

## Conference Paper

# Precursor Compounds for $\text{Cu}_2\text{ZnSe}_2$ Structure

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## Abstract

Chemical deposition from aqueous environments has significant perspective among existing methods of obtaining  $\text{Cu}_2\text{Se}$  and  $\text{ZnSe}$  thin films. This method eliminates using complex expensive equipment, high-temperature heating, and deep vacuum. In this work, the calculation method for predicting the border conditions for the formation of individual metal chalcogenides phases was presented and widely tested on practice. Energy-dispersive analysis was used to investigate the elemental composition of the films. According to the results of thermoelectric power method, the layers had hole type conductivity.

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**Keywords:** thin films, chemical bath deposition, ion equilibrium, border conditions for deposition, copper (I) selenide, zinc selenide

## 1. Introduction

Previously, much attention was paid mainly to cadmium telluride  $\text{CdTe}$ , chalcopyrite compounds  $\text{CuInSe}_2$ ,  $\text{CuGaInSe}_2$ , which were step by step replacing traditional crystal silicon plates [1]. By replacing In/Ga by Zn/Sn in chalcopyrite, kesterite structure was obtained. This structure represents an alternative perspective material for light-absorbing layer in thin-filmed solar elements. Kesterite thin-filmed compounds  $\text{Cu}_2\text{ZnSnSe}_4$  attract attention of researchers due to their cost, environmental safety, and high efficiency of photovoltaic devices [2]. Present research attempts are pointed on alloying  $\text{ZnSe}$  film with Cu or making triple compounds Cu-Zn-Se (CZSe) including solid solutions  $\text{Zn}_{1-x}\text{Cu}_x\text{Se}$  ( $x \leq 0,10$ ), which are able to replace multicomponent chalcopyrite and kesterite structures.

One of the typical representatives of  $A^{\text{II}}B^{\text{VI}}$  compounds is  $\text{ZnSe}$ , which can be used for creation of semiconductor electronic devices and information display systems, as

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active laser medium, color TV displays, optical light modulators, and other optoelectronics devices. From the ecological point of view, it is very important that ZnSe is a nontoxic material due to absence of heavy metals in its compound.

The thin film copper (I) selenide is under increased attention of specialists in solar energy, micro- and optoelectronics, because it can express wide spectrum of semiconductor and specific electrophysical properties due to its elemental composition and microstructure. Band gap of copper (I) selenide thin films with nonstoichiometric compound  $\text{Cu}_{2-x}\text{Se}$  is 1.1–2.3 eV. These values are optimal for using  $\text{Cu}_{2-x}\text{Se}$  films as an absorbing layer and as a precursor for multicomponent kesterite  $\text{Cu}_2\text{ZnSnSe}_4$  structure. The present work is about chemical bath deposition of ZnSe and  $\text{Cu}_2\text{Se}$  thin films, which are the precursors for  $\text{Cu}_2\text{ZnSe}_2$  structure, and exploration of their elemental composition, morphology, and conductivity type.

## 2. Methods

Thin films of copper (I) selenide were obtained by chemical deposition from two reaction mixtures of different compositions. In the first case, the film was deposited from aqueous solution of copper chloride  $\text{CuCl}_2 \cdot 2\text{H}_2\text{O}$  and sodium selenosulfate  $\text{Na}_2\text{SeSO}_3$  with hydrochloric hydroxylamine  $\text{NH}_2\text{OH} \cdot \text{HCl}$ . The film obtained from this solution will be further referred to as  $\text{C}_2\text{Se-1}$ . In the second variant of synthesis, copper selenide film was obtained in the same conditions, but with addition of potassium thiocyanate KSCN to the solution as ligand for copper ions ( $\text{Cu}_2\text{Se-2}$ ). To create reducing medium for conversion bivalent copper  $\text{Cu}^{2+}$  into monovalent one  $\text{Cu}^+$ , hydrochloric hydroxylamine  $\text{NH}_2\text{OH} \cdot \text{HCl}$  was added to the reaction mixture, because it has sufficient value of reducing potential ( $\varphi_{\text{NH}_3\text{OH}^+/\text{N}_2} = -1.87 \text{ V}$ ) [3].

Zinc selenide thin films obtained by chemical bath deposition method from the reaction mixture containing zinc chloride  $\text{ZnCl}_2$ , sodium citrate  $\text{Na}_3\text{C}_6\text{H}_5\text{O}_7$  ( $\text{Na}_3\text{Cit}$ ), hydrochloric hydroxylamine  $\text{NH}_2\text{OH} \cdot \text{HCl}$ , and sodium selenosulfate  $\text{Na}_2\text{SeSO}_3$  were used as a chalcogenizer. To create alkaline medium sodium hydroxide, NaOH was used.

Sodium selenosulfate  $\text{Na}_2\text{SeSO}_3$  was obtained by dissolution of amorphous selenium in solution of sodium sulfite  $\text{Na}_2\text{SO}_3$  at the temperature of 363 K. As a substrate material for copper selenide thin films deposition, sital plates ST-50-1 with size of  $30 \times 24 \text{ mm}^2$  were used. The plates were degreased in advance. The synthesis of films was carried out at the temperature of 373 K in hermetic molybdenum glass reactors, which contained substrates fixed in specially prepared fluoroplastic holders. Reactors were

placed in thermostat TS-TB-10, which ensured accuracy of maintaining the temperature with an error  $\pm 0.1^\circ$ . Duration of the synthesis was 120 min.

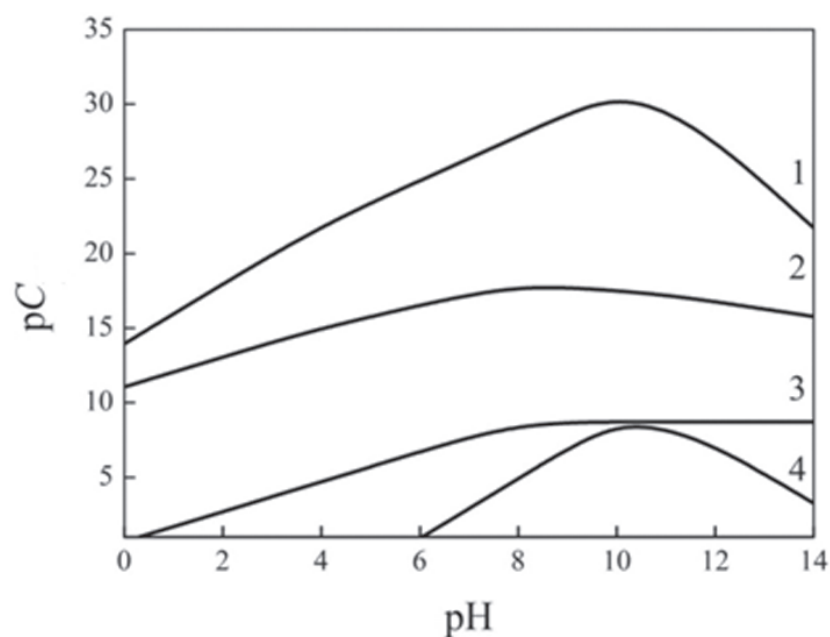
Films thickness was measured with interference microscope (Linnik's microinterferometer) MII-4M with measure error of 22%.

Study of structure-morphological characteristics and elemental compound was carried out by scanning electron microscopy method using MIRA3LMV microscope at accelerating voltage of electron bundle of 10 kV and scanning electron microscope JOEL JSM-5900 LV with attachment for energy-dispersive (EDX) analysis (EDS IncaEnergy 250). Accuracy in determination of the film's elemental composition was approximately 10%.

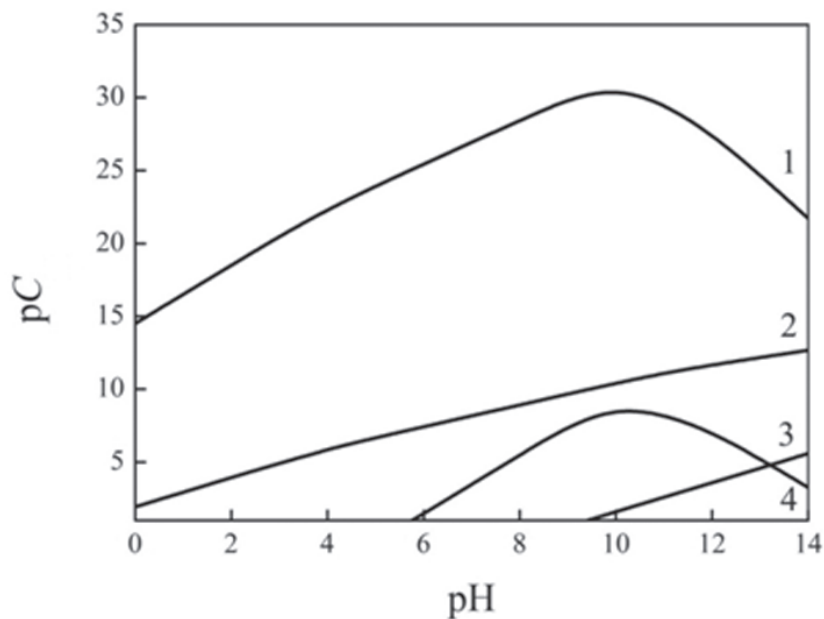
Conductivity type of deposited layers was determined using hot probe having the sign of thermoelectric power compared with semiconductor silicon of KDB brand.

### 3. Results

Thermodynamics calculations allowed revealing concentration areas and optimal pH values for the formation of mono- and bivalent copper (Figures 1 & 2) and zinc (Figure 3) selenide, as well as hydroxide phases. It made significantly easier to form the reaction mixtures concentration composition.



**Figure 1:** Border conditions of potential formation of selenides (1) CuSe and (2) Cu<sub>2</sub>Se, and hydroxides (3) CuOH and (4) Cu(OH)<sub>2</sub> in the system 'CuCl<sub>2</sub> - NH<sub>2</sub>OH·HCl - Na<sub>2</sub>SeSO<sub>3</sub>' with [CuCl<sub>2</sub>] = 0.2 mol/L, [NH<sub>2</sub>OH·HCl] = 0.2 mol/L, and [Na<sub>2</sub>SeSO<sub>3</sub>] = 0.04 mol/L; T = 298 K.



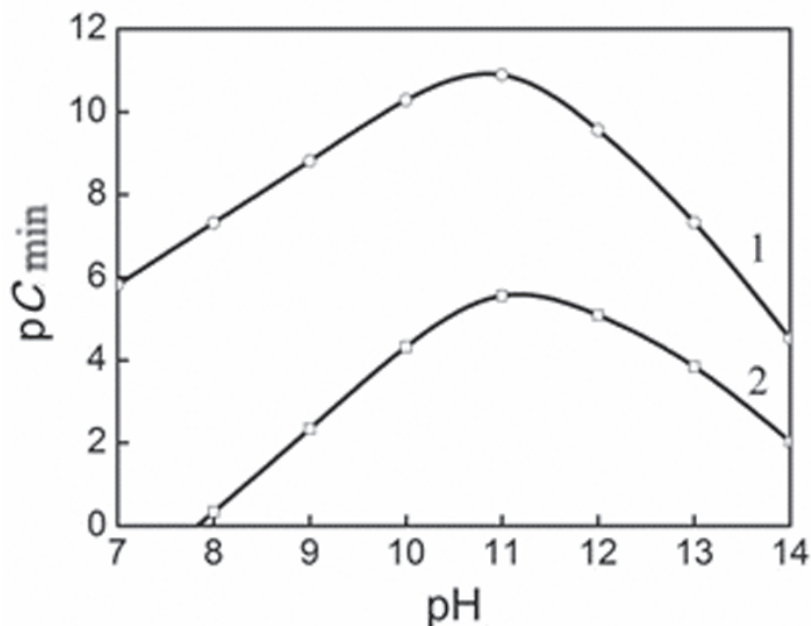
**Figure 2:** Border conditions of potential formation of selenides (1) CuSe and (2) Cu<sub>2</sub>Se, and hydroxides (3) CuOH and (4) Cu(OH)<sub>2</sub> in the system 'CuCl<sub>2</sub> – KSCN – NH<sub>2</sub>OH·HCl – Na<sub>2</sub>SeSO<sub>3</sub>' with [CuCl<sub>2</sub>] = 0.2 mol/L, [KSCN] = 0.001 mol/L, [NH<sub>2</sub>OH·HCl] = 0.1 mol/L, and [Na<sub>2</sub>SeSO<sub>3</sub>] = 0.04 mol/L; T = 298 K.

As a result of chemical deposition at the temperature of 363 K from reaction mixtures containing 0.2 mol/L of CuCl<sub>2</sub>, 0.1 mol/L NH<sub>2</sub>OH·HCl, 0.04 mol/L Na<sub>2</sub>SeSO<sub>3</sub> (pH = 3.3), and with addition of 0.001 mol/L of KSCN (pH = 4.0) to bath with the same composition, we synthesized homogenous mirror films Cu<sub>2</sub>Se-1 and Cu<sub>2</sub>Se-2, grey colored, with good adhesion to sital substrate (Figure 4).

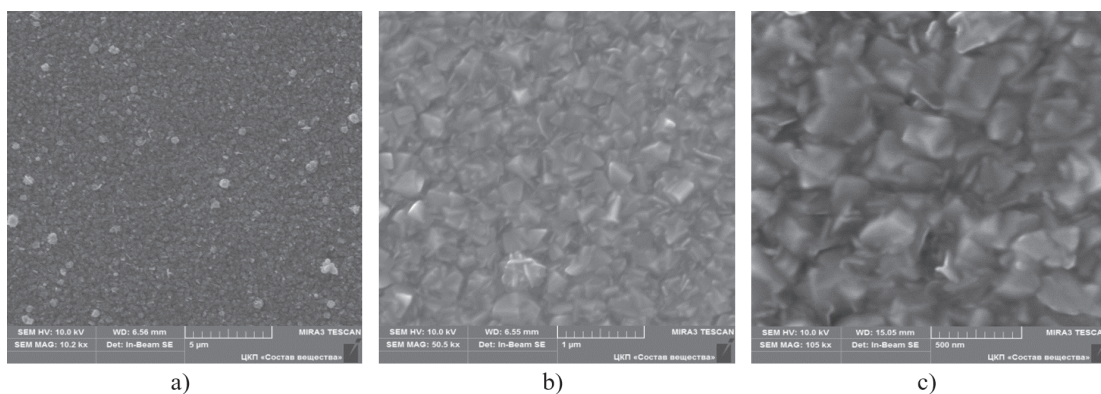
As a result of chemical deposition at 353 K from reaction mixture containing 0.03 mol/L ZnCl<sub>2</sub>, 0.35 mol/L Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>, 0.36 mol/L NH<sub>2</sub>OH·HCl, 0.99 mol/L NaOH, and 0.04 mol/L Na<sub>2</sub>SeSO<sub>3</sub> (pH = 10.5), mirror films of ZnSe were synthesized having lemon-yellow color with good adhesion to sital substrate (Figure 5).

Thickness of synthesized layers varied from 100 to 800 nm depending on the reaction mixture composition and temperature of the synthesis.

The results of EDX-analysis made us to conclude that in deposited layers there was almost exact ratio equal to two between main elements Cu/Se. Therefore, by chemical bath deposition in used reaction mixture, stoichiometric layers of monovalent copper selenide Cu<sub>2</sub>Se were obtained. Stoichiometry ratio of basic elements Zn and Se (51.61 and 48.36 at. %, correspondingly) is not respected. Nonstoichiometry can be related with presence of oxygen-containing phases in form of zinc hydroxide in the film. This was predicted by thermodynamic calculation: with pH > 10 almost 50% of metal exists in the form of neutral hydroxo-complex Zn(OH)<sub>2</sub>.



**Figure 3:** Border conditions of (1) selenide ZnSe and (2) zinc hydroxide Zn(OH)<sub>2</sub> formation in the system 'ZnCl<sub>2</sub> – Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> – NH<sub>2</sub>OH·HCl – Na<sub>2</sub>SeSO<sub>3</sub>' with the following concentrations, mol/L: [Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub>] = 0.35, [NH<sub>2</sub>OH·HCl] = 0.36, and [Na<sub>2</sub>SeSO<sub>3</sub>] = 0.04; T = 298 K.

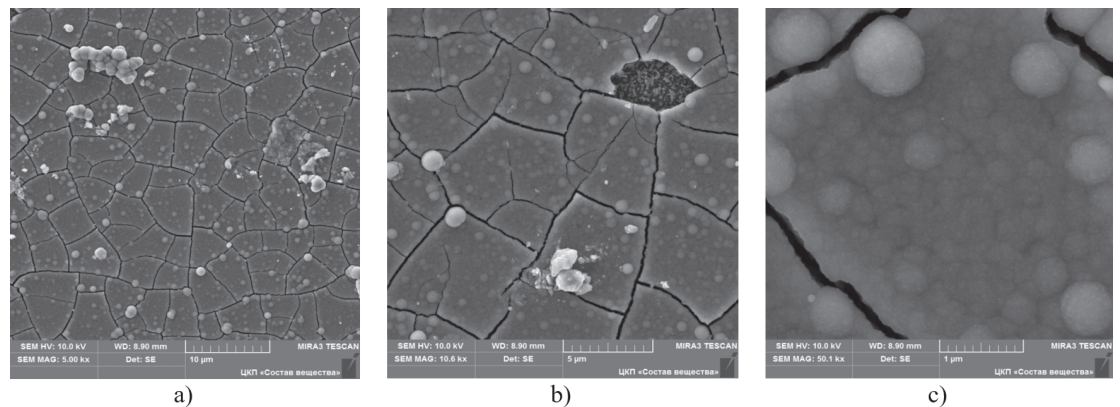


**Figure 4:** Electron microscopic images of Cu<sub>2</sub>Se-2 film obtained from reaction system containing potassium thiocyanate. Duration of the synthesis 120 min at the temperature 343 K. Magnification: (a) 10000, (b) 50000, and (c) 100000.

According to carried out research, freshly-deposited Cu<sub>2</sub>Se and ZnSe layers have a hole-type conductivity.

## 4. Conclusion

Analysis of ion equilibrium at the temperature 298 K in the reaction systems 'CuCl<sub>2</sub> – NH<sub>2</sub>OH·HCl – Na<sub>2</sub>SeSO<sub>3</sub>', 'CuCl<sub>2</sub> – NH<sub>2</sub>OH·HCl – Na<sub>2</sub>SeSO<sub>3</sub> – KSCN', and 'ZnCl<sub>2</sub> – Na<sub>3</sub>C<sub>6</sub>H<sub>5</sub>O<sub>7</sub> – NH<sub>2</sub>OH·HCl – H<sub>2</sub>O' established prevailing copper and zinc complex forms. The border conditions and concentration areas of mono- and bivalent copper, as well as zinc



**Figure 5:** Electron microscope image of ZnSe film obtained from the reaction system ' $\text{ZnCl}_2 - \text{Na}_3\text{C}_6\text{H}_5\text{O}_7 - \text{NH}_2\text{OH}\cdot\text{HCl} - \text{Na}_2\text{SeSO}_3$ ' at the temperature of 353 K and duration of the synthesis – 120 min. Magnification: (a) 5000, (b) 10000, and (c) 50000.

selenides formation were determined. The possibility of arising admixture phases in the form of copper and zinc hydroxides was evaluated. Alkaline area of pH was shown to be the most favorable for chemical copper (I) selenide solid phase deposition.

Energy dispersive analysis established that using sodium selenosulfate as chalcogenizer and presence of hydrochloric hydroxylamine in the solution provided creation of reducing medium and transformation of bivalent copper into monovalent state, leading to the formation of  $\text{Cu}_2\text{Se}$  solid phase. It was established that using sodium selenosulfate as chalcogenizer provided formation of ZnSe solid phase characterized by nonstoichiometry of selenium, which could be related to formation of zinc oxygen-containing phase of  $\text{Zn}(\text{OH})_2$  apart from metal selenide.

Copper (I) selenide films with stoichiometric composition were obtained by chemical bath deposition from the explored reaction mixtures on sitall substrates. Thickness of the films depended on initial conditions, being in the range of 100–500 nm; the films had a good adhesion to the substrate. According to electron microscopy, the films were formed from crystallites with size of 80–450 nm.

From citrate-hydroxylamine reaction mixture by chemical bath deposition, semiconductor films of zinc selenide were obtained. The films had a good adhesion to sitall substrate; their thickness was 100–800 nm depending on the given conditions. According to electron microscopy, ZnSe film consisted of globular formations with average size in substrate plane ~200–500 nm. These formations, in their turn, were made of nanoglobules with 30–50 nm size.

Thermoelectric power research proved that obtained  $\text{Cu}_2\text{Se}$  and ZnSe semiconductor layers had a hole type conductivity.

## References

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