CIS(CIGS) thin films prepared for solar cells by one-step electrodeposition in alcohol solution

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Abstract: The precursors of CIS and CIGS thin films were prepared by one-step electrodeposition in alcohol solution and then annealed in Ar atmosphere at 550 ℃ for 30min. The influences of deposition potentials and salt concentrations on the morphology and composition of the thin films were studied in details. The films were characterized by X-ray diffraction(XRD), scanning electron microscopy(SEM), and energy-dispersive X-ray spectroscopy(EDS). The results show that annealed films have pure CIS or CIGS phases with good crystallization and the morphology of the films are very uniform and dense. The high quality precursor films were obtained using optimized deposition parameters. Moreover the electrodeposition mechanism of CIS thin films was briefly discussed.

1. Introduction
Thin layers of CuInSe2 (CIS) and CuIn1-xGa_xSe2 (CIGS) are considered as the most promising material for low cost and high-efficiency solar cells, because of their high absorptivity (>10^5cm^-1) and stability against photo-degradation. Solar cells based on CuInSe2 (CIS) and Cu(In,Ga)Se2 (CIGS) have reached conversion efficiencies as high as 18.8% and 19.5% [1]. Several methods for preparation CIS(CIGS) absorber films have been reported, such as co-evaporation [2], sputtering and selenization [3], and electrodeposition [4]. Until now, co-evaporation is the most successful technique for the preparation of CIS(CIGS), which achieved the highest efficiency CIGS-based solar cells, but it seems difficult to scale up nowadays. In all these methods, Electrodeposition technique is potentially suitable to obtaining good-quality, large-area CIGS precursor films. CIS and CIGS films have been reported by several groups with the so-called one-step electrodeposited route [5], and the NREL group has also demonstrated an efficiency of 15.4% used a hybrid approach consisting of the “adjustment” of the electrodeposited precursor by evaporating 300nm Ga and 700nm In [6]. However, in aqueous deposition baths, In and Ga deposition efficiencies are limited by H^+ reduction, which causes composition inhomogeneity and the pinholes in the film and hence limits the cell efficiencies. For this reason, the present study examined the feasibility of using the alcohol as solvent for the deposition of Cu-In-Se and Cu-In-Ga-Se precursor films.
2. Experimental details
Electrodeposition of CIS and CIGS precursors was carried out potentiostatically in a three electrode cell in which the substrate was Mo foil, the counter was Pt gauze, and reference electrode was saturated calomel electrode (SCE). A Zahner IM6ex Electrochemical workstation was used for the preparation. The electrodeposition was performed from a bath containing 0.005M CuCl₂, 0.05M InCl₃ (0.03M GaCl₃), 0.025M H₂SeO₃, and 0.1M LiCl dissolved in alcohol. In the experiments, the applied potential was -0.6V for CIS deposition and -1.6V for the CIGS deposition. The pH of the chemical bath was adjusted between 1.9 and 2.2 by adding drops of concentration HCl. The obtained thin films were rinsed with bi-distilled water and dried under a nitrogen flux, then thermal annealed at 550°C for 30min in Ar atmosphere.

The X-ray diffraction (XRD) patterns of the precursors and annealed thin films were characterized by glancing angle X-ray diffraction (GAXRD) using X'Pert PRO X-Ray MPD employing CuKα radiation (λ=1.54 Å). The surface morphology was investigated using a JEOL JSM-6380LV SEM. The composition of the film was analyzed with an OXFORD-IE350 energy dispersive spectrometer (EDS) attached to SEM.

3. Electrodeposition studies in the CIS(CIGS) system
The electrodeposition of multinary semiconductors containing more than two constituent elements was expected to be more complex owing to a large difference in the deposition potentials of the elements. During CIS and CIGS film formation, the general reaction occurring at the working electrode surfaces was as follows:

\[
\begin{align*}
\text{Cu}^{2+} + \text{In}^{3+} + 2\text{H}_2\text{SeO}_3^- + 13\text{e}^- + 8\text{H}^+ & \rightarrow \text{CuInSe}_2 + 6\text{H}_2\text{O} \\
\text{Cu}^{2+} + (1-X) \text{In}^{3+} + X\text{Ga}^{3+} + 2\text{H}_2\text{SeO}_3^- + 13\text{e}^- + 8\text{H}^+ & \rightarrow \text{Cu(In, Ga)}\text{Se}_2 + 6\text{H}_2\text{O}
\end{align*}
\]

This is an ideal situation but in practice it is a combination of electrochemical and chemical reactions that occur at certain pH values. The electrochemical aspects are becoming even more complex, with the possibility of forming either the elements in their elemental form, or as binary compounds (Cu₅Se, In₂Se₃, Ga₂Se₃) in addition to the desired ternary CIS phase and CIGS. It can be seen in XRD patterns of precursor (Fig.1), several binary compounds have been founded. These binary compounds formed compliance Kroger’s mechanism [7].

For long time the formation of the quaternary phase with gallium by one step electrodeposition was a difficult problem, because the Ga³⁺ was far more difficult deposition from others. In our study, this serious bottleneck seems to have been overcome by electrodeposition in alcohol solution, the alcohol solution provide a wide electrochemical window, so CIGS precursor films could be deposition at -1.6V. Alcohol also act a surface modifiers which affect markedly the quality of the films or electrochemical kinetics.

![Figure 1. XRD patterns of as-deposited CIS thin film](image1)

![Figure 2. XRD patterns of CIS and CIGS films after annealing](image2)
4. Results and discussion

Fig. 2 shows the XRD patterns of CIS and CIGS films after annealing at 550°C for 30 min in Ar atmosphere, and they were indexed with the tetragonal chalcopyrite structure. No detectable secondary phase could be seen. The strongest diffraction peak around $2\theta = 26.74^\circ$ corresponds to diffraction from the (112) planes while the other peaks at $2\theta = 44.35^\circ$, and $52.74^\circ$ are due to diffraction from the (220) plus (204), and the (312) planes, respectively. The small positive shift in $2\theta$ value of (112) peak for the CIGS sample indicated that gallium takes partly the place of indium in the tetragonal CIS phase and then results in the tetragonal CIGS phase.

![Fig. 3. SEM images of CIS and CIGS film before annealing (a.CIS, b.CIGS)](image)

![Fig. 4. SEM images of CIS and CIGS film after annealing (a.CIS, b.CIGS)](image)

The as-deposited CIS film consists of grains with the order of 500 nm. The grain size is generally improved with a second processing step, where the material is annealed at higher temperature. And the thin film was dense and compact and shows a smooth surface morphology (Fig. 4). The SEM images of CIGS thin films (Fig. 4) showed large grains (~2 μm). From these images we can infer that the surface roughness appear to decrease as grain size get larger with higher temperature. From the above analysis it is concluded that the annealing process is important to fabricate CIS(CIGS) films.

![Fig. 5. EDS patterns of CIS and CIGS films after annealing](image)
Fig. 5 shows EDS patterns of CIS(CIGS) thin films after annealing. The EDS results show that the films composition were only slightly Cu-poor with respect to the anticipated composition of CIS(CIGS). The [Ga] to ([Ga]+[In]) ratio for the CIGS film is 0.25. This ratio span the range necessary to achieve CIGS band gaps which are optimized for the terrestrial solar spectrum.

5. Conclusions
One-step electrodeposition of CIS(CIGS) thin films in alcohol solution was studied in this article, satisfactory control of film composition was achieved by the choice of deposition potential and simple combinatorial variation in bath concentrations. An annealing process in Ar atmosphere was developed for CIS(CIGS) growth. The results indicate CIS(CIGS) thin films little deviate from the ideal stoichiometric one and single chalcopyrite structure. The SEM pictures show CIS(CIGS) thin films have uniform grain size and compact. Further work is in progress to achieve the incorporation of higher levels of gallium and better definition of the electrochemical and annealing process so that the process can be developed to produce absorber layers for efficient cells.

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