Title: **Electrodeposition of $CuInSe_2$**

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The present project was inspired by two projects: The NASA's GAS payload program by the growth of $CuInSe_2$ crystals in microgravity [1] and a not published work about electroplating of silver-selenide alloy [3].
Electrodeposition of $CuInSe_2$ has been investigated with the aim to produce low-cost thin film solar cells. Electrochemical synthesis of $CuInSe_2$ thin films from ternary electrolytes was carried out potentiostatic at various potentials. The potentials for the electrochemical deposition was chosen from studies of the polarization curves obtained from the ternary electroplating bath. A standard three-electrode cell with inert anodes of platinized titanium and a SCE reference electrode was used for the experiments in connection with a potentiostate. The substrates was 2x2x0.1 cm electropolished SS316 covered with a thin strike nickel layer (1 min., 10 A/dm^2 in a chloric acid strike nickel electroplating bath). The substrates was used as cathodes in the experiments. The deposited layers was investigated by SEM, EDS-analysis and LOM.
An aqueous solution [2] containing $CuSO_4/In_2(SO_4)_3 \cdot 5H_2O/SeO_2$ together with citric acid as complexing agent and ethanol for lowering the water activity, was used as source for the electrochemical deposition of the thin film and for obtaining polarization curves.

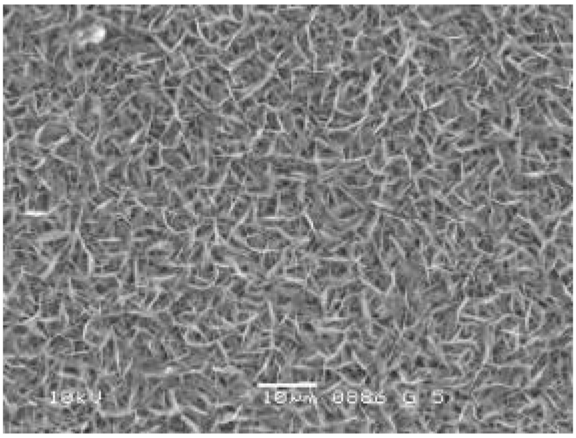

Fig 1: Surface view in SEM

For a sample held at a constant potential of -222 mV (SCE) between the working electrode and the reference electrode the as-deposited layer was a nearly stochiometric CuSe film with a dull darkblue/black look and composition of 49.8 atom% Cu and 50.2 atom% Se. The layer was powder-like on top and did not show mechanical stability. Figure 1 shows a SEM image of the surface structure.

The electrochemical bath [1] did not show chemical stability over time, because of precipitation at the anode. The precipitate was separated and analyzed by EDS. The composition was found being close in atomic ratio to In/Se/O 1/1/4. The electrochemical bath [1] was modified by adding H_2SO_4, and the experiments was continued with an electrochemical solution with good chemical stability.

The potentials for the potentiostatic deposition of the material were chosen to be -500 mV SCE (-278 mV SHE), -735 mV SCE (-513 mV SHE) and -1000 mV SCE (-778 mV SHE). The deposited layers had atomic compositions ranging from “30.5% Cu, 6.5% In and 63.0% Se” to “30.9% Cu, 19.2% In and 49.9% Se”. At the potential -735 mV (SCE) the deposited layers shows roughly stochiometric composition, which is confirmed by further experiment done in the area of the potential. The deposits were all dull and black having uniform powder-like appearance. Figure 2 show a topographic view obtained by SEM of the layer deposited at -1000 mV (SCE).

The study confirmed that a roughly stochiometric $CuInSe_2$ structure (having the exact atomic composition of $Cu_{1,2}In_{0,8}Se_2$) can be obtained by electrolytical deposition from an aqueous ternary bath with a potential of -735 mV (SCE).

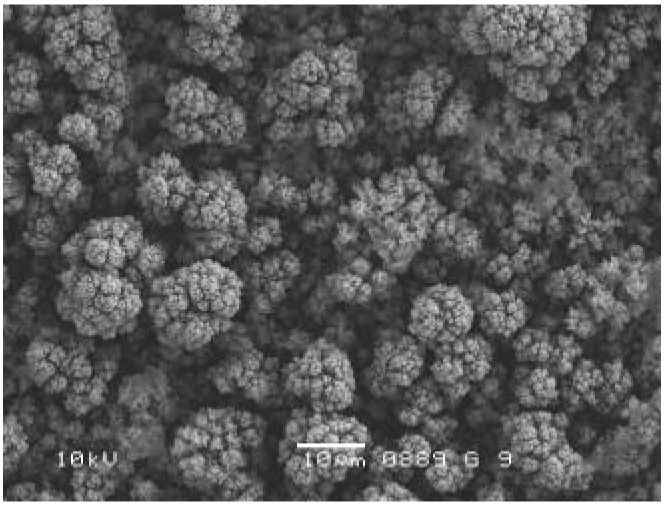

Fig. 2
SEM image of sample deposited at –1000mV (SCE).
The surface appears cauliflower like.

References:

[1] J. M. Ritter, R. Branly, E. Ackerman, R. Friedfeld, J. Bickham, A. Blitz, J. Faranda, C. Dahl, C. Theodorakis “An Interdisciplinary Payload to Perform Space Based Remote Sensing and to Measure Microgravity and Radiation Effects”, http://personal.mia.bellsouth.net/atl/j/o/jonfa/Payload.pdf, January 03, 2002

[2] Akshay Kamdar, “Thin film solar cell materials”, http://www.rit.edu/~bekpph/sem/Projects/Kamdar, January 07, 2002

[3] Per Moeller, Confidential research work, *Electroplating of silver-selenide alloys* (Institute for Product Development), 1983.