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# Chemical bath deposition of $In_2S_3$ thin films

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## Abstract

$In_2S_3$ thin films were grown by means chemical bath deposition from acid solution. Calculation of ionic equilibrium with using of thermodynamic constants for systems defines boundary conditions of formation $In_2S_3$. Films were characterized by means of XRD, SEM, EDX and XPS methods. According to XRD films have cubic structure of $In_2S_3$. XPS method was shown that the surface of $In_2S_3$ thin film includes oxygen and carbon contained impurities. SEM confirmed ***nanosized*** nature of thin films. Optical band gap of indium(III) sulfide equal to 2.3 eV.

**Keywords:** boundary conditions of deposition; chemical bath deposition; indium(III) sulfide; XRD, XPS.

## Introduction

Newsday indium (III) sulfide has wide application in a micro- and optoelectronics thanks to unique electrical and physical properties [1] such as picture tubes for color television, ionized radiation detectors and in the photovoltaic such as buffer layer and main material for $CuInS_2$ solar cells [2, 3]. $In_2S_3$ are simplest compound among chalcogenide group that possess a high energy band gap [4], n-tape conductivity, high absorption coefficient of radiation, longtime stability.

All deposition methods of $In_2S_3$ semiconductor material we are divide on physical and chemical methods. The physical methods include thermal evaporation in vacuum, spraying of water solutions with pyrolysis on a heating substrate [5], physical deposition from gas phase, molecular-beam epitaxy [6]. The chemical thin film methods include electrochemical deposition and chemical bath deposition [7]. As using of physical methods is being connected with composite equipments, deep vacuum and high-purity precursors but the chemical bath deposition has weak deposition condition, simple apparatus design, composition control mode and doping operations.

## Materials and Methods

Deposition of indium sulfide thin films was carrying out on preliminary defatting pyroceramic substrates from reaction mixture containing indium nitrate $In(NO_3)_3$, thioacetamide $CH_3NH_2CS$, tartaric acid $C_4O_6H_6$, hydroxyl amine $NH_2OH{\cdot}HCl$. The optimal pH was about 1.7. Synthesis of thin films was carried out in the range of temperature 70–90 °C in Mo-glass beaker reactors. Reactors were located in thermostat TC-TB-10. Crystal structure of thin films investigated by method of X-ray diffraction (XRD) on diffractometer Shimazu XRD – 7000 with using monochromatic $Cu/K_{\alpha 1}$ radiation, $\lambda$ = 1.54056 Å. 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 Mg$K_\alpha$ (1253.6 eV). The C1*s* line was calibration line. Scanning electron microscopy (SEM) of a simple surface was occurred on Mira-3-LMY instrument in second electron (SE) with JED 2300 tool for energy dispersive X-ray (EDX) analysis. Thickness of simples has been measured on an interferometer MII-4M.

## Discussion

The choice of reaction mixture composition and definition of colloidal chemical deposition conditions of indium sulfide $In_2S_3$ thin films is considerably facilitated after carrying out of the preliminary thermodynamic calculations.

In a basis of the deposition condition analysis from the solutions containing thioacetamide has laid a rule about reversible hydrolytic decomposition character of the sulfur-supplier [8, 9]. Thus TAA decompose in acid solution according to equal:

$$CH_3CSNH_2+2H_2O+H_3O^+ \leftrightarrow Ac^-+NH_4^++H_2S \quad (1)$$

In equal (1) yielded hydrogen sulfide quickly decompose (2) and (3) as indium-ions $In^{3+}$ combine with sulfide-ions on equal (4):

$$H_2S + H_2O \leftrightarrow H_3O^+ + HS^- \quad (2)$$

$$HS^- + H_2O \leftrightarrow S^{2-} + H_3O^+ \quad (3)$$

$$InL_x + S^{2-} \rightarrow In_2S_3 + xL \quad (4)$$

The content of $Me^{n+}$ ions had been calculated by means of the analysis ionic balances in system with the complexing account with present ligands. Result of calculation which characterized placed balance in $InCl_3$ – $C_4O_6H_6$ – $NH_2OH{\cdot}HCl$ – $CH_3NH_2CS$ system between a sediment $In_2S_3$ (curve 1), $In(OH)_3$ (curve 2) and indium complex compounds in a solution are showed on Fig. 1. Deposition of this sulfide in investigated system is placed in a wide range pH from 3 to 15. Also indium hydroxide form at the same conditions. The region pH less then 3 without formation of indium hydroxide for synthesis is optimal.

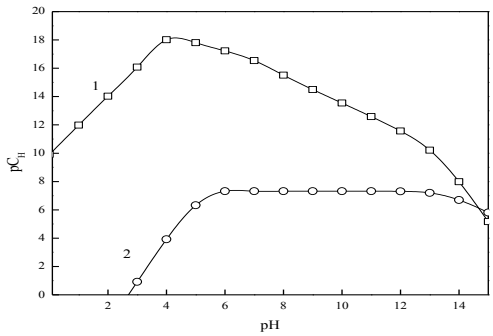


Figure 1. The region of $In_2S_3$ solid phase deposition in system $In(NO_3)_3$ – $C_4O_6H_6$ – $NH_2OH{\cdot}HCl$– TAA (1), $In(OH)_3$ line (2). The calculation carried out at 80 °C

According to calculation it was deposited uniform orange films which were observed on pyroceramic substrates and walls of beakers with good adherent. Thin films were washed and dried. Thickness of obtained thin films was up to 3500 nm.

The XRD patterns of the deposited $In_2S_3$ thin films confirmed that it crystallized in cubic structure (XRD patterns no shown). Diffraction peaks (311), (400), (422) and (440) observed on typical XRD pattern of the $In_2S_3$ prepared on pyroceramic at 80 ºC (a film thickness 700 nm) indicate about this [10]. It is noticed that lines with least *hkl* indexes on XRD pattern of thin film are absent because of the strong substrate background is presence, and also the accurate crystal structure is not formed completely.

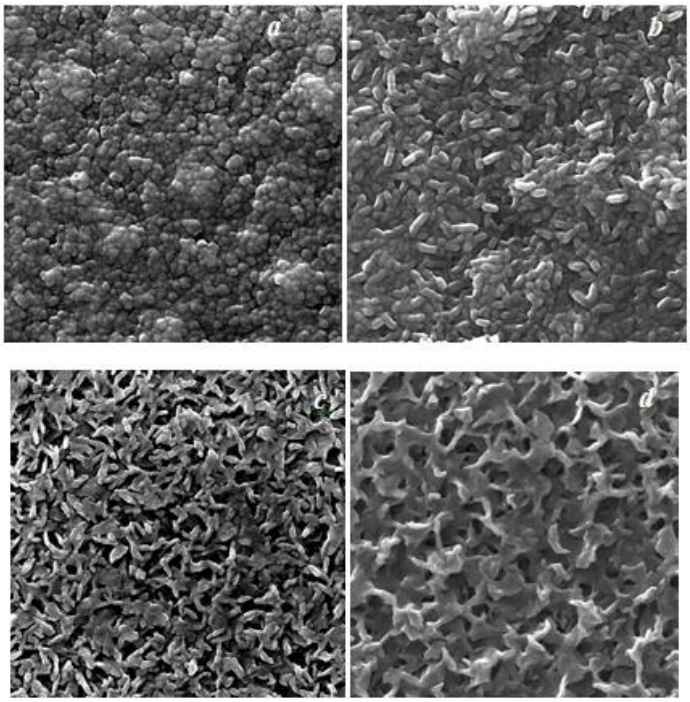


Figure 2. SEM images of as-deposited (*a, b, c*) and heat treatment at 300 ºC (*d*) $In_2S_3$ thin films prepared at, ºC: 70 (*a*), 80 (*b, d*), 90 (*c*). Magnification is 50000

SEM micrographs of the deposited films at different synthesis temperature are presented on Fig. 2. The study of as-deposited indium(III) sulfide thin films at 70 ºC (Fig. 2*a*) shown that it has a fine-crystalline structure with an average crystal size to 70-120 nm. It is a good agreement with literature date to deposition in a more acid solution [11]. The modification of film surface and mesh fractal structure were observed at increasing of a synthesis temperature (Fig. 2*b,c*) [12]. The average size of thread-crystals is 90-150 nm. We can see a particular flash-off of crystals after heat treatment on air condition in the SNOL furnace. The EDX-analysis shown that films contain up to 10 at.% of oxygen by means of oxidation process.

The $In_2S_3$ films were investigated by XPS using $Ar^+$ etching on 12 nm into depth. All films include characteristic In4*d*, S2*p*, C1*s*, In3*d* and O1*s* core levels of indium, sulfur, carbon and oxygen (Fig. 3*a*). We can see that overview XSP spectra after etching not contain C1*s* and O1*s* core levels. It means that volume material is pure. We obtained by means of XPS that surface of thin films include some oxidation phases (no more 8.5 at.% of oxygen) on surface. For example, it is may be different carbonates and organic impurities. Opposite EDX-analysis shown absents of oxygen in thin films and confirmed formation of $In_2S_3$ with small indium excess [13].

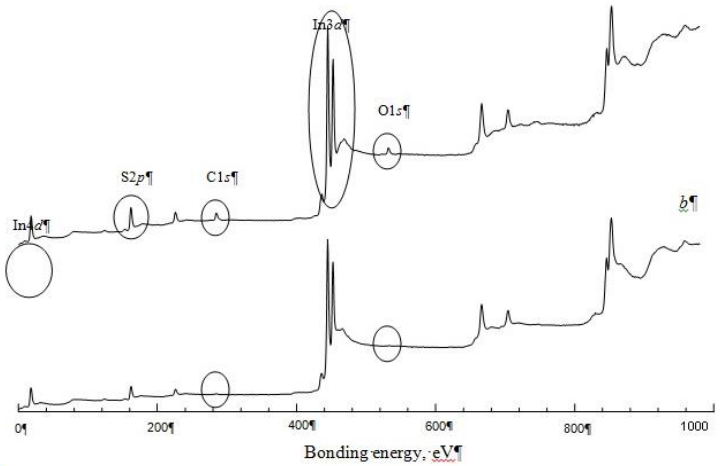


Figure 3. Overview XPS spectra of the simples with shown In4*d*, S2*p*, C1*s*, In3*d* and O1*s* core level spectrum of $In_2S_3$ before (*a*) and after (*b*) etching on 12 nm.

As can be observed (Fig. 3) all peaks are accurate and good define. The In3$d_{5/2}$ core shall with energy approximately 444.9 eV correspond to nonoxide form and it is correspond to $In_2S_3$ (444.7 eV). We cannot see any width and asymmetry of the In3*d* peak which indicate purity of compound. S2*p* peak is accurate and good define. Its bonding energy (161.4 eV) interquartile correspond to sulfide phases. The α-parameter gave us more information about compound. This value is 852.2 eV but it is some less then literature date for $In_2S_3$ (852.5 eV) and we refer this α-parameter to indium(III) sulfide.

The measure of optical properties of $In_2S_3$ thin films carried out from 300 to 1000 nm. The thin layers with 300 nm thickness for these measurements were deposited on glass substrates.

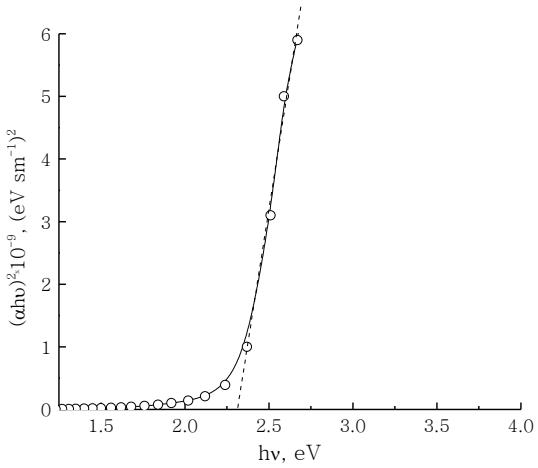


Figure 4. The plot of $(\alpha h\upsilon)^2$ versus hυ of thin film deposited at 80 ºC by CBD.

The dependence of $(\alpha h\upsilon)^2$ on energy of incident photons hυ show on Fig. 4. The $E_g$ for as-prepared $In_2S_3$ thin film has been determined by extrapolating the linear portion of $(\alpha h\upsilon)^2$ vs. hυ on x-line and has made 2.3 eV that have good agreement with literature data. The increasing of the $E_g$ more then 2.03 eV for $In_2S_3$ material is explained by the smaller size of crystal and chemical composition of a film. The oxygen on film surface indicates on thin oxidation layers that increase $E_g$

## Conclusion

The theoretical study of ion balance in $InCl_3$ – $C_4O_6H_6$ – $NH_2OH{\cdot}HCl$ – TAA system confirmed that deposition of $In_2S_3$ is accompany with formation of indium hydroxide $In(OH)_3$ steady in wide pH region. The $In_2S_3$ thin films with thickness up to 3.5 μm from tartaric solution with 1.7 pH were obtained. It was confirmed that deposited thin films has cubic structure of indium(III) sulfide by means of XRD. The surface layer of $In_2S_3$ thin film up to 12 nm includes a small amount of oxygen and carbon

contained impurities. Nanosized nature of thin films and modification of their morphology depend on temperature were shown by means of SEM. So, the increasing of synthesis temperature in rang from 70 to 90 ºC lead to increasing of average crystal size from 70 to 150 nm. It was obtained optical band gap of indium(III) sulfide equal to 2.3 eV.

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