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Al/CZTS/ZnS solar cells.

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Abstract – In this work, we report some preliminary results concerning the fabrication of quaternary semiconductor Cu2ZnSnS4 (CZTS) thin films on a flexible substrate through the simultaneous electrodeposition of elements having different standard electrochemical potentials. CZTS thin films were obtained by deposition from aqueous baths at room temperature and varying bath composition. Chemical composition and structure of the electrodeposited films were evaluated by SEM and XRD. Preliminary results on the photoelectrochemical behaviour of the films will be also presented. We obtain ZnS thin films with good physical properties, these samples can be used as window material in ZnS/CZTS solar cells to improve the photovoltaic efficiency.

Keywords – Cu2ZnSnS4, CZTS, ZnS, Thin Films, Solar Cells.

Introduction

Energy is a great issue for the development of society. Since the amount of fossil fuel is limited, a sustainable development of society requires the development of novel sustainable energy resources. In such a context, solar energy meets the requirement. Recently, Cu(In,Ga)Se_2-based thin film solar cells have achieved efficiencies as high as 20.4 % in the lab scale [1-4]. However, due to the scarcity and high cost of indium constituent, this material cannot meet the long term goal of the solar energy development. To solve this issue, it is necessary to develop alternative light absorbing materials which are composed of relatively earth abundant elements. In recent years, kesterite $CuZnSnS_4$ (CZTS) has emerged as one of the promising candidates for thin film solar cells due to its direct optical band gap of 1.0 to 1.5 eV, high absorption coefficient (over 10^4 cm^{-1}) above the optical band gap and abundant elements on Earth [5, 6]. The $CuZnSnS_4$-based thin film solar cells have achieved an efficiency as high as 11.1 % using a hydrazine-based processing CZTS absorbers [7]. This device performance points to the significant promise of CZTS as emerging and interesting materials for solar cell applications. However, hydrazine is toxic and explosive, and therefore not favorable for further up-scaling development. Therefore, an alternative deposition approach for the CZTS thin film absorber is preferable [8]. In this thesis, a solution processed approach for the deposition of CZTS thin film absorbers is presented using binary and ternary chalcognide nanoparticles as precursors. The aim of this work is firstly to develop a solution deposition process for CZTS thin film absorbers, which does not rely on hydrazine solvent and secondly to study the influence of the processing conditions such as ink precursors and annealing conditions on the structural, optical and electrical properties of CZTS thin film absorbers [9].

In the following, a brief description of the structure of this thesis and the main contents is given. starts with a brief introduction of the material properties of CZTS and the evolution of $Cu_2ZnSn(S_xSe_{1-x})_4$-based thin film solar cell efficiency. Furthermore, a literature review on the advance of various deposition techniques for CZTS thin films and the best/

Preparation, morphology and structure of Cu2ZnSnS4 thin films

As it is known that the optoelectronic properties of semiconductor materials are closely related to materials properties such as crystal quality, chemical composition and phase purity, it is essential to understand the detailed morphological and structural properties before their further application in devices. Will investigate the preparation conditions on the morphological and structural properties of CZTS thin films. The experimental details on the deposition of CZTS thin films by spin coating of the mixed precursor inks consisting of ZnS, SnS and Cu_3SnS_4 nanoparticles dispersed in hexanethiol. Two series of thin films deposited by both non-ligand-exchange and ligand-exchange processes have been prepared. The influence of the annealing temperature on the morphological and structural properties of CZTS thin films was examined by XRD and SEM. In the following we examined the effect of ligand-exchange processes on the morphological properties of the resulting thin films.

Alluminium and indium tin oxide (ITO) glass slides were used as the substrate during the deposition process polycrystalline CZTS thin films. The substrates were first cleaned in ethanol then ultrasonically washed with distilled water. Finally, substrates were dried in an oven at 90°C. In the typical synthesis, CuCl (1mmol), $ZnCl_2$ (0.75 mmol), and $SnCl_2$ (0.6mmol) were added into pyridine as a metal source and the Cu/Zn/Sn molar ratio was determined to be 2/1.5/1.2. Then, 25 mL of sodium selenite (0.15 M) was added and the pH of the solution was adjusted to 3 by addition of hydrochloric acid using pH meter. The composition can be controlled by changing the ratio of the nanoparticle precursors. The second step is to deposit Cu-Zn-Sn-S precursor films by spin coating nanoparticle precursor inks at a certain rotating speed. After that, Cu-Zn-Sn-S precursor films were subjected to a heat treatment step at 170-200 and 350 °C for 2 min respectively. The aim of this step is to remove the organic solvent as well as part of the surfactants surrounded the nanoparticle precursors. In addition, the heat treatment process also helps to dense the film on the substrates otherwise the deposited layers may be dissolved back into the solvent again when the second spin coating processes. To obtain desired thickness (less than 5 µm), the steps II and III should be repeated before going to the final annealing step.

Zinc acetate dehydrate [$Zn(CH_3COO)_2,2H_2O$] and thioacetamide (CH_3CSNH_2), of analytical reagent grade were purchased from Merck Chemical company. All the reagents were used as received. Aqueous solutions of 1M zinc acetate dehydrate, 0.5M thioacetamide (TAA) and 2MHCl were used for ZnS thin films deposition. First, 5 ml zinc acetate and 10 ml Ethylenediamine were mixed in a beaker and stirred for several minutes to get a clear and homogeneous solution. The pH value of the obtained solution was measured to be 8.4, and then some small amount of HCl was added to the solution in order to reduce the pH to 6.5. Thereafter, 40 ml TAA was added under stirring condition. Finally, a few drops of HCl were added to fix the solution pH at the value of 6.0. The glass or CZTS substrates were then immersed vertically in the solution. The beaker was sealed with a teflon tape and was placed in a thermostat bath set at a desired temperature (70 ± 5^0C)). The depositions were carried out in the time intervals of 4 hours. The deposition process was then repeated in order to obtain the filmswith different thicknesses.After each deposition stage, the samples were taken out from the beaker and cleanedwith deionized water.The powdery and less-adherent ZnS particleswere removed bywashing the samplewith distilledwater.The films, as they were grown appeared to be in a gray-blue color -exhibit a good uniformity and adherence and they can be used as new substrates to deposit thicker films.

To examine the effect of ligand-exchange with ammonium sulphide ($(NH_4)_2S$) of the precursor thin films on the morphology of the resulting CZTS thin films, the precursor thin films were treated with 0.04 M $(NH_4)_2S$ methanol solution for 30 s after heat treatment at 170 °C for 2 min to allow the ligand exchange between organic surfactants and ammonium sulphide. Finally, the resulting precursor films were subjected to annealing process at 400 to 580 °C under different sulphur and/or selenium containing atmosphere, which allows the formation of CZTS absorbers by reaction of the nanoparticle precursors.

The CZTS thin films were analyzed by grazing incidence X-ray diffraction (GIXRD) using a PANalytical XpertPro MPD system (CuKa1,2 radiation) and an incident angle of 0.58. Scanning electron microscopy on cross-sections was used to analyze the film morphology and thickness. Energy-dispersive X-ray spectroscopy (EDX) mappings and linescans were also performed on cross-sections using an acceleration voltage of 7 kV. For both analyses a LEO1530
(Gemini) with a field emission cathode was used. The overall chemical composition was determined by EDX from top in a LEO440 SEM with hairpin cathode using an acceleration voltage of 12–20 kV. The characteristic L-lines of zinc and tin and the K-lines of copper and sulfur were used for the quantitative composition determination. The J–V characteristics of CZTS-ZnS solar cells under illumination were measured with a solar simulator under standard test conditions without light soaking. External quantum efficiencies were analyzed using monochromatic illumination under short-circuit conditions.

Results and discussions

Results and discussions of the influence of annealing temperature and atmosphere on the mophoological and structural properties of the resulting Cu_2ZnSnS_4 thin films will be presented in this section. In addition, the effect of ligand-exchange processes of the precursor layers on the morphology of CZTS thin films will also be discussed.

The influence of the annealing temperature and atmosphere on the morphological and the structural properties will be investigated. The aim of this study is to determine the suitable temperature and atmosphere for preparation of the CZTS thin film absorbers. The morphology was studied by scanning electron microscopy while the structural properties were characterized by XRD

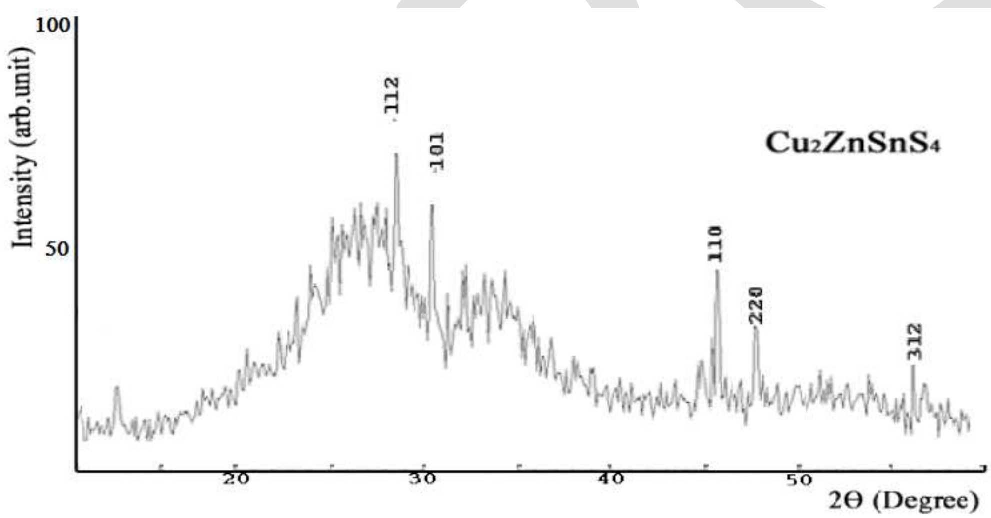

Figure 1. XRD patterns of CZTS film.

Figure 2 shows the surface and cross section SEM images of the as-deposited sample and after heat treatment process. When taking a close look at the surface of the sample, one can find that there are some nanoplates on top or embedded in the nanoparticle layers as marked by circles. The size of the ZnS and CTS nanoparticles is rather small (less than 50 nm) and the shape of these two kinds of nanoparticles are spherical; but the shape the SnS nanoparticles are composed of sphere and nanoplates. Therefore, it is clear that the nanoplates observed from the surface view of SEM image should be SnS precursor. In addition, pinholes can also be observed in the sample, however, it is not clear whether these pinholes last until the substrates or not. The films were prepared using layer by layer deposition process. This process allows the further coverage of the pinholes or cracks existed in the pre-deposited layers. Hence, the pinholes are more probably present only on the surface layers. Figure 2 (b) illustrates that the film is densely packed. The thickness of the sample is around 0.9 μm.

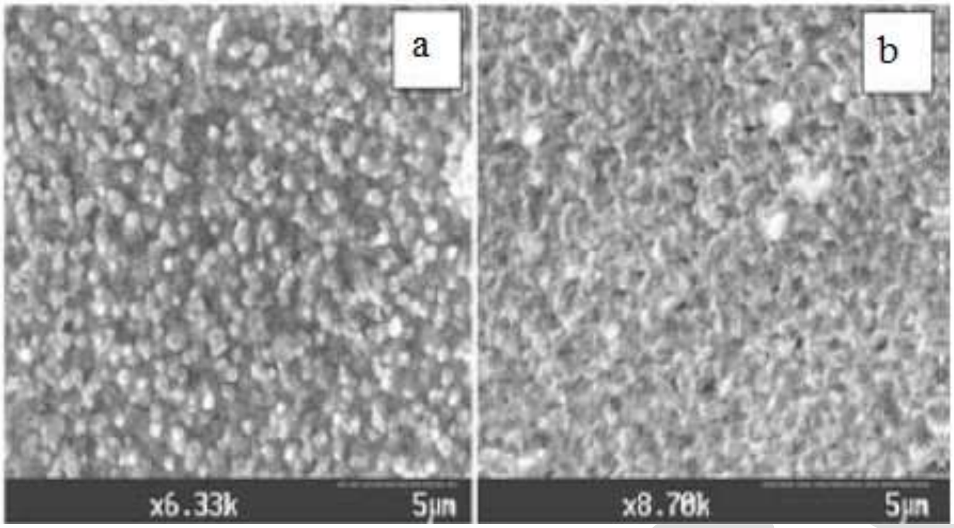

Figure 2. SEM images of CZTS film of the as-deposited sample(a) and after heat treatment process (b).

This solar cell device configuration has been developed and used for solar cells and modules and has not been specifically optimized for the CZTS absorber layers. Figure 3 depicts the J–V characteristics of the best device measured at standard test conditions. To our knowledge this is the highest efficiency obtained for a coevaporated CZTS-device up to date.

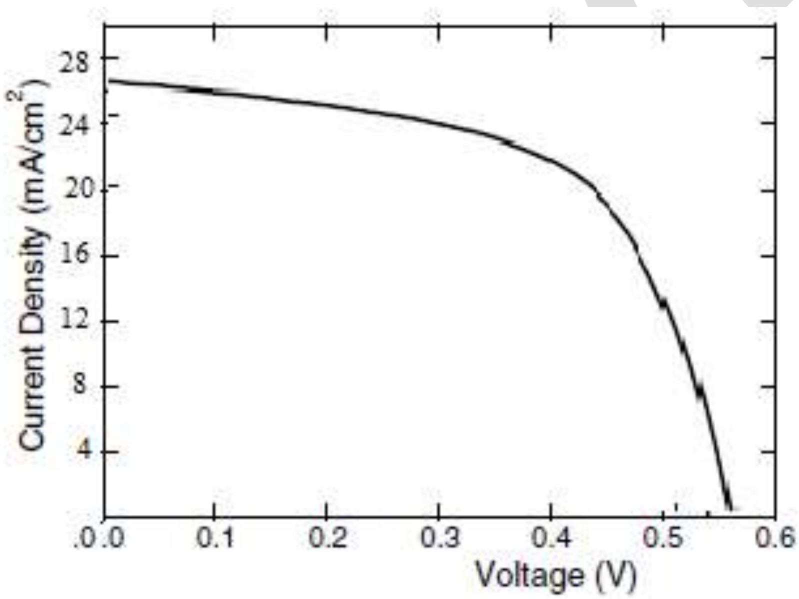

Figure 3. J–V characteristics of solar cell with deposited CZTS absorber.

To gain further insights in the device performance and loss mechanisms the external quantum efficiency (EQE) was measured on the same solar cell as shown in Figure 4.

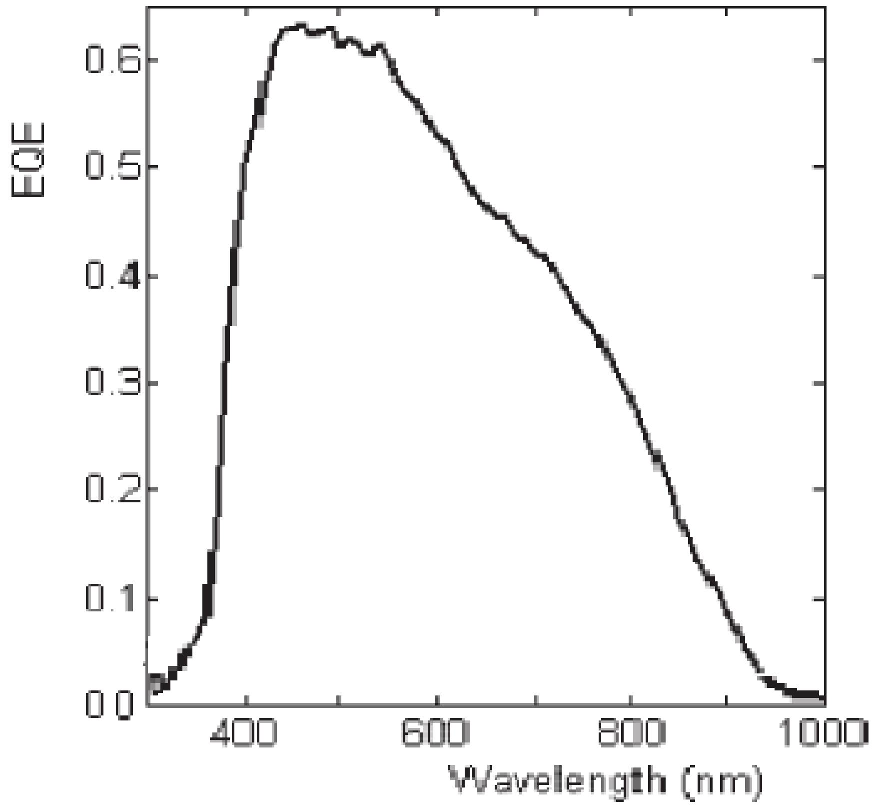

Figure 4. External quantum efficiency (EQE) of solar cell with CZTS absorber.

The EQE shows a steep increase around 350 nm related to the absorption edge of the ZnS window layer, a maximum value of about 60% at wavelengths between 400 and 500 nm and a subsequent broad decline for wavelengths above 520 nm. The optical gap of the CZTS absorber layer can be estimated from this EQE measurement, if the absorption coefficient for the material is modeled assuming a direct band gap semiconductor with parabolic bands close to the band edge. A band gap of 1.51±0.01 eV is obtained from the linear extrapolation of $(h\nu \ln(1\text{-EQE}))^2$ vs. hν. This value is in very good agreement with two recent theoretical calculations putting the value of the band gap in CZTS at 1.5 eV [10,11]. For wavelengths larger than the estimated optical gap (820 nm) significant photocurrent collection is observed in the EQE. This is likely due to substantial band tailing due to large amount of lattice disorder in the CZTS film. The collection length can be estimated by analyzing the electrical characteristics of the Al/CZTS/ZnS solar cells.

CONCLUSION

We report some preliminary results concerning the fabrication of quaternary semiconductor Cu_2ZnSnS_4 (CZTS) thin films on a flexible substrate through the simultaneous electrodeposition of elements having different standard electrochemical potentials. CZTS thin films were obtained by deposition from aqueous baths at room temperature and varying bath composition. Chemical composition and structure of the electrodeposited films were evaluated by SEM and XRD. Preliminary results on the photoelectrochemical behaviour of the films will be also presented. We obtain ZnS thin films with good physical properties, these samples can be used as window material in ZnS/CZTS solar cells to improve the photovoltaic efficiency.

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