Investigation of Some Regularities of ZnS and ZnSe Films Synthesis

Martyn Sozanskyi[1], Ruslana Chaykivska[2], Ruslana Guminilovych[1], Pavlo Shapoval[1], Yosyp Yatchyshyn[1]

[1]Analytical Chemistry Department, Lviv Pol ytechnic National University, UKRAINE, Lviv, S. Bandera Street 12, E-mail: sozanskyi.m@gmail.com

[2]Department of Technology of Organic Materials, Lviv Polytechnic National University, UKRAINE, Lviv, St. Yura square 2, E-mail: Ruslana.chaikivska.xt.2013@lpnu.ua

Abstract – The process of synthesis ZnS and ZnSe thin films by a chemical bath deposition method (CBD) has been investigated. The phase composition, surface morphology and thickness of ZnS and ZnSe films were studied. The kinetic curves of ZnS and ZnSe synthesis was obtained and activation parameters were calculated. The correlation between thickness, morphology and activation energy have been established.

Key words – semiconductor films, chemical bath deposition, structure and morphology of thin films.

I. Introduction

Zinc sulfide (ZnS) and zinc selenide (ZnSe) films due to their properties are widely used in various electronic optical devices. ZnS buffer layers are a cadmium free, wider energy band gap, alternative to the cadmium sulfide buffer layers commonly used in solar cells. ZnSe is a preferred material for lenses, windows, output couplers and beam expanders for its low absorptivity at infrared wavelengths and its visible transmission. The chemical deposition method is one of the most profitable ways of their growth [1].

II. Experimental

Zinc sulfide and zinc selenide films were synthesized from working solutions, which had been prepared by mixing of aqueous solutions of zinc chloride ($ZnCl_2$), complexing agent, chalcogenizing reagent (thiourea ($(NH_2)_2CS$) or selenium (Se)) and ammonium hydroxide (NH_4OH) or hydrazine hydrate ($N_2H_4 \cdot H_2O$), as auxiliary components. The duration of synthesis was 5-75 min, the temperature – 60-90 °C. As complexing agents were: tri-sodium citrate ($Na_3C_6H_5O_7$) for ZnS films and sodium hydroxide (NaOH) for both – ZnS and ZnSe films. The concentration of the initial solutions of zinc chloride was equal to 1.0 M; trisodium citrate – 0.5 M; sodium hydroxide – 7.0 M; thiourea – 1.0 M; ammonium hydroxide – 14.28 M; hydrazine hydrate – 5.0 M. Only freshly prepared reagents entered the working solutions for synthesis of ZnS and ZnSe thin films. The deposition has carried out on pre-prepared glass substrates with an area of 3.24 cm^2. After the end of the reaction the substrates were taken out from the bath; the surface was washed with a jet of distilled water to take off the remains of working solution and dried in air.

The phase composition of the ZnS and ZnSe was investigated by X-ray powder diffraction (diffractometer DRON-3.0, Cu*K*α-radiation). Primary processing of the experimental diffraction data in order to identify the phases was made using the PowderCell program [2]. The investigation of surface morphology of the films was carried out using a raster electron microscope REM-106Y equipped with a system for microanalysis. The thickness of films was measured on profilometer DEKTAK IIA (SLOAN). The kinetic curves of ZnS and ZnSe synthesis was obtained turbidimetricly at the 900 nm wavelenght on spectrophotometer Xion 500 «Dr. Lange».

III. Results and discussion

The phase analysis of ZnS and ZnSe films on glass substrates has been held (Fig. 1 and Fig. 2). It can be see that films are single-phase. Peaks that corresponded to the cubic phase of ZnS or ZnSe (sphalerite) on all diffractograms can be identified. The lines of theoretical diffractograms of phases, mentioned above are shown for comparison.

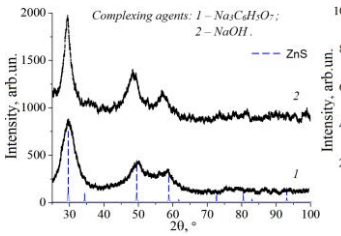


Fig. 1. X-ray diffractograms of ZnS films

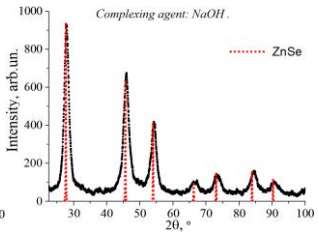


Fig. 2. X-ray diffractogram of ZnSe film

Investigation of films surface morphology (Fig. 3-5) showed that the films are solid, homogeneous, with a small amount of surface defects. In the case of using sodium hydroxide (Fig. 4-5) there is seen spherical particles. Microanalysis of films showed that the atomic ratio of zinc to the chalcogens was almost stoichiometric. There was a slight excess of the zinc in the case of using tri-sodium citrate and slight excess of chalcogens in the case of using sodium hydroxide.

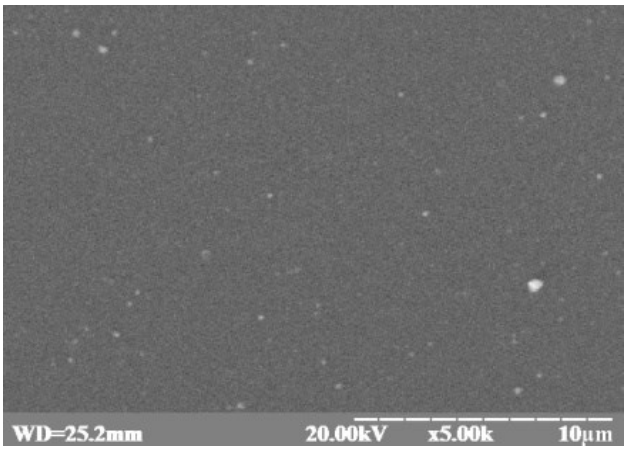


Fig. 3. Surface morfology of ZnS film, synthesized with using $Na_3C_6H_5O_7$

Lviv Polytechnic National University Institutional Repository http://ena.lp.edu.ua

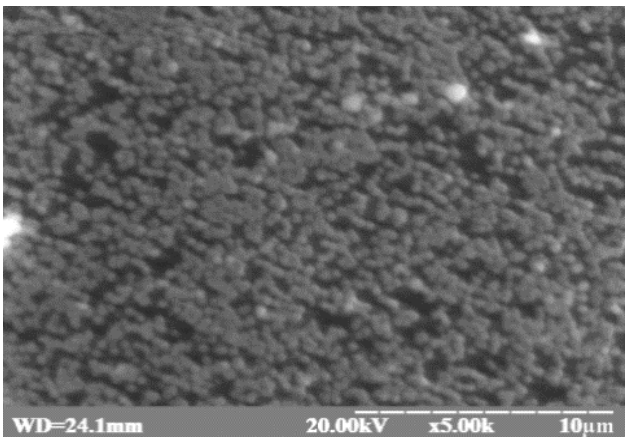


Fig. 4. Surface morfology of ZnS film, synthesized with using NaOH

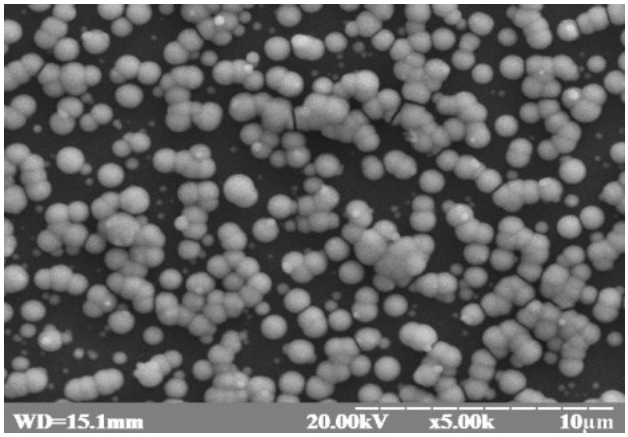


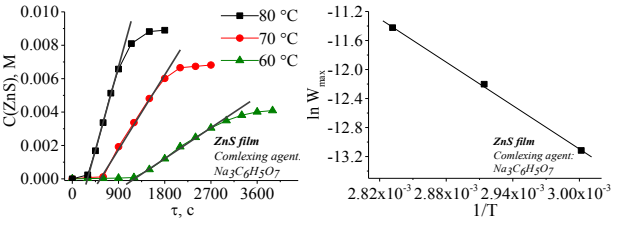
Fig. 5. Surface morfology of ZnSe film, synthesized with using NaOH

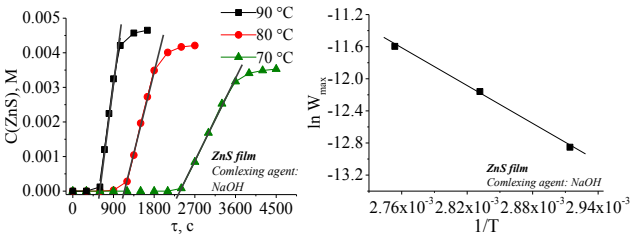
Activation parameters of the synthesis of ZnS and ZnSe films have been investigated. The study was done – the temperature effect on an accumulated amount of insoluble reaction product, during a certain time (Fig. 6). The curves has S-like form. It's indicates that synthesis of ZnS and ZnSe have autocatalytic character.

According to the temperature dependences of ln W_{max} – 1/T (Fig. 7), the values of effective activation energy (E_a) was calculated (Table 1). It can be seen that the greatest E_a value has ZnS, synthesized with trisodium citrate, and the lowest value is reached in the case of zinc selenide. It can be explained by its lower solubility than the zinc sulfide.

The thickness of ZnS and ZnSe films, taken out from the bath at the end of synthesis, was determined. When the results of thickness and activation energy had been compared (Table. 1), the same character of these values was observed. The ZnSe film with lowest value of E_a has the greatest thickness and the ZnS films with greather values of activation energies has lower thicknesses.

Also, there can be seen a correlation between a morphology and activation energy. The ZnSe and ZnS (obtained by using NaOH) films surface with big and average size of spherical particles are the most and medium energetically profitable. Therefore, it is logical that zinc sulphide films, obtained by using $Na_3C_6H_5O_7$, are without visible spherical particles, because their synthesis are the most energetically demanding.





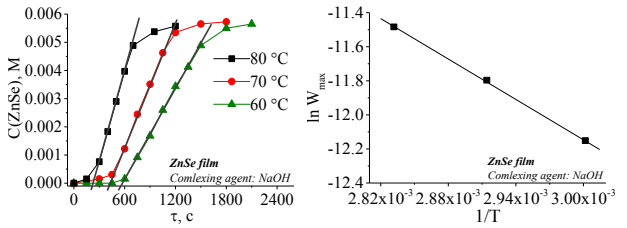


Fig. 6. Kinetic curves of ZnS and ZnSe synthesis with different complexing agents at different temperatures

Fig. 7. Temperature dependences of reaction rates in the coordinates of Arrhenius equation

TABLE 1

EFFECTIVE ACTIVATION ENERGIES OF SYNTHESIS AND THICKNESSES OF OF ZINC SULPHIDE AND ZINC SELENIDE THIN FILMS

Film	Complexing agent	Activation energy (E_a), kJ/mol	Thickness, nm
ZnS	$Na_3C_6H_5O_7$	82.85±5.40	83
ZnS	NaOH	65.16±4.62	193
ZnSe	NaOH	32.66±2.63	450

Conclusion

The ZnS and ZnSe thin films were synthesized by the CBD method. The single-phase composition of the samples was confirmed by X-ray analysis. Surface morphology of films were investigated. According to the results of kinetic curves of ZnS and ZnSe synthesis the activation parameters were calculated. The correlation between thickness, morphology and activation energy have been established.

References

[1] Pawar S.M. Recent status of chemical bath deposited metal chalcogenide and metal oxide thin films / S.M. Pawar, B.S. Pawar, J.H. Kim et. all // Curr. Appl. Phys., vol. 11(2), pp.117-161, 2011.

[2] W. Kraus, G. Nolze PowderCell for Windows (version 2.4). – Berlin: Federal Institute for Materials Research and Testing, March 2000.

Lviv Polytechnic National University Institutional Repository http://ena.lp.edu.ua