Formation of Cu$_2$ZnSnSe$_4$ thin films by selenization of electrodeposited stacked binary alloy layers

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Abstract

Brass-Bronze thin-stacked layers electrodeposited in Potentiostatic conditions were selenized in an iso-thermal quartz tubular reactor. The ratio of metal components in selenized films was adjusted through appropriate choice of composition and thickness of the constituent layers. Focus is on the influence of annealing conditions on crystalline structure, phase composition, surface morphology and optical properties of the obtained Cu$_2$ZnSnSe$_4$ (CZTSe) thin films and peculiarities of formation CZTSe thin films.

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1. Introduction

Future development of thin film photovoltaics depends on the deployment of low cost and easily up scalable deposition methods for abundant and non-toxic compounds [1]. Ternary chalcopyrites CuInS$_2$ (CIS) and Cu(In,Ga)Se$_2$ were a promising solution but increasing prices of the rare metals In and Ga have affected the cost-efficiency ratio. Replacement of III group metals with cheap and widespread Zinc and Tin serve as another opportunity for diversification and industrialization of compound thin film photovoltaics [2]. Cu$_2$ZnSnSe$_4$ (CZTSe) is a structure analog of CIS where III group (Indium or Gallium) atoms are exchanged with Zinc and Tin. CZTSe is a prospective material with a direct band gap near 1.44 eV, close to the optimum for the solar irradiation spectra and a high absorption coefficient ranging to 10$^4$ cm$^{-1}$ [3].

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There are numerous investigations on the sulfur compound Cu₂ZnSnS₄ developed by atom beam sputtering [4], thermal evaporations [5] and electron beam evaporated precursors processed in H₂S atmosphere [6]. Later, electrodeposition routes [7,8] for the formation of substrate metallic precursors subjected subsequently to sulfurization were explored. Abou-Ras et al. [7] studied Electrodeposition route developed specifically by the formation of metallic alloy Cu-Zn-Sn precursor layers [9] to build solar cells.

The Selenium compound CZTSe thin layer absorbers were grown by pulsed laser ablation [10], one step RF magnetron sputtering [11] or with sequential selenization [12] as well as synthesis from melts [13]. The monograin thin film Cu₂ZnSnSe₄ solar cell recently developed has given Voc = 422 mV, Jₚ = 21.3 mA/cm² and FF 44% with an overall efficiency of 2.16% [14].

This article focuses on the formation of Cu₂ZnSnSe₄ absorber layers by sequential electrodeposition of the Cu-Zn alloy and Cu-Sn stacked precursors, followed by reactive annealing in the atmosphere of selenium vapors.

2. Experimental details

Electrodeposition of precursor layers was performed in a potentiostatic condition with Wenking Bank PGstat 3440 in a three-electrode configuration at room temperature (20°C). Reference was a Saturated Silver Chloride electrode (Ag/AgCl: 3M KCl) and Platinum gauze with much higher active surface than the cathode served as a counter electrode. The working electrodes were molybdenum covered (near 1 µm thick) soda-lime glass substrates sized approximately 1 X 2.5 cm² or molybdenum foils with the same dimensions. Solutions for deposition Cu-Zn and Cu-Sn layers contained 0.6M Potassium Pyrophosphate and salts of Cu²⁺, Zn²⁺ and Sn²⁺ following formulations in [15]. Due to the oxidizing ability of Sn²⁺ on the anode or by the oxygen from air, the electrolytic cell for the deposition of Bronze layers was divided and the anode compartment was isolated through an ion (Na⁺) selective membrane. Anolyte was 0.2M Na₂CO₃ and to keep constant cation equilibrium concentrations for the membrane the catholyte contained 0.2M Na₃P₂O₇ and 0.4M K₃P₂O₇ as well as 0.1M Hydroquinone as an antioxidant.

Substrate layers Cu-Zn/Cu-Sn were selenized under isothermal conditions in evacuated 5-cm long quartz ampoules at 530°C – 560°C during 15 minutes at a 1.5-m thermal tubular reactor. In order to perform the thermal annealing samples with ampoules were placed in a preliminary preheated quartz holder pipe with wall thickness of 2mm, length of 60 cm and with inner diameter of 2.5 cm. After that the pipe with the ampoule inside was comparatively slowly moved out for cooling down to near 50 °C for another 20 minutes. Estimated annealing temperature profile is shown schematically in Fig.1. Other annealing experiments were performed for 1 h at 400°C preliminary preheating in a vacuum of 150 Torr for metal alloy sublayer homogenization and reactive selenization for 1 h at 560°C. Some singles, high temperature experiments, were performed at 750°C for 2 hours with alloy substrate samples deposited onto molybdenum foil.

![Fig. 1. Scheme of time-temperature profile for fast annealing experiments](image)

![Fig. 1. Thermal profile for selenization of thin alloy Brass – Bronze layers](image)
ULTRA 55 at accelerating voltage 1.74 kV through an In lens. The room temperature (RT) micro – Raman spectra were recorded by Horiba LabRam 800 high-resolution spectrometer equipped with a multichannel detection system on backscattering configuration. The spectrometer operated by Green 532 nm wavelength laser focused within a 1 μm spot diameter providing the incident light with a spectral resolution of 0.5 cm⁻¹.

X – ray diffraction analysis (XRD) was performed on Rigaku Ultima IV with Cu - Kα radiation (λ=1.5418Å) and 4 kV accelerating voltage. The diffracted beam was scanned in steps by 0.01° for 2 sec in an angular range from 10 to 80 degrees in 2θ. A comparison with JCDPS file cards [16] was made to assign the observed peaks. Phases manifested at least with three reflexes are taken into considerations. Optical investigations for determining the type and width of the band gap were carried out on UV-VIS-NIR spectrophotometer JASCO V-670 in the range of 200 to 2500 nm.

3. Results and discussion

Metal substrate layers were formed by two-step electrodeposition of alloys Brass (Cu-Zn) and Bronze (Cu-Sn) films, respectively. Final total film composition depends on the ratio of metals in the pair sublayers and its relative thickness. Total metal film thickness is defined by the sum of the thickness of the partial layers. The sequence of depositing Cu-Sn onto Cu-Zn was followed but an opposite order is possible as well. A 40-minute electrodeposition of Brass layer was followed by a 3-minute electrodeposition of Bronze layer to ensure formation of 1.5 – 2 μm thick CZTSe layer after selenization.

Fig.2. X-Ray diffraction patterns of thin layer Cu₂ZnSeSe₂ annealed in different regimes: Sample 36-5/8 – selenization of 15 minutes at 530 °C and 20 minutes slow cooling down; 36-8/4 – 1 hour annealing in vacuum and 1 hour selenization at 560°C

Fig.2 presents XRD patterns of samples 36-8/4 and 36-5/8. The first one had passed preliminary homogenization annealing in vacuum for 1 hour at 400°C, followed by reactive isothermal annealing in Selenium vapors for 1 hour at 560°C. The other sample had been treated for a short time (15 minutes) at 530°C and slow cooling down, following the procedure described by Fig.1. In both cases typical main reflexes of CZTSe at 45.1°, 27.16° and 53.52° in scale 2θ as well as minorities at 17.44°, 36.25°, 65.98° and 72.65° can be seen. Signals are strong and sharp indicating a well-crystallized Stannite – JCDPS 01-070-8930. Well-defined reflexes from the Molybdenum substrate layer at 40.18°, 56.03° and 72.45° in units 2θ were detected. There are other peaks, which could be attributed to the Molybdenum substrate as well - reflexes at 11.54° and 31.66°. If we assume the tall peak at 45.1° as a compound caused not only by the Stannite, there is obviously Mo₃Se₄ (JCDPS 03-06503701) - a product of selenization of the substrate. Detailed structural analysis has revealed non-mono-phase thin film materials in both cases. There are minor but well distinguished reflexes at 26.58°, 28°, 31.2° and 50.02° obviously related to CuSe (Klockmanite – 01-070-8576). Further, following the thesis for a compound character of the XRD pattern, another issue should be
mentioned. Probably it is possible that a thin film material consists of a cubic ZnSe (Stilleite – JCDPS 01-080-0021) the pattern of which coincides with the Stannite one at 27.16°, 45.1° and 53.52° in 2θ scale. In addition, a scrupulous analysis supposes the existence of another phase – Cu1.8Se (Bercelianite – JCDPS 01-071-0044) with reflexes at 27.16°, 45.1° and 56.03°.

Fig. 3 shows the RT Raman spectra of samples 36-8/2 and 36-5/7 deposited and annealed in the same conditions as sample 36-5/8 in Fig. 2. The patterns present defined spectra for the well-formed Stannite by almost all important vibrations at 79 cm\(^{-1}\), 173 cm\(^{-1}\), 196 cm\(^{-1}\), 231 cm\(^{-1}\) and 390 cm\(^{-1}\), respectively. There are two peaks that could be attributed to CuSe – at 94 cm\(^{-1}\) and near 263 cm\(^{-1}\). Another signal at 247 cm\(^{-1}\) was registered, which may be due to the cubic ZnSe. The weak vibration at 443 cm\(^{-1}\) could be attributed to the bond Si-O-Si from the substrate [17]. As the samples are similar in composition and are annealed in the same conditions, the differences in signal intensities in the spectra should be related to the differences in layer thickness.

Fig. 4 presents a SEM microgram of sample 36-8/4 preliminarily annealed in vacuum for 1 hour at 400°C and selenized at 560°C for 1 hour. As we could take insights from the XRD and Raman spectra, the CZTSe thin layer was found to consist of large grains sized more than 1 μm. More detailed observations revealed fine grains situated...
mainly on the large grain boundaries at the bottom of the layer and flat hexagonal well-formed crystals situated mainly on the surface of the layer. High definition EDX allowed us to determine the composition peculiarities of the described objects. Large grain composition (measured at point +) indicates to slightly Tin rich CZTSe (23.77 at% Cu - 11.30 at% Zn - 13.67 at% Sn – 51.25 at% Se) thin film material. Fine powder crystallites on the interface Mo - CZTSe indicated as o shows a composition of 52.65 at% Zn – 47.35 at% Se that corresponds to the Stilleite phase presented in Fig.2. Flat plate crystal grains on the surface – indicated as x were defined to correspond to the Klockmanite (Fig.2), giving 47.48 at% Cu – 52.52 at% Se.

Fig.5. Plot for determining the band gap of Cu2ZnSnSe4 films selenized in different conditions: 36-8/4 -1 hour at 400°C in vacuum +1 hour at 560°C and 36-8/2&36-5/7 for 10 minutes at 530 °C. The analysis is based on the assumption that CZTSe is a direct band gap material.

Fig.5 shows the dependence of the curves of \((\alpha h \nu)^2\) on the dropping optical light energy \(h \nu\) for layers CZTSe deposited in similar conditions but annealed both by fast (10 minutes selenization at 530°C -36-8/2&36-5/7) or through preliminary metal alloy homogenization at 400°C for 1 hour and 1 hour selenization at 560°C – sample 36-8/4. The direct optical band gap was approximated by plotting \((\alpha h \nu)^2\) versus the energy in eV and extrapolating the linear part of the spectrum \((\alpha h \nu)^2 = f (h \nu)\) to zero. Thus, the band gap of the CZTSe thin films was estimated to be 1.31 eV ± 0.01 eV. This value is much lower than those reported earlier [3,5] 1.44 eV and 1.56 eV. It seems closer to those close to 1 eV proposed recently in the investigations of monograin materials [18]

Comparison of the data in Fig.2 enables to conclude that a longer annealing time acts favourably to the formation of well-crystallized Stannite Cu2ZnSeSe4 and different binaries (Klockmanite - CuSe and Stilleite - ZnSe) as well as those for thicker under-layer of Mo3Se4.

4. Conclusions

Electrodeposition of alloys Brass and Bronze substrate layers followed by selenization results in successful formation of well-crystallized Stannite thin film structures. Shorter annealing time may lead to favorable formation of Stannite thin films but the system is still not a perfect mono phase. All thin layer materials showed similar optical properties and a band gap near 1.31 eV.

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6. References

15. Ямпельский А.М., Ильин В.А., Краткий Справочник Гальванотехника, Ленинград “Машиностроение”, 1981