MOLECULAR LAYER ELECTRODEPOSITION FOR SEMICONDUCTOR COMPOUNDS

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Stringent material quality requirements for opto-electronic devices have excluded electrodeposition as an acceptable method for the synthesis of semiconductor compounds, despite its many advantages. Conventional electrodeposition leads to small-grained and non-stoichiometric compounds, caused primarily by the co-deposition of elements with highly disparate reduction potentials. Chemical and electrochemical epitaxial methods can produce very thin films or superstructures [1-7]. This paper presents an alternate approach — molecular layer electrodeposition (MLE), to synthesize semiconductor films at practical deposition rates.

MLE entails the successive electrodeposition of monolayers of a compound from a single electrolyte containing all the constituent elements [8]. This work uses a Cu-In-Se based model system because it illustrates the complexities of ternary compound formation, as well as the versatility of the MLE approach; it also includes a commercially important solar cell component, $CuInSe_2$ [9]. MLE of $CuInSe_2$ takes advantage of the self-limiting reactions and the low free energy compound formation, to directly form a stoichiometric $CuInSe_2$ monolayer in each step, as schematically illustrated in Fig. 1. Theoretical treatments demonstrate that a compound deposits at a more positive potential than one or both component elements and its stoichiometry is preserved via thermodynamics [10,11]. In the case of $CuInSe_2$, a monolayer of the compound does form at a more positive potential than at least one constituent, In. However, the kinetics for Cu-In-Se system is fairly complex. Despite the favorable thermodynamics, the electrodeposited $CuInSe_2$ films invariably contain one or more phases of Se, CuSe, Cu_2Se and In_2Se_3. Controlling the kinetics of competing reactions is essential to produce a stoichiometric film. The standard parameters used to control the kinetics include: temperature, electrolyte composition and deposition potential, E. This work introduces new parameters to manipulate the film stoichiometry – (i) solution volume, (ii) cell geometry and (iii) anodic dissolution potential.

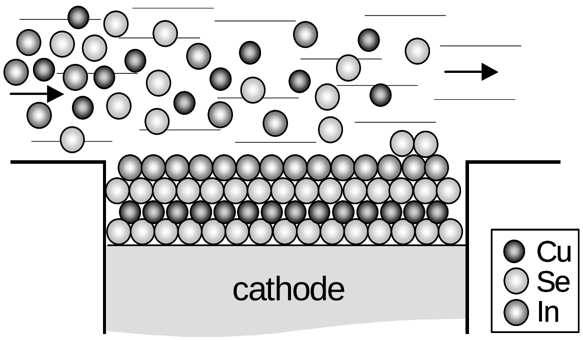

Figure 1: Schematic of $CuInSe_2$ molecular layer electrodeposition from an electrolyte containing all three constituent ions: Cu^{2+}, In^{3+}, and Se^{4+}.

MLE controls the solution volume with a thin layer flow cell. This paper investigates the effects of solution volume by comparing voltammetric characteristics, pulsed flow/deposition waveforms and film composition with different deposition system configurations.

The results reveal different reaction mechanisms for $CuInSe_2$ formation in bulk and thin layer electrolytes. The three new control parameters provide a new route to control film morphology and a straightforward means to increase the content of difficult-to-co-deposit metals like In in $CuInSe_2$ films.

MLE combines the advantages of epitaxial and conventional electrodeposition while circumventing the problems. It avoids the post-annealing step needed for conventionally electrodeposited films. It allows the deposition of more than one monolayer of the compound per cycle. It eliminates multiple electrolytes, rinse cycles and under layer dissolution, thus extending the utility of epitaxial deposition to device fabrication at low temperatures, with simpler apparatus and practical deposition rates. MLE could evolve into an integrated system for manufacturing entire devices on temperature-sensitive polymeric substrates such as lightweight flexible solar cells. MLE also provides interesting possibilities to create a range of nanoscale structures and superlattices.

This work is sponsored partly by an EISG grant from the California Energy Commission and a SBIR grant from the Missile Defense Agency.

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