coming decade, depending on assumptions made [1]. In one scenario, where every planetary citizen is provided access to 2 kW of electricity supply by the middle of the century (the U.S.A. is at 3 kW per capita), the peak demand for electrical power increases from 4 terawatt (1TW = 10^{12} W) to 18.4 TW (Table I). It is both unlikely and undesirable that the increase in demand will be fulfilled by traditional hydrocarbon energy resources.

Table I: Electrical demand estimates

	World Pop.	Per Capita Demand	Peak Demand[a]	Peak Demand[b]
2004	6.38 B	0.6 kW	4.0 TW	4.0 TW
2050	9.22 B	2.0 kW	11.4 TW	18.4 TW

[a] 2050 demand from pop. growth & per capita demand
[b] 2050 demand from IEA growth rate of 2.3%

Clean energy resources, such as wind and solar, have the opportunity to backfill the demand. Of all non-carbon based resources, solar is believed to be the only energy resource that can ubiquitously meet the "Terawatt Challenge" [2]. With a current annual global production capacity of approximately one gigawatt (1GW = 10^9 W), the photovoltaics (PV) industry requires substantial growth in order to effectively meet the challenge. Additionally, the cost of components throughout the PV system product chain must be significantly reduced to achieve improved cost-competitiveness.

Keshner and Arya [3] recently examined this issue and came to three primary conclusions:

1. $1.00 /watt at the system level is required to achieve cost-competitiveness with traditional power generation choices.
2. The $1.00/watt benchmark cannot be achieved with crystalline Si solar cell technologies.
3. Multi-GW factories producing thin-film PV modules is the enabling factor in achieving the $1.00/W cost benchmark.

This paper examines a specific roadmap for the achievement of 2.0 GW/yr production of $Cu(In,Ga)Se_2$ ("CIGS") solar cells and modules. In contrast to the aforementioned study, we consider the following:

1. The production of CIGS solar cells by a continuous in-line process at higher unit volumes (200 MW / machine) offers capital investment advantages relative to the manufacture of traditional monolithically integrated panels.
2. Flexible solar cells offer opportunities for non-rigid packaging that can lower implementation costs in the field. On-site Glass and aluminum sub-factories, considered a requirement to lower module costs, can be replaced with polymer, polymer composite, and steel finishing factories.
3. Control of the raw material supply chain, especially In, Ga and Se, and their synthesis and formation into source materials, such as sputtering targets, will be an important component in realizing full cost reductions.
4. Higher profit margins in the near-term resulting from system sales prices of $1-$3/W offer accelerated return-on-investment opportunities to justify the up-front capital investment required to achieve multi-GW scale manufacturing in multiple locations.

2 CIGS SOLAR CELLS AND MANUFACTURING

2.1 CIGS Solar Cell Technology

Solar cells based upon the CIGS p-type absorber have been under development for over 25 years. CIGS has proven to be both highly efficient, with laboratory performance approaching 20% [4], and highly reliable in the field, with lifetimes exceeding 18 years with little or no degradation. Unfortunately, there has not been substantial market penetration by this technology, in part

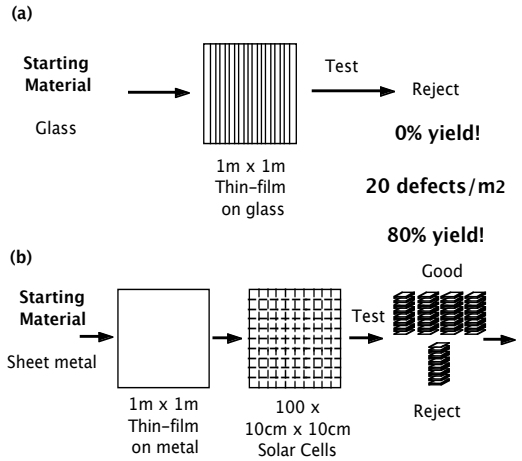

Figure 1: Illustration of (a) dis-economy of yield associated with monolithic integration of thin-film PV in contrast to (b) production of discrete solar cells.

A 15.2% AM0 / 1433 W/KG THIN-FILM CU(IN,GA)SE_2 SOLAR CELL FOR SPACE APPLICATIONS

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ABSTRACT

Thin-film CIGS solar cells have been investigated for use in the space environment. The study includes deposition on lightweight metal substrates, measurement under AM0 light, and irradiation by electrons and protons. A 15.2 % AMO cell performance has been achieved, resulting in a specific power of 1433 W/kg & 1235 W/kg for bare and SiOx "coverglass" cells, respectively. No degradation has been observed after e^- irradiation. A 24-cm^2 cell design has achieved 1100 W/kg specific power.

INTRODUCTION

Si and III-V photovoltaic (PV) technologies have dominated the satellite power market since its inception nearly 50 years ago. Multi-junction III-V cells have surpassed Si technologies in power density (W/m^2), specific power (W/kg), and relative degradation (End-of-life (EOL) η / beginning-of-life (BOL) η), but have lagged in cost ($/W) competitiveness. Generally, it is a variable combination of these factors that determine the cell material of choice for a particular satellite application.

As the number of government and commercial satellite constellations increase, and the satellite unit size decreases, there has emerged an increasing demand for PV cells and arrays with a lower cost-basis and lighter mass (also translating into lower cost). The only technologies with a promise to reduce costs by 50-90% are cells and arrays based upon thin-film PV technologies. At present, the selection includes amorphous Si and Cu(In,Ga)Se_2 (CIGS)-based PV cells and integrated panels. In this contribution, we present results from recent studies involving CIGS thin-film cells fabricated on ultra-lightweight metal substrates. Fabrication, cell testing, and manufacturing issues will be presented.

CELL DESIGN & FABRICATION

Cell Design

Thin-film PV was first developed as the next generation successor to wafer-Si technologies with the intention of breaking the $1/Wp cost barrier for terrestrial markets. Cost reduction is realized through material reduction and economies of scale and volume (EOSV). 1-10 μm thin-film solar cells represent a greater than 95% reduction in semiconductor material costs. EOSV for terrestrial products was to be realized through in-line cell fabrication processes (in contrast to batch processes for wafer-Si) and monolithic integration (a process of concurrent cell fabrication and series interconnection). These goals have been been difficult to achieve and have slowed the progress of commercialization of thin-film PV technologies.

The solar cell under investigation in this work is illustrated in Fig. 1. The primary difference between this cell design and a standard CIGS cell lies in the use of thin, flexible metal substrates (in contrast to rigid glass) and a proprietary buffer layer that contains Na. Present state-of-the-art performance for cells fabricated on soda-lime glass and 150-μm stainless steel (SS) is 18.8%[1] and 17.5%[2], respectively, both measured under AM1.5 simulated illumination.

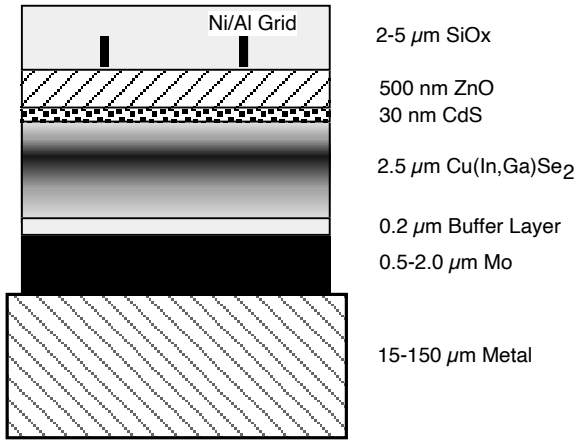

Fig. 1 Schematic of thin-film CIGS space solar cell

The use of a metallic substrate also deviates from the norm in that it does not support a monolithic integration scheme. Monolithic integration, on paper, provides for streamlined interconnection during the cell fabrication process. Unfortunately, this has not been realized in

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Special Issue

Perspective on High-efficiency Cu(In, Ga)Se_2-based Thin-film Solar Cells Fabricated by Simple, Scalable Processes

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We have fabricated high-efficiency Cu(In, Ga)Se_2(CIGS)-based photovoltaic (PV) devices by four different processes. Each process may be characterized as either sequential or concurrent deposition of the metals with or without an activity of selenium. A world-record, total-area efficiency of 17.1% has been achieved by the concurrent delivery of the metals in the presence of selenium. Gallium has been introduced into the device in such a manner as to produce homogeneous, normal profiling and double-profiling graded bandgap structures. This has resulted in an open-circuit voltage (V_{oc}) parameter of 680 mV and a fill factor of over 78%. A growth model has been developed allowing for simple translation of these processes to a manufacturing environment for the large-scale production of modules.

INTRODUCTION

The National Renewable Energy Laboratory (NREL), under contract to the United States Department of Energy, has been involved in the research and development of thin-film photovoltaics since 1982. The primary charter of the photovoltaics program is to develop new and better PV technologies and to support industry in doing the same. The goal is to introduce photovoltaics as a cost-effective alternative to conventional utility power generation. This goal is accomplished by an approach that first considers basic materials research, followed by solar cell development, and concludes with technology transfer to industrial organizations and market development.

To establish cost effectiveness in PV technology, both performance and cost are considered. Solar cells and modules fabricated from polycrystalline CIGS-based thin films are strong candidates for high performance and low cost.[1] Laboratory-scale device efficiencies in excess of 15% have been reported by several groups.[2–4] The low-cost criterion is satisfied for most thin-film technologies through low material usage, monolithic integration and low manufacturing costs, to name a few. Several industrial groups have produced large-area (sub) modules with a performance in excess of 7%.[5,6] One company has successfully produced a 10% module with an aperture area near 4000 cm^2.[4] In this work, laboratory-scale device absorbers are fabricated by physical vapor deposition (PVD) processes that may be conducive to industrial scale-up.[7,8] An additional advantage for the thin-film CIS technology developed at the NREL is the potential for high yield through greater-than-average process tolerances and self-limiting

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Structure, chemistry, and growth mechanisms of photovoltaic quality thin-film $Cu(In,Ga)Se_2$ grown from a mixed-phase precursor

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The formation chemistry and growth dynamics of thin-film $CuInSe_2$ grown by physical vapor deposition have been considered along the reaction path leading from the Cu_xSe:$CuInSe_2$ two-phase region to single-phase $CuInSe_2$. The $(Cu_2Se)_\beta(CuInSe_2)_{1-\beta}$ $(0<\beta\leq 1)$ mixed-phase precursor is created in a manner consistent with a liquid-phase assisted growth process. At substrate temperatures above 500 °C and in the presence of excess Se, the film structure is columnar through the film thickness with column diameters in the range of 2.0–5.0 μm. Films deposited on glass are described as highly oriented with nearly exclusive (112) crystalline orientation. $CuInSe_2$:Cu_xSe phase separation is identified and occurs primarily normal to the substrate plane at free surfaces. Single-phase $CuInSe_2$ is created by the conversion of the Cu_xSe into $CuInSe_2$ upon exposure to In and Se activity. Noninterrupted columnar growth continues at substrate temperatures above 500 °C. The addition of In in excess of that required for conversion produces an In-rich near-surface region with a $CuIn_3Se_5$ surface chemistry. A model is developed that describes the growth process. The model provides a vision for the production of thin-film $CuInSe_2$ in industrial scale systems. Photovoltaic devices incorporating Ga with total-area efficiencies of 14.4%–16.4% have been produced by this process and variations on this process. © *1995 American Institute of Physics.*

I. INTRODUCTION

Photovoltaic (PV) devices fabricated with a thin-film $Cu(In,Ga)(S,Se)_2$-based chalcopyrite absorber continue to advance towards economic viability with active-area conversion efficiencies exceeding 17%.[1,2] Critical developments include processing temperatures greater than 500 °C and the utilization of $CuIn_{1-x}Ga_xSe_2$ $(1.0\leq E_g\leq 1.7$ eV) and $CuIn(S_{1-y}Se_y)_2$ $(1.0\leq E_g\leq 1.5$ eV) alloys as absorbers to better match the absorber band gap to the AM1.5 solar spectrum. In this report we focus on the common basis of these quaternary alloy systems, thin-film $CuInSe_2$. It is the formation chemistry within the Cu:In:Se system and the resulting properties of the binary and ternary products[3–5] that govern the performance of the alloys within the compositional range of interest. In most cases, the results presented here for the ternary $CuInSe_2$ system apply equally well to the quaternary $Cu(In,Ga)Se_2$ system. Fundamental studies of the ternary $CuGaSe_2$ and the quaternary $Cu(In,Ga)Se_2$ material systems can be found elsewhere in the literature.[6–9]

To date, the absorbers for the high-efficiency devices are fabricated by either physical vapor deposition (PVD) of the constituent elements,[10–13] or by the selenization of the metal precursors. PVD is a viable technology for the fabrication of $CuInSe_2$-based absorbers and modules and is utilized as a prototyping tool for the development of novel fabrication processes.[1] Several industrial participants[14,15] have developed the selenization process for large-area PV module production. Successful introduction of a profitable product, however, has been hindered by a compound formation chemistry that encourages spatial nonuniformities and poor adhesion to the underlying Mo back contact.

Previously, we briefly reported on a novel two-stage PVD process for the fabrication of high-quality ternary and quaternary thin films.[5] The process relies on the superior film morphology of a very Cu-rich Cu:In:Se mixture, or Cu_xSe binary, with a simple reaction chemistry for the subsequent formation of the single-phase ternary product. The resulting polycrystalline aggregate exhibits larger grains and higher preferred orientation relative to other processes. This structure is defined by non-interrupted columnar grains with lateral dimensions of 2–10 μm. This structure allows for continuous carrier transport between the interface and the back contact, and minimizes deleterious grain-boundary effects. A growth model incorporating the formation chemistry was described, and we argued for its universal application to other PVD and non-PVD absorber fabrication processes. The process has been successfully applied to both the $CuInSe_2$ and $CuGaSe_2$ ternary and combined quaternary alloy systems. $Cu(In,Ga)Se_2$ thin-film devices fabricated by this process have total-area efficiencies in excess of 14%. In this paper, we focus on presenting the supporting evidence and expanding on the details of the growth model and formation chemistry. Elsewhere in the literature,[1,10] we report on two other PVD processes that, in part or whole, invoke this formation chemistry and have produced total-area PV device efficiencies of 16.4% and 15.1%, respectively.

Supporting data include structural characterization by x-ray diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) and diffraction (TED) that identify $CuInSe_2$:Cu_2Se phase segregation and anomalous CuPt ordering[16] of the $CuInSe_2$ lattice. XRD indicates a qualitative relationship between grain size, preferred orientation, and Cu content. A liquid-phase-assisted growth mechanism involving the Cu_xSe binary is suggested as the primary factor influencing the observed phenomena. Bulk and surface film compositions ranging from $CuInSe_2$ to In_2Se_3 are observed by XRD and x-ray photoelectron spectroscopy

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Thin-film $Cu(In,Ga)Se_2$ materials and devices: A versatile material for flat-plate and concentrator photovoltaic applications

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ABSTRACT

Thin-film $Cu(In,Ga)Se_2$(CIGS) is used as the absorber in an all-thin-film solar cell for both conventional 1-sun and concentrator applications. The absorber fabrication process is represented by time-dependent profiles of elemental Cu, In, Ga, and Se fluxes. The Cu/(In+Ga) ratio determines the phase chemistry during growth whereas the Ga/(Ga+In) ratio determines the CIGS band gap profile. All film-growth processes enter the CIGS:Cu_xSe two-phase field where the Cu_xSe facilitates large grain growth. Characterization of cells under 1-sun illumination reveals world-record total-area performance of 17.1%. Improvements relative to previous cells are linked to decreased inter-diffusion of In and Ga within the absorber. Cell parameters include an open-circuit voltage (V_{oc}) of 654 mV and short-circuit current (J_{sc}) of 33.9 mA/cm^2. A second cell was fabricated for operation under concentration. The 1-sun, direct-spectrum measurement yielded a 15.1%-efficient cell. Under 5- and 22-sun concentration, the cell improved to 16.5% and 17.2%, respectively. This achievement is significant in that it proves a compatibility of polycrystalline thin-film and concentrator technologies. Further optimization could yield 1-sun performance in excess of 18% and concentrator performance in excess of 20%. A path to this goal is outlined.

Keywords: Thin films, Photovoltaics, Copper Indium Gallium Selenide, Concentrator Cell, Process Modeling

1. INTRODUCTION

Photovoltaics (PV) is a critical power generation technology for applications ranging from third-world and domestic rural electrification (near-term) to peak-power generation (mid-term). The key element to the implementation of PV lies in developing devices and modules with crystalline-level performance at thin-film costs. This is rapidly becoming the case for thin-film CIGS-based PV technology. Thin-film CIGS solar cells are presently being investigated worldwide by industrial, academic, and institutional facilities. Laboratory-scale device efficiencies in excess of 15% have been reported by several groups.[1-3] In this contribution, we are pleased to report on significant progress that includes world-record device performance of 17.1% total-area (18.0% active-area) conversion efficiency for conventional flat-plate 1-sun applications and 17.2% conversion efficiency for device operation under 22-sun concentration.

The National Renewable Energy Laboratory's (NREL) PV Program is chartered to develop state-of-the-art laboratory-scale processes and transfer the technology to industry for scale-up. For manufacturing, the configuration of choice is that of a flat-plate module with monolithic interconnection of series-connected cells. This module integration approach allows for large-area deposition on inexpensive glass substrates, with an interconnect scheme that minimizes area loss and is not labor intensive. Several industrial groups have produced large-area (sub)modules with performance in excess of 7%.[4,5] One company has successfully produced a 10% module with an aperture area near 4000 cm^2.[3] In this work, laboratory-scale device absorbers are fabricated by physical vapor deposition (PVD) processes that may be conducive to industrial scale-up.[6,7] The absorber processing techniques are described in terms of source material delivery, compound formation, recrystallization, and surface termination.[6,8] The cells are characterized under standard AM1.5 illumination.

Alternatively, concentrator module geometries offer advantages due to savings in cell manufacturing costs per unit of power produced. Historically, concentrator studies have focused on high-efficiency crystalline III-V and Si-based [9,10] devices as the cell component. As the performance of thin-film CIGS solar cells approaches the 20% level, however, the differentiation arguments begin to break down. Previous modeling work [9] predicted that 1.14 eV is the optimum direct band gap for operation under a wide range of concentration levels and temperatures. This, conveniently, is the band gap of the CIGS absorbers that have produced record device efficiencies. In this work, we describe the fabrication of thin-film CIGS solar cells for operation under concentration. In general, the device design and fabrication are identical to that used for 1-sun operation, except for the front-contact grid pattern. Finished cells are characterized under the direct spectrum at various levels of concentration. The results shed important light on the robust nature of this particular thin-film solar cell system.

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