Ministry of Education and Science of Ukraine Ivan Franko National University of Lviv Faculty of Chemistry Shevchenko Scientific Society The National Academy of Sciences of Ukraine



Ist INTERNATIONAL RESEARCH and PRACTICE CONFERENCE «NANOOBJECTS & NANOSTRUCTURING» (N&N-2020)

September 20–23, 2020, Lviv, Ukraine

BOOK of ABSTRACTS



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THE EFFECT OF LOW-TEMPERATURE ANNEALING TREATMENTS ON THE STRUCTURE AND CHEMICAL COMPOSITION OF CU₂ZNSNS₄ FILMS DEPOSITED ONTO FLEXIBLE POLYIMIDE SUBSTRATES

Dobrozhan O.¹, <u>Kakherskyi S.</u>¹, Opanasyuk A.¹ ¹Sumy State University, Sumy, Ukraine ololoh0pper@gmail.com

Kesterite Cu₂ZnSnS₄ (CZTS) compound has been extensively explored during the last decades due to the promising application in the thin film solar cells as an alternative absorber material to the traditional Si, CdTe, Cu(In,Ga)(S,Se)₂ compounds. The major reason for the low efficiencies of CZTS based solar cells might be dedicated to weakly controlled fundamental properties of films (e.g. phase composition, crystalline quality, scattering domain sizes). Besides that, the final price of the solar cell includes the cost of production process of films including substrate choice. Thus, this work is aimed to obtain CZTS thin films onto flexible polyimide substrates by spraying polyol mediated nanocrystals with subsequent low-temperature annealing to prove that such approach allows to access the nanocrystalline quality and chemical composition stability suitable for low-cost, flexible nanostructured solar cells.

With this in mind, firstly, CZTS nanocrystals with the kesterite structure were synthesized in the diethylene glycol medium and stabilized with polyvinylpyrrolidone additives. Afterward, nanocrystals were dispersed in the water/(ethylene glycol) mixture and sprayed onto the preheated flexible polyimide substrates. In the last step, the deposited CZTS films were annealed at 200 °C for (10-120) min in Argon atmosphere to evaporate the solvents, increase film-to-substrate adhesion and induce nanograin growth.



Fig. 1. XRD patterns of CZTS nanocrystals grown at a different time (a) and CZTS films annealed at 200 °C for different times (b). The blue vertical lines correspond to JCPDS card #00-026-0575 of hexagonal CZTS crystal structure. The orange vertical lines correspond to polyimide substrate, data were taken from reference.

XRD and Raman studies showed that nanocrystals and films mainly composed of CZTS kesterite phase with the presence of minor secondary phases of Cu-S and Cu-Sn-S materials. This observation is in line with another research works. Although, we have observed improvement of the crystalline quality and chemical stability in nanocrystals and films with the increase of growth and annealing time. The average CSD sizes of CZTS nanocrystals and films increase from ~8 nm at $t_g = 1$ min to ~10 nm at $t_g = 60$ min; ~10 nm at $t_a = 0$ min (as-deposited films) to ~18 nm at $t_a = 120$ min, respectively. These values are well-correlated with XRD and TEM data. Annealing time increase led to increase of CSD sizes inside CZTS materials evidencing the crystalline quality improvements. CZTS films obtained at higher annealing time have larger defect-free crystalline regions.

The value of band gap of the obtained samples was $E_g = (1.4-1.5) \pm 0.2$ eV that is optimal for solar spectrum absorption. The deposited nanostructured CZTS thin films are suitable to operate as absorbers in the flexible solar cell.