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Pulse-plating electrodeposition and annealing treatment of $CuInSe_2$ films

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Abstract: $CuInSe_2$ (CIS) thin film was prepared on molybdenum substrate using pulse-plating electrodeposition in aqueous solution. The most suitable pulse potential range for co-deposition is found to be from −0.55 to −0.75 V (vs SCE) from linear potential scanning curve. The electrodeposited films were characterized by X-ray diffractometry (XRD), scanning electron microscopy(SEM) and energy dispersive X-ray analysis (EDS). The annealing effects on electrodeposited precursors were investigated. And the influence of pulse parameters on film quality was studied. The chalcopyrite phase $CuInSe_2$ films with smooth surface and stoichiometric composition are obtained at a pulse potential from −0.65 to −0.7 V (vs SCE), a pulse period of 1−9 ms with a duty cycle of 33% and annealing treatment.

Key words: $CuInSe_2$; thin films; pulse-plating electrodeposition; annealing; solar cells

1 Introduction

Copper indium diselenide ($CuInSe_2$, CIS)-based photo-voltaic materials are one of the most important and promising candidates in developing polycrystalline thin film solar cells[1−2]. CIS materials have large optical absorption coefficient(10^5 cm^{-1}), which results from a direct energy gap, and permits thin films with the thickness of only 1−2 μm. They also have long-term opto-electronic stability.

CIS-based solar cells have already surpassed the conversion efficiency of 19.5% based on a multistep process using PVD[3]. The PVD technology is excellent for good quality film growth, but difficult to scale up because of its high cost. Currently, a great deal of effort is directed to a large-scale, high-quality and low-cost technology for preparing CIS-based thin films. Electrodeposition is highly suitable to achieve that goal [4]. The efficiency of 11.3% is reported for a cell using electrodeposition route[5].

There are two methods used for electrodeposition, the direct current (d.c.) method where the cathode potential is biased by a direct potential, and the pulsed-plating one where the cathode potential is modulated in the pulsed potential. The d.c. electrodeposition of CIS-based thin films has been studied widely[6−7], but its application is restricted by its only one controlling variable (current or potential), which is not enough to control the films growth. The pulsed-plating electrodeposition allows independent variation of three parameters: potential or current, period and duty cycle. It has some advantages over the d.c. electrodeposition, namely, improvement of deposition distribution and adhesion[8−9]. It can result in a smoother, more compact and more homogeneous surface and a more expedient composition controlling of the deposited film[10].

In this work, CIS thin films are prepared by pulsed-plating electrodeposition and annealing treatment.

2 Experimental

$CuInSe_2$ thin film was cathodically electrodeposited onto Mo substrate (d 8 mm) at room temperature using a three electrode system with a saturated calomel electrode (SCE) as reference electrode and a Pt foil as counter electrode. The Mo substrates were treated in ammonia solution ($V(H_2O)$:$V(NH_3)$=5:1) to remove the thin surface oxide layer[11], ultrasonically cleaned with acetone, washed with distilled water and dried.

The constituents of the electrolyte used for the

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electrodeposition of CIS thin films were 5 mmol/L $CuCl_2$, 50 mmol/L $InCl_3$, 10 mmol/L SeO_2. In addition, 300 mmol/L KCl and 500 mmol/L Na-citrate were used as a supporting electrolyte and complexing agents, respectively. The pH value of the solution was adjusted to 1.7 with HCl.

The deposition of the Cu-In-Se precursor was carried out under non-stirring with various square-pulse potentials (initial pulse potential 0 V and a step potential (from −0.6 to −0.8 V (vs SCE)), duty cycle θ ($\theta=t_{on}/(t_{on}+t_{off})$) and pulse period T ($t_{on}+t_{off}$).

Fig.1 illustrates a pulse potential that was applied to work electrode (cathode). The wave form of these trains of pulses is square and unipolar. Although these potential pulses applied between the cathode and anode are of square in shape, the corresponding current form is differently modulated due to the presence of an electric double layer at the cathode electrolyte interface forming a capacitor of molecular dimension[12].

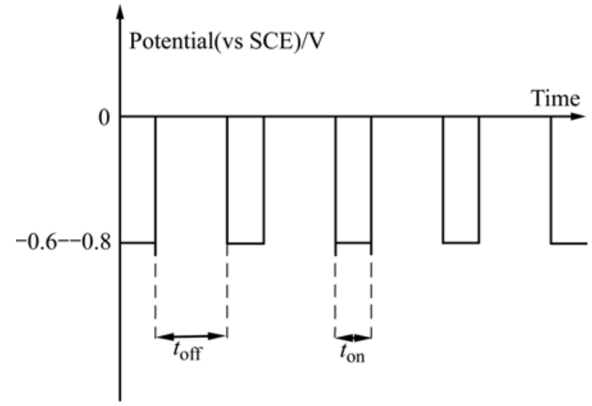

Fig.1 Schematic diagram of pulse potential used to deposit CIS films

The deposition time was 60 min. The as-deposited films were annealed at 450 ℃ for 30 min in flowing Ar. The crystalline properties, surface morphology and the chemical composition of the as-deposited and annealing-treated films were characterized by X-ray diffractometry (XRD, Rigaku3014), scanning electron microscopy (SEM, JSM-6360LV) and energy dispersive X-ray spectroscopy (EDS, EDAX-GENSI-S60S), respectively.

3 Results and discussion

3.1 Electrochemical analysis

The electrodeposition of CIS film on cathode is most likely caused by the combination of electrochemical and chemical reactions as follows:

$$Cu^{2+}+2e \rightarrow Cu \quad E^0=0.342\ \text{V (vs NHE)} \tag{1}$$

$$In^{3+}+3e \rightarrow In \quad E^0=-0.338\ \text{V (vs NHE)} \tag{2}$$

$$H_2SeO_3+4H^++4e \rightarrow Se+3H_2O \quad E^0=0.74\ \text{V (vs NHE)} \tag{3}$$

$$Cu,\ In,\ Se \rightarrow Cu_aIn_bSe_c \tag{4}$$

Linear potential scan (Fig.2) was conducted by EG&G PAR 273A to estimate the reduction potential of each element. The optimum potentials for reduction of Cu^{2+}/Cu, SeO_3^{2-}/Se, In^{3+}/In elements are −0.38, −0.47 and −0.55 V (vs SCE), respectively. As the potential moves to more negative value than −0.75 V (vs SCE), hydrogen bubble generates. The polarization of these reduction potential to the theoretically expected values is caused by various factors, such as the constituents and concentration of the electrolyte, pH, substrate, the absence or presence of stirring, complexing agents[13−14]. From the curve, the suitable potential range for co-deposition is found to be from −0.55 to −0.75 V (vs SCE).

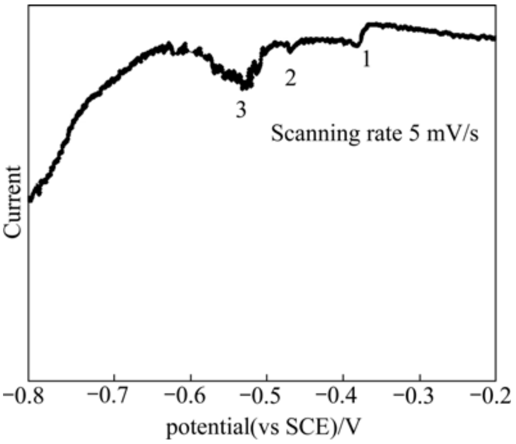

Fig.2 I—V curve of linear potential scan

The theoretical thickness of the electrodeposited $CuInSe_2$ thin films is determined by Faraday's law as following relationship:

$$d=\frac{i\times t\times m}{n\times F\times A\times \rho} \tag{5}$$

where n is the number of electrons transferred, F is Faraday's number, A is the electrode area, i is the current delivered, t is the deposition time, m is the relative molecular mass (366.28 g/mol) and ρ is the density of the electrodeposited CIS film(5.77 g/cm^3). The number of electrons transferred is taken as 13, if the total electrode reaction is assumed to occur:

$$Cu^{2+}+In^{3+}+2H_2SeO_3+8H^++13e \rightarrow CuInSe_2+6H_2O \tag{6}$$

In this work, the value of $i\times t$ is obtained from Fig.1, and the n-value is determined as 13.4[6]. On the basis of the theoretical calculation using Enq.(5), the deposited thickness of the CIS material is controlled in the range between 0.8 and 1.5 μm. Since the as-deposited films are not compact, we consider that the theoretical thickness is close to that of the films annealed[15].