Chapter 5
Electro-Deposition of Cu_2ZnSnS_4 Solar Cell Materials on Mo/SLG Substrates

Min Yen Yeh, Yu-Jheng Liao, Dong-Sing Wuu, Cheng-Liang Huang and Chyi-Da Yang

Cu_2ZnSnS_4 (CZTS) absorber layers, treated with post sulfurization, were successfully grown on Mo/soda lime glass substrates by electro-deposition at room temperature. Electro-deposition is such a method that has the advantages of high quality, low-cost, high-efficiency, high production, vacuum-less and good void fill ability. In this work, a two-electrode arrangement system was used and worked at galvanostat setting. The CZTS was electro-deposited through single-step processes using sodium citrate ($Na_3C_6H_5O_7$) and tartaric acid ($C_4H_6O_6$) as the complexing agents. The as electro-deposited CZTS films were treated with post sulfurization using sulfur vapor. The crystallinity of the as electro-deposited CZTS was improved through the post-sulfurization. The as-formed CZTS was analyzed using FE-SEM, XRD and Raman Spectrometer. The CZTS films exhibit polycrystalline kesterite structures with preferred XRD orientation on (112), (220), (312) planes. The optical band gap energy was $\sim$1.25 eV which was a suitable value for solar cell application.

5.1 Introduction

Humans have achieved a level of material progress based on continuous invention in science and technology. The endeavor on developing science and technology to meet the need of comfortable live consumes lots of energy resources. The conventional energy resources include oil, gas, coal, etc. The increase of energy usage exhausts the storage of conventional energy resources year by year. It is a suffering

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experience of oil crisis happened in 1970s. Today we face more serious global energy problems which involve not only the shortage of conventional energy, but the impact to the environment. The insurmountable energy problems challenge people to find out suitable alternative resources. The choices and development of alternative resources urge the requirement of recycle and green to our environment. Nowadays, development of solar energies, wind and hydrogen fuel cells are the popular subjects.

The application of solar energy is based on the developments of solar cells. Common use of solar cell devices include silicon based (single, multiple, amorphous crystalline), compound (GaAs, CdTe, $CuInSe_2$), and dye-sensitized (TiO_2) solar cells. Since silicon material is abundant in the Earth crust and Si process is a high developed technology, silicon solar cells are dominant in the commercial photovoltaic market. Most of the commercial Si solar cells are made of crystalline Si based on Si bulk substrates. The solar cell structures only occupy few micrometers of thickness onto bulk Si. Most of raw bulk Si material is wasted and causing high cost production. High-efficiency thin-film solar cells may hold the key to the cost consideration.

The development of thin-film compound semiconductor such as CIGS, and CZTS has the potential to meet the requirements of solar cells. Though, the ZnO/CdS/CIGS thin-film solar cells had reached 19.2 % efficiency [1], lower reserve of indium (In) in the earth's crust and toxic element of Se to our environment would become the barrier for mass production. In recent years, Cu_2ZnSnS_4 is the most promising absorber layer material for solar cell to replace CIGS, although CZTS solar cells have less efficient than CIGS solar cells reported by the National Renewable Energy Laboratory 19.9 % [2] and the German solar and hydrogen energy research institutions 20.3 % [3]. Since CZTS constituents of copper, zinc, tin and sulfur are plenty in the earth and non-toxic, and this makes it a suitable candidate for replacing CIGS solar cells. Nowadays, non-toxic, low-cost and high efficiency CZTS thin film solar cells have been developed by IBM 8.4 % [4] and 11.1 % in 2012 [5].

CZTS can be prepared by various methods, such as spray-pyrolysis deposition [6], electron-beam evaporation [7], radio-frequency magnetron sputtering deposition [8], electroplated deposition [9], pulsed laser deposition [10], and sol-gel deposition [11]. The advantages of low cost materials, large area deposition, low temperature process and easy equipment, make electro-deposition an attractive technique as compared to vacuum system processes like e-beam evaporation, rf-sputtering, and pulse laser deposition. Generally it is easier to deposit mono-element by electro-deposition in a single-step. A quaternary compound is more difficult to deposit in one-step through electro-deposition. Single-step electro-deposition of CZTS thin films from aqueous is difficult since the reduction potential range of these metal ions is considerably large [12]. CZTS films prepared by single-steps electro-deposition remain still a challenge to obtain stoichiometry composition [12–14]. For obtaining stoichiometric CZTS, complexing agents are used to decrease the gap in the reduction potentials of species and improve the lifetime of deposition bath as well as the adhesion of the deposited film on the

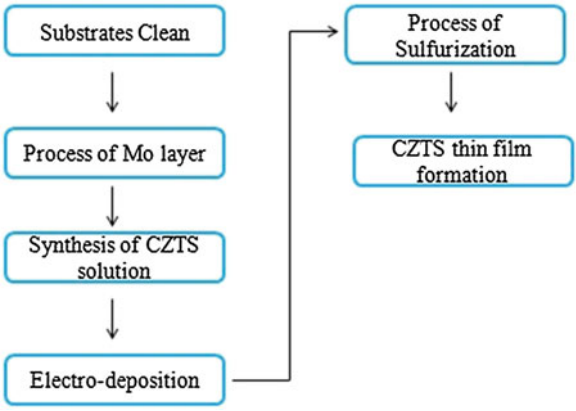


Fig. 5.1 Flow chart of Cu_2ZnSnS_4 electro-deposition process

substrate [12, 15]. Tri-sodium citrate (Na_3-citrate) was used as the complexing agent in quaternary electrolytic bath for electro-deposition of CZTS thin films [14]. In this work, tri-sodium citrate was used as the agent for single-step electro-deposition on Mo/SLG substrate. The structural properties of the as-electro-deposited and sulfurized thin films were investigated using X-ray diffractometry (PANalytical X'pert Pro with CuKα radiation, $\lambda = 1.5406$ Å). The morphological and compositional characteristics of the as-prepared CZTS thin films are characterized using field emission scanning electron microscopy (JEOL, JSM-6700F), and energy dispersive X-ray spectroscopy (EDX, OXFORD INCA). Raman spectral analysis was performed by using 532 nm laser exited line. Optical transmittance & reflectance spectra are performed using N&K UV-visible analyzer in the range of 190 $\sim$ 1000 nm.

5.2 Experimental Methods

CZTS thin film was prepared by electro-deposition technique through a single-step process in a non-vacuum system at room temperature. The processes have several advantages, such as low cost source materials, large area deposition, cheap capital equipment, solution synthesis and room temperature growth. Molybdenum (Mo) widely used in industry is suitable used as the back contact for CZTS solar cells. Most of CZTS thin films deposited on Mo/SLG substrate may encounter the problems of adhesion and contact resistance between CZTS layer and Mo metal. The interface quality often affects the solar cell performance. Poor interface quality will increase series resistance of solar cells, and deteriorate the device efficiency. Direct electrochemical growth of CZTS onto Molybdenum surface may be a possible way to improve the interface quality and access higher-quality CZTS film.

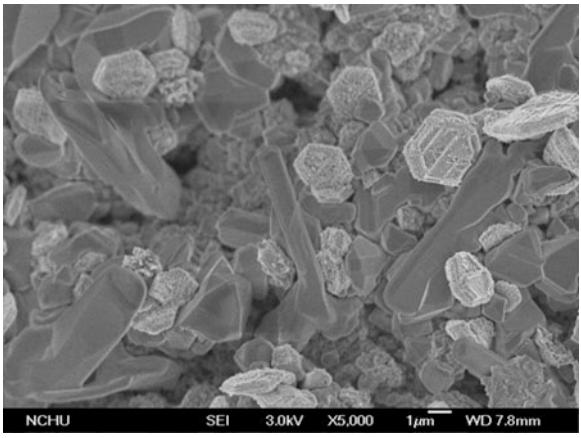


Fig. 5.2 Surface morphologies of as electro-deposited CZTS treated with post sulfurization

In this work, the deposition process of Cu_2ZnSnS_4 thin film is shown in Fig. 5.1. Soda lime glass (SLG) with 2×4 cm^2 dimension was used as substrates. SLG substrates were cleaned in ultrasonic bathes of acetone and D.I. water, successively, and dried flown nitrogen. Molybdenum layers were chosen as the starting layer for electro-deposition and prepared on SLG substrates by D.C. sputtering. The sputtering chamber was pumping down to a back ground pressure of 5×10^{-6} torr, and working pressure was kept at 6 mtorr. A 2-inch diameter and 6-mm thickness Molybdenum with 99.95 % purity was used as the target. A rotatable substrate holder was fixed at 10 cm from the Molybdenum target. The electrolyte aqueous for CZTS electro-deposition was prepared using metal sulfates ($CuSO_4$, $ZnSO_4$, $SnSO_4$) at 2 : 1 : 2 mol ratios mixed in D.I. water. Sodium citrate ($Na_3C_6H_5O_7$) and tartaric acid ($C_4H_6O_6$) were used as the complexing agents. The electro-deposition was carried out at room temperature using a double-electrode configuration in galvanostat with a maximum current of 3 mA. The working and counter electrodes dipped into electrolyte were 1×1 cm^2. After electro-deposition, the obtained CZTS thin films were treated with sulfurization using a conventional tube furnace filled with nitrogen. Sulfur vapor sublimated from sulfur powder was used for the CZTS sulfurization process at 400 °C for 10 min.

5.3 Results and Discussion

The surface morphology of the as-deposited and sulfurized CZTS thin films was investigated by using scanning electron microscopy (SEM). CZTS thin films were electrochemically deposited in galvanostat at 3 mA. Figure 5.2 presents SEM surface micrographs of as-deposited CZTS thin films onto Mo/SLG substrate. It is observed that the film shows non-uniform distribution of agglomerated particles with dense packing. The agglomerated particles with well-defined boundary reveal

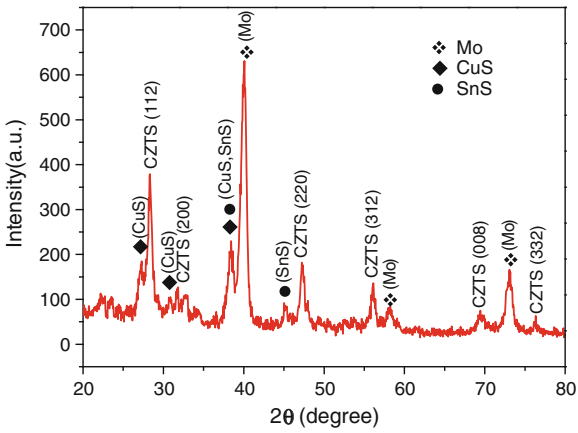


Fig. 5.3 XRD patterns of as electro-deposited CZTS treated with post sulfurization

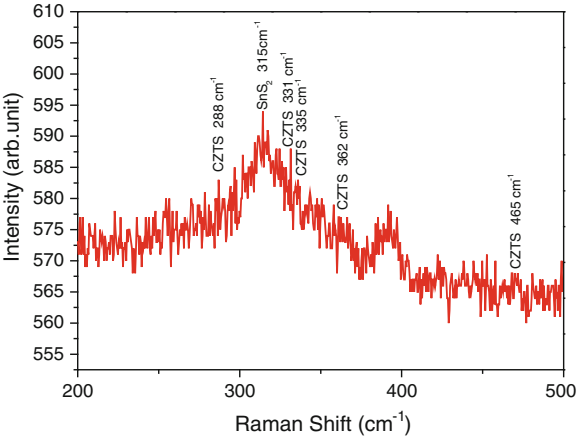
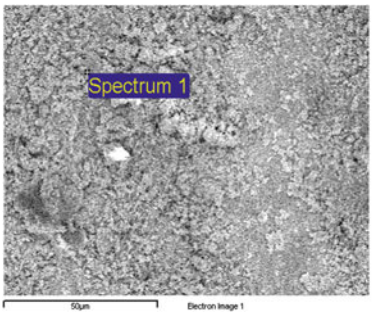


Fig. 5.4 Raman shift spectrum of as electro-deposited CZTS treated with post sulfurization

rectangle and pebble shapes have a size range of 1 ∼ 8 μm. The obtained grain sizes seem to be larger than those reported in literatures [12, 14]. The larger size of particles might be the effect of sulfurizing process using sulfur vapor in this work, as comparing to other's annealing works using ambient gas of nitrogen or Ar. It had been found that surface morphologies of prepared CZTS thin films were affected by annealing condition [12].

Structural properties of as electro-deposited CZTS treated with post-sulfurization at 400 °C were analyzed using XRD measurement with 2θ scanning from 20 to 80°. The XRD spectrum of as sulfurized CZTS thin films electro-deposited from quaternary electrolyte aqueous containing sodium citrate and tartaric acid on Mo/SLG substrates are presented in Fig. 5.3. The XRD peaks diffracted at the positions indexed as (112), (200), (220), (312), (008), and (332) attribute to different crystallographic planes of Cu_2ZnSnS_4. The XRD pattern of the as electro-deposited CZTS treated with post-sulfurization reveals polycrystalline and



Element	Weight%	Atomic%
S K	34.02	59.30
Cu L	15.07	13.26
Zn L	9.02	7.71
Sn L	41.89	19.73
Totals	100.00	

Fig. 5.5 EDS analysis of as electro-deposited CZTS treated with post sulfurization

kesterite structure. Besides polycrystalline CZTS, other secondary phases such as CuS and SnS are found in the films. The secondary phases of copper sulfides and tin sulfides were also frequently observed in CZTS films in other reports [12, 16].

As we can see that it is hard to distinguish some of the XRD diffraction peaks of CZTS from secondary phases such as CuS, SnS and ZnS since they stand too close. XRD seems no a very precise way to distinguish CZTS and its secondary phases. Raman spectroscopy may become an alternative method to identify the structure of the as-deposited CZTS and secondary phases. Figure 5.4 shows Raman spectroscopy results of as electro-deposited CZTS treated with sulfurization. From the Raman spectrum, we can observe scattering peaks at 288, 331, 335, 362 and 465 cm^{-1} defined as the characteristic peaks of Cu_2ZnSnS_4 [17–21]. The existence of SnS peak scattering at 315 cm^{-1} is also found in the as electro-deposited CZTS thin films treated with sulfurization by the Raman test [22–24]. From the XRD and Raman test we know that there are still numerous challenges to electro-deposit CZTS in which no secondary phase is accompanied.

The composition of the CZTS film was analyzed by EDS. Figure 5.5 shows that the content of sulfur in the as electro-deposited CZTS film is compensated enough through the sulfurization treatment. The constituent of copper seems poor in the film. The content of Zn seems to be lost a little during high temperature process (sulfurization) similar to the report [17]. It can be seen that the as deposited CZTS film treated with sulfurization does not reveal a close stoichiometric composition. A close stoichiometric composition was found to relate to an optimal volume of complexing agent added into the quaternary electrolyte for single-step electro-deposition [12].

The transmittance and reflectance of the CZTS films were examined using UV-visible spectra from 200 to 1000 nm. Optical absorption coefficients were then calculated as [27]

$$\alpha = \frac{1}{t}[\ln(1 - R_\lambda) - \ln T_\lambda], \tag{5.1}$$

where t is the film thickness, R_λ and T_λ are reflectance and transmittance coefficients, respectively.

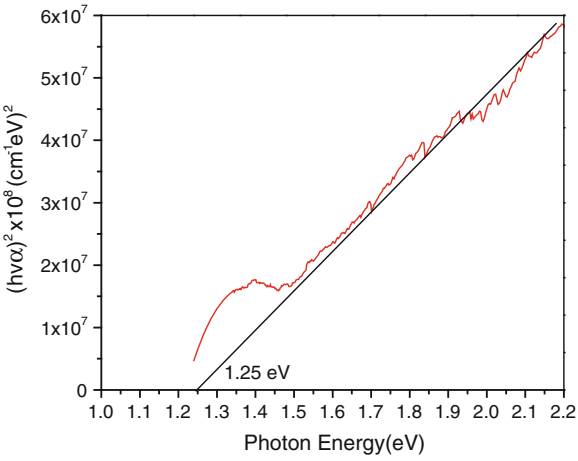


Fig. 5.6 Absorption spectrum of CZTS as a function of photon energy, the CZTS is electro-deposited on Mo/SLG and treated with post sulfurization

The absorption coefficients of the CZTS are higher than 1×10^4 cm^{-1} in the visible range. A high absorption property over the solar radiation band is thought to be an attractive candidate for solar cells applications. The as electro-deposited CZTS film treated with post-sulfurization, has a high absorption spectrum over a larger photon energy region. From [27], we know that the absorption coefficient related to direct transitions has the following spectral dependence:

$$\alpha = A(hv - E_g)^{1/2}, \tag{5.2}$$

where A is a constant, hv is the photon energy and E_g is the energy band gap. A direct transition can then be found by the linear dependence of $(\alpha hv)^2$ versus hv. Thus optical-energy gap can be determined by extrapolating the linear part of the spectrum of the square absorption coefficients of the CZTS to zero absorption coefficient as a function of photon energy. As shown in Fig. 5.6, the CZTS optical energy gap is $\sim$1.25 eV which is suitable to be the absorber layer for solar cells [25, 26].

5.4 Conclusion

Cu_2ZnSnS_4 thin films were successfully prepared on Mo/SLG substrates at room temperature by Galvanostat electro-deposition method. The as electro-deposited CZTS films were treated with post sulfurization using sulfur vapor in a conventional tube furnace filled with nitrogen. The one-step electro-deposited processes use sodium citrate ($Na_3C_6H_5O_7$) and tartaric acid ($C_4H_6O_6$) as the complexing agents to decrease the gap in the reduction potentials of species. Non-uniform agglomerated particles with well-defined boundary rectangle and pebble shapes in a size of 1 $\sim$ 8 μm were observed from the as prepared CZTS SEM surface

morphology. The obtained grain sizes larger than other's work might be the effect of sulfurizing. The as electro-deposited CZTS treated with post-sulfurization reveals polycrystalline and kesterite structure from XRD test. Secondary phases such as CuS and SnS are found in the CZTS films from XRD and Raman examination. Using an optimal volume of complexing agent may be a way to improve the secondary phases, and this may be also useful to obtain a close stoichometric CZTS. The as electro-deposited CZTS films are suitable to be the absorber layer for solar cells, since they have high absorption efficiencies in the visible range with the optical energy gap of ~ 1.25 eV.

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