

## (Ag<sub>x</sub>Cu<sub>1-x</sub>)<sub>2</sub>ZnSnS<sub>4</sub> THIN-FILMS PREPARED BY SPRAY PYROLYSIS

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**ABSTRACT:** One of the most detrimental problems in the further development of thin film solar cells based on kesterite type compound semiconductors is the limitation in open circuit voltage ( $V_{oc}$ ). The latter, according to many theoretical and experimental studies, is mostly related to the high concentration of intrinsic defects, mainly with  $Zn_{Cu}$  antisites. Recently, a way for overcoming this problem by partial substitution of Cu cations by Ag was proposed. This may lead to a strong decrease of intrinsic defects due to higher formation energy of  $Zn_{Ag}$  defects and as result to increase of  $V_{oc}$ . Taking this into account, we performed an investigation of  $(Ag_xCu_{1-x})_2ZnSnS_4$  thin films deposited by the spray pyrolysis method. The as-deposited thin films with 10, 15 and 20 % of Ag were annealed at 450 °C for 60 min in presence of elemental sulfur. Structural investigations by XRD, as well as Raman spectroscopy studies confirmed the formation of solid solutions. Photoluminescence investigations showed one broad band, which exhibits the blue shift with the increase of Ag concentration. This could be explained by changes in the activation energy of the defect levels involved in radiative transition rather than with the band gap change.

Keywords: Kesterite, Thin Film, Spray Pyrolysis, XRD, Raman Spectroscopy

### 1 INTRODUCTION

In the past few years  $Cu_2ZnSn(S,Se)_4$  (CZTSSe) have been considered as a promising material for the development of cheap and effective thin-film solar cells. In favor of this was the fact that the composition consists not scarce and not toxic elements. The maximum energy conversion factor obtained on solar cells with CZTSSe as an absorber showed 12.6 % in the laboratory [1]. However, further improvements have stopped due to the low open circuit voltage ( $V_{oc}$ ). The latter, according to many theoretical and experimental studies, is mostly related to the high concentration of intrinsic defects, leading to a low minority carrier lifetime, electrostatic potential fluctuations, tail states etc. [2-4]. The main defect is related with  $Zn_{Cu}$  antisites, which leads to creation of the defect acceptor band inside the band gap [5]. Predominance of this defect is provided by the low formation energy, which could be explained by the small difference in the sizes of atoms and chemical properties of Cu and Zn.

Ag was proposed as a promising candidate for substitution of Cu, since it belongs to the same chemical group as copper, but its radius is 16 % larger, which leads to an increase in the formation energy of  $Zn_{Ag}$  disorder defects in the cell [6-10]. However, pure  $Ag_2ZnSn(S,Se)_4$  (AZTSSe) is a semiconductor with n-type conductivity, which strongly limits its utilization as absorber in thin film solar cell [11]. Therefore, it is necessary to consider the transition series of solid solutions from CZTSSe to AZTSSe in order to overcome the difficulties arising in pure CZTSSe and AZTSSe.

The present study is the first attempt to obtain thin films of  $(Ag_xCu_{1-x})_2ZnSnS_4$  (ACZTS) solid solutions by the non-vacuum spray pyrolysis method. In this way the positive influence of Ag on the intrinsic defects of kesterite type compounds was combined with one of the easiest and cheapest deposition methods. Taking this into account, the main purpose of this work was to obtain ACZTS thin films by spray pyrolysis, and to investigate their structural and optical properties for future photovoltaic application. The samples were prepared by spray pyrolysis of an aqueous solution onto soda-lime glass (SLG). The main characteristics of the samples were obtained from the X-ray diffraction (XRD), Raman spectroscopy and photoluminescence (PL) analysis.

### 2 EXPERIMENTAL DETAILS

The deposition was performed using self-made spray pyrolysis system placed in the glovebox filled with  $CO_2$ . The XRD data were collected using a PANalytical X'pertPro MPD diffractometer equipped with  $CuK\alpha$

radiation ( $\lambda = 1.54056 \text{ \AA}$ ). Detector scans were obtained in Bragg-Brentano geometry, with the step size of  $0.02^\circ$ .

The Raman spectra were obtained with an HR800 Horiba Jobin Yvon spectrometer, matched with a metallographic microscope and a CCD detector. Measurements in backscattering configuration were done using He-Ne laser as excitation source (laser line  $632.8 \text{ nm}$ ). The Raman shift of all measured spectra was calibrated using intercalated spectra obtained from the Si monocrystal reference sample and imposing its main band position at  $520 \text{ cm}^{-1}$ .

The photoluminescence spectra were measured at room temperature by a  $0.5\text{m}$  grating spectrometer coupled with InGaAs detector and excited with a  $660 \text{ nm}$  laser line with excitation energy about  $0.4 \text{ kW/cm}^2$ .

### 3 RESULTS AND DISCUSSIONS

#### 3.1 Solution preparation and deposition

The solution for the deposition of ACZTS thin films was prepared from two precursor solutions. The first initial solution (IS1) consisted of Cu- and Ag- containing complexes, while the second (IS2) one of Zn- and Sn-containing complexes. This separation to IS1 and IS2 is caused by their high stability and homogeneity, these precursor solutions could be stored for a long time (up to 14 days) without being influenced by possible temperature fluctuations. With temperature decrease precipitated crystals could be formed, however they are easily dissolved with a temperature increase.

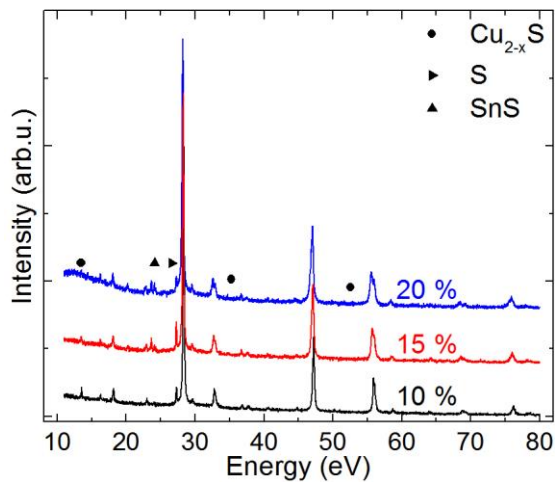
The first precursor solution IS1 was prepared as described earlier in [12], the only adjustment to the previous routine being the replacement of a part of CuCl by AgCl to ensure the formation of solid solutions. As the result  $25 \text{ ml}$  of solution IS1 containing water ( $\text{H}_2\text{O}$ ), thiourea ( $\text{CS}(\text{NH}_2)_2 - \text{Th}$ ), CuCl and AgCl was obtained. It is worse to be mentioned that chlorides with  $\text{Cu}^+$  cations were used for the IS1 to ensure the formation of the  $[\text{Cu}^+(\text{Th})_n]^+$  complex with  $n > 3$ , which improves the homogeneity of the solution. While the use of chlorides with  $\text{Cu}^{2+}$  cations, together with  $[\text{Cu}^+(\text{Th})_n]^+$  complex formation leads to the formation of an additional  $1/2(\text{Th})_2^{2+}$ (Formamidine disulfide) complex, which dissolves in time with precipitation and has a strong influence on the sulfur concentration in the final solution. Details of the IS2 preparation were described elsewhere [12].

The final solution was prepared just before the deposition process in proportion of: IS1:IS2 = 3:1, which provides a stoichiometric composition of the precursors. The final solution has the concentration of  $0.33 \text{ M}$ .

The deposition of the final solution was performed in air on the SLG substrate heated up to  $420 - 430 \text{ }^\circ\text{C}$  with a spraying rate  $\sim 5 \text{ ml/min}$ . As result a series of three thin films with 10, 15 and 20 % of Ag was obtained. These concentrations were aimed, based on the previous analysis of the band gap of the ACZTS solid solutions, which was found to decrease slightly for thin films with 20 % of Ag and increase up to  $2 \text{ eV}$  for the pure  $\text{Ag}_2\text{ZnSnS}_4$  compound [13]. Finally, to increase the crystalline quality, the as-deposited samples were annealed in vacuum at  $450 \text{ }^\circ\text{C}$  for  $60 \text{ min}$  in presence of elemental sulfur to prevent it loss.

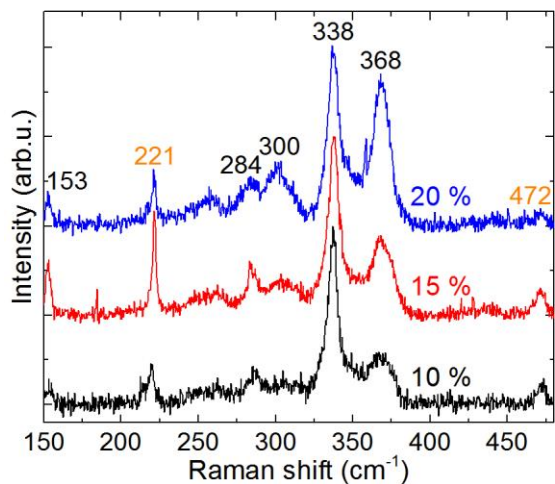
#### 3.2 Thin films characterization

In order to analyse the quality of obtained thin films X-ray diffraction (XRD), Raman spectroscopy and photoluminescence measurements were applied. In the obtained diffraction patterns (see Figure 1), the most intense Bragg peaks can be attributed to kesterite type structure (space group  $I\bar{4}$ ) [14], wherein the peaks positions are shifted to lower  $2\theta$  angles which is due to the incorporation of Ag in the crystal structure forming an ACZTS solid solution. It is important to emphasize that the shift is higher for samples with higher initial Ag concentration, which supports the possibility of control of the Ag/Cu ratio by changing the IS1 composition. However, it should be mentioned that small amounts of secondary phases ( $\text{Cu}_{2-x}\text{S}$ , SnS and S) were also found in the samples, while a relatively low signal to noise ratio and wide peaks denotes the relatively low crystalline quality of the thin films. This could be related to the fact that the conditions of sample annealing were selected similar to that previously used for standard  $\text{Cu}_2\text{ZnSnS}_4$  (CZTS) thin films, while for the ACZTS solid solutions other conditions could be optimal.

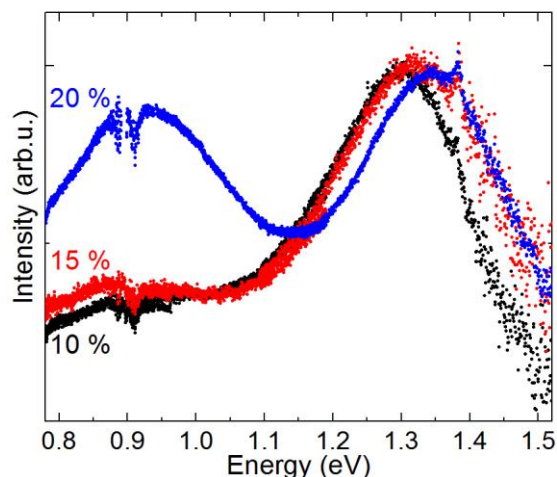


**Figure 1:** XRD diffractograms of ACZTS thin films.

The most intense peak in the Raman spectra (Figure 2) at  $338\text{ cm}^{-1}$  has a similar position with the main Raman peak of a CZTS kesterite type compound [15]. Most probably this similarity is related with nature of this peak – vibrations of the anion atoms [15], which are almost independent from the Cu/Ag substitution. However, it was found that the peaks at  $300$  and  $368\text{ cm}^{-1}$  increase with an increasing Ag concentration. According to the analysis of Raman spectra of CZTS compounds, in these regions there are the E and B symmetry modes [15], which could be related with vibrations of all atoms, including Cu cations. Partial substitution of copper cations to silver ones could be a reason for the observed changes of intensity of the peaks at  $300$  and  $368\text{ cm}^{-1}$ . It should be noted that the additional peaks at  $221$  and  $472\text{ cm}^{-1}$  could be attributed to SnS and  $\text{Cu}_{2-x}\text{S}$  phases, respectively, also found from XRD analysis.



**Figure 2:** Raman scattering spectra of ACZTS thin films. With orange are marked peaks attributed to the secondary phases.



**Figure 3:** PL spectra of the ACZTS thin films.

In the PL spectra (Figure 3), measured at room temperature a broad band with maximum shifting from 1.30 to 1.34 eV with an Ag concentration increase was observed. Due to the slight band gap decrease in the samples with up to 20 % of Ag [13], most probably this shift is related to a change of the activation energy of defect levels involved in the radiative recombination. At lower energies an additional PL band at about 0.9 eV was also detected, which is probably related to the secondary phases found from the XRD and Raman spectroscopy studies.

#### 4 CONCLUSIONS

From the presented characterization of the ACZTS solid solutions deposited by spray pyrolysis it could be concluded, that this method could be successfully used for the preparation of thin films with a control of Ag concentration. However, additional process optimizations should be performed in order to achieve higher crystalline quality of the thin films as well as to avoid the formation of secondary phases.

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#### REFERENCES

- [1] W. Wang, M.T. Winkler, O. Gunawan, T. Gokmen, T.K. Todorov, Y. Zhu, D.B. Mitzi, *Adv. Energy Mater.* 4 (2013) 1301465.
- [2] O. Gunawan, T.K. Todorov, D.B. Mitzi, *Appl. Phys. Lett.* 97 (2010) 233506.
- [3] I.L. Repins, H. Moutinho, S.G. Choi, A. Kanevce, D. Kuciauskas, P. Dippo, C.L. Beall, J. Carapella, C. DeHart, B. Huang, S.H. Wei, *J. Appl. Phys.* 114 (2013) 084507.
- [4] T. Gokmen, O. Gunawan, T. K. Todorov, D. B. Mitzi, *Appl. Phys. Lett.* 103 (2013) 103506.
- [5] K. G. Lisunov, M. Guk, A. Nateprov, S. Levchenko, V. Tezlevan, E. Arushanov, *Sol. Energ. Mater. Sol. Cells* 112 (2013) 127.
- [6] S. Chen, J.H. Yang, X. Gong, A. Walsh, S.H. Wei, *Phys. Rev. B* 81 (2010) 245204.
- [7] Z.-K. Yuan, S. Chen, H. Xiang, X.-G. Gong, A. Walsh, J.-S. Park, I. Repins, S.-H. Wei, *Adv. Funct. Mater.* 25 (2015) 6733.
- [8] E. Chagarov, K. Sardashti, A.C. Kummel, Y.S. Lee, R. Haight, T.S. Gershon, *J. Chem. Phys.* 144 (2016) 104704.
- [9] T. Gershon, Y.S. Lee, P. Antunez, R. Mankad, S. Singh, D. Bishop, O. Gunawan, M. Hopstaken, R. Haight, *Adv. Energy Mater.* 25 (2016) 1502468.
- [10] C.J. Hages, M.J. Koeper, R. Agrawal, *Sol. Energ. Mater. Sol. Cells* 145 (2016) 342.
- [11] T. Gershon, K. Sardashti, O. Gunawan, R. Mankad, S. Singh, Y.S. Lee, J.A. Ott, A. Kummel, R. Haight, *Adv. Energy Mater.* 6 (2016) 1601182.

- [12] L. Dermenji, N. Curmei, M. Guc, G. Gurieva, M. Rusu, V. Fedorov, L. Bruc, D. Sherban, S. Schorr, A. Simashkevich, E. Arushanov, *Surf. Eng. Appl. Electrochem.* 52 (2016) 509.
- [13] W. Gong, T. Tabata, K. Takei, M. Morihama, T. Maeda, T. Wada, *Phys. Status Solidi C* 12 (2015) 700.
- [14] G. Gurieva, M. Guc, L.I. Bruk, V. Izquierdo-Roca, A. Pérez Rodríguez, S. Schorr, E. Arushanov, *Phys. Status Solidi C* 10 (2013) 1082.
- [15] M. Guc, S. Levchenko, I.V. Bodnar, V. Izquierdo-Roca, X. Fontane, L.V. Volkova, E. Arushanov, A. Pérez-Rodríguez, *Sci. Rep.* 6 (2016) 19414.