The Next Frontier: Electrodeposition for Solar Cell Fabrication

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The world's predicted energy demand will reach 28 Terawatt (TW) by 2050.[1] Meanwhile the earth receives about 10,000 times more energy from the Sun than the global energy consumption.[2] In order to meet a sizeable part of the world's demand solar energy conversion will have to reach TW size.

Over 80% of the solar market is dominated by technology based on silicon[3] partially due to the maturity of the silicon industry. Silicon is an indirect gap semiconductor and requires silicon wafers thicker than 200 microns to work well as a solar cell.

On the other hand, thin film technologies such as CdTe and $CuInGaSe_2$ (CIGS) use direct band gap compound semiconductors.[4] Despite the fact that these materials are used as thin films with thickness varying between 1-3 microns, there may be significant limitations in materials availability and higher cost at TW scale.[5,6] An Earth-abundant and environmentally friendlier version than $CuInGaSe_2$ is Cu_2SnZnS_4 (CZTS) where indium is substituted by tin, gallium by zinc, and selenium by sulfur. CZTS is also a direct band gap semiconductor with band gap reported values between 1.45-1.6 eV.[7-9]

To put things in perspective regarding the status and the potential of each technology, Fig. 1 shows the best obtained laboratory cell efficiencies for the different technologies. The best crystalline silicon solar cells boast 27% efficiency, the best thin film solar cells are in the 20% range, triple junction solar cells have reached up to 41% efficiency, and the best organic and emerging inorganic solar cells reach between 8 and 11% percent.

Electrodeposition has been shown to provide improved benefits in several solar cell technologies. It is one of the most selective processes because deposition only occurs at positions on a substrate where the substrate conductivity is highest.

Unlike evaporation, sputtering, chemical vapor deposition, and some of the wet chemical processes, the materials utilization rate in electrodeposition is better than 90% partly due to the selectivity and partly because there is extensive know-how on the re-use and recycle of electrodeposition chemistries.

In terms of processing conditions, it is a low temperature atmospheric process that allows the fabrication of 3D nanometer scale or nanometer planar devices with great precision and control.
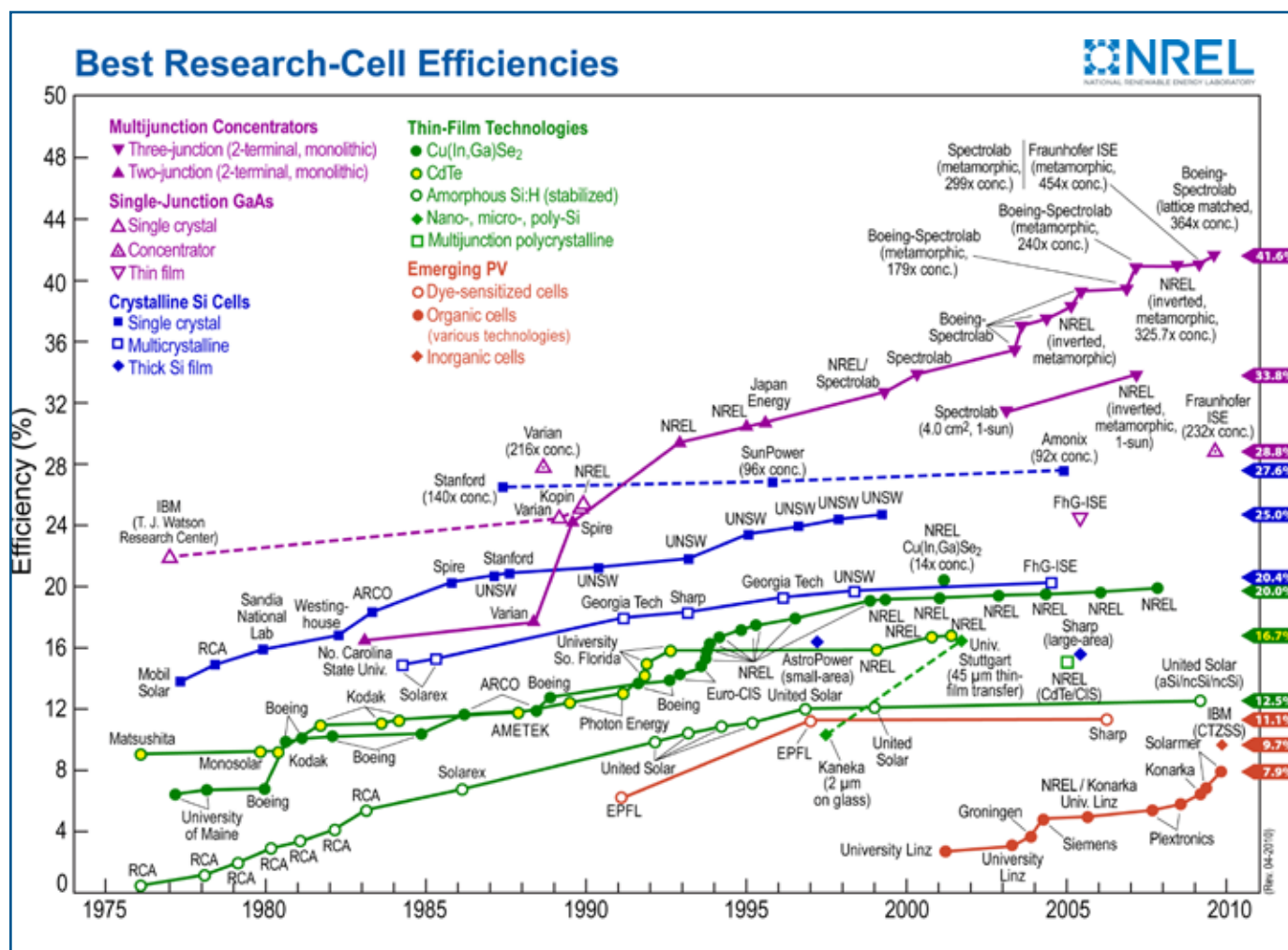
Fig.1. *Best laboratory solar cell efficiencies from the National Renewable Energy Lab in Golden, Colorado.*

Last but not least, significant progress has been made toward the scaling up of electrodeposition processes (both electrolytic and electroless) in microelectronics for printed circuit boards and for semiconductor wafers. The scale of substrates for the solar industry varies between 156 mm² to m² and within the range of the microelectronics processing. This scaling has been done on both rigid and metallic flexible substrates for different applications.

The remainder of the discussion focuses on a more detailed description of the research that has been reported for the different solar technologies. (Editor's Note: See also related article on inorganic photovoltaic cells, *Interface*, Vol. 17, p. 30, 2008.)

Contacts for Crystalline and Multi-crystalline Silicon Solar Cells

A silicon solar cell is a simple *p-n* junction. The *p-n* junction is formed by diffusing phosphorus into the wafer as an impurity dopant. Screen-printed Ag contact fingers are used on the *n*-type surface to make electrical contact at the top surface of the cell. Aluminum paste is used to make contact at the back *p*-type surface. The structure is annealed to introduce a *p+* doped region at the back of the cell to lower the contact resistance and supply a back surface field that reflects minority carriers back toward the junction. An antireflection (A/R) coating, typically silicon nitride, is deposited over the top surface to complete the device.[10]

Green and coworkers[11,12] from the University of New South Wales (UNSW) have pointed out that there is a high penalty for using screen-printed contacts. Large shading losses, the high resistivity of the screen-printed Ag grids at 3.5-4 mohm cm compared with pure Ag at 1.5-1.6 mohm cm (three times as high), a high contact resistance between the grid and Si, and poor aspect ratio reduce device efficiencies to approximately 14%. This has led the researchers to develop solar cells in which the contacts are defined either using photolithography or laser scribing. A typical 'UNSW cell structure' is shown in Fig. 2 where the contacts are either exposed or buried. In these structures the Ag paste has been substituted by nickel silicide for improved contact resistance, a layer of nickel, copper for improved conductivity, and finally a layer of tin or solder in order to create a solderable surface.

For the design shown in Fig. 2b,[10,13] the surface of the Si has been oxidized in order to passivate the front surface of the cell and contact grooves were cut using laser scribing. In this "buried contact" design, the contact metals, Ni, Cu, and then Ag or Sn, are deposited using electroless and light induced electrolytic methods. The higher doping concentration of this *n+* region and the NiSi that forms reduces the contact resistance at the grid contact. This type of cell is used in the high efficiency Saturn modules produced by BP Solar.[13]

Nguyen et al.[14] demonstrated that light induced electroplating of copper metal on top of the front contact grid has shown promise in reducing line resistance and increasing cell power output. Preliminary cell performance study data with Ag plating have shown that front side resistance before plating was on average 0.122 ohms while after plating it was improved to 0.054 ohms,

potentially producing 100% more current and therefore more power output. In addition, electroplated deposits have better selectivity and throwing power, so they can be deposited in a thinner conductor, resulting in less shading of the PV material and greater electricity production by the module.

The Light Induced Plating (LIP) method has received only limited acceptance in the industry due to the cost of plating precious metal layers such as silver. The feasibility of using this technique to plate non-precious metals, such as nickel (Ni), copper (Cu), or tin (Sn) is preferable from a lower cost perspective. Cu has higher electrical resistivity compared to Ag but is a less expensive material. Using Cu instead of Ag as the primary current carrier for the contact metallization should allow the same benefits with a substantially lower manufacturing material cost.

In the study by Nguyen et al.,[14] solar cells were processed in a LIP tool where light was injected into the cell to generate electrons needed for the electrodeposition process. A rectifier was used to apply a voltage on the backside of the cell to protect the backside Al contact from becoming the anode and dissolving during the electrochemical reaction. Plated Ni followed by plated Cu produced a line resistivity of 1.75 μOhm-cm in a 100 micron contact opening. This line resistivity is close to that of bulk Cu.

In the study of Rao et al.,[15] a NiSi layer followed by electroplated copper was introduced into the contacts. The contact resistance between Cu and the emitter was minimized with the use of metallic interfacial layers such as silicides that formed either by sputtering or by electrodeposition. It was found that increasing the thickness of the plated Cu reduces the device series resistance, and increases the solar cell efficiency. A plateau in efficiency was reached for the same substrate when the Cu thickness was higher than 8 micrometers.
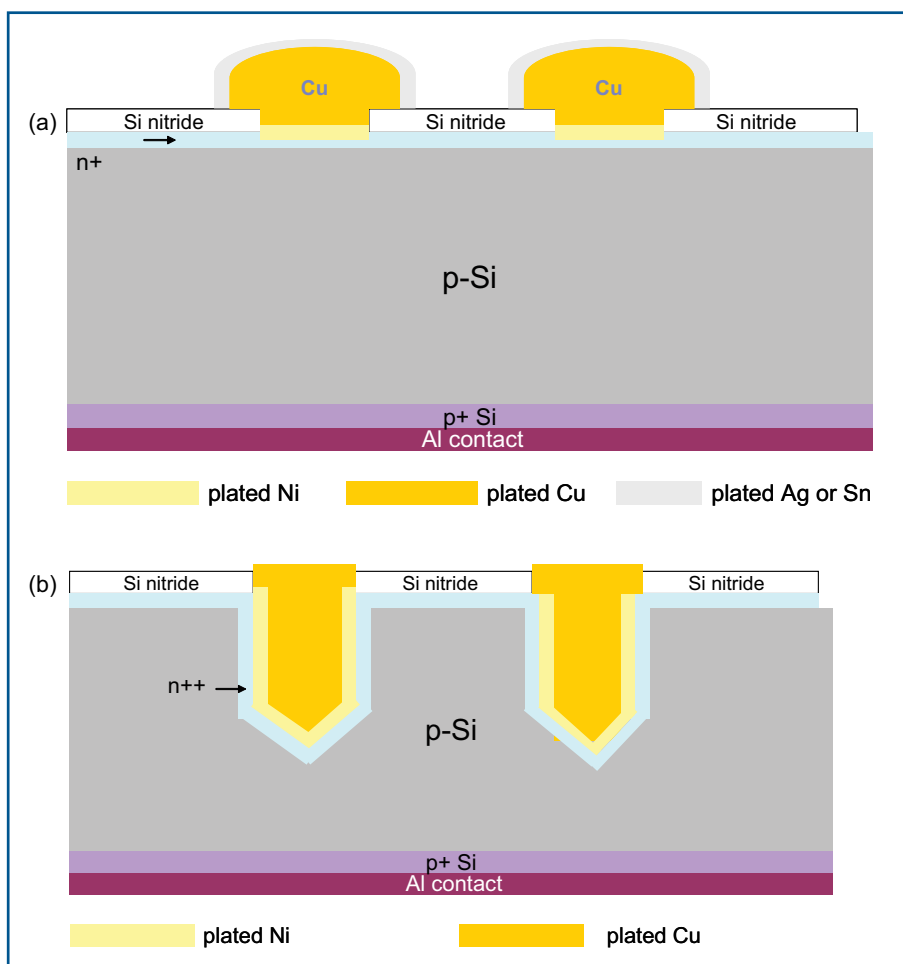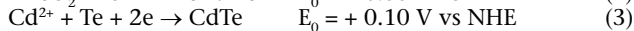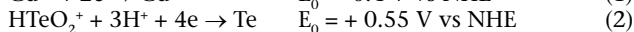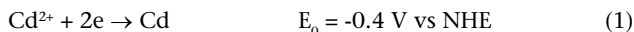

Fig. 2. *(a) Schematic cross-section of a Si solar cell that has the screen printed silver contacts substituted by NiSi silicide, plated Ni, plated Cu, and Sn. (b) Schematic cross-section of buried contacts with NiSi, plated Ni, and Cu.*

Electrodeposition Technology for the Fabrication of Chalcogenide CdTe and $CuIn_xGa_{1-x}(Se_yS_{1-y})_2$ Thin Film Solar Cells
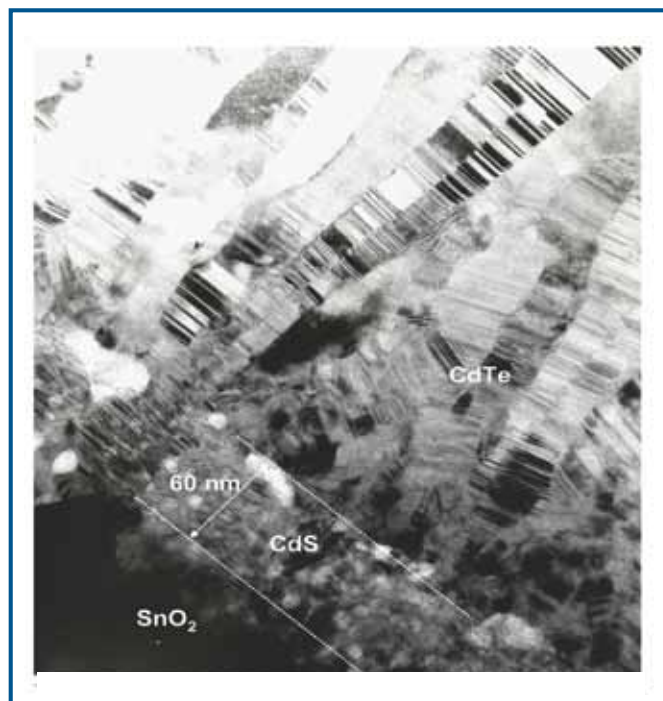
Cadmium telluride is the most extensively studied chalcogenide material in the field of electrodeposition. The free energy of formation of the compound plays a major role in allowing self regulation of the composition, close to stoichiometry, over a wide range of potential as illustrated by the following electrochemical reactions taking place in acidic solutions.

$$Cd^{2+} + 2e \rightarrow Cd \qquad E_0 = -0.4 \text{ V vs NHE} \qquad (1)$$
$$HTeO_2^+ + 3H^+ + 4e \rightarrow Te \qquad E_0 = +0.55 \text{ V vs NHE} \qquad (2)$$
$$Cd^{2+} + Te + 2e \rightarrow CdTe \qquad E_0 = +0.10 \text{ V vs NHE} \qquad (3)$$

A window of 0.5 V exists for the formation of CdTe between the deposition potentials of pure tellurium and pure cadmium. This deposition mechanism, which is analogous to underpotential deposition (UPD) on surfaces, is a driving force for the formation of high quality crystalline CdTe films at near room temperature. Lincot[16,17] has demonstrated polycrystalline CdTe films can be obtained on CdS by electrodeposition in acidic conditions as shown in Fig. 3.

Single crystalline columns with a preferential orientation (111) perpendicular to the substrate (here CdS) are evident, which extend throughout the entire thickness of the film that is 1-2 microns thick. The as grown CdTe films have semiconducting properties, making them directly suitable for optoelectronic applications. Depending on the deposition potential, *n* type or *p* type semiconductors are obtained.

Despite these encouraging results, evaporation is used in the manufacturing of CdTe thin film solar cells. First Solar[18] is the largest manufacturer of CdTe thin film solar cells with production greater than 1 GW/yr, manufacturing cost of $0.75/W, the lowest in the industry, and module conversion efficiency of 11.6%. As this article was being written, GE[19] announced that they have made record efficiency cadmium telluride modules at almost 13%. GE claimed that the best way to reduce manuf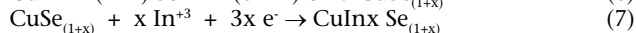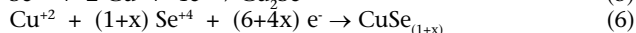acturing solar cost, was by improving efficiency, also stating that each percentage point in efficiency lowers cost by 10%. GE plans to start a 400 MW factory in 2013, with module efficiency higher than 13%. Will GE use electrodeposition to realize these goals? It remains to be seen.

$CuInGaSe_2$ (CIGS) solar cells have been touted to be one the most promising of the thin film solar cell technologies.[20] Efficiencies higher than 20% (Fig. 1) have been demonstrated in several laboratories with the CIGS material. Shafarman and Stolt[20] have done a very comprehensive review of the CIGS device physics, electrical characterization, the CIGS materials, and a review of the co-evaporation technology used to produce some of the champion CIGS cells.

Despite the fact that laboratory results are outstanding and several companies with different process technologies have rushed to scale the CIGS technology up, there is still a gap between the small cell efficiencies of 20%[21] and the large module efficiencies which are between 10-12%. This is partly due to the complex nature of the quaternary material and partly due to the difficulties inherent in scaling up the expensive vacuum-based CIGS deposition approaches that were adapted in the early '90s 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.

Basol et al.[22] recently reported on a roll-to-roll electrodeposition based CIGS technology. 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 by electrodeposition of precursor CIGS layers that are converted to high quality chalcopyrite through Rapid Thermal Annealing (RTA) as shown in Fig. 4. Solar cells were fabricated in a roll form and then cut and sorted for module manufacturing. Large area solar cell efficiencies of over 12% were demonstrated using this technology. Modules with 10% efficiency and 1 m² area were fabricated.

We recently reported on the challenges of the fabrication of $CuInSe_2$, $CuInS_2$ and $CuInGaSe_2$ by electrodeposition.[23] We investigated the co-deposition of an $CuInSe_2$ precursor layer in a citrate solution without organic additives. Figure 5 shows the voltammetric data and the resulting as deposited microstructure that is mostly nodular.[23] At the initial stages of film growth, copper rich selenium phases form during deposition. Roussel et al.[24] suggested that copper rich phases facilitate the incorporation of selenium and the formation of $CuInSe_2$.

$$Cu^{+2} + 2e^- \rightarrow Cu \qquad (4)$$
$$Se^{+4} + 2\ Cu + 4e^- \rightarrow Cu_2Se \qquad (5)$$
$$Cu^{+2} + (1+x)\ Se^{+4} + (6+4x)\ e^- \rightarrow CuSe_{(1+x)} \qquad (6)$$
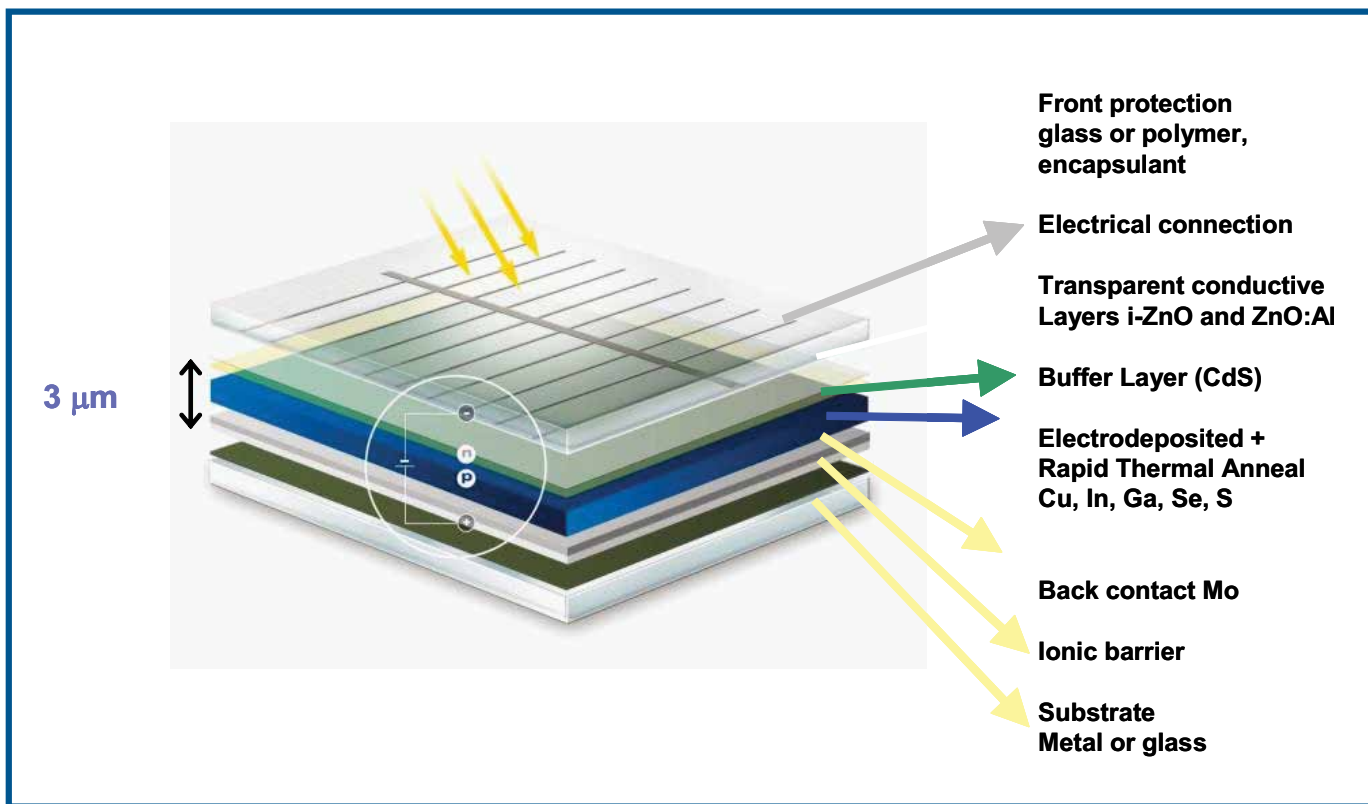$$CuSe_{(1+x)} + x\ In^{+3} + 3x\ e^- \rightarrow CuInx\ Se_{(1+x)} \qquad (7)$$

As a result of this mechanism, incorporation of indium in the $CuInSe_2$ film is facilitated by the formation of CuSe phases.

This type of mechanism results in a non-uniform composition of the precursor layer $CuInSe_2$ layer with a Cu_2Se layer next to the Mo interface, and with a CuSe and a $CuInSe_2$ layer on top. Both the compositional non-uniformities and the modular microstructure make the $CuInSe_2$ material difficult to electrodeposit from simple complexed chemistries.

Aksu et al.[25] recently reported on an 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. 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.

A more successful approach for achieving compositional uniformity is the metal stack approach. As shown in Fig. 6, a Cu/In/Cu/In precursor structure was used to convert the metals to the chalcopyrite $CuInS_2$. Control of the composition of the

FIG. 3. *High resolution transmission electron microscopy view of a CdTe layer electrodeposited at 2 microns per hour in an acidic solution at 70°C. The substrate is glass covered by a tin oxide conductive layer and a microcrystalline CdS layer deposited chemically.[16, 17] (Reproduced by permission of The Electrochemical Society)*

FIG. 4. *Schematic of a thin film CuInGaSe$_2$ solar cell.[23](Reprinted with permission from the ARCSIS Photovoltaic Technical Conference)*
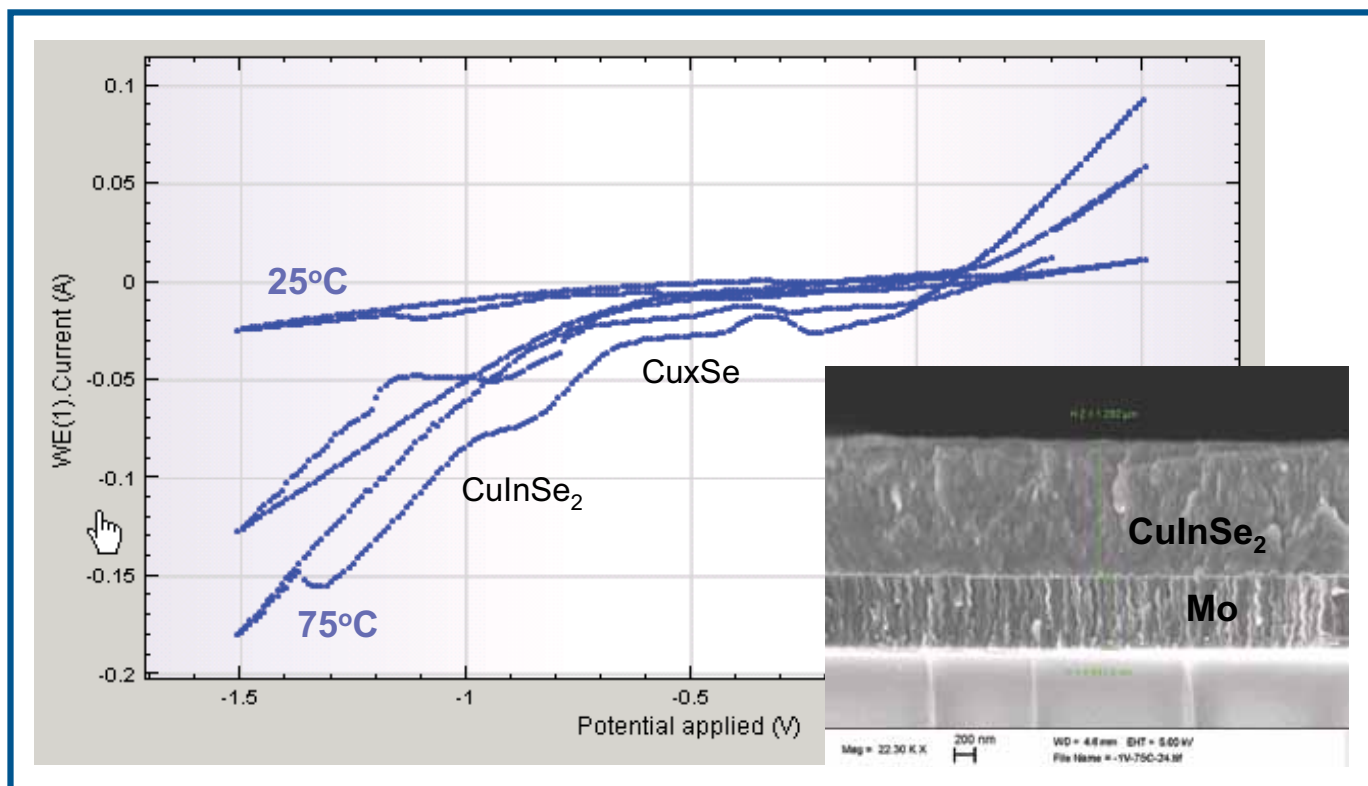
FIG. 5. *Cyclic voltammograms of a molybdenum electrode in a solution containing 5mM CuSO$_4$, 15mM InSO$_4$, and 10mM selenous oxide, sodium citrate solution at pH 2.5 and at 25°C and 75°C. A cross-section of the resulting deposit at -1.3 V vs. MSE and at 75°C is shown.[23] (Reprinted with permission from the ARCSIS Photovoltaic Technical Conference)*
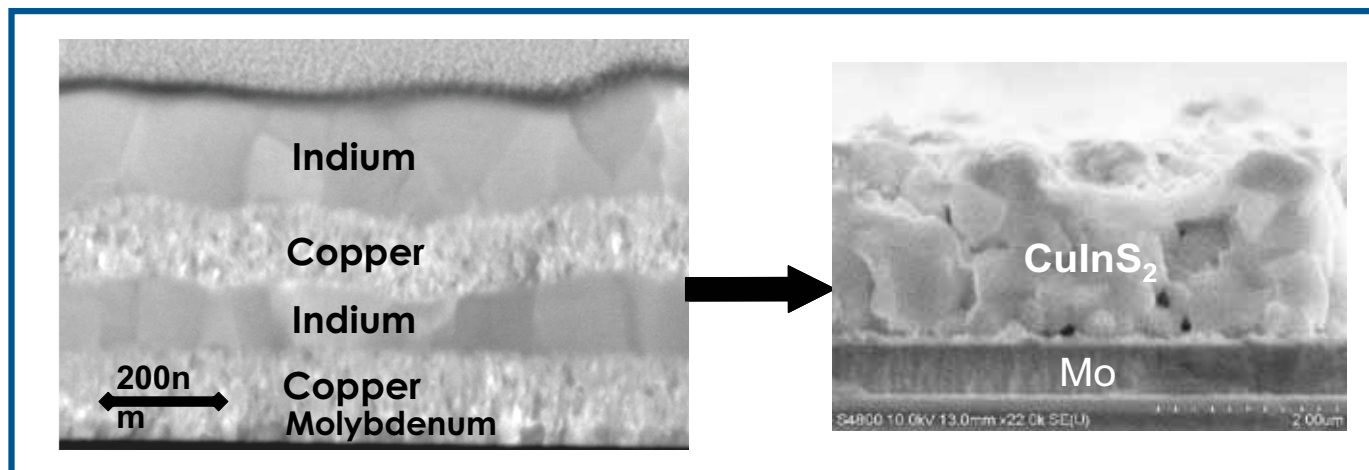
Fig. 6. *A multilayer structure of Cu/In/Cu/In can be converted to CuInS$_2$ by annealing at 550°C in a Rapid Thermal Anneal (RTA) furnace in a sulfur atmosphere.[23] (Reprinted with permission from the ARCSIS Photovoltaic Technical Conference)*

chalcopyrite film is achieved by precise control of the thickness of the nanometer thick metal layers. Reproducibility with minimal thickness variations and minimal surface roughness of all layers have been found to be critical for a well-controlled absorber.[26]

Surface roughness and thickness control are highly influenced by nucleation and growth of indium on copper. This was studied in depth by Huang et al.[26] who determined that the electrodeposition of indium on copper in a sulfate solution showed a two-step film growth behavior, a conformal smooth film growth followed by a 3D island growth. Fast interdiffusion was observed between the electroplated copper and indium and a CuIn$_2$ alloy phase formed during the indium deposition at room temperature. The alloy formation is believed to promote a conformal deposition of a few indium mono-layers; the fast interdiffusion counterbalances the indium mono deposition and lowers the indium content at the surface. The 3D island growth is believed to be delayed until a threshold value of indium content is reached at the surface. The time when this threshold value is reached depends on the indium deposition rate and the grain size and the diffusivity of the copper.

The metal stack process was scaled up to a panel size of 30 cm x 60 cm. We have demonstrated[23] cell efficiencies between 8-10% with champion cells at over 10% solar cell efficiency.

Emerging Materials for Thin Film Solar Cells: Cu$_2$ZnSn(Se$_y$S$_{1-y}$)$_4$

A promising candidate for low cost absorber layers is the quaternary compound of Cu$_2$ZnSnS$_4$ (CZTS) which is the equivalent of CuInS$_2$ when replacing In with Sn and Zn in a 50/50 ratio.[6] The need to replace indium stems from the fact that indium is two orders of magnitude more expensive than Sn, Zn, and Cu. In terms of availability on the planet, In is about as available as Cd and Se and one or more orders of magnitude less available than Sn, Cu, Sn, and S.

Ennaoui et al.[27] reported on an electroplated CZTS film using a CuZnSn alloy precursor. The pyrophosphate alkaline bath contained about 3mM of Cu^{+2}, and Zn^{+2} and 30 mM of Sn^{+2}, along with complexing agents and additives. Sulfur was added by annealing using a gas mixture of Ar with 5% H$_2$S at 550° C for 2 hours. The resulting kesterite composition was Cu-poor with Cu/(Zn+Sn) of 0.97. The CZTS layer exhibited very large grains and had secondary phases such as ZnS and Cu$_2$SnS$_3$ in addition to the Cu$_2$SnZnS$_4$ phase. The devices showed an efficiency of 3.4%.

Scragg et al.[28] used an electrochemical stacked metal layer approach to fabricate CZTS solar cells. As with CuInS$_2$ and CIGS, the advantage of this approach is the improved control of the composition of the CZTS, which is achieved by controlling the order of deposition of the metal layers and their thickness. A Cu/Sn/Cu/Zn metal stack was used in this study. Copper was electroplated using an alkaline chemistry that contained a surfactant. The surfactant allowed a lower surface roughness of the deposits. Zinc was plated from a sulfate bath at pH of 3 and Sn from a methanesulfonic acid bath that also contained a surfactant. An oxide layer of the Sn prevented Zn nucleation on top of Sn but not on top of Cu. It was hypothesized that a UPD layer of Cu-Zn facilitates nucleation of Zn on Cu. As a result, a metal stack with Cu/Sn/Cu/Zn was produced.

Similar to the previous study,[27,28] secondary phases of ZnS and Cu$_2$SnS$_3$ were apparent along with the Cu$_2$SnZnS$_4$ phase. An additional issue encountered was the weak adhesion of the kesterite material to the Mo backside electrode interface. The electrodeposited cells yielded solar cell efficiency of 3.2%.

In 2010, Mitzi et al.[5] reported Cu$_2$SnZn(SeS)$_4$ devices with world record efficiency of 9.7% using a hydrazine-chemical-based solution deposition that contained a mixture of selenium and sulfur species.

We have deposited Cu$_2$SnZnS$_4$ using an electroplated metal stack precursor.[29] The metal precursor was converted to kesterite by annealing for 10-15 min in a sulfur containing atmosphere. Figure 7 shows the microstructure of the resulting absorber layer, consisting of large grains up to 1 micron in size; most importantly, only the Cu$_2$SnZnS$_4$ phase was detected using Raman spectroscopy.

So far very good progress has been made with the electrodeposited kesterite materials. Based on our results, we are confident that efficiencies similar to the ones achieved previously with evaporation and the chemical solution process[5] can also materialize using electrodeposition.

Conclusion and Future Outlook

Electrodeposition for solar cells is an active area of research and it has been shown to provide improved benefits in several solar technologies. For the silicon solar cell contacts, electrodeposited metal contacts result in 1-2% solar cell efficiency improvement due to a lower processing temperature with better yield than screen printing, improved contact resistance, lower overall resistance, and the ability to fabricate small contacts that reflect the sunlight less.

For the chalcopyrite and the kesterite thin films, electrodeposition offers very low cost of manufacturing with a continuous reel-to-reel or roll-to-roll process. Rigid glass or flexible metallic substrates can be used with these thin films, potentially opening up new applications for solar energy.
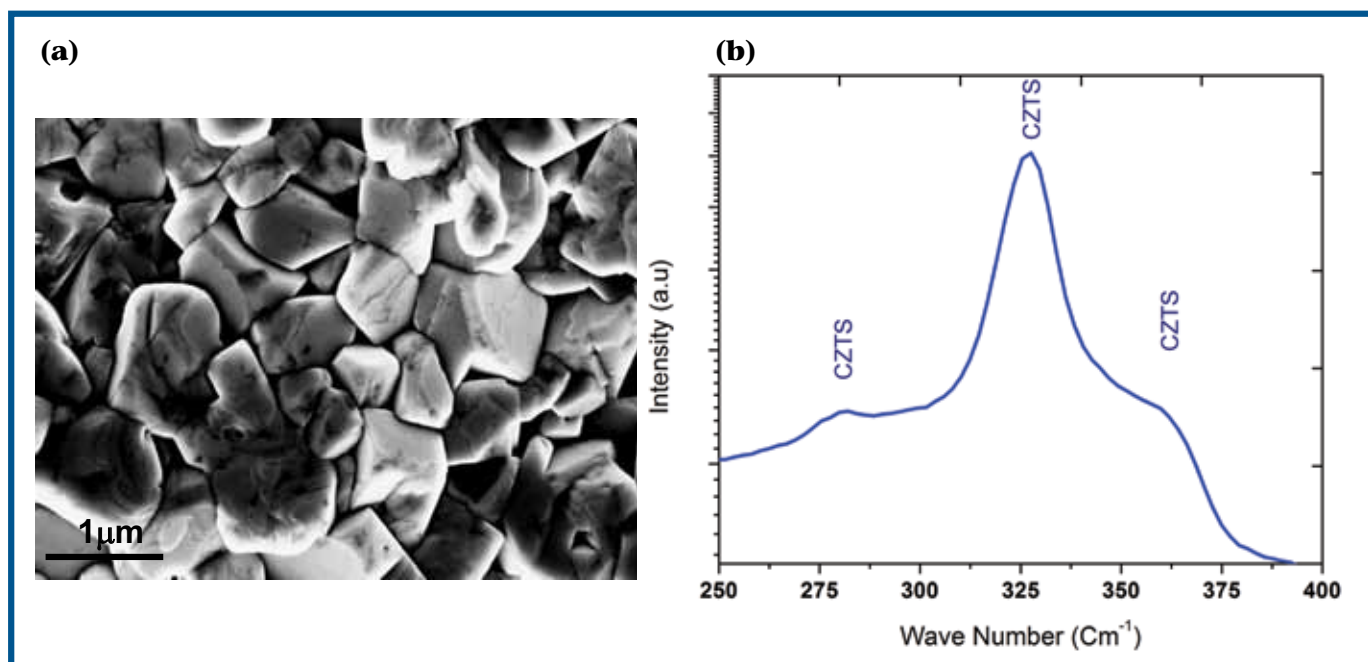
Fig. 7. *(a) Top-down SEM of electrodeposited Cu_2SnZnS_4 with a well defined grain size of about 1micron. (b) Raman spectroscopy of the electrodeposited Cu_2SnZnS_4 showing only the CZTS kesterite phase.*[29]

These applications span from energy generation for energy utilities to building integrated materials, solar-powered cars, and electronic devices.

Electrodeposited CIGS is already scaled-up for manufacturing by Solopower Inc. For these applications, we expect that electrodeposition will become a game changer in its ability to lower manufacturing costs to less than $0.50/W, making solar energy affordable to the public.

Unlike CIGS and CdTe, which have issues of materials availability such as indium, gallium, cadmium, and tellurium and that are high cost, CZTS does not have these issues.[6] Electrodeposited kesterite has the potential of reaching terawatt scale with the widest deployment in the marketplace.

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Dr. Romankiw was Chair of the ECS Electrodeposition Division, is a Fellow and Honorary Member of ECS, Fellow and lifetime member of IEEE, lifetime member of the Shevchenko Scientific Society, member of the IBM Academy of Science and Technology since 1987, and a member of the Academy of Engineering of Ukraine since 1992. IBM has honored Dr. Romankiw with several Outstanding Invention and Contribution Awards and 30 Invention Achievement Awards. Dr. Romankiw was honored by the ECS Electrodeposition Division Award in 1984, received the Inventor of the Year Award of New York State in 2001, the ECS Vittorio de Nora Award in 1994, the Morris A. Lieberman Award by IEEE in 1998, and the Perkin Gold Medal by the Societies of Chemical Industries in 1993. He may be reached at romankiw@us.ibm.com.

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