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Pulsed electrodeposited CZTS thin films: Effect of duty cycle

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ABSTRACT

The kesterite Cu_2ZnSnS_4 (CZTS) thin films are deposited by a novel pulsed electrodeposition method. The pulse potentials are kept at −1.1 V (SCE) and −0.7 V (SCE). The duty cycle is varied from 33% to 67% by varying pulse durations. The effect of duty cycles on the properties of CZTS thin films is investigated. The films deposited using an optimized duty cycle condition exhibit phase pure CZTS with nearly stoichiometric composition and have a compact morphology with optical band gap energy of 1.5 eV.

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1. Introduction

The photovoltaic quality thin films of Cu_2ZnSnS_4 (CZTS) have been prepared using a plethora of techniques, which are subdivided as physical (vacuum) and chemical (non-vacuum) processes [1]. The highest efficiency of 11.1% has been reported for spin-coated CZTS thin films [2]. The chemical processes offer many attractive features like, simplicity, scalability, cost-effective, low temperature deposition capability over large areas and manufacturability over their physical counterparts. Electrodeposition is an attractive electrochemical process that enables high quality metallic and semiconducting thin films. It has also been used widely to prepare photovoltaic quality quaternary compound thin films of CZTS. So far, three different approaches have been employed to electro-synthesize precursors for CZTS thin films on Mo substrates; (i) sequential electrodeposition of metallic stacked layers on copper (Cu), zinc (Zn) and tin (Sn) [3], (ii) simultaneous electrodeposition of metallic Cu, Zn, and Sn thin films [4], and (iii) single step electrodeposition of CZTS thin films from an electrolyte containing mixed Cu, Zn and Sn cationic precursors [5]. The precursors are further subjected to high temperature sulfurization (~550 °C) to obtain phase-pure CZTS thin films.

The electrodeposition of CZTS thin films involves deposition of Cu, Zn and Sn and/or their sulfides usually from an electrolytic bath. The standard reduction potentials of these elements differ widely and hence cause problems and impose certain limitations for straight forward single step electrodeposition. The electrodeposition of CZTS is complicated because electrodeposition of Zn competes with hydrogen evolution reaction (HER) and causes hydrogen embrittlement that hampers growth of smooth electrodeposits, required for photovoltaic quality CZTS absorber layers [3]. Sn electrodeposits are often porous, coarse, and non-adherent with formation of whiskers, needles, and dendrites. Therefore the use of surfactants, additives and leveling agents become imperative for obtaining smooth photovoltaic quality electrodepositions of Sn and Zn [6].

The pulsed electrodeposition (PED) has been widely used in metal electrodeposition to increase deposition rate and modify film quality [7]. The PED has also been used in the $CuInSe_2$ deposition to improve film quality [8]. However, it has not yet been employed for the growth of CZTS thin films. PED is similar to the conventional direct current electrodeposition, except that the plating currents are turned on and off in a controlled fashion, resulting in a square wave with pulse duration, T_{ON}, time between pulses, T_{OFF} and overall deposition duty cycle. PED has the advantage of flexibly creating complex alloy composition. By controlling metal ion concentrations, current density and pulse durations, nucleation of new crystals can be favored over growth of existing crystals, resulting in films with ultrafine grain structure [9].

In this endeavor, we report on the PED of CZTS thin films with smooth morphology merely by controlling the pulse amplitude, duration and duty cycle. The growth of CZTS thin films with controlled stoichiometric ratios and phase purity without use of surfactants and additives is demonstrated. The effect of duty cycle on the electrodeposits is explained explicitly.

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2. Experimental

The PED process was carried out with a conventional three electrode potentiostat (Wontech WMPG 1000). The graphite electrode was employed as a counter electrode and SCE electrode served as the reference electrode. The Mo-coated glass substrate (2.5×2.5 cm^2) was used as a working electrode. An aqueous electrolytic bath contains copper sulfate pentahydrate ($CuSO_4 \cdot 5H_2O$), zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$), tin sulfate ($SnSO_4$) and sodium thiosulfate ($Na_2S_2O_3$), with trisodium citrate as a complexing agent and pH of the bath was maintained at 5.0 by adding an appropriate quantity of tartaric acid.

The precursor films were deposited for 45 min using the PED method. The pulse waveform was applied between two potentials, $V_1 = -1.1$ V and $V_2 = -0.7$ V. After the PED the films were further annealed under normal pressure using a gas mixture of 5 vol% Ar/H_2S.

The structural properties of the films were carried out using a high resolution X-ray diffractometer (XRD, X'pert Pro), a field-emission scanning electron microscope (FE-SEM, JEOL-6300), attached with an energy dispersive X-ray spectrometer (EDS) and an UV–vis spectrometer (Cary-100, Varian).

3. Results and discussion

The pulse potentials and their respective durations have been fixed such that during time t_1, potential V_1 (−1.1 V (SCE)) and during time t_2, potential V_2 (−0.7 V (SCE)) get imposed on the working electrode for 330 ms and 670 ms respectively. Further, the time durations were varied as 500 ms and 670 ms for t_1 and 500 ms and 330 ms for t_2, so as to vary duty cycles from 33% to 67%.

During t_1, at −1.1 V (SCE) a very thin layer of Zn–S/Cu–Sn–S was electrodeposited, followed by a thin layer of Cu–Sn–S during t_2, at −0.7 V (SCE). Thus many thin layers were deposited with alternating stacks and varying pulse time durations caused their thicknesses to vary. The thickness of an individual layer can be controlled precisely by maintaining time, t_1 or t_2 constant, and thus to accomplish desired stoichiometric Cu/(Zn+Sn), Zn/Sn and S/metal ratios. The variation of time durations t_1 and t_2 also facilitates formation of CZTS films with Cu-poor and Zn-rich compositions, known to be superior for getting an excellent photovoltaic property.

The compositions of the CZTS films deposited at various duty cycles have been determined from EDS analysis and are given in Table 1. As expected, Zn concentration increases with the increasing duty cycle and is higher for 67%. Similarly Sn concentration also gets incremented with duty cycle and becomes higher for 67% duty cycle. There is a minor change in the concentration of S species, while Cu concentration decreases with increasing duty cycle. The mechanism of lowering Cu content is not very clear. However some complex chemical/electrochemical reactions lead to such reduction in Cu content in the films with increase duty cycle. The results were analyzed for multiple samples and did not vary from Table 1. Further focused work is warranted to understand the Cu deposition mechanism in these precursor films. Nonetheless, it is possible to vary stoichiometric ratios precisely by merely varying duty cycles. Jeon et al. [9] have also used PED for CZTS thin films; however, the deposited CZTS films showed composition far from stoichiometry leading to many secondary phases.

Table 1
Chemical composition of pulse electrodeposited CZTS films at various duty cycles.

Duty cycle (%)	t_1 (ms)	t_2 (ms)	Atomic (%)					
			Cu	Zn	Sn	S	Cu/(Zn+Sn)	S/metal
33	330	670	27	6.5	10.5	56	1.5	1.27
50	500	500	26	9	11	53	1.1	1.12
67	670	330	24	12	13	52	0.96	1.08

Fig. 1(a) shows the XRD spectra for the CZTS films deposited at various duty cycles. All the samples are polycrystalline and exhibit four characteristic peaks of CZTS along (112), (200), (220) and (312) at 2θ values of 28.53°, 32.98°, 47.32° and 56.17°, respectively (JCPDS 26-0575). The intensity of a major peak along (112) plane increases with decrement in duty cycle, whereas there is no much variation in the intensities of other peaks. The crystallinity of the samples improves slightly with decrease in duty cycle from 67% to 33%.

It is well-known that the X-ray diffraction peaks of CZTS coincide exactly with ZnS and Cu_2SnS_3 (CTS) compounds (JCPDS 89-2426 and 89-4714). Therefore structural characterization and phase analysis were performed using Raman spectroscopy. Fig. 1 (b) shows Raman spectra for all the samples over 200–600 cm^{-1}. The peaks at 338, 318 and 288 cm^{-1} clearly indicate formation of CZTS phase for all the samples. However, a close inspection of the Raman spectrum for the film deposited at 33% duty cycle reveals a peak at 310 cm^{-1}, a signature of Cu_2SnS_3 phase. Hence it is clear that these samples contain mixed CZTS and CTS compounds and this may be the reason of getting slightly higher Cu concentration in EDS analysis.

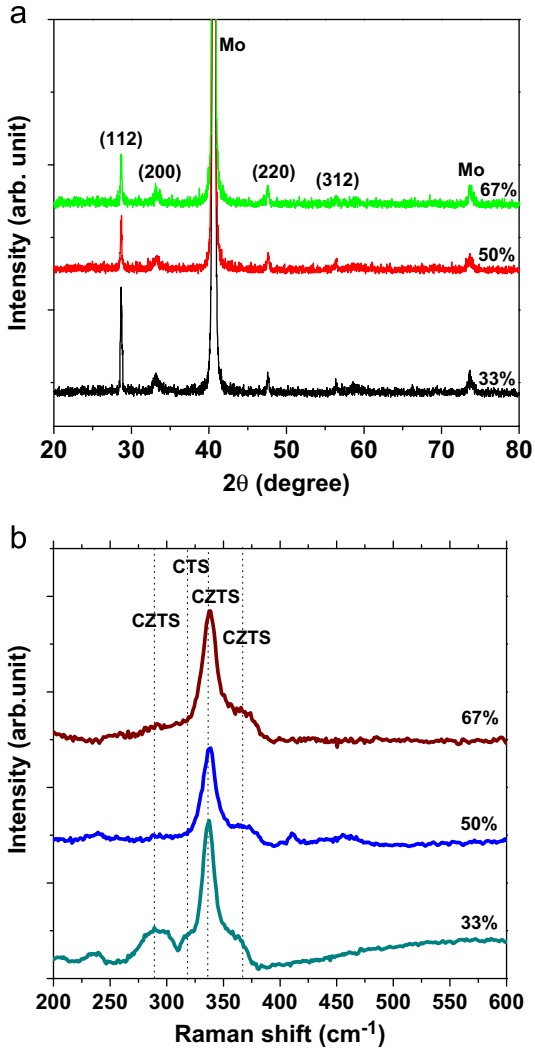

Fig. 1. (a) XRD and (b) Raman spectra of the CZTS films deposited at various duty cycles.

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