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Effect of Trisodium Citrate on the Properties of Electrodeposited Cu_2ZnSnS_4 (CZTS) Layers on ZnS Thin Films Using a 2-Electrode Method

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Abstract

Electrodeposition of CZTS thin films on ZnS was carried using a 2-electrode method to fabricate superstrate structure solar cells. A comprehensive study was performed on the effects of trisodium citrate on the CZTS electrolyte bath. In the present investigation, it is demonstrated that using a CZTS electrolyte with a concentration of 0.2 M trisodium citrate yields CZTS thin films with an electronic bandgap of 1.52 eV, a p-type nature, and good uniformity, which are all results desired for the fabrication of thin film solar cells. Characterization was performed using UV-Vi-IR optical absorption, SEM imaging, Raman spectrometry, and photoelectrochemical cells conducted for electronic bandgap, morphology, chemical composition, and semiconductor conductivity, respectively.

Keywords

Electrodeposition, Complexing Agents, CZTS Thin Films, Semiconductors

1. Introduction

With the increasing demand of solar energy harvesting devices, many materials have been looked upon to increase the efficiency of existing solutions as well as reduce the cost of generating renewable energy. Cu-In-Ga-S (CIGS) and CdTe thin film solar cells have been extensively researched upon to replace silicon solar cells. However, the high toxicity and scarcity of materials have limited long term usage of these technologies. In contrast, Cu_2ZnSnS_4 (CZTS) is a promising material to overcome the obstacles CIGS present. CZTS is a p-type quaternary compound with a bandgap of 1.4 - 1.5 eV and a high absorption coefficient ($>10^4$ cm^{-1}), which makes it an ideal candidate for photovoltaic applications [1].

Different methods have been used to fabricate CZTS thin films, which include vacuum methods such as sputtering [2], thermal evaporation [3], pulse laser deposition [4], and chemical vapor evaporation [5], as well as non-vacuum methods such as spray pyrolysis [6], electrochemical deposition [7], and chemical bath deposition [8]. Among the aforementioned methods, electrodeposition stands out as an attractive fabrication method due to its simple experimental setup, inexpensive equipment, low-wastage generation, low-temperatures of operation, and scalable ability. Nevertheless, electrodeposition of four compounds from a single electrolyte can prove to be a difficult task. There is a difference of 1.2 V in the reduction potential of Cu, Zn, Sn, and S [9]. Complexing agents can be used to reduce the gap between the reduction potential of Cu, Zn, and Sn ions to facilitate the fabrication of CZTS from a single bath.

Pawar, *et al*. have studied the effects of trisodium citrate on the synthesis of CZTS thin films on ITO. Their findings reported stoichiometric composition of CZTS with the usage of citrate for electrodeposition [10]. In this study, a citrate complex system was used to fabricate CZTS on glass/FTO/ZnS, for the fabrication of thin film solar cells. The surface, composition, conductivity, and reduction potential of the ions in electrolytes with different concentrations of trisodium citrate were studied.

2. Experimental Procedure

Glass/FTO/ZnS annealed substrates with an area of 4 cm^2 were used as the cathode for the electrodeposition of the CZTS thin films. A two-electrode configuration was used, with a carbon rod working as the counter electrode. The CZTS films were prepared from an electrolyte containing 0.02 M copper (II) sulfate ($CuSO_4$), 0.01 M zinc sulfate heptahydrate, 0.02 M tin (II) sulfate ($SnSO_4$), and 0.02 M sodium thiosulfate ($Na_2S_2O_3$). Tartaric acid was used to adjust the pH of the electrolyte to 5.0 ± 0.05 [10]. Different chemical baths were used with varying concentrations of trisodium citrate ranging from 0 to 0.4 M. The total time of deposition of the films was of 45 minutes at room temperature. Post-deposition, the films were annealed under normal atmospheric conditions at 400˚C with an up rate of 10˚C/min to avoid damage to the glass substrate.

Different analytical techniques were used to analyze the CZTS layers deposited on ZnS. To study the conductivity type of the films, photoelectrochemical (PEC) cell tests were carried under dark and illuminated conditions. Raman spectroscopy was used to study the structure and molecular vibration of the films. An Innovative Photonic Solutions Raman probe with a stabilized hybrid external cavity laser (HECL) was used in this research. Ultraviolet-visible-near infrared spectrometry was used to analyze the optical properties of the films using a UNICO UV/Vi/IR spectrometer. A VersaSTAT 3 from Princeton Applied Research was used to carry chronoamperometry and cyclic voltammetry measurements, which were carried out from 0.8 to −1.8 V (vs. OC) with a scan rate of 10 mV/s. A Thermo Scientific Lindberg Blue M furnace was used to perform

the annealing process.

3. Results and Discussion

CV was conducted to identify initial growth range for CZTS layers followed by optimization using characterization using PEC tests, optical absorption, Raman and SEM methods.

3.1. Cyclic Voltammetry

Cyclic voltammetry analysis was used to understand the reaction of the ions at different applied voltages for each electrolyte fabricated. The cyclic voltammograms were generated with a scan rate of 10 mV/s from 0.8 to −1.8 V vs OC. Figure 1 shows that the bath containing 0.2 trisodium citrate had stronger peaks for the reduction potential of all ions.

The CV for 0.2 M shows that Zn-reduction ($Zn^{2+} + 2e \rightarrow Zn$) was taking place at −1.25 V. The reduction of Sn ($Sn^{2+} + 2e \rightarrow Sn$) was found at −1.1 V, and the peak reduction of Cu ($Cu^{2+} + 2e \rightarrow Cu$) was found at −0.9 V. Sulfur exhibited a reduction peak ($S^{2+} + 2e \rightarrow S$) at −0.75 V. In contrast with the bath without citrate, the difference between S and Zn reduction peaks was of 0.95 V. The citrate complex was able to bring the reduction peaks of the ions present in the electrolyte closer together, facilitating the process of electrodeposition.

3.2. Photoelectrochemical Cell Tests

Photoelectrochemical cell (PEC) tests were used to determine the conductivity type of the thin film layers. PEC cells consist of forming a solid/liquid junction with the glass/FTO/CZTS and a suitable electrolyte. In this case, a 0.2 M $Na_2S_2O_3$ electrolyte was used for the liquid junction. The sample was immersed in the electrolyte and the open circuit (OC) current was measured against a carbon rod

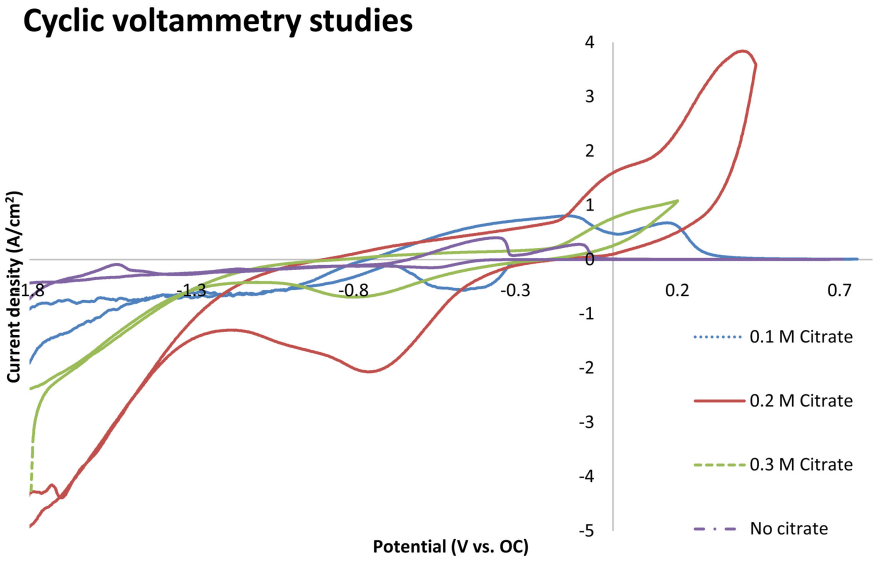

Figure 1. CVs recorded at a scan rate of 10 mV/s with varying citrate composition.

(cathode). The solid/liquid junction acts as a weak Schottky diode and the difference between the OC current in dark and illuminated conditions yields the PEC signal. The PEC signal provides with useful information on the strength of the depletion region which can help interpret the quality of the thin film. The PEC cell was calibrated against CdS, a well-known n-type semiconductor [11]. A negative signal was obtained from this n-type semiconductor, meaning that any positive signal pertained to a p-type semiconductor.

Several samples with growth voltage ranging from −1.0 V to −1.2 V were fabricated and tested. Table 1 shows the change of electrical conductivity with respect to the growth voltage and the citrate concentration. In all cases, the electrodeposited CZTS thin films showed a p-type nature. However, the films deposited in the bath containing 0.3 M trisodium citrate showed poor electrical conduction and quality overall.

3.3. Optical Absorption

The optical properties of the annealed thin films were studied using a UV-Vi-near IR spectrometer. The optical absorption measurements were carried on a light wavelength range of 300 to 1100 nm. Tauc plots were generated as shown in Figure 2 and the electronic bandgap of the materials were determined. To obtain these plots, Stern's Relation shown in Equation (1) was used.

$$\alpha = \frac{k\left(hv - Eg\right)^{\frac{n}{2}}}{hv} \tag{1}$$

Table 1. The electrical conductivity vs growth voltage for CZTS with varying trisodium citrate concentration.

Growth voltage (mV)	Citrate concentration (M)	As-deposited PEC signal (mV)	Heat-treated PEC Signal (mV)
1000	0	7	14
1050	0	11	19
1100	0	12	21
1150	0	17	24
1000	0.1	11	17
1050	0.1	21	24
1100	0.1	25	29
1150	0.1	34	37
1000	0.2	18	26
1050	0.2	22	34
1100	0.2	31	38
1150	0.2	34	47
1000	0.3	3	7
1050	0.3	8	15
1100	0.3	9	20
1150	0.3	13	17

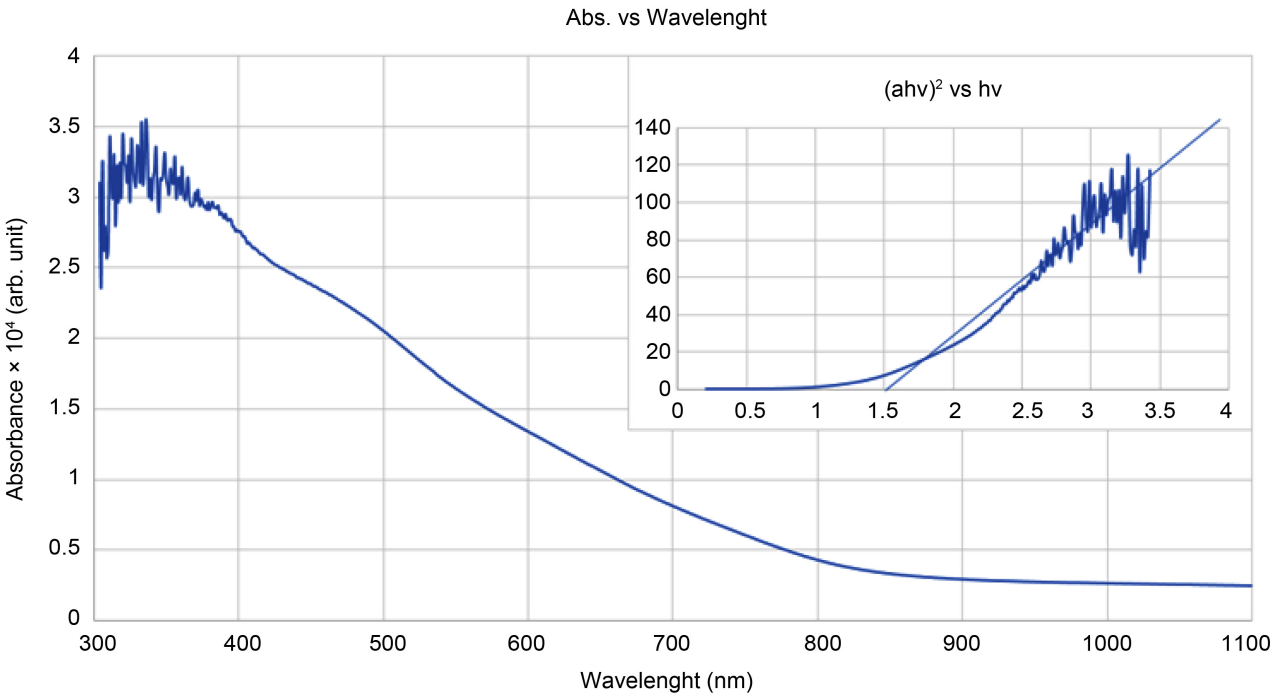

Figure 2. Optical absorption spectra and insert Tauc plot of CZTS deposited in a 0.2 M Citrate bath. The bandgap was found to be 1.52 eV.

where v is the frequency of the photon, h is the Planck's constant (6.63 × 10^{-34} Js), Eg is the bandgap, k is the band tailing parameter and n is 1 for direct bandgap materials [9]. Hence Equation (2) can be obtained:

$$(\alpha hv)^{\frac{1}{2}} = k\left(hv - E_g\right) \tag{2}$$

By plotting $(\alpha hv)^{\frac{1}{2}}$ versus the photon energy (hv), the semiconductor's direct bandgap can be found. It is necessary to extrapolate the straight-line portion of the curve to the hv axis. The intercept will correspond to the bandgap of the material.

The bandgap of the CZTS was found to be 1.49, 1.51, 1.52, and 1.48 eV for baths without citrate, and with 0.1 M, 0.2 M, and 0.3 M trisodium citrate concentrations, respectively. The obtained values are in accordance with previously reported values of CZTS of 1.54 eV. The bandgap obtained from the samples produced in the 0.2 M bath were those closest to the ideal direct bandgap for an absorber layer in a p-n-junction solar cell.

3.4. Raman Spectrometry

To confirm the presence of secondary phases, Raman spectrometry analysis was performed. The data were matched with published data of CZTS and it was found that the strongest peaks in the spectra obtained corresponded to kesterite CZTS, found at 462 cm^{-1} and peaks of lower intensity of CZTS past the main peak [3]. ZnS is known to exhibit strong peaks at 352 and 271 cm^{-1} and such peaks were found in the results obtained [12]. Crystalline SnS_2 phase was

matched to the peak found at 225 cm^{-1} [13]. Figure 3 shows the Raman spectra for CZTS deposited in the 0.2 M citrate bath.

3.5. Scanning Electron Microscope Imaging

SEM imaging was used to analyze the annealed samples. Figure 4 shows the surface morphology of a sample produced using 0.1 M citrate bath (a) and a sample fabricated using a 0.2 M citrate bath (b). SEM images revealed that the films prepared on the 0.2 M citrate solution had a uniform topography. The surface showed a compact grain structure with more uniform grain sizes throughout. The small size of the grains signifies good adhesion of CZTS to the ZnS layer. No evident voids were found using SEM. The samples produced with the 0.1 M citrate bath showed bigger clusters of CZTS crystals with a varying grain size. The structure of this CZTS layer is non-uniform and pores can be observed in the images, showing the ZnS layer underneath.

4. Conclusion

CZTS films have been deposited on ZnS for the fabrication of substrate thin film solar cells. Using Trisodium Citrate as a complexing agent, it was possible to bring together the reduction potential of the four different compounds present in the electrolyte to facilitate electrodeposition. It was found that the best samples for solar cell purposes were obtained from an electrolyte containing 0.2 M Trisodium citrate. Raman spectrometry revealed the presence of secondary phase ZnS on the CZTS surface that could reduce the efficiency of the solar cell. SEM revealed a uniform surface with indications of good adhesively to the ZnS underlying surface. In this research, it was possible to fabricate stable n-p layers

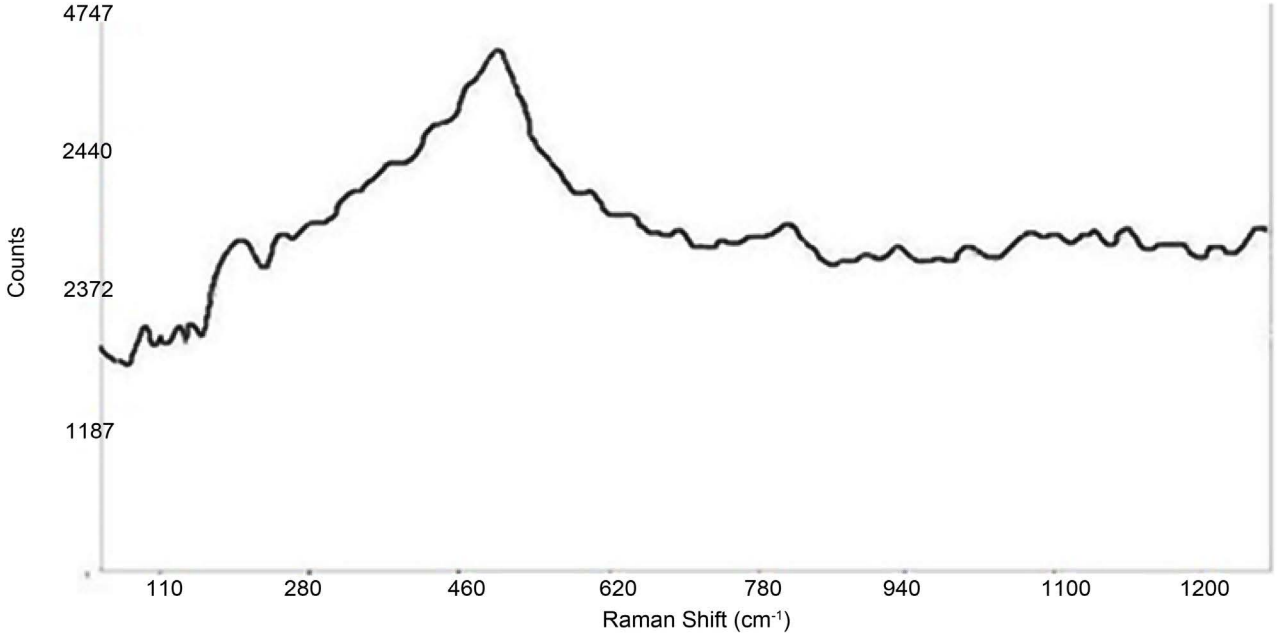

Figure 3. Raman spectra for CZTS films deposited using 0.2 M trisodium citrate.

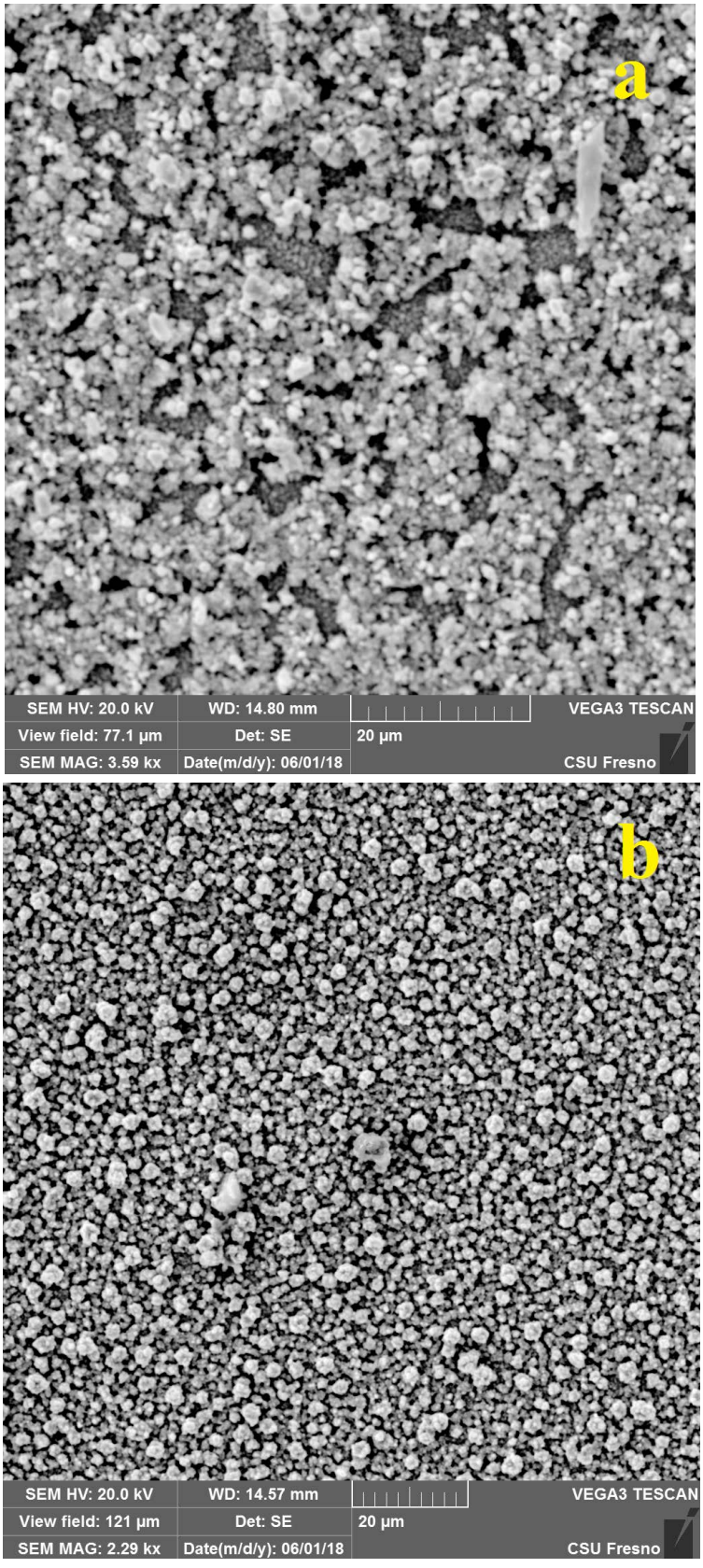

Figure 4. Surface morphology of CZTS fabricated using a 0.1 M (a) and 0.2 M (b) citrate complex.

for the production of thin film solar cells. Such solar cells have the superstrate structure increasing the light penetration to the n-p junction without the hindrance of the grid on the solar cells on substrate structures.

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Conflicts of Interest

The authors declare no conflicts of interest regarding the publication of this paper.

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