STATUS OF ELECTROPLATING BASED CIGS TECHNOLOGY DEVELOPMENT

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ABSTRACT

CIGS is the leading thin film PV material in terms of it capability to yield high efficiency solar cells. Co-evaporation method already yielded solar cells with close to 20% efficiency. Despite this success, however, commercialization of CIGS has not been aggressive. One reason for this is the fact that CIGS is a complex material. The other reason is the difficulty of scaling up this technology while keeping the cost structure competitive. SoloPower has developed a low cost electrodeposition-based CIGS technology for large scale roll-to-roll manufacturing. The substrate is a flexible metallic foil. CIGS absorber layers are formed through annealing and thermal activation of electrodeposited precursor layers. Top and bottom contacts are formed by roll-to-roll sputtering approaches. The technique has excellent ability to control the composition of the deposited layers over large are substrates. After forming a roll of solar cells, devices are cut and then packaged in module structures. Flexible solar cells with an area of over 100 cm^2 were fabricated with over 12% efficiency. Over 1 m^2 area modules with an efficiency of 10% were also fabricated.

INTRODUCTION

CIGS is a leading thin film PV material that demonstrated small area solar cell efficiencies close to 20% [1]. Despite this success however, commercialization of CIGS technologies has been slow. This is partly due to the complex nature of this quaternary material and partly due to the difficulties inherent in scaling up the expensive vacuum-based CIGS deposition approaches that were adapted in early 90's during the research and development phase of this material system. Therefore, there is a drive to identify lower cost processing methods for CIGS film growth with the ability to yield high efficiency solar cells at high yield.

Electrodeposition is a low cost method that has been explored for CIS and CIGS film formation since early 1980's. Some electrodeposition approaches concentrated on the deposition of the compound or a mixture of various Cu, In, Ga and Se phases from a single electrolyte [2], [3], [4]. The deposited films were then often subjected to a high temperature reaction/crystallization step to improve their photovoltaic properties. In other approaches, various constituents of the compound were first electrodeposited on a substrate in the form of a precursor film and then the precursor film was reacted and homogenized through high temperature processing forming the CIS or CIGS compound layer. These two-stage techniques included approaches such as; electrodeposition of thin Cu and In layers forming a Cu/In precursor stack and reaction of the metallic stack with gaseous Se species to form the compound [5], electrodeposition of a Cu/In/Se stack on a substrate and rapid thermal annealing of the stack to form CIS [6], electrodeposition of In-Ga [7], Cu-Ga [8] or Cu-In-Ga [9] metal alloys to form precursor layers and reaction of these precursor layers with Se to form the compound, and electrodeposition of In-Se and Cu-Se on a substrate forming a stacked precursor such as a Cu/In-Se/Cu-Se structure and annealing of the structure to form CIS [10]. We recently reported on a novel electroplating bath with the capability to deposit In-Se as well as Ga-Se layers that can be used for the preparation of Ga containing precursors and CIGS layers [11]. It should be noted that most of the above mentioned studies were aimed at growing CIS layers rather than CIGS films. This is partly due to the fact that addition of Ga into electrodeposited films is challenging because of the high negative plating potential of Ga compared to Cu, In and Se. Such high plating potential gives rise to excessive hydrogen evolution on the cathode surface during plating of the films out of aqueous electrolytes. Hydrogen evolution reduces the plating efficiency of Ga and causes defects such as pinholes in the grown layers since the small gas bubbles stick to the surface of the growing film and prevent proper deposition at that location. Reduced plating efficiency also results in poor control of the Ga content of the plated layers.

As the review above demonstrates electrodeposition is a versatile technique with the ability to yield thin films of metals, metal alloys, mixtures and compounds, which may be used for the preparation of precursor layers of various structures and chemical content. These precursor layers may then be converted into CIS or CIGS absorbers through thermal processing. However, development of specialized electrolytes with long term stability and ability to control the crucially important Cu/(In+Ga) and Ga/(Ga+In) molar ratios are of utmost importance for the successful application of electrochemistry to CIGS film growth. We recently

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reported on an electrodeposition based CIGS technology that yielded close to 14% efficient small area cells and over 11% efficient devices with over 100 cm^2 area [12]. Modules with an area of about 1 m^2 and an efficiency of about 9% were also demonstrated. This paper will summarize the present status of the electrodeposition based CIGS technology at SoloPower.

EXPERIMENTAL

CIGS layer growth

CIGS layers were formed over 50μm thick flexible stainless steel foil substrates which were in the form of 150-500 meter long rolls. The width of the foil substrates was 0.34 meters. After cleaning, the rolls were coated with a Mo-based contact layer using a roll-to-roll sputtering tool. The rolls were then transferred to the electrodeposition station where a Cu-In-Ga-Se precursor film containing the preselected composition was electrodeposited on the contact layer in a roll-to-roll electroplating machine. The precursor layers were then subjected to an RTP-type annealing/crystallization process step which converted them into device quality CIGS layers. The typical temperature range employed in this process step was 500-550 °C, although CIGS film formation could be achieved in a wider temperature range of 450-600 °C. The thickness of the CIGS layers was in the range of 1-2 μm, typically in the range of 1.1-1.3 μm.

Compositional analysis of the precursor layers and the CIGS films was carried out by XRF measurements. Results were also confirmed by inductively coupled plasma (ICP) analysis after cutting coupons from various regions of the processed rolls and then chemically dissolving these coupons to prepare ICP samples.

Solar cell fabrication

A typically 100 nm thick CdS buffer layer was deposited on the CIGS absorber by the chemical bath deposition (CBD) approach using a roll-to-roll deposition system. An intrinsic-ZnO/conductive-TCO stack was then sputter deposited over the buffer layer using a roll-to-roll sputtering tool. The sheet resistance value of the TCO layer was in the range of 40-60 Ω/□ and the transmission within the visible range of the spectrum was over 90%.

The roll of the solar cell stack obtained after the TCO sputtering step was coated with a large number of silver- based finger patterns using a roll-to-roll screen printing tool, which employed a low temperature ink that can be cured at below 250 ºC. As a result of this process step, a roll containing thousands of solar cells was obtained. Figure 1 shows the re-wind port of the finger deposition tool where the web with solar cells and a paper interleaf are being wrapped around the re-wind spool.

Module fabrication and testing

Grid patterns deposited on the roll of solar cell structure define the shape and the size of the devices that are later cut from the roll. We used three different finger patterns and three different cell sizes (nominal areas of 100 cm^2, 120 cm^2 and 180 cm^2) in our development efforts. An automated roll-to-roll cutter was utilized to cut the cells from the rolls based on the pre-selected sizes of the devices. Cut cells were sorted and binned according to their current and efficiency values using an automated testing/sorting tool. Sorted and binned flexible cells were then interconnected using standard copper ribbons to form cell strings. The stringing method used low temperature solders or conductive adhesives that cured at temperatures below 250 ºC. Modules with front glass sheets were fabricated in a standard vacuum lamination machine. The back sheet was either a flexible polymeric foil or a glass sheet. I-V characteristics of the cells and modules were measured at SoloPower and NREL under standard AM1.5 conditions.

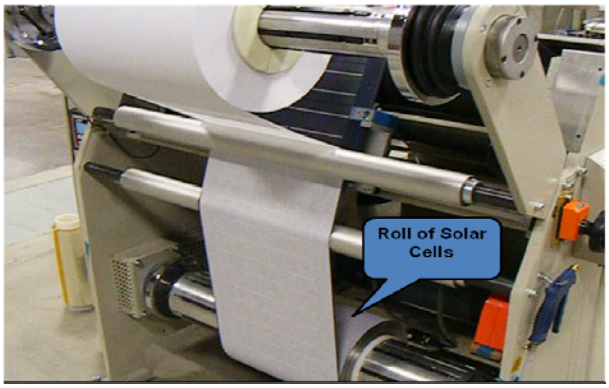

Fig. 1. The last step of the solar cell fabrication process flow is the grid pattern application which forms a roll of solar cells at the re-wind port of the roll-to-roll screen printing tool.

RESULTS AND DISCUSSION

One of the important prerequisites for successful application of an electrodeposition technique to CIGS absorber film formation is the demonstration of composition control in a reliable and repeatable manner. Figures 2 and 3 show the results of an experiment carried out to demonstrate such ability for SoloPower's roll-to-roll electrodeposition process. In this experiment a 240 meters long roll was processed through the roll-to-roll electrodeposition tool and the targeted Cu/(In+Ga) ratio was changed in the middle of the roll, during processing, while keeping the Ga/(In+Ga) ratio constant. The change was accomplished through the controls available in the plating process. As can be seen from Figure 2 the measured Cu/(In+Ga) molar ratio responded very fast (within a few meters) to the change made in the process parameters after running the first

120 meters of the web under the first process condition (condition 1). Furthermore, after switching to the new condition, the process kept the new Cu/(In+Ga) molar ratio (condition 2) very stable until the end of the roll.

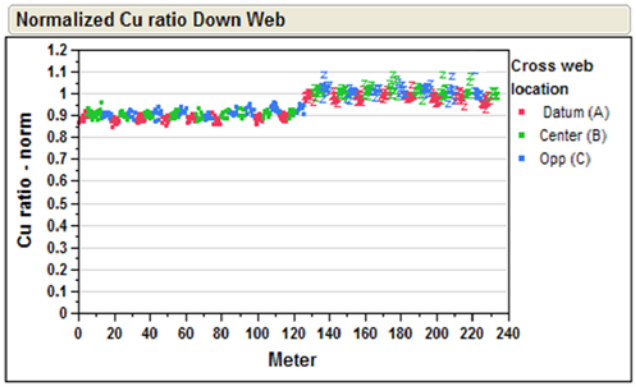

Fig. 2. The Cu/(In+Ga) molar ratio measured on an electrodeposited precursor layer formed on a 240 meters long 0.33 meters wide web. Process parameters were changed to increase the ratio after running the first 120 meter portion of the web.

Figure 3 shows the measured Ga/(In+Ga) molar ratio for the same web. As can be seen from this data the Ga composition is stable throughout the 240 meters of the web as dictated by the process parameters of the roll-to-roll electrodeposition tool. These results demonstrate the ability of the technique to independently adjust and control the two important metals ratios in CIGS processing. It should be noted that the cross web uniformity of the two ratios were also demonstrated in the above data which shows measurements from the center of the web (labeled as Center-green) as well as the two sections along the two edges of the web (labeled as Datum-red and Opp-blue).

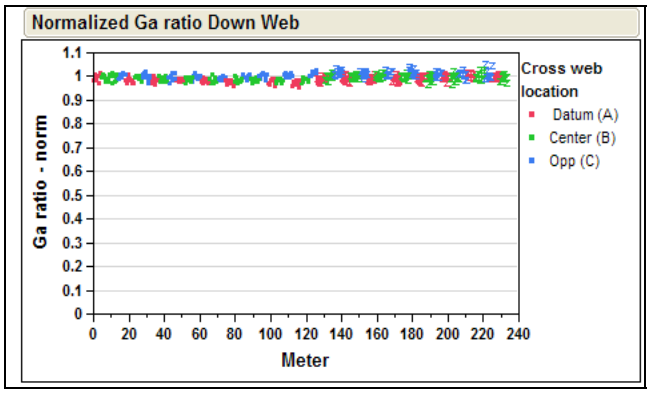

Fig. 3. The Ga/(In+Ga) molar ratio data collected from the web of Figure 2.

The CIGS layers grown from the electrodeposited precursor layers were of good crystalline quality and displayed a preferred <112> orientation. The grain size was found to be a strong function of the Ga content of the film as well as the details of the crystallization process step.

Dependence of the solar cell efficiencies on the Cu/(In+Ga) and Ga/(In+Ga) metal ratios of the precursor layers and the distribution of the efficiency values along and across the long flexible substrates were also studied. Data in Figure 4 shows the relative efficiency distribution of nominally 180 cm^2 area solar cells made on the experimental roll of Figures 2 and 3. It should be noted that about 60 meters long sections from the beginning and the end of this roll were cut to carry out other experiments. The rest of the roll was then taken through the complete process flow to finish the devices. Therefore the data of Figure 4 was collected from only the middle 110 meters long section of the roll.

As can be seen from the data of Figure 4 the solar cell efficiencies obtained from the section of the web run under “condition 1” in the electroplating tool (see Figure 2) are 50-80% of the values obtained from the section of the web run under “condition 2”. Furthermore, the amount of the cross-web scatter in the device efficiency values from the portion processed under “condition 1”, which corresponds to a lower than ideal Cu/(In+Ga) ratio, is much larger than the scatter in the region of the roll that was processed under “condition 2”. The data of Figure 4 demonstrates the importance of compositional control for device efficiency and the ability of the electrodeposition method to yield solar cells with consistent conversion efficiency once the composition is fixed within the established process window. Work is now in progress to further tighten the efficiency distribution of the over 9% efficient solar cells processed within the experimentally determined process window.

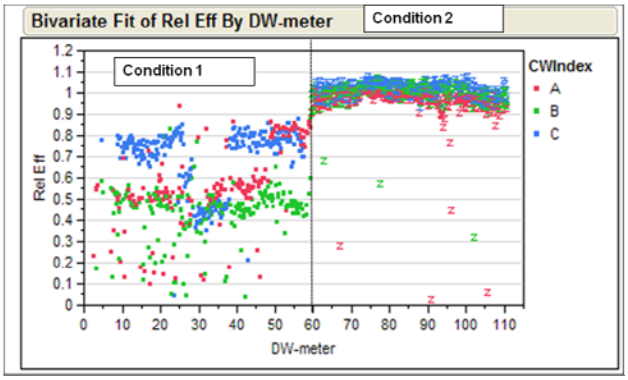

Fig. 4. Relative distribution of the efficiencies of nominally 180 cm^2 area solar cells fabricated along and across a 110 meters long section of the web cut from the middle portion of the 240 meters long web of Figures 2 and 3.

The illuminated I-V characteristics of a 102 cm^2 area solar cell measured at NREL is shown in Figure 5.

The total area efficiency of this device is 12.25%. The V_{oc}, J_{sc} and FF values are 0.54 V, 34.4 mA/cm^2 and 65.7 %, respectively. This efficiency value corresponds to an active area efficiency of about 13.5%.

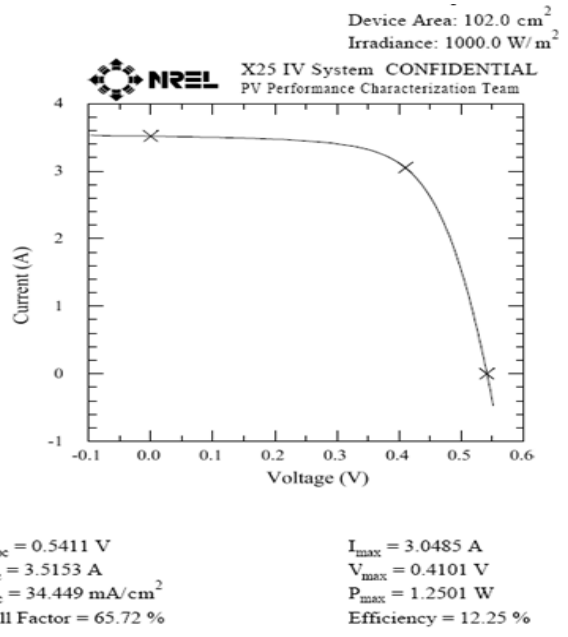

Fig. 5. Illuminated I-V characteristics of a 102 cm^2 area flexible CIGS solar cell with 12.25% efficiency.

Figure 6 shows the illuminated I-V characteristics of a module fabricated by bussing and packaging ten cell strings. Each string contained ten interconnected

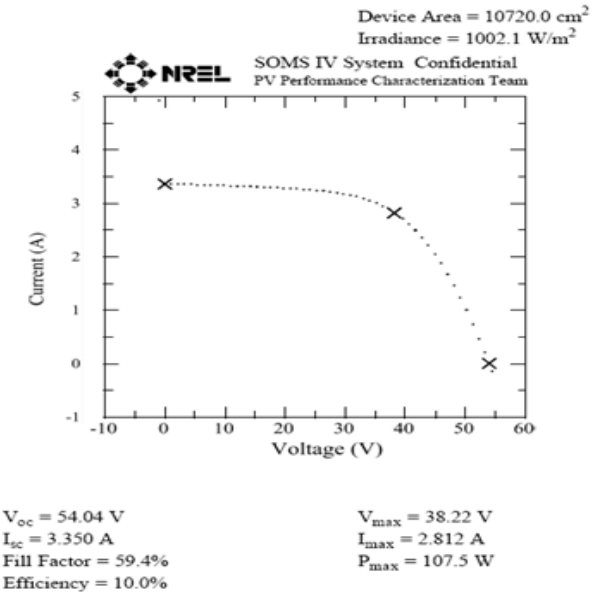

Fig. 6. The illuminated I-V characteristics of a 1.07 m^2 area module with 10% conversion efficiency.

cells. The total aperture area of the module is 1.07 m^2. After lamination and framing, the module was sent to NREL for measurement. As can be seen from the data of Figure 6, the total power output was measured to be 107.5 W with V_m, I_m and efficiency values of about 38.2 V, 2.8 A and 10%, respectively.

Reliability studies

CIGS device structure is known to be sensitive to moisture at elevated temperatures. Therefore, it is essential that the module structure provide hermetic sealing to the solar cells packaged within it. In absence of moisture the device is stable as exemplified by the data of Figure 7, which shows the results of a stability test carried out on a group of five solar cells. The devices were unprotected and were kept in an air oven at 85 ºC for 1000 hours. As can be seen from the data, the device structure is very stable under these dry conditions. When similar experiments were repeated under 85% relative humidity conditions, the unprotected cell efficiencies went down in an irreversible manner.

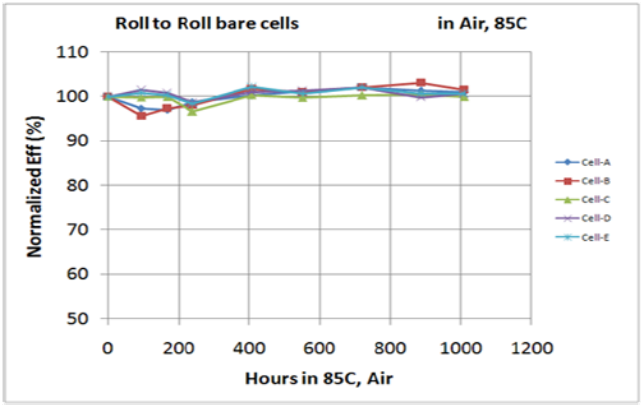

Fig. 7. Normalized efficiencies of five different cells annealed at 85 ºC for 1000 hrs demonstrating the stability of the CIGS cells under dry heat conditions.

Studies carried out to identify the component(s) of the solar cell most affected by the damp heat conditions included testing of each of the components individually under damp heat conditions. These components included the substrate/CIGS/CdS structure, the TCO layer, the TCO/grid interface, and the front and back contacts made to the solar cell. Figure 8 shows the results of a study carried out on the back contact quality and reliability. The study compared four different contacting processes, some using different contacting materials. After measuring the initial contact resistance, the samples were subjected to damp heat conditions (85 ºC/85% RH) in an environmental chamber for a period of 456 hours without any protection. Variation in the contact resistance values was monitored at intervals. As can be seen from this data, the back contact resistance values for “process-2” and “process-4” are much lower than “process-1” and they are

relatively stable under damp heat conditions. In the case of “process-3”, although the starting contact resistance is low, it gets deteriorated fast through the 456 hours of testing. These results demonstrate the importance of carrying out highly accelerated damp heat tests on each component of the CIGS solar cell structure to evaluate its sensitivity to damp heat so that the stability of these components may be optimized yielding a more robust and moisture resistant solar cell.

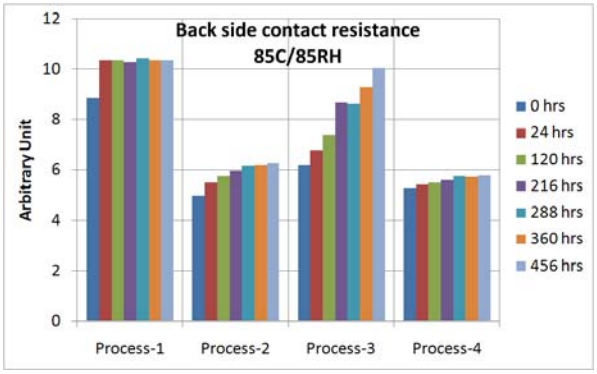

Fig. 8. Variation of the back contact resistance of flexible CIGS solar cells as the cells are aged unprotected in a damp heat environment. Four different types of contacting approaches were evaluated.

The above mentioned sensitivity of the CIGS cell structure to moisture is the primary reason for the failure of modules which are not properly sealed. Figure 9 exemplifies the evolution of the module packaging activity at SoloPower through evaluation of various packaging materials and procedures to attain stable operation for modules under damp heat conditions.

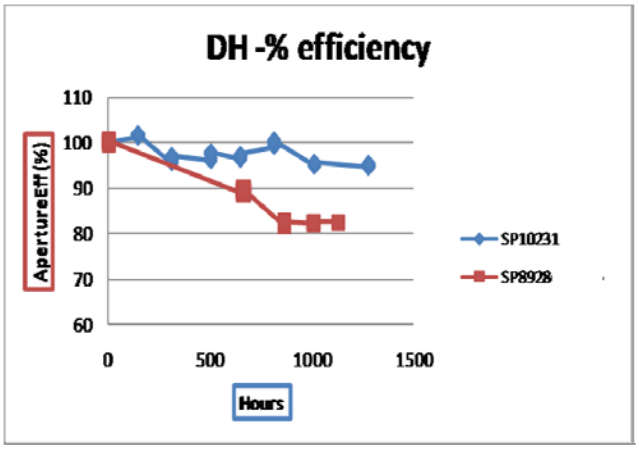

Fig. 9. Efficiency data collected from two modules tested in an environmental chamber under damp heat conditions. Packaging of module SP8928 was defective allowing the water vapor to enter the package.

Figure 9 displays two sets of efficiency stability data obtained from two modules that were subjected to 1200-1300 hrs of testing in an environmental chamber kept at 85 ºC and 85% relative humidity. One data set belongs to module SP8928, which was packaged in a glass/film structure using materials and procedures that we identify as “rev-3”. The other data set belongs to the module SP10231, which was fabricated using “rev-4” materials and procedures. As can be seen from this data the stabilities of the two modules are drastically different under damp heat conditions. The post-mortem analysis of the module SP8928 clearly demonstrated that the culprit for its failure was moisture digression into the module through the junction box location on the back sheet of the module. Figure 10 shows a picture of that location taken through the front glass sheet. As can be seen from this photo, moisture entering through the back sheet and the junction box discolored the sections (circled) of the solar cells across from the junction box.

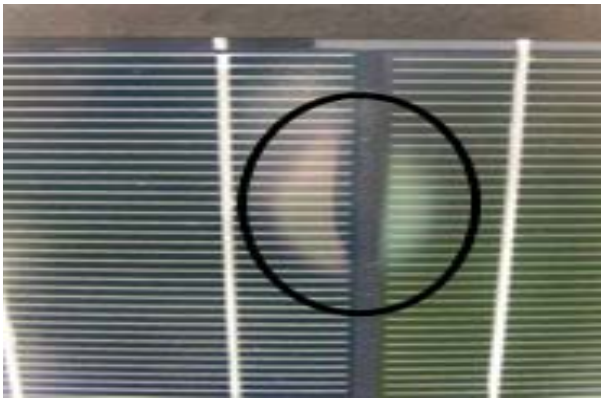

Fig. 10. Photograph of the section of module SP8928 (see Fig. 9) discolored (circled) due to moisture digression into the structure through the junction box.

In-house module structure reliability studies included passing groups of modules through the IEC61730 / IEC61646 / UL1703 test sequences which include dry and wet hi-pot tests, temperature cycling, damp heat testing, humidity freeze and UV exposure tests. In addition to the in-house reliability studies SoloPower recently established a roof-top laboratory (see Figure 11) to collect performance data from individual modules as well as from a string of modules tied to a 3 kW inverter. The lab is complete with a weather station, collecting data on variables such as ambient temperature, irradiance, wind speed/direction, relative humidity and precipitation. Individual modules are also being tested for shading effects, dirt accumulation effects, temperature effects and light soaking effects. Once enough data is collected valuable information about system yield, system performance ratio and performance indexes will be determined.

Fig. 11. A view of SoloPower's roof-top testing facility with CIGS modules manufactured by SoloPower's electrodeposition based technology.

CONCLUSIONS

A roll-to-roll electrodeposition based CIGS technology was developed. The electrodeposition step of the process has the capability to control the Cu/(In+Ga) and Ga/(In+Ga) metal ratios reliably. CIGS layers are formed through RTP of the electrodeposited precursors. Solar cells are fabricated in a roll and then cut and sorted for module manufacturing. Large area solar cell efficiencies of over 12% were demonstrated using the technology. 10% efficient modules with nominally 1 m^2 area were also fabricated. Reliability studies showed that the cells needed to be packaged in hermetically sealed module structures for long term stability under damp heat conditions. A roof-top testing facility with an array of modules was established to collect outdoors performance data.

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REFERENCES

[1] I. Repins, M. Contreras, B. Egaas, C. DeHart, J. Scharf, C. Perkins, B. To and R. Noufi, "19.9% efficient ZnO/CdS/CIGS solar cell with 81.2% fill factor", *Progress in Photovoltaics: Research and Applications* **16**, 2008, p. 235.

[2] R. Bhattacharya, "Solution grown and electrodeposited CIS thin films", *J. Electrochem. Soc.* **130**, 1983, p. 2040.

[3] R. Bhattacharya, W. Batchelor, J. Granata, F. Hasoon, H. Wiesner, K. Ramanathan, J. Keane and R. Nouifi, "CIGS based photovoltaic cells from electrodeposited and chemical bath deposited precursors", *Solar Energy Materials and Solar Cells* **55**, 1998, p. 83.

[4] D. Guimard et al., "Efficient CIGS based solar cells prepared by electrodeposition", *MRS Sym. Proc. vol.763,* 2003, p. B6.9.1.

[5] V. Kapur, B. Basol and E. Tseng, "Low cost methods for the production of semiconductor films for CIS/CdS solar cells", *Solar Cells* **21**, 1987, p. 65.

[6] H. Fritz and P. Chatziagorastou, "A new electrochemical method for selenization of stacked CuIn layers and preparation of CIS by thermal annealing", *Thin Solid Films* **247,** 1994, p. 129.

[7] J. Zank, M. Mehlin and H. Fritz, "Electrochemical co-deposition of indium and gallium for chalcopyrite solar cells", *Thin Solid Films* **286**, 1996, p. 259.

[8] R. Friedfeld, R. Raffaelle and J. Mantovani, "Electrodeposition of CIGS thin films", *Solar Energy Materials and Solar Cells* **31**, 1999, p. 163.

[9] M. Ganchev, J. Kois, M. Kaelin, S. Bereznev, E. Tzvetkova, O. Volobujeva, N. Stratieva and A. Tiwari, "Preparation of CIGS layers by selenization of electrodeposited Cu-In-Ga precursors", *Thin Solid Films* **511-512**, 2006, p. 325.

[10] A. Fernandez, M. Calixto, P. Sebastian, S. Gamboa, A. Hermann and R. Noufi, "Electrodeposited and selenized CIS thin films for photovoltaic applications", *Solar Energy Materials and Solar Cells* **52**, 1998, p. 423.

[11] S. Aksu, J. Wang and B. Basol, "Electrodeposition of In-Se and Ga-Se thin films for preparation of CIGS solar cells", *Electrochemical and Solid-State Lett.* **12**, 2009, p. D33.

[12] B. Basol, M. Pinarbasi, S. Aksu, J. Wang, Y. Matus, T. Johnson, Y. Han, M. Narasimhan and B. Metin, "Electroplating based CIGS technology for roll-to-roll manufacturing", *Proc. 23rd European PVSEC*, 2008, p. 2137.