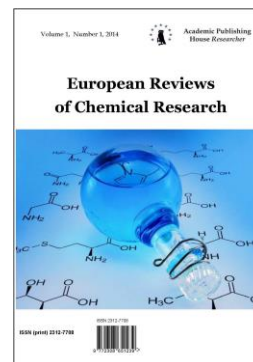


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Chemical Bath Deposition and Study of Semiconductor Thin Films in $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3$ System

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Abstract

In the first time thin films of $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ composition with the content of indium up to 9.63 at% were obtained by means of a chemical bath deposition from a system “indium chloride – copper chloride – sodium hydroxide – thiourea” and “indium chloride – copper chloride – sodium hydroxide – trilon B – thiourea”. The experimental data on the distribution and the atomic ration of elements in synthesized patterns obtained by the x-ray photoelectron spectroscopy were discussed. The change in the surface microstructure of thin films depending on the temperature and the composition of reaction bath were determined by means of scanning electron microscopy. The structure of obtained thin films has *n*-type of conductivity.

Keywords: copper sulfide (I), indium sulfide(III), thin films, solid solutions of replacement, x-ray photoelectron spectroscopy.

1. Introduction

The people stands near to a new discover that connected with solution of difficult problems. As last decades a great force was direct to solution of removable energy problem. The scientific attention in any removable field direct to a new semiconductor material and this deposition method. The thin film chalcopyrite structures we can refer to promising material for solar cells.

The first representative in a line of chalcopyrite semiconductor is copper(I)-indium(III) disulfide $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3$. Collection of a properties such as high absorption factor of incident sunlight α ($\sim 10^{-5} \text{ cm}^{-1}$) (Jing-Jing et al., 2012), optimal energy band gap (1.5 eV) (Novoselova, 1979), rather high efficiency factor ($\sim 13\%$) (Fiechter, 2008), radiation stability (Maier et al., 2011), low industrial cost and environment safety in comparison with CdS is causing that these semiconductors use for solar cells preparation. Moreover a improvement of optical properties of chalcopyrite thin films $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3$ is caring out by means of control doping by elements such as Ga, Zn, Fe, Se doping (Yanfeng et al., 2011; Kuan-ting et al., 2013; Sharma et al., 2009).

There are different deposition methods for semiconductor material in a system $\text{Cu}_2\text{S}-\text{In}_2\text{S}_3$. For example, it is high-speed magnetron spraying in a vacuum, spraying of water solutions with pyrolysis on heating a substrate (Lee, JunHo, 2010), physical deposition from gas phase, molecular-beam epitaxy (Chepra, Das, 1986), deposition by a sulfidization method on separate

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layers Cu-In (Merdes et al., 2011), electrochemical deposition (Jing-Jing et al., 2012) and chemical bath deposition (CBD) (Sharma et al., 2009; Yoon et al., 2012).

Attractiveness of CBD is not only its technology simplicity, the absence of deep vacuum or high temperature but also a deposition possibility for supersaturated solid solution, flexible control of a film properties that is vary difficult or impossible to achieve. As a result these factors are promising a low-temperature chemical deposition methods for copper(I)-indium(III) disulfide. However, literature data about complex physical and chemical studies for thin films of copper (I) and indium (III) sulfides and this replaced solid solution by CBD is absent.

Earlier we noticed from carried out thermodynamic researches (Fedorova et al., 2015; Maskaeva et al., 2012) that is a concentration region for copper (I) and indium (III) sulfides codeposition in two different system: hydroxide-system and trilonate-system. Also we showed that is a wide region of indium hydroxide steady which can impede a sulfide phase formation.

Purpose of the present work is carrying out of chemical bath co-deposition of thin films of copper (I) and indium sulfides and physical and chemical studies of their composition and microstructure.

2. Materials and methods

Deposition of Cu(I)-In-S thin films was carrying out on preliminary defatting sitall substrates (CT-50-1 mark) from two different reaction mixture. The first of them contained indium chloride InCl_3 , copper chloride CuCl_2 , sodium hydroxide NaOH , thiourea $\text{N}_2\text{H}_4\text{CS}$. The second reaction mixture additionally contained trilon B $\text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O}$. The $\text{NH}_2\text{OH} \cdot \text{HCl}$ addition in reaction mixture had entered to transfer the copper Cu^{2+} in Cu^+ . The synthesis of thin films was carried out in a range of temperatures 333–353 K in glass leak proof reactors in which substrates fixed in specially made ftoroplaste device were placed. Reactors were located in thermostat TC-TB-10 with the accuracy of maintenance of temperature $\pm 0.1^\circ$. Deposition time 120 minutes was fixed for all thin films. Thickness of obtained simples has been measured on interferometer Linnik's MII-4M. Dark resistance measurements of semiconductor Cu(I)-In-S thin films has been measured on equipment K.54.410. Composition and main form of compounds in thin films were studied by means of X-ray photoelectron spectroscopy (XPS) method on ESCALAB MK II (VG Scientific, Great Britain) X-ray photoelectron spectrometer using magnesium cathode $\text{MgK}\alpha$ (1253.6 eV) as the non-monochromatized X-ray excitation source. The $\text{Cu}2p_{5/2}$ line was calibration line with energy 932.5 eV. Scanning electron microscopy (SEM) of a simple surface was occurred on JEOL JSM-6390 LA instrument in second electron (SE) with JED 2300 tool for energy dispersive X-ray (EDX) analysis. Semiconductor type of obtained thin films was studied by means of a generated voltage measures.

3. Results and discussions

Concentration region and codeposition pH for copper (I) and indium sulfides was obtained by predicted calculation of CBD condition in $\text{Cu}_2\text{S-In}_2\text{S}_3$ system. For this aim analyses of ion balances in two complex systems was carried out (Maskaeva et al., 2012) that revealed which copper (I) and indium sulfides co-deposition is possible in wide pH region from 3.5 to 10, but in the case of trilon B is the only possible in a high alkaline condition.

Smooth Cu-In-S thin films with rather good adhesion to sitall substrate were deposited in experiment from carried out thermodynamic researches. Colour of thin films changes from light-brown (send-coloured) up to dark-brown with green shade.

The study of a main element forms and them composition in Cu-In-S thin films were carried out by means of XPS. For this survey spectra, region $\text{In}3d$ electron core level of indium, region $\text{Cu}2p$ electron core level of copper, region $\text{S}2p$ electron core level of sulfur and region from 10 to 90 eV containing $\text{In}4d$ and $\text{Cu}3p$ peaks were recorded.

The XPS data showed that chalcopyrite thin film content indium from 4.05 to 9.63 at% with deposition condition and initial reagent concentrations (see table). The copper amount exceed indium and fluctuate from 25.76 to 49.43 at%, and sulfur is in deficiency (12.99–26.28 at%). High oxygen quantity, except for main elements, from 20.14 to 52.36 at% in studied films was obtained.

Table

Simple	In, at%	Cu, at%	S, at%	O, at%	[Trilon], M	T, K
1	8.89	25.76	12.99	52.36	–	343
2	4.15	49.43	26.28	20.14	–	353
3	4.05	47.08	20.74	28.13	0.03	343
4	9.63	40.65	18.46	31.26	0.03	353
CuInS ₂ (monocr.)	25.00	25.00	50.00	–		

We suggest that oxygen is being included in the different oxygen-keeping impurities such as Cu₂O, In(OH)₃, In₂O₃ entering into Cu₂S-In₂S₃ thin film composition at chemical deposition process. The formation of these metal sulfides in reaction deposition mixtures was confirmed by ionic balances calculation in (Maskaeva et al., 2012).

The chemical condition of elements in thin film surface layers was being determined by the position of In3*d*, Cu3*p*, S2*p* and O1*s* peak of electron core levels spectra of In, Cu, S and O atoms accordingly.

The In4*d* peak indicates a present of indium in deposited films. It consists of two components: the first with energy ~18.53 eV (fig. 1a), how we suggesting, is an indium oxide form, and the second with energy ~19.6 eV refer to sulfide form. The In3*d* electron core level with energy ~444.75 eV is more informative line. One a few deviate to high energy compared to standard peak energy 444.45 eV for indium sulfide. All over indicate that indium particularly remains in an oxide or hydroxide phase in Cu-In-S surface layers.

Spectral analyses revealed that a main chemical form of sulfur in Cu-In-S surface layers is copper (I) sulfide (fig. 1b). Thus a bounding energy ~161.48 eV for S2*p* electron core levels spectra of sulfur in all over cases was interpreted as formation of the copper (I) sulfide solid phase. It compare to creating of a good conditions in the reaction bath for Cu₂S formation that possible activates a sulfidization process of indium hydroxide and Cu-In-S thin film deposition. Present of the some peak with deviation to high energy show that sulfur has positive charge and enter to composition of a sulfates or sulfites.

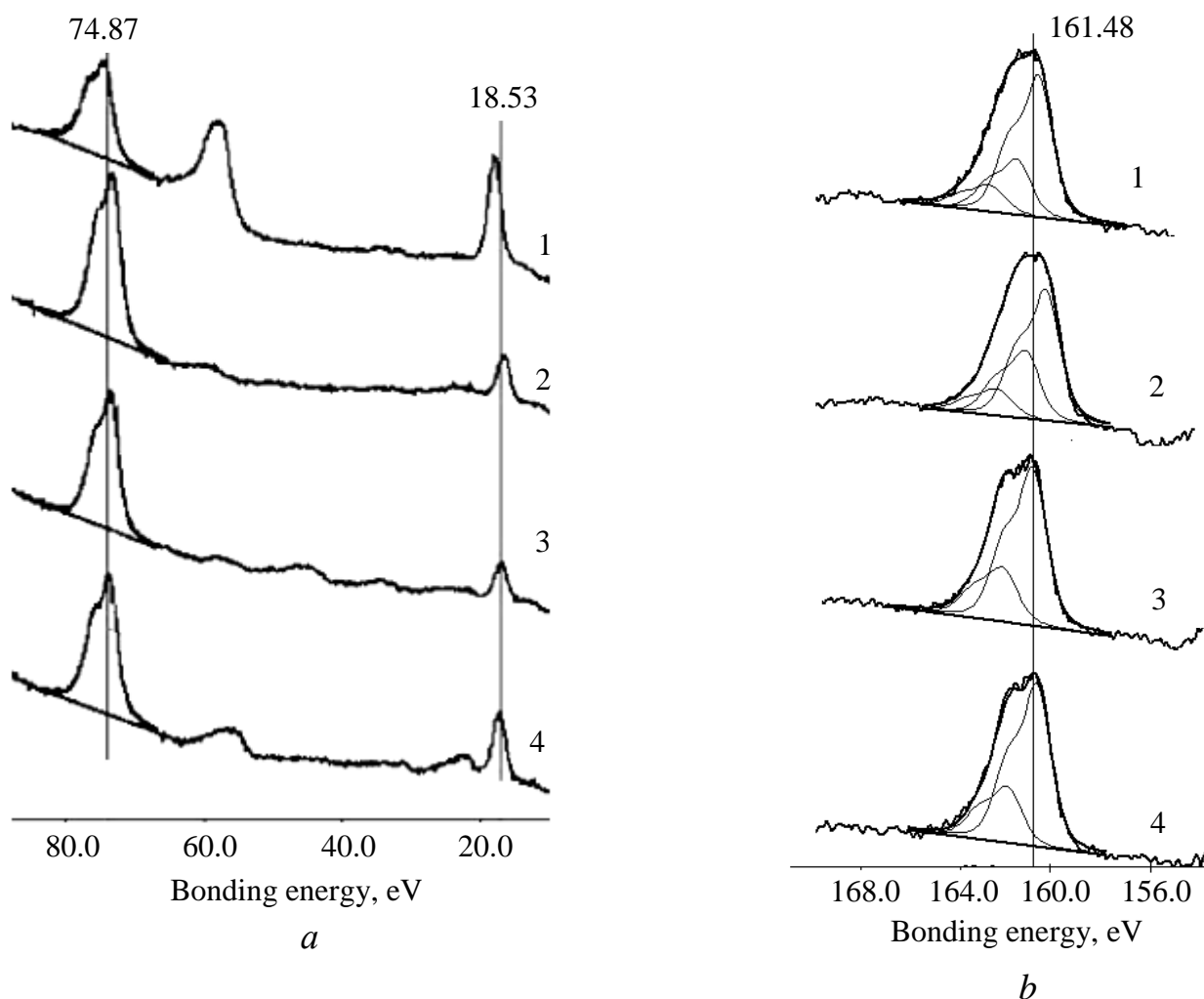


Fig. 1. XPS spectra of the samples: Cu_{3p}, In_{4d} (a) и S_{2p} (b) electron core levels spectra of copper, indium and sulfur in Cu₂S–In₂S₃ films. The photoelectron registration angle is 90° (analysis depth for layer is 2-4 nm)

XPS spectra of Cu_{2p} electron core level of deposited thin films with bonding energy 932.5 eV. On obtained spectra we clearly see that copper in layers fully is Cu⁺ due to hydroxide amine hydrochloride addition in reaction mixture. Apparently from [fig. 2](#) oxygen in films exist in two forms: oxide or hydroxide. There are peak with small bonding energy ~531.37 eV and peak with high bonding energy that refer to different organic, sulfate and sulfite impurities said about it. From XPS data we can conclude that the compound In_xCu_{1-x}S_yO_{1-y} with complex composition is formed in surface layers.

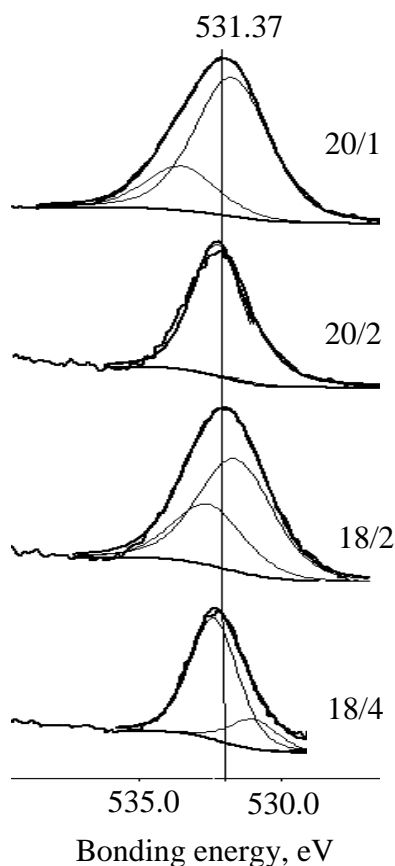


Fig. 2. XPS spectra of the samples: Cu2p (a) и O1s (b) electron core levels spectra of copper and oxygen in Cu-In-S

The SEM study of a deposited Cu_2S thin film structure (fig. 3) showed that it consists of sickle-like particles which don't have accurate crystallographic facet with size 110–500 nm. We can see small spherical agglomerates on surface with the same composition as main layer.

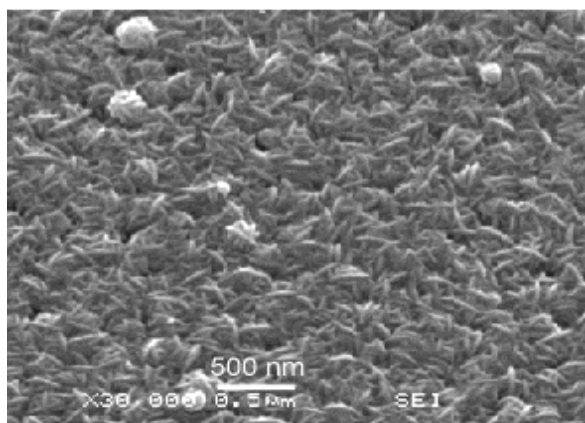


Fig. 3. SEM microphotograph of the make-up deposited Cu_2S film in second electron (magnification 30000)

The SEM data showed that addition of indium salt in reaction mixture is leading to decrease in particle size up to 76–230 nm (fig. 4) and formation of aggregates not possessing express habitus.

This is formation of $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thin films from particles with average size 100–230 nm due to increase CBD temperature. Morphology don't have visual transformation due to increase

temperature up to 353 K (fig. 4c), but pellet size non-uniformity simultaneous increase.

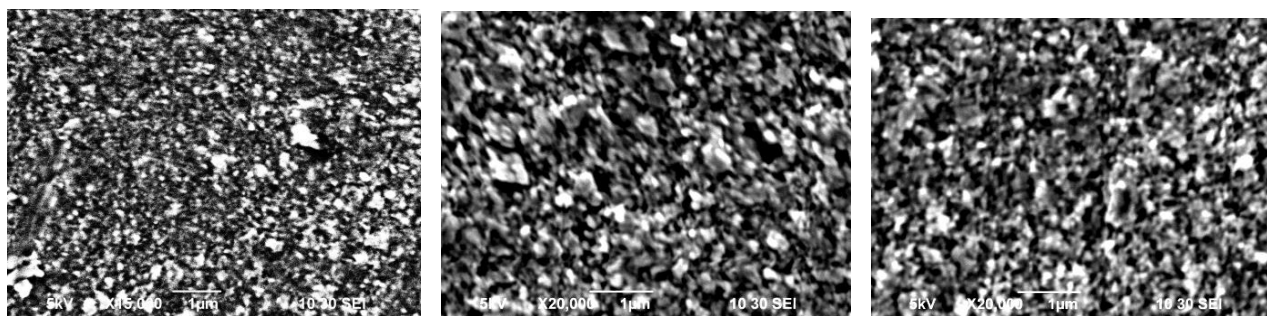


Fig. 4. SEM of the make-up deposited $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ film from reaction mixture including copper chloride, indium chloride, sodium hydroxide, hydroxide amine hydrochloride and thiourea, at temperature, K: 333 (a), 343 (b) и 353 (c)

We notice that a measured film $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thickness by interferential microscope (Linnik's interferometer) depend on temperature at 333–353 K and increase from 320 to 570 nm. Reaction mixture, in it case, consists of copper chloride, indium chloride, sodium hydroxide, hydroxide amine hydrochloride and thiourea.

The complexing agents to inhibit extraction of copper in the precipitate in considered system in a number with copper hydroxides CuOH ($pK_{\text{H}} = 14.70$), CuOH^+ ($pK_{\text{H}} = 7.0$), $\text{Cu}(\text{OH})_2$ ($pK_{\text{H}} = 13.68$), $\text{Cu}(\text{OH})_3^-$ ($pK_{\text{H}} = 17.0$), $\text{Cu}(\text{OH})_4^{2-}$ ($pK_{\text{H}} = 18.50$) were Y^{4-} -ions giving more strong copper trilonat complex – CuY^{2-} ($pK_{\text{H}} = 18.80$) (Lure, 1989). Indium in reaction bath form complexes with following indexes of instability constants InOH^{2+} ($pK_{\text{H}} = 7.55$), $\text{In}(\text{OH})_2^+$ ($pK_{\text{H}} = 17.94$), $\text{In}(\text{OH})_3$ ($pK_{\text{H}} = 26.95$), $\text{In}(\text{OH})_4^-$ ($pK_{\text{H}} = 31.07$), InY^- ($pK_{\text{H}} = 24.95$) (Kumok et al., 1983).

Origin condition of copper (I) sulfide solid phase is essential change with trilon B addition as degree of copper salt transformation to sulfide is decreasing. Thus a velocity of Cu_2S formation decrease, but it almost don't have any change for indium sulfide deposition because trilon B addition in reactor given't a changes in In_2S_3 deposition conditions. It results to formation a more uniform film consisted of particles with average size 50–130 nm.

Growth dynamic of thin film with trilon B addition in mixture (second case of the synthesis) essential differ from first one. Thickness of semiconductor layer $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ varying from 115 to 405 nm possesses exponential temperature dependence.

Dark resistance of make-up deposited semiconductor $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ in second case of the synthesis is constant in all over temperature interval and equal to 3–5 kOm on a square. One can observe that dark resistance for synthesized films in second case is decreasing from 32 to 8 kOm on a square. Probably this dependence connects with thickness increasing of the semiconductor layers.

Important characteristic of the semiconductor layer promising material in solar cells is a conductivity type. Conductivity type of $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thin films was obtained by means of a thermo-emf sign that in all over intervals of In/Cu ratio and temperature is negative, i.e. a film have p -type conductivity as well as In_2S_3 monocrystal (Bereznev et al., 2013). The individual copper sulfide possess p -type conductivity which full correspond to literature data: Cu_2S is the hole conductor (p -type) (Abrikosov et al., 1975).

Semiconductor p -type material is necessary for creating p - n -junction in solar cells with $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thin films. As p -type semiconductor represent itself a thin films such as lead and tin sulfides deposited by CBD. Also change of semiconductor type is possible by means of a copper quantity varying which is added into $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thin film. Just copper will supply n -type due to excess of that. If CuInS_2 will possess p -type conductivity CdS or GaP thin films can be use for p - n -junction.

4. Conclusion

For the first time $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thin films were deposited by means of CBD in $\text{InCl}_3 - \text{CuCl}_2 - \text{NaOH} - \text{N}_2\text{H}_4\text{CS}$ and $\text{InCl}_3 - \text{CuCl}_2 - \text{Na}_2\text{C}_{10}\text{H}_{14}\text{O}_8\text{N}_2 \cdot 2\text{H}_2\text{O} - \text{NaOH} - \text{N}_2\text{H}_4\text{CS}$ systems at 333–353 K with thickness 115–570 nm and good adhesion to siall substrate. XPS data showed that surface of thin film in $\text{Cu}_2\text{S} - \text{In}_2\text{S}_3$ system include 4.05–9.63 at% of indium, 25.76–49.43 at% of copper, 12.99–26.28 at% of sulfur. Moreover, film composition is including metal oxide phases with 20.12–52.36 at% of oxygen which predicted from ion balance calculation. SEM showed that composition of reaction mixture and deposition temperature depends on morphology of $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ nanostructured films. The *n*-type conduction of $\text{In}_x\text{Cu}_{1-x}\text{S}_y\text{O}_{1-y}$ thin films was obtained. The dark resistance varies from 3 to 5 kOm on square meter for deposited films from trilonate-system and from 32 to 8 kOm on square meter for deposited films from second system.

5. Acknowledgements

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