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Co-sprayed manganese doped zinc sulfide films

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ABSTRACT

Manganese doped zinc sulfide thin films were deposited on glass substrates using co-spray method. Different characterization techniques such as XRD, FESEM, AFM, UV–vis and PL have been used in order to investigate the structural, morphological and optical properties of these films. X-ray diffraction (XRD) analysis indicated that pure and Mn-doped films showed only hexagonal polycrystalline wurtzite structure with [0 0 1] vertical preferential direction. SEM images revealed that manganese inclusion has a significant effect on the morphological structure; films have nano-sized grains with a size of approximately 100 nm. All films have high transmittance of about 82% in the visible region. Manganese inclusion has been shown to decrease overall optical gap from 3.69 to 3.63 eV. The photoluminescence intensity was found to reach a maximum and decline at higher manganese content, assisting to the well-known concentration quenching effect. The critical doping level of Mn ions has been determined to be 2%.

1. Introduction

Belonging to binary II–VI compounds, zinc sulfide (ZnS) is by far one of the most interesting semiconductor materials which has a direct band gap of 3.68 eV at room temperature and 40 meV as exciton binding energy, together with some advantages such as long-term environmental stability, biocompatibility, non-toxicity and low cost [1]. Additionally, it can be synthesized through chemical routes by simply using thiourea and zinc organometallic precursors which are cheaper, non toxic, abundant and highly stable compounds. Due to its large band gap, ZnS can be used as buffer layer in thin film solar cells [2], infrared transparents [3], photoelectrodes [4] and other optoelectronic devices [5]. Besides, this material can host diverse transition metal ions as luminescent centers (Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}…) which can promote its optoelectronic properties (create discrete energy states in the band gap region) and favor its practical applications in various domains such as thin film electroluminescence devices (TFEL), field emission displays, solid state lighting and sensing technologies.

Manganese doped zinc sulfide (ZnS:Mn) is a well known phosphor with interesting photoluminescence, electroluminescence, upconversion luminescence and triboluminescence [6]. Photoluminescence is the emission of light by a material after it has been exposed to an electromagnetic radiation (excitation). The luminescence intensity is basically related to the impurities and defects created in the host matrices. Normally, more impurities and higher density defects will produce higher luminescence emission intensity [7]. However and according to several experimental results, the luminescence emission intensity of many phosphors as a function of activator concentration initially increases and then declines, going through a maximum at some concentrations [8].

Even though manganese doped zinc sulfide phosphors have been extensively studied for a long time, there are still inconsistent reports about the exact amount of such activator which cause concentration quenching effect. Actually, this varies considerably from approach (method) to another one; even it can show different comportment when prepared by the same method depending upon the preparation conditions. Until now, nearly all reported ZnS phosphors (films) have been synthesized using physical approaches, which require expensive and complicated equipments along with high vacuum for some techniques [10]. The elaboration step of thin film phosphors is being considered part of the answer to move to high-quality and low-cost production of efficient phosphor-emitting materials. For that reason, significant efforts have emerged in search for alternative synthesis routes (taking into account their strengths and weaknesses) that possess environmentally-friendly and economically-friendly characteristics. Among the chemical candidate method, spray or more especially co-spray is the procedure of choice in

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a sense that it can be used to grow films with an easier way, ensured reproducibility, overall short deposition time, low energy cost and it can be scaled to generate large areas coating without causing any environmental harms (green synthesis route).

Zinc sulfide can be found under two allotropic forms: zinc blende (cubic) and wurtzite (hexagonal) [11], but the latter one is much more desirable for its superior electronic and optoelectronic properties [12]. Highly crystalline ZnS film is difficult to obtain using classical spray techniques (the obtained films are either cubic polycrystalline or amorphous). According to previous studies, the application of wurtzite ZnS film is still rarely reported because of the high required temperature fabrication process [13]. Very recently, we have successfully obtained high quality ZnS (wurtzite) hexagonal-structured films using this method at a relatively moderate temperature [9]. Continuing, manganese doped ZnS films with 0–5% (at%) were prepared using co-spray technique. The main objective of the investigation is to study the influence of Mn incorporation on the structure, optical and photoluminescence properties of these films, allowing us to determine the optimum amount of Mn ions which produces the highest PL intensity.

2. Experimental

In the present work, Mn-doped ZnS films were prepared using co-spray technique. Detail of the synthesis procedure is fully described elsewhere [9].

Zinc acetate dihydrate (Zn $(CH_3COO)_2 \cdot 2H_2O$) and thiourea (CH_4N_2S) were used as the starting salts to supply Zn^{2+} and S^{2-} ions respectively. In this work, each solution has been prepared separately, i.e., precursor of cationic and anionic solution. A mixture at 1:1 volume ratio of distilled water and absolute methanol was used as solvent in all prepared solutions. Few drops of acetic acid were added to cationic solution in order to prevent the formation of zinc hydroxide. The concentration of zinc precursor was fixed at 0.2 M (the same goes for anionic solution). After maintaining the resulting solutions under magnetic steering for 30 min, clear solutions were obtained.

The substrates used for the present work were commercial microscope glass slides with the size of 10 mm × 10 mm × 1 mm. Before starting, the substrates were chemically cleaned with hydrochloric acid (HCl), acetone, ethanol and distilled water in order to remove all contaminants on the surface of substrates. The substrate temperature was kept constant at 380 °C during deposition.

X-ray diffraction (XRD) measurements were performed by using a Shimadzu 6000 powder X-ray diffractometer with Cu Kα irradiation at $\lambda = 1.5406$ Å. Field emission scanning electron microscope (FESEM) (FEI Nova-Nano SEM-600) was applied for morphological study. Atomic force microscopy (AFM) (INNOVA-Veeco) was used to observe the morphology of the samples surface. The optical transmittance was determined using Shimadzu (UV-1800) UV–vis Spectrophotometer in the wavelength range from 200 to 1100 nm. Photoluminescence measurements were performed at room temperature by exciting the samples with a 325 nm He–Cd laser (IK3301R-G).

3. Results and discussion

3.1. Structure analysis

X-ray diffraction spectra of the as-synthesized Mn-doped ZnS films are presented in Fig. 1. All the diffraction peaks of ZnS films can be well indexed as the hexagonal wurtzite ZnS phase structure, which are consistent with the standard card (JCPDS no. 36-1450). The existing of a dominating peak is an indicative of high preferential orientation. Generally, at initial stage of the growth all orientations have the same chance to take up. The preferential orientation along (0 0 2) direction may be related to the lower formation energy of this plan [14]. The (0 0 2) peak intensity of Mn-doped ZnS is higher than that of the undoped film. As we can see, the intensity of (0 0 2) plan increases as a function of manganese content reaching a maximum at 2% Mn and the intensity of this peak become gradually lower with further Mn doping. That is to say the crystal quality of ZnS film could be improved by the addition of a suitable amount of manganese (1–2 at% in this experiment). However, more doping concentration (beyond this limit) deteriorated the crystallinity of films, which may be due to the formation of the stress by the difference in ion size between zinc and manganese, and the segregation of dopants in grain boundaries for high doping concentrations.

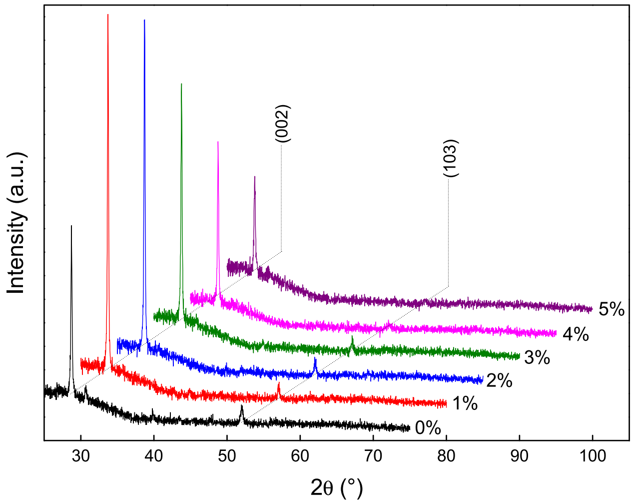

Fig. 1. Diffractograms of ZnS films as a function of Mn content.

Generally speaking, X-ray peak shift occurs due to three reasons: lattice parameter change, presence of residual stress and defect concentration. It is well-known that Mn^{2+} can substitute for Zn^{2+} ions in the ZnS crystal lattice because of their close ionic radii (0.83 and 0.74 Å for Mn^{2+} and Zn^{2+} respectively). The ionic radius of Mn^{2+} is slightly higher than that of Zn^{2+}, so with doping of manganese ions the lattice constant could be expanded (decrease in the Bragg position). We found that the (0 0 2) peak position of the Mn-doped ZnS samples (1–2 at%) shifted a little toward lower angle compared with that of undoped sample, implying that the Mn-ions substitute the zinc ions as we can see in Fig. 2a.

Fig. 2b shows the full width at half maximum (FWHM) of the (0 0 2) peak as a function of Mn content. We found that the FWHM of the (0 0 2) peak decreases with increasing Mn content reaching a minimum at 2%, and then increases noticeably with further increasing of Mn beyond that point. The introduction of more Mn-ions into the lattice of ZnS leads to the large structural strain which creates more defects in the films. The decrease in the crystallite size with respect to doping reflects the possible obstruction of crystalline growth by the presence of foreign atoms.

3.2. Morphological analysis

Fig. 3 presents the SEM images of the as-prepared Mn-doped ZnS thin films. Undoped ZnS films consist of irregular crystals of 50–150 nm in size. A slight decrease in crystallite size to 50–100 nm could be observed as 1% Mn is doped with ZnS. However,