

## INTERMEDIATE COMPOUNDS IN FORMATION OF COPPER SULFIDES BY SPRAY PYROLYSIS

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**Abstract.** The chemical processes of the formation of copper sulfide and copper indium disulfide by chemical spray pyrolysis were investigated. The use of  $\text{CuCl}_2$  or  $(\text{CuCl}_2 + \text{InCl}_3)$  and  $\text{SC}(\text{NH}_2)_2$  as precursors led to intermediate metalorganic complex compounds in the starting water solutions. It was established that copper oxidation state is +1 in these intermediates and coordination of ligand to metal atom occurs through the sulphur atom. The chemical composition of the compound on the base of  $\text{CuCl}_2$  and  $\text{SC}(\text{NH}_2)_2$  responded to  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  which crystallised in tetragonal crystal system. Lattice parameters for  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  were calculated. Dehydration temperature for  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  is  $120^\circ\text{C}$  and thermal destruction temperature was  $210^\circ\text{C}$  at which copper sulfide as one of the pyrolysis products formed.

**Key words:** spray pyrolysis, formation chemistry, copper sulfide, copper indium disulfide, copper chloride thiourea compounds, thermal destruction.

### 1. INTRODUCTION

As compared to the standard techniques of vacuum deposition and chemical vapour deposition, chemical spray pyrolysis (CSP) is an inexpensive method for depositing large area thin films of different materials. CSP is often used for producing thin film gas sensors and component layers in  $\text{ZnO}/\text{CdS}/\text{CuInS}_2(\text{CIS})$  type solar cells.

The properties of sprayed metal oxide films correspond to the requirements, which are presented for gas sensors and optical windows in solar cells [1, 2]. During last years, an interest in the sprayed CdS films [3–5] and CIS adsorber layers [6–8] has increased due to the possibility to produce  $\text{ZnO}/\text{CdS}/\text{CIS}$  type solar cells completely by CSP. Although cell efficiencies are markedly lower than those produced by standard techniques (4 versus 10%) [5], it is believed that further efforts could reduce this difference [5, 9].

Several authors have studied the influence of technological parameters, such as chemical composition of spraying solution, molar ratio of precursors, growth temperature and type of carrier gas, to obtain thin films of CIS type materials with parameters acceptable for solar cells [6-8, 10]. Their results confirm that properties of thin films depend on the above-mentioned parameters. But only few authors have investigated the chemistry of CIS formation during the spray process [9, 11]. It is established that a similarity exists between the chemical processes occurring in CdS formation and in CIS type material thin films, if appropriate metal chlorides and thiourea or its derivatives are used as precursors [9]. The mechanism of CIS formation by spray pyrolysis is not clear yet, but our investigations on sprayed CdS films [12, 13] confirm the importance of researches in the field of formation chemistry. The results obtained provide us with data prerequisite to produce films with predicted parameters.

The aim of this study was to investigate the interaction of precursors as  $\text{CuCl}_2$  and  $\text{SC}(\text{NH}_2)_2$  or  $\text{CuCl}_2$ ,  $\text{InCl}_3$  and  $\text{SC}(\text{NH}_2)_2$  in starting water solutions. The spraying of these solutions onto heated substrate gave  $\text{Cu}_{2-x}\text{S}$  or  $\text{CuInS}_2$  thin films as a desired final product. The phases formed in starting solution and their thermal stability will be discussed.

## 2. EXPERIMENT

Copper(II)chloride dihydrate GR (Merck index 1.02733), thiourea for synthesis (Merck index 818591) and indium(III)chloride prepared from indium (extra pure) and hydrochloric acid GR (Merck index 1.00319) were used as initial chemicals in our experiments. Deionised water was used for solutions.

The precipitation of the intermediate compound occurred during 2 up to 12 hours in diluted water solutions containing  $\text{CuCl}_2$  (or  $\text{InCl}_3 + \text{CuCl}_2$ ) and  $\text{SC}(\text{NH}_2)_2$  with concentrations typical of spraying solutions (Table 1, section 1). Deposition did not occur in solutions containing  $\text{InCl}_3$  and  $\text{SC}(\text{NH}_2)_2$ . Larger amounts of intermediate compounds were obtained by mixing more concentrated water solutions of precursors at different molar ratios of cation and ligand (Table 1, section 2) and used for X-ray diffraction (XRD), chemical and thermal analysis. All precipitates were separated at room temperature, filtered, rinsed with deionised water and dried in a thermostat at 50°C.

$\text{Cu}_{2-x}\text{S}$  and  $\text{CuInS}_2$  thin films were prepared by the spray pyrolysis process using compressed air or nitrogen as carrier gases and the set-up described earlier [14].

The intermediates formed were characterised by infra-red (IR) spectroscopy, XRDA and chemical analysis. The FTIR spectra was obtained in 4000-400  $\text{cm}^{-1}$  range with a Nicolet Magna IR 750 instrument using the KBr pellet technique or with Bomen FTIR MB 122 instrument. The XRD patterns of the intermediates and thin films were recorded using a DRON-2 diffractometer with monochromatic  $\text{Cu K}_\alpha$  radiation. The



elemental composition of the samples was checked by energy dispersive spectroscopy (EDS). Concentrations of copper and chlorine in the intermediate were determined by atom absorption spectroscopy and amperometric titration with rotating Pt electrode, respectively. Thermal stability of the intermediates was examined on OD-102 type derivatograph.

Table 1

List of the prepared solutions

Section	Material index	Precursors	c, mol/l
I	11	CuCl <sub>2</sub>	0.005
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.01
	12	CuCl <sub>2</sub>	0.01
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.01
	13	CuCl <sub>2</sub>	0.01
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.02
	14	InCl <sub>3</sub>	0.005
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.01
	16	CuCl <sub>2</sub>	0.002
		InCl <sub>3</sub>	0.002
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.006
II	III-21-2	CuCl <sub>2</sub>	0.2
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.4
	III-21-3	CuCl <sub>2</sub>	0.2
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.6
	III-29-2	CuCl <sub>2</sub>	0.033
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.066
	III-30-3	CuCl <sub>2</sub>	0.033
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.033
	III-30-2	CuCl <sub>2</sub>	0.02
		InCl <sub>3</sub>	0.02
		SC(NH <sub>2</sub> ) <sub>2</sub>	0.06

### 3. RESULTS AND DISCUSSION

Precipitation was observed in spraying solutions kept in laboratory conditions. The precipitate appeared during 2 up to 12 hour period depending on the solution concentration. Table 1 shows the compositions of prepared solutions and their concentrations.

The changes in solution colour were observed when higher concentrations of CuCl<sub>2</sub> and SC(NH<sub>2</sub>)<sub>2</sub> solutions were mixed. The blue colour, typical of CuCl<sub>2</sub> solution, changed up to green after mixing with SC(NH<sub>2</sub>)<sub>2</sub> solution. The acidity of the solution increased simultaneously

with the solution colour change. Mixing of 50 ml  $\text{CuCl}_2$  ( $c = 0.1 \text{ mol/l}$ ,  $\text{pH} = 3.9$ ) and of 100 ml  $\text{SC}(\text{NH}_2)_2$  ( $c = 0.1 \text{ mol/l}$ ,  $\text{pH} = 6.4$ ) water solutions gave the final solution with  $\text{pH} = 2.8$ . An increase in acidity was observed also in the diluted solutions. The observed phenomena indicated to the change of the oxidation state of copper from +2 to +1 in the solution [15]. A white precipitate formed in colourless solution as a final result of the interaction of precursors. The precipitate consisted of needle shape crystallites of size from some twenty up to some hundred micrometers (Fig. 1).

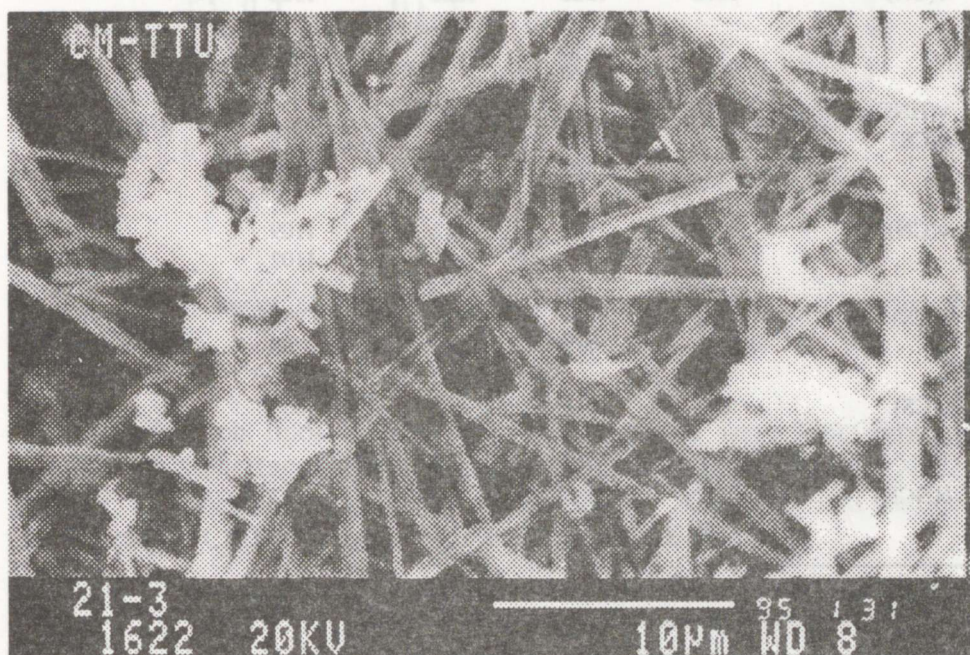


Fig. 1. SEM micrograph of copper chloride thiourea complex compound.

The vibration frequencies for the characteristic groups of ligand and formed intermediates synthesised at different molar ratios and concentrations of precursors (Table 2) revealed that  $\nu(\text{CN})$  were shifted to higher frequencies while  $\nu(\text{CS})$  were shifted to those lower than the frequencies of the free ligand – thiourea. The result confirms that coordination of ligand to metal atom occurs through the sulphur atom [16]. The results of IR measurements confirm the formation of coordination compound in  $\text{CuCl}_2 + \text{SC}(\text{NH}_2)_2$  solution as well as in  $\text{CuCl}_2 + \text{InCl}_3 + \text{SC}(\text{NH}_2)_2$  solution.

The X-ray diffraction patterns of the intermediates separated from the solutions with different molar ratios and concentrations of  $\text{CuCl}_2$  and  $\text{SC}(\text{NH}_2)_2$  (Table 1, section 2) were identical, and diffractogram of III-29-2 is demonstrated in Fig. 2.



Oscillation frequencies ( $\text{cm}^{-1}$ ) of the characteristic groups of ligand and intermediate compounds

Characteristic group	SC(NH <sub>2</sub> ) <sub>2</sub>	Material No.12* Cu:S 1:1	Material No. 13* Cu:S 1:2	Material No. 16* Cu:In:S 1:1:3	Material III-29-2** Cu:S 1:2
v(CN)	1472	1520	1520	1520	
		1512	1512	1512	1516
		1470	1470	1494	
v(HNC)	1414	1450	1450	1440	1432
		1415	1419	1418	1417
v(CS)		1400	1400	1400	1400
v(CN)	1086	1103	1112	1109	1109
			1101	1102	
v(CS)	732	724	713	732	698
		713	704	706	
v(CS)	632	611	610	607	608
$\delta$ (NCN)					
$\delta$ (NCN)	487	483	483	467	474

\* IR spectra measured on Bomen FTIR MB 122 instrument.

\*\* IR spectra measured on Nicolet Magna IR 750 instrument.

The XRD pattern of the intermediate separated from  $\text{CuCl}_2 + \text{InCl}_3 + \text{SC}(\text{NH}_2)_2$  solution was different from that presented in Fig. 2. Thus, formation of copper sulfide and copper indium disulfide passes through different complex compounds. This paper studied the intermediate formed in  $\text{CuCl}_2 + \text{SC}(\text{NH}_2)_2$  solution.

AXES 1.4A program was used to identify the diffractograms. The diffractograms do not belong to tris(thiourea)copper chloride –  $\text{Cu}(\text{SCN}_2\text{H}_4)_3\text{Cl}$  (PDF 18-1964), the only copper chloride thiourea compound is presented in JCPDS files (PDF-1, sets 1-42). Five more intensive experimental XRD peaks without specification of crystal system for  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}$  and  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl} \cdot 1/2\text{H}_2\text{O}$  are described in [17]. The recorded X-ray diffraction patterns of the investigated compounds were close to the XRD pattern of hydrate phase. Chemical analysis of the intermediate confirmed that concentrations of Cu and Cl in the intermediate respond to concentrations of Cu and Cl in mono(thiourea)copperchloride hydrate  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl} \cdot \text{H}_2\text{O}$  (Calc.: Cu, 32.9; Cl, 18.4 (mass %); Found: Cu, 32.1; Cl, 18.2 (mass %) for the material III-29-2).

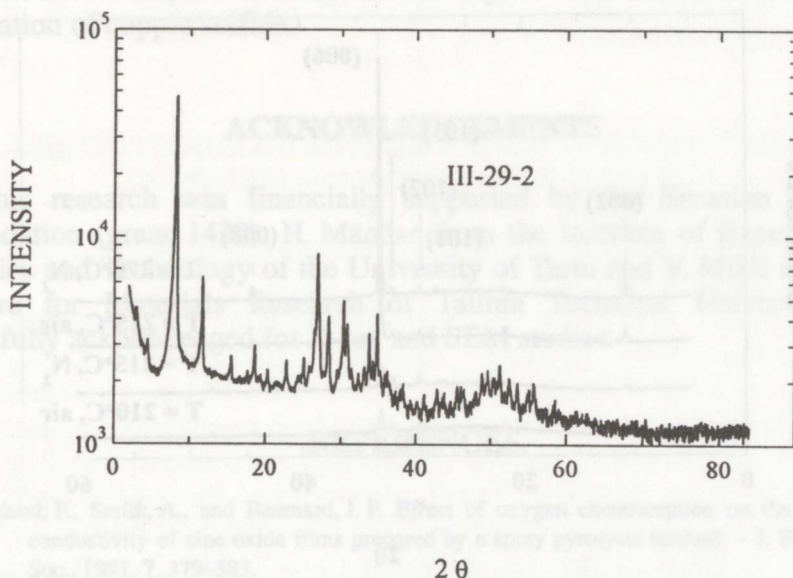


Fig. 2. X-ray diffractogram of the intermediate complex compound formed in solution of  $\text{CuCl}_2 + \text{SC}(\text{NH}_2)_2$ .

The diffraction lines of the complex compound were identified as belonging to the tetragonal crystal system by the analogy of recorded XRD patterns to  $\text{RbBr}$ -thiourea XRD pattern (PDF 20-1485), and lattice parameters for  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  were calculated (Table 3).

Table 3

**Unit cell data for  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$**

Formula	$\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$ (III-29-2)
Radiation	$\text{CuK}\alpha$ ( $\lambda = 1.5405980 \text{ \AA}$ )
Unit cell data	$a = 21.2137 \pm 0.0187 \text{ \AA}$ $b = 21.2137 \pm 0.0187 \text{ \AA}$ $c = 8.7952 \pm 0.0014 \text{ \AA}$ $\alpha = \beta = \gamma = 90.000 \pm 0.000^\circ$
Crystal system	Tetragonal

Thermal analysis (TG, DTG, DTA) of  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  indicated the dehydration at  $120^\circ\text{C}$  and the thermal destruction at temperatures higher than  $210^\circ\text{C}$ . Metal sulfide is one of the thermal decomposition products.



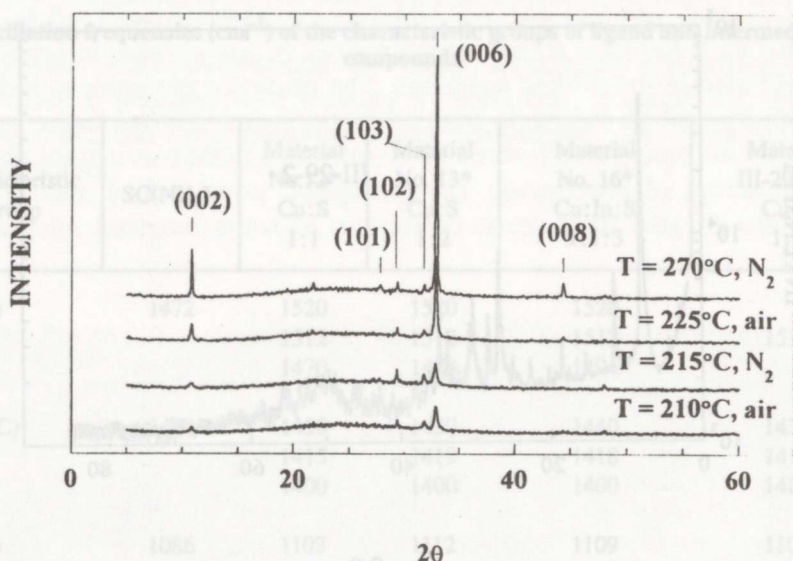


Fig. 3. X-ray diffractograms of copper sulfide thin films sprayed at different temperatures. Initial solution:  $\text{CuCl}_2 + \text{SC}(\text{NH}_2)_2 = 1:2$ ,  $[\text{CuCl}_2] = 0.002 \text{ mol/l}$ .

The spray process of the solutions of  $\text{CuCl}_2$  and  $\text{SC}(\text{NH}_2)_2$  as precursors leads to copper sulfide thin films (Fig. 3). The concentrations of the precursors in the initial solutions for CSP of copper sulfide were the same as shown in Table 1 (section 1) (0.005 – 0.01 mol/l, Cu:S = 1:1, 1:2). Pressured air and nitrogen were used as carrier gases and temperature of soldered tin bath varied from 250 up to 450°C. The formation of hexagonal copper sulfide films was detected at growth temperature about 210°C. The increase in the growth temperature up to 270°C gave CuS films exhibiting a strong orientation in the (001) direction. At higher temperatures, the formation of copper sulfate was detected. An inert media is needed to avoid the formation of copper sulfate by the oxidation of copper sulfide.

#### 4. CONCLUSIONS

It was established that the formation of copper sulfide (or copper indium disulfide) films by CSP of water solutions of  $\text{CuCl}_2$  (or  $\text{CuCl}_2 + \text{InCl}_3$ ) and  $\text{SC}(\text{NH}_2)_2$  onto heated substrate passes through the stage of the intermediate complex compound formed in initial solution. Copper oxidation state is +1 and coordination of ligand to metal atom occurs through the sulphur atom in these compounds. As a result of interaction of  $\text{CuCl}_2$  and  $\text{SC}(\text{NH}_2)_2$  in initial solutions, the intermediate complex compound  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  forms. The lattice parameters for  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  were calculated. Thermal destruction of the

intermediate complex at temperatures higher than 210°C leads to the formation of copper sulfide.

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## VAHEÜHENDID VASKSULFIIDIDE MOODUSTUMISEL KEEMILISE PIHUSTAMISE MEETODIL

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On uuritud vasksulfiidi ja vaskindiumdisulfiidi moodustumist keemilise pihustamise meetodil. Kasutades lähteainetena  $\text{CuCl}_2$  või ( $\text{CuCl}_2 + \text{InCl}_3$ ) ja  $\text{SC}(\text{NH}_2)_2$  toimub metallorgaaniliste kompleksühendite moodustumine lähtevesilahustes. Vase oksüdatsiooniaste nendes ühendites on +1 ja ligandi koordinatsioon metalli aatomiga toimub väevli aatomi kaudu.  $\text{CuCl}_2$  ja  $\text{SC}(\text{NH}_2)_2$  baasil moodustunud kompleksühendi keemiline koostis vastab  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  koostisele ja ühendil on tetragonaalne kristallstruktuur. On määratud  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  võreparameetrid.  $\text{Cu}(\text{SCN}_2\text{H}_4)\text{Cl}\cdot\text{H}_2\text{O}$  dehüdradatsiooni temperatuur on  $120^\circ\text{C}$  ja termiline lagunemine toimub  $210^\circ\text{C}$  juures vasksulfiidi kui ühe pürolüüsi produkti moodustumisega.