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Ministry of Education and Science of Ukraine
Sumy State University
IEEE Nanotechnology Council
IEEE Magnetics Society
The International Union of Pure and Applied Physics

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Synthesis and Structural Properties of $\text{Cu}_2\text{ZnSnS}_4$ and Cu Nanoparticles for Printed Electronics

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Abstract — Metal (Cu) and semiconductor ($\text{Cu}_2\text{ZnSnS}_4$) nanoparticles were successfully synthesized by the chemical methods. Morphological and structural properties of nanoparticles were investigated. Synthesized nanoparticles were used for development of nanoinks, which are promising for 3D printing of the electronic circuit components and solar cells.

Keywords — nanoparticles, morphology, structure, XRD, printed electronics.

I. INTRODUCTION

Nowadays four-component compound $\text{Cu}_2\text{ZnSnS}_4$ (CZTS) is considered as a promising alternative to the traditional materials for absorber layers of thin-film solar cells, such as Si, CdTe, $\text{Cu}(\text{In,Ga})(\text{S,Se})_2$. This is due to CZTS has optimal electrical and optical properties (*p*-type conductivity; bandgap, which corresponds to the Shockley-Quieser maximum $E_{g\text{CZTS}} = 1.5$ eV; large light absorption coefficient, $\alpha \sim 10^4\text{-}10^5$ sm^{-1} etc) [1-3]. It was lasted more than 20 years from the moment of production of the first solar cell based on CZTS films in 1996 [4], however maximal efficiency of such devices haven't exceed 12,6% yet [5]. The difference between theoretical (32-34 % [6]) and experimental values of efficiency of solar cells based on CZTS is explained by non-optimal structural characteristics and stoichiometry of the films, as well as by the presence of secondary phases with different bandgap. This leads to high sequential and low shunt resistance, high recombination speed of light generated charge carriers, and short lifetime of minority charge carriers, which significantly deteriorates characteristics of developed devices [7].

Formation of ohmic contact to the active layers of solar cells is an important part of device development. Usually as a material for ohmic contact to CZTS, which has *p*-type conductivity, such metals as Mo, W, Au, Pd, Pt, Ni are used [8]. Respectively, for formation of ohmic contact to window layers of solar cells, which have *n*-type conductivity, such metals as Al, Ag, Cu are mostly applied [9].

At present time many physical and chemical methods are used for deposition of CZTS films [10-14]. As a result, the

price of thin-film solar cells is varied in the range from \$ 0.50 to \$ 1.00 / W, which is usually determined by the cost of their fabrication [15]. Further decreasing of the price is possible due to application of new methods of CZTS films deposition [16].

One of the promising ways of decreasing the production cost is application of flexible substrates, and low-temperature methods of film deposition, which include printing of the films using 2d and 3d printers. This principle can be easy realised in laboratory and in manufacture [17, 18]. Further removal of organic solvents in the films is usually carried out by their decomposition and evaporation at high temperatures of annealing of the product [19].

Conventional inkjet printers use water based ink pigments that can be replaced with ink containing a suspension of nanoparticles of various materials [20]. In our time, a large variety of nanocrystals of metals, semiconductors, insulators and intermetallic materials has been synthesized [21]. Development of a stable colloidal solution of nanoparticles, which is used as ink, with appropriate viscosity and surface tension, which is environmentally friendly and non-toxic is further scientific and technological problem.

In the presented work results of optimization of synthesis of CZTS and Cu nanoparticles depending on the time of their synthesis are presented.

II. MATERIAL AND METHODS

CZTS nanoparticles were obtained by polyol synthesis in an inert argon atmosphere. As an environment for synthesis, diethylene glycol (DEG) was used. A mixture of salts 0.334 g (2 mmol) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$, 0.220 g (1 mmol) $\text{Zn}(\text{CH}_3\text{COO})_2 \cdot 2\text{H}_2\text{O}$, 0.226 g (1 mmol) $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ and 60 ml DEG was placed into a three-necked flask and was heated using an oil bath with intense stirring with a teflon stirrer. After reaching a temperature of 130 °C, the mixture was kept for 10 minutes then there a solution of 0.304 g (4 mmol) $(\text{NH}_2)_2\text{CS}$ into 10 ml DEG was added dropwise. After that, the purge of the flask by Ar started. The resulting reaction mixture was heated to a temperature of 240 °C during definite time period. In the

process of synthesis, we obtained CZTS samples at different time intervals of exposition at temperature of reaction environment, namely $\tau = 0, 15, 30, 60, 90$ and 120 min. Subsequently, the mixture was cooled to room temperature and the synthesized product was separated from the organic component (DEG) by centrifugation. The residues of DEG were washed using ethanol with intense shaking followed by centrifugation. The washed CZTS samples were dried at room temperature for 24 hours. The scheme for the synthesis of CZTS nanoparticles is presented in Fig. 1.

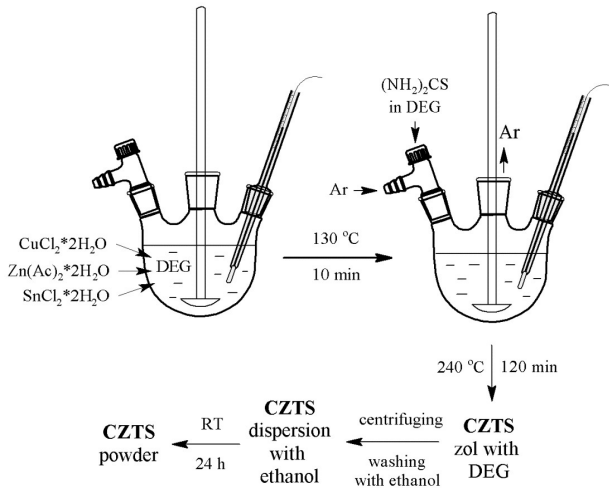


Fig. 1. Schematic of CZTS nanoparticles synthesis

Synthesis of Cu nanoparticles was carried out in an aqueous solution in air at room temperature. At first, 0.9 g of gum acacia was dissolved in 30 ml of water. The dissolution process lasted 30 minutes at an intensive mixing of the solution in a chemical glass at 150 ml using a magnetic stirrer. Gum acacia was used as a protective environment for Cu nanoparticles against oxidation after the addition of reducing agent. In other glass the solution 0.428 g (2.5 mmol) $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$ in 20 ml of water was prepared. Then a solution of copper salt was added to the solution of gum acacia, continuing to stir it intensively for 10 minutes. After that 0.9 ml $\text{N}_2\text{H}_4 \cdot \text{H}_2\text{O}$ was added dropwise to the solution. This amount of reductant corresponded to the molar ratio to the used salt as 1:10.

After adding of hydrazine hydrate, the mixture was stirred for 1 hour. The resulting solution was centrifuged for 20 minutes with a rotational speed of 5000 rpm. The separated product was washed from the organic compound three times using ethanol followed by centrifugation and, last time, was washed using acetone. Moist powder of copper was dried during 3 hours in vacuum at room temperature. The synthesis scheme is presented in Fig. 2.

X-ray diffractometer DRON 4-07 in Ni-filtered K_α radiation of copper anode was used to determine the structural properties. Sampling was carried out in continuous registration mode (speed – $16^\circ/\text{min}$, step 0.1 deg.) in the angle range 2θ from 10° to 80° , where 2θ is the Bragg angle. Experimental results were transmitted directly to the DifWin software package for pre-processing. X-ray radiation was focused according to the Bragg-Brentano method.

The peak intensities were normalized to the intensity of (112) peak of the tetragonal phase. Phase analysis was

performed by comparison of the inter-planar distances as well as relative intensities measured from the samples and reference data JCPDS (CZTS – № 00-026-0575).

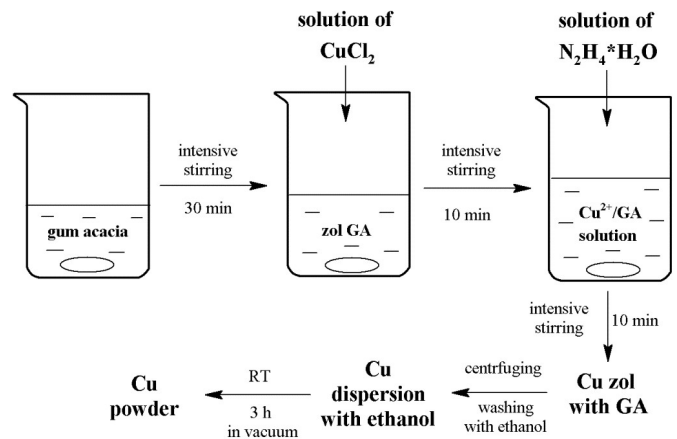


Fig. 2. Schematic of Cu nanoparticles synthesis

Lattice parameters a and c of the tetragonal phase for CZTS were calculated according to the next relations [22-23]:

$$a_{\text{CZTS}} = \frac{\lambda}{2 \sin \theta} \sqrt{h^2 + k^2 + l^2 \left(\frac{a}{c}\right)^2},$$

$$c_{\text{CZTS}} = \frac{l}{\sqrt{-\frac{h^2 + k^2}{a^2} + \left(\frac{2 \sin \theta}{\lambda}\right)^2}},$$

where 2θ is the Bragg angle; λ is X-ray wavelength; (hkl) – Miller indexes.

The value of elementary cell volume of CZTS was calculated using equation

$$V_{\text{cell(CZTS)}} = a^2 \cdot c$$

Average size L of the coherent scattering domains (CSD) and microstrain level ε in CZTS samples were calculated from broadening of (112) diffraction peak using equations [24-25]:

$$L = \frac{0.94 \cdot \lambda}{\beta \cdot \cos \theta}, \quad \varepsilon = \frac{\beta}{4 \cdot \tan \theta},$$

where λ – wavelength; β – value of broadening of corresponding diffraction peak; θ – diffraction angle.

III. RESULTS AND DISCUSSION

The XRD patterns of CZTS nanoparticles, synthesized at different time are presented in Fig. 3. As follows from Fig. 3, peak at $(28.75-28.85)^\circ$ angles which corresponds to the reflection from the (112) plane of the tetragonal phase of CZTS is dominant. Also peaks at $(32.55-33.25)^\circ$, $(47.75-47.90)^\circ$, $(56.40-56.65)^\circ$, $(69.55-69.85)^\circ$ and $(76.45-77.25)^\circ$

which correspond to reflections from (220) and (312) planes of CZTS compound are detected on XRD spectra. Peaks which correspond to oxide phases of components, were not observed on XRD patterns, unlike our work [23, 25], where small amount of SnO₂ and Cu₂S exterior phases was present. This indicates that the concentration of uncontrolled phases in the samples does not exceed 3-5% [26]. It should be noted that with increasing synthesis time, the intensity of peaks on XRD patterns is slightly increasing, and their half-width is decreasing (Fig. 4).

As it is known, the intensities ratios for series of diffraction reflections from the crystallographic planes of the kesterite and stannite phases are different [27]. That's why, definition of these ratios makes it possible to establish accurately the dominant phase in the material. Calculated ratio $I_{(112)}/I_{(220)}$ of reflections intensities from (112) and (220) crystallographic planes for the samples was (2.15-2.29). These values are close to the value of $I_{(112)}/I_{(220)}$ ratio in undoped films with kesterite phase, which was of about 2.80 [28]. Thus, we assume that studied nanoparticles had kesterite structure. This assumption is confirmed by experimental calculations of crystalline lattice parameters ratio ($c/2a = 0.97782-0.99732$) of a material, which was close to 1, and this is characteristic of kesterite phase [29].

Thereby analysis of XRD patterns shows, that single-phase CZTS samples with tetragonal crystal lattice (I-42m group) and kesterite structure, were obtained in result of synthesis (Fig. 3).

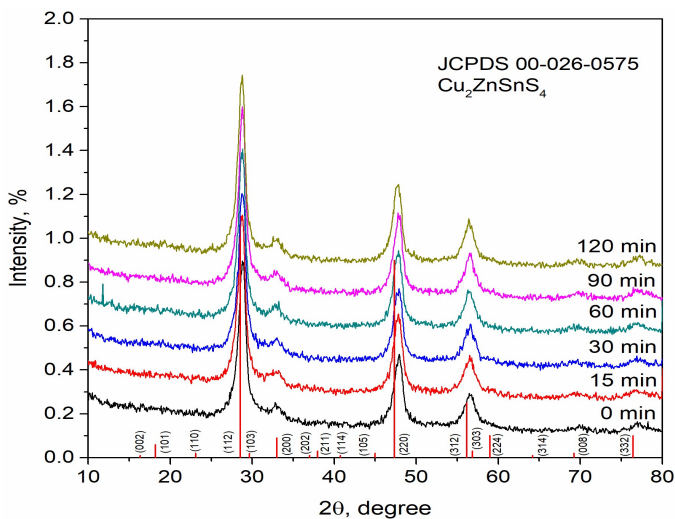


Fig. 3. XRD patterns of CZTS samples, synthesized at different time

As it was noted, for CZTS samples the time interval of exposition at the temperature of reaction camera of 240 °C was varied in the range $\tau = (0 - 120)$ min. It was established, that the duration of synthesis has a weak effect on the process of material crystallization and particle size. In all cases, well-crystalline, single-phase products were obtained (Fig. 3).

It was determined, that average CSD size of CZTS nanoparticles was slightly increasing from 7.9 to 8.4 nm (Fig. 4, Table 1) with increase of synthesis time. At the same time the microstrain level in the samples is decreasing from $4.58 \cdot 10^{-3}$ ($\tau = 0$ min) to $4.29 \cdot 10^{-3}$ ($\tau = 120$ min) (Fig. 4, Table 1). It should be noted, that CSD size practically was equal to

the size of obtained nanoparticles and was approximately two times smaller, than in our previous work [23].

Lattice parameter of the material is very sensitive to the changes of stoichiometry, introduction of impurities, oxidation etc. That's why precise determination of lattice parameter value allows to study relevant processes.

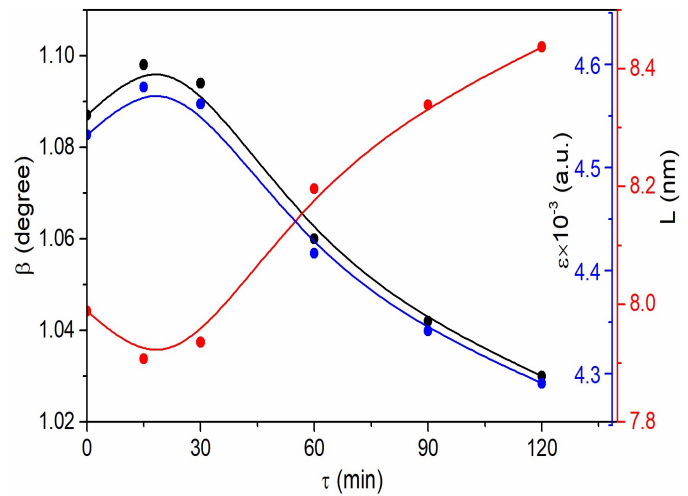


Fig. 4. Dependence of broadening of (112) diffraction peak (β), CSD size (L) and microstrain level (ϵ) in CZTS samples on synthesis time

Calculated values of lattice parameters are presented in Table 1. It was determined, that lattice parameters were changed in following ranges: $a_{CZTS} = (0.53568 - 0.54212)$ nm, $c_{CZTS} = (1.04429 - 1.08133)$ nm, $c/2a_{CZTS} = (0.97782-0.99732)$. As it seen from Table 1, with increasing of synthesis time the values of a and c parameters are decreasing, and their difference from reference data increases. The closest values of a and c parameters to reference data were obtained time of synthesis $\tau = 0$ min. The value of elementary cell volume was varied in the range $V_{cell(CZTS)} = (0.2997-0.3178)$ nm³. These values were smaller, than reference data for massive material [30] and values for CZTS films, obtained by spray-pyrolysis method in works [31-32].

Unfortunately, we could not obtain a stable suspension of synthesized nanoparticles. In the synthesis process, they cluster and form aggregates and conglomerates (Fig. 5) Our attempts to split conglomerates of particles with size of $D = 2-5$ microns using ultrasound disperser UZDN-A hadn't led to positive results. Thus, the obtained nanoinks can be used for printing of films using 3d printers. However, when printing with inkjet 2d printer a quick "clogging" of nozzles, that have a size of 20 microns, was observed. Currently, our scientific group conducts work on stabilizing the suspension of nanoparticles to ensure the printing of films inkjet printers.

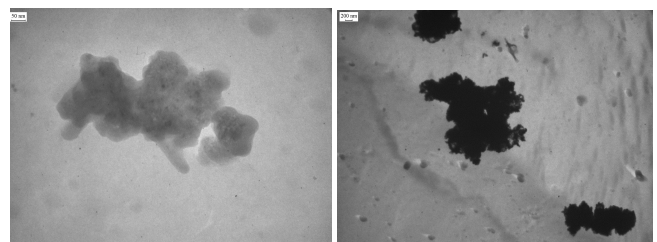


Fig. 5. SEM images of obtained aggregates and conglomerates of CZTS nanoparticles

TABLE I. SOME STRUCTURAL PROPERTIES OF SYNTHESIZED CZTS NANOPARTICLES

Synthesis time τ , min	Broadening of peak (112) β , degrees	L , nm	$\varepsilon \cdot 10^{-3}$	a , nm	c , nm	$c/2a$	V_{cell} , nm ³
0	1.087	7.99	4.53	0.54212	1.08133	0.99732	0.3178
15	1.098	7.91	4.58	0.53659	1.04937	0.97782	0.3021
30	1.094	7.94	4.56	0.53659	1.04937	0.97782	0.3021
60	1.060	8.20	4.42	0.53750	1.05452	0.98095	0.3047
90	1.042	8.34	4.34	0.53568	1.04429	0.99062	0.2997
120	1.030	8.44	4.29	0.53659	1.04937	0.99394	0.3021
Reference data	$a = 0.54270$ nm, $c = 1.0848$ nm, [JCPDS № 00-026-0575]			$c/2a = 0.9994$,		$V_{cell} = 0.3195$ nm ³	

As a result of Cu nanoparticles synthesis, single-phase crystalline samples with an average CSD size of about 20 nm were obtained (Fig. 6). It was determined that the purity of the final product depends on two factors: 1) the amount of the added reducing agent (hydrazine hydrate) to the salt solution of copper with the polymer, which act as a stabilizer of the colloidal solution, 2) the method of washing and drying of the separated metal copper precipitate. After the using of water or isopropyl alcohol for washing and drying in air atmosphere the obtained copper was partially oxidized to hydroxocarbonate.

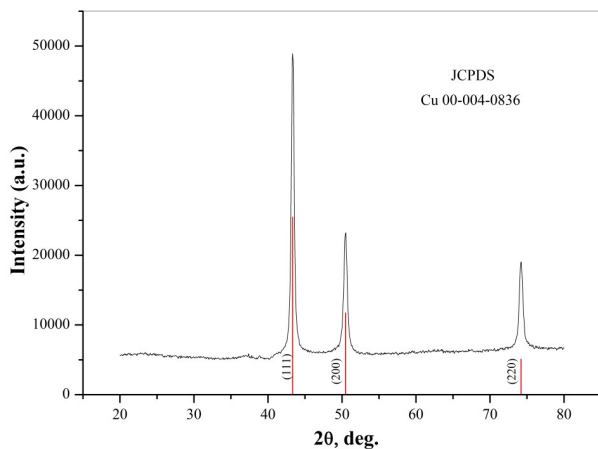


Fig. 6. XRD pattern of Cu sample

CONCLUSIONS

In this work we studied the influence of synthesis time (τ) on the phase composition, parameters of the crystalline lattice (a , c , $c/2a$), elementary cell volume (V_{cell}) and the coherent scattering domains size (L) of the CZTS nanoparticles obtained by polyole synthesis in the inert atmosphere of argon. Phase analysis showed that the synthesized nanocrystals of the four-component compound increasing from $L = 7.9$ nm to $L = 8.4$ nm. At the same time the microstrain level decreases from $\varepsilon = 4.58 \cdot 10^{-3}$ to $\varepsilon = 4.29 \cdot 10^{-3}$.

Calculated values of lattice parameter were smaller, than that in massive material, and varied in the ranges $a_{CZTS} = (0.53568-0.54212)$ nm, $c_{CZTS} = (1.04429-1.08133)$ nm, $c/2a_{CZTS} = (0.97782-0.99732)$, with increase of synthesis time

these values were decreasing. It was shown that optimal characteristics (the smallest CSD size, the value of lattice parameter is close to the reference data) were observed for the nanoparticles synthesized at $\tau = 0$ min.

As a result of copper nanoparticles synthesis, single-phase crystalline samples with an average CSD size of about 20 nm were obtained. It was shown, that using of water or isopropyl alcohol for washing and drying in air atmosphere leads to partial oxidation to copper hydroxocarbonate.

Obtained suspensions of CZTS and Cu nanoparticles can be used for printing the corresponding films using 3d printers.

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