ABSTRACT

Formation of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ by chalcogenisation of electrochemically deposited precursor layers

The aim of the doctoral thesis was to investigate the formation of Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ compounds during chalcogenisation of electrochemically deposited thin layers.

CZTS(Se) is a novel and promising semiconductor-absorber material for the solar cell industry as it consists of earth-abundant and non-toxic elements (except Se). One of the advantages of this quaternary compound is its high absorption coefficient of more than 10^4 cm^{-1}. Additionally, CZTS(Se) has a direct band gap of approximately 1 eV for $Cu_2ZnSnSe_4$ and 1.5 eV for Cu_2ZnSnS_4. The preparation method for precursor films in this study is electrochemical deposition. Benefits of this method include performance at, or near room temperature, cost-efficiency, small chemicals wastage and relatively fast deposition rate. Using non-toxic materials, it can be considered an environmentally friendly production technique. Electrochemical deposition of metals, alloys and compounds can be controlled through some of the electrical parameters of the deposition process, as well as by chemical parameters of the prepared electrolyte (concentration of constituents, pH, complexing agents), and by the duration of the process. Through all these variables composition, morphology and thickness of deposited layers can be regulated.

In the present work, the influence of the initial composition of precursors as well as the influence of different conditions in the chalcogenisation process on the synthesized CZTS(Se) phase and its chemical composition was investigated. Two different approaches for preparation of precursor films were performed and compared: 1) simultaneous co-deposition of elemental Cu-Zn-Sn-S elements and 2) sequential deposition of various stacked alloys (Cu-Zn, Cu-Sn) and metal (Sn). Three different complexing agents (SCN^-, $P_2O_7^{4-}$, $C_6H_5O_7^{3-}$) were applied in order to find best conditions for precursor preparation. The novelty of this work is the electrodeposition of binary compounds to form precursor layers and their subsequent chalcogenisation to form CZTS(Se) thin films.

Electrodeposited precursor layers were annealed in two different ways:

1) isothermal annealing in selenium vapour or

2) sulphurisation in H_2S atmosphere in an infrared furnace (rapid thermal annealing).

The main advantage of rapid thermal annealing is the fast heating and cooling rate that can save time and energy, both of which is important for potential future industrial production. Electrochemically deposited precursors and thermally treated films were investigated with cyclic voltammetry, polarography, SEM, EDX, AFM, XRD and Raman spectroscopy.

It was found that use of a rotating disc electrode leads to formation of precursors with uniform thickness and homogenous structure. The complexing agent $C_6H_5O_7^{3-}$ led to deposition of dense and smooth metallic precursor layers. The investigations also showed the occurrence of underpotential deposition phenomenon of Zn^{2+} on a primordial copper layer. Moreover, it was found that for stacked precursor structures like Cu-Zn/Sn and Cu-Zn/Sn-Cu, Zn tends to dissolve from the initially deposited Cu-Zn layer in copper-tin or pure tin containing electrolytes. It was concluded that very Zn-rich (40 – 50 at% of Zn) initial Cu-Zn layer is required in order to get Cu-poor or stoichiometrically stacked precursors and subsequently CZTS(Se) films. The primary phases formed in metallic precursors (Cu-Zn-Sn) are Cu_5Zn_8, Cu_6Sn_5, $Cu_{0.7}Zn_{0.3}$ and elemental Sn. The Cu-rich phase $Cu_{0.7}Zn_{0.3}$ arose only after deposition of Sn.

Thiocyanate ligand used for deposition of Cu-Zn-Sn-S thin films showed the possibility of simultaneous co-deposition of Cu-Zn-Sn-S compounds. The Cu:Sn ratio in the co-deposited films is controlled through preparation of the electrolyte with the desired Cu:Sn ratio, whereas the Zn concentration is determined by applied potential. The sulphur concentration in the co-deposited layers depends on the duration of deposition, but the films are as a rule sulphur poor and need additional treatment in chalcogen atmosphere. After annealing in H_2S gas CZTS films were formed and XRD and Raman spectroscopy measurements indicated the absence of other phases in the film.

Optimal sulphurisation parameters for rapid thermal annealing were found to be 2°C/s ramp up rate and cooling down to 25°C for 15 minutes at 470ºC.