JOURNAL OF OPTOELECTRONICS AND ADVANCED MATERIALS Vol. 13, No. 11-12, November – December 2011, p. 1548 - 1552

Growth and characterization of chemical bath deposited zinc sulphide thin films

M. STEFAN*, E.-J. POPOVICI[a], I. BALDEA[b], R. GRECU[a]
National Institute for R &D of Isotopic and Molecular Technology, 71 – 103Donath Str., 400295, Cluj-Napoca, Romania
[a] *"Raluca Ripan"Institute for Research in Chemistry, "Babes-Bolyai" University, 30 Fantanele Str , 400294Cluj-Napoca, Romania*
[b] *Faculty of Chemistry and Chemical Engineering, "Babes-Bolyai" University, 400028Cluj-Napoca, Romania*

Zinc sulphide thin films were deposited on optical glass platelets, from chemical bath containing variable amounts of thiourea, zinc acetate, ammonia and sodium citrate. The growth aspects of ZnS/glass/ZnS heterostructures by monolayer technique and their subsequent characterization were studied.The samples were investigated by FT-IR and UV-VIS absorption spectroscopy, photoluminescence measurements, scanning electron microscopy and X-ray diffraction. The optical and morpho-structural characteristics of zinc sulphide layers are strongly influenced by reagent concentrations as well as by deposition time.

(Received June 2, 2011; accepted November 23, 2011)

Keywords: Zinc sulphide, Chemical bath deposition, Optical properties, Thin films

1. Introduction

The synthesis of binary metal chalcogenides has been a rapidly growing area of research due to their important physical and chemical properties. Zinc sulphide is an important II–VI semiconductor with a wide band gap which is suitable for applications in solar cells, solar selective decorative coatings, UV light emitting diode, photocatalysis and phosphors in flat panel displays [1-4].

The films obtained by chemical deposition methods are found to be of comparable quality to those obtained by more sophisticated and expensive physical deposition processes [5-8]. Among the chemical methods, chemical bath deposition (CBD) is a very attractive way for producing ZnS thin films, due to the possibility of large-area deposition at low cost and simple instrumentation. At present, much work has been carried out to obtain high quality thin films by optimizing the parameters of chemical bath deposition process, such as the ratio of the reagents, pH value of the solution, temperature and duration of the procedure [9-10].

The paper presents some of our results on the growth and characterization of chemical bath deposited zinc sulphide thin films. The effects of the preparative conditions on deposition rate, optical and morpho-structural properties of ZnS thin films are discussed.

2. Experimental part

The chemical bath deposition process uses a controlled chemical reaction for the precipitation of the thin film. In our experiments, optical glass substrates (30mm x 45mm x 1 mm) are immersed in an alkaline solution containing zinc acetate as the zinc ion source, thiourea as the sulphur source, NH_3 aqueous solution and sodium citrate as a complexion agent and ammonia to adjust the pH value. The bath temperature during the deposition was maintained in the range of 82-86°C and the pH of the solution within the values of 9.5-10.5. The details of experimental technique have been described in our previous works [11-12]. Thin films of zinc sulphide were produced by monolayer technique. In order to evaluate the photoluminescence ability of films, some samples were prepared with or without copper doping and with chloride co-doping (NaCl flux). The doping stage was performed during the films growing stage, by introducing the Cu–salts into the chemical bath. The co-doping stage was achieved by immersing the ZnS/glass/ZnS heterostructures in NaCl-containing solution. After drying the doped/co-doped ZnS/glass/ZnS heterostructures were annealed at 500°C, in nitrogen atmosphere.

FT-IR spectra of the powders from chemical bath before and after the thermal treatment were recorded in the 500-4000 cm^{-1} range, on JASCO 610 Spectrometer (KBr pellets technique).The optical properties of ZnS thin films were evaluated with an UNICAM Spectrometer UV4. Scanning electron microscopy (SEM) with a JOEL-JSM 5510LV microscope was achieved in order to evaluate the films morfology. The measurements were performed using Au-coated films. Photoluminescence characteristics of ZnS thin films was evaluated by a Perkin Elmer 204

Fluorescence Spectrofotometer. Film thickness (h) was evaluated by the micro-weighing method [13, 14].

3. Results and discussion

The deposition of zinc sulphide thin films by CBD technique in zinc acetate–sodium citrate –thiourea system consists of complexation of the zinc cations with sodium citrate and the consecutive reaction with the sulphide ions provided by the hydrolysis of thiourea. Ammonia was used to adjust the pH value.

ZnS thin films were grown by monolayer technique, from chemical bath with the following composition: [zinc acetate] = $15x10^{-3}$ M; [sodium citrate] = $7.5x10^{-3} \div 60x10^{-3}$ M; [ammonia] = $300x10^{-3}$ M; [thiourea] = $150 \text{ x } 10^{-3}$ M. Two samples series were obtained namely:

- Series A: one 2 hrs deposition, from bath containing different $[Zn^{2+}]$: $[Cyt^{3-}]$ ratios as follows: 1:4 (sample F1.6); 1:3 (sample F2.4); 1:2 (samples F3.4, F3.6); 1:1.5 (samples F4.4, F4.6) and 1:0.5 (samples F7.4).
- Series B: one deposition, from bath containing $[Zn^{2+}]$: $[Cyt^{3-}]$ =1:3 , using a variable growing time as follows: 0.5h (sample F8.1); 1h (sample F8.2); 1.5h (sample F8.3); 2.5h (sample F8.4); 3h (sample F8.3); 4h (sample F8.6);

Under the above-mentioned conditions, adherent and homogeneous ZnS thin films were grown on both sides of the glass substrates to give the ZnS/glass/ZnS heterostructures. It is well known that it is difficult to deposit ZnS thin film due to its small solubility product (Ksp = $10^{-24.7}$). The formation of the ZnS thin films takes place either in the bulk of the solution due to the spontaneous ZnS precipitation, by a homogeneous reaction, or at the surfaces of the substrate leading to the formation of the film, by a heterogeneous reaction**.** The general reaction involved in the deposition process was:

$$Zn(CH_3COO)_2 + (NH_2)_2CS + 2OH^- \rightarrow ZnS + H_2CN_2 + + 2H_2O + 2CH_3COO^- \quad (1)$$

In the deposition process of ZnS thin films, a series of complex reactions are involved, with the formation of intermediates [15-16]. To highlight this, FTIR spectra of bulk ZnS from chemical bath before and after thermal treatment in air were recorded (figure 1).

The bands appearing in the 3200–3600 cm^{-1} regions can be assigned to the O-H stretching modes of water. This very weak peak indicates the presence of trace amount of adsorbed water in the powder. The peak at 2900 cm^{-1} attributed to C-H bonds of sodium citrate is removed with thermal treatment.The isothiocyanate group (- N= C= S) shows a strong peak in the 2000–2273 cm^{-1} domain. The presence of sodium citrate is evidenced by bands at 1600 -1400 cm^{-1} that are characteristic for the vibrations of the carboxyl group, COO^-. The peaks at 1115 cm^{-1} and 648 cm^{-1} can be attributed to Zn - OH stretching mode and Zn OH bending mode, respectively.

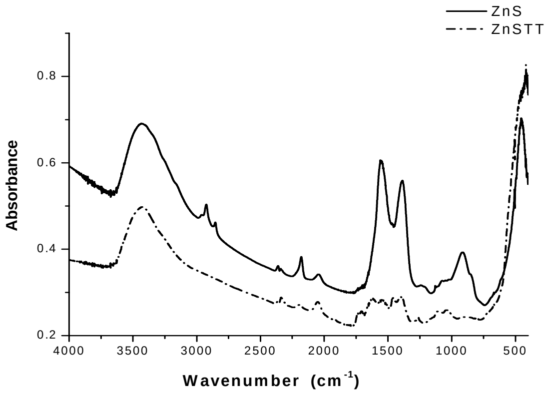

Fig. 1. FT-IR spectra of bulk zinc sulphide before (ZnS) and after thermal treatment (ZnS TT).

By heat treatment at 350°C sodium citrate and cyanamide are removed. The strong band at 490 cm^{-1} is attributed to the Zn-S bond.

Several experimental parameters have been modified in order to establish the optimum ones for the thin films growth including reagents concentrations, deposition technique; etc

The influence of the concentration of the complexing agent (sodium citrate) on the ZnS films thickness has been investigated at constant zinc acetate and thiourea concentrations

The molar ratio between Zn^{2+} and $C_6H_5O_7^{3-}$ (abbreviated as Cyt^{3-}) species was varied between 1.0: 0.5 and 1.0: 4.0. The dependence of ZnS film thickness on sodium citrate concentration is illustrated in Fig. 2.

The concentration of complexing agent influences both the growing rate and the film quality. Formation of high-quality films, adherent to the substrate is conditioned by the presence of sodium citrate in the bath, which serves as a complexing agent, deposition rate regulator. Under employed experimental conditions, two categories of samples could be prepared namely adherent and homogeneous films at high Na-citrate concentration ($[Zn^{2+}]$: $[Cyt^{3-}]$ = 1:2÷ 1:4) and powdery and less adherent films at relatively low citrate concentration ($[Zn^{2+}]$: $[Cyt^{3-}]$ = 1:0.5÷ 1:1.5). Based on this study and after repeated experiments it was found that the optimal $[Zn^{2+}]$: $[Cyt^{3-}]$ ratio was 1:3.

In order to elucidate some kinetics aspects for the ZnS films growing process, using the monolayer technique, the evolution of film thickness depending on the duration of deposition was plotted (fig.3). One note that the film thickness tends to a limit. The film growing curve can be described by a linear equation (1) of the form:

$$h = \frac{at}{1 + bt} \quad (2)$$

where h is the film thickness, t deposition time and a, b are constants. The equation can be linearized in double reciprocal form (2):

$$\frac{1}{h} = \frac{b}{a} + \frac{1}{a}\frac{1}{t} \qquad (3)$$

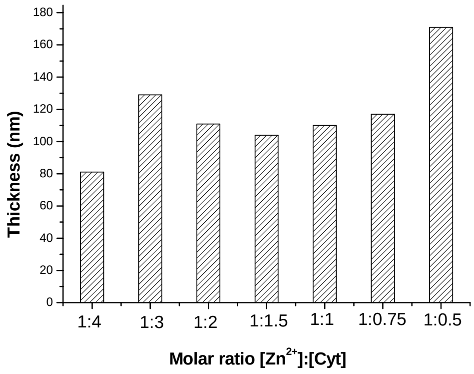

Fig. 2. Variation of films thickness, using different [Zn^{2+}]:[Cyt^{3-}] ratios (Series A).

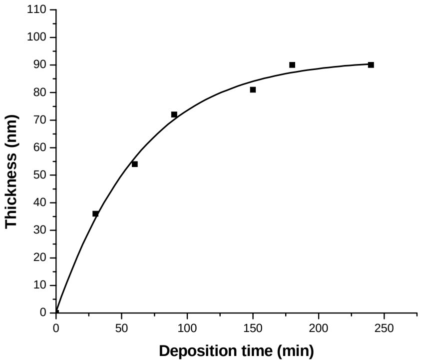

Fig. 3. Variation of films thickness with deposition time (Series B).

The reciprocal values of thickness and time were calculated and then were plotted as illustrated in Fig. 4. The o correlation coefficient is 0.9946. In the experimental conditions selected for preparation of ZnS from CBD and from the right parameters, constants a and b respectivelly from equation (1) are calculated. Thus, a = 1/slope = 1 / 0.6194 = 1.61 nm / min and b = ordered / slope = 0.0074/0.6194 = 0.012 min^{-1}. These constants are "constants rate."

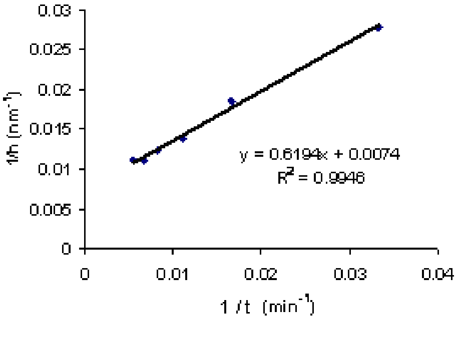

Fig. 4. Linearization curve of the growing process of monolayer films for series B.

This graph illustrates the variation of ZnS film thickness with time, for monolayer deposition. A similar approach could be made for the deposition of the second layer, and so on.

The optical properties of the ZnS films deposited on glass substrates were determined from the transmission measurements. Fig. 5 presents the comparative transmittance spectra of some ZnS/glass/ZnS heterostructures grown by monolayer technique at different sodium citrate concentrations (Fig. 5a) and different deposition time (Fig. 5b), respectively.

The optical transmittance of ZnS thin films is strongly influenced by the preparation conditions of ZnS/glass/ZnS heterostructures. The optical homogeneity of the films prepared in baths with relatively low citrate concentration is poor. As expected, the film transmission decreases as the thickness increases. The pattern of interference fringes suggests that the films do not have a uniform thickness. At reagent molar ratio [Zn^{2+}]: [Cyt^{3-}] = 1:3 the films exhibit more than 70% transmittance. The optimal deposition bath, considering all ingredients, corresponds to the reagent ratio of: [Zn^{2+}]: [Cyt^{3}]: [NH$_3$]: [thiourea] =1:3:20:10. These conditions were considered as standard.

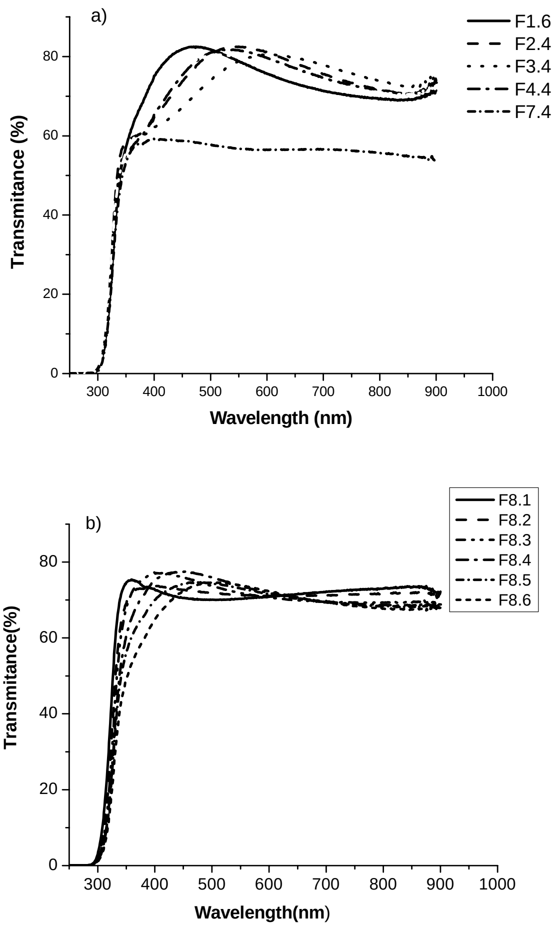

Fig. 5. Comparative transmittance spectra of some ZnS/glass/ZnS heterostructures prepared by monolayer technique in: (a) different molar ratio and (b) different deposition time.

The surface structure and morphology of the films were evidenced by SEM investigations. Fig. 6 shows the surface of some ZnS/glass/ZnS heterostructures obtained by monolayer technique, from bath with different sodium citrate concentrations (F3.6; F4.6). Both ZnS samples showed uniform, continuous smooth surfaces with few spherical blobs scattered over them; there are adsorbed particles on films formed in the saturation phase. The small and regular cracks on the surface of the films suggest the amorphous character of the layer. There are adsorbed particles on films formed in the saturation phase.

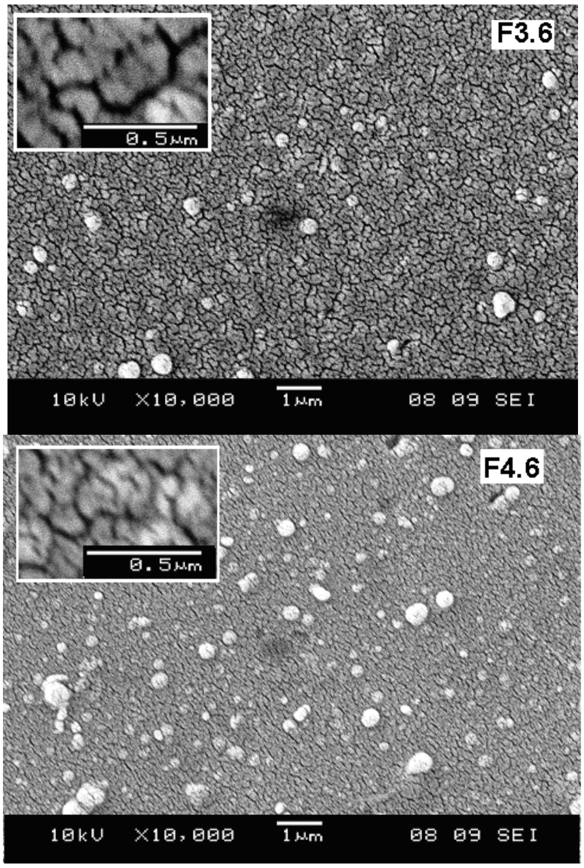

Fig. 6. SEM images of some ZnS/glass/ZnS heterostructures prepared using different [Zn^{2+}]:[Cyt^{3-}] ratios.

The crystallographic properties of ZnS thin films have been investigated by XRD technique. The X-ray diffractograms of the heat-treated ZnS thin films are typical for the non-crystalline structures. It was found that the light emitting properties of ZnS and other luminescent thin films and powdes are highly influenced by the annealing regime as well as doping conditions [17-21].

Preliminary tests were performed on monolayer ZnS thin films to develop luminescent properties.

The effect of the doping/co-doping on the photoluminescence (PL) characteristics of ZnS/glass/ZnS heterostructures prepared by monolayer technique is illustrated in Fig. 7.

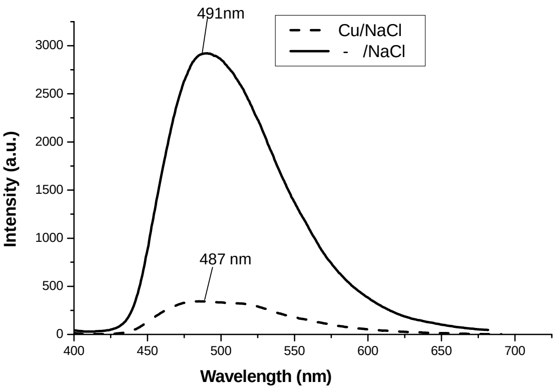

Fig. 7. Emission spectra of ZnS/glass/ZnS heterostructures obtained in different conditions.

The photoluminescence measurements revealed that films doped by introducing Cu-ions into the chemical bath and successively co-doped by immersion in flux (NaCl) containing solution show the ability to develop light emitting properties.

PL spectra of heterostructures obtained with copper and sodium chloride i.e. ZnS(Cu, NaCl)/glass/ ZnS(Cu, NaCl) heterostructures and only with sodium chloride flux i.e. ZnS(NaCl)/glass/ ZnS(NaCl) presents a broadband emission with variable intensity, depending on the doping conditions.

The copper containing films do not reveal a significant effect of the Cu-doping (Figure 7).The sample presents a weak green emission at 487 nm. Emission intensity is much higher in the sample without copper activator. In this case, the peak position (491 nm) suggests that, in our experimental conditions, ZnS layer is contaminated with small amounts of oxygen, taken from the aqueous precipitation medium, or during the annealing stage. Generally, O-doped zinc sulphide (ZnS:O) has a maximum emission at about 500 nm.

4. Conclusions

Zinc sulphide thin films were successfully prepared by chemical bath deposition onto optical glass platelets using zinc acetate– sodium citrate – ammonia – thiourea system, by monolayer technique. By optimizing the experimental parameters such as the reagents ratio, pH value of the solution, temperature and duration of the procedure, high quality films were obtained. Some kinetic aspects were highlighted on the formation of ZnS films by monolayer technique.

The Uv-Vis investigations on ZnS thin films evidenced that films show good transmittance and the optical properties change, depending on the experimental conditions.

Surface morphology is different for films obtained from bath with different sodium citrate amounts and different deposition time.

Photoluminescence investigations revealed that all the samples show a weak luminescence in the green spectral range. It is very possible that this was due to the oxygen doping, for the deposition was performed in an aqueous medium.

References

[1] S. M. Pawar, B. S. Pawar, J. H. Kim, Oh-Shim Joo, C. D. Lokhande, Current Appl. Phys. **11**, 117 (2011).

[2] X. Fang, T. Zhai, U. K. Gautam, L. Li, L. Wu, Y. Bando, D. Golberg , Progress in Mat. Sci. **56**, 175 (2011).

[3] X. Wu, F. Lai, L. Lin, J. Lv, B. Zhuang, Q. Yan, Z. Huang, Appl. Surf. Sci. **254**, 6455 (2008).

[4] H. K. Sadekar, N. G. Deshpande, Y. G. Gudage, A. Ghosh, S. D. Chavhan , S. R. Gosavi, Ramphal Sharma , J. Alloys Comp. **453**, 519 (2008).

[5] T. Nakada, M. Hongo, E. Hayashi, Thin Solid Films **431-432**, 242 (2008).

[6] L. X. Shao, K. H. Chang, H. L. Hwang, Appl. Surf. Sci. **212-213**, 305 (2003).

[7] P. K. Ghosh, Sk.F. Ahmed, S. Jana, K. K. Chattopadhyay, Optical Mat. **29**, 1584 (2007).

[8] N. K. Allouche, T. B. Nasr, N. T. Kamoun, C. Gausch, Mat. Chem. Phys. **123**, 620 (2011).

[9] F. Long, W. M. Wang, Z. K. Cui, L. Z. Fan, Z. G Zou, T. K. Jia, Chem. Phys. Lett. **462**, 84 (2008).

[10] Y. Zhang, X. Y. Dang, J. Jin, T. Yu, B. Z. Li, Q. He, F. Y. Li, Y. Sun, Appl. Surf. Sci. **256**, 6871 (2010).

[11] M. Lădar, E.- J. Popovici, L. Pascu, R. Grecu, I. C. Popescu, E. Indrea, Studia Universitas Babes-Bolyai, Physica **2,** 469 (2003).

[12] R. Grecu, E.- J. Popovici, M. Lădar, E. Indrea, J. Optoel Adv. Mat. **6**(1), 127 (2004).

[13] L. Pascu, E.- J. Popovici, C. Dan, R. Grecu, E. Indrea, Proceedigs of SPIE **4430**, 267 (2001).

[14] M. C. Rosu, R. C. Suciu, S. V. Dreve, T.D.Silipas, I. Bratu, E. Indrea, Rev. Roum. Chim. **56**(6), 601(2011).

[15] J. M. Dona, J. Herrero, J. Electrochem. Soc. **141**(1), 205 (1994).

[16] R. Sahraei, G. M. Aval, A. Goudarzi, J. Alloys Comp. **466**, 492 (2008).

[17] M. Ladar , E. J. Popovici, I. Baldea, R. Grecu, E. Indrea, J.Alloys Comp. **434-435**, 697 (2007).

[18] J. Ebothe, T. A. El Hichou, M. Troyon, Thin Solid Films **487,** 54 (2005).

[19] W. Q. Peng, G. W. Cong, S. C. Qu, Z. G. Wang, Optical Mat. **29**, 313(2006).

[20] A. Mesaros-Hristea, O. Alm, E.J. Popovici, M. Boman,Thin Solid Films, **516**, 8431 (2009).

[21] A.I. Cadis, E. J. Popovici, E.Bica, I. Perhaita, L. Barbu-Tudoran, E. Indrea, Chalcogenide Lett., **7**(11), 631(2010).

---

[*] Corresponding author: marialadar@yahoo.com