

## Effects of non-complexing additives on electrodeposited Cu(InGa)Se<sub>2</sub> (CIGSe) thin film

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Thin film of Cu(InGa)Se<sub>2</sub> (CIGSe) is a very promising semiconductor material as absorber layers for solar cell [1] and photoelectrochemical hydrogen production application [2]. The band gap of this quaternary semiconductor varies between 1.04 eV and 1.68 eV (1.04 eV of the CuInSe<sub>2</sub> and 1.68 eV of the CuGaSe<sub>2</sub>). Amid various fabrication methods available, vacuum based techniques promote the growth of high quality films, but they are expensive and difficult to scale up. Thus, electrodeposition may be the most effective alternative to these methods [1]. Several studies on electrodeposition of CIGSe thin film have been reported, but there are few studies about the effects of non-complexing additives on electrodeposited films. The use of additives in electrodeposition can to cause interesting effects on the growth and structure of the films. Glycerol (GLR) and Triton 100-X (TRT) have been used as nonionic and non-complexing additives in alloys plating, resulting in higher deposition efficiency and improvement in the microstructure of deposits [3,4]. Cyclic voltammetric (CV), Raman spectroscopy, Energy Dispersive X-ray (EDX) and UV-vis spectroscopy, Scanning Electron Microscopy (SEM), Photocurrent (PC) and Mott-Schottky analyses were carried with the aim to gain an insight into the effects of non-complexing additives (GLR and TRT) on electrodeposited CIGSe thin films.

Electrochemical experiments were carried out in a three-electrode cell configuration with a fluorine-doped tin oxide (FTO) coated glass as working electrode, a Pt-plate as auxiliary and a Ag/AgCl/Cl<sup>-</sup>(sat. KCl) as reference electrodes. The electrolytic bath contained 4 mM CuSO<sub>4</sub>, 2 mM In<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 10mM Ga<sub>2</sub>(SO<sub>4</sub>)<sub>3</sub>, 8 mM SeO<sub>2</sub>, 0.3 M Na<sub>2</sub>SO<sub>4</sub> / H<sub>2</sub>SO<sub>4</sub> - pH 1.5 (as supporting electrolyte) and different additive concentrations (0.1, 1.0, 10 mM). The electrodeposition of the all films was performed in a stationary bath at -0.80 V for 15 min at 25 °C. The PC and Mott-Schottky experiments were performed in 0.1 M NaNO<sub>3</sub>. From CV measurements, it was observed an increase in the peak current in the presence of additives, which can be associated with throwing power effect. The Raman spectra of the CIGS films showed an enlarged peak located at about 174-184 cm<sup>-1</sup>, attributed to the A1 symmetry mode of vibration of CuInSe<sub>2</sub>/CuGaSe<sub>2</sub>/CIGSe (CuInSe<sub>2</sub> = 174 cm<sup>-1</sup> and CuGaSe<sub>2</sub> = 184 cm<sup>-1</sup> [5]), and a defined peak associated to Se at about 240 cm<sup>-1</sup> [5]. For the films electrodeposited from bath containing 0.1 mM of additives, it was also observed a peak at about 258 cm<sup>-1</sup> [5], which can be related to presence of Cu<sub>x</sub>Se phases. The results of the characterizations obtained by EDX, Mott-Schottky, UV-vis and PC are presented in the Table 1. It can conclude that the CIGSe films are In-rich and with low Ga content. However, the Ga content was sufficient to shift the band gap (E<sub>g</sub>) from 1.04 eV (CuInSe<sub>2</sub> band gap) to 1.33-1.35 eV, indicating the formation of the CIGSe phase. The films electrodeposited from solution containing 10 mM of additives showed more positive flat band potential (E<sub>FB</sub>) and low photocurrent. It should be considered whether this reduction in photocurrent can be interference of the n-type FTO substrate, as reported in previous work [6]. Nevertheless, the more positive E<sub>FB</sub> is ideal to application in photoelectrochemical hydrogen production. The low

photocurrent of these films can be also associated with the increase of defects or of the recombination surface, compared with the others films. Annealing treatment can improve the photocurrents performed by electrodeposited CIGSe films. Mott-Schottky analysis also proved that all films were p-type semiconductors.

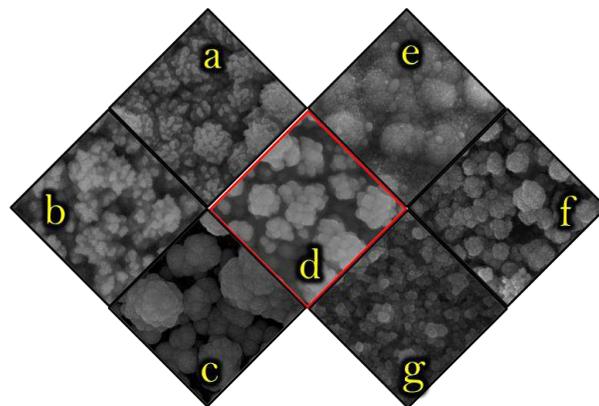
**Table 1.** Physical properties of the electrodeposited CIGSe thin films with electrolytic bath containing different concentration of GLR and TRT.

[Additives] (mM)	%atm				E <sub>FB</sub> (V*)	E <sub>g</sub> (eV)	PC** (μA/cm <sup>2</sup> )	
	Cu	In	Ga	Se				
GLR	0.1	8	32	1.4	59	0.33	1.34	2.16
	1.0	11	29	0.9	58	0.31	1.34	4.35
	10	13	23	1.0	63	0.72	1.33	1.25
0	10	28	0.7	61	0.42	1.34	2.74	
TRT	0.1	5	30	0.5	65	0.46	1.35	2.85
	1.0	19	20	1.5	59	0.25	1.35	1.93
	10	18	20	1.4	60	0.74	1.34	1.13

\* vs. Ag/AgCl/Cl<sup>-</sup>(sat. KCl) electrode. \*\*Solar simulator, AM 1.5G lens and 100 mW cm<sup>-2</sup>.

The main effect of the additive presence was observed in the microstructure of the films. Figure 1 shows the SEM images for films electrodeposited from electrolytic bath containing different concentrations of additives.

**Figure 1.** SEM images of the CIGSe thin films prepared from electrolytic bath containing: (a) 0.1 mM GLR, (b) 1 mM GLR, (c) 10 mM GLR, (d) 0 mM of additives, (e) 0.1 mM TRT, (f) 1 mM TRT and (g) 10 mM TRT.



It can be observed that the presence of additives in the deposition bath causes change in the grain size of the films. The electrodeposits obtained from 10 mM GLR showed non-compact morphology and with large grains. This can explain its low photocurrent, since there is limited contact between the grains to transport the charge carriers. In future work, it is interesting to evaluate the effect of this morphology changes in the photocatalytic properties of these films.

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### References

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