

## ELEMENTAL SULFUR AS A PRECURSOR FOR $\text{Cu}_x\text{S}$ LAYER FORMATION

A. BRONUSIENE, I. ANCUTIENE\*

*KTU, Department of Physical and Inorganic Chemistry, Radvilenu pl. 19, LT-50254 Kaunas*

We present a simple route for the formation of copper sulfide ( $\text{Cu}_x\text{S}$ ) layer on glass substrate using molten sulfur and copper(II/I) salt solution. A sulfur layer and copper sulfide layer obtained were investigated in detail by X-ray diffraction analysis (XRD), scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). The surface morphology studies showed that sulfur layer on glass substrate consisted of large agglomerates and copper sulfide as nanoplates or particulated agglomerates were formed. Analysis of elemental composition showed that with the increase of the temperature of copper (II/I) salt solution and the treatment time the amount of copper in the layer increased. The XRD analysis showed the polycrystalline in nature with various phases of copper sulfides such as djurleite, digenite, anilite, talnakhite and covellite. The phase composition of sulfide layer depended on the treatment time in the copper(II/I) salt solution.

(Received February 19, 2018; Accepted October 9, 2018)

*Keywords:* Elemental sulfur, Copper sulfides, SEM-EDS, XRD

### 1. Introduction

Various metal sulfides such as  $\text{Cu}_x\text{S}$ ,  $\text{CdS}$ ,  $\text{ZnS}$ , and  $\text{SnS}$ , have been intensively studied in the past two decades due to their excellent physical and chemical properties [1–3]. A study of copper sulfide layer has given much attention due to numerous technological applications in achievement of solar cells, in photochemical conversion of solar energy as solar absorber coating, as selective radiation filters on architectural windows for solar control in the warm climates, as electroconductive coatings deposited on organic polymers, etc. [2, 4].

Copper sulfide layers are one of the potentially useful metal chalcogenides with significant variation in properties depending on the stoichiometry ( $\text{Cu}_x\text{S}$ ,  $1 \leq x \leq 2$ ). Copper sulfide is a semiconductor material, that optical and electrical properties varying significantly as a function of its composition. At room temperature, five stable phases of  $\text{Cu}_x\text{S}$  are known to exist in the bulk form:  $\text{CuS}$  (covellite),  $\text{Cu}_{1.75}\text{S}$  (anilite),  $\text{Cu}_{1.8}\text{S}$  (digenite),  $\text{Cu}_{1.95}\text{S}$  (djurleite),  $\text{Cu}_2\text{S}$  (chalcocite) [3–6]. The different phases of  $\text{Cu}_x\text{S}$  exhibit considerable variations of properties, therefore they can be used in different potential applications.  $\text{Cu}_x\text{S}$  layers have been prepared by various techniques: the liquid-liquid interface reaction, chemical vapor deposition, chemical vapor reaction, electrochemical methods, successive ionic layer adsorption and reaction, etc. [5]. Physical techniques are suitable for synthesizing uniform and high quality layers, but they are more expensive and highly energy consuming. Chemical methods are economic and beautiful structures can be obtained with them.

For the sulfurization of dielectrics various solutions were proposed, e.g. the solution of elemental rhombic sulfur in carbon disulfide [7], the aqueous solutions of sodium polysulfides [8] and polythionic acids [9]. In this study copper sulfide layers on glass have been formed by the use of molten elemental sulfur as a precursor of sulfur. The use of elemental sulfur could be most convenient way to form copper sulfide by avoiding hazardous sulfurization process. For the characterization of the obtained layers scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS) and X-ray diffraction (XRD) methods were used.

---

\* Corresponding author: ingrida.ancutiene@ktu.lt

## 2. Experimental

### 2.1. Cu<sub>x</sub>S layer formation

The glass substrates of 25×25×1 mm with a matte finish on a single side were used. All substrates with liquid soap and distilled water were washed, then they were cleaned ultrasonically in acetone bath at 40 °C for 10 min, rinsed with distilled water and dried. For the formation of copper sulfide layers the glass slide was dipped in molten sulfur at 150 °C for 10 s and then sulfurized sample was treated with a copper (II/I) salt solution. 0.4 M Cu(II/I) salt solution was made from crystalline CuSO<sub>4</sub>×5H<sub>2</sub>O and a reducing agent, hydroquinone, as described in [10]. The experimental conditions are shown in Table 1.

Table 1. Conditions of treatment with copper (II/I) salt solution.

Sample No	1	2	3	4	5	6
Temperature of Cu(II/I) salt solution, °C	40				60	
Treating time in Cu(II/I) salt solution, min	1	5	10	20	1	5

Sulfur (powder, 99.98% trace metals basis from Sigma–Aldrich), crystalline copper sulfate pentahydrate (CuSO<sub>4</sub>·5H<sub>2</sub>O) (crystals and lumps, 99.999% trace metals basis from Sigma–Aldrich), and hydroquinone (C<sub>6</sub>H<sub>4</sub>(OH)<sub>2</sub>) (flakes, ≥99% ReagentPlus® from Sigma–Aldrich) for experiments were used.

### 2.2. SEM-EDS characterization

The scanning electron microscope (SEM) equipped with an energy dispersive spectrometer Quantax 200 with a detector XFlash 4030 (Bruker AXS Microanalysis GmbH, Germany), was applied for surface of formed layers analysis.

### 2.3. XRD characterization

The XRD studies of the layers on glass substrate on a DRON-6 diffractometer operating with Cu K<sub>α</sub> radiation (Ni filter) at the tube voltage of 30 kV and tube current of 20 mA were performed. X-ray diffractograms of samples were treated using the programs Search Match, ConvX, Xfit and Microsoft Office Excel.

## 3. Results and discussion

### 3.1 The layer morphology and elemental composition

Scanning electron microscopy was used to characterize the morphology of obtained sulfur and copper sulfide layers. Typical SEM images of the samples can be seen in Figs. 1 and 2. SEM images of sulfur layer on the glass slide are shown in Fig. 1. Fig. 1a shows that the surface of the layer is completely covered by sulfur agglomerated particles. A magnified SEM image (Fig. 1b) shows that sulfur layer is uniform and consists of large agglomerates.

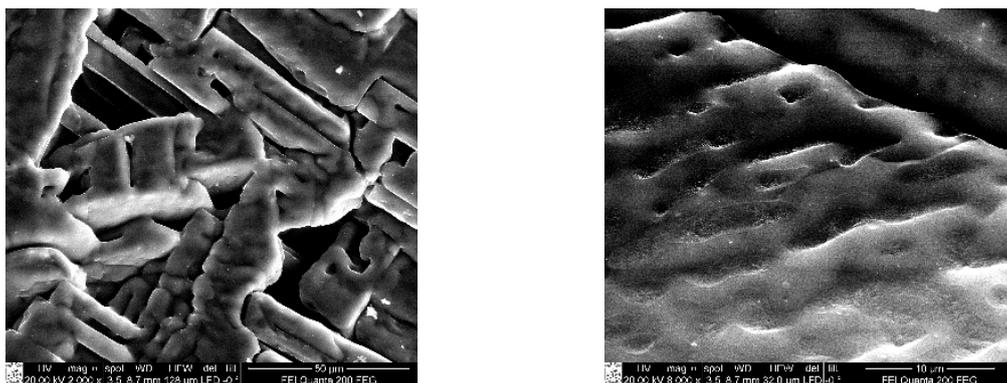


Fig. 1. SEM images of sulfur layer on the glass substrate

Fig. 2 shows SEM images of copper sulfide formed on glass with sulfur layer. It can be seen in Fig. 2a that small particles of copper sulfides cover the sulfur layer.

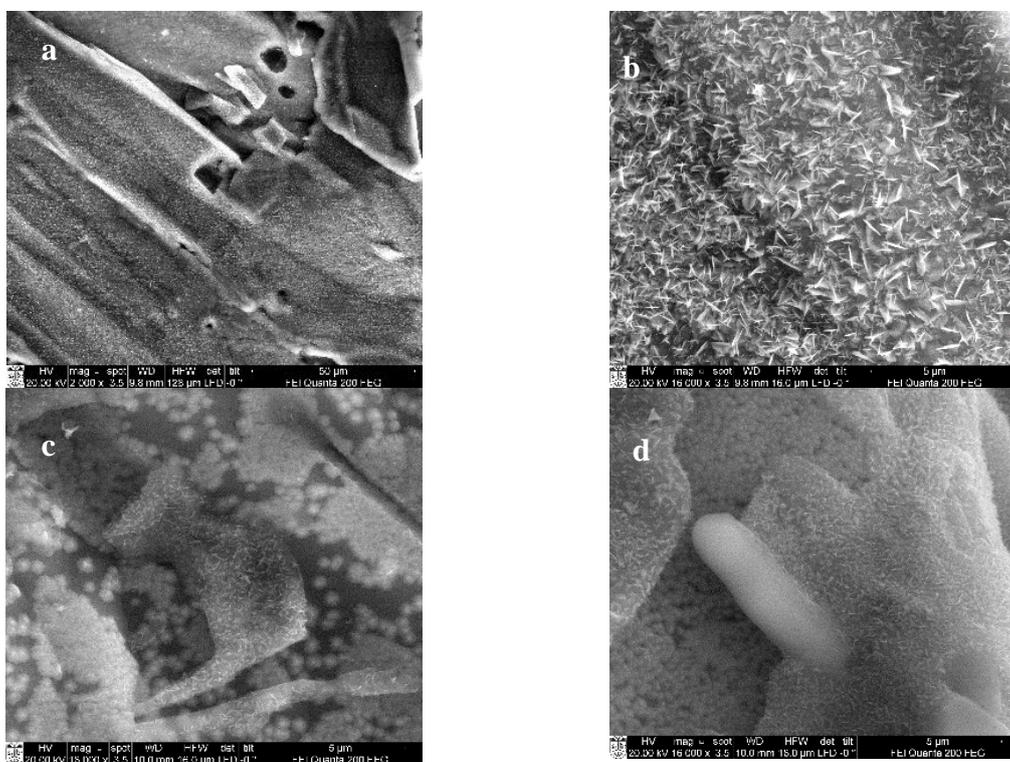


Fig. 2. SEM images of copper sulfide layer on the glass substrate: a, b – sample No 1, c – sample No 2, d – sample No 5.

A magnified SEM image (Fig. 2b) revealed the formation of  $\text{Cu}_x\text{S}$  small crystallites with angular shape as nanoplates. The influences of treating time and the temperature of copper salt solution on the layer morphology were investigated. With the increase of treating time in  $\text{Cu(II/I)}$  salt solution (Fig. 2c) particulated agglomerates of  $\text{Cu}_x\text{S}$  are formed. With the increase of the temperature of copper salt solution the formed layer is denser and more uniform.  $\text{Cu}_x\text{S}$  layer consists of nanoplates and particulated agglomerates.

The elemental composition of the obtained layer was analyzed by energy dispersive spectrometry. EDS shows the presence of S, Cu, C, O and N peaks. The graphical representation of the EDS analysis of copper sulfide layer on glass is presented in Fig. 3.

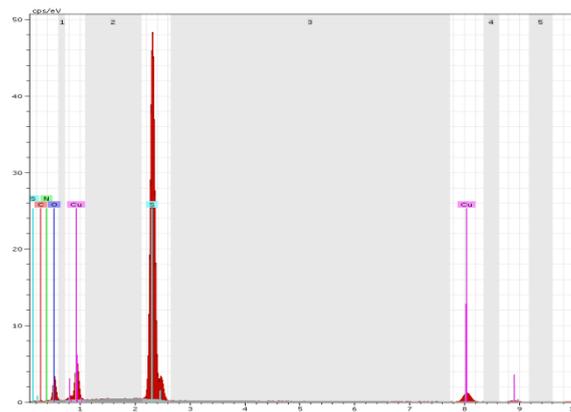


Fig. 3. EDS spectrum of copper sulfide layer. Sample No 5.

EDS data revealed large quantities of oxygen (15 – 30 wt. %), the existence of carbon (1 – 2 wt. %) and nitrogen (4 – 5 wt. %) in the samples. The existence of those elements is believed originated from the sample surface contamination in the atmosphere. Elemental compositions of the layers are summed up in Table 2. Comparison of sulfur and copper is made using the S(K) and Cu(K) lines.

Table 2. Elemental composition of  $\text{Cu}_x\text{S}$  layers (excluded C, O and N elements).

Sample	1	2	3	4	5	6
S (norm. wt. %) <i>K-series</i>	53.3	52.3	34.1	29.0	56.7	55.4
Cu (norm. wt. %) <i>K-series</i>	9.1	16.2	30.9	34.7	13.3	23.8

It can be seen that the copper amount in the formed layer increases with the increase of treating time in Cu(II/I) salt solution (samples No 1-4). With the increase of the temperature of copper salt solution the formed layer is also rich in copper (samples No 5-6). The copper amounts in the samples No 5 and 6 are approximately 1.5 times greater than those found in the samples No 1 and 2, respectively.

### 3.2 The copper sulfide layer phase composition

Elemental sulfur on the glass substrate reacts with the copper ( $\text{Cu}^+$ ) ions in the copper salt solution to form copper sulfide ( $\text{Cu}_x\text{S}$ ) compounds:



The phase composition of the obtained sulfide layer was established by comparing its X-ray diffraction patterns with those of known minerals [11–13]. The chemical composition and crystal structure of the majority of  $\text{Cu}_x\text{S}$  minerals such as chalcocite, djurleite, digenite, anilite, yarrowite, covellite were investigated [14]. The crystal structure of  $\text{Cu}_x\text{S}$  depends on the chemical composition and conditions of synthesis.

On keeping glass samples with sulfur layer for a different period in the copper salt solution at 40 °C,  $\text{Cu}_x\text{S}$  layers of different composition were obtained. The X-ray diffraction patterns of the layers showed that peaks of various copper sulfide phases exist in the layer rather than only of one (Fig. 4).

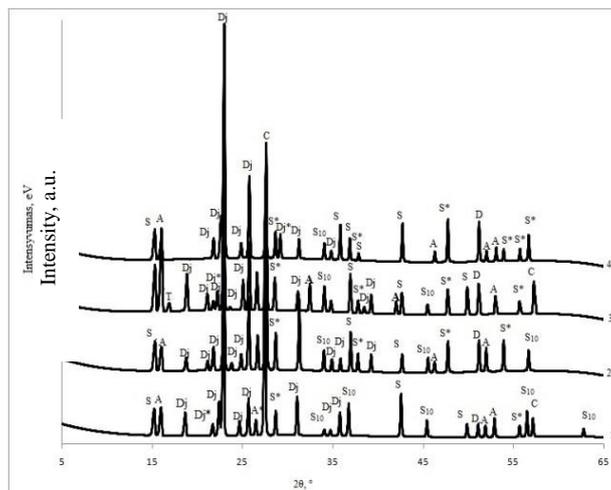


Fig.4. XRD patterns of obtained layer (peak of sulfur (JCPDS: 1-478)–S, sulfur syn (JCPDS: 24-733)–S\*, sulfur S<sub>10</sub> (JCPDS: 77-227)–S<sub>10</sub>, djurleite Cu<sub>31</sub>S<sub>16</sub> (JCPDS: 42-564)–Dj, djurleite syn Cu<sub>31</sub>S<sub>16</sub> (JCPDS: 34-660)–Dj\*, digenite Cu<sub>9</sub>S<sub>5</sub> (JCPDS: 47-1748)–D, anilite Cu<sub>7</sub>S<sub>4</sub> (JCPDS: 72-617)–A, anilite syn Cu<sub>7</sub>S<sub>4</sub> (JCPDS: 33-489)–A\*, talnakhite Cu<sub>34</sub>S<sub>32</sub> (JCPDS: 71-2438)–T, covellite CuS (JCPDS: 78-880)–C). Treatment time of glass sample with sulfur layer in the Cu(II/I) salt solution at 40°C, min: 1 – 1, 2 – 5, 3 – 10, 4 – 20.

Analysis of the diffraction patterns of samples also showed some peaks of unreacted elemental sulfur S (JCPDS card No 1-478), S<sub>10</sub> (JCPDS: 77-227) and synthetic sulfur (JCPDS: 24-733). When the period of treatment with the Cu(II/I) salt solution was 1 min (curve 1), the phases of djurleite (JCPDS: 42-564 and 34-660), anilite (JCPDS: 72-617 and 33-489), covellite (JCPDS: 78-880) and digenite (JCPDS: 47-1748) are observed. This XRD pattern shows numerous peaks of djurleite Cu<sub>31</sub>S<sub>16</sub> phase (JCPDS: 42-564) at  $2\theta=18.65, 22.26, 22.89, 24.68, 25.66, 31.06, 34.74, 35.75^\circ$ . The peak of djurleite at  $2\theta=22.89^\circ$  predominates in the X-ray diffraction pattern. The peaks of anilite Cu<sub>7</sub>S<sub>4</sub> (JCPDS: 72-617) at  $2\theta=15.96, 51.90, 52.89^\circ$  are observed too. When the period of treatment was 5 min (curve 2), the same phases of sulfur and copper sulfides are detected. The XRD pattern shows numerous peaks of synthetic sulfur at  $2\theta=28.72, 37.79, 47.75, 53.92^\circ$ . The peaks of djurleite and covellite CuS at  $2\theta=27.61^\circ$  dominate in this X-ray diffraction pattern. When the treatment time was prolonged until 10 min (curve 3), a negligible peak of talnakhite Cu<sub>34</sub>S<sub>32</sub> (JCPDS: 71-2438) at  $2\theta=16.88^\circ$  is noticeable. After 20 min of treatment time with copper salt solution (curve 4) the djurleite phase remains as dominating phase in copper sulfide layer. Hence, the phase composition of copper sulphide layer depends on the treatment time of glass sample with sulfur layer in the Cu(II/I) salt solution. The dominated phase in the composition of sulfide layer is djurleite Cu<sub>31</sub>S<sub>16</sub>. When the period of keeping in the copper salt solution is prolonged, more copper sulfides form and the intensity of copper sulfide peaks increases.



- [4] J. Podder, R. Kobayashi, M. Ichimura, *Thin Solid Films*. **472**, (2005).
- [5] M. Xin, K. Li, H. Wand, *Applied Surface Science*. **256**, (2009).
- [6] S. Li, T. Zha, Q. Wang, C. Wang, Y. Ren, Y. Chen, D. Pan, *J. Alloys Compd.* **716**, (2017).
- [7] I. Ancutiene, V. Janickis. *Centr. Eur. J. Chem.* **8**, (2010).
- [8] A. Zebrauskas, Copper sulfide formation on polymers materials. *Habil. Doct. Thesis*, 1995.
- [9] I. Ancutiene, V. Janickis, R. Giesa. *Polish J. Chem.* **78**, (2004).
- [10] I. Ancutiene, V. Janickis, S. Grevys. *Chemistry*. **8**, (1997).
- [11] A. Zebrauskas, A. Mikalauskiene and V. Latvys, *Chemistry*. **3**, (1992).
- [12] T. Yamamoto, T. Kamigaki, E. Kubota, *Kobunshi Ranbunsku. Soc. Polym. Sci.* **44**, (1987).
- [13] R. Nomura, K. Konyao, H. Matsuda, *Ind. Eng. Chem. Res.* **28**, (1988).
- [14] R. Goble, *Canad. Mineral.* **23**, (1985).