IEEE UKRAINE SECTION

IGOR SIKORSKY KYIV POLYTECHNIC INSTITUTE

2020 IEEE 40th INTERNATIONAL CONFERENCE ON ELECTRONICS AND NANOTECHNOLOGY (ELNANO)

CONFERENCE PROCEEDINGS

APRIL 22-24, 2020
KYIV, UKRAINE

2020 IEEE 40th International Conference on ELECTRONICS AND NANOTECHNOLOGY (ELNANO)

IEEE Catalog Number: CFP2005U-USB
ISBN: 978-1-7281-9712-8

Organizing Committee of IEEE ELNANO-2020
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Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$ Nanocrystals As Absorbers In 3rd Generation Solar Cells

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Abstract - Cu_2ZnSnS_4 and $Cu_2ZnSnSe_4$ semiconductor nanocrystals were synthesized by polyol method. The morphological and structural properties were investigated by transmission electron microscopy and X-ray diffraction methods. The nanocrystals growth behavior for both compounds were compared. Showed that the synthesized nanocrystals of the four-component compounds have a single phase structure of tetragonal modification of the kesterite type. It has been found that secondary phases are not detected in the materials with the method precision. It is established that the lattice period closest to the bulk materials of stoichiometric composition has CZTS nanocrystals synthesized at a time of 60 min and CZTSe particles obtained at a synthesis time of 30-45 min. The obtained nanocrystals were used to develop nanoinks to print absorbers of solar cells by 2d and 3d printers.

Keywords - Cu_2ZnSnS_4, $Cu_2ZnSnSe_4$, morphology, nanocrystals, solar cells, structure, thin films, XRD.

I. INTRODUCTION

Nowadays, solar cells (SC) based on silicon, 1st generation, are widely used to convert solar to electrical energy but in the recent years thin-film solar cells based on heterojunctions with absorbers of GaAs, InP, $CuIn_{1-y}Ga_ySe_2$ (CIGS), CdTe and with various window and charge collector layers that belong to the second generation of such devices have been increasingly developed [1].

Today for these SC, efficiency of 21.0% for CdTe, 23.35% for CIGS, 24.2% for InP and 29.1% for GaAs has been obtained, approaching theoretical maximum (28-32%) [2]. However, disadvantages such as high cost of In, Ga, and Te, toxicity of Cd, give impetus to search a new alternative materials for absorbers and third-generation SC designs for large-scale terrestrial application [1]. The materials such as Cu_2ZnSnS_4 (CZTS), $Cu_2ZnSnSe_4$ (CZTSe) $Cu_2ZnSnS_{4-y}Se_y$ (CZTSSe) have been proposed as absorption layers of the third generation of SC [3]. This is due to being close to the optimal for converting sunlight energy bandgap (E_g) (Shockley-Queisser optimum), high light absorption coefficient (~10^5 cm^{-1}), *p*-type conductivity, long lifetime and high mobility of charge carriers [4-5]. Unlike other semiconductors, such compounds do not contain rare and environmentally hazardous components, in contrast, the elements are widespread in the earth's crust and the cost of the production is low. In addition, the change of concentration of sulfur and selenium in a five-component compound CZTSSe allows to regulate band gap of the material from E_g = 1.0 eV (CZTSe) to 1.5 eV (CZTS) fine-tuning it to Shockley-Queisser optimum. At the same time, to reduce the production costs SCs, the active layers might be obtained by low energy processes [6].

However, synthesis of nanocrystals and deposition of films for CZTS, CZTSe, CZTSSe compounds is associated with some difficulties, because their components have significantly different vapor pressure values, and the area of homogeneity is quite narrow [7]. As a result, the resulting layers often contain several phases with different bandgaps, and their structural quality is low, accordingly, the record SC efficiency based on these compounds is relatively low (11.3% - CZTSSe; 10% - CZTS) [2].

The trend towards developing of the electronics devices applying 2d and 3d printers is becoming popular, which makes it possible to significantly simplify the procedure of its production and reduce the cost. For 2d printing simple home printers have been used, in which the inks are replaced by special nanoinks containing a suspension of metal or semiconductor nanoparticles [8].

The next scientific and technological problem is the synthesis of nanoparticles of various materials with controlled characteristics and the development of their stable colloidal solutions with the specified viscosity and surface tension, which can be used as nanoinks. Many physical and chemical methods are used to obtain CZTS, CZTSe, CZTSSe materials [9-12]. The first methods provide higher quality of films but later are simpler and provide reduced costs of solar devices. 2d and 3d chemical printing methods are more economical, flexible and waste-free technology [13].

In this work, the synthesis procedure of CZTS, CZTSe nanocrystals has been improved, their morphological and structural characteristics were studied depending on the synthesis time with the aim of further synthesis of the five-component compound CZTSSe.

978-1-7281-9713-5/20/$31.00 ©2020 IEEE