Cu-In-Ga electrodeposition on Mo substrate is carried out in acidic aqueous media. Subsequent selenization leads to Cu(In,Ga)Se$_2$ absorber for thin film solar cells. First, conditions to achieve one-step Cu-In-Ga electrodeposition are analysed. Then, Cu-In and Cu-Ga systems are studied. Cu-In electrodeposition is realized under diffusion-control conditions. For Cu-Ga system, first Cu(II) diffusion-controlled reduction occurs, followed by kinetic under-potential deposition (UPD) of Ga, leading to the formation of CuGa$_2$ compound. Finally Cu-In-Ga electrodeposition is investigated. For Cu-In-Ga system, CuGa$_2$ compound is not noticed, Ga-O codeposition is favored. In presence of citrate, Ga metal is deposited without oxide. Cu(II) and In(III) reductions are both diffusion-controlled, and Ga(III) kinetically controlled, allowing composition control at fixed pH and potential, but with dendritic growth. After selenization, complete Ga insertion is noticed in the formed chalcopyrite absorber. Solar cells with 4% efficiency were achieved despite porous morphology of the absorber.

**Introduction**

Solar cells based on Cu(In,Ga)Se$_2$ (CIGS) chalcopyrite absorbers have demonstrated high conversion efficiencies up to 19.9% (1). Electrodeposition is a major technology to achieve low-cost production of these absorbers (2). However, obtaining a semiconductor material with good properties is still a challenge. In particular, for Cu(In,Ga)Se$_2$ thin films, co-electrodeposition of the different elements is difficult, essentially due to Ga(III) low reduction potential and its affinity for oxygen. Its electrodeposition is then problematic in aqueous solutions. Several studies have already dealt with quaternary electrodeposition, often failing at inserting high In and Ga content in a satisfactory way in the deposit (3-4). On the contrary, stacked metallic electrodeposition followed by selenization enabled synthesis of 13.6% CIGS-based solar cells (5). In our case, Cu-In-Ga metallic codeposition is investigated.

Cu(II), In(III), Ga(III) have standard reduction potentials of -0.32, -1.00 and -1.19 V/MSE respectively. To achieve co-deposition, strong complexing or diffusion-control of Cu, and, in a least extent, of In, is necessary, to be able to deposit the three species at one potential. Cu-In-Ga layers of graded composition electrodeposited from complex thiocyanate electrolyte have already been investigated (6). In this study, simple aqueous baths without complexing agent are studied first. In this case, an acid pH, typically lower than 2.5 is necessary to avoid Ga and In oxide precipitation (along with
low concentrations of these elements). Effect of citrate complexation will then be discussed.

In a first approach, Cu-In and Cu-Ga electrodeposition will be investigated, then Cu-In-Ga electrodeposition on Mo substrate, leading to a metallic precursor of around 700 nm thickness. Subsequent selenization leads to CIGS absorber, with a thickness around 2 μm. Characteristics of the obtained absorber will be examined, with a focus on Ga insertion in the absorber material. Finally, solar cells are completed with CdS and ZnO, and electrically characterized.

**Experimental**

The solutions were prepared from analytical grade purity chemicals dissolved in high purity water (18.2 MΩ·cm). They contained copper sulfate, gallium sulfate, indium sulfate in mM concentrations and sodium chloride (0.4 M) as supporting electrolyte, with a pH close to 2.2. In certain conditions, sodium citrate is added in mM concentrations. The electrolytes were deaerated by argon bubbling prior to experiment and an argon pressure was maintained over the solutions during the experiment. If necessary, the pH was adjusted with concentrated hydrochloric acid or sodium hydroxide.

A three electrode cell with a 0.125 L capacity was used at room temperature. The reference electrode was a saturated mercurous sulfate electrode (MSE, E° = 0.65 V/NHE). The anode was a Pt coil. The substrate was a 6 cm² electrode made of glass covered by sputtered Mo layer (500 nm) provided by Saint-Gobain. Prior to each experiment, the Mo substrate was cleaned in 25% ammonia solution for 15 min, rinsed under flowing high purity water. For some experiments, a Cu layer (200 nm) was pre-electrodeposited from a citrate bath.

A Biologic VSP2 potentiostat was used for the electrochemical experiments. Electrodepositions were carried out typically at a given potential of –1.5 V/MSE, to reach a thickness of around 700 nm. Cathodic potentiostatic polarizations were carried out from open-circuit potential (OCP) to –2.2 V/MSE, with a scan rate of 5 mV/s.

Selenization of the metallic precursor was achieved by Rapid Thermal Annealing using elemental Se powder in a closed furnace at temperatures around 600°C.

The chemical analysis of the deposited/annealed layers was carried out by means of X-Ray fluorescence (XRF, Fischerscope). The surface morphology was examined by field emission gun-scanning electron microscope (FEG-SEM, Leo Supra) (secondary electron in-lens observation, 3-5 kV, 4-7 mm working distance) coupled with an energy dispersive spectroscopy (EDS) detector. The crystalline structure was examined by X-ray diffraction (cobalt anticathode λKα1 = 0.17889 nm). Raman microprobe measurements were made using a HR800-UV Horiba-Jobin Yvon spectrometer, coupled with an Olympus metallographic microscope (frequency cut-off at 42 cm⁻¹), and using the red line of an He-Ne laser (λ = 632.8 nm) as excitation light.

CdS thin buffer layer with a thickness of about 50 nm was chemically deposited onto the CIGS layer. The solar cell structure was completed with 80 nm intrinsic ZnO and 400 nm Al₂O₃:ZnO top-window layer by radio-frequency (RF) sputtering. Electrical
parameters of the solar cells were measured using a solar simulator with AM 1.5 at the power density of 100 mW/cm².

Results and discussion

Cu-In-Ga electrodeposition

Voltammetric study. Figure 1 presents cathodic polarization curves in solution for several pHs. The curves show a current plateau, whose magnitude increases with decreasing pH. The high current densities noticed (higher than 5 mA.cm⁻²) are characteristic of proton diffusion wave, due to high proton diffusion coefficient (9.3.10⁻⁵ cm²/s compared to less than 1.5.10⁻⁵ cm²/s for the metallic ions used) and low pH. In the potential range necessary for Cu-In-Ga co-electrodeposition (lower than the standard potentials of the elements), quite important H₂ evolution is taking place, lowering the Faradaic efficiency. A pH value of 2.2 is chosen for subsequent experiments as a compromise, enabling to limit hydrogen evolution, and a sufficient solubility of Ga and In species. Potentiostatic electrodeposition has been studied at −1.5 V/MSE, enabling high Ga content in the electrodeposit.

Figure 1. Cathodic polarization curves in Cu-In-Ga solution at different pHs (1 mM Cu(II), 0.5 mM In(III), 20 mM Ga(III), scan rate: 5 mV/s). In grey is the potential range necessary for Cu-In-Ga co-electrodeposition.

Figure 1. Cathodic polarization curves in Cu-In-Ga solution at different pHs (1 mM Cu(II), 0.5 mM In(III), 20 mM Ga(III), scan rate: 5 mV/s). In grey is the potential range necessary for Cu-In-Ga co-electrodeposition.

Cu-In electrodeposition. The Cu-In system has been extensively studied before (7-8). On the basis of reference (8), at these potential and concentrations, diffusion-controlled deposition of both elements is reached. As a consequence, the In/Cu ratio in the film is monitored through the In(III)/Cu(II) ratio in solution (not shown).

Cu-Ga electrodeposition. As for Cu-In electrodeposition, diffusion-controlled deposition is achieved for Cu (same potential and range of concentrations). This leads to dendritic growth, because of high overpotentials (higher than 800 mV) for Cu (9). Electrodeposited thickness is found proportional to Cu(II) concentration (Figure 2 (a)). Ga(III) reduction is realized at relatively high concentrations and low overpotentials, so
kinetically controlled electrodeposition of Ga should be favored, induced after Cu(II) reduction, as no Ga deposition is noticed without Cu in solution.

Figure 2. (a) XRF composition and thickness analysis as a function of Cu(II) concentration in the electrodeposition bath; 20 mM Ga(III), 0.05-4 mM Cu(II), E = -1.5 V/MSE, pH 2.2 (b) X-Ray diffractogram of Cu-Ga electrodeposit on Cu/Mo substrate

Chemical analysis (Figure 2(a)) shows a constant atomic ratio Ga/Cu equal to 2 with varying Cu(II) concentrations in the range 0.25-3 mM. Little O insertion is noticed in that film (EDS analysis: 9 at%). XRD (Figure 2 (b)) confirms that CuGa₂ is present (JCPDS file n° 25-0275), in this case on Cu/Mo substrate. So deposition of Ga occurs through compound formation, which can shift slightly Ga deposition to more positive potentials (as calculated: 50 mV, with a Gibbs Energy for CuGa₂ formation of 27 kJ/mol). Although the potential applied should be cathodic enough to enable Ga reduction, this reaction may be kinetically very slow and therefore not be noticed in these experiments. More experiments with varying potentials are in progress to confirm this. A two-step mechanism can be proposed: first Cu(II) reduction under diffusion control [1], then CuGa₂ compound formation, kinetically controlled [2]. The possible effect of chloride ions on Cu(II) reduction, through Cu(I) stabilization, is not taken into account here due to the high overpotential considered.

\[
\text{Cu(II) + 2 e}^- \rightarrow \text{Cu} \quad [1]
\]

\[
2\text{Ga(III) + 6 e}^- + \text{Cu} \rightarrow \text{CuGa}_2 \quad [2]
\]

**Cu-In-Ga electrodeposition.** On the diffractogram (Figure 3), almost no definite compound deposition is noticeable. Only weak Cu-In alloy peak is measured (possibly Cu₂In; JCPDS file n° 42-1475), although there is a high amount of Ga in the precursor. On SEM pictures (Figure 4 (a)) a compact oxide layer can be seen at the basis of the electrodeposit, that EDS reveals to be a Ga-O phase, amorphous as it is not revealed by XRD. Using citrate as a complexing agent (Figure 4 (b)), only pure Ga electrodeposition is noticed, in the shape of spheres, due to the low melting point of Ga (29.8°C) (EDS detector on these spheres does not reveal any significant amount of O).
Figure 3. XRD of electrodeposited Cu-In-Ga; from a bath containing: 1 mM Cu(II), 0.5 mM In(III), 20 mM Ga(III), pH 2.2-2.3. Composition: Cu/(In+Ga)=1.04; Ga/(In+Ga)=0.48.

(a) (b)

Figure 4. SEM images of Cu-In-Ga electrodeposits: (a) no complexing agent, E = -1.4V/MSE and (b) 3 mM citrate, E = -1.5 V/MSE; 1 mM Cu(II), 0.5 mM In(III), 20 mM Ga(III), pH 2.2-2.3; at the right of the pictures, EDS analysis of the circled area.

To understand this behaviour, speciation diagrams of Ga in aqueous solution were simulated using the Medusa/Hydra software package (Figure 5). At the working electrode, proton reduction causes a small pH increase. In 4 mM Ga(III) solution, when pH goes over 2.2 (which is the working pH), GaOOH becomes the predominant species and leads to precipitation; whereas with 3 mM citrate, Ga(cit) is then predominant, whatever pH around 2-3, and then limits Ga-O co-deposition. In the real solution, Cl⁻ and SO₄²⁻ ions tend also to complex Ga³⁺ (to a least extend than citrate, and at pH below 2.5), and contribute also to reduce Ga-O codeposition.

To conclude on this electrodeposition part, Cu and In are deposited mainly by diffusion control, as for the Cu-In system, so the In/Cu ratio in the film is controlled through the In/Cu in solution; elemental Ga deposits kinetically, with citrate in solution: the Ga content in the film is controlled through the Ga amount in solution. This leads to the schematic diagram (Figure 6), where composition in the film is linked to composition in solution, in the conditions of pH and potential used. That enables to control the deposit composition, for example to synthesize Cu rich or Cu poor precursors, that will result after selenization in absorbers with different optoelectronic properties.
Figure 5. Predominance diagrams of 4 mM Ga(III) in H2O in the pH range 1.5-3 (a) without and (b) with presence of 3 mM citrate.

Figure 6. Schematic composition diagram corresponding to pH 2.2, E = -1.5 V/MSE, 45 min deposition.

Characterization after selenization of the CIGS absorbers

The XRD diagram (Figure 7(a)) shows Cu(In,Ga)Se2 chalcopyrite phase (JCPDS file n°40-1487, 35-1102 and 35-1101 for CIGS chalcopyrite with 0, 0.3, 0.6 Ga/(In+Ga) respectively), with part of the substrate selenized as MoSe2 (JCPDS file n°29-0914). The Ga insertion in the chalcopyrite is emphasized through the shift of the peaks (Figure 7(b)), shift that does not occur with an electrodeposition in the absence of citrate where Ga segregates as an oxide phase. Using Vegard’s law, i.e. assuming a linear relationship between the crystal lattice parameter and the concentrations of the constituent elements (here, In and Ga), the Ga content in the chalcopyrite phase can be obtained, and was comparable to the Ga content measured by XRF, showing complete Ga insertion in the chalcopyrite phase.
Figure 7. (a) XRD pattern of a selenized sample, corresponding to average composition of CuIn$_{0.65}$Ga$_{0.35}$Se$_2$. (b) zoom on (112) peak, showing Ga insertion related shift. Values indicate % Ga/(Ga+In) calculated using linear extrapolation of the JCPDS file peaks.

Micro-Raman analysis (Figure 8) on a cross section confirmed these results, with presence of the A1 chalcopyrite mode. A slight shift of this mode is showing Ga enrichment towards the back contact. MoSe$_2$ E1/A1 modes are present, along with elemental Se at the CIGS/MoSe$_2$ interface, and slight Cu$_x$Se binary phase at the surface.

Figure 8. Micro-raman spectra along a CIGS absorber cross-section: continuous line: at the top of the absorber, dashed line: near to the CIGS/MoSe$_2$ interface, on CIGS side, dotted line: on MoSe$_2$ side; (a) whole spectra; (b) zoom at 170-175 cm$^{-1}$ showing shift related to Ga enrichment.

The electrodeposit structure was dendritic (Figure 9(a)), due to Cu deposition under diffusion control at high overpotentials, as seen before. This morphology could actually enable a quicker selenization, due to the high surface-to-volume ratio. Selenization enabled to form more compact films, with crystals of about 500 nm, but porosity
remained (Figure 9(b)). MoSe₂ sub-layer was more than a micron-thick, which is detrimental for the overall conversion efficiency of the solar cell. The structure of the complete device is presented in Figure 9(c), with CdS and ZnO layers.

![SEM cross-section picture of a sample](image)

Figure 9. SEM cross-section picture of a sample (a) as electrodeposited (Mo/Cu-In-Ga); (b) annealed under Se atmosphere (Mo/MoSe₂/CIGS); (c) cell completed with CdS/ZnO.

**Device results**

Solar cells with 4.06% efficiency were achieved (V<sub>oc</sub> 415 mV; j<sub>sc</sub> 23.5 mA/cm²; FF 41.7%; area 0.1 cm²). The absorber composition was: Cu/(In+Ga)=0.8; Ga/(In+Ga)=0.37, which is comparable to the best efficiency CIGS solar cells. Efficiency achieved in this study is comparable to previous devices based on Cu-In-Ga electrodeposition in a high complexing media, that demonstrate 4.35% efficiency (6). These results are promising, considering the nanostructured absorber, that induces a highly developed interface, so higher recombination probability through interface defects: high efficiency improvement is expected when optimizing the morphology.

**Conclusion**

One-step electrodeposited Cu-In-Ga thin films with composition control have been achieved. In particular, no Ga-O electrodeposition is noticed in adequate conditions, enabling selenization without high reducing atmosphere (no toxic H<sub>2</sub>Se annealing) contrary to previous studies (4), and complete Ga insertion in the chalcopyrite absorber. However, compact films are required for better efficiency material, further studies are in progress to reduce porosity during the electrodeposition step and optimize annealing.

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References


