Potential of Copper Indium Selenide Compounds for Various Solar Energy Conversion Devices

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The optimal properties of copper indium selenide (CIS) and its alloys to produce efficient, reliable solar cells have long been demonstrated in PEC and PV devices. Its proven performance in low visible light, radiation hardness, and low degradation enables a wide range of PV applications. Its direct bandgap and high absorption coefficient enables using $\sim 1 \mu m$ thin layers in devices. This presentation will outline our work on CIS photoelectrochemical (PEC) and photovoltaic (PV) devices, underscoring the influence of Adam Heller's groundbreaking accomplishments in the development of PEC cells and photoelectrolysis. His contributions to materials electrochemistry continue to impact diverse areas of electrochemistry, including semiconductor electrochemistry. The latter paved the path for subsequent solar cell research for those of us that were fortunate to actively interact with Adam during the early evolution of PEC devices. It certainly impacted our work on CIS based PEC and PV devices.

The CIS PV development path has primarily focused on CIS-alloys, such as CuInGaSe₂, CuInGa(SeS)₂ (CIGS). The alloying unfortunately complicates the transition to large-area deposition, impeding CIGS PV scalability and cost-effectiveness. Drawing upon our early research that led to a 12% efficient and stable solar cell [1], we have been developing an off-mainstream technology based on CIS ordered defect chalcopyrites (ODC) selected from the $(Cu_2Se)(In_2Se_3)_{x+1}$ series of compounds. ODC formation is attributed to the exceptionally low ΔH for the formation of charge compensated defect pairs, e.g. $(2V_{Cu} + In_{Cu}^{2+})$ [2]. It produces stable stoichiometric ODC compositions and dictates their properties. The CIS-ODCs offer special attributes to manufacture high-efficiency devices on large areas [3,4]. For example:

- Thermodynamically driven CIS-ODC formation leads to self-stabilizing compositions, which simplifies large-area deposition.
- Variable wide bandgaps increase photon absorption, offering potential for higher efficiency.
- Ability for self-doping into *n*-CIS, *i*-CIS or *p*-CIS compounds enables new device architectures.

The CIS-ODC materials easily adapt to low-cost processes such as electrodeposition. The CIS film can be synthesized using our extremely low-cost and highly reproducible single-step electrodeposition approach. This process allows wide tolerance to process variability and easily scales up for continuous roll-to-roll production. Besides this processing advantage, the unique attributes of CIS ODCs offer a direct route to a full spectrum of 3rd generation (3G) CIS PV devices [5]. Our research to date has revealed many unexpected features for our electrodeposited CIS-ODC films. We exploit these attributes to develop spin-off technologies that could lead

to the next performance leap [6] and generate low cost solar power. This paper will track the evolution of CIS PV, highlighting the developments that have the potential to achieve high performance and easy manufacturability. Our CIS-based developments include various device structures that have evolved from CIS-ODC for solar energy conversion:

- The original *n*-CIS PEC solar cell and electrochemical formation of *np* heterojunction offers high stability and efficiency
- The transition to thin film *n*-CIS PV cell enables cost effective, flexible solid state PV devices
- Roll-to-roll system allows continuous electrodeposition of compositionally homogenous CIS absorbers for mass production
- Bi-hybrid CIS-based photoelectrodes address the issue of voltage matching in water splitting PEC systems.
- Advanced 3G solar cells based on nanostructured CIS can maximize solar conversion efficiencies.

Projects underway attempt to pursue the above and related concepts, in order to realize the potential of the special CIS materials for solar energy conversion.

Acknowledgements

National Science Foundation, Air Force and Xcel Energy awards provided support for our work.

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