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Synthesis of thin Cu–Zn–Sn–S films for solar batteries by one-stage electrodeposition followed by annealing in a reactive atmosphere

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The thin Cu–Zn–Sn–S films for solar batteries were prepared by the one-stage electrodeposition of precursors from a citrate buffer solution followed by annealing in a sulfur atmosphere.

Quaternary copper compounds $Cu_2ZnSn(S,Se)_4$ (CZTS, CZTSe) play a special role among promising solar energy converters. These compounds have the same tetragonal structure as Cu–In–Ga–S (CIGS), but indium and gallium atoms are replaced by zinc and copper atoms.[1] These semiconductor materials have an optimum band gap (1.0–1.5 eV) and a high light absorption coefficient ($> 10^4$ cm^{-1}). Therefore, films as thin as 1–2 μm suffice for the efficient operation of solar batteries of this type.[2,3] Furthermore, these compounds are composed of low-toxic elements that are abundant in nature.

Vacuum methods are most popular for the preparation of absorbing CZTS(Se) layers.[4–9] However, these techniques employ high temperatures, and they are hardly scalable and expensive. In turn, liquid-phase methods such as electrochemical deposition can be more promising as they do not use high temperatures and allow a film to be deposited on substrates of any shape and on large areas.[10–12]

Two versions of this method can be used to obtain thin CZTS films. The first one is the sequential galvanic coating, in which the final film is formed by the sequential deposition of metal layers with predefined thicknesses followed by additional sulfurization/selenization. The second variety involves one-stage electrodeposition, where all of the four components are deposited from one working solution. The advantage of the latter procedure is obvious: one can work with a single solution, which accelerates the process and simplifies the regeneration of working solution.

However, there are very few studies on CZTS synthesis by one-stage electrodeposition. Furthermore, devices based on films obtained by this method have low efficiency at this point. The reasons of this remain as yet unclear. It may be a consequence of our insufficient knowledge of the synthesis and subsequent annealing of samples. Difficulties are also created by the narrow potential range where CZTS compounds of required stoichiometry are formed.[1,13,14]

Attempts were made to obtain thin CZTS films by one-stage electrodeposition from a buffer solution containing citrate and tartrate ions.[2,15–17] However, this system is unstable and stable tartrate deposits can be formed upon prolonged use. They impair the experiment reproducibility. Furthermore, annealing was carried out in an atmosphere containing no sulfur, which also affects the final film composition: in certain cases, the resulting films are not monophase and contain impurities, which can be easily determined by XRD analysis.

A new method for the preparation of thin CZTS films for solar batteries by one-stage electrodeposition of precursors from a citrate buffer solution followed by annealing in sulfur atmosphere is proposed here.

The electrodeposition was carried out in a three-electrode electrochemical cell using a working electrode [glass/Mo or glass/ITO (In_2O_3–SnO_2) substrate], a counter electrode (platinum or graphite), and a reference electrode [3M silver/silver chloride electrode (SSCE)].The working solution contained 0.02 mol dm^{-3} $CuSO_4$, 0.01 mol dm^{-3} $ZnSO_4$, 0.02 mol dm^{-3} $SnSO_4$ and 0.02 mol dm^{-3} $Na_2S_2O_3$. A mixture of trisubstituted sodium citrate and citric acid (0.2 M Na_3Cit + 0.1 M H_3Cit), pH 5–5.5, was used as a buffer solution. Electrodeposition of thin CZTS films results from a combination of the following electrochemical and chemical reactions:

$$Cu^{2+} + 2e \rightarrow Cu^0,$$
$$Zn^{2+} + 2e \rightarrow Zn^0,$$
$$Sn^{2+} + 2e \rightarrow Sn^0,$$
$$S_2O_3^{2-} + 6H^+ + 4e \rightarrow S^0 + 3H_2O,$$
$$2Cu^0 + Zn^0 + Sn^0 + 4S^0 \rightarrow Cu_2ZnSnS_4 \text{ (chemical reaction).}$$

After electrodeposition, samples were annealed for 30–60 min at 500–550 °C in a three-zone furnace under a sulfur atmosphere.[16]

The cyclic voltammograms obtained during CZTS synthesis from a citrate buffer solution on glass/Mo supports (Figure 1)[†] exhibited well-resolved cathodic peaks in the following regions: –1045 mV typical of hydrogen evolution processes (curve *1* for the reference buffer solution), –380 and –1022 mV typical of copper reduction (curve *2*), –1120 mV typical of zinc reduction (curve *3*), –874 and –1073 mV typical of tin reduction (curve *4*) and –1060 mV – reduction of the sulfur-containing component (curve *5*) from individual citrate buffer solutions. Note that more than one peak is present for copper and tin, which suggests that reduction of these metals occurs *via* intermediate oxidation states and that reduction of the corresponding metal complexes is involved.[‡] Curve *6* in Figure 1 corresponds to the cyclic current–potential curve in the citrate buffer solution containing all of the

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[†] The voltammetric characteristics and specific features of electrodeposition were studied using an IPC Pro potentiostat/galvanostat. Cyclic voltammetric curves were recorded at a potential sweep rate of 10 mV s^{-1}. A constant potential was maintained during electrodeposition. The films were studied by XRD analysis (DRON-4, CuKα irradiation), scanning electron microscopy (Zeiss LEO SUPRA 25) and optical spectroscopy (Shimadzu UV-3101PC). Elemental compositions were studied by X-ray fluorescence analysis (X-Art, COMITA).

[‡] Two additional peaks with maxima around –700 and –800 mV are observed on the cyclic voltammogram of the original buffer solution in the syntheses on glass/ITO substrates. These peaks are apparently due to the reduction of tin and indium contained in ITO.

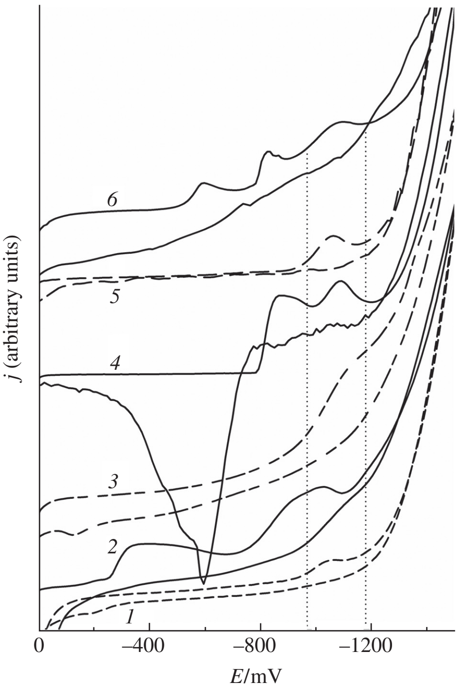

Figure 1 Cyclic voltammograms on a Mo support in (*1*) 0.2 M Na_3Cit + + 0.1 M H_3Cit; (*2*) 0.02 M $CuSO_4$ + 0.2 M Na_3Cit + 0.1 M H_3Cit; (*3*) 0.01 M $ZnSO_4$ + 0.2 M Na_3Cit + 0.1 M H_3Cit; (*4*) 0.02 M $SnSO_4$ + 0.2 M Na_3Cit + + 0.1 M H_3Cit; (*5*) 0.02 M $Na_2S_2O_3$ + 0.2 M Na_3Cit + 0.1 M H_3Cit; (*6*) 0.02 M $CuSO_4$ + 0.01 M $ZnSO_4$ + 0.02 M $SnSO_4$ + 0.02 M $Na_2S_2O_3$ + 0.2 M Na_3Cit + + 0.1 M H_3Cit.

four components. A peak in the range from –1090 to –1190 mV, where all the four components can be reduced simultaneously, is of particular interest. Based on these data, the potential range was selected for scanning in 50 mV steps in order to find the deposition potential with a higher accuracy.

Analysis of XRD data† showed that the resulting non-annealed precursor films were amorphous, apparently, due to hydrogen evolution in this potential range. The minimum content of impurity phases is characteristic of films obtained in a range from –1090 to –1140 mV followed by annealing in a sulfur atmosphere. Figure 2 shows X-ray diffraction patterns of CZTS samples. It is evident that all the lines can be attributed to the kesterite phase (tetragonal lattice, $I\bar{4}2m$). The lattice parameters are a = 5.433 Å, c = 10.843 Å for the samples obtained at E = –1090 mV, and a = 5.426 Å, c = = 10.831 Å for the samples obtained at E = –1140 mV [the parameters of CZTS powders obtained by solid phase synthesis are a = 5.427 Å, c = 10.84 Å (JCPDS card 26-0575)]. It is important that the intensity ratio of the lines characteristic of the kesterite phase is close to that of the polycrystalline reference sample (JCPDS card 26-0575), which indicates that the sample contains no manifest textures. The CZTS sample obtained at E = –1190 mV contains a considerable amount of impurity phases (X): SnS, Cu_xS, Cu_xSn_y, *etc*.

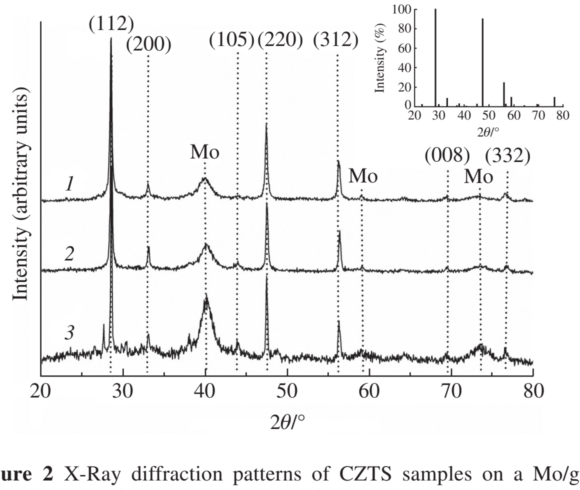

Figure 2 X-Ray diffraction patterns of CZTS samples on a Mo/glass support obtained from Na_3Cit + H_3Cit buffer solution at (*1*) –1090, (*2*) –1140 and (*3*) –1190 mV with subsequent annealing for 30 min at 550 °C in a sulfur atmosphere.

Table 1 Chemical composition of CZTS films obtained at E = –1140 mV with the subsequent annealing at 550 °C in a sulfur atmosphere.

Empirical formula	Cu (%)	Zn (%)	Sn (%)	Cu/(Zn+Sn)
$Cu_{1.19}Zn_{0.4}Sn_{1.96}S_4$	15.06	13.10	46.34	0.50
$Cu_{0.42}Zn_{0.31}Sn_{1.68}S_4$	7.13	5.41	53.26	0.21

Table 1 presents the empirical formulas and element ratios in the CZTS films obtained at –1140 mV and subsequently annealed in sulfur vapour at 550 °C. Apparently, the films are depleted in zinc because zinc has the lowest reduction potential in comparison with all the other elements (E = –762 mV),[18] whereas the higher tin content in the samples is due to the lower complex stability in comparison with copper.[19,20]

Figure 3 demonstrates a plot in the $(\alpha h\nu)^2$–$h\nu$ coordinates for CZTS samples deposited at E = –1140 mV, which allows the semiconductor band gap to be estimated. Intersection of extrapolated straight line with the x axis (α = 0) gives the band gap E_g = 1.55 eV. These values are in good agreement with published data.[9,21–23]

The photoactivity of CZTS films was determined by a photoelectrochemical method based on charge transfer between a photoelectrode (CZTS sample) and a counter-electrode in a specially selected electrolyte.[16] Current–voltage plots were recorded for all CZTS samples in aqueous Eu^{3+} solution under chopped light conditions (100 mW cm^{-2}) at potentials from –1000 to 0 mV (*vs.* 3M SSCE). For demonstration purposes, Figure 4 presents data on the photoactivity of CZTS films obtained at E = –1140 mV. The instants when light was intermittently turned on/off are shown with arrows. One can see that the segments of photocurrent raise and decay relative to the dark current consist of two components: fast (shown as circles in the figure) and slow. In this case, we are only interested in the fast component, which indicates that the film conductivity changes under illumination with light due to the generation of new mobile charge carriers. The observed photoconductivity directly evidences that the samples synthesized possess photoactivity.§ Since photoresponse was observed in the cathodic region, it can be concluded that the samples are p-type semiconductors.

Thus, we developed a new method for synthesizing monophase CZTS films. It involves electrodeposition from a citrate

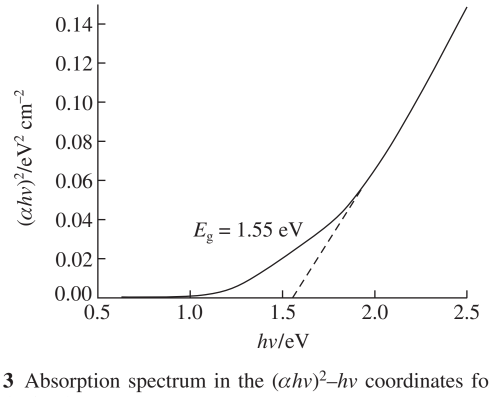

Figure 3 Absorption spectrum in the $(\alpha h\nu)^2$–$h\nu$ coordinates for a CZTS sample obtained at E = –1140 mV.

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§ For comparison, Figure 4 shows the potential *vs.* current density plot for a non-photosensitive film (dashed line).

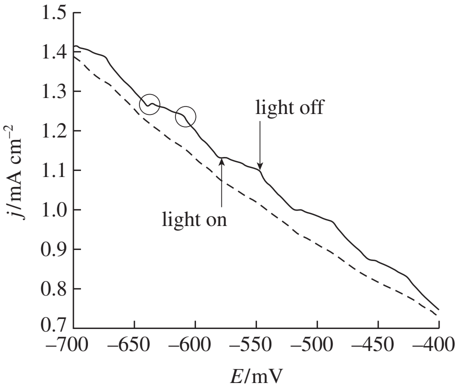

Figure 4 Dependence of current *vs.* voltage in a photoelectrochemical cell under chopped light for a CZTS sample obtained at $E = -1140$ mV.

buffer solution followed by annealing in a sulfur atmosphere. The method allows one to obtain CZTS films with the composition and properties that meet the requirements for absorbing layers in solar batteries.

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