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Electrodeposition of CZTS thin film at different concentration of glycine

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Advances in technologies and modernization of the society have influenced the energy demand directly. Increase in energy demand in upcoming years will be very challenging because the consumption of fuel to achieve the energy demand will not be that much promising, since it would be getting vanished very soon. The alternative source which can help to achieve this demand could be solar energy. Solar cell is ought to be the finest application of solar energy. The chalcogenide based absorber materials for thin film solar cells (TFSC) have gained more attention in recent years. However among all the absorber materials the copper zinc tin sulfide (CZTS) found to be an efficient option. It is earth abundant material and relatively benign. CZTS is a p-type semiconducting material possess optical band gap of 1.5 eV, high absorbance coefficient 10^4 cm^{-1}. In this work, formation of CZTS thin film is done by electrodeposition technique in a single step with glycine complexing agent. Different concentration of glycine for the development of CZTS thin film is studied. Analysis of obtained this films were characterized by adopting various techniques.

Keywords: Electrodeposition, thin film, glycine, concentration.

Introduction

Absorber materials for TFSC plays major role, it can be also called as “Heart” for TFSC. Currently the chalcogenide based absorber materials for TFSC gained more interest due to its capable characteristics. At present copper indium gallium diselenide, $CuInSe_2$ and CdTe are the chalcogenide based absorber materials are in use for thin film solar cells [1]. But some demerits are faced by these materials. The accessibility for indium and selenium is limited thus causes it cost immoderate. On other hand the element cadmium (Cd) is toxic in its nature[2]. Among from these the copper zinc tin sulfide (CZTS) was found to be suitable option for thin film solar cells as an absorber material. CZTS is a quaternary semiconducting material composed by earth abundant material and as a result makes its availability easy as well as low cost material. Beside from these properties the CZTS have direct band gap 1.5 eV which is an ideal optical band gap value for thin film solar cells[1,3]. A 12.6% of efficiency was recorded for CZTS based thin film solar cells[4]. Preparation of CZTS thin film can be accomplished by various routes such as physical and chemical techniques[3]. The electrochemical deposition could be the first choice among all due to its excellent advantages[5]. It allows the smooth, scalable and uniform deposition of desired material with desired stoichiometry and thickness[6]. There are plenty of works done by researcher to achieve the CZTS thin film by using electrochemical deposition. But they are of multistep and addition of sulfur was done at annealing time with high temperature[7].

In present work the formation of CZTS thin film in a single-step on gold coated glass substrate. For single-step deposition glycine served the purpose of a complexing agent. At different concentration of glycine the deposition study were carried out. The obtained CZTS thin film were analyzed using SEM to investigate the surface morphology, EDX done to study the atomic % of elements, X-ray diffraction to know the nature of the sample and current-voltage studies was carried out in presence and absence of light source (200 W incandescent lamp) to know the resistance of the obtained sample.

Material and method

The material and experimental procedure is explained elsewhere[8]. Depositions were done at potentiostatic mode.

The concentration of glycine in precursors solution was varied from 90 mM to 110 mM. The electrolyte pH was kept constant at 2.5.

Results and discussion

Cyclic voltammetry:

Fig. 1 presents the obtained cyclic voltagrams at different concentration of glycine. It is believed to be that for single-step electrochemical deposition of more than one metal ions to the desired substrate, the complexing agent plays major role. It helps to reduce the deposition potential window between all the present metal ions and gives the optimal reduction potential value[9]. The well defined peaks were observed for 100 mM of glycine concentration with respect to other concentration, this could be due to the better complexation effect of glycine concentration. However, the optimal deposition potential was found to be nearly same for all the cases at –0.89 V (vs Ag/AgCl)[10].

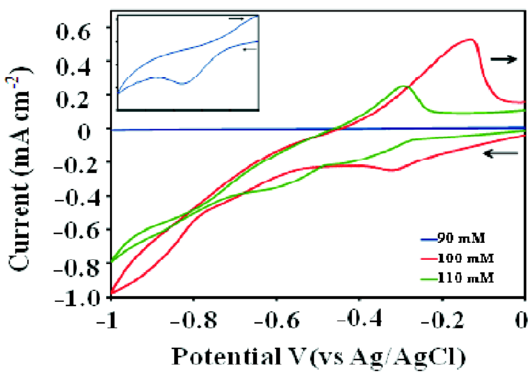

Fig. 1. Cyclic voltagrams at different concentration of glycine.

Current-time transient:

Fig. 2 shows the current-time transients during deposition of CZTS thin film at different concentration of glycine. The plot is mainly divided by three regions. In region I, a fall in cathodic current density was observed to be very fast which is attributing the starting of nucleation process of metal ions present in electrolyte bath. After the nucleation process the cathodic current density shows lesser drop (region II) to some extend which revels the starting phase of formation of CZTS thin film. As the deposition time passes the cathodic current

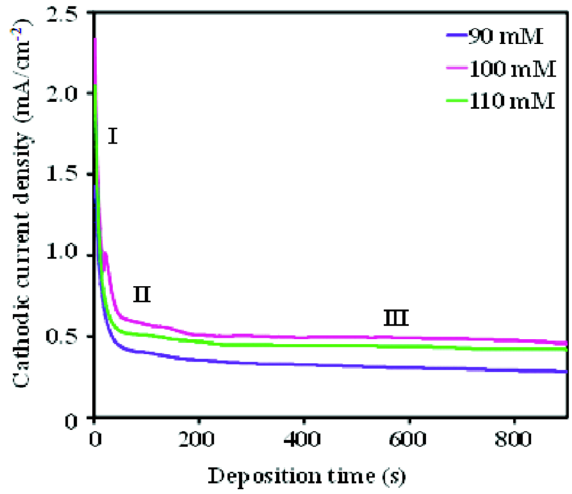

Fig.2. Current-time transients during the deposition of CZTS at different concentration of glycine.

density was observed to be constant (region III) which attribute the growth of CZTS thin film[8].

Scanning electron microscopy:

Fig. 3 shows the SEM results for the films deposited at different concentration of glycine. Increase in concentration of glycine showed increase in surface roughness[10]. The particles for all the cases were agglomerated with each other and this is the desirable characteristic for solar cells application[11]. Table 1 gives the EDX results for the films deposited at different concentration of glycine. At higher concentration of glycine the film was found to be out of stoichiometry. The closer stoichiometry was recorded for the film deposited from 90 mM and 100 mM of glycine.

X-Ray diffraction:

Fig. 4 gives XRD spectra obtained for various concentra-

Table 1. Atomic % of as deposited CZTS thin film formed with different concentration of glycine

Atomic %			
Elements	Glycine concentration		
	90 mM	100 mM	110 mM
Cu	28.51	37.54	48.99
Zn	7.39	5.77	5.59
Sn	6.98	6.23	6.32
S	57.11	50.46	39.10
Total		100	

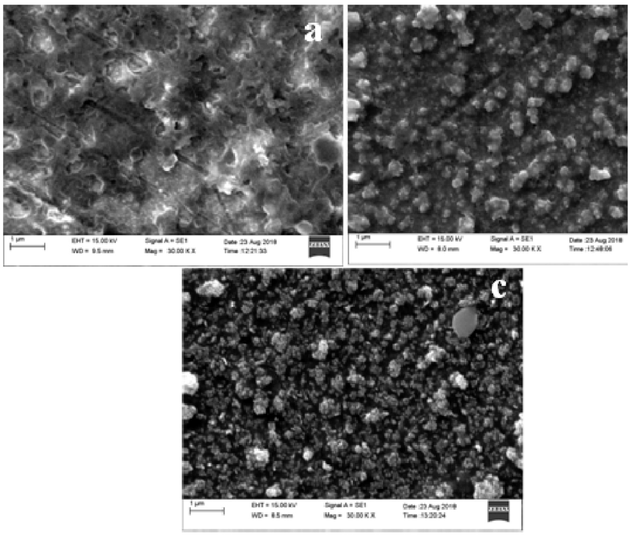

Fig. 3. SEM images for as-deposited CZTS thin films: (a) 90 mM glycine, (b) 100 mM glycine and (c) 110 mM glycine.

tion of glycine. According to the obtained spectra deposits showed polycrystalline in its nature. The recorded spectra also reveal kesterite structure of CZTS with $Cu_2Sn_3S_7$ as secondary phase. The better crystalinity was observed for the deposit with 100 mM of glycine concentration.

Current-voltage study:

Fig. 5 gives the I-V plot for glycine concentration of 90 mM and 100 mM in presence and absence of light source.

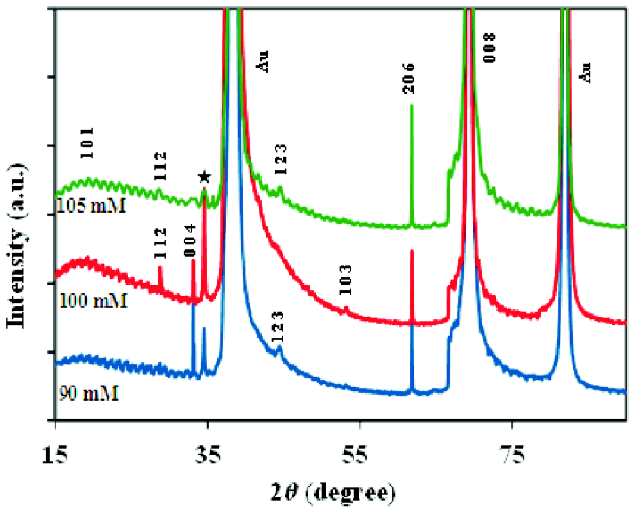

Fig. 4. XRD spectra recorded for different concentration of glycine.

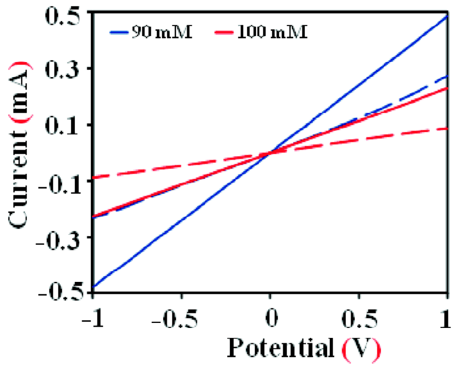

Fig. 5. Current-voltage (IV) recorded for different concentration of glycine in presence and absence of light, solid lines represents data recorded in presence of light and dash line in absence of light.

The sandwich Au/CZTS/Au was used for the present study. The ohmic nature was followed by the sample in both the cases was observed. The average resistance values in presence of light for 90 mM and 100 mM of glycine concentration was found to be 20.8 Ω and 44.2 Ω respectively. Similarly in absence of light it was found to be 41.4 Ω and 110 Ω for 90 mM and 100 mM respectively. The fall in resistance value when film is exposed to light suggest that the obtained films are suitable for thin film solar cells application[8].

Mott-Schottky:

Fig. 6 reveals the Mott-Schottky plot for CZTS thin film prepared by using 90 mM of glycine concentration. The plots slope confirms the nature of material. A positive slope implies the n-type material having electron as a charge carrier and a negative slope implies the p-type material with holes as a charge carrier[8]. The negative slope of Mott-Schottky was observed for the present CZTS thin film which confirms the p-type material. The charge carrier concentration was calculated by using the following relation (eq. (1)):

$$N = -\frac{2}{e\varepsilon\varepsilon_0 S} \quad (1)$$

where N is the number of charge carriers in cm^{-3}, the static relative dielectric constant for CZTS is represented using ε and it is considered to be 4.27, the permittivity of free space in F cm^{-1} is denoted by ε_0 and e is the charge of the electron in Coulombs[8]. The charge carrier was calculated for the CZTS

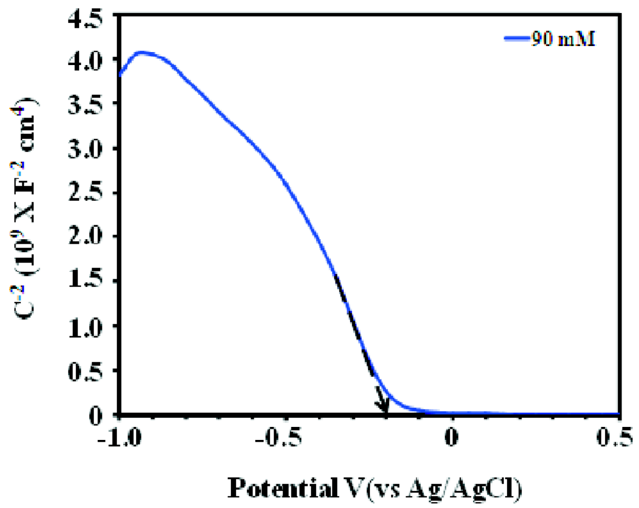

Fig. 6. Mott-Schottky plot for CZTS thin film using 90 mM of glycine concentration.

thin film formed by 90 mM of glycine was 1.58×10^{23} cm^{-3}.

The flat band potential of the formed film is also calculated by extrapolating the linear section of the curve to x axis. The obtained flat band value was found to be –0.20 V.

Conclusions

At different concentration of glycine the CZTS thin film were deposited successfully in single-step on gold coated substrate. Surface roughness was observed to escalate with rise in glycine concentration. At higher concentration of Glycine stoichiometry was found to be deviating by desired stoichiometry. The films deposited with 90 mM concentration of glycine showed closer to required stoichiometry. The drop in resistance value when samples are exposed to light said to be suitable characteristics for the application of solar cells. The negative slope confirmed the p-type material with charge carrier concentration and flat band value of 1.58×10^{23} cm^{-3}, –0.20 V respectively.

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