The Phase and Morphology of CuInSe₂ Film Prepared by One-Step Electrodeposition

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crossref http://dx.doi.org/10.5755/j01.ms.23.4.17447

Received 18 January 2017; accepted 05 March 2017

CulnSe₂ with chalcopyrite structure has become one of the most promising photoelectric materials for its high optical absorption coefficient and conversion efficiency. Electrodeposition has the advantages of low cost and easy operation. CuInSe₂ films were prepared by one-step electrodeposition with CuCl₂·2H₂O, InCl₃ and SeO₂ as raw materials. Cyclic voltammetry curves of the solutions were tested by electrochemical workstation. The phases of product thin films were analyzed by X-ray diffraction (XRD) and the surface morphology was characterized by scanning electron microscope (SEM). Experimental results show that the continuous, uniform and dense CuInSe₂ thin films can be obtained under conditions of deposition potential -0.5 V and sodium citrate as complexing agent with concentration of 5mmol/L. The XRD diffraction peaks of CuInSe₂ thin film are corresponding to the crystal planes of (112), (220) and (312) respectively.

Keywords: CulnSe₂, thin film, photoelectric, one-step electrodeposition.

1. INTRODUCTION

CulnSe₂ belongs to I-III-VI group and has chalcopyrite structure with band gap about 1.04 eV. It is a semiconductor material with a direct band gap and its energy gap covers a wide range of solar spectrum and can be adjusted within the scope of 1.0 ~ 1.5 eV through doping with other elements such as Ga and Al. CulnSe₂ has high thermal stability, better resistance to radiation and high optical absorption coefficient of about 10⁶ cm⁻¹. Moreover, its conversion efficiency of CulnSe₂ reached 19.2 %. Therefore, CulnSe₂ has become one of the most promising photoelectric materials [1].

The methods for preparing CulnSe₂ photoelectric materials include sputtering [2, 3], solvothermal [4], chemical bath deposition [5] and electrodeposition [6, 7], etc. As a ternary photoelectric material, CulnSe₂ has a strict demand of manufacturing process. For instance, the properties of precursor [8] such as composition, reaction time and heat treatment conditions [9, 10] have a significant impact on the performance of CulnSe₂. Therefore, it is necessary to choose a suitable method to obtain stable CulnSe₂ photoelectric materials. The uniform, dense thin films can be prepared at room temperature by electrodeposition with advantages of non-vacuum and low cost [11, 12]. Under the action of the electric field, the redox reaction occurs between the cations and anions, and the films are obtained by electrodeposition on the substrate.

The films of ternary compound CulnSe₂ prepared by electrodeposition are often treated by selenization for improving the composition, crystallinity and photoelectric performance [13]. Since the chalcopyrite crystal structure is required for photoelectric film, it needs to make the amorphous film crystallizing by heat treatment. In the study for preparing CulnSe₂ photovoltaic materials, researchers frequently adopt the assisted electrodeposition [14] and multi-step method [15, 16] to obtain a ternary compound CulnSe₂, and the works of studying one-step electrodeposition for CulnSe₂ are relatively few [17], so one-step electrodeposition for photoelectric material should be investigated further.

In this work, the electrochemical properties of the electrodeposition solution were analyzed by cyclic voltammetry curves, and then the CulnSe₂ films were prepared with CuCl₂·2H₂O, InCl₃ and SeO₂ as raw materials. The effect of electrodeposition process such as deposition potential and the concentration of complexing agent on the phase and morphology of CulnSe₂ thin film were studied.

2. EXPERIMENTAL DETAILS

Solution preparation: 6 mmol/L CuCl₂·2H₂O, 8 mmol/L InCl₃, 6 mmol/L SeO₂ and a certain concentration of complexing agent with sodium citrate, sodium gluconate, potassium sodium tartrate or ethylenediamine tetraacetic acid. The chemicals used in this work were supplied by National Pharmaceutical Chemical Reagent Co., Ltd. CulnSe₂ thin films were deposited at different potentials for 30 min with different concentrations of the complexing agent on the glass substrates with SnO₂ conducting layer after pretreatment. The size of the glass substrate is 40 mm × 20 mm × 4 mm.

The cyclic voltammetry curves were carried out on the PARSTAT 2273 electrochemical workstation with a scan...
rate of 10 mV/s and a range of -1~ 0 V; the phases of product samples were analyzed by X-ray diffraction (XRD) on the Bruker D8 XRD system with Ni filtered Cu-Kα (λ=1.5059 Å). The surface morphology of the product films was observed using scanning electron microscope (SEM) with a model of JSM-6380LA.

3. RESULTS AND DISCUSSION

3.1. The effect of different complexing agent on the electrochemical performance of solution

The complexing ability of different complexing agents to metal ions in solution was studied. The plating solution consists of 6 mmol/L CuCl₂·2H₂O, 8 mmol/L InCl₃, 6 mmol/L SeO₂ and 5 mmol/L complexing agent which was selected as sodium citrate, sodium gluconate, potassium sodium tartrate or ethylenediamine tetraacetic acid.

Fig. 1 shows the cyclic voltammetry curves of solution containing various complexing agents. It indicates that the effects of different complexing agents on solution are various. The beginning of reduction and oxidation even the reduction and oxidation potentials is changed in the solutions with different complexing agents. When the complexing agent is sodium citrate, the oxidation and reduction potentials both move negatively, and the oxidation potential moves more obviously which moves by 0.22 V as opposed to ethylenediamine tetraacetic acid. The difference of oxidation-reduction potential has the minimum value when the complexing agent is sodium citrate, which is more conducive to achieve co-deposition, so it chooses sodium citrate as complexing agent for later experiments. According to cyclic voltammetry curves it was found that the ion discharge potentials were among – 0.3 ~ – 0.8 V, so it selected – 0.3 ~ – 0.8 V as the potential range in experiments.

![Cyclic Voltammetry Curves](image)

**Fig. 1.** The cyclic voltammetry curves of the solution with different complexing agents: a – ethylenediamine tetraacetic acid; b – potassium sodium tartrate; c – sodium gluconate; d – sodium citrate

3.2. The effect of electrodeposition process on phase formation of CuInSe₂ thin films

3.2.1. The effect of deposition potential on phase formation of CuInSe₂ thin films

Fig. 2 shows the phase of target product CuInSe₂ except the phase of SnO₂ conducting layer on glass substrates can be obtained when the deposition potentials are – 0.3 V, – 0.5 V, – 0.6 V and – 0.8 V according to the standard PDF card No.87-2265. The films with different compositions can be prepared under different deposition potentials. There are SnO₂ and CuSe which are obtained when the deposition potential is – 0.3 V. The main peaks of the product film is preferably corresponding to the CuInSe₂ peaks when the deposition potential is – 0.5 V, so CuInSe₂ compounds are obtained by deposition method according to the standard PDF card No.87-2265 for XRD. It indicates that the CuInSe₂ thin films can be obtained by electrodeposition under – 0.5 V. When the deposition potential is – 0.6 V, the product has a high diffraction peak intensity of Cu₂Se₂ phase in addition to CuInSe₂ phase. According to the experimental results, the phase formation of thin films can be affected by the deposition potential. The optimal deposition potential is – 0.5 V in this experimental system.

![XRD Patterns](image)

**Fig. 2.** XRD patterns of the CuInSe₂ films under different deposition potentials and other experimental conditions of 6 mmol/L CuCl₂·2H₂O, 8 mmol/L InCl₃,6 mmol/L SeO₂, 5 mmol/L complexing agent, Deposition time 30min and the bath pH 2.0

3.2.2. The effect of concentration of sodium citrate on phase formation of CuInSe₂ thin films

Fig. 3 shows XRD patterns of the CuInSe₂ thin films that were obtained by adding different concentrations of sodium citrate.

![XRD Patterns](image)

**Fig. 3.** XRD patterns of the CuInSe₂ thin films under different concentrations of sodium citrate and other experimental conditions of 6 mmol/L CuCl₂·2H₂O, 8 mmol/L InCl₃,6 mmol/L SeO₂.
When the concentration of sodium citrate is 5 mmol/L, diffraction peaks of CuInSe₂ appear in the XRD patterns, it indicates that CuInSe₂ was obtained. When the concentration of sodium citrate is 25 mmol/L CuSe phase appeared. When the concentration of sodium citrate is 50 mmol/L Cu₃Se₄ was obtained. When the concentration is greater than 5 mmol/L, the films surface appears gully and becomes rougher with the increasing concentration of sodium citrate. When the concentration of sodium citrate is up to 20 mmol/L, the powder deposition phenomenon occurs on the films, the binding force of the films with the substrate becomes weak and shedding occurs easily. Therefore, it is more conducive to form the desired product when the concentration of complexing agent sodium citrate, when the deposition potential is −0.5 V, the film surface becomes denser, the film becomes more uniform, its flatness and compactness have increased. Therefore, the optimal deposition potential can be chosen as −0.5 V for preparing CuInSe₂ thin films.

4. CONCLUSIONS

Electrochemical properties of the solutions were tested by electrochemical workstation. Important experimental conditions are selected as follows: Sodium citrate as a complexing agent, −0.3 ~ −0.8 V as the deposition potential range and 5 mmol/L as the complexing agent concentration. CuInSe₂ thin films were prepared by one-step electrodeposition with CuCl₂·2H₂O, InCl₃, SeO₂ as raw materials and the 5 mmol/L complexing agent sodium citrate. When the deposition potential is −0.5 V and the deposition time is 30 min, the continuous, dense, uniform CuInSe₂ thin films can be obtained. The XRD diffraction peaks of CuInSe₂ thin film are corresponding to the crystal planes (112), (220) and (312) respectively.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No.51272140).

REFERENCES


