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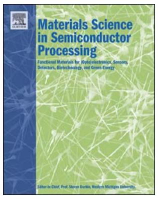

Study of the structure and optical properties of Cu and Mn *in situ* doped ZnS films by chemical bath deposition

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ABSTRACT

The *in situ* doping of ZnS films with Cu and Mn ions was obtained by the chemical bath deposition method. The resulting films, with cubic crystalline structure, were specular, adherent, and optically transparent. The analysis from X-ray photoelectron spectroscopy confirmed the effective insertion of Cu and Mn ions and the formation of defects in the crystalline structure of the ZnS films. Moreover, the morphology analysis showed that the presence of the doping ions in the reaction solution promoted the deposition of films with better uniformity. The effects of the doping agents in the optical properties of the ZnS films were also analyzed. First of all, it was observed a red-shift of the optical absorption edge, and therefore, the decrease of the optical band gap. Afterwards, the room-temperature photoluminescence spectroscopy confirmed the effective activation of the ZnS film with Cu and Mn ions, when the luminescence emission centered at 470 nm was shifted to longer wavelengths (green-orange emissions centered at 530 nm). Based in these results, it is concluded that the process reported here could be used as an original alternative for the preparation of ZnS films with a mixture of other doping agents.

1. Introduction

Among the great variety of semiconductor materials, ZnS has been extensively studied since several years ago due to its high optical transmittance, high refractive index (2.35), wide energy gap (3.68 eV) and luminescence emissions from the ultraviolet to the visible spectrum [1–3]. These properties and the versatility of the ZnS material to adopt different morphologies at microscopic level has been the basis for its applications in UV and X-ray sensors [4,5], gas sensors [6], biosensors [7], solar cells [8], and light emitting devices [9]. ZnS thin films can be deposited by methods such as spray pyrolysis [10], plasma-assisted metalorganic chemical vapor deposition (PA-MOCVD) [11], sputtering [12], sol-gel [13], successive ionic-layer adsorption reaction (SILAR) [14], thermal evaporation [15] and chemical bath deposition (CBD) [16]. Particularly, it is well-known that CBD is a simple and cost-effective method for the deposition of highly reproducible ZnS films. The deposition parameters such as bath temperature, solution pH, deposition time and chemical reagents define the growth rate, structure, chemical composition, and physical properties of these films [17–23]. Moreover, the CBD method has been used for the doping of ZnS films in mild conditions by adding small amounts of the doping precursors in the reaction solution. The resulting films have undergone significant changes in their optical and electrical properties. For instance, the study of Sahraei et al. indicated that the saturation of ZnS nanocrystals by Ni^{2+} ions decreases the optical transmittance. This report also shows that the photoluminescence (PL) emission intensity increases for low Ni^{2+} concentrations and quenches for high Ni^{2+} concentrations [24]. Chen et al. reported that La-doping cause the effective shift of the absorption edge from UV to the visible-light region [25]. Furthermore, Mn-doped ZnS films have shown high optical transmittance ($> 80\%$) and the enhancement of the fluorescence emission intensity [26]. Our research group, in a previous study, reported the decrease of the optical transmittance and sheet resistance with the incorporation of the Cu ions in ZnS films [27]. In addition, the conductivity of the film with higher Cu^{2+} concentration changed from n-type to p-type.

ZnS films co-doped with two or more metal ions are attractive for its application as active layers in photocatalysts and radioluminescent nuclear batteries which, until now, have been only developed with nanoparticles [28,29]. So far, the literature reports a unique study to produce luminescent ZnS films by adding Mn and Cu ions directly into an alkaline chemical bath system [30]. However, the activation of the resulting film was only achieved by its thermal treatment at 500 °C. The

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aim of this paper is to demonstrate the effectiveness of the (Cu, Mn) *in situ* co-doping of ZnS films by a chemical bath deposition process that uses slightly acidic solutions. The film deposition was influenced by the presence of complexes of ethylenediaminetetraacetic acid (EDTA) with Zn, Cu and Mn ions. The effectiveness of the doping ions insertion in the ZnS structure was confirmed by X-ray photoelectron spectroscopy (XPS). It is important to remark that no further annealing treatments were required to activate the luminescence of the ZnS films doped with Cu and Mn ions. As evidence, photoluminescence spectroscopy results showed that the ZnS:(Cu, Mn) film exhibited the ability to emit green-yellow light by absorbing UV light. Thus, this film is a good candidate to be applied as a luminescent down-shifting layer for the enhancement in solar cells conversion efficiency [31].

2. Experimental

2.1. Preparation of the films

Soda-lime glass slides were used as substrates for the deposition of the ZnS, ZnS:Cu and ZnS:(Cu, Mn) films. Before the deposition process, all substrates were cleaned in an ultrasonic cleaner with a mixture of ethanol and isopropyl alcohol (1:1), aqueous solution of HCl (1:10) and deionized water. The clean substrates were finally dried at room temperature.

Aqueous solutions with concentrations of 0.1 M zinc acetate dihydrate [$Zn(OAc)_2{\cdot}2H_2O$], 0.1 M copper sulfate [Cu_2SO_4] and 0.1 M manganese acetate tetrahydrate [$Mn(OAc)_2{\cdot}4H_2O$] were used as Zn, Cu and Mn precursors, respectively. Also, solutions of 0.1 M thioacetamide [C_2H_5NS] and 0.1 M EDTA [$C_{10}H_{16}N_2O_8$] were used as sulfur precursor and complexing agent, respectively. The ZnS film was then deposited by immersing each glass substrate in a beaker with a reaction solution previously prepared by the sequential addition of 15 ml of Zn precursor, 5 ml of EDTA, 15 ml of thioacetamide and 5 ml of deionized water. This process was also used for the preparation of the ZnS films with the doping agents, but instead of the Zn precursor, 15 ml of a mixture of the different metal precursor was used. Thus, the ZnS:Cu film was prepared with a mixture of 3.6 parts of the Zn precursor and 0.4 parts of the Cu precursor. Meanwhile, the ZnS:(Cu, Mn) film was prepared with a mixture of 3.6 parts of the Zn precursor, 0.2 parts of the Cu precursor and 0.2 parts of the Mn precursor. In all cases, the temperature of the reaction solutions was kept at 80 °C by immersing each beaker in a water bath system. After 3 h, the substrates with the deposited films were removed from the reaction solutions and washed with deionized water.

2.2. Characterization

The crystalline structure of the films was analyzed by a Bruker D8 Advance X-ray diffractometer (XRD) with Cu-Kα ($\lambda = 1.5418$ Å) radiation (40 kV, 40 mA). This system is equipped with a thin film accessory equivalent to the asymmetric Bragg–Brentano geometry for grazing angle mode measurements. X-ray photoelectron spectroscopy (XPS) was used to analyze the elemental composition and bonding interactions of the elements on the films surface by a PHI 5000 VersaProbe II system equipped with a focused monochromatic X-ray beam with Al-Kα ($\lambda = 1486.6$ eV) radiation (15 kV and 10 mA). The scanning electron microscopy (SEM) images of the films surface were obtained with a Philips Model XL30ESEM microscope operating at 30 kV. High-resolution transmission electron microscopy (HRTM) images were taken to the cross-sections of the films with a FEI-TITAN microscope working at 80–300 kV. The optical transmittance of the films was determined with a USB2000 + Ocean Optics spectrometer in the wavelength range from 250 to 800 nm. The thickness of the thin films was measured using a Contour GT-K 3D optical microscope in VSI mode. The room temperature photoluminescence (PL) spectroscopy was carried out with a 27.5 cm focal length Acton monochromator equipped with a 1200 g/mm diffraction grating blazed at 500 nm. The emission of a He-Cd laser at 325 nm was used as excitation source and the modulated PL signal was detected with a Hamamatsu photomultiplier tube.

Table 1
Elemental content, average thickness, and optical band gap of the films.

Sample	Elemental content (at%)				Average thickness (nm)	Optical band gap (eV)
	S	Zn	Cu	Mn		
ZnS	54.5	34.8	–	–	105.3	3.88
ZnS:Cu	47.69	47.69	4.62	–	55.4	3.73
ZnS:(Cu, Mn)	46.99	49.18	2.15	1.76	51.7	3.8

3. Results and discussions

The reaction solutions used to prepare the films exhibited changes in color along the deposition time. This is, the reaction solution used for preparing the ZnS film went from clear to whitish, whereas, those used for preparing the ZnS:Cu and ZnS:(Cu, Mn) films went from clear blue to brownish. At the end of the deposition process, all deposited films were homogeneous, specular, well-adhered to substrate and highly transparent. The average thickness of the ZnS, ZnS:Cu and ZnS:(Cu, Mn) films, listed in Table 1, were 105.3, 55.4 and 51.7 nm, respectively.

3.1. Crystalline structure and chemical composition

X-ray diffraction patterns of ZnS, ZnS:Cu and ZnS:(Cu, Mn) thin films are shown in Fig. 1. In all cases, peaks identified at 28.9°, 48.4° and 57.1° were assigned to the reflections of the planes (111), (220) and (311), respectively, which are in good agreement with those identified for the cubic type crystalline structure (JCPDS 05–0566). Diffraction

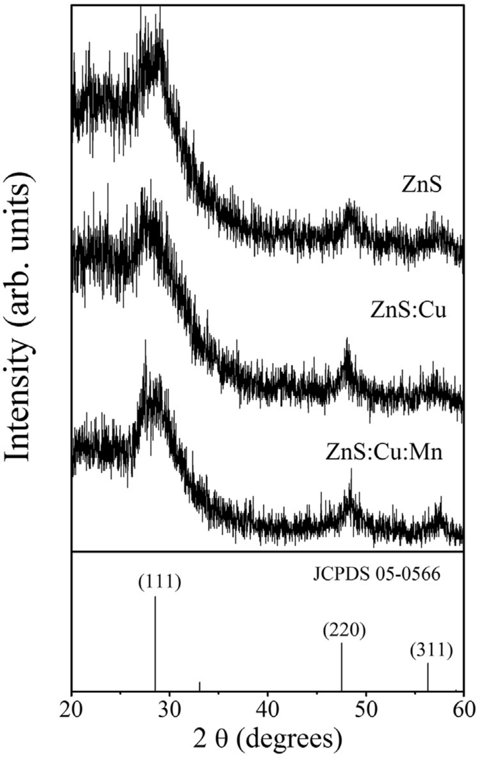

Fig. 1. XRD patterns of the films on glass substrates.