

Tuning the Gallium Content of Metal Precursors for Cu(In,Ga)Se₂ Thin Film Solar Cells by Electrodeposition from a Deep Eutectic Solvent

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(1) We present the mathematical development that via the mass fluxes (J), the Ga/III ratio of the deposits can be controlled.

According to Fick's Law, during codeposition of two elements, in a system under diffusion control, the composition of a deposit is dictated by the ratio of the mass fluxes, J . Therefore, for In and Ga one can write:

$$\frac{J_{Ga}}{J_{In}} = \left(\frac{n_{Ga}}{n_{In}} \right)_{deposit} \quad (1)$$

a) Considering $J_{Ga}/J_{In} = A$ one can prove that:

$$\frac{Ga}{Ga+In} = \frac{Ga}{III} = \frac{A}{A+1} \quad (2)$$

This equation establishes a relation between the mass fluxes and the expected Ga/III ratio, thus evidencing, theoretically, that via the mass fluxes one can control this ratio. The next steps will focus on proving that the charge passed during deposition, Q , ensures the desired stoichiometry.

When performing electrodeposition of two different species, the total current flowing, j_t , is the sum of the individual currents. Thus, in our system the currents generated by the reduction of In and Ga during deposition:

$$j_t = j_{In} + j_{Ga} \quad (3)$$

b) Therefore, by integration in time, one obtains the charge, Q :

$$Q_t = \int_0^t j_{In} dt + \int_0^t j_{Ga} dt \quad (4)$$

Since the deposition is performed under a diffusion control regime and the working electrode is rotated, any time dependent behaviour of the current is eliminated and one can directly write:

$$Q_t = Q_{In} + Q_{Ga} \quad (5)$$

c) Using Faraday's Law, one can write explicitly both components of Q_t .

$$Q_{In} = \frac{kFn_{In}}{\eta} \quad (6)$$

$$Q_{Ga} = \frac{kFn_{Ga}}{\eta} \quad (7)$$

Where k is the number of transferred electrons, F is the Faraday constant (96485 C.mol⁻¹), n is the number of moles deposited (mol) and η is the plating efficiency. The latter variable will be considered 90% for both species.

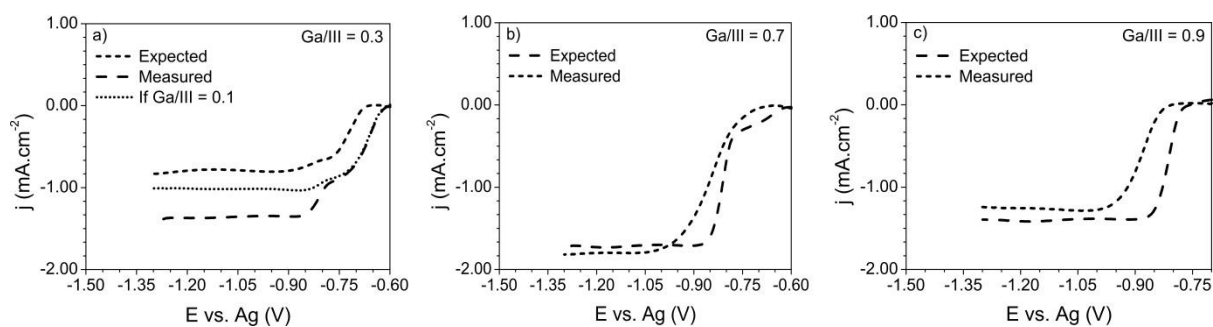
d) One can then write:

$$Q_{Ga} = Q_{In} \cdot \frac{n_{Ga}}{n_{In}} \Leftrightarrow Q_{Ga} = Q_{In} \cdot \frac{J_{Ga}}{J_{In}} \quad (8)$$

$$Q_t = Q_{In} \left(1 + \frac{J_{Ga}}{J_{In}} \right) \quad (9)$$

Equation 9 shows the total charge passed during deposition will be divided into 2 components, where the latter is related to Ga and includes a correction term J_{Ga}/J_{In} which ensures the expected stoichiometry of the deposit.

(2)



Expected and measured CVs of $\text{ChCl:U-GaCl}_3\text{-InCl}_3$ on a Mo electrode with $\text{Ga/III} =$ a) 0.3, b) 0.7 and c) 0.9. The expected CVs were calculated from the sum of the single element systems ChCl:U-GaCl_3 and ChCl:U-InCl_3 on a Mo electrode. All CVs were baseline corrected.