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Study and Characterization of Nanocrystalline ZnS: Tb Thin Films deposited by Sol-Gel Method

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Abstract The thin layers of undopedZnS and ZnS doped Tb (4%) were deposited on glass substrates using sol-gel and dip-coating methods. Thermal treatments have been carried out at 500 °C for 1 hour. The structural characterization of these samples was carried out by the X-rays diffraction (XRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). UV-visible spectrophotometry and Fourier Transform Infrared spectroscopy (FTIR) have been used to study the effect of deposition layers on the optical properties of ZnS doped Tb thin films. X-ray diffraction measurements show that the films are amorphous. Atomic force microscopy images of the films have revealed homogeneous and granular structure and the SEM micrographies show a uniform and porous structure of deposit films. The optical transmission spectra in the UV - visible range have shown that the doped film present a good optical transmission ranging between 60% and 86% in the visible. The gap values are decreasing with doping. FTIR analysis confirm the presence of ZnS band vibration at 617.187 cm^{-1}.

Key words.ZnS doped Tb,UV-visible, sol-gel method, XRD, SEM.

1. Introduction

Recently, researches on properties of nanocrystalline semiconductors have attracted much attention [1]. II-VI semiconductors have an immense scientific and technological importance. Among them, Zinc sulfide (ZnS) is the most important with a wide optical band gap (3.6 eV). Because of its favorable electronic and optical properties, ZnS have a many applications such as solar cells [2], electro-luminescent and optoelectronic devices [3]. Various physical and chemical methods are used to prepare ZnS thin films such as rf sputtering [4], hydrothermal method [5], spray pyrolysis [6], chemical bath deposition [7] and sol-gel [8].

The sol-gel technique is a simple technique based on the series of hydrolysis and condensation reactions to form a wet-gel structure. This method has been extended to the fabrication of thin films or coatings on different substrates.

In this work zinc sulfide doped terbium (ZnS:Tb) thin films were deposited on glass substrates by sol-gel method using dip-coater.

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2. Experimental

ZnS doped Tb thin films with different concentrations (0 and 4%) were prepared by following steps: zinc acetate dihydrate Zn $(CH_3COO)_2.2H_2O$and terbium III nitrate hexahydrate (Tb III $(NO_3)_3.6H_2O$) were firstly dissolved in propanol-1. Thiourea CH_4N_2S was dissolved in propanol-1 separately by stirring (300 rpm) at room temperature. Triethanolaminewas added to the first solution drop by drop. Then, a solution of NaOHwas added to adjust the pH at 12 and to obtain a homogeneous transparent solution. Finally, the solution of thioureawas added to this solution and mixed in the same flask. A constant agitation is maintained during 2 hours, at 300rpm. Thin films of ZnS doped Tb were deposited on properly cleaned glass substrates by dip-coating with a velocity of 170 mm/s. This operation was repeated for 10 times.

The deposited films were dried at 423 K to remove the mixed solvent and organic substances such as C, H and N.

The structural characterization of these samples was carried out by the X-rays diffraction (XRD) using a (XPert PRO PANatycal) with Cu Kα radiation (λ = 1.54051A°), scanning electron microscopy (SEM) (SEM Quanta 200, FEI France) and atomic force microscopy (AFM) with three-dimensional (3D) and two dimensional (2D). The grain sizes were

determined by the scherrer formula. UV-visible using UV / visible spectrophotometry (SHIMADZU UV 1800 PC) in the range of 200-1100 nm at room temperature and Fourier Transform Infrared spectroscopies (FTIR) (Iraffinity-1 Shimadzu) between 400 and 4000 cm^{-1} have been used to study the effect of deposition layers on the optical properties of ZnS doped Tb thin films.

3. Results and discussion

3.1. XRD Analysis

X-ray diffraction (XRD) analysis were carried out at room temperature for all samples with a powder diffractometerXPert PRO PANatycal (λ (CuKα) = 1.54051 Å) at 40 kV and 30 mA, using silicon as internal standard. The spectra were recorded in 2θ between 20° and 80 °.

Figure 1 shows the XRD patterns of ZnS:Tb^{3+} thin films deposited on glass substrate.

The analysis present amorphous structures for all deposits thin layers, and no peak were detected which means that the crystallinity of these thin layers is insignificant.After thermal treatment, the characteristic peaks of hexagonal ZnO appear at 2θ =31,812° and 36,196°. This wurtzite structure was indexed by isotypie with card ASTM (number: 01-089-1397). A numerous works explained this phenomenon by the oxidation of ZnS due to oxygen in air during heat treatment [9, 10].

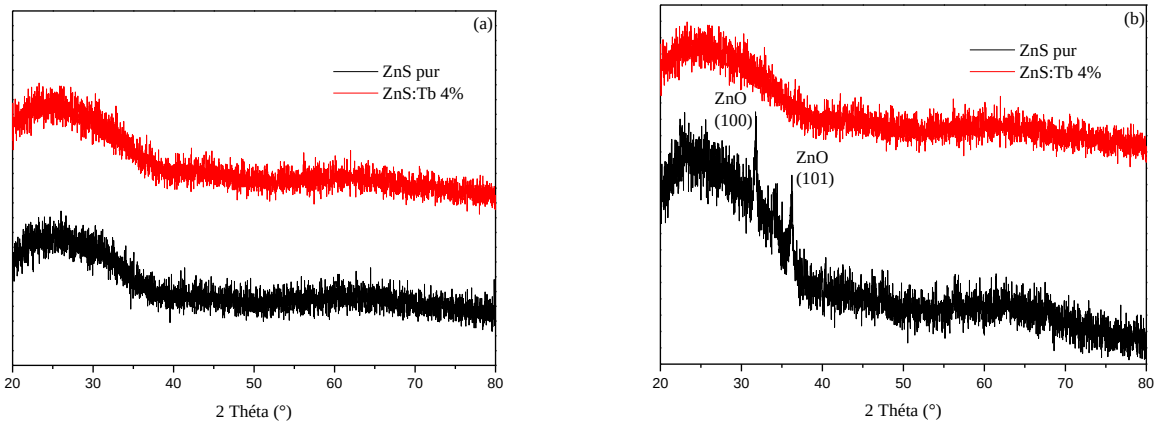

Fig.1. X-ray diffraction of ZnS:Tb^{3+} thin films (0-4%), a) before annealing, b) after annealing (500 ° C, 1h).

3.2. AFM Analysis

Figure 2 shows the surface morphology of the thin layers of pure ZnS and ZnS:Tb^{3+} (4%), deposited on glass substrate characterized by the atomic force microscopy (AFM) with three-dimensional (3D) and two dimensional (2D). The RMS values (surface roughness) of the samples are shown in Table (1).

Thin film of pure ZnS shows no planar surface with a very important roughness (RMS = 61.610 nm). Doping greatly decreases roughness (ZnS:Tb^{3+} 4% = 12.605 nm).The thermal treatment revealed quite homogeneous form of agglomerates which are uniformly distributed on the surface. This is due to the crystallization. Furthermore, the thin layers of ZnS:Tb^{3+} exhibit columnar grains along the c-axis perpendicular to the surface and the roughness increases (ZnS:Tb^{+3} 4% = 40.845 nm).

3.3. SEM Analysis

The morphology of the film was examined by scanning electron microscopy (SEM Quanta 200, FEI France).

Figure 3 shows micrographies of the pure ZnS and ZnS:Tb^{3+} (4%) before and after heat treatment . The deposit carried out at room temperature is amorphous, with uniform and porous structure.

After thermal treatment at 500°C during 1h, we observed the formation of agglomerates composed of small grain sizes (5-6 µm). These grains have homogeneous spherical shapes. This result confirms the XRD analysis. ZnS becomes ZnO after 500 ° C.

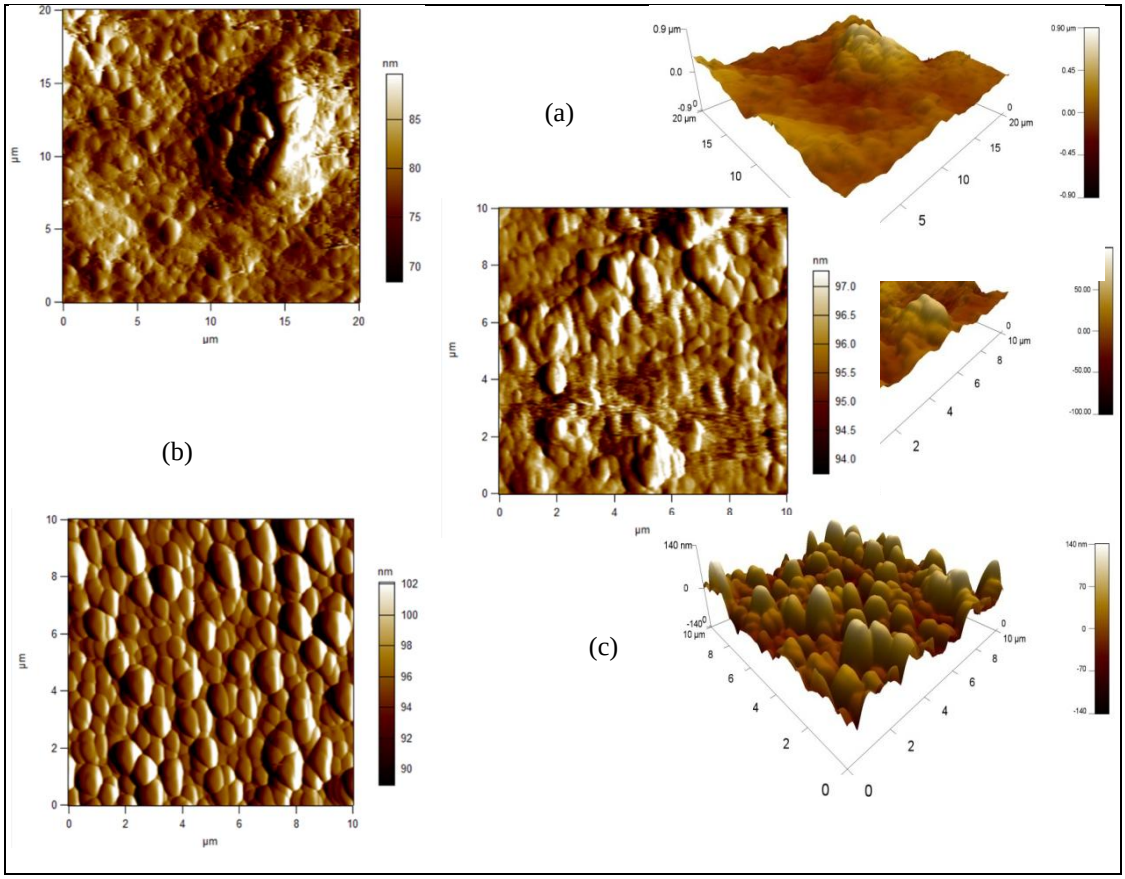

Fig.2. AFM image 2D and 3D of the surface of ZnS:Tb^{3+}thin films: (a) pure ZnS, (b) ZnS:Tb^{3+} 4% before annealing, (c) ZnS:Tb^{3+} 4% after annealing (500 ° C, 1h).

3.4. UV-Visible Analysis

The optical properties of the zinc sulfide doped terbium (ZnS:Tb^{3+}) thin films were determined from transmittance measurements using UV / visible spectrophotometry (SHIMADZU UV 1800 PC) in the range of 200-1100 nm at room temperature. Figure 4 shows the transmittance spectra of ZnS:Tb^{3+} thin films according to the wavelength. The behavior of curves before and after annealing (500°C, 1h) show that the deposits are of good quality.

The thermal treatment does not reveal defects in the crystal. Transmittances of the compositions of ZnS:Tb^{3+} (4%) is improved of approximately 25% compared to that of pure ZnS (from 57 to 83%).

Table 1.The values of the RMS (the surface roughness) of our samples.

RMS (nm)		
Compositions	Before annealing	After annealing (500°C, 1h)
ZnS:Tb^{+3} 0%	161,610	-
ZnS:Tb^{+3} 4%	12,605	40,845

In order to understand the performance of thin films ZnS with dopant concentration, it's necessary to determine the direct band gap (Eg). The relationship between the absorption coefficient (α) and the photon energy (h ν) for direct allowed transition is given by the theory of optical absorption:

$$\alpha (h\nu) = A(h\nu - Eg)^{n/2}$$

Where A is constant and n is equal 1 for direct band gap semiconductors. The direct optical band gap value is determined from the intercept of

the straight line portion of the $(\alpha h \nu)^2$ against the graph and the $(h \nu)$ axis.

Table 2 summarizes the gap values and the maximum transmittance of ZnS thin films doped with terbium (0-4%).The band gap of ZnS thin film has more great that of bulk ZnS, which is gives in the literature at 3.66 eV. This increase in gap is induced by the reduction of the crystallite size (nanometer order) which causes a quantum confinement effect. Several authors [1] have reported this behavior.

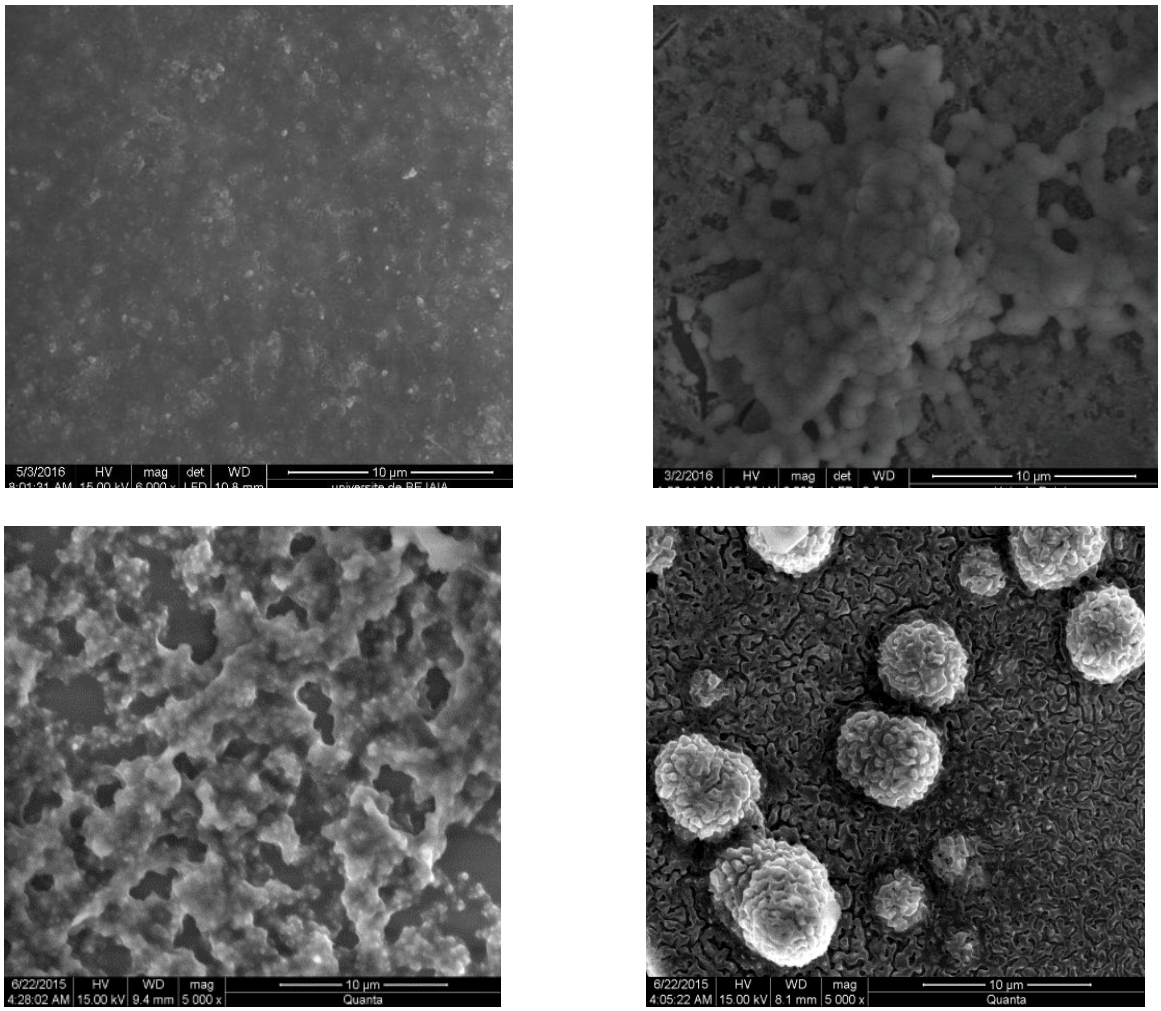

Fig.3. The SEM images of ZnS:Tb^{3+} : (a,c) ZnS :Tb^{3+} (0-4%) before treatment and (b, d) ZnS :Tb^{3+} (0-4%) after heat treatment.

Table 2. The gap values and the maximum transmittance of ZnS:Tb (0-4%) thin films.

Compositions	Optical Gap E_g (eV)		Maximal Transmittance T_{max} (%)	
	Beforeanneling	Afteranneling	Beforeanneling	Afteranneling
ZnS:Tb 0%	3.83	3.53	57	67
ZnS:Tb 4%	3.97	3.72	83	86

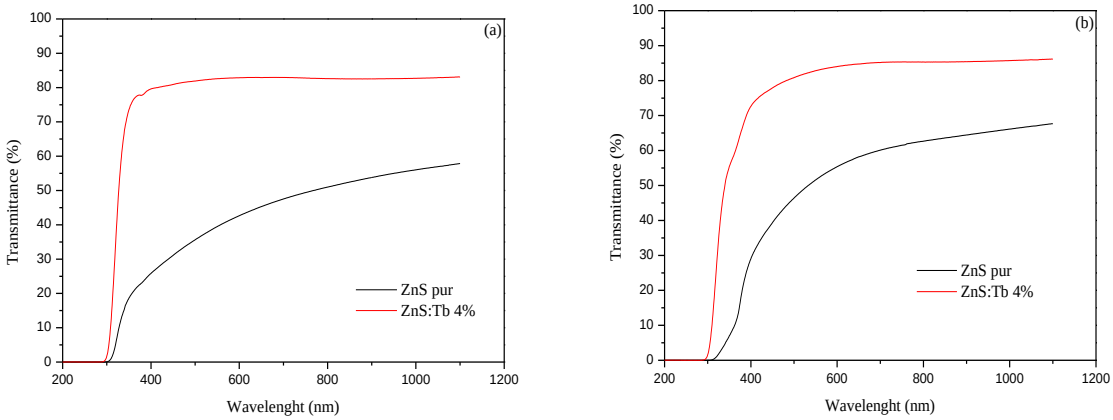

Fig.4: Transmittance spectra of ZnS:Tb^{3+} thin films (0-4%), (a) before annealing, (b) after annealing (1H, 500°C).

3.5. FTIR Analysis

IR spectra of samples were recorded with the FTIR (Iraffinity-1 Shimadzu) between 400 and 4000 cm^{-1}. Figure 5 shows the transmittance spectra of ZnS:Tb^{3+} thin film.

The spectra show peaks at 3410.37; 2363.63; 1525.4; 1022.52 and 617.187 cm^{-1}. The broad peak located at 3410.37 cm^{-1} are attributed to the vibrations of the bond - OH which indicate the presence of ions hydroxyl and/or adsorbed water due to the presence of humidity. The band observed at 1525.4cm^{-1} is attributed to the vibration of valence C=O present in acetate. The C-OH bond is situatedat 1022.52 cm^{-1}. The band corresponding to Zn-S liaison appears at 617.187 cm^{-1}.

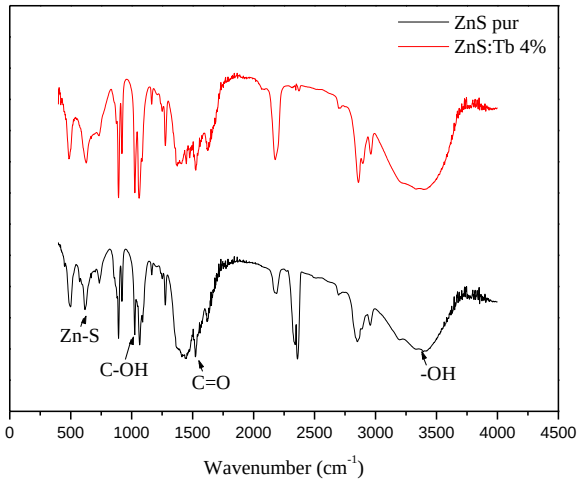

Fig.5. FTIR spectra of ZnS: Tb^{3+} thin films (0-4%).

4. Conclusion

Zinc sulfide doped terbium (ZnS:Tb^{3+}) with different concentrations (0-4%) thin films were deposed on glass substrates by a dip-coater using sol-gel method.

X-ray diffraction analysis has revealed that the thin layers for all compositions are amorphous. Atomic force microscopy images of the films have revealed a homogeneous and granular structure. Doping decreases roughness. The optical transmission spectra in the UV - visible range have shown that all the doped films present a good optical transmission in the visible. The values of gap were between 3.83 and 3.97 eV. Analysis FTIR of the powders confirms the presence of the vibration band of Zn-S at 617.187 cm^{-1}.

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