Electrodeposition Technology for the Fabrication of $CuIn_xGa_{1-x}(Se_yS_{1-y})_2$, and Cu_2ZnSnS_4 Thin Film Solar Cells

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Electrochemical technology has been an integral part of major advances in semiconductor technology of the 20th century. While, the microelectronics industry is rapidly reaching maturity, its explosive start and sustained growth has been partly enabled by the use of scalable electrochemical processes. These processes [1,2,,3,4] have been scaled to different wafer sizes - from 125 mm to 200mm and to 300mm diameter wafers, while feature size has to satisfy a continuous shrinkage from micron size to nanometer size. The precise control and accommodation of different length scales has been possible due to the basic treatment and understanding of current distribution and physico-chemical phenomena from the molecular level to the mm scale.

The solar industry is still in early development. While the dominating solar technology is based on single crystal and polycrystalline silicon, thin film photovoltaic materials such as CdTe, $CuInS_2$ (CIS), $CuInGaSe_2$ (CIGS) and its earth abundant version offer a lower cost alternative[5, 6, 7,8]. $CuInGaSe_2$ (CIGS) solar cells have been touted to be one the most promising of the thin film solar cell technologies. Efficiencies higher than 20% have been demonstrated in several laboratories with the CIGS material.

These materials can be electroplated to form the p-type absorber layer of a hetero-junction PV cell. Different processing approaches have been tried such as electrodeposition of Cu/In/Ga/Se thin films or alloy deposition of binary, ternary or even quarternary alloys such as $CuInS_2$ or $CuInGaSe_2$ (CIGS)[8]. All these precursor processing approaches require a subsequent high temperature 530 – 590°C rapid thermal annealing step in a selenium or sulfur atmosphere. A key challenge is to deposit very uniform nm scale thin films on meter large resistive substrates. Controlling nucleation and growth phenomena and tailoring the microstructure of the thin film is essential for controlling the composition and microstructure of the final chalcopyrite layer. A key challenge is to convert by annealing the uniform metal layers to good quality semiconductor material.

For the fabrication of the $CuInS_2$ precursor material, 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[9] who determined that the electrodeposition of indium on copper showed a two-step film growth behavior, a conformal smooth film growth followed by a 3D island growth. The metal stack process was scaled up to a panel size of 30 cm x 60 cm. We have demonstrated that we were able to reach cell efficiencies between 8 % - 10% with champion cells at over 10% solar cell efficiency[8].

A promising candidate for low cost absorber layers is the quarternary compound of Cu_2ZnSnS_4 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 and gallium stems from the fact that these are two orders of magnitude more expensive than Sn, Zn and Cu. In terms of availability on the planet these are about as available as Cd and Se and one or more orders of magnitude less available than Sn, Cu, Sn and S.

Using a similar methodology as in $CuInS_2$, we have deposited Cu_2SnZnS_4 using an electroplated metal stack precursor[10]. The metal precursor was converted to kesterite by annealing for 10-15 min in a sulfur containing atmosphere. The microstructure of the resulting absorber layer, the different phases detected by X-ray diffraction and Raman spectroscopy will be discussed as well as cell efficiencies achieved to-date.

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