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Study of Chemical Bath Deposited In_2S_3 Thin Films

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Indum(III) sulfide (In_2S_3) thin films were grown by means of 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 shown that the surface of In_2S_3 thin film includes oxygen and carbon contained impurities. SEM confirmed nanosize nature of thin films. Optical band gap of indium(III) sulfide equal to 2.3 eV.

Keywords: Boundary conditions, Chemical bath deposition, Indium(III) sulfide, XPS.

INTRODUCTION

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

There are two methods *i.e.*, physical and chemical methods for deposition of indum(III) sulfide films. 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.

EXPERIMENTAL

Deposition of indium sulfide thin films was carrying out on preliminary defatting sitall substrates from reaction mixture containing indium nitrate (1 M), thioacetamide (CH_3CSNH_2), tartaric acid ($C_4O_6H_6$), hydroxylamine ($NH_2OH{\cdot}HCl$). The indium precursor in the solution gave indium-ions. The tartaric acid (1 M) was used for complexation of indium-ions which inhibited reaction of sulfide formation. Also, hydroxylamine (1 M) was used as additional stabilizing. A precursor of sulfide-ions was 1 M thioacetamide (TAA) that is unstable in a solution. 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 in which substrates fixed in specially made ftoroplaste device were placed. Reactors were located in thermostat LOIP LT-116 with the accuracy of maintenance of temperature ± 0.1°. Deposition time 120 min has been fixed for all thin films.

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. Shooting led at a room temperature in a scanning mode with step 0.03° and time of accumulation of a signal 20 s. Measurement of value of the lattice period and specification of structural parameters of thin films were led with FULLPROF program use.

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 MgK_α (1253.6 eV) as the non-monochromatized X-ray excitation source. The C1*s* line was calibration line with energy 284.5 eV.

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.

RESULTS AND 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 allowing to find boundary conditions of deposition of these compounds from water solutions.

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 thioacetamide decompose in acid solution according to equal:

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

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

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

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

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

As criterion of a solid phase metal sulfide formation taking into account the criteria of the necessary supersaturation (Δ) which provide nucleation of the critical size used the ratio:

$$SC_{Me_2S_n} \cdot \Delta = [Me^{n+}]_H^2 [S^{2+}]_H^n = IC_{Me_2S_n} \quad (5)$$

where SC = solubility creation corresponding to metal sulfide; IC = ionic creation, *i.e.* creation of free ions concentrations of metal [Me^{n+}] and sulfur-ions [S^{2-}].

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 in 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 found region of deposition indium sulfide has been used for choice a pH region and a concentration components into a reaction mixture. For example, the region pH less then 3 without formation of indium hydroxide for synthesis is optimal.

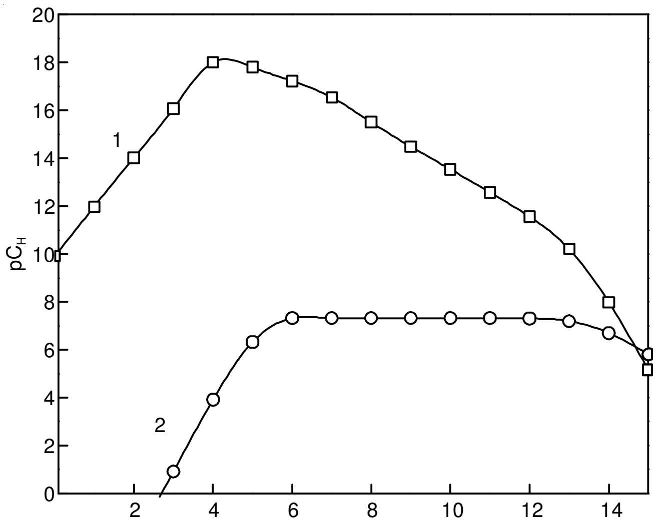

Fig. 1. Region of In_2S_3 solid phase deposition in system $In(NO_3)_3 - C_4O_6H_6 - NH_2OH \cdot HCl - CH_3CSNH_2$ (1), $In(OH)_3$ line (2). The calculation carried out at 80 °C

According to calculation it was deposited uniform orange films, which were observed on sital 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 sital at 80 °C (a film thickness 700 nm) indicate about this pattern [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 present and also the accurate crystal structure is not formed completely.

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 °C (Fig. 2a) shows that it has a fine-crystalline structure with an average crystal size to 70-120 nm. There are large aggregates on film surface that has a size to 800 nm. It is a good agreement with literature data 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. 2b,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 shows that films contain up to 10 at. % of oxygen by means of oxidation process. The ratio of basic elements is not changed.

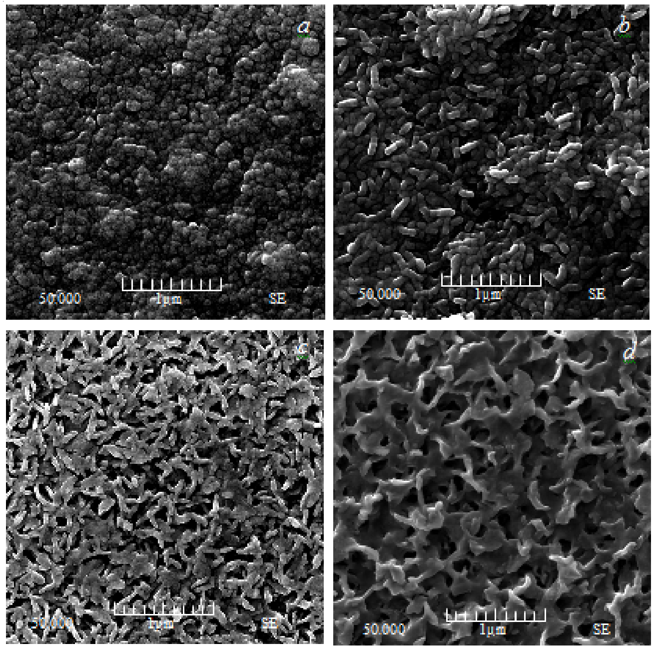

Fig. 2. SEM images of as-deposited (a, b, c) and heat treatment at 300 °C (d) In_2S_3 thin films prepared at, °C: 70 (a), 80 (b, d), 90 (c)

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, accordingly (Fig. 3a). It is observed 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 may be different carbonates and same other organic impurities. Opposite EDX-analysis shown absents of oxygen in thin films and confirmed formation of In_2S_3 with small excess of indium [13].

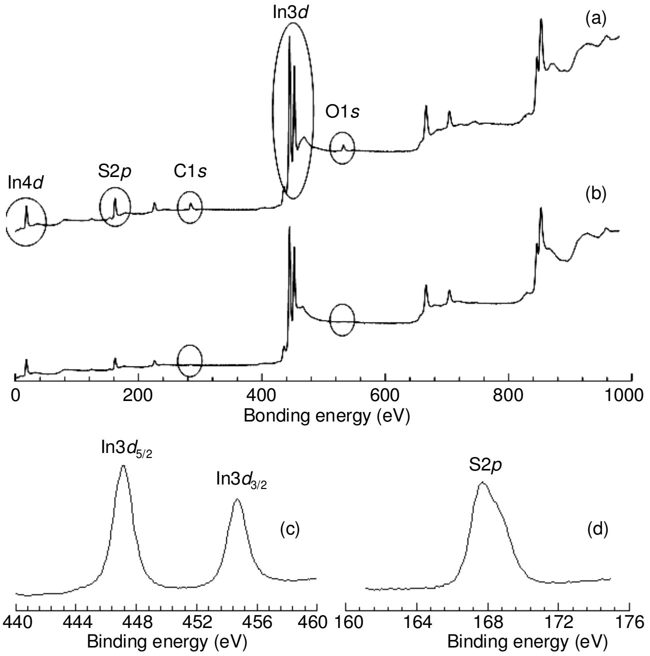

Fig. 3. Overview XPS spectra of the simples with shown In4*d*, S2*p*, C1*s*, In3*d* and O1*s* core level spectrum of In_2S_3 before (a) and after (b) etching on 12 nm into depth and XPS for In3*d* (c) and S2*p* core levels (d)

Fig. 3 shows the XPS of In3*d* and S2*p* core levels. As can be observed that all the peaks are accurate and well defined. The $In3d_{5/2}$ core shall with energy approximately 444.9 eV correspond to nonoxide form and it is corresponded to In_2S_3 (444.7 eV). Any width and asymmetry of the In3*d* peak are observed, which indicate purity of compound. S2*p* peak is accurate and good define. Its bonding energy (161.4 eV) interquartily 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 data for In_2S_3 (852.5 eV) and we refer this α-parameter to indium(III) sulfide.

The measured of the 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 at the same condition as that on sital. The material absorption factor (α) is related with energy of incident photons hν by following equation:

$$\alpha h\nu = A(h\nu - E_g)^n \qquad (6)$$

were A – factor depending on transmission properties and thickness d of thin film, E_g – optical band gap, n - factor equal to 0.5 for direct junction in case of In_2S_3.

The dependence of $(\alpha h\nu)^2$ on energy of incident photons (hν) show on Fig. 4. The E_g for as-prepared In_2S_3 thin film has been determined by extrapolating the linear portion of $(\alpha h\nu)^2$ *vs.* hν on absciss and has made 2.3 eV that have good agreement with literature data. The increasing of the E_g more than 2.03 eV for In_2S_3 volumetric material is explained by the smaller size of crystal (up to 70 nm at a film thickness 300 nm) and chemical composition of a film. The oxygen on film surface present according to EDX and XPS analyses that indicate on a thin oxidation layer. It can increase E_g value shifting absorption edge in short-wave range of a spectrum.

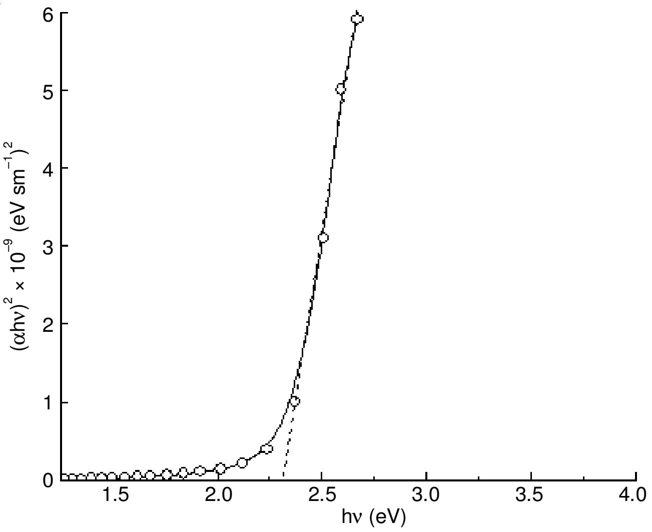

Fig. 4. Plot of $(\alpha h\nu)^2$ *versus* hν of thin film deposited at 80 °C by chemical bath deposition

Conclusion

The theoretical study of ion balance in $InCl_3 – C_4O_6H_6 – NH_2OH{\cdot}HCl – CH_3CSNH_2$ system confirmed that deposition of In_2S_3 is accompanied 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 acid 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. Nanosize nature of thin films and modification of their morphology depend on temperature were shown by means of SEM. So, the increasing of synthesis temperature ranging from 70 to 90 °C 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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