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Tin Sulfide Films by Chemical Spray Pyrolysis: Formation and Properties

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Declaration:

Hereby I declare that this doctoral thesis, my original investigation and achievement, submitted for the doctoral degree at Tallinn University of Technology has not been submitted for doctoral or equivalent academic degree.

Svetlana Polivtseva

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Tinasulfiid kiled keemilise pihustuspürolüüsi meetodil: moodustumine ja omadused

SVETLANA POLIVTSEVA

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List of Publications

The list of author's publications, on the basis of which the thesis has been prepared:

- I **S. Polivtseva**, I. Oja Acik, M. Krunk, K. Tõnsuaadu, A. Mere. Thermoanalytical study of precursors for tin sulfide thin films deposited by chemical spray pyrolysis, J. Therm. Anal. Calorim. 121 (2015) 177–185.
- II **S. Polivtseva**, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunk. Spray pyrolysis deposition of Sn_xS_y thin films, Energy Procedia 60 (2014) 156–165.
- III **S. Polivtseva**, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunk. Tin sulfide films by spray pyrolysis technique using L-cysteine as a novel sulfur source, Phys. Status Solidi C 13 (2016) 18–23.
- IV **S. Polivtseva**, A. Katerski, E. Kärber, I. Oja Acik, A. Mere, V. Mikli, M. Krunk. Post-deposition thermal treatment of sprayed SnS films, Thin Solid Films 633 (2017) 179–184.

Copies of these articles are included in Appendix.

Author's Contribution to the Publications

Contribution to the papers in this thesis are:

- I** Synthesis of the precursors for thermal analysis; their characterisation by XRD and FTIR spectroscopy; participation in conduction of thermal analysis of dried precursors (TG/DTA/EGA–MS measurements); characterisation of solid intermediates and final products by XRD and FTIR spectroscopy; analysis of the obtained results; major role in writing.
- II** Deposition of SnS thin films by the chemical spray pyrolysis method (CSP); films characterisation by XRD and UV–Vis spectroscopy; analysis of the results; major role in writing.
- III** Synthesis of the precursors and their characterisation by XRD and FTIR spectroscopy; deposition of SnS thin films by the chemical spray pyrolysis method (CSP); films characterisation by XRD and UV–Vis spectroscopy; analysis of the results; major role in writing.
- IV** Deposition of SnS thin films by the chemical spray pyrolysis method (CSP); participation in conduction of post-deposition thermal treatments; films characterisation by XRD and Raman, FTIR and UV–Vis spectroscopy methods; analysis of the results; major role in writing.

Abbreviations

AA-CVD	Aerosol-Assisted Chemical Vapour Deposition
ALD	Atomic Layer Deposition
CBD	Chemical Bath Deposition
CSP	Chemical Spray Pyrolysis
RF	Radio-frequency sputtering
CVD	Chemical Vapor Deposition
DTA	Differential Thermal Analysis
DTG	Differential Thermogravimetry
EBE	Electron Beam Evaporation
ECD	Electrochemical Deposition
EDX	Energy Dispersive X-ray Spectroscopy
Eg	Optical bandgap
EGA	Evolved Gas Analysis
FTIR	Fourier Transform Infrared Spectroscopy
HVE	High Vacuum Evaporation
L-cys	L-cysteine
MS	Mass Spectroscopy
Ort	Orthorhombic
pH	Potential of hydrogen
PVD	Physical vapor deposition
RS	Rocksalt
SILAR	Successive Ionic Layer Adsorption and Reaction
SEM	Scanning Electron Microscopy
TA	Thermal Analysis
Tcc	Thiocarbonyl compound
TG	Thermogravimetry
Ts	Substrate temperature
Tu	Thiourea
TTU	Tallinn University of Technology
UV–Vis	Ultraviolet-Visible (Spectroscopy)
XRD	X-Ray diffraction
ZB	Zinc blende

Introduction

Developments in science and technology fundamentally alter the needs of modern society and modern life. Significant changes in the structure of human life have been mainly associated with the discovery and production of materials. In general, materials are milestones of civilization. Technologies that use novel materials make human life safer and more sustainable. The rapid growth of human population along with the electricity consumption and the continuous decrease of the classical energy sources (oil, gas etc.) have forced scientists to study and to develop alternative energy systems. Furthermore, recent large accidents including the Fukushima Daiichi nuclear disaster (2011) and the Deepwater Horizon drilling rig explosion (2010) have confirmed the necessity for the development of green technologies for energy, which will become crucial in this global society. The use of solar energy is just one of the new “green” initiatives presented to the community. As with any new solution for human life, there is always a compromise between the efficiency, safety, materials and production costs. The use of nontoxic, earth-abundant materials produced by simple and cost-effective methods can respond to some above mentioned issues.

Tin monosulfide (SnS) can be recommended as an alternative absorber instead of Cu(In,Ga)Se₂ or CdTe for multi-layered thin film solar cells. In general, SnS thin films can be fabricated using a variety of physical and chemical deposition techniques. However, the structure and structure-dependent properties as well as the purity of prepared films have been found to depend on the deposition method applied. The chemical spray pyrolysis (CSP) is a representative of fast atmospheric methods, which is suitable for large-area film deposition in industry. In the Laboratory of Thin Film Chemical Technologies at Tallinn University of Technology (TTÜ), CSP has been a major method to produce different layers such as TiO₂, ZnO, NiO, ZnS, CdS, In₂S₃, CuInS₂ and to implement them in a thin film or nanostructured solar cell.

In general, aqueous or alcoholic solutions containing tin(II) chloride (SnCl₂) and thiocarbonyl compounds, preferably thiourea (SC(NH₂)₂), have been used for growing SnS films by spray. Before this study was initiated, deposition of SnS films by CSP had been mainly performed not taking into account any possible interactions of precursors in the spray solution. Furthermore, a better understanding of the thermal behaviour of precursors produced in the CSP process allows researchers to choose the optimal deposition conditions and thereby to control properties of formed tin sulfide films.

This dissertation clarifies the complexation occurring in spray solutions containing tin(II) chloride and thiourea or L-cysteine. It contains studies on the formation chemistry of tin sulfide in the CSP process when SnCl₂ and SC(NH₂)₂ are used as starting precursors. The thesis research focuses on studying the effects of the molar ratios of precursors (SnCl₂ to SC(NH₂)₂ or L-HSCH₂(NH₂)CHCO₂H) in aqueous solutions and different deposition temperatures on the properties of sprayed SnS films. The effect of post-deposition annealing in flowing N₂ and dynamic vacuum on the properties of SnS films is studied.

This dissertation contains four Chapters. Chapter 1 includes a literature overview describing the main properties of tin (II) sulfide, fabrication methods for SnS films and the properties of sprayed SnS films. Chapter 2 describes experimental details: the synthesis and characterisation of the precursors for process chemistry studies incl. thermal analysis studies; deposition of SnS films by CSP and procedures of post-deposition thermal treatments of SnS films grown by CSP, and techniques applied to characterize the film physical properties. Chapter 3 focuses on obtained results and

discussion. The chapter is divided into two sections. The first section introduces the complexation of starting chemicals in spray solutions and the formation of complex compounds as precursors for SnS films [I, III], followed by the analysis of thermal analysis results of synthesised precursors, the results and detailed discussion of tin sulfide formation in the CSP process. The second section is dedicated to the influences of deposition temperature and the molar ratio of starting chemicals (SnCl_2 to $\text{SC}(\text{NH}_2)_2$) in aqueous solutions on the thin film physical properties [II]; the effect of post-deposition thermal treatments in flowing N_2 and dynamic vacuum on the properties of sprayed SnS films [IV]; and the effects of deposition temperature and the molar ratio of starting chemicals (SnCl_2 to $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$) in aqueous solutions on the thin film physical properties [III]. Chapter 4 summarises the results obtained in this thesis research.

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1 Literature review and aim of the study

1.1 Tin sulfide

Tin as a heavy element in group 14 of the Periodic Table exhibits two main oxidation states of +2 and +4. Tetravalent oxidation state with the $4d^{10}5s^05p^0$ electronic configuration is slightly more stable than divalent one, having an electronic configuration $4d^{10}5s^25p^0$. For this reason, both tin(II) and tin(IV) compounds are known to exist, including a variety of tin sulfide forms [1-3].

The Sn-S system contains three main thermodynamically stable phases, tin monosulfide (SnS), tin sesquisulfide Sn_2S_3 and tin disulfide (SnS_2), and their polymorphs (Fig. 1.1). In addition, there are two metastable phases of tin sulfide, Sn_3S_4 [4] and Sn_4S_5 [5, 6], which are postulated as intermediate products in the decomposition of SnS_2 [7] and not considered as a part of the equilibrium S–Sn phase diagram presented in Fig.1.1 [8].

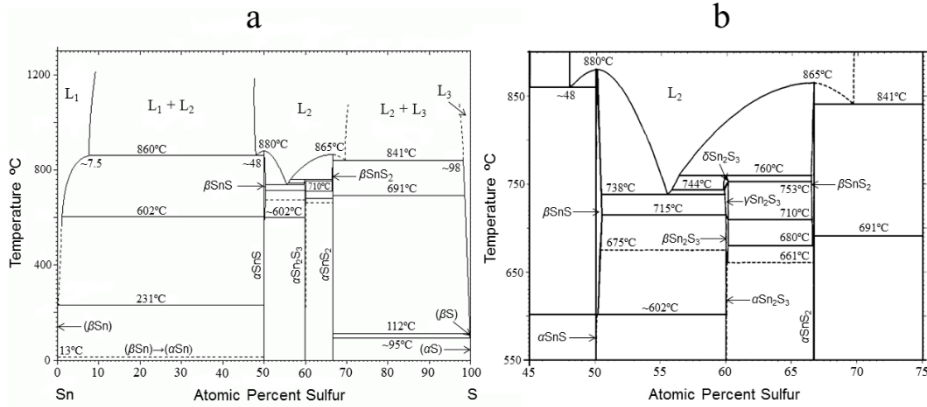


Fig. 1.1 Sn-S phase diagram: a) between 0 and 100 at. % S; b) between 45 and 75 at. % S, by Sharma and Chang [8].

SnS appears in several crystallographic forms. Orthorhombic α -SnS is the equilibrium structure in the Sn–S system. Depending on the experimental conditions, SnS can crystallise in the metastable cubic structure that has several polymorphs such as the rocksalt (RS) and the zinc blende (ZB) types. Table 1 summarises roughly the conditions of existence for crystallographic forms of SnS and ground-state crystal structures of Sn_2S_3 and SnS_2 and in the Sn–S system.

Most authors have agreed that orthorhombic α -SnS single crystal has a direct bandgap of ~ 1.3 eV, while orthorhombic β -SnS has a slightly higher bandgap value of 1.4 eV [2, 9, 10]. The optical transition of the cubic SnS material is questionable. The direct bandgap of 1.6–1.8 eV has been estimated for the films composed of the zinc blende SnS phase [11], whereas cubic SnS nanoparticles tend to show an indirect bandgap of 1.53 eV [12].

Single phase of orthorhombic SnS exhibits p-type behaviour based on the formation of tin vacancies according to the defect reaction [1, 5]:

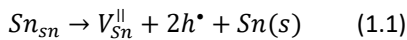
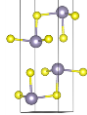
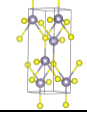
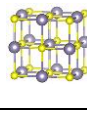
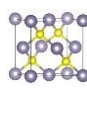
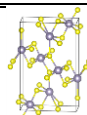
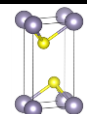


Table 1. Conditions of existence for crystallographic forms of SnS and ground-state crystal structures of Sn₂S₃ and SnS₂ in the Sn–S system.

Compound	Lattice parameters	Existence criteria	Crystal structure	Ref.
	Polymorph		Space group	
SnS	a= 11.254 Å b= 4.023 Å c=4.294 Å	Orthorhombic tin monosulfide comprises ~50 at.% of tin and occurs in several polymorphs, α and β . In the Sn–S system, α -SnS is thermodynamically stable at temperatures below 605 °C.		[1]
	α = orthorhombic		<i>Pnma</i>	
	a= 4.148 Å b= 11.480 Å c=4.177 Å	β -SnS exists at temperatures above 605 °C.		[1]
	β = orthorhombic		<i>Cmcm</i>	
	a=b=c= 6.000 Å (equilibrium)	SnS occurs as RS-SnS with a cubic (Fm-3m) space group under epitaxial growth on a freshly cleaved NaCl seed layer.		[1, 13]
	Cubic (rocksalt, RS)		<i>Fm-3m</i>	
	a=b=c= 5.445 Å (experimental)	ZB-SnS crystallises in a cubic (F-43m) space group with measured lattice parameters which are very similar to the equilibrium lattice parameters of RS-SnS. ZB-SnS may form in a highly strained medium and is stabilized by a high concentration of lattice defects.		[1, 14]
	Cubic (zinc blende, ZB)		<i>F-43m</i>	
α -Sn ₂ S ₃	a= 3.747 Å b= 8.864 Å c=14.020 Å	Sn ₂ S ₃ contains ~40 at.% of tin and appears in α -, β -, γ - and δ -Sn ₂ S ₃ modifications (Fig. 1). α -Sn ₂ S ₃ is stable below 661 °C.		[1]
	orthorhombic		<i>Pnma</i>	
α -SnS ₂	a=b= 3.645 Å c=5.891 Å	SnS ₂ contains ~33-34 at.% of tin and exists in α - and β -SnS ₂ forms (Fig. 1). α -SnS ₂ converts to β -SnS ₂ at temperatures above 691 °C.		[1]
	hexagonal		<i>P-3m1</i>	

According to some authors, zinc blende SnS material exhibits p-type conductivity [11, 15], while other investigators demonstrated the ambipolar conductivity [16, 17], as probably both tin and sulfur vacancies have been presented. Thus, a contradiction exists in the literature data concerning the conductivity type of the cubic SnS materials.

For the α -Sn₂S₃ phase, there is no agreement in the literature concerning the transition type, direct or indirect. Several authors reported the direct optical bandgap of 0.85–1.16 eV for α -Sn₂S₃ [18-20], while other research groups vindicated an indirect bandgap for α -Sn₂S₃ in the range of 1.09–2.20 eV [2, 21]. Sn₂S₃ as a compound composed of Sn(IV) and Sn(II) cations may display mixed-type conductivity, appearing from Sn and

S vacancies, which are both possible [2]. Still, most of the studies have reported the n-type conductivity for the Sn_2S_3 materials [2, 22, 23].

$\alpha\text{-SnS}_2$ single crystal has been shown to exhibit an indirect bandgap of ~ 2.3 eV, as reported in [2, 24-27] and n-type conductivity, coming from the favourable sulfur vacancies [2].

In summary, tin sulfides, particularly SnS, can appear in a variety of crystallographic forms depending on the synthesis protocols. The crystallographic forms determine the optical and conductivity properties of tin sulfides.

1.2 Deposition methods for tin sulfide films

Various physical and chemical techniques have been used for the deposition of SnS films.

1.2.1 Physical deposition methods and film properties

The physical techniques, which are mainly represented by radio-frequency (RF) sputtering [28, 34], physical vapor deposition (PVD) [35], electron beam evaporation (EBE) [36], and high vacuum evaporation (HVE) [37-39], can be used for the fabrication of SnS thin films. A stoichiometric SnS powder is used as a source material for film deposition.

Structure and structure-dependent properties of SnS films as well as the purity of films and chemical composition have been found to depend on the deposition method used [11, 15, 16, 40]. Controlled atmosphere methods such as RF sputtering and HVE yield films composed of the orthorhombic SnS (ort-SnS) phase [28, 35, 41]. Often, due to possible oxidation state of tin (+2 and +4), other tin sulfide phases like Sn_2S_3 and SnS_2 have been presented in the SnS films deposited by HVE and EBE at substrate temperatures below 300 °C [33, 36-38, 42]. For this reason, relatively high process temperatures have been used in these deposition methods to prevent the formation of higher tin sulfide phases [35-38].

Despite significant SnS research pool, the transition type of SnS films, be it direct or indirect, is still questionable [2, 28, 34, 36]. According to the most published studies, ort-SnS films have direct transition and optical bandgap values lying in the region of 1.3–2.0 eV [28, 35, 34, 38, 42]. The optical direct bandgap values of HVE-deposited ort-SnS films have been found to be between 1.3 eV and 1.9 eV depending on film thicknesses and deposition temperatures, as the stoichiometry of films varied with both these parameters [39, 42-44]. Hartman et al. [28] reported an indirect bandgap in the range of 1.08–1.2 eV for the ort-SnS films deposited using RF sputtering. Banai et al. [34] advocated both direct and indirect transitions for ort-SnS films grown by RF sputtering, and reported the indirect bandgap of 1.2 eV for films grown at 60-mtorr total pressure and target power of 105 W. For the EBE-prepared ort-SnS films, Tanusevski et al. [36] determined bandgap values of 1.2 eV and 1.4 eV for the indirect and direct transitions, respectively. Despite some uncertainty in the transition type of SnS films, all researchers agree that an efficient optical absorption lies in the range of 1.4–1.8 eV.

The resistivity value of $9.7 \times 10^4 \Omega \text{ cm}$ has been reported for slightly tin rich SnS film (Sn/S ratio of 1.10) grown by RF sputtering [28].

1.2.2 Chemical deposition methods and film properties

The wide group of chemical methods represented by chemical bath deposition (CBD) [11], successive ionic layer adsorption and reaction (SILAR) [45], aerosol-assisted chemical vapour deposition (AA-CVD) [16], electrochemical deposition (ECD) [46], atomic

layer deposition (ALD) [32, 40, 47], chemical vapor deposition (CVD) [41], spin coating [48], and chemical spray pyrolysis (CSP) [17, 49-51], operate with processes driven by different chemical reactions for SnS film formation.

The orthorhombic SnS (ort-SnS) films have been grown using the ALD method with well-controlled atmosphere [41]. The zinc blende SnS films can be produced by solution-based methods such as SILAR or CBD [11, 45] at deposition temperatures around ~20–30 °C, and by the physicochemical AA-CVD method at 300 °C [16].

The bandgap values of chemically-grown films depend mainly on the crystal structure of SnS, orthorhombic (ort-SnS) or cubic (ZB-SnS) [2, 11], and deposition temperature. For ort-SnS films deposited by ALD at temperatures around 180 °C, direct bandgap values vary in the range of 1.3–1.9 eV, as the film composition may change depending on the precursor used and film thicknesses [41, 47]. The direct bandgap values in the region of 1.6–1.9 eV have been reported for the CBD [11] or SILAR [45] grown films composed of ZB-SnS, while indirect optical bandgap of 1.1 eV has been determined for the CBD-prepared films consisting of ort-SnS [52].

The use of chemical methods such as AA-CVD [16], CSP [10, 49], SILAR [45], and electrodeposition [46] yielded SnS films contaminated by impurities such as oxygen, chlorine and carbon in detectable concentrations of around 10 at.%. The deposition temperature and precursors have been found to control phase composition of formed films, type and amount of impurities in the films as tin oxide(s) and hydroxide(s) or higher tin sulfides can form during deposition processes [16, 45, 49]. It is known that impurities may introduce a perturbation into the host band structure of semiconductors [53]. Oxygen contamination may lead to larger than expected bandgap values [54].

It is known that conductivity type of SnS films can be changed from p-type to n-type by the variation of Sn/S ratios [51].

It can be concluded that SnS films have promising physical properties for different applications. The crystallographic modification and structure-dependent properties of SnS films are controlled by the deposition method and the experimental parameters applied.

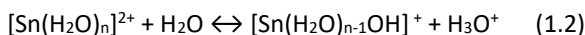
1.2.3 Choice of precursors for tin sulfide film deposition by chemical methods

As stated above, tin has four electrons in its valences-orbital, resulting in multiple oxidation states of 0, +2 and +4. Thus, the choice of Sn precursor is of prime importance in order to obtain tin monosulfide films using chemical deposition methods. As tin needs to keep its less stable oxidation state during SnS film formation, the oxidation state of its precursor (Sn(II)) can make crucial impact on the phase composition of formed films. It has been shown that application of organotin(II) sulfide [$\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}\text{Sn}\}_2(\mu\text{-S})$] or organotin(IV) heptasulfide [$\{2,6-(\text{Me}_2\text{NCH}_2)_2\text{C}_6\text{H}_3\}_2\text{Sn}_2\text{S}_7$] as single-source precursors in the spin-coating method yielded films composed of SnS and SnS₂, respectively [48]. Similarly, Ahmet et al. demonstrated that the use of dimethylamido-(N-phenyl-N', N'-dimethylthiouriate) tin(II) [$\text{Sn}\{(\text{C}_6\text{H}_5)\text{NCSN}(\text{Me}_2)\}(\text{NMe}_2)$] as a single-source precursor in the AA-CVD process gives the unmatched ability to control oxidation state in the deposition of SnS films [16]. The highest efficiency of 4.6% for SnS-based solar cells has been also reported for the ALD-grown films using tin bis(N,N'-diisopropylacetamidinato) (Sn(amd)₂), in which the Sn centre exhibits the +2 oxidation state [32].

The oxidation state is not only determined by the tin source but also by ligands that may behave as soft reducing or oxidizing agents, or as a stabilizing agent. Commonly, in solution-based deposition methods, it is desired that solvents display only a dissolving

role for the precursor compounds without pronounced ligand competition, which causes changes in the precursors. Such conditions are probably realized in spin coating [48] and in AA-CVD [16], in which single-source precursors for SnS dissolved in aprotic low-polar solvents (toluene, dichloromethane, etc.). Whereas the polar solvents like water and alcohols may induce the ligand competition around Sn centres of precursors, it may result in the precursor transformation.

It is known that all the tin(II) halides are highly soluble in aqueous and alcoholic solutions due to strong complex formation [7]. Tin(II) chloride, which is widely used as a tin precursor in the CBD and CSP methods, has great reactivity and tends to hydrolysis in aqueous solutions. Semenov et al. [55] reported that the formation of tin hydroxo species starts at pH above 1 for the 0.01 M aqueous solution of SnCl₂ (Fig. 1.2) according to the reaction:



On the other hand, in acidic media, SnCl₂ acts as a strong reducing agent due to a high redox potential of Sn²⁺/Sn⁴⁺ [56].

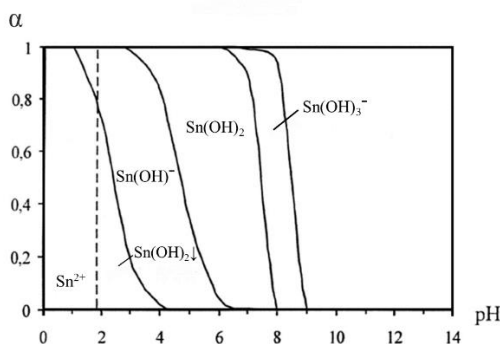


Fig. 1.2 Distribution diagrams for the formation of Sn²⁺ hydroxo complexes. The proportions of Sn(II) aqua and hydroxo complexes, α , depending on calculated pH values of 0.01M solutions [55].

Oxidation and hydrolysis of Sn(II) cations are two undesired processes occurring in aqueous solutions during the SnS film deposition. To minimise those unwanted reactions of Sn(II), complexation with different ligands can be used. Indeed, it has been reported that use of triethanolamine (N(CH₂CH₂OH)₃) and ammonia (NH₃) [11] or tartaric acid (HOOC-CH(OH)-CH(OH)-COOH, C₄O₆H₆) [57, 58] as stabilizing agents in CBD allows researchers to prevent the precipitation of tin hydroxo species even at pH = 6–8. Relatively higher electron-donating ability of sulfur in thiourea compared to oxygen in water results in a higher ability of thiourea to form a complex. Formation of Sn(II) thiourea complexes leads to shifting of the formation of tin hydroxo species to slightly higher pH values [59]. Therefore, especially for the solution-based methods utilizing aqueous solutions, two key factors should be followed: 1. suppression of tin(II) cations hydrolysis and 2. stabilisation of the less stable divalent state of tin.

In summary, the hydrolysis and oxidation processes of tin(II) cations should be controlled in order to fabricate tin monosulfide thin films using chemical deposition methods.

1.2.4 Chemical spray pyrolysis

Chemical spray pyrolysis (CSP) belongs to a family of solution-based methods operating in ambient conditions. CSP offers great advantages with relative simplicity, rapidness, cost-effectiveness and suitability for large area deposition. The first study concerning the usage of the CSP method for the film deposition (CdS films) was reported by Chamberlin and Skarman in 1966 [60]. Up to now, sprayed films such as metal oxides e.g. SnO₂ [61], ZnO [62, 63], NiO [64], TiO₂ [65] and metal sulfides like CdS [66], ZnS [67], In₂S₃ [68, 69], SnS [51] and CuInS₂ [70, 71], have been implemented in many devices.

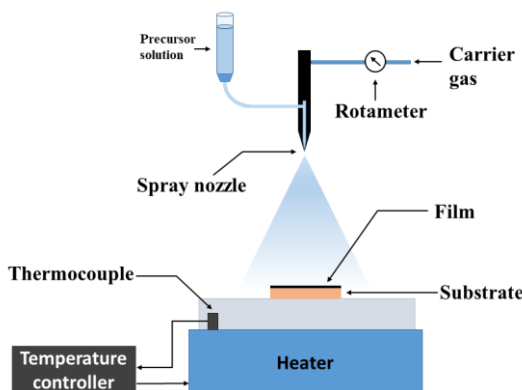


Fig. 1.3 Scheme of the spray pyrolysis system.

In the CSP method, thin films are synthesised by nebulising fine droplets of precursor solutions containing metal salts and different additives (acids, complexing agents etc.) onto preheated substrates. The schematic diagram of the spray pyrolysis system is presented in Fig. 1.3. The typical CSP system is composed of an atomiser, which helps to produce aerosols, a solution vessel, a heater, and a temperature controller [60, 72]. The solution droplets are generated by an atomiser (e.g. pneumatic, ultrasonic or electrostatic nebulisers). Depending on the atomiser type used, the CSP method can be categorised into three modes: pneumatic, ultrasonic and electrostatic [60, 73, 74].

Commonly, aqueous or alcoholic solutions containing a metal salt are used to grow metal oxide thin films using the CSP method. In some cases, when hydrolysis reactions are pronounced in the spray solution, dissolving suitable complexing agents is needed, as it makes the spray pyrolysis process possible. For the fabrication of metal sulfide films, the precursor solutions must contain a metal salt (usually metal chloride, MeCl_x) and a sulfur source (usually thiourea, SC(NH₂)₂, tu), which might form a variety of complex compounds. For the reasons listed above, starting chemicals and formed complex compounds must be soluble in the used solvent for successful deposition of the film.

Different parameters such as the deposition temperature, carrier gas, solution spray rate, concentration of starting chemicals in a solution, the distance between a spray nozzle and substrates, nature of the substrates and solvents have been reported to influence the film properties [75, 76].

In summary, the CSP method has been successfully used for the fabrication of different metal sulfide and metal oxide films. It has been found that solution composition, along with other experimental parameters, affects the phase composition and the film properties.

1.3 Metal sulfide films by chemical spray pyrolysis

Formation of metal sulfides in the chemical spray pyrolysis process

Different metal sulfide (Me = Cd, Zn, In, Cu) films have been grown using the CSP method [51, 66-71]. In the spray pyrolysis processes using aqueous solutions with dissolved metal halides and thiourea as starting chemicals, the formation of various metal sulfides passes through the formation of intermediate complex compounds. Formed complex compounds can be described using a general formula $[\text{Me}(\text{tu})_x]\text{X}_y \cdot n\text{H}_2\text{O}$, in which Me is a coordination centre, X is a halogen (Cl, Br) and x, y and n are the number of a surrounding array of molecules or ions, as reported by several authors [77-85]. In those complex compounds, thiourea molecules behave as neutral ligands, which coordinate the metal ion through the sulfur atom of the thiocarbonyl group [78-80, 82, 85, 86].

Several authors have studied the thermal behaviour of a variety of metal thiourea complexes by using simultaneous TG/DTA/EGA techniques in different atmospheres [77-79, 81, 83, 84, 86, 87]. According to the results in [77-79, 81, 83, 84, 86, 87], the thermal degradation of $\text{Me}(\text{tu})_x\text{X}_y \cdot n\text{H}_2\text{O}$ is a multistep process occurring mainly at temperatures above 200 °C. The formation of metal sulfide phases and the main evolution of gaseous products of thermal degradation have been recorded at temperatures above 200 °C, irrespective of the atmosphere used [85, 87]. Moreover, metal sulfides are final decomposition products in inert atmosphere, while the thermal degradation of metal thiourea complexes performed in an oxidative atmosphere leads to metal oxides as resultant products at high temperatures [79, 88]. The presence of additional uncomplexed thiourea in precursors, in comparison with the corresponding amount needed for the formation of metal chloride thiourea complex compound, can suppress the formation of the metal oxide phase [79, 89].

The decomposition of organic matter in most of the metal thiourea complex compound has been completed in air at temperatures below 700–800 °C [79, 88].

Properties of metal sulfide films

In the CSP process, the growth temperature and the molar ratio of metal and sulfur sources (Me:S) in the spray solution have shown to have strong effect on the properties of formed films [90, 91]. For instance, ZnS films produced by spray at 400 °C were found to be amorphous in nature, while those films deposited at temperatures above 500 °C were crystalline regardless of the molar ratio of ZnCl_2 and $\text{SC}(\text{NH}_2)_2$ (Zn:S) in solution [91]. Furthermore, ZnS films grown by spray at 550 °C using aqueous solution containing ZnCl_2 and $\text{SC}(\text{NH}_2)_2$ at the Zn:S molar ratio of 1:1 were composed of a mixture of ZnO and ZnS phases. Changing the Zn:S molar ratio in the spray solution from 1:1 to 1:3 yielded films consisting of the ZnS phase only [91]. Similar influences of deposition temperatures as well as molar ratios of indium and sulfur sources (In:S) in the spray solution have been observed for sprayed In_2S_3 films [68].

The properties of metal sulfide films might be influenced by several other technological aspects as well like nature of used starting chemicals and solvents, deposition atmosphere, substrate type, spray set-up, droplet size, etc. [68, 69, 72, 90, 92]. For instance, the 1:3 In_2S_3 films derived from ethanol-based solutions with the In:S molar ratio of 1:3 grown by spray at 250 °C were three times thinner and with lower bandgap than those deposited using aqueous solutions [69].

In summary, metal halides and thiourea, mainly used as starting chemicals to obtain metal sulfide films by CSP, interact in aqueous solutions and form intermediate complex compounds. To clarify chemical processes underlying the mechanism of metal sulfide formation upon the thermal decomposition of intermediates, simultaneous thermal analysis techniques have been employed. The thermal degradation temperature and the temperature of metal sulfide oxidation specify the temperature range in which metal sulfide films could be deposited using CSP. The properties of films grown by CSP have been found to depend on the deposition temperature, the molar ratio of starting chemicals along with other experimental parameters.

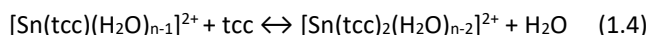
1.4 Tin sulfide films by chemical spray pyrolysis

1.4.1 Formation of tin sulfide in the chemical spray pyrolysis process

The chemicals traditionally employed for the preparation of sprayed SnS films have been tin(II) chloride (SnCl_2) in combination with sulfur source with a general formula $\text{R}_1\text{C}(\text{S})\text{R}_2$ ($\text{R}_1, \text{R}_2 = -\text{CH}_3, -\text{NH}_2, -\text{NH}(\text{CH}_3)$ or $-\text{NH}(\text{C}_2\text{H}_5)$) [49-51]. When thiocarbonyl group containing ligands (tcc) are added to the highly acidic ($\text{pH} < 2$) aqueous solution of Sn^{2+} , replacement of water molecules in the coordination sphere occurs, with the resultant formation of a variety of complexes [59, 87, 93]. Such replacement is a stepwise process that can be illustrated by the following series of reactions:



With an increasing amount of tcc in the solution, the equilibrium is shifted towards the formation of complexes with a higher number of tcc molecules surrounding tin atoms in the coordination sphere:



The complexation processes in aqueous solutions (Eqs. 1.2, 1.3 and 1.4), and, as a result, the composition of complex compounds have been found to depend on the solution pH and the molar ratio of starting chemicals [77, 80, 86]. Thus, in highly acidic aqueous solutions containing tin(II) chloride and thiourea, the formation of two single source precursors like $\text{Sn}(\text{tu})\text{Cl}_2$ and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ has been reported [77, 94-96]. The complex compound of $\text{Sn}(\text{tu})\text{Cl}_2$ forms when solutions with the Sn:tu molar ratio of 1:1 are used. Alternatively, the formation of $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ occurs when Sn:tu molar ratios in solutions are taken from 1:2 to 1:6 [96].

Madarász et al. have performed thermal analysis studies of $\text{Sn}(\text{tu})\text{Cl}_2$ and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ as single source precursors for tin sulfide [77, 94, 95]. TG and DTA curves of both precursors reveal the thermal decomposition profile, which occurs through several stages (Fig. 1.4). The thermal decomposition processes of both precursors in air are mostly endothermic at temperatures below $\sim 250^\circ\text{C}$ and exothermic at temperatures above 300°C .

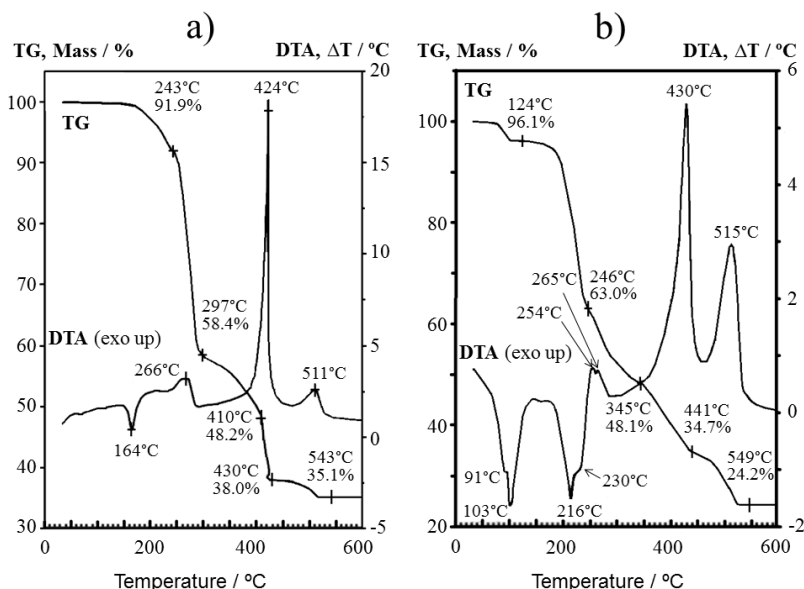


Fig. 1.4 TG/DTA curves of dried complex precursors: a) $\text{Sn}(\text{tu})\text{Cl}_2$ and b) $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. TG/DTA curves are recorded in flowing air using the heating rate of $10^\circ\text{C min}^{-1}$ [94, 95].

To clarify the processes taking place during the thermal decomposition of both precursors, the gaseous species evolved have been simultaneously recorded by EGA–MS and EGA–FTIR methods. Thermal degradation of both tin-thiourea complexes and the formation of tin sulfide have been shown to start at temperatures above 200°C [77, 94, 95]. The main evolved gaseous species include NH_3 , CS_2 , H_2NCN , HNCS , HCN , HCl , COS , SO_2 , and CO_2 [94, 95]. Importantly, the evolution of SO_2 from both precursors was completed by 430°C as an oxidation product of tin sulfide phases [94, 95].

It has been reported that metal halides ($\text{Me} = \text{Cu}, \text{Sn}, \text{Hg}, \text{Ni}, \text{Co}$) and L-cysteine ($\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$) also form complex compounds in aqueous solution [106–108, 109]. L-cysteine molecules coordinate the metal ion through sulfur (thiol group), nitrogen (amino group) and oxygen (carboxyl group) atoms [106–108, 109]. Thus, L-cysteine acts as a chelating agent in aqueous solutions. Authors in [107] have studied the thermal behaviour of $\text{Sn}(\text{L-cysteine})$ complex compound in air. According to the results in [107], the main thermal decomposition of $\text{Sn}(\text{L-cysteine})$ appears in the temperature region of 220 – 560°C .

It can be concluded that tin (II) chloride and thiourea form two intermediate complexes, $\text{Sn}(\text{tu})\text{Cl}_2$ and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, in solutions depending on the solution composition. The thermal analysis studies have been conducted for both complexes [77, 94, 95]. L-cysteine might be potentially used as a sulfur source in spray solutions for the deposition of SnS films, as it produces soluble complexes with metal halides in aqueous solutions. No reports have appeared on the use of L-cysteine as complexing agent and sulfur source for metal sulfide film preparation. It has been shown that tin sulfide films should be fabricated in a fairly narrow temperature range of 200 – 400°C . There is no clear understanding of effects caused by an excess of thiourea in the spray solution on the formation of tin sulfide.

1.4.2 Effect of starting chemicals molar ratio in the spray solution on the properties of tin sulfide films

Aqueous solutions containing tin(II) chloride (SnCl_2) and thiourea ($\text{CS}(\text{NH}_2)_2$) or alcoholic solutions containing the same tin source and substituted thiourea (N,N-diethyl or N,N-dimethyl thiourea) have been used to grow SnS films using pneumatic CSP [49-51, 97-102]. A major parameter affecting the properties of tin sulfide films deposited using CSP has been found to be the substrate temperature.

Despite a pool of studies within the last 20 years demonstrating that the precursors' molar ratio (Me:S) in the spray solution affects significantly the reactions of metal sulfide formation [79, 86, 88] as well as the properties of sprayed metal sulfide films [67-69, 91], tin monosulfide thin films have been mainly grown at $\sim 375^\circ\text{C}$ using the spray solution with the Sn:S molar ratio of 1:1 [49, 50, 98, 99, 101, 102].

To our best knowledge, before our early research, only one report focused on the influence of Sn:S molar ratios in the spray solution on the phase composition of tin sulfide films. Sajeesh et al. [51] demonstrated that the phase composition of sprayed tin sulfide films varies significantly with the changes in the precursors (Sn:S) molar ratio in spray solutions. According to the results in [51], the use of the 1:1 solution at substrate temperatures of 375°C resulted in films composed of a mixture of Sn_2S_3 and SnS phases. SnS was a main crystalline phase of films produced using the solutions with the Sn:S ratio of 1:2. The deposition performed at the similar temperature employing the solutions with a triple or quadruple excess of thiourea yielded films composed of a mixture of SnS and dominating SnS_2 phases [51].

1.4.3 Effect of substrate temperature on the properties of tin sulfide films

Several authors demonstrated that the growth temperature controls the phase and elemental compositions, optical properties as well as crystallite size and thickness of sprayed SnS films [49-51, 97-102]. According to Koteswara Reddy et al., sprayed films deposited at temperatures below 200°C are amorphous in nature [49, 97, 102]. White spots of unreacted precursors have been observed all over the surface of films formed at substrate temperatures below 250°C [49, 51, 97].

In general, films deposited at relatively low temperatures ($< 300^\circ\text{C}$) using solutions with the Sn:S molar ratios of 1:1 or 1:2 were composed of a mixture of SnS and Sn_2S_3 and/or SnS_2 phases [51, 97, 98]. SnS became a main crystalline phase in the films when the deposition temperature was increased up to $\sim 350^\circ\text{C}$ [97]. The formation of SnO_2 and/or SnS_2 phases, in addition to SnS, have been detected in the films grown at temperatures above 400°C regardless of the precursors molar ratios (1:1 or 1:2) in the solution [51, 97, 98].

Calixto-Rodriguez et al. [99] demonstrated that films deposited at the growth temperatures of $350\text{--}400^\circ\text{C}$ have larger SnS crystallite size than those grown at 320 or 455°C . However, Sajeesh et al. [51] reported a slight decrease in SnS crystallite size when the deposition temperature was increased from 300°C to 400°C . It has been shown that the thickness of SnS films decreases with the increase in the growth temperature [51]. Observed behaviour is characteristic of different films prepared by spray [74, 68].

The elemental composition of the films has been affected by the changes in the deposition temperature, which consequently affects the optical properties of formed films. In general, low deposition temperatures ($\leq 320^\circ\text{C}$) led to the slightly Sn deficient films [49, 51, 99, 102]. The concentration of chlorine in the sprayed tin sulfide films has been decreased by increasing the deposition temperature, and chlorine has not been

detected in the film grown at temperatures above 250 °C [49]. SnS films grown at 350–375 °C were nearly stoichiometric, while higher deposition temperatures (above 400 °C) resulted in films with considerable sulfur deficiency [49, 100, 102]. Furthermore, the concentration of oxygen in the film increases with increasing deposition temperatures above 400 °C [100]. The observed effects on sulfur deficiency in films grown at higher growth temperatures have been explained by the probable sulfur re-evaporation [51, 100]. The explanations given on the formation of tin oxide and increase in the oxygen content in the films deposited at temperatures above 400 °C seems to be insufficient in the light of the results reported for the sprayed In_2S_3 thin films [68, 69]. According to the results in [68, 69], gradual increase in the deposition temperature leads to a gradual increase in the oxygen content of In_2S_3 films. It has been shown that the formation of indium oxide phase in the films produced by spray at 410 °C was not due to the oxidation of In_2S_3 phase, as post-deposition thermal treatment of indium sulfide films at 450 °C in air did not lead to the formation of metal oxide [68], and was probably due to the oxidation of uncomplexed InCl_3 [79].

1.4.4 Effect of post-deposition thermal treatments on the properties of tin sulfide films

In general, post-deposition thermal treatment in various media has been found to improve the properties of metal sulfide thin films. It has been shown that annealing of sprayed CuInS_2 in a H_2S atmosphere improves the chemical purity and increases the material crystallite size [103]. A shift in optical bandgap values towards the bulk value of 1.3 eV has been reported for HVE-grown SnS films annealed in a sulfur containing atmosphere [10]. A structural transition from cubic to orthorhombic along with changes in the optical bandgap from 1.75 to 1.0 eV have been reported for CBD-deposited SnS films after annealing in N_2 atmosphere at 600 °C [104].

To our best knowledge, no comprehensive studies on the effects of post-deposition thermal treatment in different atmospheres on the properties of sprayed tin sulfide films have been reported. Few reports have presented supplementary results on the post-deposition annealing of tin sulfide films grown by the CSP method [10, 100, 105]. Ramakrishna Reddy et al. [10] reported significant improvement in the crystallinity of SnS films by annealing in sulfur atmosphere at 300 °C. According to the results in [100], the resistivity of tin-rich SnS films grown by spray at 350 °C has been slightly decreased and a minor improvement in the carrier density has been recorded after annealing in vacuum at 200 °C for 2 h. Compared to as-grown films, a decrease in the electrical resistivity by four orders of magnitude along with an increase in the carrier concentration has been shown for sprayed SnS films treated at 400 °C in flowing argon atmosphere [105]. The observed effects have been associated with improvements in film crystallinity and grain growth [100, 105].

In summary, according to the literature, deposition temperature is the main deposition parameter controlling properties of sprayed tin sulfide films; crystalline nearly stoichiometric tin monosulfide films can be grown at 350 °C using a solution with a Sn:S molar ratio of 1:1. Sajeesh et al. [51] demonstrated that the molar ratio of starting precursors varying from 1:1 to 1:4 affected the phase composition of SnS films grown at 375 °C. However, the experimental data for the properties of films grown using solutions with different Sn:S molar ratios at other deposition temperatures were not included in [51]. The annealing studies for the sprayed SnS films have been described only in general terms. No sufficient argumentation for the observed improvements in electrical

resistivity and carrier density have been presented in [10, 100, 105], as the data on the phase composition of thermally-treated films were overlooked.

1.5 Application of tin sulfide films

Tin(II) sulfide (SnS) is a non-toxic material exhibiting a direct optical bandgap of 1.3–1.8 eV, a high absorption coefficient (above 10^4 cm^{-1}) and p-type conductivity [1, 2, 9, 11, 28]. In addition to its remarkable physical properties, the earth-abundance of the constituent elements, Sn and S, makes tin sulfide attractive for a variety of applications including photoelectrochemical cells [29], chemical sensors [30], solid-state batteries [31] and thin film solar cells [32, 33].

The use of tin monosulfide films in solar cells [32, 33] provides the ability to replace the widely used absorbers containing scarce or toxic constituents (Cu(In,Ga)Se_2 , CdTe, etc.) and therefore makes the production of final products safer and more profitable. It has been shown that the efficiency of RF-sputtered orthorhombic SnS solar cells reaches 2% using Zn(O,S) [125] or $\text{Zn}_{(1-x)}\text{Mg}_x\text{O}$ [126] buffer layers. The solar cell with CBD-grown cubic SnS absorber and CdS buffer films exhibited an efficiency of around 1.3% [120]. To date, the best efficiency of cells with HVE-grown SnS films has been recorded at 3.9% [33]. Despite the efforts made during recent years to improve SnS-based solar cells, the highest efficiency recorded is 4.6% for solar cells with ALD-grown SnS films [32], which is still significantly lower than the theoretical value of 24% [3].

1.6 Summary of the literature review and the aim of the study

The studies on tin sulfide films can be summarized as follows:

1. Different physical and chemical methods have been used to grow tin sulfide films. Chemical spray pyrolysis method can offer a number of advantages such as simplicity, rapidness, cost effectiveness and suitability for large area depositions.
2. Metal halides ($\text{Me} = \text{Cd}, \text{Zn}, \text{In}, \text{Cu}$) and thiourea form complexes in aqueous solutions. Metal sulfides are the products of the thermal decomposition of metal thiourea halide complex compounds. The thiourea content in intermediates higher than required for a corresponding complex (e.g. $\text{In(tu)}_3\text{Cl}_3 + 3\text{tu}$; $\text{Zn(tu)}_2\text{Cl}_2 + \text{tu}$ etc.) may suppress the formation of the metal oxide phase.
3. Aqueous or alcoholic solutions containing tin(II) chloride and a thiocarbonyl compound (thiourea or substituted thiourea) at the Sn:S molar ratio of 1:1 have been generally used for the deposition of SnS films by spray.
4. Tin(II) chloride and thiourea form complexes in aqueous solution. Thermal analysis studies of two single source precursors, Sn(tu)Cl_2 and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, have been performed in synthetic air. No thermoanalytical studies on precursors containing tin(II) thiourea chloride complex compounds and an excess of thiourea have been reported. L-cysteine, as it forms complex compounds with different metal cations, might be potentially used as a sulfur source in the chemical spray pyrolysis method.
5. The deposition temperature and the molar ratio of tin and sulfur sources in the spray solution are key technological parameters affecting the properties of sprayed SnS films.

- *The effect of the deposition temperature*

Crystalline tin monosulfide can be grown at deposition temperatures of 350–400 °C. The increase in the deposition temperature above 400 °C leads to the

formation of the tin oxide phase. The effect of the growth temperature on the impurities content (e.g. oxygen) in the films has not been sufficiently studied.

- *The effect of the molar ratio of starting chemicals (Sn:S) in the spray solution*

In general, SnS films have been deposited by spraying of aqueous solutions containing tin(II) chloride (Sn) and thiocarbonyl compounds (S) at a Sn:S molar ratio of 1:1. It has been demonstrated only in one report that the phase composition of sprayed tin sulfide films depends on the molar ratio of precursors in the spray solution. No systematical studies on the influences of starting chemicals (Sn:S) molar ratios in the spray solution on the properties of sprayed tin sulfide films have been reported.

No comprehensive studies covering the effects of the deposition temperature coupled with varied precursors' $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratios in the spray solution on the phase and elemental compositions, morphological and optical properties of tin sulfide films have been conducted. Neither have any studies focused on the deposition and the properties of sprayed tin sulfide films grown using any alternative sulfur source.

6. Annealing of HVE-grown SnS films in sulfur atmosphere yielded films with decreased optical bandgap values. Post-deposition thermal treatment of CBD-grown SnS films in nitrogen led to the transition from the cubic to the orthorhombic phase. No comprehensive studies on the effects of post-deposition thermal treatment in different atmospheres on the properties of sprayed tin sulfide films have been reported.
7. Tin sulfide thin films can be potentially used for a variety of applications due to their appropriate physical properties, chemical stability and cost-effectiveness of Sn and S elements. Tin monosulfide can be used as an absorber material in thin-film solar cells instead of $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CdTe , as it exhibits a direct optical bandgap of 1.3–1.8 eV, a high absorption coefficient (above 10^4 cm^{-1}) and p-type conductivity.

Based on the main conclusions listed above, the objectives of the current doctoral thesis research were:

1. To investigate the formation of tin sulfide in the CSP process:
 - to study the composition of intermediate compounds formed in aqueous solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ as starting chemicals at different molar ratios and acting as precursors for tin sulfide films using dried precursors
 - to study the thermal decomposition of intermediate compounds applying a complex of simultaneous thermal analysis techniques.
2. To study the influence of the deposition temperature and the molar ratio of SnCl_2 and $\text{SC}(\text{NH}_2)_2$ in an aqueous spray solution on the phase and elemental compositions, optical and morphological properties of tin sulfide films grown by the CSP method.
3. To study the effect of the post-deposition thermal treatment in nitrogen and vacuum on the properties of sprayed tin sulfide thin films.
4. To investigate possibilities of using an alternative sulfur source instead of thiourea.

2 Experimental

The main experimental details are presented in two subsections. The first subsection describes the synthesis, characterisation and thermoanalytical studies of precursors for SnS films. The deposition and characterisation of sprayed tin sulfide films are introduced in the second subsection. The detailed description of the experiment is introduced in published papers [I-IV].

2.1 Synthesis and characterisation of precursors for tin sulfide films

2.1.1 Synthesis of precursors

Two types of precursor solutions were prepared by dissolving a corresponding amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1M acidic aqueous solutions of $\text{SC}(\text{NH}_2)_2$ (pH <1) or L- $\text{HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ (pH <3) at molar ratios of 1:1 (named as **1**) and 1:8 (named as **2**) [I], or 1:1 (named as **3**) and 1:4 (named as **4**) [III], respectively. The solvent was slowly evaporated at room temperature for 5 days, followed by further drying at 35 °C for 24 h in air.

2.1.2 Characterisation of precursors

The obtained dried powders **1** and **2** were characterised using XRD, EDX and FTIR methods and then used for thermoanalytical investigations. The dried powders **3** and **4** were characterised by FTIR spectroscopy. The analytical methods employed for the characterisation of precursors for the deposition of tin sulfide films by CSP are summarized in Table 2.1. More details are specified in articles [I, III].

Table 2.1 Methods used for the characterisation of precursors for SnS films

Properties	Analytical method	Apparatus	Ref.
functional groups	FTIR spectroscopy	Perkin-Elmer GX1	[I, III]
phase composition	XRD	Rigaku Ultima IV	[I]
elemental composition	EDX	Zeiss HR FESEM Ultra 55	[I]
thermal decomposition (temperatures, endo/exo type of reactions, evolved gases)	TG/DTG/DTA	SetSys-Evolution 1600	[I]
	TG/ EGA-MS	SetSys-Evolution 1600 + OmniStar quadrupole mass spectrometer	[I]

2.2 Deposition of tin sulfide films by chemical spray pyrolysis and characterisation

2.2.1 Deposition of tin sulfide films

Tin sulfide films were deposited onto preheated soda-lime glass substrates (30x10x1 mm³) in air using the pneumatic chemical spray pyrolysis technique (sketch of the spray set-up in Figure 1.3) [II, III, IV]. The precursor solutions were prepared by dissolving stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and thiourea ($\text{CS}(\text{NH}_2)_2$, tu) [II, IV] or L-cysteine (L- $\text{HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$, L-cys) [III] as sulfur sources in deionized water containing a few

drops of concentrated HCl, pH values were fixed as 1 and 3, respectively. For all the samples the concentration of the Sn^{2+} cation in the spray solution was 0.01M and the molar ratio of precursors (Sn:S) was varied from 1:1 to 1:8. The deposition temperatures were changed from 200 to 370 °C. The spray solution volume was 50 ml and the spray rate was kept at ca. 3.0 mL/min for all the deposition experiments [II, III, IV].

2.2.2 Post-deposition thermal treatment of sprayed tin sulfide films

In order to study the effect of post-deposition thermal treatment, SnS films were grown onto soda-lime glass substrates at 200 °C using acidic aqueous solutions containing tin chloride and thiourea at Sn:S molar ratios of 1:1 or 1:8 [IV]. The films were subjected to annealing in vacuum or nitrogen atmosphere at 450 °C for 1 h. The temperature and experiment duration were chosen according to preliminary studies. The pressure in the chamber during vacuum annealing of the samples was 5×10^{-6} Torr. Alternatively, the samples were loaded into a quartz tube; the tube was purged with nitrogen (5N), and, after the N_2 flow rate was set to 18 mL/min, the quartz tube was inserted into a preheated tube furnace [IV].

2.2.3 Characterisation of as-deposited and thermally-treated tin sulfide films

The phase and elemental compositions, morphological and optical properties of as-deposited tin sulfide films and those of annealed in different atmospheres were studied using the characterization methods summarized briefly in Table 2.2.

Table 2.2 Methods used for the characterisation of as-deposited and annealed tin sulfide films

Properties	Analytical method	Apparatus	Ref.
phase composition, crystallite size, orientation of crystallites	XRD	Rigaku Ultima IV	[II, III, IV]
phase composition	Raman spectroscopy	Horiba's LabRam HR800	[IV]
elemental composition	EDX	Zeiss HR FESEM Ultra 55 + Bruker ESPRIT 1.8 system	[II, III, IV]
morphology, film thickness	SEM	Zeiss HR FESEM Ultra 55	[II, III, IV]
functional groups	FTIR spectroscopy	Perkin-Elmer GX1	[IV]
total transmittance, total reflectance	UV-Vis spectroscopy	Jasco V-670	[II, III, IV]

3 Results and discussion

3.1. The formation of tin sulfide in the chemical spray pyrolysis process

In order to simulate the CSP process and to find a proper spray solution composition and thermal conditions for the deposition of sprayed tin sulfide films, the formation chemistry of tin sulfide was studied. Aqueous solutions were prepared using SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at the two extreme molar ratios of 1:1 (**1**) and 1:8 (**2**), then the solvent was slowly evaporated, and the dried powders were characterised and used for TA investigations [I]. A similar procedure was used to prepare the dried precursors derived from solutions containing SnCl_2 and L- $\text{HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ as a sulfur source at the molar ratios of 1:1 (**3**) and 1:4 (**4**) [III].

3.1.1 Characterisation of intermediates formed in aqueous solutions containing SnCl_2 and thiourea or L-cysteine as starting chemicals for tin sulfide films

Dried thiourea-based precursors **1** and **2** were characterised using XRD, FTIR spectroscopy and EDX analysis. Dried L-cysteine-based precursors **3** and **4** were characterised using FTIR spectroscopy. The results are summarised in this subsection and published in [I, III].

Interaction of SnCl_2 and $\text{SC}(\text{NH}_2)_2$ in aqueous solutions

The IR spectra of the dried thiourea-based precursors **1** and **2** and that of $\text{SC}(\text{NH}_2)_2$ (thiourea, tu) are compared in Fig. 3.1. The spectrum of thiourea shows a vibration at 1470 cm^{-1} , being characteristic of CN group stretching vibrations, $\nu(\text{CN})$ [78]. The IR spectra of **1** and **2** show that the $\nu(\text{CN})$ is shifted to higher wavenumbers, viz. 1500 and 1490 cm^{-1} , respectively. The increased wavenumbers of the CN group vibration in **1** and **2** show the strengthening of the bond between carbon and nitrogen atoms [78, 110]. The characteristic stretching vibrations of CS group, $\nu(\text{CS})$, are peaked at 1415 and 730 cm^{-1} in the spectrum of thiourea. In **1** and **2**, these vibrations are shifted to 1385 and 700 cm^{-1} , respectively. The shift of the CS group stretching vibrations towards lower wavenumbers in **1** and **2**, compared to that of tu, is due to the reduced double bond character between carbon and sulfur atoms [79, 80, 110, 111]. This shows that the coordination of ligand to metal cations occurs through the sulfur atom in **1** and **2**. Moreover, the spectrum of **2** shows additional vibrations at 1470 and 730 cm^{-1} . These vibrations are characteristic of $\nu(\text{CN})$ and $\nu(\text{CS})$ in noncomplexed thiourea, respectively.

According to XRD studies, **1** is composed of $\text{Sn}(\text{tu})\text{Cl}_2$ (JCPDS Card 01-075-1290) only [112], and **2** contains crystalline phases of thiourea (JCPDS 00-009-0790) [112] and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, which is isostructural with the $\text{Sn}_2(\text{tu})_5\text{Br}_4 \cdot 2\text{H}_2\text{O}$ [85].

According to EDX studies, the elemental composition of **1** (found, in at. %) is: Sn 22.4%, S 22.1% and Cl 42.5%; and of **2** is: Sn 5.9%, S 48.9% and Cl 19.0%. The Sn:Cl:S ratio of 1:1.9:1.0 in **1** is very close to that calculated for $\text{SnCl}_2 \cdot (\text{SCN}_2\text{H}_4)$, where Sn:Cl:S ratio is 1:2:1. In the case of **2**, the Sn:Cl:S ratio of 1:3.2:8.3 is close to that calculated for a mixture of $(\text{SnCl}_2 \cdot 2.5(\text{SCN}_2\text{H}_4) \cdot \text{H}_2\text{O} + 5.5(\text{SCN}_2\text{H}_4))$, with the Sn:Cl:S ratio of 1:2:8.

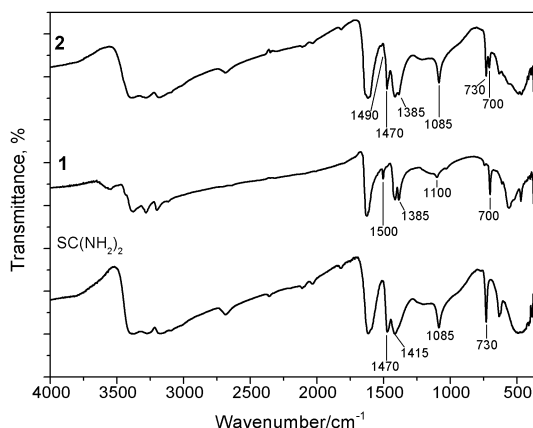


Fig. 3.1 FTIR spectra of dried samples **1**, **2** and $\text{SC}(\text{NH}_2)_2$ recorded at room temperature.

Comparing the results obtained from FTIR, XRD and EDX studies, it can be concluded that sample **1** is a complex compound with a formula $\text{SnCl}_2 \cdot (\text{SCN}_2\text{H}_4)$, in which the thiourea molecule is coordinated to the tin centre via its sulfur atom. Sample **2** is composed of a mixture of a complex compound and free thiourea and can be expressed as $\text{SnCl}_2 \cdot 2.5(\text{SCN}_2\text{H}_4) \cdot \text{H}_2\text{O} + 5.5(\text{SCN}_2\text{H}_4)$ [I].

Interaction of SnCl_2 and $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ in aqueous solutions

Figure 3.2 presents the IR spectra of $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ and dried L-cysteine-based samples obtained from solutions with SnCl_2 :L-cysteine of 1:1 (**3**) and 1:4 (**4**). The IR spectra of **3** and **4** show significant differences in the positions and intensities of functional groups characteristic of L-cysteine.

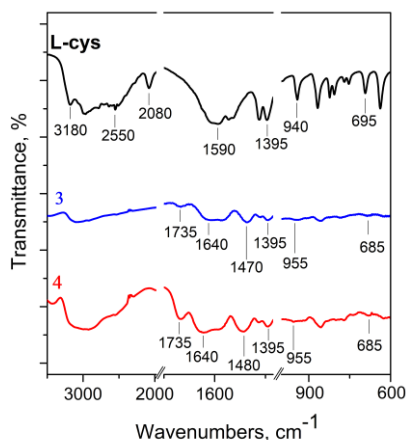


Fig. 3.2 FTIR spectra of dried samples **3**, **4** and $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ recorded at room temperature.

The absence of vibrations of the $-\text{SH}$ group placed at 2250 cm^{-1} , weakening and shifting characteristic frequencies of CS bond from 695 to 685 cm^{-1} in the IR spectra of **3**

and **4** indicate that L-cysteine is coordinated to Sn^{2+} cation through a sulfur atom. The disappearance of vibrations characteristic of the $-\text{NH}_2$ group located at 3180 and 2080 cm^{-1} in the spectrum of L-cysteine, the appearance of new vibrations at 1470 and 1480 cm^{-1} for samples **3** and **4**, respectively, and the shifting of the band from 1590 cm^{-1} to 1640 cm^{-1} refer to the complex formation via nitrogen atom [106, 107]. The appearance of the stretching vibrations for $\text{C}=\text{O}$ at 1735 cm^{-1} in the spectrum of **3** and **4**, and weakening of the stretching vibration for COO^- at 1395 cm^{-1} indicate that double-bond character between carbon and oxygen atoms increased upon protonation. It demonstrates that the cysteine molecule is bound to the Sn^{2+} cation through an oxygen atom.

The changes observed in the positions and intensities of vibrations of functional groups characteristic of L-cysteine in **3** and **4** compared to those of free L-cysteine indicate the formation of Sn-L-cysteine complex compound [III].

To summarise, both sulfur sources form intermediate complex compounds with SnCl_2 . It is shown that thiourea is coordinated to tin cations via sulfur atoms, while L-cysteine is connected to Sn(II) cations through sulfur, nitrogen and oxygen atoms. The formation of complexes between tin(II) chloride and sulfur sources, soluble in spray solution, is an important step for the chemical spray pyrolysis process, as it makes the CSP procedure possible.

3.1.2 Thermal analysis study of precursors for tin sulfide films

The thermoanalytical studies were performed for the thiourea-based precursors as thiourea is commonly used as a sulfur source for the sprayed tin sulfide films. The thermal behaviour of the dried precursors, Sn(tu)Cl_2 (**1**) and that containing a complex compound $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ and free thiourea (**2**), were studied by simultaneous TG/DTA/EGA-MS and TG/DTA measurements, respectively, in flowing (80% Ar + 20% O_2 , synthetic air) atmosphere in the temperature range of $30\text{--}700^\circ\text{C}$ using the heating rate of $10^\circ\text{C min}^{-1}$ [I].

Thermal analysis of precursor 1

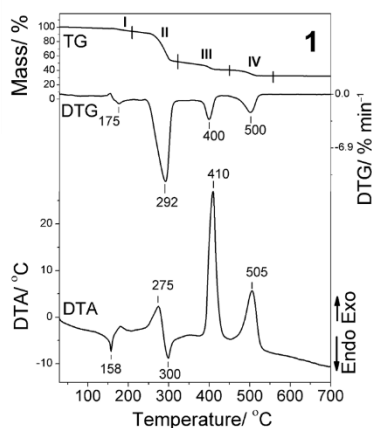


Fig. 3.3 Simultaneous TG/DTG/DTA curves of **1**. Flowing (80% Ar + 20% O_2): flow rate 60 mL min^{-1} , heating rate: $10^\circ\text{C min}^{-1}$. The initial mass of samples **1** was 15.0 mg .

According to the DTG curve, four mass loss steps could be detected for **1** (Fig.3.3, see Table 1 in [I]). The first mass loss step of **1** occurs in the range of $30\text{--}210^\circ\text{C}$ after the

endothermic melting of the compound at 158 °C. According to the DTA curve (Fig. 3.3), the second decomposition step in the temperature range of 210– 320 °C shows an exothermic process at 275 °C and an endothermic process at 300 °C. The mass loss steps 3 and 4 are exothermic reactions with DTA maxima peaked at 410 and 505 °C, respectively. The total mass loss of **1** in the temperature interval of 30–700 °C is 68% (calculated 56.4%). According to the XRD analysis, SnO₂ is the final decomposition product of **1** at 700 °C. The calculated mass loss of **1** is much lower than the experimental one, indicating the release of some volatile Sn species (e.g. SnCl₄).

Gaseous products evolved during the thermal decomposition of precursor 1

Figure 3.4 presents the evolution profiles of gaseous species as monitored by simultaneous TG/DTA/EGA–MS for **1** [I].

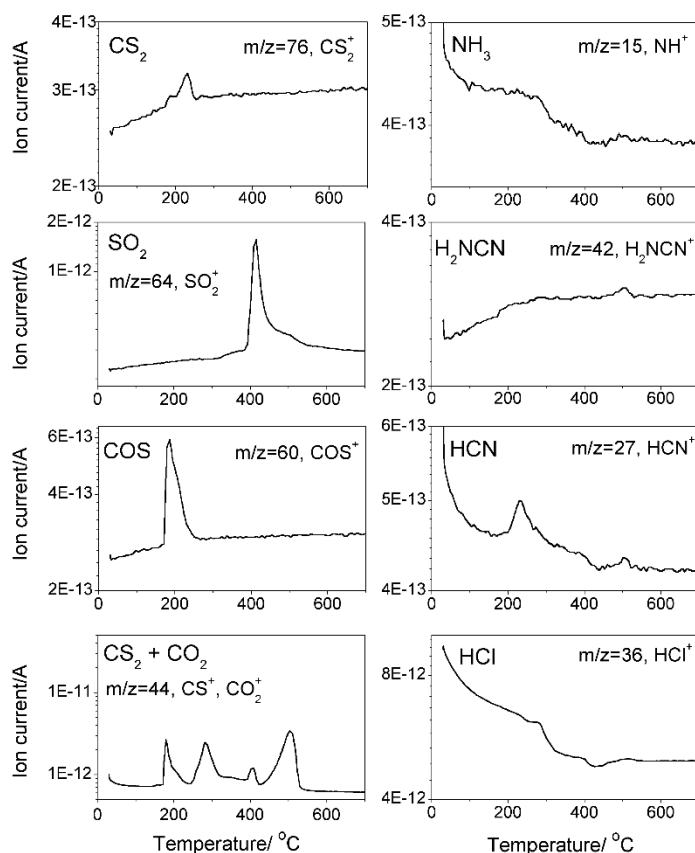
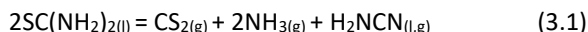


Fig. 3.4 Gas evolution profiles of various gaseous species, as determined by TG/DTA/EGA–MS of **1**. Flowing (80% Ar + 20% O₂): flow rate 60 mL min⁻¹, heating rate: 10 °C min⁻¹. The initial mass of sample **1** was 15.0 mg.

In the first decomposition step (30–210 °C), the evolution of gaseous species starts at around 170 °C with the evolution of carbon disulfide (CS₂), ammonia (NH₃) and

cyanamide (H_2NCN) (Fig. 3.4), which are the decomposition products of adjacent thiourea ligands in the melt (3.1) [89, 113]:

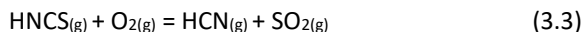


The evolution of carbonyl sulfide (COS) was found to start shortly after the evolution of CS_2 . COS is one of the oxidation products of the CS_2 vapor according to the reaction (3.2) [89, 113]:

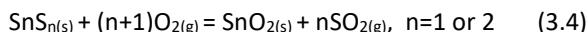


In the second decomposition step (210–320 °C), the evolution of CS_2 and COS continues up to 260 °C, and the release of H_2NCN and NH_3 , HCl and HCN continues until the end of the decomposition step.

The evolution of isothiocyanic acid (HNCS) could not be detected by EGA–MS and has been detected by EGA–FTIR during the thermal decomposition of $\text{Sn}(\text{tu})\text{Cl}_2$ in the temperature region of 200–300 °C [95]. Thus, the evolution of HCN with the maximum at 230 °C can be considered as the oxidation product of HNCS according to the reaction (3.3), as reported in [78, 81]:



In the third decomposition step of **1** (320–450 °C), the highly exothermic effect at 410 °C (Fig. 3.3) is accompanied by an intensive evolution of SO_2 (320– 550 °C) and minor release of CO_2 and H_2NCN . This indicates the oxidation processes of tin sulfides, according to the reaction (3.4) [95] as well as the decomposition and the oxidation of organic residues:



In the fourth decomposition step of **1** (450–550 °C), an exothermic effect at 505 °C is accompanied by an intensive evolution of CO_2 and the release of SO_2 and H_2NCN . Evolution of gaseous species such as CO_2 and H_2NCN evidences the decomposition and oxidation of an organic matter.

The results of the thermal decomposition study of **1** were used to describe the decomposition of the thiourea-rich precursor **2**, as both were measured with the same experimental apparatus and under similar experimental conditions.

Thermal analysis of precursor 2

The characteristic TG/DTG/DTA curves of sample **2** are presented in Fig. 3.5. According to the DTG curve, the thermal degradation of **2** in the temperature range of 30–700 °C in air consists of four mass loss steps (Fig. 3.5, see Table 1 in [I]) with a total mass loss of 84.5% (calculated 81.9%). Thermal behaviour of **2** is more sophisticated than that of **1** and that of $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ reported in [77, 94] and shown in Fig. 1.4b.

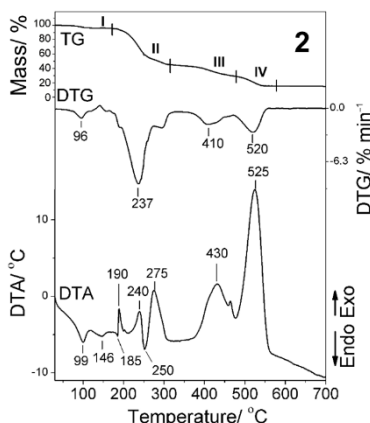


Fig. 3.5 Simultaneous TG/DTG/DTA curves of **2**. Flowing (80% Ar + 20% O₂): flow rate 60 mL min⁻¹, heating rate: 10 °C min⁻¹. The initial mass of samples **2** was 15.0 mg.

The first decomposition step of **2** is in the temperature interval of 30–175 °C with a DTG maximum at 96 °C and a mass loss of 4.8%. The DTA curve shows endothermic peaks with a maximum at 99 °C and a broad band with a maximum at 146 °C. The mass loss of 4.1% in the temperature range of 30–120 °C corresponds to the dehydration of **2**. A broad endothermic effect in the temperature range of 120–160 °C with a maximum at 146 °C probably belongs to the melting of **2**. The melting of **2** was confirmed by the visual inspection of **2** when heated in a laboratory oven.

The second decomposition step of **2** takes place in the temperature range of 175–320 °C with a mass loss of 50.5% and a DTG maximum at 237 °C. According to the DTA curve, the decomposition of **2** in this temperature region is a complicated multistep process with several overlapping endothermic and exothermic effects.

The third decomposition step of **2** in the temperature interval of 320–475 °C is an exothermic process with maxima at 430 and 460 °C. Compared to **1**, the first exothermic effect in this temperature region occurs at ca 20 °C higher temperatures. In the case of **1**, this exothermic effect was accompanied by the evolution of SO₂, due to the oxidation of sulfur-containing phases. Thus, the oxidation of sulfide phases in **2** is shifted to higher temperatures than that observed in **1**. The mass loss of **2** in this decomposition step is only slightly higher than that recorded for **1**. The mass losses are 12.0% for **1** and 15.5% for **2**. The DTA curve of **2** exhibits a plateau in the temperature range of 315–345 °C. However, the DTA curve of **1** (Fig. 3.3) shows no plateau in this temperature region.

The fourth decomposition step of **2** in the temperature range of 475–570 °C is a highly exothermic process with a DTA maximum at 525 °C. Compared to **1**, the DTA maximum of **2** is shifted to a higher temperature, from 505 °C (**1**) to 525 °C (**2**). A similar shift of the exothermic effect to a higher temperature has been observed for thiourea-rich precursors for In₂S₃ [79] and CuInS₂ [89].

The mass loss of **2** in the fourth decomposition step is 13.7%, which is significantly higher than that observed for **1** (8.0%). This shows that the content of organic matter at the beginning of the last decomposition step of **2** is significantly larger than in **1**. The decomposition of **2** is completed by 570 °C. The total mass loss of **2** in the temperature interval of 30–700 °C is 84.5 %. According to XRD, the final decomposition product of **2** at 700 °C is SnO₂. The calculated mass loss of **2** (81.9%) is close to the experimental one

(84.5%), indicating that the excess of thiourea in the precursor hinders the release of volatile tin species from the system.

Comparison of solid decomposition products of **1** and **2**

The solid intermediates and the final products of thermal decomposition of **1** and **2** were characterised using *ex situ* FTIR and XRD. The FTIR spectra of the solid intermediate products of **1** and **2** heated up to various temperatures are compared in Fig. 3.6. The FTIR spectra of **1** and **2** heated up to 190 °C (Fig. 3.6) show no vibrations characteristic of **1** and **2** (Fig. 3.1), confirming the destruction of **1** and **2** already at 190 °C. This is in correspondence with the TG/DTA data (Figs. 3.3, 3.5), showing that the decomposition of **1** and **2** starts at 170 and 150 °C, respectively. FTIR spectra of both **1** and **2** obtained by heating up to 190 °C and the spectrum of **2** at 210 °C (Fig. 3.6) exhibit a vibration at 2070 cm⁻¹. This can be assigned to the stretching vibrations of both thiocyanate (SCN) and hydrogen-bonded RNH³⁺ groups and indicates isomerisation of thiourea into ammonium thiocyanate (NH₄SCN) [83, 114]. The absorption peak at 2070 cm⁻¹ has been detected in the decomposition products of thiourea [115], Cu(tu)₃Cl•H₂O [84], Cd(tu)₂Cl₂ [78], Zn(tu)₂Cl₂ [83] and In(tu)₃Cl₃ [114]. The isomerisation of SC(NH₂)₂ to NH₄SCN is presented in [115], and the decomposition of the latter explains the evolution of gaseous species such as HNCS and NH₃ (see reaction 5 [I]) and the formation of ammonium tin chlorides as solid intermediates in the first decomposition step of **1** and **2** (see Table 2 in [I]).

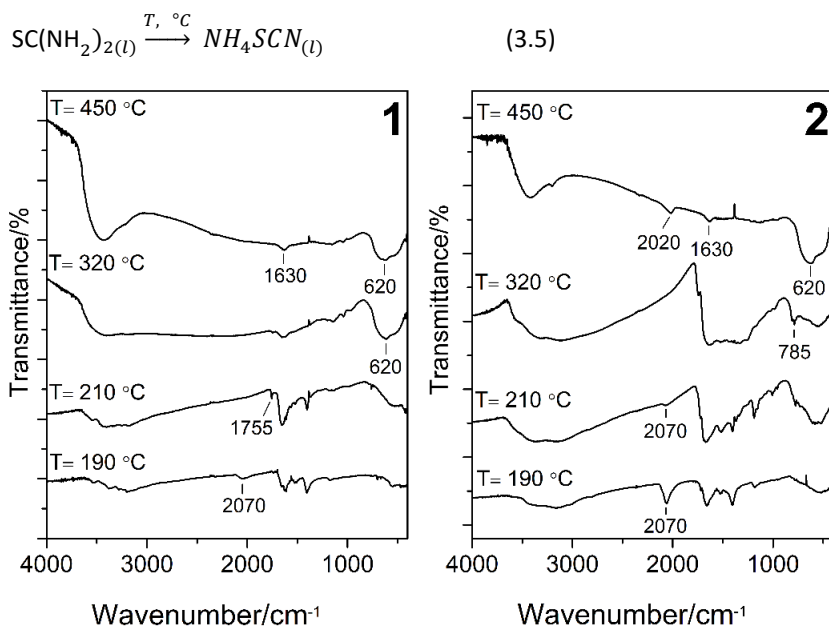
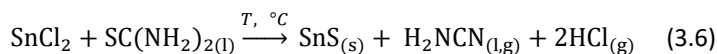


Fig. 3.6 FTIR spectra of the solid residues obtained by heating of **1** and **2** at 190, 210, 320, and 450 °C.

XRD studies reveal that the solid residue of **1** heated up to 210 °C contains crystalline phases of SnS₂, ammonium hexachlorostannate (NH₄)₂Sn^{IV}Cl₆ and guanidinium

trichlorostannate $C(NH_2)_3Sn^{III}Cl_3$. The solid product of **2** at 210 °C contains SnS_2 , SnS , $(NH_4)_2SnCl_6$, and NH_4Cl (see Table 2 in [I]).

Taking into account the thermal effects, gaseous and solid decomposition products of **1** and **2**, the formation of SnS upon the thermal decomposition of precursors can be presented as the following schematic reaction:



The FTIR spectra of **1** and **2** heated up to 320 °C (Fig. 3.6) are different. The spectrum of **2** reveals strong absorptions in the wavenumber range of 1665–1200 cm^{-1} and at 785 cm^{-1} , which can be assigned to the polymerized product of cyanamide [78, 116]. The FTIR spectrum of **1** heated up to 320 °C reveals a broad and intensive band at 620 cm^{-1} , characteristic of SnO_2 [117]. XRD analysis confirms the presence of a mixture of SnO_2 and SnS_2 phases in the solid products of **1** heated up to 320 °C. However, the solid product of **2** heated up to 320 °C still consists of SnS_2 (Table 2 in [I]).

FTIR spectra of **1** and **2** heated up to 450 °C are similar. Both **1** and **2** show a broad band at 620 cm^{-1} , characteristic of SnO_2 [117]. XRD analysis shows that the crystalline solid product of **1** and **2** heated up to 450 °C is SnO_2 . The absorption bands in the region of 1600–1000 cm^{-1} indicate the presence of some organic residues in **1** and **2**. In addition, the spectrum of **2** shows the absorption at 2020 cm^{-1} belonging to the cyanamide group. Thus, the intensive exothermic effects at 505 °C in **1** and 525 °C in **2** are caused by the decomposition and combustion of organic residues.

Summary of the formation and thermal analysis of precursors for SnS films

It was shown that $SnCl_2$ and $SC(NH_2)_2$ form two complex compounds, $Sn(tu)Cl_2$ and $Sn_2(tu)_5Cl_4 \cdot 2H_2O$, derived from aqueous solutions with the molar ratios of starting chemicals of 1:1 (**1**) and 1:8 (**2**), respectively. In both complexes, thiourea acts as a monodentate ligand and is coordinated to tin cations through sulfur atoms. Uncomplexed thiourea is additionally present in **2**. $L-HSCH_2(NH_2)CHCO_2H$ forms intermediate complex compounds with $SnCl_2$. L-cysteine acts as a tridentate ligand and is connected to $Sn(II)$ cations through sulfur, nitrogen and oxygen atoms. The formation of intermediate complexes between tin(II) chloride and sulfur sources soluble in the spray solution, is a necessary step for the chemical spray pyrolysis process, as it makes the CSP procedure possible.

The thermal decomposition of **1** occurs in the temperature region of 170–530 °C in synthetic air. The thermal decomposition of **2** takes place in the temperature range of 150–570 °C in synthetic air. The final decomposition product of **1** and **2** is SnO_2 at 570 °C. The experimental mass loss of **1** in synthetic air is higher than the calculated value, indicating the release of volatile Sn species (e.g. $SnCl_4$). The total mass loss of **2** in synthetic air is close to the calculated value. This fact indicates that excess of thiourea retards the formation of volatile Sn species and, as a result, the loss of Sn from the system.

According to the thermal analysis studies, the degradation of **1** and **2** and the formation of tin sulfide occur at temperatures around 200 °C. The formation of $C(NH_2)_3Sn^{III}Cl_3$ is detected in **1** heated up to 210 °C and not detected in **2**. The $C(NH_2)_3Sn^{III}Cl_3$ phase might form $SnCl_2$ upon the thermal degradation, which can be easily oxidised. Thus, the formation of crystalline SnO_2 phase for **1** is detected at the lower

temperature of 320 °C compared to that for **2** at 475 °C according to XRD. Although the results of thermoanalytical investigations cannot be directly forwarded to the chemical spray pyrolysis process, it is clearly seen that the use of thiourea-rich precursors retards the formation of SnO₂.

3.2 Tin sulfide films grown by the chemical spray pyrolysis method

This section summarises the effects of the substrate temperature and starting chemicals (tin(II) chloride and thiourea or L-cysteine) molar ratio in a spray solution on the properties of tin sulfide films. Tin sulfide films were grown using aqueous solutions containing SnCl₂ and SC(NH₂)₂ [**II**] or HSCH₂(NH₂)CHCO₂H [**III**] at molar ratios varied from 1:1 to 1:8. Hereinafter the abbreviation "Sn:S" is employed for SnCl₂:SC(NH₂)₂ and SnCl₂:HSCH₂(NH₂)CHCO₂H molar ratio in a spray solution. The substrate temperature (Ts) in [**II**, **III**] implies the growth temperature measured on the substrate surface during the deposition process. Films were deposited in ambient conditions at different substrate temperatures varied in the region of 200–370 °C.

3.2.1 Tin sulfide films by chemical spray pyrolysis using thiourea as a sulfur source

Effect of the growth temperature

The structural properties such as phase compositions, crystallite sizes, the preferred crystallite orientation of sprayed tin sulfide films were characterised using XRD. Figure 3.7 compares X-ray diffractograms of the films grown at various substrate temperatures. At the early stage of this study, the data on the existence of various tin monosulfide polymorphs were insufficient. For this reason, in [**II**, **III**], the diffraction peaks located at 2θ values of 23.0, 26.7, 30.9, 31.8, 38.8, 44.3, and 45.0° were assigned to the orthorhombic SnS phase (PDF 01-083-1758) [112].

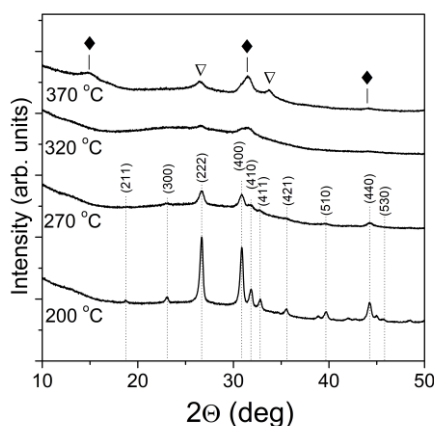


Fig. 3.7 XRD patterns of SnS films grown at $T_s = 200\text{--}370\text{ }^{\circ}\text{C}$ using a SnCl₂:SC(NH₂)₂ molar ratio of 1:2 in the spray solution. The peaks marked with (hkl) indices belong to the cubic SnS [119], «▽» belong to SnO₂ phase (JCPDS 01-077-0452), «◆» belong to SnS₂ phase (JCPDS 01-089-2028). (A modified version of Fig. 1 in [**III**]).

XRD peaks located at 2θ values of 18.8, 32.8, 35.5, 39.7, 42.2, 42.9, 45.8, and 48.5° remain unidentified (See Fig. 1 in [II] and Fig. 2 in [III]). Thus, in that stage, we concluded that sprayed films contain an unknown crystalline phase in addition to orthorhombic SnS.

At the end of 2015, it was reported that a new cubic SnS (C-SnS) phase may exist in the Sn–S binary system [118]. The unit cell of this structure is a large cube with a cube edge of $a \approx 11.6 \text{ \AA}$ [12, 118, 119], twice that of the zinc blende structure [119]. Tin sulfide films deposited by CBD [119] and AA-CVD [16] as well as nanocrystals synthesized by a hydrothermal chemical process [12] are composed of the C-SnS phase and show XRD patterns with the characteristic triple peaks in the 2θ regions of 30–33° and 43–46° [12, 119]. Considering the recently published papers [12, 118, 119], and taking into account the results of the XRD studies, we concluded that the sprayed tin sulfide films exhibiting diffractograms with the characteristic triple peaks in the 2θ regions of 30–33° and 43–46° are composed of the recently reported C-SnS phase. According to XRD, the films contain no unidentified "x" phase.

Diffractograms of the films deposited at 370 °C do not show the XRD peaks characteristic of C-SnS (Fig. 3.7). Peaks located at 2θ of 15.0, 31.6, and 44.0° correspond to the SnS₂ phase (JCPDS 01-089-2028), and those at 2θ of 26.5 and 33.8° belong to the SnO₂ phase (JCPDS 01-077-0452).

According to XRD (Fig. 3.7), the formation of higher tin oxides and sulfides is favourable in the films grown at temperatures above 320 °C. To find the reason of tin oxide phase formation at 370 °C, the films produced at 200 °C using 1:2 thiourea-based solutions were annealed for 1 h at 350 and 425 °C in air. The XRD patterns of as-grown and annealed in air C-SnS films can be found in Fig. 2 in [I]. The films annealed at 350 °C are composed of C-SnS as a main crystalline phase, diffraction peaks characteristic of Sn₂S₃ phase (JCPDS 01-075-2183) can be also detected on the XRD pattern. The SnO₂ phase was detected in addition to C-SnS and Sn₂S₃ when films were annealed at 425 °C in air. This experiment shows that the formation of SnO₂ phase in the films deposited at 370 °C is not caused by the oxidation of the C-SnS film.

Effect of the starting chemicals molar ratio in the spray solution

Figure 3.8 compares XRD patterns of SnS films deposited by spray of aqueous solutions containing SnCl₂ and SC(NH₂)₂ at molar ratios of 1:1, 1:2, 1:4 and 1:8 at 200 °C. Similar diffractograms were recorded for the films grown at 270 °C. According to XRD (Fig. 3.8) and Raman (see Fig. 1b in [IV]) studies, films consisted of cubic SnS as the only crystalline phase regardless of the molar ratio of the precursors in the spray solution.

Film parameters such as the films thickness, the crystallite size of C-SnS phase and the preferred orientation of SnS crystallites were affected by the Sn:S molar ratios in solutions. By increasing the sulfur source content in spray solutions, it seems that SnS crystallites have a preferred growth along the (222) plane, as the (222) peak is more pronounced in the 1:4 and 1:8 films compared to that in 1:1 and 1:2 films (Fig. 3.8).

For the C-SnS films grown at similar deposition temperatures, the increase in the crystallite size was observed with a gradual increase in the amount of thiourea in the spray solution. For instance, the crystallite sizes of C-SnS phase sprayed at 200 °C using 1:1 and 1:8 solutions were 17 and 35 nm, respectively (Table 3.2).

The crystallite size decreased with increasing the deposition temperature. For example, the crystallite sizes of C-SnS phase in films grown at 200 to 270 °C using the 1:1 solution were 17 and 9 nm, respectively (Table 3.2). In general, crystallite size in sprayed

films increases with an increase in the growth temperature. A reverse effect in C-SnS films could be explained by the formation of a secondary phase, likely tin oxide (see results of EDX studies, Table 3.2), which may retard the growth of SnS crystallites.

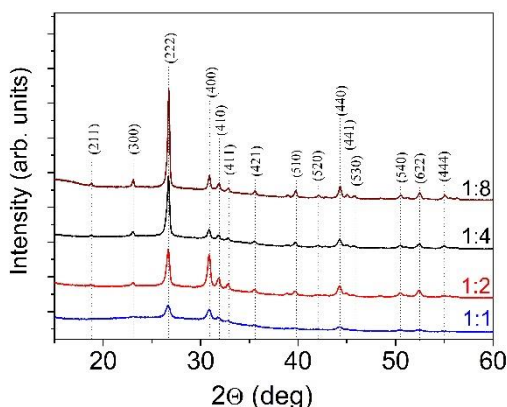


Fig. 3.8 XRD patterns of C-SnS films grown at $T_s = 200$ °C using the $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratios of 1:1, 1:2, 1:4 and 1:8 in the spray solution. All the peaks marked with (hkl) indices belong to the C-SnS phase [119]. (A modified version of Fig. 3 in [II]).

Table 3.2 The atomic ratio of Sn/S, and the atomic percentage of chlorine and oxygen according to EDX, crystallite size, film thicknesses and optical bandgap (E_g) of sprayed SnS films grown at 200 and 270 °C using solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at various Sn:S molar ratios.

Sn:S molar ratio in solution	T_s , °C	Sn/S atomic ratio in film	Cl, at. %	O, at. %	Crystallite size, nm	Film thickness, nm	Optical E_g , eV
1:1	200	1/0.5	7	41	17	445	2.1
	270	1/0.4	3	54	9	290	2.6
1:2	200	1/0.7	5	38	25	1160	1.9
	270	1/0.6	2	48	14	480	2.2
1:4	200	1/0.8	3	33	28	750	1.9
	270	1/0.7	1	43	15	610	2.1
1:8	200	1/0.9	2	29	35	1030	1.8
	270	1/0.9	1	32	23	1020	1.9

The phase composition of the films is affected by the amount of sulfur source in the spray solution and this effect becomes notably visible at growth temperatures above 320 °C. XRD patterns of the films deposited at 370 °C at different Sn:S molar ratios in spray solutions are compared in Fig. 3.9. Firstly, films prepared using the 1:1 thiourea-based solution consisted of SnO_2 . Secondly, spraying the solution with the $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratio of 1:2 yielded films composed of a mixture of SnS and SnS_2 phases. Finally, deposition performed using 1:4 solutions yielded films that consisted of a mixture of SnS + SnS_2 .

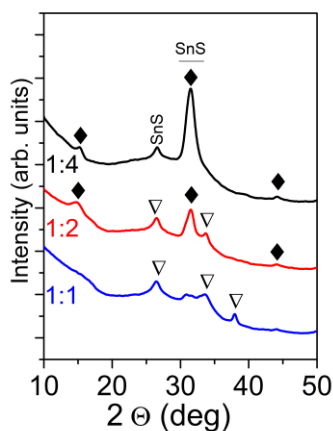


Fig. 3.9 XRD patterns of films grown at $T_s = 370^\circ\text{C}$ using $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratios of 1:1, 1:2 and 1:4 in the spray solution. The peaks marked with « ∇ » belong to SnO_2 phase (JCPDS 01-077-0452) and « $\blacklozenge$ » belong to SnS_2 phase (JCPDS 01-089-2028) [112].

Elemental composition and morphology of SnS films

EDX studies were used to evaluate the effect of the various deposition parameters on the chemical composition of sprayed SnS films. The chlorine impurities were detected in all the films grown below 320°C (Table 3.2). The Cl concentrations in the films decrease with an increase in the deposition temperature and in the amount of sulfur source in the spray solution.

All the films produced using tu-based solutions are sulfur-deficient irrespective of the growth temperature (Table 3.2). At similar growth temperatures, the sulfur deficiency is more apparent for films grown using low concentration of thiourea in the spray solution. For instance, the films deposited at 270°C using the 1:1 solution exhibit the Sn/S ratio of 1/0.4 in sprayed film, while a spray of 1:4 solution results in films with the Sn/S ratio of 1/0.7 (Table 3.2). The excess of tin notably decreased with a gradual increase in the amount of thiourea in the spray solution, the Sn/S ratio of 1/0.9 is characteristic of the film grown at 270°C from a highly thiourea-rich solution (1:8).

SEM studies of the sprayed films were performed in order to investigate the influence of the different experimental conditions on the morphological properties and film thicknesses. According to SEM images, the SnS films deposited using tu-based solutions are compact and crack and pin-hole free regardless of the molar ratio of starting chemicals (Fig. 3.10). The amount of sulfur source in the spray solution affects the thickness of films (Table 3.2, Fig. 3.10). At similar growth temperatures, the use of thiourea-rich solutions produces thicker films. For example, SnS films grown at 200°C using the 1:8 tu-based solutions show a thickness of ca 1030 nm, while spraying solutions with Sn:S molar ratio of 1:1 yielded films with a thickness of ca 440 nm.

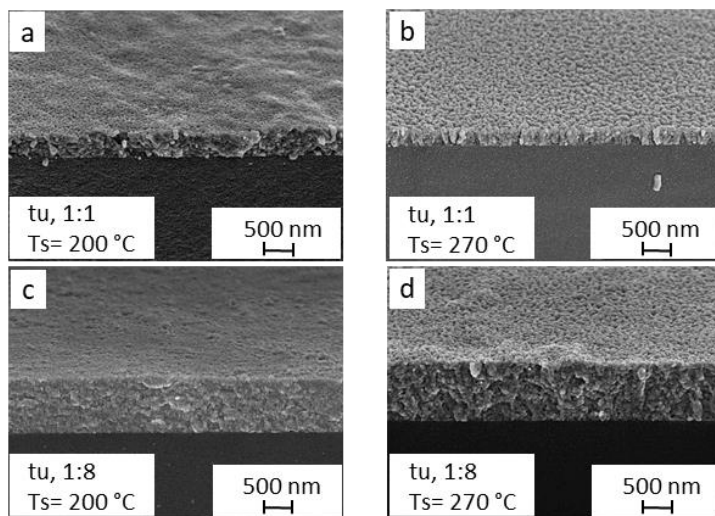


Fig. 3.10 SEM images of films grown at 200 and 270 °C using spray solutions with the $\text{SnCl}_2\text{:SC(NH}_2)_2$ molar ratios of (a, b) 1:1 and (c, d) 1:8. (A modified version of Fig. 5 in [II]).

Optical properties of SnS films

The UV–Vis measurements were used to evaluate the total optical transmittance and the optical bandgap values of the SnS films depending on different deposition parameters. The SnS films grown at 200 °C using the 1:4 and 1:8 tu-based solutions show the total optical transmittance around 70% in the visible and near-infrared spectral region (Fig. 3.11). Total optical transparency increased slightly using a lower amount of sulfur source in spray solutions. At similar growth temperatures, the number of interference fringes on the spectra of films grown using the 1:1 and 1:2 solutions is lower compared to the films sprayed using 1:4 and 1:8 solutions (Fig. 3.11), indicating the decrease in the film thicknesses as confirmed by SEM (Table 3.2). The absorption edge shifted from lower wavelength region to higher wavelengths by increasing the amount of thiourea in the spray solution.

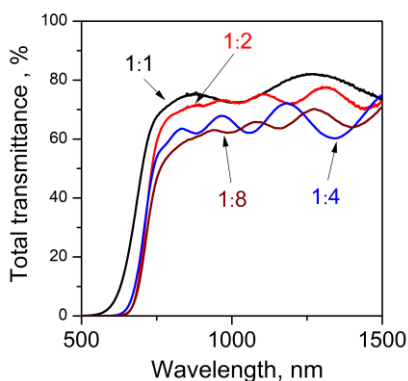


Fig. 3.11 Total transmittance spectra of SnS films grown at $T_s = 200$ °C using spray solutions with the $\text{SnCl}_2\text{:SC(NH}_2)_2$ molar ratios of 1:1, 1:2, 1:4 and 1:8.

The optical bandgap values (E_g) of films were determined from total transmittance spectra using the well-known Tauc equation:

$$\alpha h\nu^n = A(h\nu - E_g) \quad (3.6)$$

where α is the absorption coefficient, h is the Planck constant, A is a constant that is independent of the photon energy, E_g is the bandgap energy, $h\nu$ is the incident photon energy, and $n = 2$ for direct transitions. The E_g values were found by extrapolating the straight-line portion of the $(\alpha h\nu)^2$ versus $h\nu$ graph to a zero absorption coefficient value (See Fig. 7 in [IV]). The optical bandgap values of all the films are tabulated in Table 3.2. At similar growth temperatures, optical bandgap values of films deposited by spraying the 1:8 solutions are lower than those values calculated for the films grown using 1:1 and 1:2 solutions. For instance, the E_g value of 2.6 eV for the 1:1 film grown at 270 °C is higher than that for the 1:8 film, 1.9 eV. The difference can be explained by the presence of an amorphous oxygen-containing phase with a higher E_g value in the 1:1 film. C-SnS films deposited at 200 °C using the 1:8 solution exhibit the E_g value of 1.8 eV, similar to that reported for the CBD-grown C-SnS films having E_g values of 1.65–1.8 eV [119, 120].

Summary of the deposition of sprayed SnS films using thiourea as a sulfur source

SnS films can be deposited in air by the CSP method using aqueous solutions containing tin(II) chloride and thiourea. Films grown in the temperature range of 200–270 °C are composed of cubic SnS as a dominant phase independent of a Sn:S molar ratio used in the spray solution. At similar growth temperatures, spraying the solutions with a higher amount of thiourea yields thicker films with lower oxygen and chlorine content and lower bandgap values. Nebulizing the solutions with higher content of thiourea produces more stoichiometric films with larger SnS crystallites.

The molar ratio of starting chemicals in the spray solution controls the phase composition; this effect becomes evidential when films are grown at 370 °C. The amount of thiourea in the spray solution higher than required for the formation of intermediate complexes, $\text{Sn}(\text{tu})\text{Cl}_2$ and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, retards the formation of SnO_2 phase in sprayed films grown at temperatures above 320 °C. The formation of SnO_2 in tin sulfide films deposited at 370 °C is probably caused by the oxidation of tin chloride and not due to the oxidation of tin sulfide phases.

3.2.2 Effect of post-deposition thermal treatment on the properties of tin sulfide films grown by chemical spray pyrolysis

In order to develop a single-phase film with improved crystallinity compared to that of the as-deposited films and the optical properties required for an absorber material, C-SnS films grown at 200 °C using solutions with the starting chemicals (tin(II) chloride and thiourea) molar ratios of 1:1 and 1:8 were thermally treated in vacuum and nitrogen.

Phase composition of annealed 1:1 films

Figure 3.12a compares the XRD patterns of 1:1 films annealed in nitrogen and vacuum. According to the XRD results, the 1:1 film annealed in nitrogen at 450 °C is composed of

a mixture of C-SnS [12, 119] and SnO₂ (PDF 01-077-0452) crystalline phases. Thermal treatment of the 1:1 film in vacuum at 450 °C for 1 h yields a sample showing XRD reflections of the metallic Sn phase (PDF 01-086-2264) only [112]. The Raman spectrum of the 1:1 film annealed in flowing nitrogen (Fig. 3.12b) shows peaks at 110, 120, 175, 190, 200, and 225 cm⁻¹, which are characteristic of C-SnS [12, 16]. Raman shifts at around 175 and 260 cm⁻¹ might also belong to the mixed oxide states of SnO_x [121].

The Raman spectrum of the 1:1 film treated in vacuum reveals bands at 110, 175, 190, 200, and 225 cm⁻¹, indicating that the C-SnS phase is still present in the film, although the XRD results confirmed the presence of metallic Sn only (Fig. 3.12a).

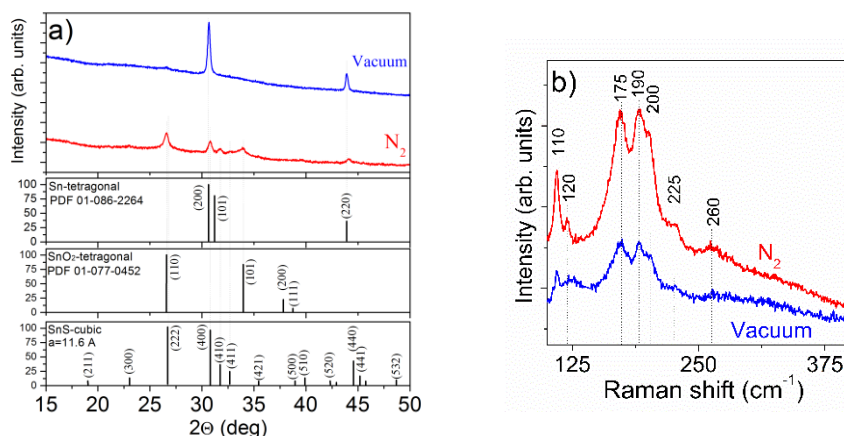


Fig. 3.12 (a) XRD patterns of sprayed films grown at 200 °C using a solution with a SnCl₂:SC(NH₂)₂ molar ratio of 1:1 and then annealed in N₂ or in vacuum at 450 °C for 1 h. (b) Raman spectra of 1:1 films annealed in N₂ or in vacuum at 450 °C for 1 h.

Phase composition of annealed 1:8 films

Figure 3.13a shows the XRD patterns of 1:8 films annealed in nitrogen and vacuum. The 1:8 film annealed in nitrogen consists of crystalline Sn₂S₃, as all the diffraction peaks could be assigned to the orthorhombic Sn₂S₃ phase (PDF 01-072-0031) [112]. The mean crystallite size of Sn₂S₃ is ca 54 nm. Annealing of the 1:8 film in vacuum at 450 °C for 1 h yields a film composed of orthorhombic SnS (PDF 01-072-8499) [112]. The mean crystallite size of the orthorhombic SnS in the vacuum-annealed film is ca 43 nm, which is slightly larger than the value of 35 nm characteristic of the as-grown C-SnS film (Table 3.2).

The Raman spectrum of the 1:8 film annealed in nitrogen (Fig. 3.13b) shows peaks at 152 and 235 cm⁻¹ and an intense peak at 307 cm⁻¹, which are characteristic of the Sn₂S₃ phase [3]. Thus, the Raman study supports the results of the XRD study regarding the presence of the Sn₂S₃ phase in the N₂-annealed 1:8 film. In addition, peaks at 110 and 175 cm⁻¹ and at around 190 cm⁻¹ are visible in the spectrum and indicate that the C-SnS phase is also present, although it was not detected by XRD. The 1:8 film annealed in vacuum exhibits Raman peaks at 156, 180, and 220 cm⁻¹ that correspond to orthorhombic SnS [122, 123]. This result is consistent with that recorded by XRD. The phase compositions of the samples according to the XRD and Raman studies are summarized in Table 3.3.

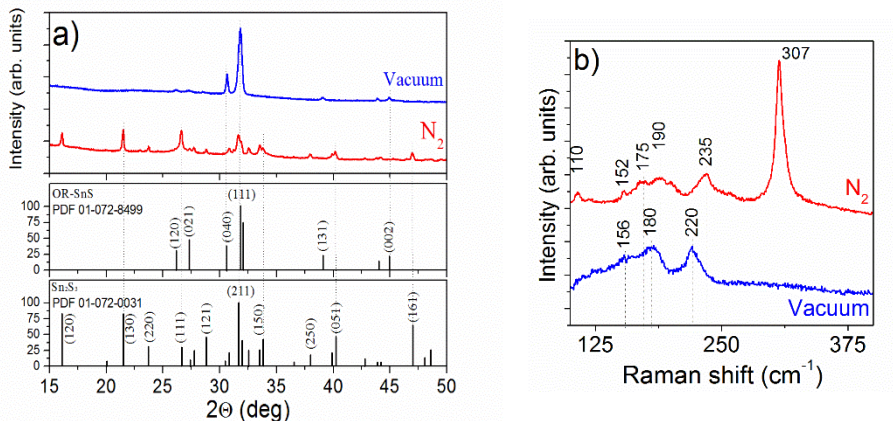
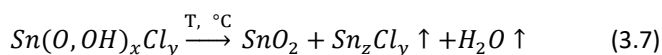


Fig. 3.13 (a) XRD patterns of sprayed films grown at 200 °C using a solution with a $\text{SnCl}_2\text{:SC(NH}_2)_2$ molar ratio of 1:8 and then annealed in N_2 or in vacuum at 450 °C for 1 h. (b) Raman spectra of 1:8 films annealed in N_2 or in vacuum at 450 °C for 1 h.

Discussion of the composition of as-deposited and annealed films

Table 3.3 lists the Sn/S atomic ratios and the atomic percentage of chlorine in the as-sprayed and annealed films based on the EDX results depending on the starting chemicals molar ratio (Sn:S) in the spray solution and the thermal treatment atmosphere. According to the EDX studies, the concentration of Cl is higher in the 1:1 as-deposited SnS film compared to the as-grown 1:8 film. Furthermore, the as-grown 1:1 and 1:8 films both are Sn-rich (Table 3.3), according to their Sn/S values of 1/0.5 and 1/0.9, compared to tin monosulfide. As the Sn excess is more pronounced for the 1:1 film, the presence of another Sn-containing phase is likely and has higher concentration in the as-grown 1:1 film. This assumption is supported by the EDX data on the Cl content (Table 3.3) and the following results from supporting studies: the FTIR spectrum of the 1:1 film material shows vibrations at around 3460–3580 cm^{-1} and at 1630–1670 cm^{-1} (see Fig. 5 in [IV]) characteristic of the (OH) group [124]; and XRD analysis confirms the formation of the SnO_2 phase during annealing in flowing nitrogen atmosphere (Fig. 3.13a). Thus, it can be proposed that the as-grown 1:1 film may contain an amorphous $\text{Sn(O,OH)}_x\text{Cl}_y$ phase.

It could be speculated that the SnO_2 phase detected in the 1:1 film annealed in N_2 forms upon the thermal decomposition of tin oxide hydroxide chloride according to the following schematic reaction:



According to the EDX result, the 1:1 film annealed in vacuum is highly tin-rich ($\text{Sn/S}=1/0.3$); the film is composed of a mixture of Sn and SnS phases, and SnO_2 was not detected (Table 3.3). The formation of Sn upon annealing of the 1:1 film in vacuum is thought to be explained by the following summary reaction:

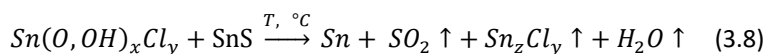


Table 3.3 Main phases according to the XRD and Raman studies, the mean crystallite size (*D*) of a main phase according to XRD data, the atomic ratio of Sn/S, and the atomic percentage of chlorine according to EDX data, and optical bandgap (*E_g*) of sprayed films grown at 200 °C using solutions containing SnCl₂ and SC(NH₂)₂ at molar ratios of 1:1 and 1:8 (Sn:S = 1:1 and SnS = 1:8) and of those annealed in N₂ and vacuum at 450 °C for 1 h.

Sn:S molar ratio in solution	Treatment	Sn/S atomic ratio in film	Cl at. %	Main phases, XRD	D nm	Main phases, Raman	E _g , eV
1:1	As-dep	1/0.5	7	C-SnS	17	C-SnS	2.1
	N ₂	1/0.5	< 1 ^a	C-SnS SnO ₂	18	C-SnS (SnO _x)	1.8
	Vacuum	1/0.3	< 1 ^a	Sn	-	C-SnS	-
1:8	As-dep	1/0.9	1	C-SnS	35	C-SnS	1.8
	N ₂	1/0.7	< 1 ^a	Sn ₂ S ₃	54	Sn ₂ S ₃ C-SnS	1.7
	Vacuum	1/0.9	< 1 ^a	Ort-SnS	43	Ort-SnS	1.4

^a below the detection limit of EDX.

Considering that the as-deposited 1:8 film shows the Sn/S ratio of 1/0.9 and the film contains 1 at. % of chlorine according to the EDX results (Table 3.3), it could be assumed that non-crystalline Sn₂Cl_y and/or Sn(O,OH)_xCl_y secondary phases may also be present in the as-grown 1:8 film. However, when present, they appear in much lower amount than in the 1:1 film as the FTIR spectrum of the as-grown 1:8 film shows no vibrations characteristic of the hydroxyl group (Fig. 5 in [IV]), and the formation of tin oxide was not detected after annealing. The as-grown and vacuum-annealed 1:8 films both show some sulfur deficiency compared to tin monosulfide. Although the N₂-annealed 1:8 film is composed of Sn₂S₃ as the main crystalline phase (Fig. 3.13a and b), the Sn/S value of 1/0.7 suggests that a secondary Sn-containing non-crystalline phase is probably present.

To summarise, the presence of secondary phases in films can be reduced by spraying the thiourea-rich solution with the Sn:S molar ratio of 1:8, followed by annealing in vacuum at 450 °C for 1 h.

Optical properties of annealed SnS films

The bandgap values of the thermally treated films evaluated from the UV–vis transmittance spectra using the Tauc relation (3.6) are presented in Table 3.3.

Post-deposition annealing in N₂ decreased optical bandgap values of 1:1 and 1:8 films compared to the as-deposited films. This effect is more pronounced for the films grown using solutions with a Sn:S molar ratio of 1:1. It might be explained by the decomposition of incorporated OH groups and the formation of tin oxide phase (see reaction 3.7), as the concentration of Sn(O,OH)_xCl_y secondary phase is probably higher in the as-deposited 1:1 films. In general, tin oxide phase(s) have lower bandgap values than the corresponding tin hydroxide(s). Thermal treatment of the 1:8 film in vacuum results in an *E_g* value of 1.4

eV (Table 3.3, Fig. 7 in [IV]), which is close to 1.33 eV reported for orthorhombic SnS films grown by HVE and CBD [104, 122].

Summary of annealing of sprayed SnS films using thiourea as a sulfur source

To summarise, in the fabrication of tin monosulfide films by the CSP methods, the amount of the sulfur source in the spray solution seems to be the key parameter. After annealing in N₂ at 450 °C for 1 h, the films deposited using the 1:1 solution were composed of a mixture of cubic SnS and SnO₂, whereas the 1:8 films annealed under similar conditions consisted of Sn₂S₃ as the main crystalline phase. After annealing in vacuum at 450 °C for 1 h, the 1:1 films mainly consisted of metallic Sn phase. Orthorhombic SnS layers with an E_g value of 1.4 eV can be produced using the 1:8 films grown at 200 °C after annealing in vacuum at 450 °C for 1 h.

3.2.3 Tin sulfide films by chemical spray pyrolysis using L-cysteine as a sulfur source

Effect of the growth temperature

Diffraction patterns of the films deposited in the temperature interval of 200–370 °C using solutions with a SnCl₂:L-HSCH₂(NH₂)CHCO₂H molar ratio of 1:1 (see Fig. 2 in [III]) are similar to those recorded for all films grown at temperatures below 320 °C using thiourea-based solutions (Fig. 3.7). Cubic SnS is the only crystalline phase of all the films deposited using the 1:1 L-cysteine-based solution. While some minor changes in SnS crystallite size were observed, there appears to be no correlation to the deposition temperature; the mean SnS crystallite size of all the films is relatively consistent at around 20 nm irrespective of the deposition temperature.

Effect of the starting chemicals molar ratio in the spray solution

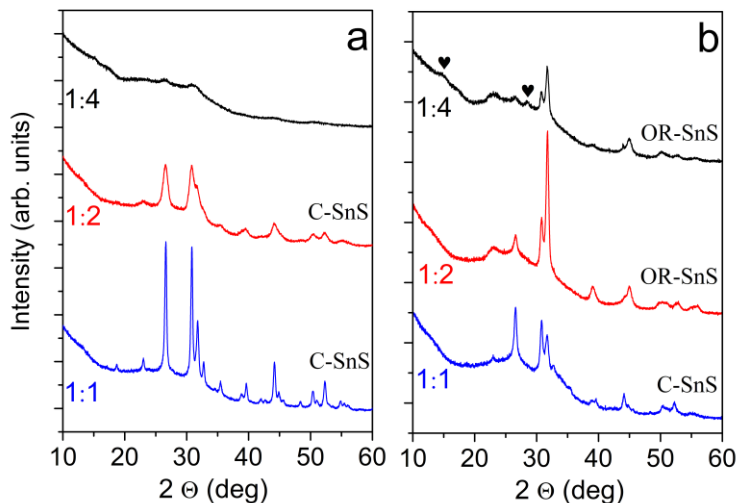


Fig. 3.14 XRD patterns of films grown at (a) $T_s = 270$ °C and (b) $T_s = 370$ °C using the SnCl₂:HSCH₂(NH₂)CHCO₂H molar ratios of 1:1, 1:2 and 1:4 in the spray solution. The peaks marked with « ♥ » belong to Sn₂S₃ phase (JCPDS 01-072-7600) [112]. (A modified version of Fig. 3 in [III]).

XRD patterns of films deposited by spraying of aqueous solutions containing SnCl_2 and L-cysteine at molar ratios of 1:1, 1:2 and 1:4 at 270 and 370 °C are presented in Fig. 3.14. C-SnS is the only crystalline phase of the films deposited at 270 °C using 1:1 and 1:2 solutions. It is clearly seen that the diffraction peaks of SnS weaken and become wider by increasing the L-cysteine concentration in the spray solution. Changing the molar ratio of starting chemicals in the spray solution from 1:1 to 1:2, the mean crystallite size decreases from 21 to 10 nm (Table 3.4). The films produced using the 1:4 solution are almost amorphous (Fig. 3.14a). Thus, there is no reason to use solutions with high amount of L-cysteine in the spray solution. These experiments demonstrate that L-cysteine as a sulfur source acts differently compared to thiourea, when an excess of thiourea in the spray solution promotes the growth of larger SnS crystallites (Table 3.2). Melted phase and /or high content of organic residues from L-cysteine could be responsible for retarding the SnS crystallite growth (Table 3.4).

The amount of sulfur source in the spray solution has a visible effect on the phase composition of films at 370 °C (Fig. 3.14b). At similar deposition temperature, spraying the 1:1, 1:2 and 1:4 solutions resulted in the films consisting of C-SnS, orthorhombic SnS and a mixture of orthorhombic SnS + Sn_2S_3 phases, respectively. Solution composition has insignificant effect on SnS crystallite size in films produced at 370 °C (Table 3.4). According to the XRD studies, at similar molar ratios of starting chemicals in spray solutions (Sn:S= 1:1 or 1:2), the use of L-cysteine as a sulfur source instead of commonly used thiourea inhibits the formation of crystalline tin oxide phase in films grown at 370 °C (Figs. 3.7 and 3.14).

Table 3.4 The atomic ratio of Sn/S, and the atomic percentage of chlorine, oxygen and carbon according to EDX, crystallite size, film thicknesses and optical bandgap (E_g) of sprayed SnS films grown at 270 and 370 °C using solutions containing SnCl_2 and $\text{HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ at various Sn:S molar ratios.

Sn:S molar ratio in solution	T_s , °C	Sn/S atomic ratio in film	Cl, at. %	O, at. %	C, at. %	Crystallite size, nm	Film thickness, nm	E_g , eV
1:1	270	1/0.8	2	31	20	21	1340	1.8
	370	1/0.7	1	41	12	15	1000	2.1
1:2	270	1/1.2	1	29	26	10	1600	1.8
	370	1/1.0	<1 ^a	30	18	19	850	1.7
1:4	270	1/1.4	<1 ^a	27	32	-	1580	-
	370	1/1.0	<1 ^a	31	19	18	750	2.0

^a below the detection limit of EDX.

To summarise, irrespective of the molar ratio of starting chemicals in the spray solution, films deposited in the region 270–370 °C using L-cysteine as a sulfur source are composed of cubic or orthorhombic SnS. Film phase composition is affected by the molar ratio of precursors in the spray solution. This effect is notable at the deposition temperature of 370 °C.

The EDX data in Table 3.4 show that regardless of the deposition temperature and Sn:S ratio in the spray solution, the films contain a considerable amount of oxygen and carbon. Carbon content is decreased with increasing the deposition temperature up to 370 °C, as the carbon residue originated from the sulfur source is decomposed. However, the carbon content is still high in the films at this temperature, indicating incomplete decomposition of L-cysteine at temperatures used for film deposition [107]. As expected, the relative amount of oxygen content in the films is reduced mostly by the higher amount of sulfur source in spray solution at both deposition temperatures (Table 3.4). The concentration of chlorine in the films decreases with increasing the deposition temperature and amount of L-cysteine in the spray solution. Observed behaviour is similar to that demonstrated for the films deposited using thiourea-based solutions (Table 3.4).

All the films sprayed using the 1:1 solution are sulfur-deficient, independent of the growth temperature (Table 3.4). The films grown at 270 °C using solutions with the Sn:S molar ratios of 1:2 and 1:4 were found to be sulfur rich with the film Sn/S ratios of 1/1.2 and 1/1.4, respectively (Table 3.4). Deposition performed at 370 °C using the 1:2 and 1:4 L-cysteine-based solutions yielded films with film Sn/S ratios of 1/1. These results differ from those reported for the films grown using thiourea as a sulfur source, as all the films were found to be sulfur-deficient irrespective of deposition temperature and the $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratio in solution.

According to the cross-sectional images, the SnS are compact and crack-free regardless of the deposition temperature and the Sn:S molar ratio in the solution (Fig. 3.15). The film thickness was found to depend on the content of L-cysteine in the spray solution (Table 3.4). According to the XRD and EDX studies, the use of L-cysteine as a sulfur source in the spray solution instead of thiourea requires higher deposition temperatures (above 270 °C) and the Sn:S molar ratio below 1:4. Films grown at 370 °C using solutions with a Sn:S molar ratio of 1:2 are thinner than those grown from 1:1 solution, thicknesses are 850 and 1000 nm, respectively (Table 3.4).

The optical bandgap values of SnS films grown using L-cysteine as a sulfur source were determined from total transmittance spectra using the Tauc relation (3.6), and tabulated in Table 3.4. The cubic SnS films sprayed at 270 °C using L-cysteine-based solutions with Sn:S molar ratios of 1:1 and 1:2 showed E_g ca 1.8 eV, similar to that measured for the C-SnS films deposited at 200 °C using thiourea-rich solutions with a Sn:S molar ratio of 1:8 (Table 3.3). Spraying the 1:2 L-cys-contained solutions at 370 °C yielded a film with a E_g value of 1.7 eV, the film was composed of orthorhombic SnS according to XRD (Fig. 3.14b). At the similar growth temperature, spraying the 1:1 and 1:4 solutions containing L-cysteine as a sulfur source yielded films with E_g values of ca 2.0 eV (Table 3.4). The variations in the bandgap values might be attributed to the presence of other tin compounds in films such as Sn_2S_3 or amorphous tin oxide (SnO_2) phases [49].

To summarise, the film thickness, the relative amount of sulfur, chlorine and carbon decreased with an increase in the deposition temperature.

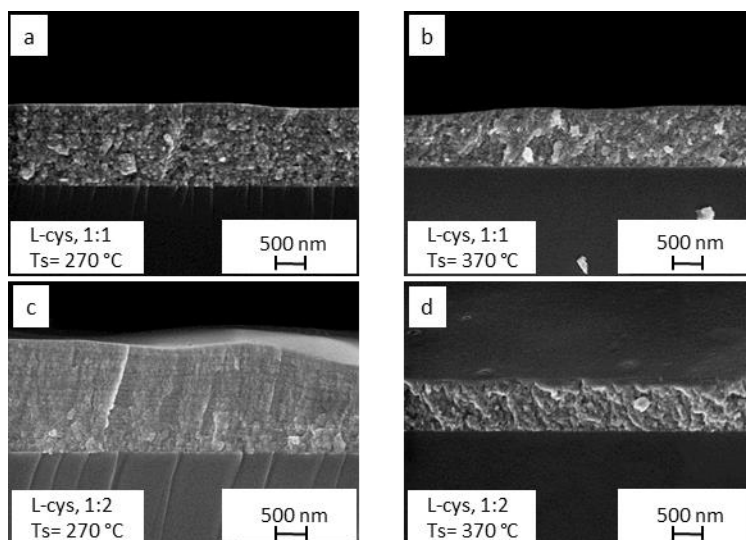


Fig. 3.15 SEM images of films grown at different temperatures using spray solutions with the $\text{SnCl}_2\text{:HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ molar ratios of (a, b) 1:1 and (c, d) 1:2. (A modified version of Fig. 4 in [III]).

Summary of the deposition of sprayed SnS films using L-cysteine as a sulfur source

SnS films can be produced by the CSP methods using aqueous solutions containing tin(II) chloride and L-cysteine as a sulfur source. Films grown at 200 and 270 °C are composed of cubic SnS as the only crystalline phase when the 1:1 and 1:2 solutions are sprayed. At similar deposition temperatures, the use of higher amount of L-cysteine in the spray solution yields films with lower content of chlorine and oxygen and higher content of carbon. The effect of a $\text{SnCl}_2\text{:HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ molar ratio in the spray solution on film phase composition becomes evidential when films are grown at 370 °C. Increasing L-cysteine amount in spray solutions leads to the phase transition from cubic to orthorhombic SnS. At the similar molar ratio of starting chemicals (Sn:S= 1:1 or 1:2), employing L-cysteine as a sulfur source instead of commonly used thiourea inhibits the formation of crystalline SnO_2 phase in the films deposited at 370 °C.

Conclusions

The main conclusions from this thesis research can be formulated as follows:

1. In aqueous solutions, the formation of tin sulfide in the CSP process started with the formation of two tin thiourea complex compounds, $\text{Sn}(\text{tu})\text{Cl}_2$ or $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$. According to XRD, EDX and FTIR, the dried precursor **1** (derived from solutions with $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratio of 1:1) was $\text{Sn}(\text{tu})\text{Cl}_2$; the dried precursor **2** (derived from the 1:8 solution) was composed of a mixture of $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ and uncomplexed thiourea.
2. The thermal decomposition of **1** and **2** in the temperature range of 30–700 °C in air consisted of four mass loss steps. The final decomposition product of **1** and **2** in air was SnO_2 . The total mass loss of **1** is 68.0% higher than the theoretical value of 56.4%; while the mass loss of **2** of 84.5% is close to the theoretical value (81.9%). The solid decomposition products at 210 °C of **1** were SnS_2 , $(\text{NH}_4)_2\text{SnCl}_6$ and $\text{C}(\text{NH}_2)_3\text{SnCl}_3$, and of **2** were SnS , SnS_2 , $(\text{NH}_4)_2\text{SnCl}_6$ and NH_4Cl . The formation of SnO_2 for **1** was detected at 320 °C and for **2** at 475 °C. Thus, an excess of thiourea in the spray solution, compared to that required for the formation of intermediate complex compounds, suppressed the formation of the SnO_2 phase and enabled the formation of tin sulfide without notable amount of tin oxide phases in the temperature range of 200–320 °C.
3. The pneumatic spray pyrolysis method can be used for the fabrication of cubic SnS films in the temperature region of 200–270 °C using aqueous solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at a molar ratio of from 1:1 to 1:8. Increasing the deposition temperature from 200 °C up to 270 °C decreased the crystallite size of C-SnS (from 17 nm to 9 nm), chlorine content (from 7at.% to 3 at.%), film thicknesses (from 445 nm to 290 nm) for 1:1 films. Similar effects were observed for films grown using other molar ratios of starting chemicals in spray solutions.
4. The molar ratio of SnCl_2 and $\text{SC}(\text{NH}_2)_2$ in the spray solution affected the properties of films as follows:
 - In the temperature interval of 200–270 °C, films were composed of the C-SnS phase irrespective of the Sn:S molar ratio in the spray solution. At 200 °C, nebulising the 1:8 solution instead of the 1:1 solution yielded thicker films (1030 nm vs. 445 nm) with larger SnS crystallite size (35 nm vs. 17 nm), a Sn/S ratio closer to stoichiometry (1/0.9 vs. 1/0.5), lower chlorine content (2 at.% vs. 7 at.%) and lower bandgap value (1.8 eV vs. 2.1 eV).
 - The films sprayed at 370 °C were composed of SnO_2 when solutions with the $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratios of 1:1 and 1:2 were used. The use of 1:4 solutions yielded films consisting of a mixture of SnS and SnS_2 phases. The formation of the SnO_2 phase in the 1:1 and 1:2 films grown at 370 °C was not due to the oxidation of the SnS phase.
5. Post-deposition thermal treatments in nitrogen or vacuum at 450 °C for 1 h controlled the properties of sprayed tin sulfide films. Thermal treatment of 1:1 films in nitrogen produced films consisting of a mixture of cubic SnS and SnO_2 phases, whereas thermal treatment in vacuum yielded metallic Sn . The 1:8 films annealed in nitrogen were composed of Sn_2S_3 as a main crystalline phase.

Orthorhombic SnS films exhibiting an E_g value of 1.4 eV can be fabricated using films deposited at 200 °C from solutions with a $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratio of 1:8 and then thermally treated in vacuum at 450 °C for 1 h. The reason for the presence of the secondary phases in the annealed films was discussed. It was proposed that tin chloride hydrolysis products were likely to be present in the as-grown films and affected the phase composition of annealed films.

6. L-cysteine can be used as an alternative sulfur source instead of thiourea for the deposition of sprayed tin sulfide films, as it forms complexes with SnCl_2 soluble in aqueous solutions. Orthorhombic SnS films can be grown at 370 °C using solutions with a $\text{SnCl}_2:\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ molar ratio of 1:2.

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Abstract

Tin sulfide films by chemical spray pyrolysis: formation and properties

Tin monosulfide (SnS) as a possible absorber material in solar cells has received much research attention in recent years due to its high absorption coefficient, a direct bandgap of approximately 1.4 eV and abundance and nontoxicity of constituents.

This PhD dissertation was performed under the research projects completed or currently running in the Laboratory of Thin Film Chemical Technologies, TUT, Estonia.

The aim of the dissertation was to study the formation of tin sulfide in the chemical spray pyrolysis process; to investigate the influence of deposition temperature, molar ratios of starting chemicals (SnCl_2 and $\text{SC}(\text{NH}_2)_2$) in aqueous solutions and post-deposition thermal treatment on properties of tin sulfide films fabricated by the chemical spray pyrolysis method; and to evaluate possibilities of using $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ as an alternative sulfur source to replace thiourea.

In order to find a suitable solution composition and thermal conditions for the deposition of tin sulfide films by CSP in air, the formation of tin sulfide was studied with the help of a complex of simultaneous thermal analysis techniques. Thermal decomposition studies of intermediates derived from aqueous solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at molar ratios of 1:1 (**1**) or 1:8 (**2**) were conducted using simultaneous TG/DTA/EGA-MS measurements accompanied with *ex situ* XRD and FTIR studies, which were used to characterize the obtained intermediates and solid decomposition products.

The intermediate **1** consisted of $\text{Sn}(\text{tu})\text{Cl}_2$, whereas **2** consisted of $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ and uncomplexed $\text{SC}(\text{NH}_2)_2$. In both complex compounds, $\text{SC}(\text{NH}_2)_2$ was connected to tin cations via sulfur atom. The thermal decomposition of **1** and **2** in the temperature range of 30–700 °C consisted of four mass loss steps with the total mass losses of 68.0 and 84.5%, respectively. The final decomposition product of **1** and **2** in air was SnO_2 . Complex compounds start to decompose at 210 °C. The formation of SnO_2 was detected at lower temperature for **1** compared to that for **2**, at 320 °C and 475 °C, respectively. We demonstrated that excess of thiourea in the spray solution hinders the release of volatile tin species from the system and suppresses the formation of the SnO_2 phase.

Films were grown by CSP using aqueous solutions containing SnCl_2 (Sn) and $\text{SC}(\text{NH}_2)_2$ (S) as starting chemicals with molar ratios varied from 1:1 to 1:8 in the temperature range of 200–410 °C. According to XRD, films deposited in the temperature region of 200–270 °C were composed of cubic SnS phase regardless of the molar ratio of SnCl_2 and $\text{SC}(\text{NH}_2)_2$ in the spray solution. The use of solutions with Sn:S ratios of 1:1 and 1:2 at 370 °C yielded films with the dominating SnO_2 phase, while spraying thiourea-rich solutions (e.g. Sn:S = 1:4) retarded the formation of tin dioxide phase in films formed at 370 °C.

Post-deposition thermal treatments were performed for as-deposited films. Thermal treatment of 1:1 films in nitrogen resulted in a mixture of cubic SnS and SnO_2 phases, whereas annealing in vacuum yielded metallic Sn. Thermal treatment of 1:8 films in nitrogen yielded Sn_2S_3 , whereas in vacuum resulted in orthorhombic SnS films having an E_g value of 1.4 eV.

Our studies demonstrated that $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ can be used as an alternative sulfur source for the deposition of tin sulfide films by CSP as it forms soluble complexes with SnCl_2 in aqueous solutions. We showed that films consisting of the orthorhombic SnS phase can be grown at 370 °C using 1:2 solutions.

According to the results obtained in the thesis research, excess of $\text{SC}(\text{NH}_2)_2$ in aqueous solution retards the formation of the SnO_2 phase and inhibits the loss of tin species from the spray system. Aqueous solutions with $\text{SnCl}_2:\text{SC}(\text{NH}_2)_2$ molar ratio of 1:8 and the deposition temperature of 200 °C are suitable for the fabrication of cubic SnS films by CSP. Thermal treatment in vacuum for 1 h of 1:8 films is required to obtain layers consisting of the orthorhombic SnS phase, which exhibit a bandgap of 1.4 eV.

Kokkuvõte

Tinasulfiid kiled keemilise pihustuspürolüüsi meetodil: moodustumine ja omadused

Tina monosulfiid (SnS) sobib kõrge neeldumiskoeffitsiendi ($10^4\text{--}10^5$ 1/cm nähtavas valguses) ja keelutsooni sobiva väärtuse (1.4 eV) tõttu kasutamiseks päikesepatareides absorbermaterjalina. Tina, väävel ja nende ühendid ei ole mürgised ja on maakoores laialdaselt levinud.

Doktoritöö valmis Tallinna Tehnikaülikooli Keemiliste kiletehnoloogiate teaduslaboratooriumi teadusprojektide raames.

Doktoritöö eesmärk oli uurida tinasulfiidi moodustumist keemilise pihustuspürolüüsi meetodil ja sadestatud tinasulfiidkilede omadusi sõltuvalt sadestustemperatuurist, lähteainete (SnCl_2 and $\text{SC}(\text{NH}_2)_2$) molaarsuhtest vesilahuses ning termilistest järeltöötlustest. Samuti uuriti $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ võimalikku kasutatavust alternatiivse väävli allikana tinasulfiidkilede sadestamisel pihustuspürolüüsi meetodil.

Doktoritöös uuriti tinasulfiidi moodustumise protsessi, et määrata sobiv pihustuslahuse koostis ja kilede kasvatamise temperatuur. Antud töös näidati, et vesilahustes, kus SnCl_2 ja $\text{SC}(\text{NH}_2)_2$ olid molaarsuhtes 1:1 (**1**) või 1:8 (**2**) tekivad vaheühendid, mille termilisel lagunemisel tekib tinasulfiid. Kuivatatud pulbriliste vaheühendite uurimiseks ja nende termilise lagunemise uurimiseks rakendati termoanalüütiliste meetodite kompleksi (TG/DTG/DTA koos EGA-MS analüüsiga) ja *ex-situ* XRD- ning FTIR-analüüsi. Leiti, et vaheühend **1** koosnes $\text{Sn}(\text{tu})\text{Cl}_2$ kompleksühendist ja vaheühend **2** oli kompleksühendi $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ ja vaba $\text{SC}(\text{NH}_2)_2$ faaside segu. Mõlemas kompleksühendis oli $\text{SC}(\text{NH}_2)_2$ seotud tina katiooniga läbi väävli aatomi. **1** ja **2** termiline lagunemine temperatuuride vahemikus $30\text{--}700$ °C õhus koosnes neljast etapist ja lõpp-produktiks 700 °C juures oli SnO_2 , summaarsed massikaod oli vastavalt 68.0% ja 84.5%. Antud uurimistöö näitas, et tinasulfiid tekib vaheühendite lagunemisel esimeses etapis ca 200 °C juures, kusjuures tiokarbamiidi liig vähendab tina sisaldavate lenduvate ühendite kadu ja pidurdab SnO_2 faasi moodustumist.

Tinasulfiidkiled sadestati pihustuspürolüüsi meetodil vesilahusest, milles muudeti lähteainete SnCl_2 (Sn) ja $\text{SC}(\text{NH}_2)_2$ (S) molaarsuhet vahemikus 1:1 kuni 1:8 ja sadestustemperatuuri vahemikus $200\text{--}410$ °C. Leiti, et kiled mis olid sadestatud temperatuurivahemikus $200\text{--}270$ °C koosnesid kuubilisest SnS faasist sõltumata SnCl_2 ja $\text{SC}(\text{NH}_2)_2$ molaarsuhtest pihustuslahuses. Kiled, mis kasvatati 370 °C juures lahusest, kus Sn:S olid molaarsuhtes 1:1 ja 1:2, sisaldasid peamiselt SnO_2 faasi. Tiokarbamiidi liig (nt Sn:S = 1:4) pihustuslahuses pärssis SnO_2 faasi moodustumist kiledes.

Pihustussadestatud tinasulfiidkiledele teostati termiline järeltöötlus 450 °C juures. 1:1 kilede termilisel järeltöötlusel lämmastiku keskkonnas saadi kiled, mis koosnesid kuubilise SnS ja SnO_2 faaside segust ning termiline järeltöötlus vaakumis päädis metallilise Sn moodustumisega. 1:8 kiledele termilisel järeltöötlusel lämmastiku keskkonnas moodustus Sn_2S_3 faas, vaakumis moodustusid ortorombilise struktuuriga SnS kiled, mille keelutsooni laius oli 1.4 eV.

Antud uurimistöö tulemusena leiti samuti, et SnCl_2 ja $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ moodustavad vesilahuses kompleksühendi ja $\text{L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ saab kasutada alternatiivse väävli allikana tinasulfiidkilede sadestamiseks pihustuspürolüüsi meetodil.

Leiti, et lähtelahusest, kus $\text{SnCl}_2\text{:L-HSCH}_2(\text{NH}_2)\text{CHCO}_2\text{H}$ on molaarsuhtes 1:2, on 370 °C juures võimalik kasvatada ortorombilise struktuuriga SnS kilesid.

Dokoritöö tulemustest võib järeldada, et $\text{SC(NH}_2)_2$ liig pihustuslahuses pärsib SnO_2 moodustumist ja tina ühendite kadu pihustuspürolüüsi protsessis. Kuubilise struktuuriga SnS kilesid saab sadestada pihustuspürolüüsi meetodil 200 °C juures vesilahustest, kus $\text{SnCl}_2\text{:SC(NH}_2)_2$ on molaarsuhtes 1:8. Saadud kilede termilisel kuumutamisel vaakumis 450 °C juures on võimalik valmistada ortorombilise struktuuriga 1.4 eV keelutsooniga SnS kilesid.

Appendix

PAPER I

S. Polivtseva, I. Oja Acik, M. Krunks, K. Tõnsuaadu, A. Mere, Thermoanalytical study of precursors for tin sulfide thin films deposited by chemical spray pyrolysis, *J. Therm. Anal. Calorim.* 121 (2015) 177–185.

Thermoanalytical study of precursors for tin sulfide thin films deposited by chemical spray pyrolysis

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Abstract Thermal decomposition of precursors for SnS thin films obtained by drying aqueous solutions of SnCl_2 and $\text{SC}(\text{NH}_2)_2$ in the Sn:S molar ratios of 1:1 (**1**) and 1:8 (**2**) was monitored by simultaneous thermogravimetry/differential thermal analysis (TG/DTA) measurements in the dynamic 80 % Ar + 20 % O_2 atmosphere. The evolved gaseous species from **1** were recorded by simultaneous thermogravimetry/differential thermal analysis/evolved gas analysis–mass spectrometry (TG/DTA/EGA-MS) measurements. X-ray diffraction (XRD) and Fourier transform infrared spectroscopy (FTIR) were used to characterize the dried precursors and products of the thermal decomposition. The precursor **1** is a complex compound, $\text{Sn}(\text{tu})\text{Cl}_2$, while **2** consists of $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot \text{H}_2\text{O}$ and noncomplexed thiourea. The thermal degradation of **1** and **2** in the temperature range of 30–700 °C consists of four steps with a total mass loss of 68.0 and 84.5 %, respectively. According to XRD, the solid decomposition products at 210 °C of **1** are SnS_2 , $(\text{NH}_4)_2\text{SnCl}_6$ and $\text{C}(\text{NH}_2)_3\text{SnCl}_3$, and of **2** are SnS_2 , SnS, NH_4Cl and $(\text{NH}_4)_2\text{SnCl}_6$. Decomposition of **1** and **2** is completed by 550 and 570 °C, respectively. The final decomposition product of **1** and **2** at 700 °C is SnO_2 . This study shows that the excess of thiourea in the spray solution, compared to that required for the formation of the intermediate tin complex compounds, suppresses the formation of tin oxide phase and depresses the loss of tin species from the system.

Keywords Simultaneous thermogravimetry (TG) and differential thermal analysis (DTA) · Evolved gas analysis (EGA) · Mass spectroscopy (MS) · Tin sulfide · Thiourea · Chemical spray pyrolysis (CSP)

Introduction

Tin sulfide (SnS) is a promising absorbing material for thin film solar cells [1]. Different physical and chemical methods have been applied to deposit SnS films. One of them is chemical spray pyrolysis, which is simple, rapid and low-cost, non-vacuum method. In the chemical spray pyrolysis (CSP) process, aqueous or alcoholic solutions containing stannous chloride (SnCl_2) as tin source and thiourea ($\text{CS}(\text{NH}_2)_2$, tu) or substituted thiourea (N,N-diethyl or N,N-dimethyl thiourea) as sulfur source at the Sn:S molar ratio of 1:1 have been used for the SnS film deposition [2, 3].

It has been shown earlier that different metal sulfide thin films with device quality properties can be deposited by the CSP method [4]. It has been demonstrated by several reports that the molar ratio of the precursors (Metal and S sources, Me:S) in the spray solution has strong effect on the phase composition of metal sulfide films deposited by the CSP [5, 6]. It has been shown that thiourea content higher than required for the corresponding thiourea complex compound (viz. $\text{Zn}(\text{tu})_2\text{Cl}_2$, $\text{In}(\text{tu})_3\text{Cl}_3$) formation suppresses the oxygen content in the sprayed films [5, 6]. It has been demonstrated in [7–9] that the phase composition of sprayed tin sulfide films, similarly to ZnS and In_2S_3 films, depends on the precursors (Sn:S) molar ratio in the spray solution. Moreover, in our previous study on sprayed SnS films we demonstrated that at similar deposition temperatures the spray of solutions with higher content of

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thiourea results in thicker SnS films with lower bandgap and decreased chlorine and oxygen content [9]. Thus, the formation chemistry studies of thin sulfides are important in order to model the process and to determine the optimal solution and thermal conditions of CSP.

Thermal decomposition of two tin complex compounds, $\text{Sn}(\text{tu})\text{Cl}_2$ and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, as single source precursors for SnS films, has been studied by Madarász et al. [10–12]. According to the results in [10], the thermal decomposition of $\text{Sn}(\text{tu})\text{Cl}_2$ in air leads to SnS_2 as a main phase at temperatures up to 290 °C, while SnO_2 phase was dominating at temperatures above 370 °C. However, in the case of the thiourea-rich complex, $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, the formation of SnO_2 phase was shifted to 400 °C. Previous studies on the thermal decomposition of precursors for In_2S_3 and CuInS_2 [16, 22] showed that an excess of thiourea in the spray solution (compared to that of the corresponding metal chloride thiourea complex compound) suppresses the formation of metal oxide phase and depresses the loss of metal species from the system. However, there is still a lack of knowledge how the excess of tu influences the formation of tin sulfide.

In this paper, we report the results on the thermal decomposition of the dried precursors for tin sulfide films, formed in an aqueous solution with Sn:S molar ratios of 1:1 and 1:8. The solid intermediates and the final products of the thermal decomposition were characterized by ex situ FTIR and XRD. The aim of the study was to get better understanding of the formation of tin sulfide films in the chemical spray pyrolysis process.

Experimental

Chemicals

Thiourea ($\text{SC}(\text{NH}_2)_2$, tu) (p.a. > 98 %, Merck-Eurolab K29087778), dihydrated stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) (p.a. > 98 %, Sigma-Aldrich SZBB2090V) and hydrochloric acid (HCl) (p.a. 37 %, Sigma-Aldrich SZBA2780) were used for synthesis. Deionised water was used for solutions. The chemicals were used as received without any further purification.

Synthesis of precursors

The precursor solutions were prepared by dissolving a proper amount of $\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ in 1 mol L⁻¹ aqueous solution of $\text{SC}(\text{NH}_2)_2$ containing few drops of concentrated HCl. SnCl_2 and $\text{SC}(\text{NH}_2)_2$ molar ratios in the solutions were 1:1 (**1**) and 1:8 (**2**). The solution was let to slowly evaporate at room temperature for 5 days, followed by further drying at 35 °C for 24 h in air.

Characterization of dried precursors and products of their thermal decomposition

Fourier transformed infrared (FTIR) spectroscopy and X-ray diffraction (XRD) analyses were used to characterize **1** and **2**, and the solid intermediates and the final products of their thermal decomposition. FTIR transmission spectra were recorded in the region of 4000–400 cm⁻¹ on a Perkin-Elmer GX1 spectrometer using the KBr pellet technique. The XRD patterns were recorded by a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.5406$ Å, 40 kV at 40 mA) using the silicon strip detector D/teX Ultra. The elemental composition of **1** and **2** was studied by energy dispersive spectroscopy (EDS). The analysis was performed on the Zeiss ULTRA 55 device with Bruker EDS detector.

Heat treatments of **1** and **2** were also performed in a preparative scale in air using a Nabertherm laboratory oven and open Al_2O_3 crucibles. Heat treatment temperatures were determined on the bases of the dynamic TG curves. The annealing time at chosen temperature was fixed to 5 min, after that the sample was taken out from the oven and cooled down under ambient conditions. The cooled residues were subjected to the analysis.

Thermal analysis

The simultaneous TG/DTA/EGA–MS measurement of **1** was performed in an apparatus consisting of a SetSys-Evo 1600 (Setaram, France) thermal analyzer and an OmniStar (Pfeiffer, Germany) quadrupole mass spectrometer. Coupling between the two components was provided through a heated capillary tube kept at 180 °C. The ion currents of the selected mass/charge (m/z) numbers were monitored in multiple ion detection (MID) mode (Quadera version 4.20 software) with the collecting time of 1 s for each channel.

The TG/DTA measurement of **2** was performed on the SetSys-Evo 1600 thermal analyzer. The TG/DTA/EGA–MS and TG/DTA measurements of **1** and **2**, respectively, were carried out in a dynamic 80 % Ar + 20 % O₂ atmosphere in the temperature range of 30–700 °C using the heating rate of 10 °C min⁻¹, the gas flow rate of 60 mL min⁻¹ and open Pt crucibles. The initial mass of sample **1** was 15.0 mg, and of **2** was 15.0 mg.

The evolved gases were identified on the basis of their MS reference spectra available on World Wide Web in the public domain spectral libraries of NIST [13].

Results and discussion

Characterization of dried samples **1** and **2**

Figure 1 shows the IR spectra of the dried samples **1** and **2** and that of thiourea (tu). The spectrum of tu shows a

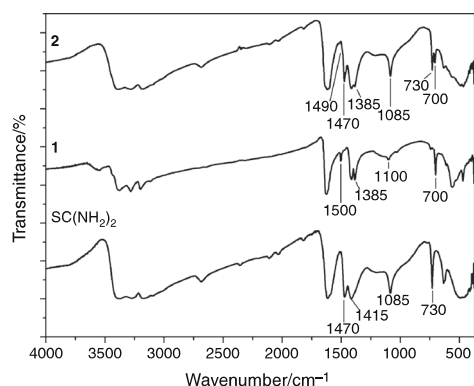


Fig. 1 FTIR spectra of dried samples **1**, **2** and thiourea ($\text{SC}(\text{NH}_2)_2$) recorded at room temperature

vibration at 1470 cm^{-1} being characteristic of CN group stretching vibrations, $\nu(\text{CN})$ [14]. The IR spectra of **1** and **2** show that the $\nu(\text{CN})$ vibration is shifted to higher wavenumbers, viz. 1500 and 1490 cm^{-1} , respectively. The increased wavenumbers of the CN group vibration in **1** and **2** show the strengthening of the bond between carbon and nitrogen atoms [14, 15]. The characteristic stretching vibrations of CS group, $\nu(\text{CS})$, are peaked at 1415 and 730 cm^{-1} in the spectrum of tu. In **1** and **2**, these vibrations are shifted to 1385 and 700 cm^{-1} , respectively. The shift of the CS group stretching vibrations toward lower wavenumbers in **1** and **2** compared to that of tu is due to the reduced double-bond character between carbon and sulfur atoms [15–18]. This shows that the coordination of ligand to metal atoms occurs through the sulfur atom in **1** and **2**. Moreover, the spectrum of **2** shows additional vibrations at 1470 and 730 cm^{-1} . These vibrations are characteristic of $\nu(\text{CN})$ and $\nu(\text{CS})$ in noncomplexed tu, respectively.

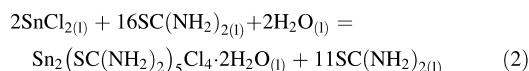
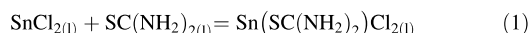
According to FTIR study, **1** is a complex compound where tu is connected to the Sn cation through the sulfur atom, while **2** is consisted of a complex compound and free thiourea.

According to the Powder Diffraction File (PDF) database [19], **1** and **2** are crystalline materials. XRD analysis showed that **1** is composed of $\text{Sn}(\text{SCN}_2\text{H}_4)\text{Cl}_2$ (JCPDS 01-075-1290) [19], and **2** contains crystalline phases of thiourea (JCPDS 00-009-0790) [19] and a phase which is isostructural with the $\text{Sn}_2(\text{SCN}_2\text{H}_4)_5\text{Br}_4 \cdot 2\text{H}_2\text{O}$ [20], and probably is its chloride analogue, $\text{Sn}_2(\text{SCN}_2\text{H}_4)_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$, as proposed by Madarász et al. [10, 11].

According to EDS, the elemental composition (found, in at. %) of **1** is as follows: Sn 22.4 %, S 22.1 % and Cl 42.5 %; and of **2** is as follows: Sn-5.9 %, S-48.9 % and Cl-19.0 %. As the light elements cannot be determined by EDS, we can only compare the ratios of atomic

percentages. The Sn:Cl:S ratio of 1:1.9:1.0 in **1** is very close to that calculated for a compound with the formula $\text{SnCl}_2 \cdot (\text{SCN}_2\text{H}_4)$, where Sn:Cl:S ratio is 1:2:1. In the case of **2**, the Sn:Cl:S ratio of 1:3.2:8.3 is close to that calculated for a mixture of $(\text{SnCl}_2 \cdot 2.5(\text{SCN}_2\text{H}_4) \cdot \text{H}_2\text{O} + 5.5(\text{SCN}_2\text{H}_4))$, with the Sn:Cl:S ratio of 1:2:8.

Based on the FTIR, XRD and EDS study, the complex formation reaction between the SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at molar ratios of 1:1 (**1**) and 1:8 (**2**) in aqueous solutions could be presented as reactions (1) and (2), respectively.



Thermal analysis

The TG, DTG and DTA curves of **1** are presented in Fig. 2. According to DTG, the thermal degradation of **1** in the temperature region of $30\text{--}700^\circ\text{C}$ in flowing (80 % Ar + 20 % O_2) consists of four mass loss steps (Fig. 2; Table 1). The first decomposition step of **1** is in the range of $30\text{--}210^\circ\text{C}$. The thermal decomposition of **1** immediately starts after the endothermic melting of the compound at 158°C [10, 12, 21]. The second decomposition step in the temperature range of $210\text{--}320^\circ\text{C}$ shows an exothermic process at 275°C and an endothermic process at 300°C ,

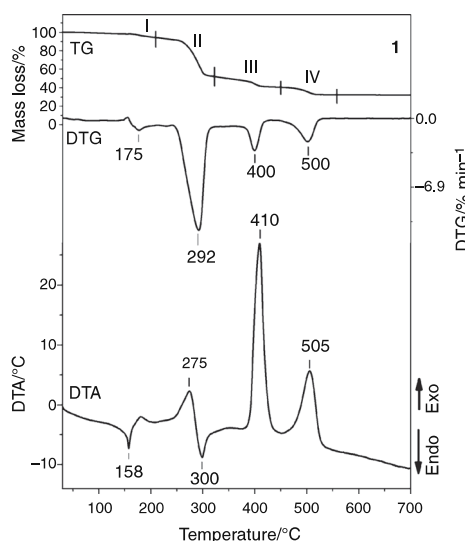


Fig. 2 Simultaneous TG/DTG/DTA curves of **1**. Flowing (80 % Ar + 20 % O_2): flow rate 60 mL min^{-1} , heating rate: $10^\circ\text{C min}^{-1}$. The initial mass of sample **1** was 15.0 mg

Table 1 Decomposition steps, mass losses and temperatures of DTA and DTG peaks of dried samples of **1** and **2**, recorded using the heating rate of 10 min^{-1} in flowing (80 % Ar and 20 % O_2) atmosphere on the SetSys-Evolution instrument

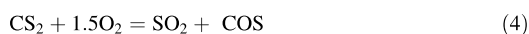
Sample	Step	TG temp. range/ $^{\circ}\text{C}$	Mass loss/%	DTG _{max} / $^{\circ}\text{C}$	DTA peak ($\pm$)/ $^{\circ}\text{C}$
1	1	30–210	6.3	175	158 (–)
	2	210–320	41.7	292	275 (+) 300 (–)
	3	320–450	12.0	400	410 (+)
	4	450–550	8.0	500	505 (+)
	Total mass loss		68.0		
2	1	30–175	4.8	96	99 (–) 146 (–)
	2	175–320	50.5	237	185 (–) 190 (+) 240 (+) 250 (–) 275 (+)
	3	320–475	15.5	410	430 (+)
	4	475–570	13.7	520	525 (+)
	Total mass loss		84.5		

according to the DTA curve (Fig. 2). The mass loss steps 3 and 4 are exothermic processes with DTA maxima peaked at 410 and 505 $^{\circ}\text{C}$, respectively. The decomposition of **1** is completed by 550 $^{\circ}\text{C}$. The total mass loss of **1** in the temperature interval of 30–700 $^{\circ}\text{C}$ is 68 % (calculated 56.4 %). According to the XRD analysis [19], the final decomposition product of **1** at 700 $^{\circ}\text{C}$ is SnO_2 . The calculated mass loss of **1** is much lower than the experimental one, indicating release of some volatile Sn species (e.g., SnCl_4) [10, 12].

Figure 3 shows the evolved gaseous species by their characteristic mass-spectroscopic ion fragments versus temperature over the thermal degradation of **1**. The evolution of gaseous species starts in the first decomposition step (30–210 $^{\circ}\text{C}$) around 170 $^{\circ}\text{C}$ with the evolution of carbon disulfide (CS_2), accompanied by the release of ammonia (NH_3) and cyanamide (H_2NCN), which are the decomposition products of adjacent thiourea ligands in the melt (3) [22, 23].



The evolution of carbonyl sulfide (COS) was found to start shortly after the release of CS_2 . COS is one of the oxidation products of the CS_2 vapor according to the reaction (4) [22, 23].

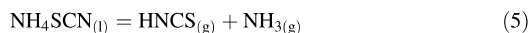


Interestingly, no evolution of sulfur dioxide (SO_2) was detected by EGA–MS around 200 $^{\circ}\text{C}$ (see Fig. 3). Similar results have been obtained by Madarász et al. [12] as no evolution of SO_2 was detected from $\text{Sn}(\text{tu})\text{Cl}_2$ by both

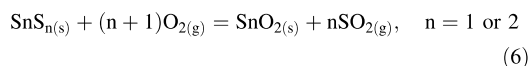
EGA–FTIR and EGA–MS at temperatures below 300 $^{\circ}\text{C}$. According to Madarász et al. [12], this phenomenon indicates that the released mixture of gases from $\text{Sn}(\text{tu})\text{Cl}_2$ was not rich enough in flammable gases containing sulfur, such as CS_2 and HNCS .

In the second decomposition step (210–320 $^{\circ}\text{C}$), the evolution of CS_2 and COS continues up to 260 $^{\circ}\text{C}$, and the release of H_2NCN and NH_3 , HCl and HCN continues until the end of the decomposition step.

The evolution of HNCS could not be detected by EGA–MS [11, 12]. However, according to the literature the release of HNCS has been confirmed by the EGA–FTIR during thermal decomposition of $\text{Sn}(\text{tu})\text{Cl}_2$ in the temperature region of 200–300 $^{\circ}\text{C}$ according to the reaction (5) [12]. Thus, the evolution of HCN with the maximum at 230 $^{\circ}\text{C}$ can be considered as the oxidation product of HNCS as reported in [14, 24].

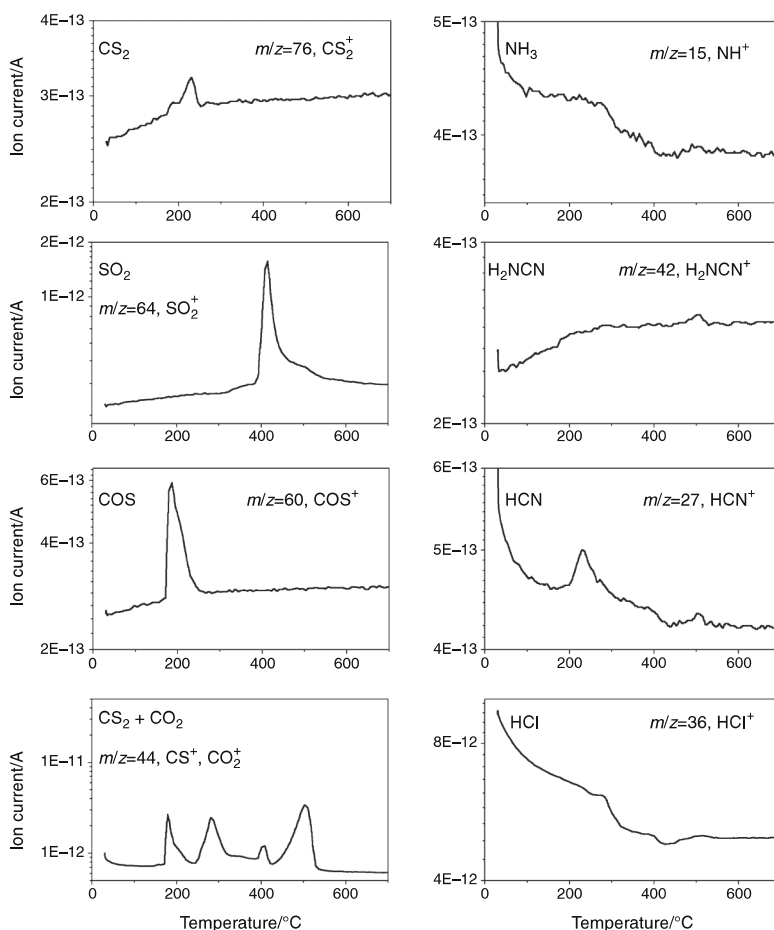


In the third decomposition step of **1** (320–450 $^{\circ}\text{C}$), the highly exothermic effect at 410 $^{\circ}\text{C}$ (Fig. 2) is accompanied by an intensive evolution of SO_2 (320–550 $^{\circ}\text{C}$) and minor release of CO_2 and H_2NCN . This indicates the oxidation processes of tin sulfides, according to the reaction (6) [12] as well as the decomposition and the oxidation of organic residues.



In the fourth decomposition step of **1** (450–550 $^{\circ}\text{C}$), an exothermic effect at 505 $^{\circ}\text{C}$ is accompanied by an intensive

Fig. 3 Gas evolution profiles of various gaseous species, as determined by TG/DTG/DTA/EGA-MS of **1**. Flowing (80 %Ar + 20 % O₂): flow rate 60 mL min⁻¹, heating rate: 10 °C min⁻¹. The initial mass of sample **1** was 15.0 mg



evolution of CO₂ and the release of SO₂ and H₂NCN. Evolution of gaseous species such as CO₂ and H₂NCN evidences the decomposition and oxidation of an organic matter.

The thermal decomposition behavior of **1** is similar to that reported for Sn(tu)Cl₂ by Madarász et al. [10, 12]. However, in [10, 12] the thermal decomposition of Sn(tu)Cl₂ was found to take place in five mass loss steps in the temperature range of 175–543 °C. According to the DTG curve (Fig. 2), the thermal decomposition of **1** takes place in four steps and the DTA maxima differ from those reported for Sn(tu)Cl₂ in [10, 12].

The differences in the DTA peak positions might be caused by the different experimental apparatus and measurement conditions used. The results of the thermal decomposition study of **1** were used to describe the decomposition of the tu-rich precursor **2**, as both were

measured with the same experimental apparatus and under the similar experimental conditions.

The TG, DTG and DTA curves of sample **2** are presented in Fig. 4. According to the DTG curve, the thermal degradation of **2** in the temperature range of 30–700 °C in flowing (80 % Ar + 20 % O₂) consists of four mass loss steps (Fig. 4; Table 1) with a total mass loss of 84.5 %. Thermal behavior of **2** is more sophisticated than that of **1** and that of Sn₂(tu)₅Cl₄·2H₂O reported in [10, 11].

The first decomposition step of **2** is in the temperature interval of 30–175 °C with a DTG maximum at 96 °C and a mass loss of 4.8 %. The DTA curve shows endothermic peaks with a maximum at 99 °C and a broad band with a maximum at 146 °C. The mass loss of 4.1 % in the temperature range of 30–120 °C corresponds to the dehydration of **2**. A broad endothermic effect in the temperature range of 120–160 °C with a maximum at 146 °C probably

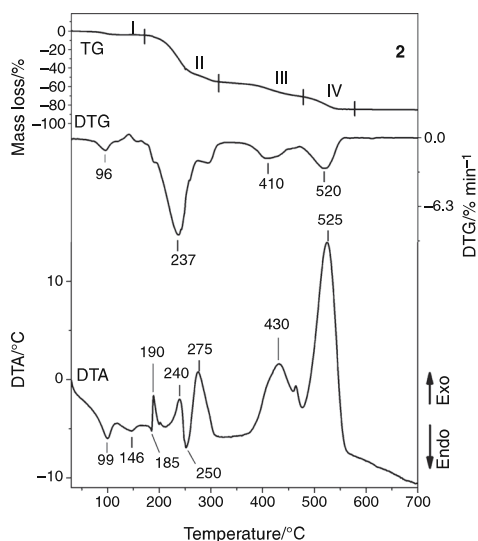


Fig. 4 Simultaneous TG/DTG/DTA curves of **2**. Flowing (80 % Ar + 20 % O₂): flow rate 60 mL min⁻¹, heating rate: 10 °C min⁻¹. The initial mass of sample **2** was 15.0 mg

belongs to the melting of **2**. The melting of **2** was confirmed by visual inspection of **2** when heated in a laboratory oven. The melting of Sn₂(tu)₅Cl₄·2H₂O has not been reported in [10, 11].

The second decomposition step of **2** takes place in the temperature range of 175–320 °C with a mass loss of 50.5 % and a DTG maximum at 237 °C. According to DTA curve, the decomposition of **2** in this temperature region is a complicated multistep process with several overlapping endothermic and exothermic effects.

The third decomposition step of **2** in the temperature interval of 320–475 °C is an exothermic process with maxima at 430 and 460 °C. Compared to **1**, the first exothermic effect in this temperature region occurs at ca 20 °C higher temperatures. In the case of **1**, this exothermic effect was accompanied by the evolution of SO₂ due to the oxidation of sulfur-containing phases. Thus, the oxidation of sulfide phases in **2** is shifted to higher temperatures than that observed in **1**. The mass loss of **2** in this decomposition step is only slightly higher than that recorded for **1**. The mass losses are 12.0 % for **1** and 15.5 % for **2**.

The DTA curve of **2** exhibits a plateau in the temperature range of 315–345 °C. Similar plateau but in a lower temperature region has been also observed in the thermal decomposition study of Sn₂(tu)₅Cl₄·2H₂O [11]. However, the DTA curves of **1** (Fig. 2) and that of Sn(tu)Cl₂ presented by Madarász et al. [12] do not show a plateau in this temperature region.

The fourth decomposition step of **2** in the temperature range of 475–570 °C is a highly exothermic process with a DTA maximum at 525 °C. Compared to **1**, the DTA maximum of **2** is shifted to higher temperature, from 505 °C (**1**) to 525 °C (**2**). Similar shift of the exothermic effect to higher temperature has been observed for tu-rich precursors for In₂S₃ [16] and CuInS₂ [22].

The mass loss of **2** in the fourth decomposition step is 13.7 %, which is significantly higher than that observed for **1** (8.0 %). This shows that the content of organic matter at the beginning of the last decomposition step of **2** is significantly larger than in **1**. The decomposition of **2** is completed by 570 °C. The total mass loss of **2** in the temperature interval of 30–700 °C is 84.5 %. According to the XRD analysis [19], the final decomposition product of **2** at 700 °C is SnO₂. The calculated mass loss of **2** (81.9 %) is close to the experimental one, indicating that the excess of tu in the precursor hinders the release of volatile tin species from the system. For comparison, the total mass loss recorded for Sn₂(tu)₅Cl₄·2H₂O was 75.8 % [11] and that is significantly higher than the theoretical 62.1 %.

Study of solid intermediate products of thermal decomposition of **1** and **2**

The FTIR spectra of the solid intermediate products of **1** and **2** heated up to various temperatures are presented in Fig. 5a, b, respectively. The FTIR spectra of **1** and **2** heated up to 190 °C (Fig. 5) do not show the vibrations characteristic of **1** and **2** (Fig. 1), confirming the destruction of **1** and **2** already at 190 °C. This is in correspondence with the TG/DTA data (Figs. 2, 4), showing that the decomposition of **1** and **2** starts at 170 and 150 °C, respectively. FTIR spectra of both **1** and **2** obtained by heating up to 190 °C and the spectrum of **2** at 210 °C (Fig. 5) exhibit a vibration at 2070 cm⁻¹. This can be assigned to the stretching vibrations of both thiocyanate (SCN) and hydrogen-bonded RNH³⁺ groups and indicates isomerization of thiourea into ammonium thiocyanate (NH₄SCN) [25, 26]. The absorption peak at 2070 cm⁻¹ has been detected in the decomposition products of thiourea [27], Cu(tu)₃Cl·H₂O [28], Cd(tu)₂Cl₂ [14], Zn(tu)₂Cl₂ [26] and In(tu)₃Cl₃ [25]. The isomerization of SC(NH₂)₂ to NH₄SCN presented as reaction (7) [27], and the decomposition of the latter explains the evolution of gaseous species such as HNCS and NH₃ (see reaction 5) and the formation of ammonium tin chlorides as solid intermediates in the first decomposition step of **1** and **2** (Table 2).



According to XRD [19] (Table 2), the solid residue of **1** heated up to 210 °C contains crystalline phases of SnS₂,

Fig. 5 FTIR spectra of the solid residues obtained by heating of **1** (a) and **2** (b) at 190, 210, 320 and 450 °C

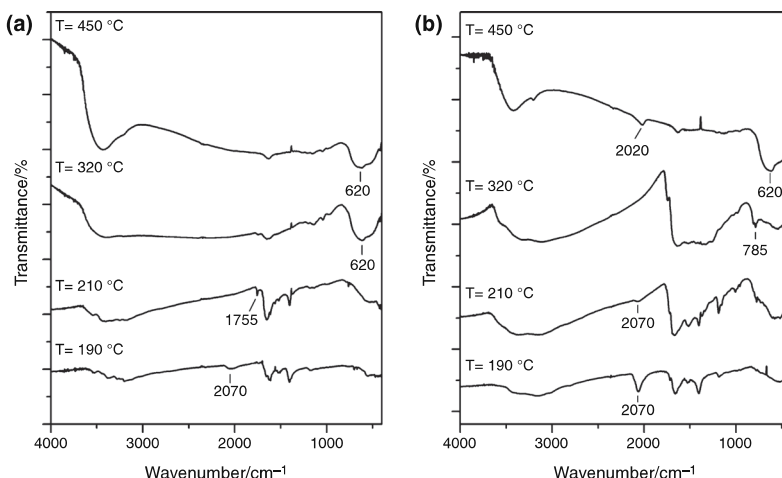


Table 2 Crystalline decomposition products of **1** and **2**, as detected by XRD. Heat treatments were performed in a preparative scale in laboratory furnace in air

1 (Sn:S = 1:1)		2 (Sn:S = 1:8)	
T/°C	Main crystalline phases and ICDD PDF-2 reference files	T/°C	Main crystalline phases and ICDD PDF-2 reference files
210	SnS ₂ (00-023-0677) (NH ₄) ₂ SnCl ₆ (01-073-1500) C(NH ₂) ₃ SnCl ₃ (01-076-9807)	210	SnS ₂ (00-023-0677) (NH ₄) ₂ SnCl ₆ (01-073-1500) NH ₄ Cl (00-007-0007) SnS (01-083-1758)
320	SnO ₂ (01-077-0452)	320	SnS ₂ (00-023-0677)
450	SnO ₂ (01-077-0452)	475	SnO ₂ (01-077-0452)
570	SnO ₂ (01-077-0452)	570	SnO ₂ (01-077-0452)

(NH₄)₂SnCl₆ and C(NH₂)₃SnCl₃. The solid product of **2** at 210 °C contains SnS₂, SnS, (NH₄)₂SnCl₆ and NH₄Cl.

The FTIR spectra of **1** and **2** heated up to 320 °C (Fig. 5a, b) are different. The spectrum of **2** reveals strong absorptions in the wavenumber range of 1665–1200 cm^{−1} and at 785 cm^{−1}, which can be assigned to the polymerized product of cyanamide [14, 29]. The FTIR spectrum of **1** heated up to 320 °C reveals a broad and intensive band at 620 cm^{−1} characteristic of SnO₂ [30]. XRD analysis [19] confirms the presence of SnO₂ and SnS₂ in the solid products of **1** heated up to 320 °C. However, the solid product of **2** heated up to 320 °C still consists of SnS₂.

FTIR spectra of **1** and **2** heated up to 450 °C are similar. Both **1** and **2** show a broad band at 620 cm^{−1} characteristic of SnO₂ [30]. XRD analysis [19] shows that the crystalline solid product of **1** and **2** heated up to 450 °C is SnO₂. The absorption bands in the region of 1600–1000 cm^{−1} indicate the presence of some organic residues in **1** and **2**. In addition, the spectrum of **2** shows the absorption at

2020 cm^{−1} belonging to cyanamide group. Thus, the intensive exothermic effects at 505 °C in **1** and 525 °C in **2** are caused by the decomposition and combustion of organic residues.

Conclusions

A comparison of the thermal decomposition of the precursors for tin sulfide thin films is presented. The precursors are obtained by drying aqueous solutions of SnCl₂ and SC(NH₂)₂ in the Sn:S molar ratios of 1:1 (**1**) and 1:8 (**2**). According to FTIR and XRD, **1** is Sn(tu)Cl₂, while **2** consists of Sn₂(tu)₅Cl₄·2H₂O and noncomplexed thiourea.

The thermal decomposition of **1** and **2** in the temperature range of 30–700 °C in synthetic air (80 % Ar + 20 % O₂) consists of four mass loss steps with total mass loss of 68.0 and 84.5 %, respectively. The final decomposition product of **1** and **2** at 700 °C is SnO₂. The

total mass loss of **1** (68.0 %) is higher than the theoretical one (56.4 %); however, for **2** the mass loss of 84.5 % is close to the theoretical one (81.9 %). According to XRD, the solid decomposition products at 210 °C of **1** are SnS_2 , $(\text{NH}_4)_2\text{SnCl}_6$ and $\text{C}(\text{NH}_2)_3\text{SnCl}_3$, and of **2** are SnS_2 , SnS , NH_4Cl and $(\text{NH}_4)_2\text{SnCl}_6$. According to the DTA curves, the oxidation of sulfide phase is peaked at 410 °C for **1** and 430 °C for **2**. The samples prepared in a laboratory oven confirm this trend. However, in case of **1** the formation of SnO_2 is detected at lower temperature.

This study shows that the excess of thiourea in the spray solution, compared to that required for the formation of the intermediate tin complex compounds, provides enough liquid phase for metal sulfide formation, depresses the loss of tin species from the system, suppresses the formation of tin oxide phase and thus enables the formation of tin sulfides without notable amount of oxide phases in the temperature region of 200–320 °C. However, thermal analysis results of tin thiourea complexes with no additional thiourea show that these precursors are not recommended for tin sulfide thin film deposition as there occurs the loss of tin from the system and tin oxide phase is present already at around 300 °C, probably due to the oxidation of tin chloride.

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PAPER II

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Spray pyrolysis deposition of Sn_xS_y thin films

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Abstract

Sn_xS_y films were grown by chemical spray method using aqueous solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at molar ratio of $\text{Sn}:\text{S}=1:1, 1:2, 1:4$ and $1:8$ in the temperature interval of $200\text{--}410\text{ }^\circ\text{C}$ in air. Films were characterized by XRD, SEM, EDX and UV-VIS spectroscopy. According to XRD, films grown below $270\text{ }^\circ\text{C}$ were composed of SnS as a main phase independent of $\text{Sn}:\text{S}$ ratio in the parent solution. It has been shown that spray of $1:4$ and $1:8$ solutions results in thicker films with lower oxygen and chlorine content, and lower optical band gap compared to the films from $1:1$ and $1:2$ solutions.

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Keywords: Chemical spray pyrolysis, thin films, SnS, morphology, optical properties, XRD, SEM, EDX

1. Introduction

Tin monosulfide is a promising candidate as an absorbing semiconductor for photovoltaic applications since its constituent elements are inexpensive, environmentally-friendly and easily available in nature. Furthermore, this material has appropriate optical properties such as a suitable direct optical bandgap (E_g) in the range of $1.3\text{--}1.5\text{ eV}$ and a high optical absorption coefficient $\alpha > 10^4\text{ cm}^{-1}$ for use in thin-film solar cells [1]. In spite of these advantages,

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solar cells based on SnS absorbers have not shown efficiencies higher than 2.46 % [2], which is significantly lower compared to the theoretical efficiency of 24% [3].

Many dry and solution-based techniques such as chemical vapor deposition [4], radio frequency (RF) sputtering [5], physical vapour deposition (PVD) [6], chemical bath deposition (CBD) [7], atomic layer deposition (ALD) [8], electrochemical deposition [9] and chemical spray pyrolysis (CSP) have been used to deposit tin sulfide films [10–22]. The CSP method was chosen for the deposition SnS thin films due to its simplicity and cost effectiveness.

The effect of growth temperature, the tin and sulfur precursors molar ratio in the spray solution (Sn:S) and the effect of post-deposition annealing on the phase and chemical composition, and optical properties of SnS films grown by CSP have been investigated in several previous studies [10–23]. Aqueous or alcoholic solutions containing stannous chloride (SnCl_2) and thiourea ($\text{CS}(\text{NH}_2)_2$) or substituted thiourea (N,N-diethyl or N,N-dimethyl thiourea) have been used for the SnS film deposition by pneumatic CSP. According to the results reported in studies listed above, the use of substituted thiourea instead of thiourea does not seriously affect the sprayed film properties.

It has been demonstrated by several studies that the main parameter influencing the SnS films properties is the deposition temperature. The substrate temperature controlled the phase composition of films. For example, Koteeswara Reddy et al. [22] have reported that films prepared from the 1:1 solution at temperatures below 300 °C consisted of a mixture of SnS, Sn_2S_3 and SnS_2 phases, while films grown at $T_s \sim 350$ °C were mainly composed of SnS phase. The films deposited at temperatures higher than 360 °C contained oxygen in addition to Sn and S [22].

Commonly, SnS thin films were deposited using the Sn:S molar ratio of 1:1 in the solution [10–16, 19–22]. However, it has been shown earlier that the precursors' molar ratio (Me:S) in the spray solution has strong effect on the metal sulfide formation reactions [27], as well as on properties of indium sulfide and zinc sulfide films deposited by CSP [28, 29]. It has been found in [18, 20] that the Sn:S molar ratio in the spray solution has influence on the film phase composition. For instance, Sajeesh et al. [18] reported that films deposited by spray of 1:3 and 1:4 solutions at 375 °C consisted of a mixture of SnS_2 and SnS phases. At the same time the films obtained by spray of 1:1 solution at similar temperature contained Sn_2S_3 phase in addition to SnS, while samples grown from 1:2 solutions consisted of SnS phase only. It has been reported that elemental composition of the SnS films deposited from 1:1 or 1:2 solutions in the temperature interval of 350–375 °C was nearly stoichiometric [10, 12, 13, 18]. Films prepared at temperatures below 300 °C were sulfur-rich with $\text{Sn/S} < 1$, while films formed at temperatures over 400 °C were sulfur deficient with an average $\text{Sn/S} > 1.23$ [10, 12]. It was demonstrated in [13, 18] that sulfur content in the films started to decrease when deposited at temperatures higher than 400 °C.

Despite the fact that the properties of sprayed tin sulfide films were found to depend on the spray solution composition and the film growth temperature, a comprehensive study on the effect of the Sn:S ratio in the spray solution at different deposition temperatures is missing in the literature. Therefore, in this paper we investigate the influence of the precursors (SnCl_2 and thiourea) molar ratio on the phase and elemental composition, morphological and optical properties of the films deposited by pneumatic CSP method at different growth temperatures.

2. Experimental details

SnS films were deposited onto preheated soda–lime glass slides with dimensions of 30 mm × 10 mm × 1 mm by pneumatic chemical spray pyrolysis technique. The glass substrates were cleaned by washing in acetone and ultrasonically in ethanol for 10 minutes. The precursor solutions were prepared by dissolving dihydrated stannous chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$) and thiourea ($\text{CS}(\text{NH}_2)_2$, tu) in deionised water containing a few drops of concentrated HCl. For all the samples the concentration of the Sn^{2+} cation in the spray solution was 0.01M and the molar ratio of Sn:S was varied from 1:1 to 1:8. Films were prepared by spraying 50 ml solution at various substrate temperatures (T_s) in the range of 200–410 °C in air. Distance of spray head from the substrate was 29 cm, the solution spray rate was maintained close to 3 ml/min, and flow rate of compressed air as carrier gas was 6 l/min.

The structural properties of the SnS films were characterized by X-ray diffraction (XRD) using a Rigaku Ultima IV diffractometer with Cu K α radiation ($\lambda = 1.54$ Å) and Ni filter. The diffractometer was equipped with a silicon strip detector D/teX Ultra. All samples were scanned in the 2θ range of 10 deg – 60 deg with the scan step of 0.02. The average size of crystallites was calculated according to the Scherrer formula using the software on the Rigaku's system (PDXL Version 1.4.0.3).

The surface morphology, cross-sections and elemental composition of SnS films were studied with the help of a high resolution scanning electron microscopy and energy dispersive X-ray analysis (EDX) using a Zeiss HR

FESEM Ultra 55 with Bruker EDS system ESPRIT 1.8. An acceleration voltage for SEM measurements was 10 kV. Optical transmission spectra of the films were recorded in the wavelength range of 200–2500 nm using UV–Vis–NIR spectrophotometer Jasco V-670 equipped with an integrating sphere.

3. Results and discussions

3.1. Effect of the growth temperature

Figure 1 presents XRD patterns of SnS films obtained by spray of 1:2 solutions. According to XRD, the films deposited in the temperature range of $T_s = 200$ – 320 °C are composed of orthorhombic polycrystalline SnS (JCPDS 01-083-1758) [30] as a dominant crystalline phase. However, the diffraction peaks at 2θ of 18.8° , 32.8° , 35.5° , 39.7° , 41.9° , 42.9° , 45.8° , 48.5° , 54.9° and 56.4° (marked with "x" in Fig. 1) are present additionally and indicate that a secondary crystalline phase(s) is (are) also present in the films deposited at temperatures 200 – 270 °C. All the diffraction peaks marked by "x" remained unidentified as not belonging to the phases of Sn_2S_3 , SnS_2 , thiourea and SnCl_2 as precursors, or two possible intermediate complexes such as $\text{Sn}(\text{tu})\text{Cl}_2$ and $\text{Sn}_2(\text{tu})_5\text{Cl}_4 \cdot 2\text{H}_2\text{O}$ [24, 25]. By increasing the growth temperature the reflections marked by "x" are vanishing and disappear when growing the film at 320 °C.

Diffractograms of the films deposited at 370 °C and 410 °C do not show diffraction peaks characteristic of SnS. Peaks located at 2θ of 15.0° , 31.6° and 44.0° correspond to the SnS_2 phase (JCPDS 01-089-2028), and those at 2θ of 26.5° , 33.8° and 51.3° belong to the SnO_2 phase (JCPDS 01-077-0452).

Our results here differ from that reported in literature by Sajeesh et al. [18] for the films deposited by spray of solutions with Sn:S of 1:2. According to the results in [18], Sn_2S_3 is the main crystalline phase in the films grown at temperatures below 300 °C, SnS is the crystalline phase in the films grown at around 370 °C, while SnS_2 phase forms in addition to SnS when growing the film above 400 °C.

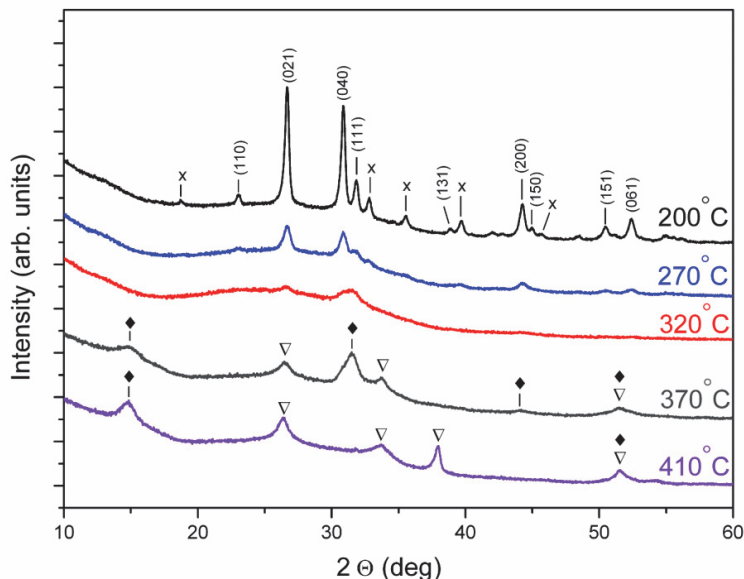


Fig.1. XRD patterns of SnS films grown at $T_s = 200$ – 410 °C using the precursors molar ratio of Sn:S=1:2 in the spray solution. The peaks marked with (hkl) indexes belong to SnS phase (JCPDS 01-083-1758) [30], «▽» belong to SnO_2 phase (JCPDS 01-077-0452), «◆» belong to SnS_2 phase (JCPDS 01-089-2028), the peaks marked by «x» remained unidentified.

The diffraction peak intensities are weakening with increasing the substrate temperature (Fig.1) as thinner films are formed at higher growth temperatures (see Table 1). Observation that thinner films are obtained at higher growth temperatures is a common characteristic of sprayed films [28]. At the same time, the diffraction peaks become wider indicating a decrease in crystallite sizes. The crystallite sizes of SnS phase, calculated from the full width at half maximum (FWHM) of the (040) diffraction peak, are presented in Table 1. By increasing the Ts from 200 to 320 °C the mean crystallite size decreases from 25 nm to 6 nm. Sajeesh et al. [18] also observed a slight decrease in the SnS crystallite size using higher deposition temperatures. Usually crystallite sizes in sprayed films are increasing with the deposition temperature. Reverse effect observed in sprayed tin sulfide films could be explained by the formation of secondary phase(s), which retard the growth of SnS crystallites. Although XRD does not show presence of crystalline oxidized phases in the film grown at 235– 320 °C, a relative increase in oxygen content is recorded in the films grown at higher temperatures (see Table 1).

In order to clarify the cause of oxide phase formation at 370 and 410 °C, the film grown at 200 °C from 1:2 solutions was annealed for one hour at 350 and 425 °C in air.

Fig. 2 presents XRD patterns of as-deposited and annealed in air SnS films. As-deposited film grown from 1:2 solution is composed of SnS phase and contains a secondary phase (marked by "x") as discussed above. The films annealed at 350 °C are composed of SnS as a main phase, diffraction peaks characteristic of Sn₂S₃ phase (JCPDS 01-075-2183) [30] can be also detected on the XRD pattern. Diffractogram of the film annealed at 425 °C confirms continual presence of SnS and Sn₂S₃ and SnO₂ phases. Interestingly, although the intensities of diffraction peaks of an unidentified phase weaken with temperature, the peaks assigned to that are still present on the XRD pattern of the sample annealed at 425 °C. This experiment shows that the formation of SnO₂ phase in the films deposited at 370 °C and 410 °C is not caused by the oxidation of the SnS film. Obtained result is similar to that reported by Otto et al. [27] for sprayed indium sulfide. Namely, it was found that the oxidation of In₂S₃ phase was not responsible for the formation of indium oxide phase in the films deposited by spray at 410 °C as annealing of thin In₂S₃ films at 450 °C in air did not cause formation of metal oxide.

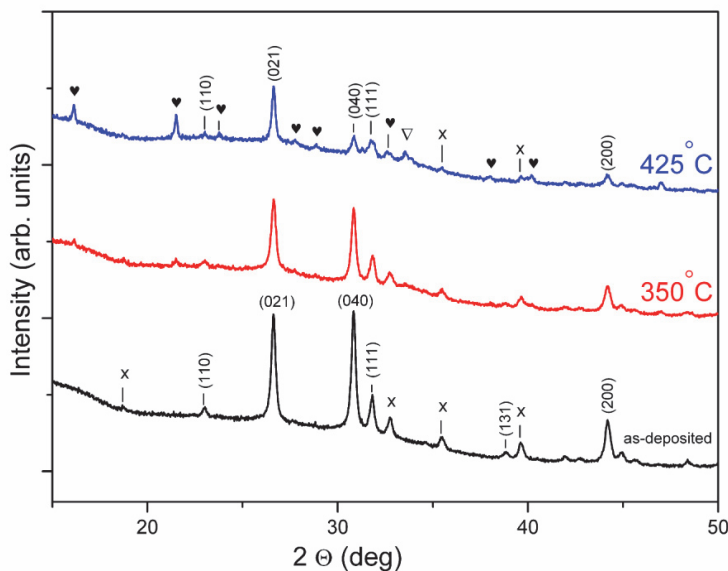


Fig.2 XRD patterns of SnS films grown at Ts= 200 °C using the precursors molar ratio of Sn:S=1:2 in the spray solution, and after annealing the films at 350 °C and 425 °C in air. The peaks marked with (hkl) indexes belong to SnS phase (JCPDS 01-083-1758), «♥» belong to Sn₂S₃ (JCPDS 01-072-7600), «∇» belong to SnO₂ and peaks marked by «x» remained unidentified.

3.2. Effect of Sn:S ratio

3.2.1. Structural analysis

Figure 3 compares XRD patterns of SnS films obtained by spray of 1:1, 1:2, 1:4 and 1:8 solutions at 200 °C. Very similar diffractograms were recorded for the films deposited at 270 °C (not presented here). According to XRD, the films are composed of polycrystalline orthorhombic SnS phase (PDF 01-083-1758) [30] as a dominant crystalline phase independent of the Sn:S ratio in the spray solution. Secondary crystalline "x" phase(s) is (are) also present, being less visible in the case of 1:1 film.

The films deposited by spray of 1:1 solutions significantly diverge from that reported in literature. Koteeswara Reddy et al. [12, 17, 22] showed that films obtained by spray of 1:1 solutions at temperatures up to 300 °C were composed of a mixture of Sn_2S_3 , SnS_2 and SnS phases. SnS was not the dominating phase in films grown below 300 °C. Lopez et al. [16] reported that the Sn_2S_3 phase is present in sprayed films grown at temperatures below 320 °C.

It can be seen that gradually increasing thiourea amount in the spray solution leads to more intense diffraction peaks which is in correspondence with increased film thicknesses (See Table 1). The result that thicker tin sulfide films are formed from thiourea-rich solutions seems surprising as similar amount of cation was used in these experiments. Based on the results of the studies on sprayed indium sulfide films [27, 28] it can be speculated that larger amount of thiourea holds back escape of metal source. Further studies are needed to confirm this hypothesis.

Comparison of diffractograms with powder reference (PDF 01-083-1758) [30] shows that the crystallites in sprayed films are preferentially oriented. The (111) diffraction peak is the strongest peak for SnS powder, the (021) diffraction peak is the most intensive for sprayed films (Fig.3). The ratios of the intensities of the (021) and (111) diffraction peaks ($I_{(021)}/I_{(111)}$) are 3.4, 3.7, 13.5 and 13.4 for 1:1, 1:2, 1:4 and 1:8 films, respectively. For the powder reference, the $I_{(021)}/I_{(111)}$ is 0.49. Thus, the SnS crystallites in the films grown at $T_s = 200$ °C are preferably grown along the (021) plane parallel to the substrate independent of the Sn:S ratio in the spray solution, however, preferred orientation is more pronounced in the films deposited from thiourea-rich solutions.

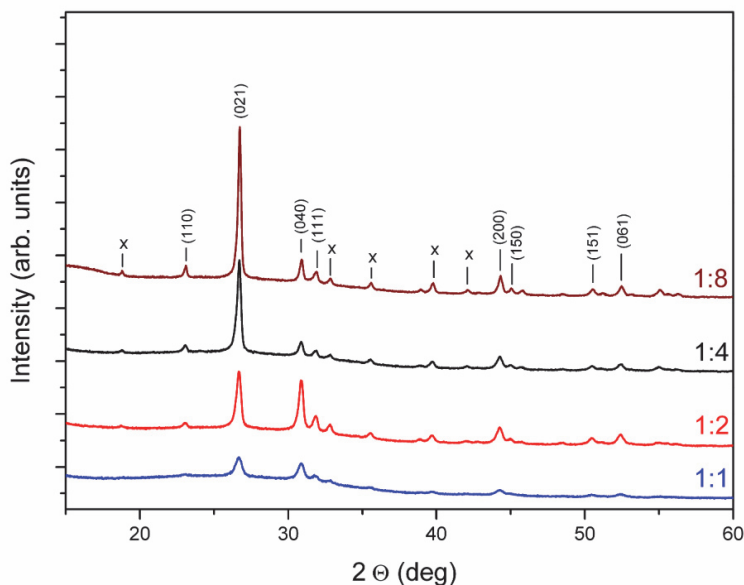


Fig.3. XRD patterns of films grown at $T_s = 200$ °C using the precursors molar ratio of Sn:S=1:1, 1:2, 1:4 and 1:8 in the spray solution. The diffraction peaks marked with (hkl) indexes belong to SnS phase (JCPDS 01-083-1758), the peaks marked by «x» remained unidentified.

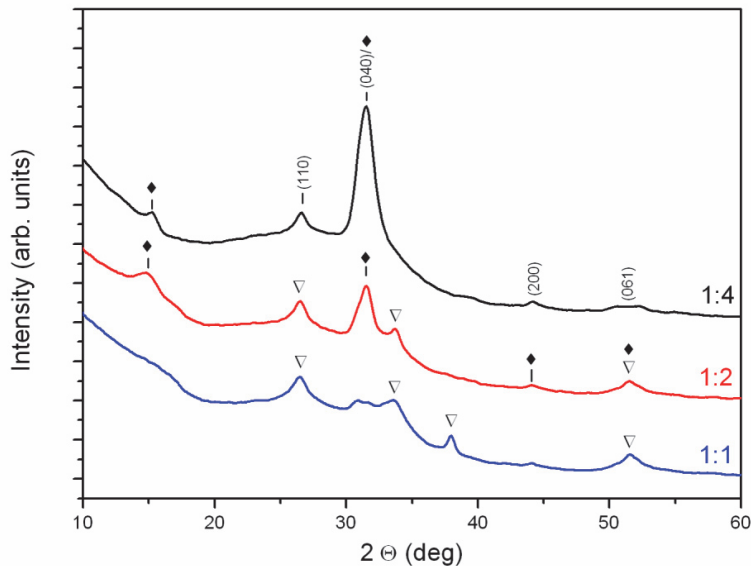


Fig.4. XRD patterns of films grown at $T_s = 370$ °C using the precursors molar ratio of Sn:S=1:1, 1:2 and 1:4 in the spray solution. The peaks marked with (hkl) indexes belong to SnS phase (JCPDS 01-083-1758), « ∇ » belong to SnO₂ (JCPDS 01-077-0452) and « $\blacklozenge$ » belong to SnS₂ (JCPDS 01-089-2028) phases.

The SnS crystallite sizes in the films grown at 200 and 270 °C by spraying solutions with different Sn:S molar ratios are presented in Table 1. The mean crystallite size is larger in the films deposited at 200 or 270 °C using thiourea-rich solutions (Sn:S=1:4, 1:8) compared to the films deposited from 1:1 and 1:2 solutions. As an example, the crystallite sizes of the SnS phase grown at $T_s \sim 200$ °C from 1:1, 1:2, 1:4 and 1:8 solutions are 17, 24, 28 and 35 nm, respectively (Table 1). For all the films a decrease in crystallite size is observed when increasing the deposition temperature as already discussed above.

The effect of use thiourea-rich solutions on phase composition becomes distinct at higher growth temperatures. XRD patterns of the films formed $T_s = 370$ °C using the precursor molar ratio of Sn:S=1:1, 1:2 and 1:4 in the spray solution are shown in Fig.4. Films prepared from 1:1 solutions are of SnO₂. Spray of 1:2 solution results in the film composed of a mixture of SnS₂ and SnO₂ phases, and spray of 1:4 solution results in the film composed of a mixture of SnS and SnS₂ phases. This result clearly indicates that the precursors' molar ratio in the spray solution controls the phase composition of sprayed films.

3.2.2. Morphology and elemental composition

Figure 5 compares the surface morphology and cross-section views of SnS films grown at 200 °C and 270 °C from 1:1, 1:2, 1:4 and 1:8 solutions. The surface of the SnS film deposited at 200 °C from 1:1 solution is more porous and is composed of agglomerates of the grains however the films deposited from 1:4 and 1:8 solutions show more homogeneous and compact structure with separately standing grains with the size of ca 25-35 nm. The surface morphology of the films grown at 270 °C from 1:1, 1:2, 1:4 and 1:8 solutions become more porous and consist of larger agglomerates of the grains compared to the films grown at 200 °C. According to the SEM cross-sectional views, the thickness of the film obtained from solution with low amount of thiourea was less compared to the films obtained from solutions with higher amount of sulfur resource (Table 1).

According to EDX analysis (Table 1) the elemental composition (Sn, S, O and Cl) of the films varied with the increase of substrate temperature and amount of thiourea in the spray solution.

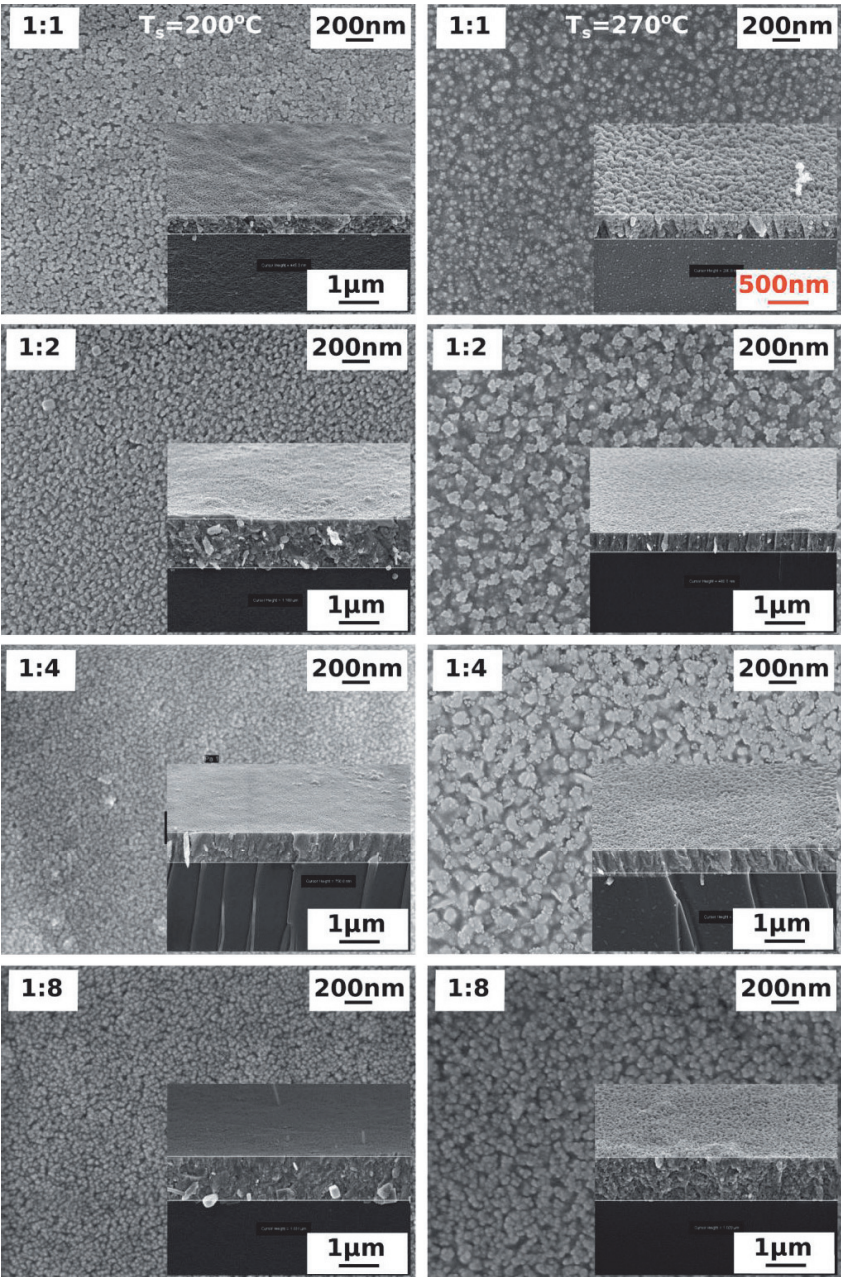


Fig.5. SEM images of films deposited on glass substrate from 1:1, 1:2, 1:4 and 1:8 solutions at $T_s= 200^\circ\text{C}$ and $T_s= 270^\circ\text{C}$. The scale bar is 500 nm on the cross-sectional image of the film deposited from 1:1 solution at 270°C .

Table 1. Elemental composition (Sn, S, O and Cl, in at %) according to EDX, film thickness (t), crystallite size (D) and optical bandgap (Eg) of SnS films deposited at various growth temperatures (Ts) and the precursors (SnCl₂ and thiourea) molar ratio (Sn:S) in the spraying solution.

Sn:S	Ts (°C)	Sn (%)	S (%)	Cl (%)	O (%)	t(nm)	Eg (eV)	D (nm)
1:1	200	34	18	7	41	445	2.1	17
	270	31	12	3	54	290	2.6	9
1:2	200	33	24	5	38	1160	1.9	25
	235	35	21	5	39	1050	1.9	17
	270	32	18	2	48	480	2.2	14
	320	28	15	1	56	370	2.4	9
1:4	200	36	28	3	33	750	1.9	28
	270	33	23	1	43	610	2.1	15
1:8	200	35	34	2	29	1030	1.8	35
	270	34	33	1	32	1020	1.9	23

By increasing the deposition temperature Ts from 200 °C to 270 °C, relative amount of S content decreases and of oxygen content increases independent of the Sn:S ratio in the spray solution, and indicates the loss of sulfur.

The elemental composition of the sprayed films does not correspond to that of pure SnS phase. Deficiency of sulfur and high excess of oxygen in the films refers to the presence of oxidated phases. However, this effect is less pronounced in the films grown by spray of solutions containing higher amount thiourea (Sn:S=1:4 and 1:8). Thus, the amount of sulfur source (thiourea) in the spray solution has an effect on the content of oxygen and sulphur in sprayed films. Further studies are needed to explain this phenomenon. The chlorine content in the films decreases by increasing both Ts and amount of thiourea.

3.2.3. Optical properties

SnS films deposited at T= 200 °C from 1:4 and 1:8 solutions show the total optical transmittance around 70 % in the visible and near-infrared spectral region (Fig. 6). The total optical transparency increased slightly using lower amount of thiourea in spraying solutions. At the same time the number of interference fringes on the spectra of the films deposited from 1:1 and 1:2 solutions is lower compared to the films sprayed from 1:4 and 1:8 solutions. Thus, films obtained by spray of thiourea rich solutions are thicker. The film thicknesses calculated from the total transmittance spectra using the refractive index $n=2$ at 1000 nm wavelength [14] and measured from the SEM cross-sectional images (Fig.5) were similar. It can be clearly seen that at similar growth temperatures, thickness of the films from 1:4 solutions was approximately twice higher than from 1:1 solutions (Table 1). The absorption edge shifted from lower wavelength region to higher wavelengths by increasing the amount of thiourea in the spray solution. Eg values were calculated from total transmittance spectra using the following well-known equation:

$$(\alpha \cdot h\nu)^n = A(h\nu - E_g) \quad (1),$$

where A is the constant which is independent from the photon energy, h is the Planck constant, Eg is a bandgap energy, $h\nu$ is the incident photon energy, and $n=2$ for the direct transitions probability. The Eg values were found by extrapolating the straight-line portion of the $(\alpha h\nu)^2$ versus $h\nu$ graph to a zero absorption coefficient value. Optical bandgap values of films deposited by spraying 1:8 and 1:4 solutions at temperatures below 300 °C are lower than bandgap values of the films from 1:1 and 1:2 solutions. As an example, Eg values of the films deposited at Ts~270 °C from 1:8, 1:4, 1:2 and 1:1 solutions were 1.9, 2.1, 2.2 and 2.6 eV, respectively (Table 1). Comparing EDX results and results obtained from the total transmittance spectra measurements, it can be explained by formation of another oxygen contained phase with higher Eg values. According to the literature results, the optical bandgap values of the films prepared by spray of 1:1 or 1:2 solutions in the temperature interval of 350-375 °C were around 1.33 eV [10, 12, 18].

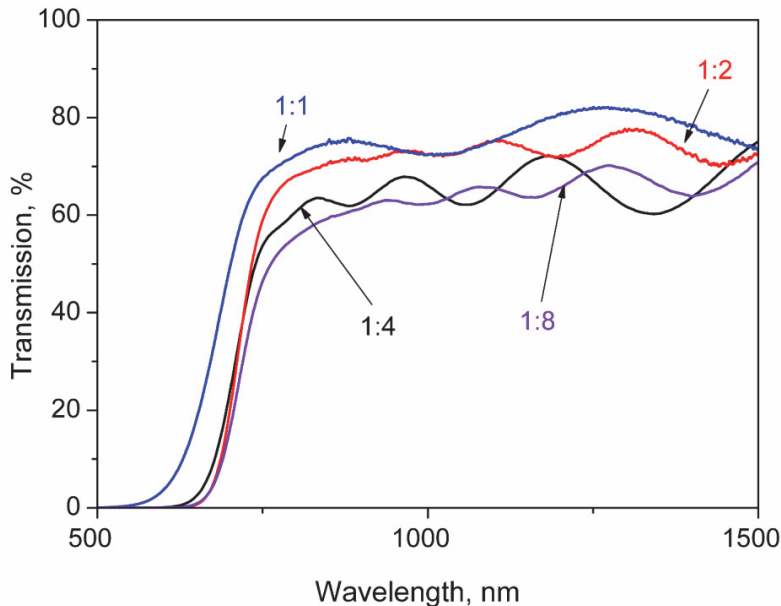


Fig.6. Total transmittance spectra of SnS films prepared from 1:1, 1:2, 1:4 and 1:8 solutions at 200 °C.

At the same time, bandgap values of the films deposited at temperatures below 300 °C or higher than 400 °C were around 2 eV. It has been explained by formation of Sn_2S_3 or SnS_2 phases at temperatures below 300 °C and SnO_2 at temperatures over 400 °C [10, 12, 13].

4. Conclusions

In this study SnS films were deposited by the pneumatic spray pyrolysis method using aqueous solutions containing SnCl_2 (Sn) and thiourea (S) with Sn:S molar ratios of 1:1, 1:2, 1:4 and 1:8 at growth temperatures $T_s = 200$ –410 °C in air. Films grown in the temperature range of 200 – 270 °C are composed of SnS as a dominant phase with preferred orientation of crystallites along the (021) plane parallel to the substrate independent of the Sn:S molar ratio in the spray solution. Secondary unidentified phase(s) is (are) also present in the films being less visible in the case of 1:1 solutions. SnS crystallite size decreases but oxygen content increases with the deposition temperature.

At similar growth temperatures, spray of solutions with higher content of thiourea in the spray solution leads to thicker films with larger SnS crystallites, decreased chlorine and oxygen content and resulted in the films with lower bandgap. The effect of the precursors molar ratio becomes evidential growing the films at 370 °C. According to XRD, films prepared from 1:1 solutions are of SnO_2 , spray of 1:2 solution leads to a mixture of SnS_2 and SnO_2 phases, and spray of 1:4 solution results in the film composed of a mixture of SnS and SnS_2 phases. In order to obtain better understanding of the effect of thiourea excess in spray solution on the film properties, the process chemistry studies are in progress.

Acknowledgements

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PAPER III

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Tin sulfide films by spray pyrolysis technique using L-cysteine as a novel sulfur source

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Tin sulfide films were deposited by spray pyrolysis method using aqueous solutions containing tin chloride (SnCl_2) and L-cysteine ($\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$) as a novel source of sulfur instead of commonly used thiourea. L-cysteine prevents SnCl_2 from hydrolysis due to a complex formation as confirmed by Fourier Transformed Infrared Spectroscopy studies. The solution that contained SnCl_2 (Sn) and L-cysteine (S) at molar ratios of Sn:S=1:1, 1:2 and 1:4 was sprayed onto glass substrates at varied temperatures between 200 °C and 370 °C. Films were characterized by X-ray diffraction (XRD), scanning electron microscopy (SEM), energy dispersive spectroscopy (EDX) and UV-Vis spectroscopy. Accord-

ing to XRD, spray of the 1:1 solution results in films that are composed of SnS as a main crystalline phase. An unidentified crystalline phase was present independent of the growth temperature. Single phase SnS films with bandgap value of 1.7 eV could be grown using the 1:2 solution at deposition temperature of 370 °C. Films grown from 1:4 solutions are amorphous using deposition temperatures below 370 °C, and composed of a mixture of SnS and Sn_2S_3 phases when grown at 370 °C. EDX study shows that SnS films contain high amount of carbon and oxygen containing residues independent of the deposition temperature and precursors' molar ratio in the spray solution.

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1 Introduction Recently, orthorhombic tin sulfide (SnS) has gained much attention as an attractive absorber material for low cost thin-film solar cells to supplant the devices based on $\text{Cu}(\text{In,Ga})\text{Se}_2$ and CdTe layers, which are composed of non-abundant In, Ga, Te and toxic Cd elements. SnS thin films have appropriate optical properties such as direct bandgap values in the region of 1.35–1.9 eV depending on the deposition technique [1–12], and absorption coefficient higher than 10^4 cm^{-1} . Single phase SnS films do not need incorporation of an extra dopant due to their intrinsic p-type conductivity caused by tin vacancies. Despite these pluses, the highest reached efficiency of 4.36 % for SnS thin film solar cells [2] is significantly lower than the theoretical value of 24% [3].

There is a variety of physical and chemical methods such as thermal evaporation [4], chemical bath deposition

(CBD) [5], electrochemical deposition (ECD) [6], chemical spray pyrolysis (CSP) [7–11], chemical vapor deposition (CVD) [12], and atomic layer deposition (ALD) [2] to deposit SnS films. Among these methods, CSP is a simple, fast and low-cost process.

Generally, aqueous or alcoholic solutions consisting tin chloride (SnCl_2) and thiourea ($\text{SC}(\text{NH}_2)_2$) are used to grow SnS films by the CSP method [7–11]. The formation of tin sulfide in the CSP process is a complicated multistep process, which started with the formation of an intermediate thiourea complex compound in a solution, followed by the thermal decomposition of the complex on a heated substrate resulting in SnS films [13, 14]. Earlier studies have demonstrated that experimental parameters such as the film growth temperature and the tin and sulfur precursors molar ratio in the spray solution (Sn:S) are mainly controlling the

phase and chemical composition of sprayed SnS films [7–11]. In case thiourea is used as sulfur source and complexing agent, highly acidic aqueous spray solutions ($\text{pH} \approx 1$) are required to avoid hydrolysis of Sn salt [8, 9]. Spraying of highly acidic solutions might cause chemical dissolution of previously deposited layers in a multilayer structure [15].

In this study we use L-cysteine ($\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$) as an alternative sulfur source instead of commonly used thiourea. According to the literature, L-cysteine forms with metal cations chelate complexes where L-cysteine ligand is bonded to the metal through the atoms of sulfur (thiol group, R-SH), oxygen (carboxyl group, R-COOH) or nitrogen (amino group, R-NH₂) [16–18]. Generally, chelate ligands are stronger complexing agents compared to a monodentate ligand like thiourea [19]. It is expected that hydrolysis of Sn precursor could be reduced and solutions with lower acidity sprayed when using L-cysteine instead of thiourea. To our best knowledge, studies on the SnS film deposition using L-cysteine as a sulfur source have not been reported in the literature.

This paper has aim to study the suitability of L-cysteine as a novel sulfur source to grow tin sulfide films by chemical spray method using aqueous solutions, and investigate the thin film structural, optical and morphological properties and elemental composition depending on the growth temperature and tin chloride to L-cysteine molar ratio in the spray solution.

2 Experimental details

2.1 Deposition of SnS films and preparation of samples for precursors interaction studies

Tin chloride ($\text{SnCl}_2 \cdot 2\text{H}_2\text{O}$ (p.a. > 98%, Sigma-Aldrich SZBB2090V)) and L-cysteine ($\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$ (p.a. > 98%, Amresco 2433C241)) were used as tin (Sn) and sulfur (S) sources, respectively. All chemicals were used as received without any further purification. Deionised water was used as a solvent. 50 ml tin chloride aqueous solution with the concentration of the Sn^{2+} cation of 0.01M was prepared. One drop of concentrated HCl was added to the solution to avoid the hydrolysis of SnCl_2 . Spray solution has $\text{pH} \approx 2.5$ after dissolution of L-cysteine in previously prepared tin chloride solution at the SnCl_2 : $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$ molar ratio (Sn:S) of 1:1, 1:2 and 1:4. The spray solutions (50 ml) were nebulized onto pre-heated soda-lime glass slides with dimensions of $30 \times 10 \times 1 \text{ mm}^3$ at different substrate temperatures (T_s) in the range of 200–370 °C in air. A detailed description of CSP procedure is presented in [9].

In order to study the possible interaction of starting precursors in aqueous solutions, deposits were extracted from the spray solutions with the Sn:S molar ratio of 1:1 (1), 1:2 (2) and 1:4 (3). To obtain deposits 1, 2 and 3, corresponding solutions at the volume of 50 ml were let to stay for 7 days at room temperature to evaporate the solvent followed by further drying at 35 °C for 24 hours in air.

2.2 Characterization of SnS films

X-ray diffraction (XRD) measurements of the films were performed on a Rigaku Ultima IV diffractometer with monochromatic $\text{Cu K}\alpha_1$ radiation ($\lambda = 1.5406 \text{ \AA}$) at 40 kV and 40 mA using the silicon strip detector D/teX Ultra. All samples were studied in the 2θ range of 10–60 deg with the scan step of 0.02 deg. The average crystallite size was calculated according to the Debye-Scherrer method using the full width at half maximum (FWHM) of the (021) XRD reflection of SnS (PDF 01-083-1758) [21] employing the software on the Rigaku's system (PDXL Version 1.4.0.3). The surface morphology, cross-sections and elemental composition of SnS films were studied with the help of a high resolution scanning electron microscopy (SEM) and energy dispersive X-ray analysis (EDX) using a Zeiss HR FESEM Ultra 55 with Bruker EDS system ESPRIT 1.8. An acceleration voltage for SEM measurements was 10 kV.

Optical spectra of the films were measured in the transmission mode employing UV–Vis–NIR spectrophotometer Jasco V-670 equipped with an integrating sphere. Transmittance spectra were recorded in the wavelength range of 200–2500 nm at room temperature.

Dried samples 1, 2 and 3 were characterized by Fourier transformed infrared (FTIR) spectroscopy on a Perkin-Elmer GX 2000 spectrometer using the KBr pellet technique.

3 Results and discussion

3.1 Interaction of L-cysteine and SnCl_2 in an aqueous solution

Figure 1 presents the IR spectra of the dried samples prepared from 1:1 (1) and 1:4 (3) solutions and $\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$. IR spectra of 2 are similar to that recorded for sample 1 (Fig. 1) and not presented here. The infrared spectrum of the L-cysteine in Fig. 1 is in good agreement with that reported in literature [20]. The IR spectra of 1 and 3 show significant differences in the positions and intensities of functional groups characteristic of L-cysteine.

The absence of vibrations at 2250 cm^{-1} , characteristic of the (-SH) group in L-cysteine, and weakening and shifting of frequencies characteristic of the (CS) group from 695 to 685 cm^{-1} in the IR spectra of 1 and 3 indicate that L-cysteine is coordinated to Sn^{2+} cation through sulfur atom. The disappearance of vibrations characteristic of the (-NH₂) group located at 3180 and 2080 cm^{-1} in the spectrum of L-cysteine, the appearance of new vibrations at 1470 and 1480 cm^{-1} for samples 1 and 3, respectively, and the shifting of the band from 1590 cm^{-1} to 1640 cm^{-1} refer to the complexation via nitrogen atom [16, 17]. The appearance of the vibrations at 1735 cm^{-1} and weakening the vibrations at 1395 cm^{-1} in the spectra of 1 and 3 indicate an increase in double-bond character between carbon and oxygen [16]. It demonstrates that coordinate bond is formed between oxygen atom of L-cysteine and Sn cation.

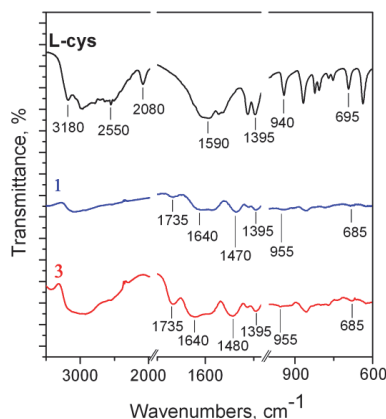


Figure 1 FTIR spectra of dried samples prepared using the precursors (SnCl_2 , L-cysteine) molar ratio of $\text{Sn}:\text{S}=1:1$ (1) and $1:4$ (3) in the solution and L-cysteine ($\text{HO}_2\text{CCH}(\text{NH}_2)\text{CH}_2\text{SH}$). FTIR spectra are recorded at room temperature.

The changes observed in the positions and intensities of vibrations of functional groups characteristic of L-cysteine in 1 and 3 compared to that of free L-cysteine indicate the formation of Sn-L-cysteine complex compound. Obtained result accords with that previously reported for cysteine complexes with Sn, Cu and Hg cations [16–18].

3.2 Effect of the growth temperature and precursors molar ratio on the film phase composition

The XRD patterns of SnS films grown from the solutions with $\text{Sn}:\text{S}$ of $1:1$ at various T_s are shown in Fig. 2. According to XRD, films deposited at temperatures between 200 and 370 °C are mainly composed of the orthorhombic polycrystalline SnS phase (PDF 01-083-1758) [21]. In addition, extra peaks placed at 2θ of 18.8°, 32.8°, 35.5°, 39.7°, 41.9°, 42.9°, 45.8°, 48.5°, 54.9° and 56.4°, denoted by "x" (Fig. 2), are present in the XRD patterns of deposited films. The diffraction peaks marked by "x" are neither belonging to the phases of Sn_2S_3 (PDF 01-072-7600), SnS_2 (PDF 01-089-2358), SnO_2 (PDF 01-071-5327), nor L-cysteine (PDF 00-032-1636) and SnCl_2 (PDF 00-001-0521) [21] as precursors. This fact indicates that unknown crystalline phase(s) is (are) also present in the sprayed films. Similar reflections have been observed on the XRD patterns of SnS films prepared by the CSP method using thiourea as a sulfur source [9]. Diffractograms of the SnS films grown by solution-based methods such as CBD [5] and ECD [6] also exhibit peaks characteristic of the "x" phase. Further studies are needed to determine this phase.

The diffraction peaks of SnS become narrower with increasing the growth temperature from 200 to 270 °C and broaden when growing the films at 320 and 370 °C. The crystallite sizes of SnS films, calculated from the FWHM of the SnS (021) reflection (Fig. 2), are presented in Table 1. The mean crystallite size increases from 18 to 21 nm

with increasing T_s from 200 to 270 °C and then decreases down to 15 nm when growing at higher temperatures. Commonly, an increase of T_s results in larger crystallite sizes of sprayed films. Opposite effect observed in SnS films prepared at $T_s > 270$ °C could be associated with the formation of additional phase(s), which hinder the growth of SnS crystallites. In spite of the fact that crystalline oxygen containing phases were not detected by XRD, oxygen content increases with increasing T_s (see Table 1). By increasing the deposition temperature thickness of the films decreased (Table 1). This is a common principle of the films grown by CSP [9].

It has been demonstrated by several reports that the $\text{Sn}:\text{S}$ ratio in the spray solution has strong effect on the phase composition of SnS films [8, 9]. XRD patterns of the films deposited by spray of $1:1$, $1:2$ and $1:4$ solutions at 270 and 370 °C are compared in Fig. 3a and 3b, respectively. According to XRD, films deposited from $1:1$ and $1:2$ solutions at 270 °C are composed of polycrystalline orthorhombic SnS phase (PDF 01-083-1758) [21] as a dominant crystalline phase and comprise a secondary crystalline "x" phase as already discussed above. The "x" peaks are more pronounced in the case of the $1:1$ film. Both $1:1$ and $1:2$ films exhibit preferential growth of crystallites along the (021) plane parallel to the substrate. Films grown by spray of $1:4$ solutions at 270 °C are found to be almost amorphous (Fig. 3a).

By changing the precursors molar ratio ($\text{Sn}:\text{S}$) in the spray solutions from $1:1$ to $1:2$, the diffraction peaks of SnS weaken and become wider, the mean crystallite size decreased from 21 to 10 nm (Table 1). These experiments show that L-cysteine as a sulfur source acts differently compared to that of commonly used thiourea when an excess of thiourea in the spray solution leads to larger crystallites [9]. Melted phase and/or high content of organic residues from L-cysteine could be responsible for retarded

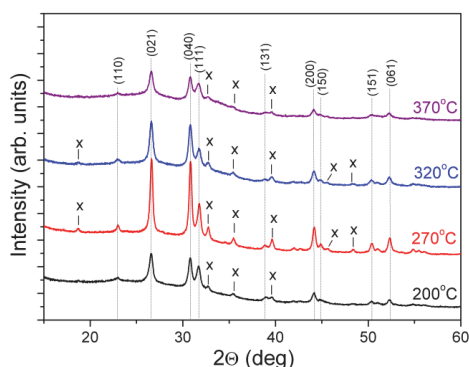


Figure 2 XRD patterns of SnS films grown at $T_s = 200$ –370 °C using the precursors (SnCl_2 , L-cysteine) molar ratio of $\text{Sn}:\text{S}=1:1$ in the spray solution. The peaks marked with (hkl) indexes belong to SnS phase (PDF 01-083-1758) [21], the peaks marked by «x» remained unidentified.

Table 1 Elemental composition (Sn, S, O, Cl and C, in at %) according to EDX, film thickness (*t*), crystallite size (*D*) and optical bandgap (*E_g*) of SnS films deposited at 270 and 370 °C and the precursors (SnCl₂ and L-cysteine) molar ratio (Sn:S) in the spraying solution.

T, °C	Sn:S in solution	[Sn] at. %	[S] at. %	[Cl] at. %	[O] at. %	[C] at. %	Sn/S	<i>t</i> , nm	<i>D</i> , nm	<i>E_g</i> , eV
270	1:1	26	21	2	31	20	1/0.8	1340	21	1.8
	1:2	20	24	1	29	26	1/1.2	1600	10	1.8
	1:4	17	24	0	27	32	1/1.4	1580	-	-
370	1:1	27	18	1	41	12	1/0.7	1000	15	2.1
	1:2	25	26	0	30	18	1/1.0	850	19	1.7
	1:4	24	25	0	31	19	1/1.0	750	18	2.0

SnS crystallite growth (Table 1). Thus, it makes no sense to use solutions with high content of L-cysteine for spraying.

Figure 3b shows the XRD patterns of the films deposited from the 1:1, 1:2 and 1:4 solutions at 370 °C. It is clearly seen that the film prepared using the 1:1 solution is composed of a mixture of SnS and "x" phases but the films deposited from the 1:2 solution contain only the SnS crystalline phase according to XRD. Spraying the 1:4 solution at 370 °C results in the film composed of a mixture of SnS and Sn₂S₃ phases. The crystallite sizes of the SnS are 16, 19 and 18 nm for the films sprayed from 1:1, 1:2 and 1:4 solutions, respectively (Table 1). Thus, the precursors' molar ratio in the solution has insignificant effect the SnS crystallite size in the film produced at 370 °C. At the same time, the Sn:S ratio in the solution has effect on the crystallite preferred orientation in the films grown at 370 °C (Fig. 3b). The SnS crystallites in the films deposited from the 1:1 solution are preferably grown along the (021) plane parallel to the substrate, while the growth along the (111)

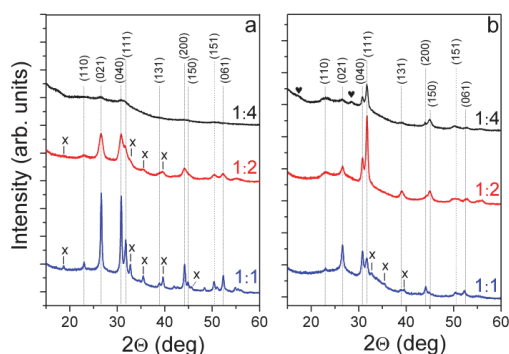


Figure 3 XRD patterns of films grown at (a) $T_s = 270$ °C and (b) $T_s = 370$ °C using the precursors (SnCl₂, L-cysteine) molar ratio of Sn:S=1:1, 1:2 and 1:4 in the spray solution. The diffraction peaks marked with (hkl) indexes belong to SnS phase (PDF 01-083-1758), «♥» belong to Sn₂S₃ (PDF 01-072-7600), the peaks marked by «x» remained unidentified.

plane is preferred in the 1:2 and 1:4 films. The difference in the XRD patterns of the 1:4 films grown at 270 and 370 °C could be due to presence of noncomplexed L-cysteine which melts at ca 240 °C and decomposes at higher temperatures [22].

3.3 Morphology, elemental composition and optical properties of sprayed films

Figure 4 shows SEM cross-sectional images of SnS films deposited at 270 and 370 °C from solutions with Sn:S ratio of 1:1, 1:2 and 1:4. According to cross-sectional views, all SnS films are compact and pin-hole free independent of the Sn:S ratio in the spray solution. The film grown at 270 °C from 1:1 solution is composed of grains with the size of ca. 20 nm. The films deposited from 1:2 and 1:4 solutions are composed of smaller grains with the size of ca 10 nm or less. L-cysteine amount in the starting solutions affects the thickness of the films (Table 1). The use of the solutions with Sn:S ratio of 1:2 and 1:4 leads to slightly thicker films compared to the use of 1:1 solutions. Films deposited at 370 °C are thinner (750–1000 nm) compared to those grown at 270 °C (1300–1600 nm) independent of the precursors molar ratio Sn:S in the spray solution. The observed phenomenon is a common characteristic of the films obtained by CSP [9]. Film thickness of the films grown at 370 °C decreased using higher amount of L-cysteine in the spray solution (Table 1).

The EDX data in Table 1 show that independent of the growth temperature and Sn:S ratio in the spray solution the

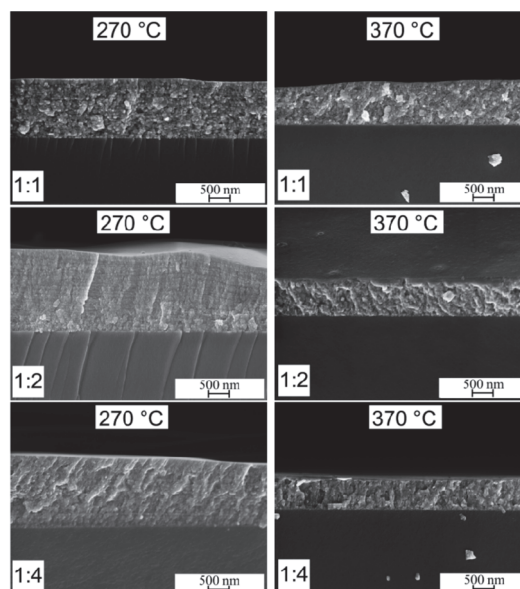


Figure 4 SEM images of films deposited on glass substrate at $T_s = 270$ °C and $T_s = 370$ °C using the precursors (SnCl₂, L-cysteine) molar ratio of Sn:S=1:1, 1:2 and 1:4 in the spray solution.

films contain high amount of carbon and oxygen. Carbon containing residues are probably originated from the L-cysteine; carbon content is higher in the films when L-cysteine enriched solutions were sprayed. Deposition at higher temperature reduces carbon content, but presence of carbon in the films deposited at 370 °C indicate that L-cysteine is not completely decomposed even at this temperature. According to the literature [22], L-cysteine is completely decomposed at temperatures above 420 °C. As expected, the oxygen content is higher in the films deposited at 370 °C. From the other hand, the higher amount of L-cysteine in the solution reduces relative amount of oxygen in the film as the films from the 1:1 solution show the highest and films from the 1:4 solution show the lowest content of oxygen at both deposition temperatures (Table 1).

The chlorine content in a film decreases by increasing both T_s and L-cysteine amount in solution. According to EDX analysis, the 1:1 films grown at 270 °C tend to be sulfur deficient ([Sn]:[S]=1:0.8), and sulfur deficiency increases when deposited at 370 °C ([Sn]:[S]=1:0.7). The films produced from 1:2 and 1:4 solutions at 270 °C are found to be sulfur rich with [Sn]:[S] of 1:1.2 and 1:1.4, respectively. Spraying the 1:2 and 1:4 solutions at 370 °C resulted in the films where atomic percentages of Sn and S are equal ([Sn]:[S] = 1:1). In spite of the fact that atomic percentages of Sn and S are equal in the film deposited at 370 °C from the 1:4 solution, the film contains relatively high amount of oxygen. As presence of SnS and Sn_2S_3 crystalline phases is confirmed by XRD, it could be supposed that amorphous oxygen containing phases could be present as well.

Figure 5 compares the optical transmittance spectra of tin sulfide films deposited at 370 °C using different Sn:S molar ratio in the spray solution. The total optical transparency is ca. 50-60 % at around 900 nm. It is clearly seen that the optical absorption edge shifted from lower wavelength region to higher wavelengths when the Sn:S ratio increased from 1:1 to 1:2. By increasing the Sn:S ratio from 1:2 to 1:4, the absorption edge shifted from higher to the lower wavelengths. The optical bandgap values (E_g) were determined from the optical transmission data using commonly known equation:

$$(\alpha \cdot hv)^n = A(hv - E_g), \quad (1)$$

where A is the constant which is independent from the photon energy, h is the Planck constant, E_g is the bandgap energy, $h\nu$ is the incident photon energy, and $n = 2$ for the direct transitions probability. The bandgap of the films is determined from the plot of $(\alpha \cdot hv)^2$ versus photon energy by extrapolating to $\alpha h\nu = 0$. Optical bandgap values are presented in Table 1. The films deposited by spray of solutions with Sn:S of 1:1 and 1:2 at 270 °C show bandgap ca. 1.8 eV, similar to that reported for the films deposited from thiourea-rich solution at 200 °C [9].

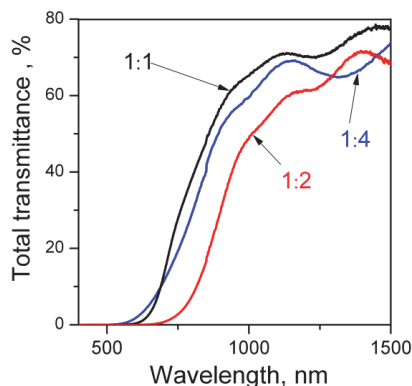


Figure 5 Total transmittance spectra of SnS films grown at 370 °C using the precursors (SnCl_2 , L-cysteine) molar ratio of Sn:S = 1:1, 1:2 and 1:4 in the spray solution.

Spraying the 1:2 solution at 370 °C results in the film with E_g of 1.7 eV, the film was single phase according to XRD (Fig. 3b). Several authors have reported that SnS films obtained by spray of thiourea-based solutions also exhibit direct bandgap of 1.7 eV [10, 11]. At the same time the spraying of 1:1 and 1:4 solutions at similar growth temperatures results in films with E_g of ca. 2.0 eV (Table 1). Many authors have supposed that the increased energy bandgap value could be attributed to the presence of other tin sulfide (SnS_2 , Sn_2S_3) or tin oxide (SnO_2) phases [7, 9].

4 Conclusions In this study we showed that L-cysteine could be employed as a novel sulfur source instead of commonly used thiourea to grow tin sulfide films by the chemical spray pyrolysis method. Use of L-cysteine as sulfur source allows using of less acidic aqueous spray solutions, with pH of 2.5, due to chelate complex formation as confirmed by IR study.

SnS films were grown by spray aqueous solutions containing SnCl_2 as a tin source and L-cysteine as a novel sulfur source at molar ratios of 1:1, 1:2 and 1:4 using deposition temperatures from 200 to 370 °C in air. According to XRD, films deposited from 1:1 solutions in the temperature range of 200-370 °C are composed of SnS as a dominant phase with preferred orientation of crystallites along the (021) plane parallel to the substrate independent of the growth temperature. Additional unidentified phase(s) is (are) also present in all 1:1 films. According to XRD, single phase SnS film could be grown by spray of 1:2 solutions at 370 °C, this film also exhibited the lowest energy gap value of 1.7 eV. Films grown from 1:4 solutions are found to be amorphous at deposition temperatures below 370 °C, and composed of a mixture of SnS and Sn_2S_3 phases when grown at 370 °C.

However, EDX study shows that SnS films contain high amount of carbon and oxygen containing residues independent of the deposition temperature and precursors'

molar ratio in the spray solution. This result indicates that deposition temperatures up to 370 °C were not enough for the thermal decomposition of residues originated from L-cysteine. Appropriate post-deposition treatment conditions (atmosphere, preferably non-oxidative, and temperature) should be found to decrease the content of residues. In order to understand the effect of the L-cysteine amount in the spray solution and determine optimal thin film deposition or annealing temperatures, the process chemistry studies, including thermoanalytical studies, should be performed.

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PAPER IV

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Post-deposition thermal treatment of sprayed SnS films



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ABSTRACT

SnS films were grown in air by chemical spray pyrolysis method using aqueous solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at molar ratios of 1:1 and 1:8 and a substrate temperature of 200 °C. As-deposited films were thermally treated at 450 °C in nitrogen or vacuum atmospheres. All samples were studied using X-ray diffractometry, Raman spectroscopy, energy-dispersive X-ray analysis, and ultraviolet–visible spectroscopy. The as-grown films consisted of cubic SnS as the only crystalline phase regardless of the molar ratio of the precursors in the spray solution. Annealing of the 1:1 films (derived from the 1:1 solution) in vacuum yielded metallic Sn, whereas annealing in N_2 produced films composed of a mixture of cubic SnS and SnO_2 phases, indicating the presence of oxygen-containing non-crystalline phases in the as-grown films. Thermal treatment of the 1:8 films in nitrogen yielded films composed of Sn_2S_3 , whereas vacuum annealing produced films consisting of orthorhombic SnS with a bandgap energy of 1.4 eV.

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1. Introduction

Tin monosulfide (SnS) is a nontoxic material exhibiting a high absorption coefficient (above 10^4 cm^{-1}) and a direct optical bandgap of 1.3–1.8 eV depending on the preparation method and crystallographic modification [1–5]. The easy availability and low cost of the constituent elements, Sn and S, and its appropriate optical properties make SnS promising for inexpensive thin-film solar cells.

SnS thin films have been fabricated by various physical and chemical deposition techniques such as high-vacuum evaporation (HVE) [4], radio frequency sputtering [5], atomic layer deposition (ALD) [6], chemical bath deposition (CBD) [2,7], aerosol-assisted chemical vapour deposition (AA-CVD) [3], and chemical spray pyrolysis (CSP) [8,9]. It has been reported that the structure and structure-dependent properties of SnS films are determined mainly by the deposition technique. For example, films obtained by HVE, ALD, and CSP are composed of orthorhombic SnS, but those prepared by AA-CVD or CBD are zinc blende SnS.

In this study, the CSP method is chosen because it requires simple, low-cost equipment and boasts scalability for large-area deposition. SnS films reportedly could be obtained by a spray technique using deposition temperatures of 200–300 °C, but the films suffered from low crystallinity and residues originating from the precursors [10,11].

Post-deposition thermal treatment of sprayed metal sulfide films in a H_2S atmosphere has been found to be effective for improving the film crystallinity and chemical purity, as reported for CuInS_2 films [12]. Compared to as-deposited films, an improvement in the film crystallinity

and a decrease in the film electrical resistivity by four orders of magnitude were reported for sprayed SnS films annealed at 400 °C in flowing argon atmosphere [8]. In addition, HVE-grown SnS films annealed in vacuum at 500 °C showed better crystallinity and photosensitivity than as-deposited films [4]. Thermal treatment of ALD-SnS films in H_2S at 400 °C significantly enhanced the grain size and increased the solar cell efficiency when SnS was used as an absorber layer [6]. Annealing of CBD-grown SnS films at 600 °C in nitrogen led to a structural phase transition from zinc blende to orthorhombic, and an increase in the film electrical conductivity was recorded [7]. To summarise, post-deposition thermal treatment of the absorber material can improve the film crystallinity and thereby contribute to enhancement of the respective solar cell efficiency. However, there are only a few reports on thermal treatment of sprayed tin sulfide films [8,9].

In this study, we investigate the effects of post-deposition thermal treatment in vacuum or nitrogen atmosphere on phase composition, elemental composition, and optical properties of tin sulfide films grown by the CSP method at 200 °C using solutions with the precursors (SnCl_2 and thiourea) molar ratios of 1:1 or 1:8. We aim to develop a single-phase film with improved crystallinity compared to the as-deposited films and the optical properties required for an absorber material.

2. Experimental details

SnS films were deposited onto soda-lime glass substrates with dimensions of 30 mm × 10 mm × 1 mm. Aqueous solutions (pH = 1) containing tin chloride (SnCl_2) and thiourea ($\text{SC}(\text{NH}_2)_2$) at Sn:S molar ratios of 1:1 or 1:8 were sprayed onto the substrate at a temperature of 200 °C in air. The process is described in detail in our previous study [10]. Films

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produced from solutions with Sn:S molar ratios of 1:1 and 1:8 are denoted as 1:1 films and 1:8 films, respectively. The as-deposited 1:1 and 1:8 films were subjected to annealing in vacuum or nitrogen atmosphere at 450 °C for 1 h. The pressure in the chamber during vacuum-annealing of the samples was 5×10^{-6} Torr. Alternatively, the samples were loaded into a quartz tube; the tube was purged with nitrogen (5N), and, after the N₂ flow rate was set to 18 mL/min, the quartz tube was inserted into a preheated tube furnace.

The X-ray diffraction (XRD) patterns of the films were measured on a Rigaku Ultima IV diffractometer with monochromatic Cu K α_1 radiation ($\lambda = 1.5406$ Å) at 40 kV and 40 mA using a silicon strip detector (D/teX Ultra). The samples were studied in a 2θ range of 10–60° with a scan step of 0.02°. The mean crystallite size was determined by the Debye–Scherrer method employing the full width at half-maximum of the cubic SnS XRD peak at a 2θ value of 26.7° [2,13] and the Sn₂S₃ XRD peak at a 2θ value of 21.5° (PDF 01–072–0031) [14] using the Rigaku system's software (PDXL Version 1.4.0.3). Raman spectra of the films were recorded at room temperature on a Horiba LabRam HR800 spectrometer using the laser line at 532 nm, which was focused on the sample with a spot diameter of 200 μ m. Spectra were recorded in the range 50–800 cm^{−1}. The surface morphologies and cross sections of the films were studied using high-resolution scanning electron microscopy (SEM), and the elemental compositions of the films were investigated by energy-dispersive X-ray (EDX) analysis using a Zeiss HR FESEM Ultra 55 scanning electron microscope with the Bruker ESPRIT 1.8 system. EDX and SEM measurements were performed at acceleration voltages of 4 kV and 10 kV, respectively. The material of as-deposited films was characterised by Fourier transformed infrared (FTIR) spectroscopy on a Perkin-Elmer GX 2000 spectrometer using the KBr pellet technique. The optical transmittance spectra of the films were recorded in the wavelength range of 200–2500 nm at room temperature using an ultraviolet-visible-near infrared (UV–Vis–NIR) spectrophotometer (Jasco V-670) equipped with an integrating sphere.

3. Results and discussion

3.1. Phase composition of as-deposited 1:1 and 1:8 films

The XRD patterns of sprayed films deposited at 200 °C using solutions with Sn:S molar ratios of 1:1 and 1:8 are shown in Fig. 1a. Similar diffractograms with characteristic triple peaks in the 2θ regions of 30–33° and 43–46° have been recorded for sprayed SnS films grown at substrate temperatures of 200–300 °C using different sulfur sources [10,11].

Analogous XRD patterns have been reported for SnS films deposited using the CBD [1,2,7] and AA-CVD [3] methods. In our previous studies [10,11] the diffraction peaks located at 2θ values of 23.0, 26.7, 30.9, 31.8, 38.8, 44.3, 45.0, 50.3, 52.4 and 54.8° were assigned to the orthorhombic SnS phase (PDF 01–083–1758) [14]. XRD peaks located at 2θ values of 18.8, 32.8, 35.5, 39.7, 42.2, 42.9, 45.8 and 48.5° were unidentified; thus, we concluded that the sprayed films contain an unknown crystalline phase in addition to orthorhombic SnS [10,11].

According to a recent report, a new cubic SnS (C-SnS) phase may exist in the Sn–S binary system [15]. The unit cell of this structure is a large cube with a cube edge of a ≈ 11.6 Å [2,13,15], twice that of the zinc blende structure [2]. Films deposited by CBD [2] and AA-CVD [3] as well as nanocrystals synthesised by a hydrothermal chemical process [13] are composed of the C-SnS phase and show XRD patterns with the characteristic triple peaks in the 2θ regions of 30–33° and 43–46° [2,13].

Raman spectroscopy is used to evaluate the vibration modes that help to identify the crystalline structure. Fig. 1b compares the Raman spectra of the as-deposited 1:1 and 1:8 films; both exhibit broad bands at around 110, 175, and 190 cm^{−1} that can be attributed to the C-SnS phase [3,13].

Considering the recently published papers [2,13,15], and taking into account the results of the XRD and Raman spectroscopic studies, it can be concluded that the films grown by spraying at 200 °C are likely composed of the C-SnS phase as the only crystalline phase regardless of the precursor molar ratio in the solution. However, the film crystallinity depends on the precursor molar ratio, as the mean crystallite size of C-SnS increases from 17 to 35 nm when the Sn:S molar ratio is changed from 1:1 to 1:8 in the spray solution (Table 1).

We invalidate the previous identification of the phase composition of the sprayed SnS films published in [10,11] and confirm that irrespective of the sulfur source used (thiourea or L-cysteine), the SnS films deposited by the CSP method at temperatures of 200–300 °C were likely to be composed of the recently reported C-SnS phase.

3.2. Phase composition of annealed 1:1 films

Fig. 2a compares the XRD patterns of 1:1 films annealed in nitrogen and vacuum. According to the XRD results, the 1:1 film annealed in nitrogen at 450 °C is composed of a mixture of C-SnS [2,13] and SnO₂ (PDF 01–077–0452) crystalline phases [14]. Thermal treatment of the 1:1 film in vacuum at 450 °C for 1 h yields a sample showing XRD reflections of the metallic Sn phase (PDF 01–086–2264) only [14].

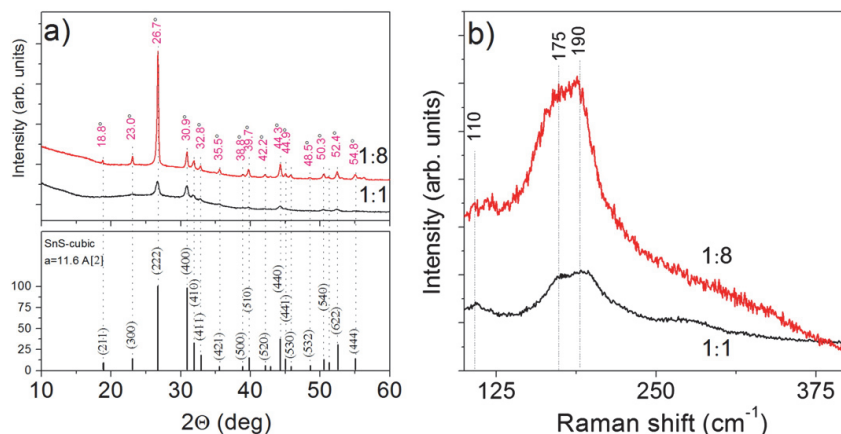


Fig. 1. (a) XRD patterns of sprayed films grown at 200 °C using solutions with SnCl₂:SC(NH₂)₂ molar ratios of 1:1 and 1:8. All the peaks marked with 2θ values belong to the cubic SnS (C-SnS) phase [2]. (b) Raman spectra of sprayed films grown at 200 °C using solutions with SnCl₂:SC(NH₂)₂ molar ratios of 1:1 and 1:8.

Table 1

Main phases according to XRD and Raman studies, the mean crystallite size (D) of a main phase according to XRD data, the atomic ratio of Sn/S, and the atomic percentage of chlorine according to EDX data, and optical bandgap (E_g) of sprayed films grown at 200 °C using solutions containing SnCl_2 and $\text{SC}(\text{NH}_2)_2$ at molar ratios of 1:1 and 1:8 (Sn:S = 1:1 and Sn:S = 1:8) and of those annealed in N_2 or in vacuum at 450 °C for 1 h.

Sn:S molar ratio in solution	Treatment	Sn/S atomic ratio in film	Cl at. %	Main phases, XRD	D nm	Main phases, Raman	E_g , eV
1:1	As-dep	1/0.5	7	C-SnS	17	C-SnS	2.1
	N_2	1/0.5	<1 ^a	C-SnS SnO ₂	18	C-SnS (SnO _x)	1.8
	Vacuum	1/0.3	<1 ^a	Sn	–	C-SnS	–
	As-dep	1/0.9	1	C-SnS	35	C-SnS	1.8
1:8	N_2	1/0.7	<1 ^a	Sn_2S_3	54	Sn_2S_3	1.7
	Vacuum	1/0.9	<1 ^a	Ort-SnS	43	C-SnS Ort-SnS	1.4

^a Below the detection limit of EDX.

Fig. 2b compares the Raman spectra of 1:1 films annealed in various atmospheres. The peaks in the Raman spectrum of the 1:1 film annealed in N_2 atmosphere show much better resolution than those of the as-grown film (see Fig. 1b); the peaks located at 110, 120, 175, 190, 200, and 225 cm^{-1} are characteristic of C-SnS [3,13]. Raman shifts at around 175 and 260 cm^{-1} might also belong to the mixed oxide states of SnO_x [16].

The Raman spectrum of the 1:1 film treated in vacuum reveals only bands at 110, 175, 190, 200, and 225 cm^{-1} , indicating that the C-SnS phase is still present in the film, although the XRD results confirmed the presence of metallic Sn only (Fig. 2a). The phase compositions of the samples according to the XRD and Raman studies are summarised in Table 1.

3.3. Phase composition of annealed 1:8 films

Fig. 3a shows the XRD patterns of 1:8 films annealed in nitrogen and vacuum. The 1:8 film annealed in nitrogen consists of crystalline Sn_2S_3 , as all the diffraction peaks could be assigned to the orthorhombic Sn_2S_3 phase (PDF 01-072-0031) [14]. The mean crystallite size of Sn_2S_3 is ca. 54 nm. Annealing of the 1:8 film in vacuum at 450 °C for 1 h yields a film composed of orthorhombic SnS (PDF 01-072-8499) [14]. The mean crystallite size of the orthorhombic SnS in the vacuum-annealed film is ca. 43 nm, which is slightly larger than the value of 35 nm characteristic of the as-grown C-SnS film (Table 1).

The Raman spectrum of the 1:8 film annealed in nitrogen (Fig. 3b) shows peaks at 152 and 235 cm^{-1} and an intense peak at 307 cm^{-1} , which are characteristic of the Sn_2S_3 phase [17]. Thus, the Raman study supports the results of the XRD study regarding the presence of

the Sn_2S_3 phase in the N_2 -annealed 1:8 film. In addition, peaks at 110 and 175 cm^{-1} and at around 190 cm^{-1} are visible in the spectrum and indicate that the C-SnS phase is also present, although it was not detected by XRD. The 1:8 film annealed in vacuum exhibits Raman peaks at 156, 180, and 220 cm^{-1} that correspond to orthorhombic SnS [4, 18]. This result is consistent with that recorded by XRD. The results of the XRD and Raman studies are summarised in Table 1.

3.4. Discussion of composition of as-deposited and annealed films

Fig. 4 shows the EDX spectra of the as-deposited 1:1 and 1:8 films. Table 1 lists the Sn/S atomic ratios in the as-sprayed and annealed films based on the EDX results, according to the precursor molar ratio (Sn:S) in the spray solution and the thermal treatment atmosphere. In the as-deposited films, the EDX spectra reveal signals of Cl and O in addition to Sn and S (Fig. 4). The relative intensities of the O and Cl signals in the as-grown 1:1 film are higher (Fig. 4a) than those of the as-grown 1:8 film (Fig. 4b), indicating higher contents of those elements in the as-deposited 1:1 film.

The as-grown 1:1 and 1:8 films are both Sn-rich (Table 1), according to their Sn/S values of 1/0.5 and 1/0.9, compared to tin monosulfide. As the Sn excess is more pronounced for the 1:1 film, the presence of another Sn-containing phase is likely and has a higher concentration in the as-grown 1:1 film. This assumption is supported by the EDX data on the Cl content (Table 1) and the following results from supporting studies: the FTIR spectrum of the 1:1 film material shows vibrations at around 3460–3580 cm^{-1} and at 1630–1670 cm^{-1} (Fig. 5) characteristic of the (OH) group [19], and XRD analysis confirms the formation of the SnO_2 phase during annealing in flowing nitrogen atmosphere (Fig. 2a).

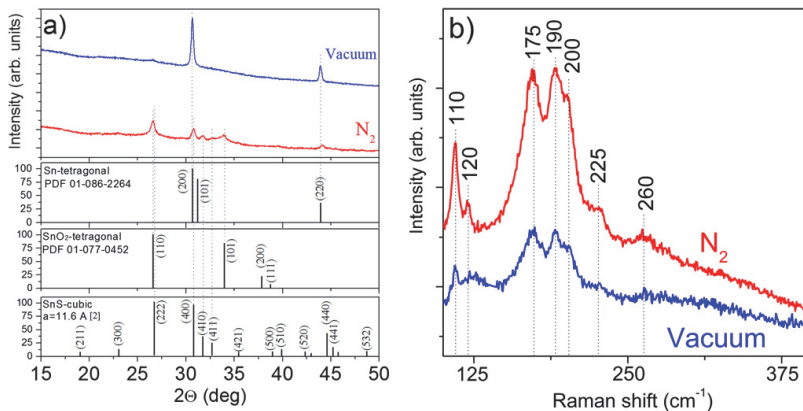


Fig. 2. (a) XRD patterns of sprayed films grown at 200 °C using a solution with a SnCl_2 : $\text{SC}(\text{NH}_2)_2$ molar ratio of 1:1 and then annealed in N_2 or in vacuum at 450 °C for 1 h. (b) Raman spectra of 1:1 films annealed in N_2 or in vacuum at 450 °C for 1 h.

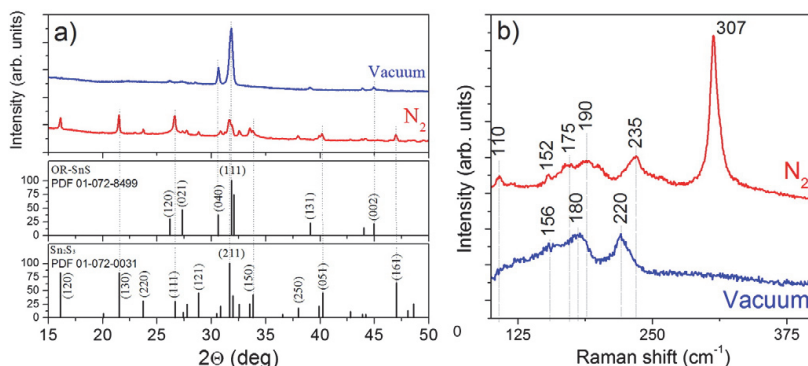
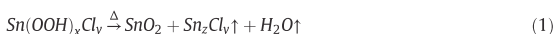


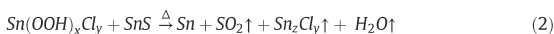
Fig. 3. (a) XRD patterns of sprayed films grown at 200 °C using a solution with a $SnCl_2:SC(NH_2)_2$ molar ratio of 1:8 and then annealed in N_2 or in vacuum at 450 °C for 1 h. (b) Raman spectra of 1:8 films annealed in N_2 or in vacuum at 450 °C for 1 h.

Thus, it can be proposed that the as-grown 1:1 film may contain an amorphous $Sn(O,OH)_xCl_y$ phase.

It could be speculated that the SnO_2 phase detected in the 1:1 film annealed in N_2 forms upon thermal decomposition of tin oxide hydroxide chloride according to the following schematic reaction:



The 1:1 film annealed in vacuum is highly tin-rich ($Sn/S = 1/0.3$) according to the EDX result; the film is composed of a mixture of Sn and SnS phases, and SnO_2 was not detected (Table 1). The formation of Sn upon annealing of the 1:1 film in vacuum is thought to be explained by the following summary reaction:



Considering that the as-deposited 1:8 film shows a Sn/S ratio of 1/0.9 and the film contains 1 at.% of chlorine according to the EDX result (Table 1), it could be assumed that non-crystalline Sn_2Cl_y and/or

$Sn(O,OH)_xCl_y$ secondary phases may also be present in the as-grown 1:8 film. However, when present, they appear in much lower amounts than in the 1:1 film, as the FTIR spectrum of the as-grown 1:8 film does not show the vibrations characteristic of the hydroxyl group (Fig. 5), and the formation of tin oxide was not detected after annealing. The as-grown and vacuum-annealed 1:8 films both show some sulfur deficiency compared to tin monosulfide. Although the N_2 -annealed 1:8 film is composed of Sn_2S_3 as the main crystalline phase (Fig. 3a and b), the Sn/S value of 1/0.7 suggests that a secondary Sn-containing non-crystalline phase is probably present.

3.5. Morphology and optical properties

The surface morphology and cross-sectional views of the as-grown 1:1 and 1:8 films and the surface morphology of the 1:8 films after annealing in nitrogen and vacuum are compared in Fig. 6. SEM images show that both as-deposited films are compact and homogeneous, with a mean grain size of ca. 20–30 nm (Fig. 6a and b). According to the cross-sectional views, the thickness of the as-grown 1:1 film, 440 nm (Fig. 6a), is less than half the value of 1030 nm for the as-grown 1:8 film (Fig. 6b). It has been shown that the precursor molar

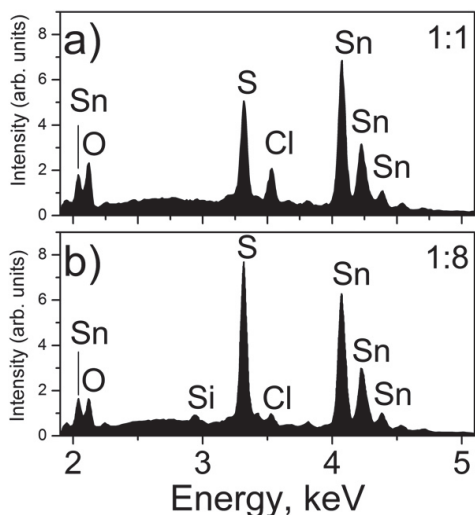


Fig. 4. EDX spectra of sprayed films grown at 200 °C using solutions with $SnCl_2:SC(NH_2)_2$ molar ratios of (a) 1:1 and (b) 1:8.

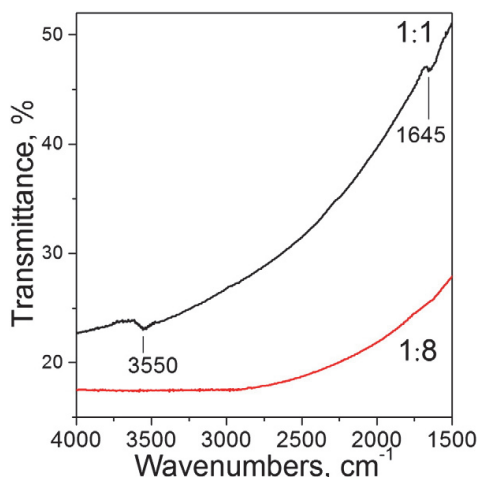


Fig. 5. FTIR spectra of sprayed films grown at 200 °C using solutions with $SnCl_2:SC(NH_2)_2$ molar ratios of 1:1 and 1:8.

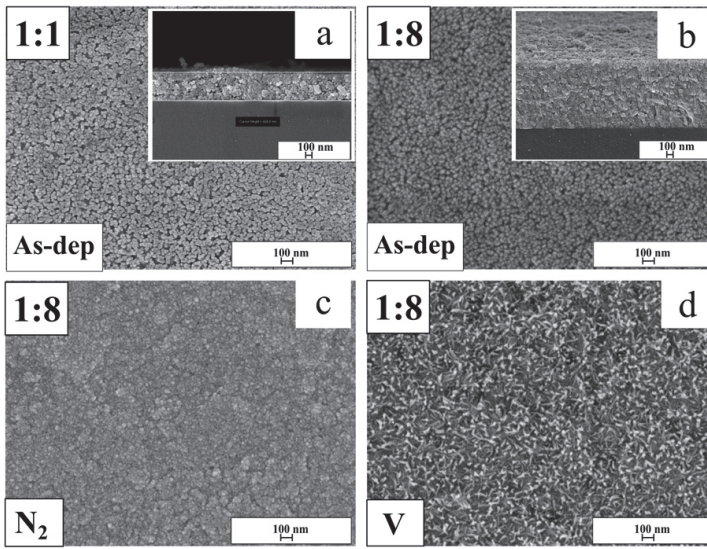


Fig. 6. SEM images of sprayed films grown at 200 °C using solutions with $\text{SnCl}_2\text{:SC(NH}_2)_2$ molar ratios of (a) 1:1 and (b) 1:8 and of 1:8 films annealed in N_2 (c) or in vacuum (d) at 450 °C for 1 h.

ratio in the spray solution affects the SnS film thickness [10,11]. Recent thermoanalytical studies have shown that an excess of thiourea in the spray solution hinders the release of volatile tin species from the system, resulting in a higher yield of the material [19]; in the present study, the SnS films grown using the 1:8 solution are found to be thicker than those grown using the 1:1 solution. Annealing of the 1:8 film in N_2 atmosphere resulted in densification of grains on the film surface (Fig. 6c). The surface morphology of the 1:8 film annealed in vacuum differs significantly from that of the as-deposited 1:8 film (Fig. 6b and d). The SEM surface image of the 1:8 film annealed in vacuum shows leaf-shaped grains (Fig. 6d), which are typical of orthorhombic SnS films produced by the HVE method [4].

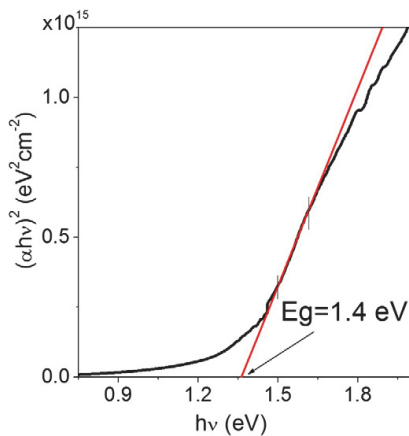


Fig. 7. Tauc plot of the sprayed 1:8 film grown at 200 °C using a solution with a $\text{SnCl}_2\text{:SC(NH}_2)_2$ molar ratio of 1:8 and then annealed in vacuum at 450 °C for 1 h.

The bandgap values of the films were evaluated from the UV–vis absorption spectra using the Tauc relation [8]:

$$(\alpha \cdot h\nu)^n = A(h\nu - E_g) \quad (3)$$

where α is the absorption coefficient, h is the Planck constant, A is a constant that is independent of the photon energy, E_g is the bandgap energy, $h\nu$ is the incident photon energy, and $n = 2$ for the direct transitions. The E_g values were found by extrapolating the straight-line portion of the $(\alpha h\nu)^2$ versus $h\nu$ graph to a zero absorption coefficient value, as shown in Fig. 7 for the 1:8 film annealed in vacuum. The optical bandgap values are presented in Table 1. The E_g value of 2.1 eV for the as-grown 1:1 film is higher than that for the as-grown 1:8 film, 1.8 eV. The difference can be explained by the presence of an amorphous oxygen-containing phase with a higher E_g value in the 1:1 film. The bandgap value of 1.8 eV for the as-sprayed 1:8 film agrees with the literature data for C-SnS films, which had E_g values of 1.65–1.8 eV [1,2]. Thermal treatment of the 1:8 film in vacuum results in an E_g value of 1.4 eV, which is close to that 1.33 eV reported for orthorhombic SnS films grown by HVE and CBD [4,7].

4. Conclusions

In this study, we showed that films grown by the chemical spray pyrolysis method at 200 °C using solutions with precursor (SnCl_2 and thiourea) molar ratios of 1:1 and 1:8 are composed of cubic SnS as the main crystalline phase.

According to XRD and Raman data, the 1:1 films annealed at 450 °C in flowing N_2 were composed of a mixture of the C-SnS and SnO_2 phases, whereas the 1:8 films annealed under similar conditions consisted of Sn_2S_3 as the main crystalline phase. The 1:1 films annealed in vacuum at 450 °C consisted of metallic Sn and cubic SnS phases. The reason for the presence of the secondary phases in the annealed films was discussed, and it was proposed that tin chloride hydrolysis products are likely present in the as-grown films and affect the phase composition of the annealed films. For fabrication of tin monosulfide films by CSP, the amount of the sulfur source in the spray solution seems to be

the principal variable, as only the films grown at 200 °C using aqueous solutions with a high excess of thiourea ($\text{SnCl}_2:\text{SC}(\text{NH}_2)_2 = 1:8$) consist of orthorhombic SnS with an E_g value of 1.4 eV after annealing at 450 °C in vacuum for 1 h.

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- [11] S. Polivtseva, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunk, Tin sulfide films by spray pyrolysis technique using L-cysteine as a novel sulfur source, *Phys. Status Solidi C* 13 (2016) 18–23.
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Curriculum vitae

Personal data

Name: Svetlana Polivtseva
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Education

Educational institution	Graduation year	Education (field of study/degree)
Omsk high school, №124	1999	Secondary education
Dostoevsky Omsk State University	2006	Organic Chemistry/ Master degree
Tallinn University of Technology	2018	Chemistry and Materials Technology

Language competence/skills

Language	Level
Russian	Native
English	Average
Estonian	Basic skills

Special courses

October, 2017 Presentation Skills training, Doctoral school of Functional materials and technologies (FMTDK)

2013–2017 UT and TUT doctoral school FMTDK, poster presentations, participation in summer schools

2013–2017 Participation at international conferences, tutorials for doctoral students, poster presentations at E-MRS Spring Meeting (2014, 2015, 2016) and 11th ESTAC (2014)

Professional employment

Period	Organisation/Country	Position
2013–2018	Tallinn University of Technology/Estonia	PhD student
2014–2014	Tallinn University of Technology/Estonia	Early-stage researcher
2007–2013	Medialogia LLC/Russia	Project Manager
2004–2007	GC Titan/Russia	Organic synthesis chemist

Research activity Projects

2016–2023	Center of Excellence project TK141 "Advanced materials and high-technology devices for sustainable energetics, sensorics and nanoelectronics"
2014–2019	Institutional Research Funding project IUT 19-4 "Thin films and nanomaterials by wet-chemical methods for next-generation photovoltaics"
2013-2015	Basis financing project of TTU B24 "Metal oxide thin films by wet chemical methods for electronic devices"
2012–2015	Estonian Science Foundation grant ETF9081 "Absorber layers by chemical spray pyrolysis for nanostructured solar cells"

Recognition

2000–2001	Fellowship award by the Vladimir Potanin Foundation, Russia
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Defended dissertations

2006 Problem-based learning as an actual pedagogical technique in teaching chemistry in secondary school, Master's dissertations, supervisor Prof. Irina Vlasova.

List of publications

1. **S. Polivtseva**, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunks, Spray pyrolysis deposition of Sn_xS_y thin films, Energy Procedia 60 (2014) 156–165.
2. **S. Polivtseva**, I. Oja Acik, M. Krunks, K. Tõnsuaadu, A. Mere, Thermoanalytical study of precursors for tin sulfide thin films deposited by chemical spray pyrolysis, J. Therm. Anal. Calorim. 121 (2015) 177–185.
3. **S. Polivtseva**, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunks, Tin sulfide films by spray pyrolysis technique using L-cysteine as a novel sulfur source, Phys. Status Solidi C 13 (2016) 18–23.
4. **S. Polivtseva**, A. Katerski, E. Kärber, I. Oja Acik, A. Mere, V. Mikli, M. Krunks, Post-deposition thermal treatment of sprayed SnS films, Thin Solid Films 633 (2017) 179–184.
5. I. Gromyko, T. Dedova, **S. Polivtseva**, J. Kois, L. Puust, I. Sildos, A. Mere, M. Krunks, Electrodeposited ZnO morphology transformations under the influence of SeO_2 additive: rods, disks, nanosheets network, In press, accepted for publication in Thin Solid Films, doi:10.1016/j.tsf.2017.12.004.

Elulookirjeldus

Isikuandmed

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Hariduskäik

Õppeasutus	Lõpetamise aeg	Haridus (eriala/kraad)
Omsk Keskkool, №124	1999	Keskharidus
Omsk F. M. Dostojevski Riiklik Ülikool	2006	Orgaaniline keemia/ magistrikraad
Tallinna Tehnikaülikool	2018	Keemia- ja materjalitehnoloogia

Keelteoskus

Keel	Tase
vene keel	emakeel
inglise keel	kesktase
eesti keel	algtase

Täiendusõpe

2017, oktoober	Esinemisoskuste koolitus, Funktsionaalsete materjalide ja tehnoloogiate doktorikool (FMTDK)
2013–2017	TTÜ FMTDK, teaduskonverents- esinemine posterettekandega, osalemine suvekoolis
2013–2017	Osalemine rahvusvahelistel konverentsidel, osalemine doktorantidele mõeldud koolitustel konverentside raames, posterettekanded E-MRS Spring Meeting'ul (2014, 2015, 2016) ja 11th ESTAC (2014)

Teenistuskäik

Töötamise aeg	Tööandja nimetus/Riik	Ametikoht
2013–2018	Tallinna Tehnikaülikool/Eesti	doktorant
2014–2014	Tallinna Tehnikaülikool/Eesti	nooremteadur
2007–2013	Medialogia LLC/Venemaa	projektijuht
2004–2007	GC Titan/Venemaa	Orgaanilise sünteesi keemik

Teadustegevus

Osalemine projektides

2016–2023	Tippkeskus TK141 "Uudsed materjalid ja kõrgtehnoloogilised seadmed energia salvestamise ja muundamise süsteemidele"
2014–2019	Institutsionaalne uurimistoetus IUT 19-4 "Õhukesed kiled ja nanomaterjalid keemilistel vedeliksadestusmeetoditel uue põlvkonna fotovoltseadistele"
2013–2015	TTÜ baasfinantseerimise projekt B24 "Keemilistel meetoditel kasvatatud metalli oksiidide õhukesed kiled elektroonikaseadistele"
2012–2015	Eesti Teadusfondi uurimistoetus ETF9081 "Absorberkihid keemilise pihustuspürolüüsi meetodil nanostruktuursetele päikesepatareidele"

Tunnustused

2000–2001 Vladimir Potanin fondi stipendium, Venemaa

Kaitstud lõputööd

2006 Probleempõhine õpe kui pedagoogiline meetod keemia õpetamiseks keskkoolis, Magistritöö, juhendaja Prof. Irina Vlasova.

Publikatsioonid

1. **S. Polivtseva**, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunk, Spray pyrolysis deposition of Sn_xS_y thin films, Energy Procedia 60 (2014) 156–165.
2. **S. Polivtseva**, I. Oja Acik, M. Krunk, K. Tõnsuaadu, A. Mere, Thermoanalytical study of precursors for tin sulfide thin films deposited by chemical spray pyrolysis, J. Therm. Anal. Calorim. 121 (2015) 177–185.
3. **S. Polivtseva**, I. Oja Acik, A. Katerski, A. Mere, V. Mikli, M. Krunk, Tin sulfide films by spray pyrolysis technique using L-cysteine as a novel sulfur source, Phys. Status Solidi C 13 (2016) 18–23.
4. **S. Polivtseva**, A. Katerski, E. Kärber, I. Oja Acik, A. Mere, V. Mikli, M. Krunk, Post-deposition thermal treatment of sprayed SnS films, Thin Solid Films 633 (2017) 179–184.
5. I. Gromyko, T. Dedova, **S. Polivtseva**, J. Kois, L. Puust, I. Sildos, A. Mere, M. Krunk, Electrodeposited ZnO morphology transformations under the influence of SeO_2 additive: rods, disks, nanosheets network, In press, accepted for publication in Thin Solid Films, doi:10.1016/j.tsf.2017.12.004.

