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*Dedicated to professor Gh. Marcu at his 80th anniversary*

# GROWTH AND CHARACTERISATION OF ZINC SULPHIDE THIN FILMS DEPOSITED ON ITO COATED GLASS

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**ABSTRACT.** ZnS thin films were grown onto ITO coated glass by chemical bath deposition. The multilayer technique was used in order to prepare ZnS/ITO/glass/ ZnS heterostructures with variable film thickness. Optical properties were investigated by UV-VIS absorption/reflection and fluorescence spectroscopy. The main ZnS films characteristics were correlated with the growing conditions and the annealing regime.

**Key words**: zinc sulphide; thin films; ITO coated glass; chemical bath deposition

## 1. INTRODUCTION

Zinc sulphide (ZnS) is a wide, direct band gap semiconductor with interesting optoelectronic properties. A large range of applications exists for thin films of ZnS such as n-window layers of solar cells, electroluminescent displays and other optoelectronic devices [1]. Different methods could be used for ZnS thin films preparation including sputtering, metal organic chemical vapour deposition (MOCVD), atomic layer epitaxy (ALE), pulsed laser deposition, chemical bath deposition (CBD) or electrodeposition [2,3]. Among them, CBD is a simple and inexpensive method and produces uniform, adherent and reproducible films. Moreover, CBD is a low temperature technique and can be used for ZnS deposition onto a variety of substrates.

The aim of this work is to study the influence of different CBD preparative parameters on the quality of ZnS thin films deposited onto ITO coated glass and, especially, on some of their optical characteristics, including their luminescence ability.

## 2. EXPERIMENTAL PART

ZnS thin films have been grown by CBD method on ITO (indium tin oxide) coated glass pieces provided by Optical Filters Ltd.(UK). The deposition of ZnS was carried out from a mixture of zinc acetate, thiourea, $NH_3$aqueous solution, and sodium citrate and twice distilled water. Prior the deposition, the platelets (50mm x 25mm x 1mm) were ultrasonically cleaned with acetone/ethanol mixture and dried. Moreover, all the deposition reagents were purified by some characteristic procedures. The multilayer deposition technique was used in order to prepare

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ZnS/ITO/glass/ZnS heterostructures with variable film thickness. The deposition temperature was 82-86ºC and pH mixture was 9.5-10.5. The details of experimental technique have been previously described [4,5]. Most of the heterostructures were obtained in a chemical bath with the standard composition: $[Zn^{2+}]$ = 0.015 M; $[C_6H_5O_7^{3-}]$ = 0.060; $[NH_3]$ = 0.300 M; [thiourea] = 0.15 M. Several samples, for luminescence investigation purpose, were prepared from chemical bath containing a smaller concentration of sodium citrate, namely 0.045 M.

The samples were washed, dried (100°C) and annealed in nitrogen (500ºC) or air (400÷550°C), using a special protecting system. In the later case, the thermal treatment was performed in special to ZnS-based mixtures containing Cu and Mn salts to generate luminescent ZnS thin films.

Zinc sulphide thin films were characterised by thickness and UV-Vis transmittance and reflectance spectra, as well as some photoluminescence investigations. Prior performing the measurements, ZnS films were partially removed with HCl (1:1) from some ZnS/ITO/glass/ZnS heterostructures to give the corresponding ZnS/ITO/glass heterostructures. Optical investigations were performed by using a UNICAM Spectrometer UV4 and photoluminescence measurements by means of a Perkin Elmer 204 Fluorescence Spectrophotometer ($\lambda_{exc}$= 365 nm). The film thickness was evaluated by the microweighing, as indicated in our previous work [6].

## 3. RESULTS AND DISCUSSION

ZnS/ITO/glass/ZnS heterostructures were prepared from chemical bath containing zinc acetate as zinc source, thiourea as sulphur source, aqueous solution of $NH_3$ as chelating and pH regulating agent, sodium citrate as chelating agent and doubly distilled water.

The chemical bath deposition process uses a controlled chemical reaction to effect the slow formation of ZnS thin films deposited onto ITO coated glass. The general chemical equation is:

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

CBD method was adapted for multilayer ZnS film formation onto ITO coated glass platelets. With this deposition technique one to five superposed ZnS layers were deposited onto ITO coated glass platelets.

In the above-mentioned conditions, adherent and homogeneous ZnS thin films were grown on both ITO coating and glass substrates to give the ZnS/ITO/glass/ZnS heterostructures. Some ZnS/ITO/glass heterostructures were obtained by the removal of ZnS films from the glass side opposite to the ITO coating

The growing parameters of the as prepared heterostructures are presented in **Table 1**. As expected, increase of zinc sulphide film thickness with the total deposition time could be noticed. The use of a high number of successively deposited layers (coatings) determines the increase of the film thickness. One can note that, the growing rate, calculated by dividing the ZnS film thickness to the total deposition time is increases with the number of coatings. According to our previous work [5,7,8], for the same deposition time, the multilayer grown film is thicker when it deposited onto the glass substrates in comparison with the film formed onto the ITO coated face of the glass platelet. Mention has to be made that, according to the manufacturer measurement, the thickness of the ITO coating is ~20 nm.

**Table 1.**
The growing parameters of some ZnS/ITO/glass heterostructures prepared by multilayer technique

| Samples code | Total deposition time n x m* | ZnS packing density (mg/cm²) | ZnS film thickness** (nm) | ZnS film growing rate (nm/min) |
|---|---|---|---|---|
| ITO 3.0 | 0 | 0 | 0 | 0 |
| ITO 3.1 | 1 x 60 = 60 min | 0.13 | 33 | 0.55 |
| ITO 3.2 | 2 x 60 = 120 min | 0.33 | 80 | 0.67 |
| ITO 3.3 | 3 x 60 = 180 min | 0.60 | 150 | 0.83 |
| ITO 3.4 | 4 x 60 = 240 min | 0.80 | 200 | 0.83 |
| ITO 3.5 | 5 x 60 = 300 min | 1.06 | 260 | 0.87 |

*Where: n = number of layers, m = deposition time; ** on the ITO coated glass face

UV-Vis absorption /reflection and photoluminescence spectroscopy were used to investigate the optical properties of different ZnS/ITO/glass or ZnS/ITO/glass/ZnS heterostructures. Moreover, in order to prove the ZnS film ability to develop luminescent properties, some of the heterostructures containing relatively thick films were annealed in special ZnS-based mixtures containing copper and manganese doping ions. The photoluminescence behaviour of the as obtained copper and manganese doped ZnS/ITO/glass/ZnS heterostructures, notated ZnS:Cu,Mn /ITO/glass/ ZnS:Cu,Mn, was evaluated from the emission spectra registered under UV excitation.

The transmission spectra (**Fig.1**) of the heterostructures that contains multilayer ZnS films illustrate the high transparency of the ITO coating over the entire visible domain (over 90%). The transparency decreases parallel with the increase of the film thickness. The multiple maxima on transparency curve of some ZnS/ITO/glass heterostructures reveal a good quality of the deposited thin film (**Fig.1**).

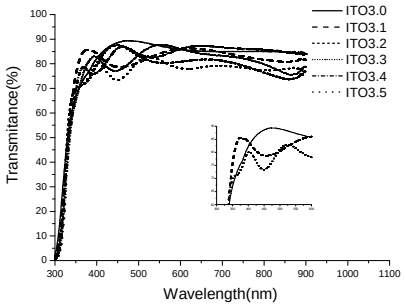


**Fig. 1.** Transmission spectra of some ZnS/ITO/glass heterostructures

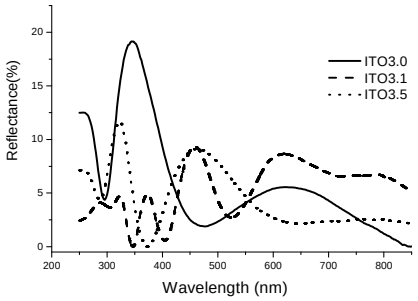


**Fig. 2.** Specular reflectance of ZnS films deposited onto ITO coated glass face

The reflectance spectra of ZnS/ITO/glass heterostructures were registered in order to evaluate the ZnS film optical quality (**Fig. 2**). The spectra registered at 0° incidence indicate the diffuse reflection of the films whereas the spectra obtained at 8º incidence of the visible light illustrate both the specular and diffuse

reflection properties of the investigated heterostructure. The specular reflectance of some samples, evaluated as the difference between the reflection measured at 8º and 0º incidence, decreases as the number of ZnS layers increases One can note the strong specular reflection properties of the ITO coated glass. A thin film of ZnS (ITO3.1) attenuates the ITO layer reflection and shows only a weak reflection characteristic to the ZnS material. This one is clearly put in evidence for the relatively thick layers (ITO3.5).

Some of the ZnS/ITO/glass and ZnS/ITO/glass/heterostructures were treated thermally either in a nitrogen atmosphere, or in some peculiar conditions that allows the evaluation of the luminescence ability of the CBD obtained ZnS films. **Table 2** presents the thickness and the thermal treatment conditions of some heterostructures containing un-doped or copper-manganese doped ZnS thin films.

The transmittance spectra of the ZnS/ITO/glass heterostructure obtained in 300 min deposition was measured before and after the thermal treatment (**Fig.3**). It is obvious that the post-growing thermal treatment decreases the film transmittance and diminishes the film optical quality.

The emission spectra of copper-manganese doped ZnS/ITO/glass/ZnS heterostructures are depicted in **Fig. 4.** The sample prepared at 400ºC shows a very weak luminescence with relatively well evidenced emission bands situated at about 467, 524 and 560 nm. These bands are correlated with the presence of some specific emission centres associated with the self-activated SA-, Cu- and Mn-luminescence in zinc sulphide layer, respectively. The weak luminescence observed for this structure could be explained either by an incomplete incorporation of the activators into the ZnS lattice generating a small number of luminescence centres, or to a poor quality of the films deposited onto ITO substrate.

In order to verify the luminescence ability of ZnS thin films, attempts were made to incorporate Cu-Mn activators by annealing the system at 550°C. The sample obtained using this thermal synthesis regime, shows a relatively strong luminescence situated mostly into the yellow spectral region. The main emission peak is observed at 577 nm, close to the theoretical value (580 nm) originated into the Mn-centres. The higher annealing temperature is in the favour of Cu-and Mn activator incorporation.

**Table 2.**

Thickness and thermal treatment conditions of some ZnS containing heterostructures

| Sample code | Thickness (nm)** | Doping and thermal treatment | Heterostructure |
|---|---|---|---|
| ITO3.5TT | 260 | 500$^{o}$C, $N_2$ | ZnS/ITO/glass |
| ITO11.3 | 320 | Cu-Mn doping, 400$^{o}$C | ZnS:Cu,Mn/ITO/glass/ZnS:Cu,Mn |
| ITO12.1 | 310 | Cu-Mn doping, 550$^{o}$C | ZnS:Cu,Mn/ITO/glass/ ZnS:Cu,Mn |

*where: n = number of layers, m = deposition time; ** mean value

The better yellow-orange emission observed for the heterostructure prepared at relatively high temperature reveals a good luminescence ability of zinc sulphide layer.

The luminescence performances of the ZnS/ITO/glass/ZnS heterostructures doped with copper and manganese are predominantly sensitive to the annealing regime and the doping conditions.

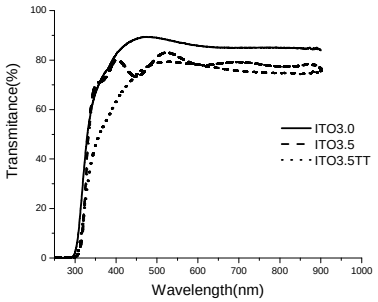


**Fig. 3.** Transmission spectra of some ZnS/ITO/glass samples before and after the thermal treatment

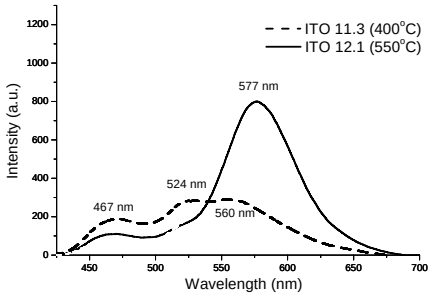


**Fig. 4.** Emission spectra of some ZnS: Cu, Mn films deposited onto ITO layer

## 4. CONCLUSIONS

The bath composition and the special CBD technique used in our experiments proved to be convenient for the deposition of adherent and homogeneous ZnS films with controllable thickness onto the ITO coated glass substrate. The growth parameters influence the optical properties of the as deposited thin films.

UV-Vis absorption /reflection investigations illustrated the quality of the as prepared ZnS/ITO/glass/ZnS heterostructures. The photo-luminescence measurements on some copper and manganese doped ZnS/ITO/glass/ZnS heterostructures proved the ability of ZnS films to develop good light emitting properties.

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