

Semiconductors for Photovoltaic Devices:  
Electrochemical Approaches

Phillip J. Dale, João Malaquias, Marc Steichen

Laboratory for Energy Materials  
University of Luxembourg  
41, rue du Brill, L-4422 Belvaux, Luxembourg

Can electrodeposition be used to synthesize high quality semiconductors for photovoltaic applications?

Thin film photovoltaic devices offer similar power conversion efficiencies to polycrystalline silicon devices and have the inherent advantages of requiring less energy and raw materials during fabrication. Thin film devices consist of a semiconductor p-n heterojunction with front and back contacts to collect charge carriers. The material properties of the p-type absorber layer are the most stringent, and determine the overall performance of the device. Common p-type semiconductors are CdTe, Cu(In,Ga)(S,Se)<sub>2</sub>, and the earth abundant Cu<sub>2</sub>ZnSn(S,Se)<sub>4</sub>. Typically the p-type semiconductor must form a two micron thick compact single phase layer over square meter areas. Most commercial producers of thin film photovoltaic modules choose high energy costing evaporation or sputtering methods to deposit the absorber. Of importance are the speed, cost, and quality of deposition.

Electrodeposition offers the ability to deposit thin films over large areas with high material usage, low energy costs, and potentially at high speed. Therefore, can electrodeposition be used to grow high quality p-type inorganic compound semiconductors?

This talk will show that it is possible to directly deposit a working p-type semiconductor, but that a two step approach of depositing metals and then annealing them in a reactive atmosphere is a simpler, easier, and more robust approach. Both approaches lead to working photovoltaic devices. However, improvements to the electrodeposition process are still required and the main challenges are outlined below.

Challenges in directly electrodepositing a p-type semiconductor are

- (i) the inherent lack of electrons necessary for a reductive deposition process
- (ii) the low thermal energy available at normal deposition temperatures to grow micron sized highly-ordered crystals.

Challenges for directly co-electrodepositing the metals Cu:In:Ga or Cu:Sn:Zn from aqueous solution are

- (iii) the competition with hydrogen reduction leading to inefficient deposition and metal oxide and hydroxide formation, embrittlement, and dendritic growth
- (iv) the control of the composition over the micrometer and centimeter length scales due to the different reduction potentials, nucleation densities, and diffusion coefficients.

In this talk it will be shown how these challenges can be met by using ionic liquids to replace aqueous electroplating baths. Ionic liquids offer larger

electrochemical windows, higher processing temperatures and the choice of new forms of starting reagent. Furthermore, task specific ionic liquids or liquid metal salts, with very high metal concentrations may even be employed to allow extremely high speed electrodeposition.

**Acknowledgements**

P.D acknowledges financial support by the Fond National de la Recherche Luxembourg for the ATTRACT research fellowship (07/06). J.M. and M.S. acknowledge financial support by the FNR-Luxembourg for the CORE Junior Track Project (C11/MS/1211521).