

# Electrochemical methods for synthesizing and characterizing copper indium diselenide (CIS) thin films

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A number of electrodeposition methods have been used to synthesize CIS pre-cursor thin films. The films have been annealed and their spectroscopic properties investigated using wet electrolyte contacts.

Electrodeposition is a proven technology which has already been used to make commercially viable CdTe cells in the BP Solar Appollo process.<sup>1</sup> It has advantages in being low energy, suitable for large area processing, and having a high material yield. Several different approaches to the electrodeposition CIS films are briefly reviewed below. All approaches start by dissolving Cu(I/II), In(III), and Se(IV) salts in aqueous solution and applying a constant negative potential at the substrate electrode to plate the dissolved ions from solution. The resulting films must then be annealed in a selenium atmosphere to give it its photovoltaic properties.

In practice, the electrodeposition of stoichiometric CIS films is non-trivial compared to that of CdTe films, as copper and selenium ions deposit under diffusion control and all the ions have different redox potentials. Thouin et al.<sup>2</sup> reported that stoichiometric CIS can be deposited by controlling the ratio of the flux of Cu and Se ions to the deposition surface. The flux is determined by the relative concentrations of Cu and Se, their diffusion coefficients, and the hydrodynamic conditions in the cell. CIS formation occurs from the reaction of stoichiometric amounts of the binaries  $\text{In}_2\text{Se}_3$  and  $\text{Cu}_2\text{Se}$  reacting together.

Another constant potential deposition strategy is to limit the concentration of Cu ions in solution so that they are supplied at a rate at which they are consumed. By changing the rate of supply of copper the composition of the films could be adjusted from indium rich to indium poor.

Kemell et al<sup>3</sup> found that stoichiometric films of CIS could be deposited at a constant potential if thiocyanate ions ( $\text{SCN}^-$ ) were added to the bath. These act by complexing strongly to copper moving its deposition potential much closer to that of indium. With  $\text{SCN}^-$  ligands CIS could be deposited by an induced co-deposition mechanism at the same potentials that  $\text{Cu}_{2-x}\text{Se}$  could be deposited. Commercially the advantage of this approach is that the stoichiometry of the deposited films did not depend heavily on the copper and indium concentrations. However our work has established that this particular ligand is unstable with respect to time, as it appears to polymerize to form a thiocyanogen polymer, losing its ability to complex the ions in solution.

Nomura et al<sup>4</sup> electrodeposited CIS films from an unstirred bath of simple salts where In was in excess by stepping the potential back and forth between the copper and the indium deposition potentials. By controlling the cycle time and deposition potentials stoichiometric films were achieved.

The photoresponse properties of CIS absorber layers were determined without completing the whole cell structure by using wet electrolyte contacts. This allows the layer type, speed of response to light, and incident photocurrent efficiency (IPCE) of the film to be determined without worrying about the quality of the window and transparent conducting layers. Examples of these measurements are given in the figures below.

Figure 1: The effect of potential on the magnitude of the photocurrent response of a CIS film under pulsed white light illumination.

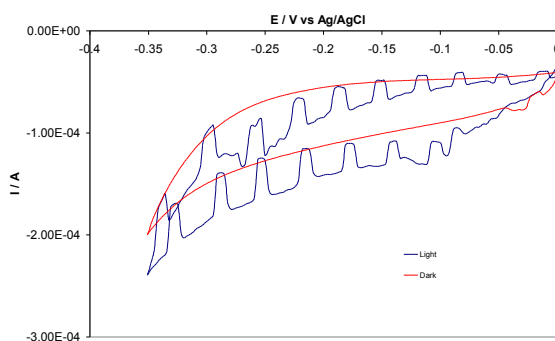


Figure 3: IPCE spectra (-) as deposited from a pulse plated bath (--) annealed film electrodeposited from an ionic liquid.

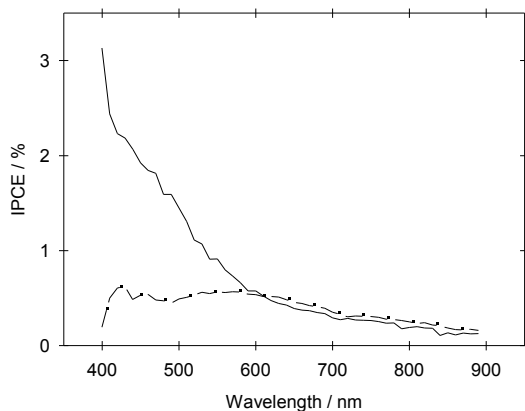


Figure 2: Photocurrent transients of three CIS films held at  $-0.3$  V vs Ag|AgCl under pulsed white light illumination.

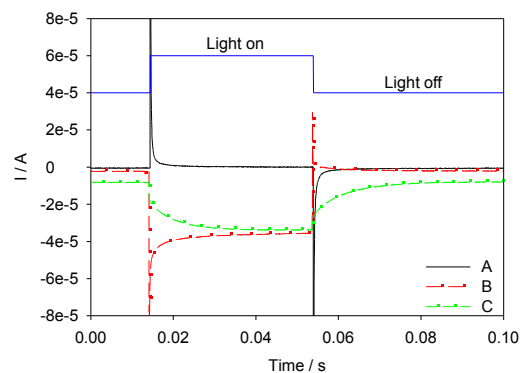
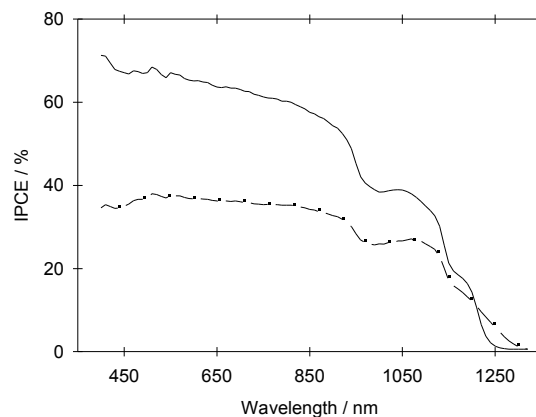


Figure 4: IPCE spectra of CIS films supplied by Northumbria University made by high vacuum deposition methods.



- (1) Duffy, N. W.; Peter, L. M.; Wang, R. L.; Lane, D. W.; Rogers, K. D. *Electrochim. Acta* **2000**, *45*, 3355-3365.
- (2) Thouin, L.; Massaccesi, S.; Sanchez, S.; Vedel, J. *J. Electroanal. Chem.* **1994**, *374*, 81-88.
- (3) Kemell, M.; Saloniemi, H.; Ritala, M.; Leskela, M. *J. Electrochem. Soc.* **2001**, *148*, C110-C118.
- (4) Nomura, S.; Nishiyama, K.; Tanaka, K.; Sakakibara, M.; Ohtsubo, M.; Furutani, N.; Endo, S. *Jpn. J. Appl. Phys. Part 1 - Regul. Pap. Short Notes Rev. Pap.* **1998**, *37*, 3232-3237.