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Study of copper diffusion under solvothermal conditions in In_2S_3 layers synthesized by spray pyrolysis

R. BANICA[a,b], D. URSU[a,b], T. NYARI[a,b], P. SVERA[b], N. VASZILCSIN[a]
[a]*University Politehnica Timisoara, 2 Piata Victoriei, 300006 Timisoara, Romania*
[b]*National Institute for Research and Development in Electrochemistry and Condensed Matter,*
144 Dr. A. Paunescu Podeanu Street, 300569, Timisoara, Romania

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$CuInS_2$ is a good material for solar cells production with thin layer of absorbent due to its high light absorption coefficient and a band gap value close to 1.5 eV. Uncontrolled heating of CIS/In_2S_3 - type junction destroys the solar cell due to a diffusion of copper from the absorber layer. In this paper the influence of solvothermal reaction conditions such as solvent type, time and Cu^+ concentration on copper diffusion in thin layers of In_2S_3 is presented. In a first step, In_2S_3 thin films were grown on glass at substrate temperatures of 320ºC and 380ºC using the ultrasonic spray pyrolysis method. The obtained layers were characterized by X-ray diffraction, scanning electron microscopy, scanning probe microscopy, absorption spectrometry and energy-dispersive X-ray spectroscopy. After that, In_2S_3 layers were subjected to the action of Cu^+ ions at high temperature and pressure in an inert environment. The diffusion process can be controlled under solvothermal conditions. The reaction time and concentration of copper ions in solution have a strong influence on the optical properties of obtained layers. This method can lead to the production of solar cells based on p-$CuInS_2$/n-In_2S_3 - type heterojunction.

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Keywords: In_2S_3, Thin film, Solar cells, $CuInS_2$

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1. Introduction

An important challenge for the scientific community is the manufacture of thin film solar cells using absorber materials with low toxicity and cheap techniques for deposition of thin films. Indium sulfide (In_2S_3) was used as absorber [1] and as buffer layer in the construction of solar cells [2-4]. $CuIn_{1-x}Ga_xS_{2-y}Se_y$ (CIGS) type absorbers are also used on an industrial scale in the construction of solar cells [5-7]. If compounds of CIGS type are deposited over In_2S_3 layer, copper diffusion into the In_2S_3 layer leads to destruction of n-In_2S_3/CIGS junction. The ternary compound semiconductor $CuInS_2$ (CIS) with a chalcopyrite structure is a perspective material for the manufacture of this type of solar cells due to the band gap value, E_g, of about 1.5 eV [8, 9] at room temperature and high absorption coefficient of light (~10^5 cm^{-1}).

The most common synthesis method of $CuInS_2$ and CIGS thin films is the sulfidation of Cu-In alloy with sulfur vapor or H_2S [10-13]. Other methods reported in literature are Atomic Layer Deposition (ALD) [14] or Chemical Bath Deposition (CBD) [15, 16], followed by annealing of resulted sulfides.

All these deposition methods are carried out at elevated temperatures at which copper diffusion in the In_2S_3 layer would result in destruction of the solar cell. The spray pyrolysis (SP) deposition of absorbent layers [17, 18] is a method by which solar cells with large surfaces can be obtained at low costs. In general, the solar cells obtained by the spray pyrolysis method have efficiencies lower than 10% [19, 20]. The grain size of $CuInS_2$ in thin films increases with the increasing of Cu:In ratio and deposition temperature [12, 21]. At high deposition temperatures, required for a well crystallized absorbent, copper diffuses into the window layer if a top-down construction of the solar cell is adopted. Diffusion of copper in chalcogenides type ZnS, CdS or In_2S_3 occurs at high speed. Thus, a solar cell of the type ZnO/In_2S_3/CuSCN degrades if it is heated over 2 minutes at 200ºC due to a diffusion of Cu^+ from the p-CuSCN in the n-In_2S_3 layer [22, 23].

Heating CIGS/In_2S_3 interface at 300ºC leads as well to Cu depletion on the CIGS layer with the formation of $CuIn_5S_8$ phase and solar cell degradation [24]. Diffusion of Cu^+ ion in the In_2S_3 lattice leads to the decrease of electronic conductivity, but does not change the type of conductivity [25]. Also, anions of copper and indium salts and thiourea decomposition products, which remain in the absorbent layer, enhance recombination processes.

The obtaining of well crystallized $CuInS_2$ grains without impurities can significantly improve the efficiency of solar cells.

Solvothermal growth of $CuInS_2$ layer on the surface of chalcogenide window layer is a new method that can lead to the formation, at low temperature, of a well crystallized absorbent layer having low concentrations of impurities. The driving force of the process of replacing indium ions with copper ions in the crystal lattice of In_2S_3 is based on lower solubility of copper sulfides relative to indium sulfides.

In this context, in the present paper the influence of substrate temperature on the physico-chemical characteristics of In_2S_3 window layers deposited by ultrasonic spray pyrolysis (USP) technique using as solvent water-ethanol mixture was studied. After the deposition and physico-chemical characterization of In_2S_3 layers, the diffusion of copper ions in the chalcogenide layer during solvothermal treatments was evaluated, for the first time.

Solvothermal treatments of In_2S_3 layers were conducted in mixtures of ethylene glycol (EG) and water containing copper (I) ions, in an inert environment and controlled pressure.

2. Experimental

2.1. Synthesis of In_2S_3 thin films by spray pyrolysis

2.1.1 Preparation of the spraying solution

A solution of $5 \cdot 10^{-3}$ M In^{3+} and $3 \cdot 10^{-2}$ M thiourea (Tu) was prepared by dissolving $InCl_3 \cdot 4H_2O$, 97% (Sigma Aldrich) and thiourea, 99% (Sigma Aldrich) in 5 ml bidistilled water. The two solutions were mixed quantitatively and a clear and colorless solution resulted. After this, 2.0 mL ethanol and distilled water up to 20 mL were added to the solution.

2.1.2 Preparation of substrates

Glass slides having the dimensions 76.2 x 25.4 x 1 mm were washed by repeated sonication for 30 minutes each in ethanol and acetone, respectively.

After this, the substrates were dried with dry nitrogen purity 4.6 (Linde-Gas, Romania) and were placed on an aluminum block. Aluminum block with substrates on it was heated to work temperature with a heating system equipped with temperature proportional-integral-derivative controller. After reaching the operating temperature, the substrates temperature was maintained constant for 30 minutes before spraying.

2.1.3 Spraying of the solution

4.0 mL of solution was sprayed on a surface of about 200 cm^2 using a liquid flow rate of 0.4 mL/min, provided with a syringe pump and an ultrasonic nebulizer. Spraying was performed using Exacta Coat (Sono-Tek Corporation) spray pyrolysis equipment. Nitrogen (4.6 purity) was used as droplets carrier. After spraying, aluminum block temperature was decreased with an average speed of 5°C/min down to a temperature of about 190°C for sample S1 and 220°C for sample S2 respectively, then at slower speeds to room temperature. The concentration of oxygen in the spray chamber was measured continuously during spraying by means of an oxygen sensor, and maintained at a value of 20 ± 1% (vol.).

2.2. Solvothermal treatment of In_2S_3 layers

In_2S_3 films on glass were cut to a size of 10 x 20 mm and were placed in Pyrex glass vials with a diameter of 25 mm covered with a PTFE cap. Subsequently, solutions of CuCl, NH_3 and water dissolved in EG were prepared, as presented in Table 1. 10 mL of these solutions was added over each In_2S_3/glass substrate which were then subjected to heat treatment at 180°C. The vials were immersed in the Synthwave (Milestone) reactor chamber in 300 mL $3.0 \cdot 10^{-2}$ M H_2SO_4 aqueous solution in order to absorb microwaves.

The reactor was pressurized twice to a pressure of 25 bar with nitrogen (5.0 purity, Linde Gas Romania), with intermediate depressurization to 100 kPa pressure in order to reduce the concentration of oxygen in the gas phase to less than 0.04% vol. The reactor was heated at a rate of 10°C/min up at a temperature of 180°C, maintained at this temperature for the necessary time (see Table 1) and then cooled at a rate of 5°C/min to room temperature. The substrates were washed with distilled water and ethanol and dried with dry nitrogen (4.6 purity).

Table 1

Sample	SP deposition temperature	CuCl concentration	NH_3 concentration	Solvent	Reaction time at 180°C. (minutes)
S1	320 - 310	-	-	-	-
S2	380 - 370	-	-	-	-
S3	380 - 370	$3.0 \cdot 10^{-3}$ M	0.74 M	96% (vol.) EG – 4 % H_2O	5
S4	380 - 370	$3.0 \cdot 10^{-3}$ M	0.74 M	96% (vol.) EG – 4 % H_2O	60
S5	380 - 370	$1.5 \cdot 10^{-2}$ M	0.74 M	96% (vol.) EG – 4 % H_2O	60
S6	380 - 370	$3.0 \cdot 10^{-3}$ M	0.74 M	75% (vol.) EG – 25% H_2O	60

2.3. Characterization

X-ray diffraction (XRD) measurements were performed using an X'Pert PRO MPD diffractometer, CuKα radiation (λ = 1.5406 Å). The CuKβ radiation was filtered off using a Ni filter.

Crystallite size was calculated using the Scherrer formula.

For the Scherrer constant a value of 0.94 was considered. Surface morphology of deposited films was studied by scanning electron microscopy (SEM) using Inspect S - FEI microscope and by scanning probe microscopy (SPM) using a MultiView 2000 ™ - Nanonics Imaging equipment.

Optical properties were determined by ultraviolet-visible (UV-Vis) transmittance spectroscopy with a Lambda 950 - PerkinElmer instrument. Compositional homogeneity of the films and elemental analysis was determined by energy dispersive X-ray analysis (EDS).

3. Results and discussion

3.1. Synthesis of In_2S_3 thin films

XRD profiles of thin films grown on glass indicate the presence of cubic In_2S_3 pure phase (PDF-03-065-0459) with a preferential growth of crystallites in the (400) direction (Figure 1) for both substrate temperatures (320ºC and 380ºC).

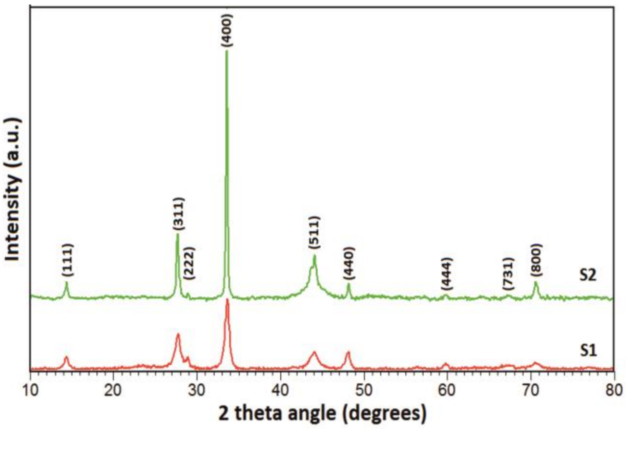

Fig. 1 XRD spectra of In_2S_3 thin films obtained at substrate temperatures of 320ºC (S1) and 380ºC (S2).

To express quantitatively the orientation of In_2S_3 layer growth on the glass support, the texture coefficient *TC*(*hkl*) was calculated, according to the relation (1) [26]:

$$TC(hkl) = \left(\frac{I_{(hkl)} / I_{r(hkl)}}{[(1/n)\sum I_{(hkl)} / I_{r(hkl)}]} \right) \tag{1}$$

where $I_{(hkl)}$ is the intensity of maxima obtained for the sample in question, $I_{r(hkl)}$ is the intensity of the peaks in the reference spectrum (JCPDS) and *n* is the number of diffraction peaks considered.

Large values of TC indicate a preferred orientation of growth relative to the crystallographic plane for which this parameter is calculated. For the calculation, the most important five diffraction peaks were considered, according to PDF-03-065-0459, cubic In_2S_3, space group Fd-3m.

The texture coefficient for In_2S_3/glass films increases from 2.7 to 3.5 with increasing substrate temperature from 320ºC to 380ºC. Average crystallite size was calculated from the full width at half maximum (FWHM) of the (400) XRD peak. Crystallite size increases with increasing substrate temperature, from 16.9 nm for sample S1 to 98.4 nm for sample S2. The transparency of the window layer is of great importance in the construction of solar cells because it is necessary that the lowest possible part of incident light to be lost through reflection and scattering processes. Therefore, the irradiance at the absorber level has to be maximum. In_2S_3 films transparency at wavelengths greater than 550 nm increases with the increasing of the substrate temperature, from lower values of 75% (absorbance values above 0.128 in the absorption spectrum) (Figure 2) for films deposited at 320ºC, up to values of over 80% for the films deposited at the 380ºC.

Basically, the lower amount of light transmitted by the layers deposited at low temperature is assigned not as much to an absorption process as to the radiation scattering process.

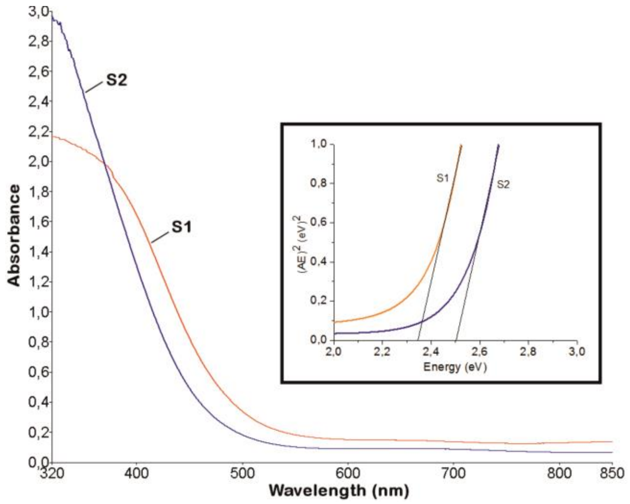

Fig. 2. UV-Vis absorption spectra of In_2S_3 films obtained at substrate temperature of 320ºC (S1) and 380ºC (S2). Inset: determination of band gap (E_g) values for In_2S_3 films grown at the two temperatures.

This interpretation is also supported by SEM image (Fig. 3a), which highlights the growth of In_2S_3 layer presenting a series of swellings.

These are probably due to the slow decomposition of the precursors at about 320ºC with the formation of a viscous film. Precursor decomposition takes place with the release of large amounts of gases.

If the time between two successive passages of the spraying head over the same area (that is of the order of several seconds) is not enough for complete decomposition of the precursors, reaction gases resulting from the pyrolysis of the $[In(Tu)_3]Cl_3$ complex accumulate between the glass substrate and the viscous film of incompletely reacted precursors, leading to bulging and cracking of In_2S_3 layers.

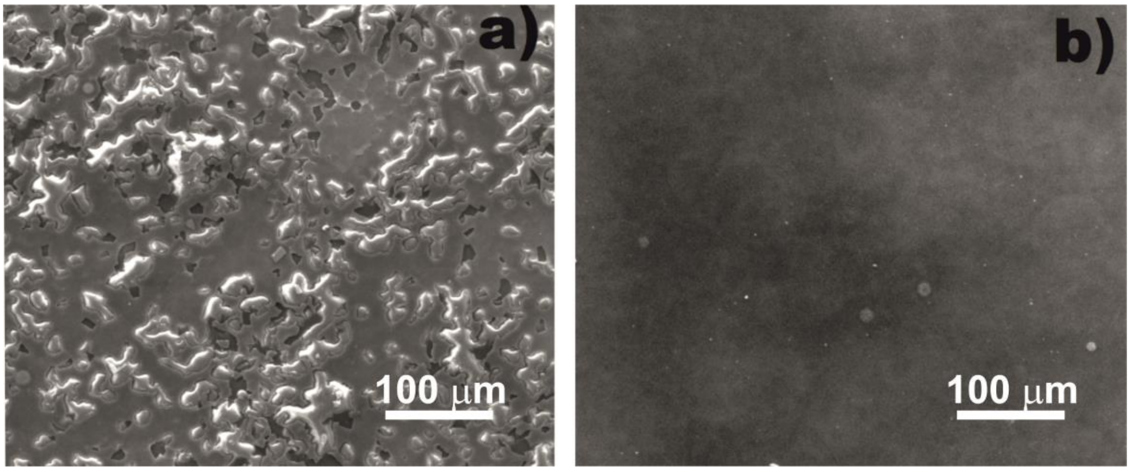

Fig. 3 SEM images of In_2S_3 films deposited on glass support at substrate temperatures of 320ºC (a) and 380ºC (b).

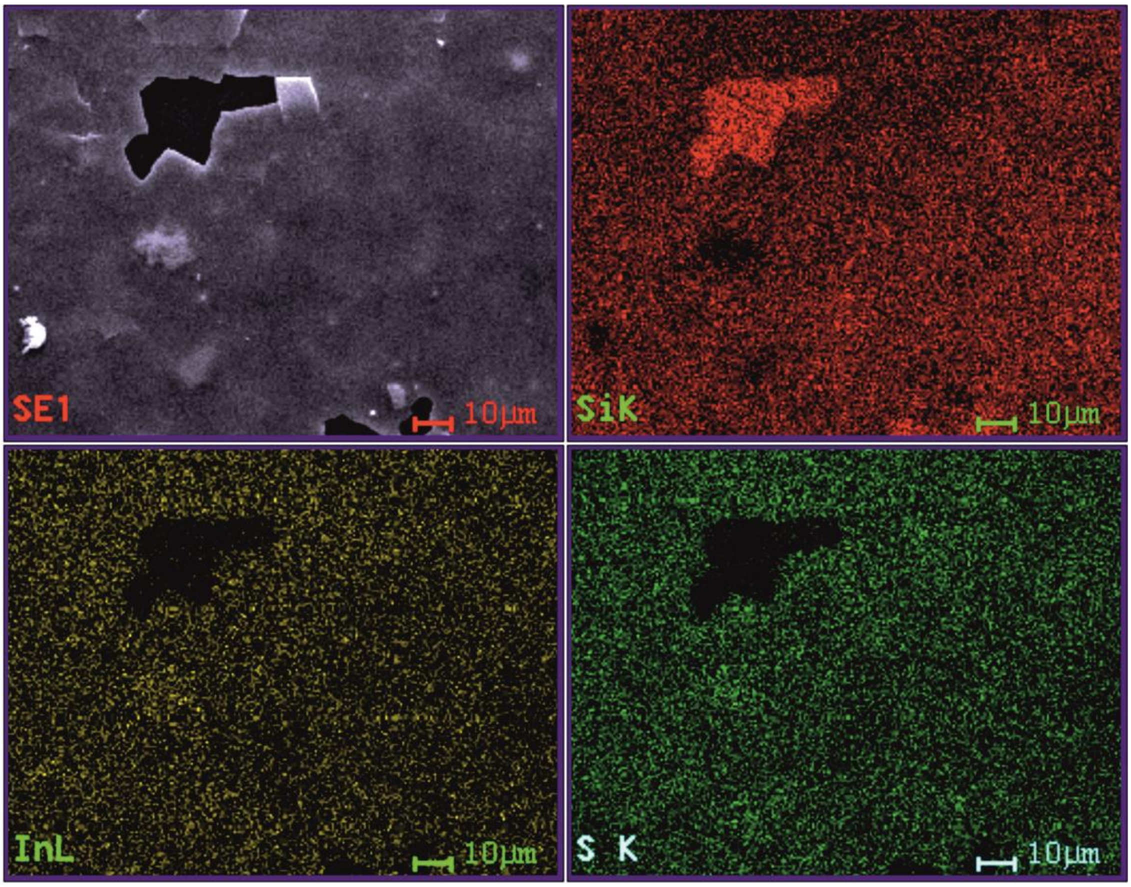

Fig. 4 EDX map for sample S1.

Also, adhesion of successively deposited In_2S_3 layers is lower for lower pyrolysis temperatures, leading to the appearance of numerous cracks in the obtained film - Figure 3a. To see if poor adhesion of In_2S_3 films to the glass substrate is the main reason for which bulging and cracking occur for layers deposited at 320ºC, a surface compositional mapping was carried out using characteristic X-ray emissions of silicon and indium for sample S1 (Fig. 4). Characteristic X-ray emissions of indium and sulfur are absent in areas with peeling of the coating. Also, the characteristic emission of silicon present in glass is much stronger in these areas. Thus, on the exfoliated areas, it cannot be emphasized the presence of an In_2S_3 layer, these areas representing penetrations of chalcogenide layer.

In conclusion, poor adhesion between the glass substrate and In_2S_3 layers deposited at low temperature is the cause of penetrations occurrence.

If the precursor decomposition occurs at high speed, dense In_2S_3 layers are obtained, as shown in Fig. 3b for the layers deposited at 380ºC. The thickness of the In_2S_3 layers deposited at 380ºC (sample S2) was determined from sectional SEM images (Figure 5a and 5d) as being of about 300 nm. The compositional map (Figure 5b and 5c) certifies the presence of sulfur in the measured layer.

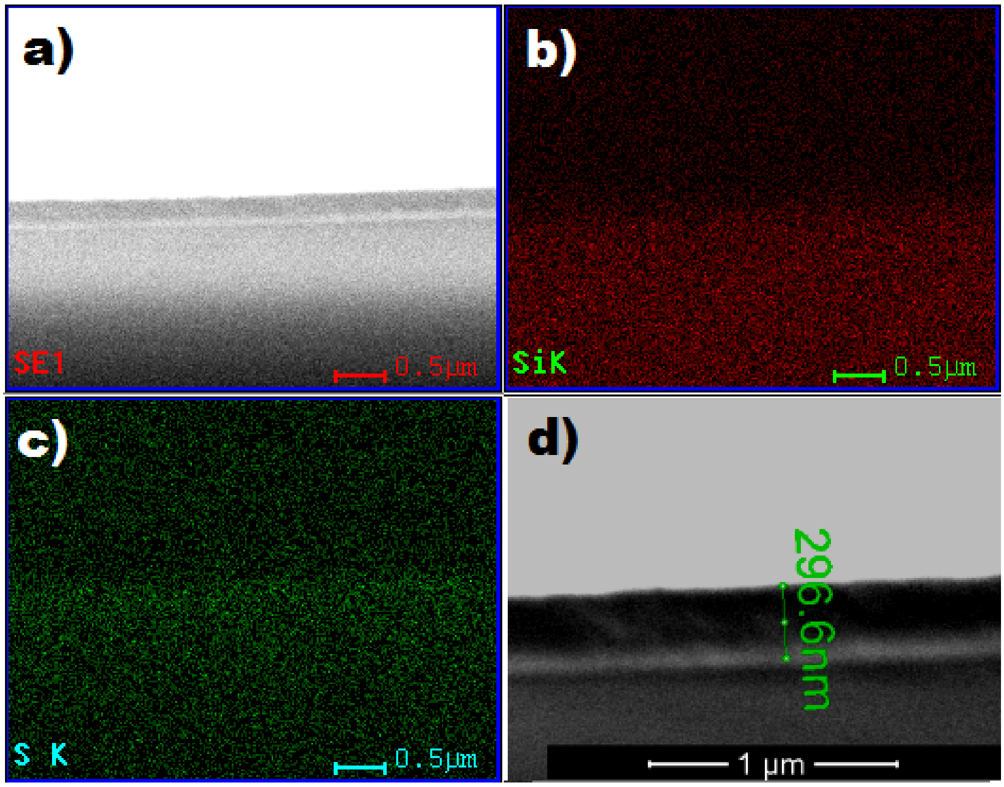

Fig. 5 Sectional SEM images of In_2S_3 layer, sample S2: secondary electron image (a), the characteristic X-ray maps of silicon (b) and sulfur (c), and high magnification SEM image (d).

At substrate temperatures below 400ºC, the inclusion of oxygen in the lattice of In_2S_3 occurs during pyrolysis of precursors. According to K. Otto and all, heating in air up to a temperature of 450ºC of In_2S_3 films deposited by SP at 230ºC does not lead to a significant oxidation of chalcogenide layers. However, pyrolysis of indium complex with thiourea on the glass surface heated to 410ºC leads to the formation of a mixture of In_2O_3 and β-In_2S_3 [27]. According to XRD spectra, In_2S_3 layers deposited by us at a support temperature of 380ºC (sample S2) do not contain indium oxide. On the one hand, this may be due to lower temperature of the substrate and, on the other hand, to the S/In ratio of 6/1, which may decisively influence the oxygen content of the layers deposited at high temperatures [27]. The oxygen content in the In_2S_3 layers obtained by spray pyrolysis increases with increasing substrate temperature, for the same S/In molar ratio in the precursor solution [27].

The optical band gap value (E_g) of In_2S_3 host layer (sample S2) was determined from the absorbance spectra. Determination of E_g for the case of direct electronic transitions can be done with the relationship (2) [28]:

$$\alpha E = C(E - E_g)^{1/2} \tag{2}$$

where: E – photon energy (eV), α – absorption coefficient of the material (cm^{-1}), C – constant, E_g – band gap width (eV).

Representing $(\alpha E)^2$ as a function of $h\nu$, E_g value can be determined for $(\alpha E)^2 = 0$. The absorption coefficient of the semiconductor can be determined using the relationship (3) [29]:

$$\alpha = \frac{\ln(1/T)}{g} \tag{3}$$

where: α – absorption coefficient of the film (cm^{-1}), g - film thickness (cm), T - transmittance.

If absorbent layer thickness is not constant, instead of absorption coefficient α, the absorbance value can be used. For dense nanocrystalline thin films in which radiation scattering is not significant, the change of absorbance per wavelength is determined by the variation of absorption coefficient α.

The increasing of substrate temperature and, by default, of the oxygen content in the chalcogenide layer, leads to an increase of the E_g value from 2.35 eV to about 2.5 eV, as shown in Figure 2 - inset.

To evaluate the roughness of the In_2S_3 film deposited at 380^{0}C, it was subjected to AFM investigation.

As shown in Figure 6 (a and b), In_2S_3 layers grown on glass are relatively smooth, with a particle size of about 200 nm, with level differences between minimum and maximum of the order of a few tens of nanometers and average surface roughness of 9.95 nm.

Under these conditions, the deposited film does not strongly scatter light, these results being consistent with the high values of transmittance at energies lower than E_g (Fig. 9, sample S2).

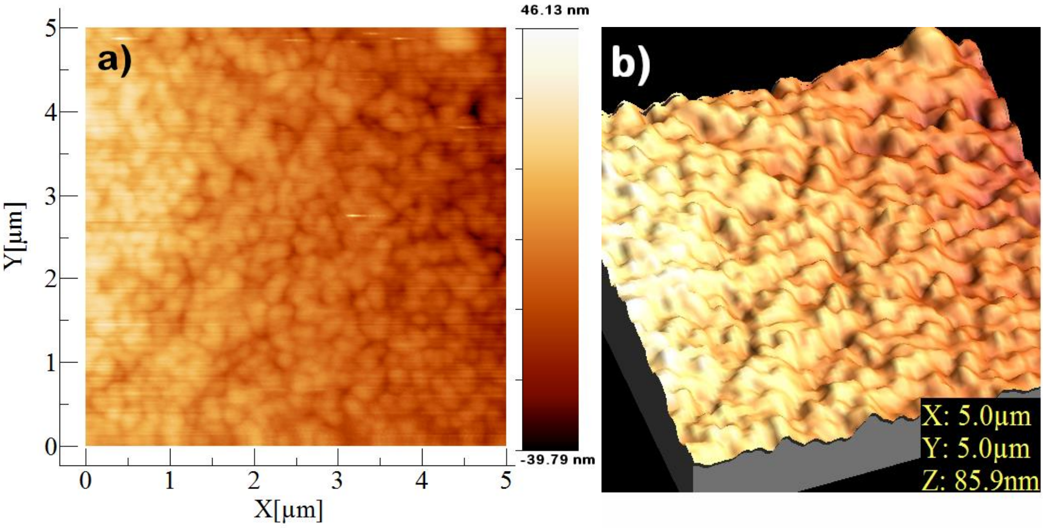

Fig. 6. 2D (a) and 3D (b) AFM images of In_2S_3 films deposited on glass at substrate temperature 380 ^{0}C.

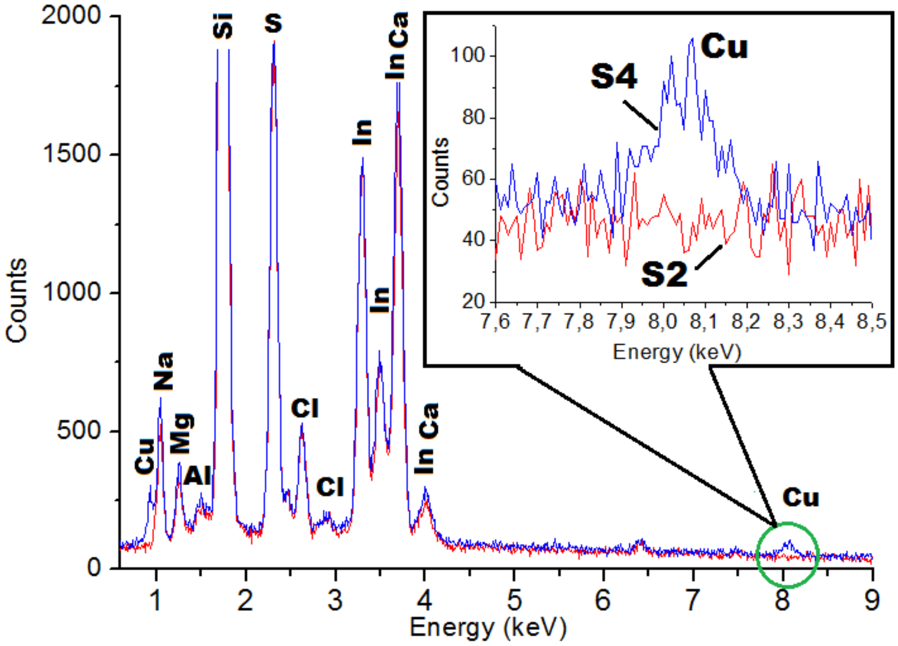

Fig. 7 EDS spectrum for In_2S_3 layer before hydrothermal treatment (red line) and after the solvothermal treatment (blue line) in 3 • 10-3 M CuCl solution for 60 minutes at 180ºC.

3.2. Solvothermal treatment of In_2S_3 films

Solvothermal treatment of the In_2S_3 layers deposited by spray pyrolysis in solutions containing Cu^+ ions can lead to obtaining of copper doped In_2S_3 layers, as it will be presented below. SEM images for samples S3-S6 (not presented here) do not highlight the appearance of cracks or peeling of In_2S_3 layer after solvothermal treatment, the morphology of the doped layers being very similar to those of pure In_2S_3. Thus, by the solvothermal treatment of In_2S_3 films in the presence of copper ions, dense films of In_2S_3:Cu can be obtained. EDS analysis of layers subjected to solvothermal treatment highlights increasing copper content of In_2S_3 layer, from 1.85% at. to 2.66% at. with increasing the reaction time from 5 to 60 minutes at a temperature of 180ºC (Fig. 7). Also, after solvothermal treatment, for sample S4 the In:S atomic ratio decreases with about 2.3%, which proves a displacement of In^{3+} ions with Cu^+ ions. Chlorine content in the layer decreases by less than 5% in all samples subjected to solvothermal treatment.

So, most chlorine is found in the deposited layer and only in a lesser extent, in a soluble form, on the layer surface. The largest decrease of indium and chlorine content after the solvothermal treatment is 3.9% and 4.4% respectively for the sample S6, which was treated in a solvent containing water. At the same time, the layer slightly enriched in sulfide and copper ions (1.86 at.%). EDS analyzes are consistent with transmission spectra that reveal a lower copper content for S3 and S6 samples and higher for samples S4 and S5.

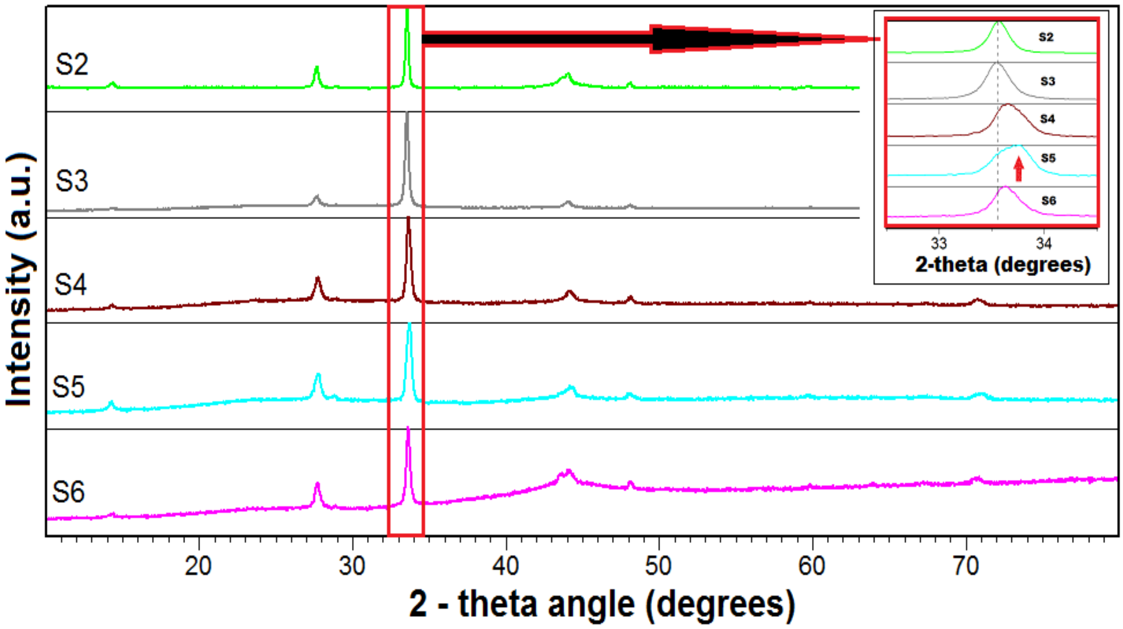

Fig. 8. XRD spectra for sample S2 and samples subjected to solvothermal treatment at 180 ℃ (S3-S6). Inset: magnified representation of (400) peak of cubic In_2S_3 for 2 theta between 32.5° - 34.5°.

Consequently, increasing polarity of the solvent by adding a small amount of water actually breaks bonds with pronounced ionic character, like In-Cl, allowing the formation of predominant covalent bonds, like Cu-S. The presence of chlorine in In_2S_3 layers obtained by ion layer gas reaction (ILGAR) method inhibit the copper diffusion by forming strong In-Cl bonds.

The In-Cl binding energy has a value of 436 kJ/mol and is greater than the binding energy of Cu-Cl (378 kJ/mol) or Cu-S (275 kJ/mol) [30]. For In_2S_3 layers obtained at high temperature, part of S^{2-} ions are replaced by O^{2-} ions, as suggested also by the increased value of E_g. Because the strength of In-O bond is higher than the In-S one, an inhibition of Cu^+ diffusion in In_2S_3 layers obtained by spray pyrolysis can occur through a similar mechanism.

Thus, the In_2S_3 layers grown at higher temperatures in the air can be more resistant to copper diffusion.

Also, larger In_2S_3 crystallites present in the layers grown at higher temperatures in air, lower density of structural defects and lower porosity of the deposited layer, all contribute to reducing the diffusion coefficient of copper. Also, chloride ions reduce the density of vacancies in In_2S_3 limiting diffusion of copper through the mechanism of vacancies.

XRD spectra for all the layers of In_2S_3/glass subjected to solvothermal treatment at 180°C highlight the displacement of the diffraction peaks due to the inclusion of copper in the lattice (Figure 8).

In the literature it is reported that the concentration of Cu^+ in In_2S_3 layers obtained by PVD (physical vapor deposition), due to diffusion from the CuSCN layer, increases from 0.01% at. to 1% at. with increasing temperature from 150°C to 175°C.

However, a layer of about 10 nm rich in copper was observed at the surface of In_2S_3 films regardless of the annealing temperature of the CuSCN/ In_2S_3 junction [30]. The appearance of a thin layer of heavily copper doped In_2S_3 was also observed by photoelectron spectroscopy [31] and HR-TEM [24, 32] studies for $CuIn_{1-x}Ga_xSe_2/In_2S_3$-type junctions heated to just 200°C.

Copper diffusion occurs due to the concentration gradient between the two surfaces of In_2S_3 layer: the first one is in contact with the electrolyte solution and the second one is in contact with the substrate surface. In the case of In_2S_3 films treated in solvothermal environment, a thin layer rich in copper can be formed at surface of In_2S_3 by the replacement reaction of In^{3+} ions with Cu^+ ions, according to the reaction:

$$In_2S_3 + 3xCu^+ \rightarrow In_{2-x}Cu_{3x}S_3 + xIn^{3+}$$

This layer rich in copper sulfide can become a barrier that limits In^{3+} ions transfer from In_2S_3 layer into solution. Thus, further diffusion of copper in In_2S_3 layer will be mostly through vacancy [33] and by insertion-substitution [34] mechanisms.

To determine whether the formation of an insoluble layer on the surface of In_2S_3 limits the diffusion of Cu^+, In_2S_3 layers were treated in solutions with different Cu^+ ions concentrations.

Increasing concentrations of Cu^+ in solution leads to right shift of the (400) peak, due to In_2S_3 lattice deformation, as suggested by x-ray diffraction spectra (Figure 8, samples S2 vs S4, S5).

The (400) peak asymmetry that appears for S4-S6 samples involves two overlapping diffraction peaks, one near $2\theta = 33.235^0$ (interplanar spacing of 2.6935 Å) corresponding to pure In_2S_3 phase, and the second shifted to higher values of 2θ corresponding to In_2S_3 layer doped with copper.

This is particularly evident for the sample S5 (peak indicated by the red arrow in Figure 8 - inset).

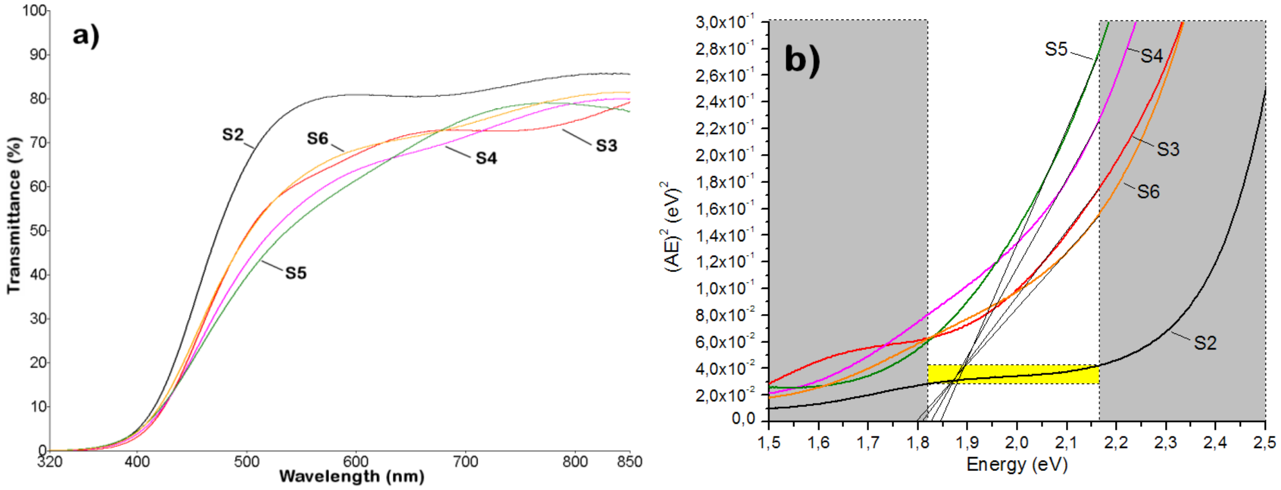

Fig. 9 UV-Vis transmission spectra for samples obtained by solvothermal treatment of the S2 sample (a), and band gap value estimation for samples S3-S6 (b).

Therefore, the concentration of Cu^+ is not uniform in In_2S_3 layer, there is a concentration gradient from the surface to the depth thereof.

No significant changes were observed in the crystal structure or displacement of the diffraction peaks with copper diffusion in polycrystalline In_2S_3 layers obtained by PVD or ILGAR for heating temperatures lower than 200ºC [30]. This is due to the existence of temperature barrier that limits the diffusion of copper in In_2S_3. This is of about 175ºC according to [30].

In the case of layers subjected to solvothermal treatment, the value of transmittance at a wavelength of 550 nm decreases with increasing the concentration of copper in solution, due to the increasing speed of displacement reaction of In^{3+} ions with Cu^+ ions, as shown in Figure 9, S4 vs S5. Increasing the layers solvothermal treatment duration at 180ºC from 5 to 60 minutes leads to the increase of copper content of the layer, as suggested by both the transmittance spectra (Figure 9, sample S3 vs S4) and EDS analysis.

For energy values greater than the E_g value of In_2S_3, the transmittance of layers subjected to solvothermal treatment is influenced both by light absorption of the host-layer In_2S_3 and by the absorption due to impurity levels. At energy levels lower than E_g of In_2S_3, the absorption of radiation is given mainly by the levels of impurities formed by diffusion of Cu^+ and by the band-to-band absorption of novel formed crystalline phases. As shown in Figure 9a, for wavelengths between 550 and 850 nm, transmittance value for sample S2 is relatively constant being influenced only by the presence of the interference fringes. Therefore, scattering radiation in this wavelength range is negligible. In addition, for energy values between 1.82 eV (681 nm) and 2.16 eV (574 nm) (the area marked with yellow rectangle in Fig. 9b), the transmittance value of the sample S2 does not vary by more than 2%. Therefore, in this area the absorption of radiation in the doped layers is due mainly to impurity levels formed by diffusion of Cu^+ in the In_2S_3 layer. E_g values determined for samples S3-S6 are lower than those obtained for undoped In_2S_3 layer, being between 1.79 and 1.85 eV. Decrease of E_g value of doped films is due to the fact that Cu3d states lead to the shift of the maximum of the valence band (VBM) to higher energies. This leads to displacement of E_g to lower values with the inclusion of Cu^+ in the In_2S_3 lattice [35].

4. Conclusions

In_2S_3 nanocrystalline layers having a thickness of about 300 nm and the transmittance of over 80% have been successfully deposited on glass by means of ultrasonic spray pyrolysis using $InCl_3$ as metal source and thiourea as sulfur source, at a substrate temperature of 380ºC. Surface morphology strongly depends on the substrate temperature. For a substrate temperature of 320ºC, slow decomposition of the indium complex leads to the formation of In_2S_3 layers showing swelling and reduced compactness. The increase of the deposition temperature leads to the obtaining of compact and transparent In_2S_3 layers having band gap value of about 2.5 eV. Solvothermal treatment of these layers at a temperature of 180^{0}C in basic solutions containing Cu^+ ions leads to the obtaining of In_2S_3 layers doped with copper. Copper content of the films increases with the solvothermal treatment duration. Morphology of the obtained doped films is similar to that of pure In_2S_3 layer but the band gap value shrinks with the inclusion of Cu^+ in the In_2S_3 lattice. Solvothermal treatment of In_2S_3 films in solutions containing copper ions can be an alternative manufacturing of $CuInS_2/In_2S_3$junctions for solar cells with thin film absorbents.

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[*] Corresponding authors: nicolae.vaszilcsin@upt.ro