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Co-electrodeposition and Characterization of Cu (In, Ga)Se_2 thin films

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Cu (In, Ga)Se_2(CIGS) thin films were electrodeposited on Mo-coated soda lime glass substrate by the electrodeposition technique. The chemical bath for co-electrodeposition was prepared from copper chloride, indium chloride, gallium chloride and selenous acid. The effect of different chemical bath concentration of the CIGS films on the microstructure and electric properties has been investigated. The microstructure and morphology of the selenized CIGS thin films were investigated by X-ray diffraction and scanning electron microscopy. The composition of the selenized CIGS thin films were characterized by energy dispersive spectroscopy. Hall coefficient, Conductivity and Mobility of the selenized CIGS thin films were measured by ACCENT HL5500 Hall System. The results indicate CIGS thin films deviate little from the ideal stoichiometric one and single chalcopyrite structure. At room temperature, electrical conductivity, Hall mobility and charge-carrier concentration of the films vary from 49.63 to 64.56 $(\Omega\cdot cm)^{-1}$,271 to 386 $cm^2V^{-1}\cdot s^{-1}$, 8.026×10^{17} to $1.4\,87\times10^{18}$ cm^{-3}, respectively, and are dependent on the composition of the films. © *2006 Springer Science + Business Media, Inc.*

Introduction

The inexpensive production of device-quality CIS-based thin films is one of the major goals of the international photovoltaics community. This is due to the fact that CIS is a nearly ideal candidate for thin film solar cells, considering that it has a direct bandgap of about 1.1 eV, has good terrestrial stability and has an extremely high optical absorption [1]. However, the band gap for $CuInSe_2$ is less than the optimum value of about 1.45 eV for the terrestrial solar spectrum. The gallium-doped $CuInSe_2$ thin films can be used to raise the bandgap to better match the solar spectrum. The optical band gap of CIGS depending on the composition varies from about 1.05 to 1.6 eV, which is within the maximum solar absorption region. This allows the band gap of CIGS to be "tailored" to the terrestrial solar spectrum [2]. Copper indium gallium diselenide ($Cu(In,Ga)Se_2$) or CIGS is a material explored extensively for the development of low-cost, high-efficiency, thin film solar cells over the past decade. Conversion efficiencies exceeding 19% for laboratory scale devices have been achieved by Ramanathan K *et al.* [3] and over 13% efficiency for solar modules on an industrial scale [4]. These factors point to a bright future for CIGS solar cells.

There have been a wide variety of vacuum-based techniques for producing CIS-based thin films such as co-evaporation [4], sputtering [5, 6], and physical vapor deposition [7]. Although these techniques have been shown to produce high-quality films, the high vacuum and thermal and/or cryogenic requirements make them expensive and inhibit their scalability. There is presently great interest in the development of low-cost processing methods for the growth of high-quality CIS-type absorber for thin film solar cell applications. Chemical bath deposition and electrodeposition deserve special attention because they have been shown to be inexpensive, low-temperature and non-polluting methods [8–10].

In the present work, Electrodeposition of the CIGS layers was carried out using the standard three-electrode system. CIGS thin films have been fabricated on Mo-coated glass substrate by the electrodeposition technique. The effect of different chemical bath concentration of the CIGS films on the microstructure and electric properties has been investigated. The purpose of our work has been to modulate the properties of CIGS by varying the Cu/(In+Ga) ratios in the compound.

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Experimental

The methods of chemical bath deposition and electrodeposition most used in practice are deposition and electrodeposition from an aqueous solution. These are complicated chemical and electrochemical processes since they involve the co-deposition of each element of the semiconductor material. The electrode reactions of Cu-In-Ga-Se taken place are as follows [11]:

$$\mathrm{Cu}^{2+} + 2\mathrm{e} \Leftrightarrow \mathrm{Cu}$$

$$\mathrm{E} = 0.34 + 0.0295 \log \left(\alpha_{\mathrm{Cu}}^{2+}/\alpha_{\mathrm{Cu}}\right)$$

$$\mathrm{In}^{3+} + 3\mathrm{e} \Leftrightarrow \mathrm{In}$$

$$\mathrm{E} = -0.34 + 0.0197 \log \left(\alpha_{\mathrm{In}}^{3+}/\alpha_{\mathrm{In}}\right)$$

$$\mathrm{Ga}^{3+} + 3\mathrm{e} \Leftrightarrow \mathrm{Ga}$$

$$\mathrm{E} = -0.56 + 0.0197 \log \left(\alpha_{\mathrm{Ga}}^{3+}/\alpha_{\mathrm{Ca}}\right)$$

$$\mathrm{HSeO}_2^+ + 4\mathrm{H}^+ + 4\mathrm{e}^- + \mathrm{OH}^- \Leftrightarrow \mathrm{H}_2\mathrm{SeO}_3 + 4\mathrm{H}^+$$

$$+ 4\mathrm{e}^- \Leftrightarrow \mathrm{Se} + 3\mathrm{H}_2\mathrm{O}$$

$$\mathrm{E} = 0.74 + 0.0148 \log(\alpha_{\mathrm{HSeO2}}^{+}/\alpha_{\mathrm{Se}}) - 0.0443\mathrm{pH})$$

Where the electrode potential E is referred with respect to the normal hydrogen electrode; $\alpha_{\mathrm{Cu}}^{2+}$, $\alpha_{\mathrm{In}}^{3+}$ $\alpha_{\mathrm{Ga}}^{3+}$ and $\alpha_{\mathrm{HSeO2}}^{+}$ refer to the activity of respective ions in the solution, and α_{Cu}, α_{In}, α_{Ga} and α_{Se} represent the activity of respective atoms in the electrolyte.

According to the Nernst equations, the electrode potentials for selenium and copper are more positive than that of indium and gallium. For the simultaneous electrodeposition of Cu, In, Ga and Se, we may adjust the pH and concentration of the electrolyte such that the deposition potentials of all the individual elements may come closer to each other. In addition, deposition potentials may be shifted by adding an appropriate complexing agent to the electrolyte.

CIGS films were prepared adopting co-electrodeposition of the four elements of Cu, In, Ga and Se. The potentiostatic technique with a conventional three-electrode cell configuration was used. The reference electrode was a saturated calomel electrode (SCE), the counter electrode was a Pt mesh, and the working electrode was a Mo-coated soda lime glass substrate. The electrodeposition bath used for the co-deposition of Cu-In-Ga-Se consisted of CuCl_2, InCl_3, GaCl_3 and $\mathrm{H}_2\mathrm{SeO}_3$. Table I shows that different chemical bath were used for CIGS thin film. The pH of the chemical bath was adjusted to be 1.5 by adding some drops of concentrated HCl (10% by volume). The bath temperature was maintained at 25°C and kept without stirring during film deposition. The experimental conditions for the co-deposition processes are the following: the applied potentials ranged from –0.6 to –0.8 V versus a saturated calomel electrode (SCE), the time of deposition was 60 min. In this present study, CIGS thin films had been successfully fabricated by the electrodeposition technique using complexing agents Na-citrate with mole concentration of 1.0 M.

The as-deposited CIGS thin films on Mo-coated glass substrate were annealed at 550°C in selenium atmosphere for 1 h in a tube furnace in a flowing argon atmosphere. Annealing temperature and time were chosen so that the single chalcopyrite structure CIGS thin films may be formed. The crystallographic properties of CIGS thin films were identified by a D/MAX-RB rotating target X-ray diffractometer using CuKα radiation, the surface and cross-sectional morphology of the CIGS thin films were observed by scanning electron microscopy (SEM). The chemical composition of the selenized CIGS thin films were characterized by energy dispersive spectroscopy. Hall coefficient, Conductivity and Mobility of the selenized CIGS thin films were measured by ACCENT HL5500 Hall System.

Results and discussion

The compositional analysis of CIGS thin films

Table I also shows the composition analysis using energy dispersive spectroscopy (EDS) for the films under identical post-annealing conditions. The data correspond to the chemical composition of the film near surface, because EDS analysis is surface sensitive. It can be seen from Table I that the atomic percentage of Ga in the films increases with the increment of the concentration of Ga^{3+}. All of the films were Cu-poor with respect to the anticipated composition of $\mathrm{Cu(In,Ga)Se}_2$. The Ga to (In + Ga) ratios for the CIGS films rang from 0.24 to 0.35. These ratios span the range necessary to achieve CIGS band gaps which are optimized for the terrestrial solar spectrum.

The XRD analysis of CIGS thin films

The XRD patterns CIGS thin films annealed at 550°C were shown in Fig. 1. The three main diffraction peaks due

TABLE I Different chemical bath used and compositional results of CIGS thin films analyzed by EDS

	Bath concentration/mM				Composition/(at%)					
Sample no	CuCl_2	InCl_3	GaCl_3	$\mathrm{H}_2\mathrm{SeO}_3$	Cu	In	Ga	Se	Cu/(In+Ga)	Ga/(In+Ga)
a	2.5	50	65	15	13.65	23.85	7.70	54.80	0.43	0.24
b	3.0	45	65	15	21.92	18.20	7.76	52.12	0.84	0.30
c	5.0	50	70	10	27.21	20.72	9.77	42.30	0.89	0.32
d	2.5	45	70	10	13.27	17.19	9.69	59.25	0.48	0.35

TABLE II The electrical properties for CIGS thin films with different bath concentration

Sample no.	Cu/(In+Ga)	Conductivity/$(\Omega \cdot \mathrm{cm})^{-1}$	Hall Mobility/$\mathrm{cm}^2\ \mathrm{V}^{-1} \cdot \mathrm{S}^{-1}$	Carrier concentration/ cm^{-3}	Conduction type
a	0.43	49.63	386	8.026×10^{17}	n
b	0.84	57.67	311	1.158×10^{18}	n
c	0.89	64.56	271	1.487×10^{18}	n
d	0.48	52.08	323	1.007×10^{18}	n

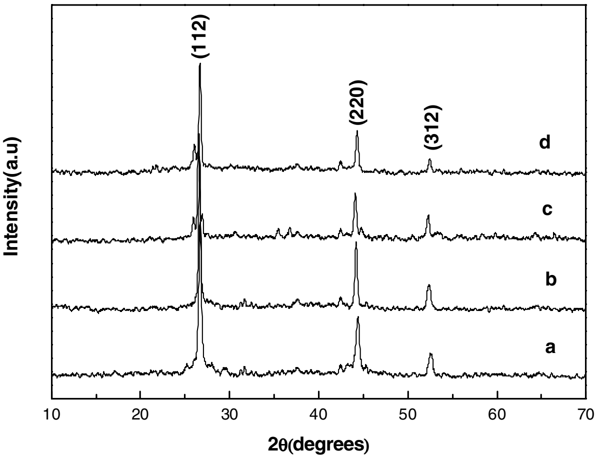

Figure 1 The XRD patterns of CIGS films annealed at 550° for 1 h

to (112), (220) and (312) planes correspond to CIGS. The most intense peak is situated at approximately 26.76°. The results indicate that the films have the single chalcopyrite structure and no secondary phase exists in CIGS thin films.

The SEM micrograph of CIGS thin films

The surface micrographs of CIGS thin films annealed in Se atmosphere for 1 h are shown in Fig. 2. The results show that the morphology is more compact and homogeneous when the amount of Cu^{2+} is more in the chemical bath. The grain size varies from 0.8 to 2.5 μm and CIGS thin films have polycrystalline structure. The grain size of sample (b) is the biggest and it is in agreement with the XRD results of Fig. 1. In Fig. 2(b), the whiskers in the CIGS films are considered to not completely volatile Se powder cling to CIGS. The SEM photo of sample (d) is due to non-uniform temperature distribution. So the heat treatment process is optimized for the future's work to fabricate high-quality CIGS thin films for solar cells.

The electrical properties of CIGS thin films

Electrical conductivity, Hall coefficient, Mobility and charge-carrier concentration of selenized CIGS thin films were measured by ACCENT HL 5500 Hall System at room temperature. The measurement conditions were the following: magnetic field intensity = 0.513 T, electrical

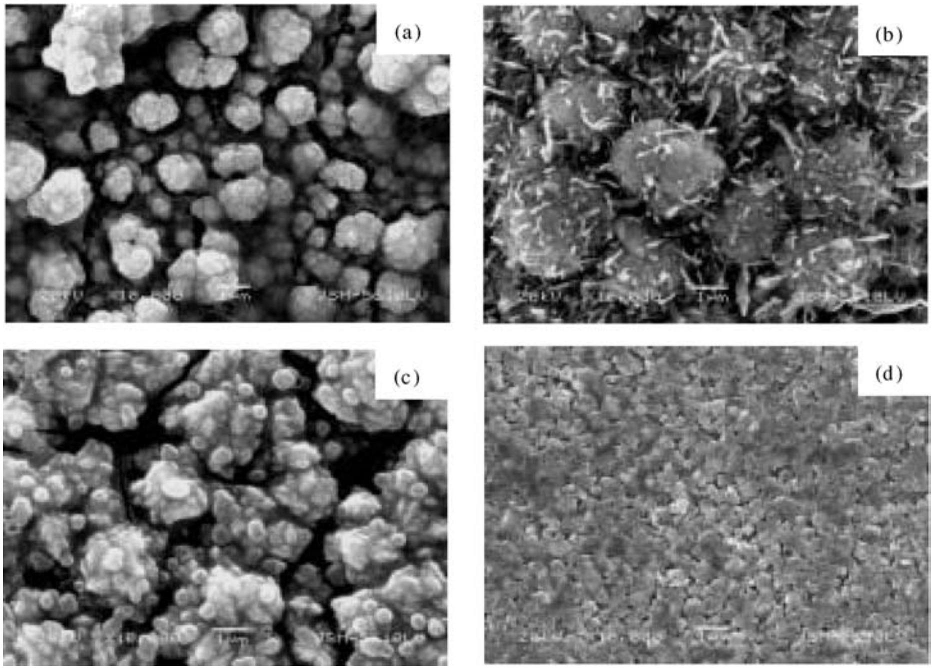

Figure 2 SEM micrographs of CIGS films with different concentration annealed in Se atmosphere at 550° for 1 h

current = 0.1 μA. Table II shows that the electrical properties for CIGS thin films annealed at 550°C. It is noted that indium-rich films have n-type conductivity, and the conductivities increase with Cu/(In+Ga) ratios. All of the films were Cu-poor because Cu/(In + Ga) ratios are all less than 1. The conductivity of thin films varies from 49.63 to 64.56 $(\Omega\cdot\text{cm})^{-1}$. The all Samples have n-type conduction because Hall coefficient is less than zero. Carrier concentration ranges from 8.026×10^{17} to 1.487×10^{18} cm^{-3}. The mobility for the thin films ranges from 271 to 386 cm^2 V$^{-1}\cdot$s^{-1}. Further observation from Table II shows that the conductivities increase as Cu/(In + Ga) ratio increases. This may be explained as follows: as the Cu/(In + Ga) ratio increases, the charge-carrier concentrations increase while the Hall mobility decreases. The conduction type of the thin films is dependent on the Cu/(In + Ga) ratio, this result is in accordance with that of CIS films [12].

Conclusions

The CIGS thin films have been fabricated on Mo-coated soda lime glass substrate by the co-electrodeposition technique. The effect of variation in bath composition on film properties was studied. The optimization of the electrochemical bath is a very important requirement to get the adequate stoichiometry for CIGS. The microstructure, composition and electrical properties of CIGS thin films were investigated. The results indicate CIGS thin films little deviate from the ideal stoichiometric one and single chalcopyrite structure. At room temperature, electrical conductivity, Hall mobility and charge-carrier concentration of the films vary from 49.63 to 64.56 $(\Omega\cdot\text{cm})^{-1}$, 271 to 386 cm^2 V$^{-1}\cdot$s^{-1}, 8.026×10^{17} to 1.487×10^{18} cm^{-3}, respectively, and are dependent on the composition of the films.

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