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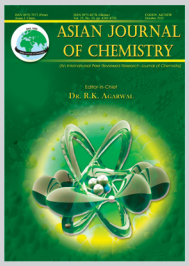

ZnS Thin Film Prepared by Using Chemical Spray Pyrolysis Method

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Zinc sulfide thin films were deposited on bare glass by the chemical spray pyrolysis technique. 10^{-2} M Zinc acetate and 4×10^{-2} M thiourea ($(NH_2)CS$) were used as a precursor solution in this work. The temperature of the substrate was set at 350 ºC. Deposited ZnS thin films show a hexagonal (wurtzite) phase structure. The crystalline quality and surface morphology of the deposited ZnS thin films were characterized using X-ray diffraction, atomic force microscopy and photoluminescence intensity. According to the XRD result, the (002) reflection is the most intense for films deposited at 350 ºC.

Key Words: Chemical spray pyrolysis, Atomic force microscopy, Thin film, ZnS.

INTRODUCTION

II-VI compound semiconductors have attracted much attention as materials in various application devices[1]. Zinc sulphide is a II-VI semiconductor with a wide direct band gap (3.7 eV), high refractive index (2.35) and high dielectric constant[2]. Zinc sulfide thin films are promising materials for their use in various device applications[3]. They can thus be used for the fabrication of optoelectronic devices such as blue light-emitting diodes, electro-optic modulators and the *n*-window layer of solar cells[4]. For example, ZnS is highly suitable as a window layer in heterojunction photovoltaic solar cells, because the wide band gap decreases the window absorption losses and improves the short circuit current of the cell[5]. It is known that ZnS phosphors have a broad-band luminescence from the near ultraviolet (UV) to the near infrared (IR). Therefore, they have often been used in the field of optoelectronic devices, such as for light-emitting diodes and flat-panel displays[6].

Zinc sulfide is the most promising because it is non-toxic and environmentally safer to handle than CdS, has a wider energy band gap than CdS and provides better lattice matching with absorbers having energy band gaps in the range of 1.3-1.5 eV[7].

There are various techniques for preparing ZnS thin films, such as pulsed laser deposition[1,4], spray pyrolysis[3-5] and chemical bath deposition[8,9]. The spray pyrolysis technique offers interesting possibilities because it is a large area technique, with a relatively low cost and a capacity to deposit optically smooth, uniform and homogeneous layers[4].

In this work, our goal is to study the structural and surface properties of ZnS thin film deposited by using chemical spray pyrolysis.

EXPERIMENTAL

We employed a spray pyrolysis deposition (SPD) technique for a thin film preparation method. Because the thin film formation is carried out in the air by a simple apparatus in spray pyrolysis deposition, the technique is one of the most attractive film preparation methods. Spray pyrolysis deposition is essentially the same film processing technique as the so-called pyrosol technique, in which a source solution is sprayed on the heated substrate to be deposited as a film. In other words, when a source solution is atomized, small droplets splash, vaporize on the substrate and leave a dry precipitate in which thermal decomposition occurs. The schematic representation of spray pyrolysis deposition apparatus is shown in Fig. 1. In the experiment, the ZnS thin films were synthesized by chemical spray pyrolysis. Bare glass was used as the substrate. First, they were cleaned with acetone for 10 min and thoroughly washed in deionized water for 480 min. The substrates were dried in a drying oven for 20 min.

Aqueous solutions of zinc acetate (anhydrous, purity 98 %) and thiourea, were chosen as main the precursors for the preparation of the ZnS thin films using this technique. The sprayed ZnS thin films were deposited using an aqueous solution. The volume of the solution for deposition was 50 mL.

The concentration of solution was fixed at 10^{-2} M zinc acetate and 4×10^{-2} M thiourea. Compressed air was used as a

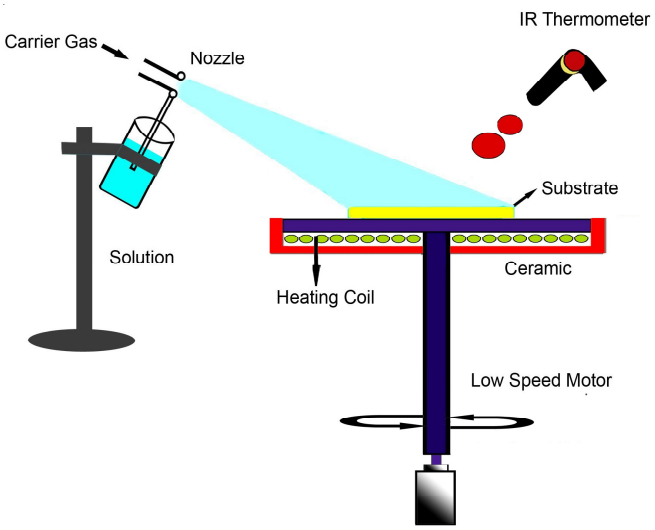


Fig. 1. Chemical spray pyrolysis system

carrier gas. The spray rate was fixed at 5 mL min^{-1}. The low-speed motor rotation speed was fixed at 0.6 cycles per second. The temperature of the substrate was determined as 350 ºC.

After the ZnS thin film deposition, the ZnS thin film had a clear grey colour. X-Ray diffraction and atomic force microscopy techniques were used to determine the structural, morphological properties of the as-deposited ZnS thin film.

RESULTS AND DISCUSSION

In order to get an X-ray diffraction pattern, an X-ray tube that emits only CuK_α X-ray by absorbing K_α X-ray by an absorber was used. The wavelength of the CuK_α X-ray is 1.54 Å. X-Ray diffraction pattern of as-deposited ZnS thin film is shown in Fig. 2. Zinc sulphide exists in sphalerite, cubic (zinc blend) and hexagonal (wurtzite) forms[10]. The cubic form is stable at room temperature, while the less dense hexagonal form (wurtzite) is stable above 1020 ºC at atmospheric pressure[6]. However the hexagonal structure for ZnS films can be obtained by the chemical spray pyrolysis method. The structural properties of the as-deposited *n*-type semi-conducting ZnS thin film prepared by chemical spray pyrolysis method were investigated using X-ray diffraction patterns. All the diffraction peaks in Fig. 2 are attributed to hexagonal ZnS. Five diffraction peaks corresponding to (100), (002), (101), (112) and (202) were detected. The (112) and (202) peaks are of much lower intensity. However, the (002) peak is the most intense peak. The XRD analysis showed that films are poly-crystalline in nature. The thin film obtained by this method was grey colour, with smooth forms.

According to Bragg's equation:

$$n\lambda = 2d \sin\theta \quad (1)$$

where n is the order of diffraction, λ is the wavelength of the incident X-rays, d is the distance between planes parallel to the axis of the incident beam and θ is the angle of incidence relative to the planes in question. The lattice spacing d was found and from (hkl) planes, lattice parameters of the unit cell a,c were calculated according to the relation,

$$\frac{1}{d^2} = \frac{4(h^2 + hk + k^2)}{3a^2 + l^2/c^2} \quad (2)$$

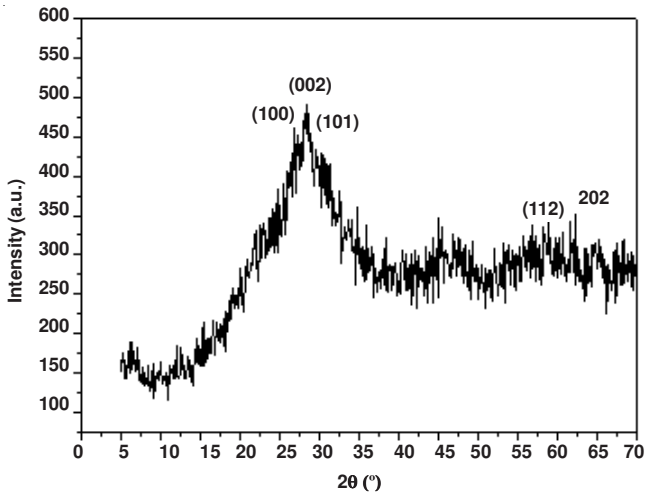


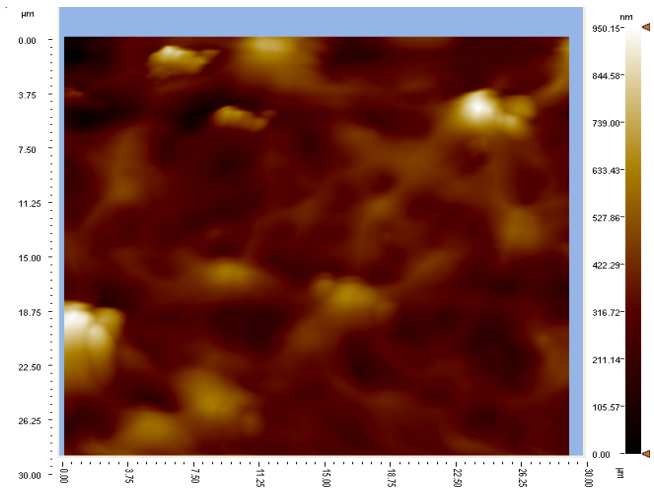
Fig. 2. X-Ray diffractograms of ZnS thin film obtained from: zinc acetate and thiourea growth by using chemical spray pyrolysis method at 350 ºC

If the broadening is due only to the effect of crystallite size, grain size can be simply determined from the (002) diffraction line using the Scherrer formula:

$$\text{Grain size} = \frac{K\lambda}{\beta\cos\theta} \quad (3)$$

where β is the full width at half maximum (FWHM) of the peak, calculated 0.148 in rad and K is the Scherrer constant, which generally depends on the crystallite shape. The grain size which is calculated by Scherrer's formula from the XRD data is *ca.* 100 nm. The grain size, which is due to the evaporation of individual fine droplets during the sprayed process, is undesirable for most semiconductor applications because of the barrier effects of grain boundary on the mobility in planar direction.

Atomic force microscopy was used for scanning the sample in XYZ directions under computer control through atomic force microscopy control electronics and atomic force microscopy software. The morphologies of as-deposited ZnS thin film characterized by two-dimensional and three-dimensional atomic force microscopy scans of the sample surface after deposition are shown in Fig. 3a-b. The images were recorded from an area of 30 m × 30 m on the film and obtained



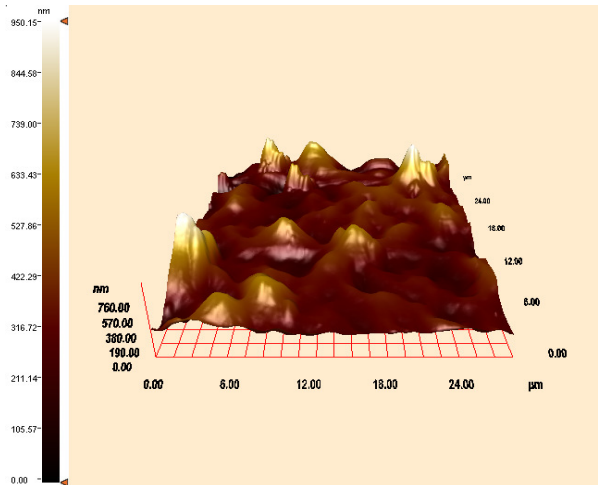


Fig. 3. AFM photographs of ZnS thin film obtained from: (a) two-dimensional AFM photograph (b) three-dimensional AFM photograph

in tapping mode. Fig. 3a a shows two-dimensional atomic force microscopy image of ZnS thin film. One can see several sizes of grains in the images, which had a tendency to be directed to the same plane which is probably the (002) plane because obtained the most intensity XRD peak. According to Fig. 3a-b, dark grain colours are smaller in size.

Fig. 3b shows a three-dimensional AFM image of ZnS thin film. One can see that the surfaces of as-deposited thin film hills are of various sizes. In Fig. 3b, it is shown that hill heights of growth ZnS thin film are up to 700 nm. Fig. 4 shows a histogram image of grain ranges. It reveals that grain sizes change between 0-1000 nm ranges.

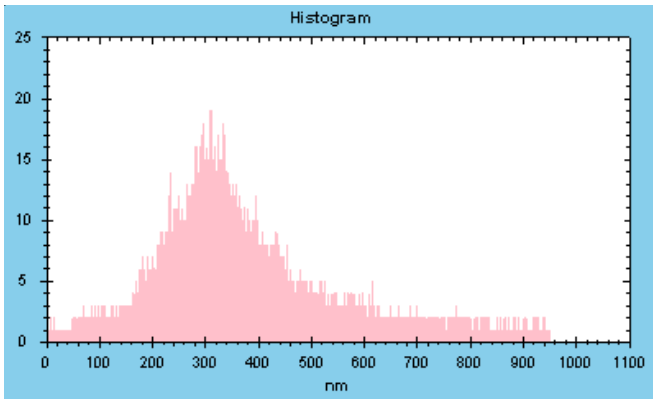


Fig. 4. AFM Histogram image of ZnS thin film obtained by using chemical spray pyrolysis method

Photoluminescence was investigated in the 3650-5500 Å wavelength range using an 325 nm HeCd laser. Fig. 5 shows the photoluminescence spectra for all the analyzed samples registered at 300 K. It should be noted on the figure that photoluminescence spectra are defined by a broad emission band for all samples, but their peak position and intensity vary depending on the stoichiometry. In the analysis of film, the photoluminescence emission maximum is *ca.* 4000 Å.

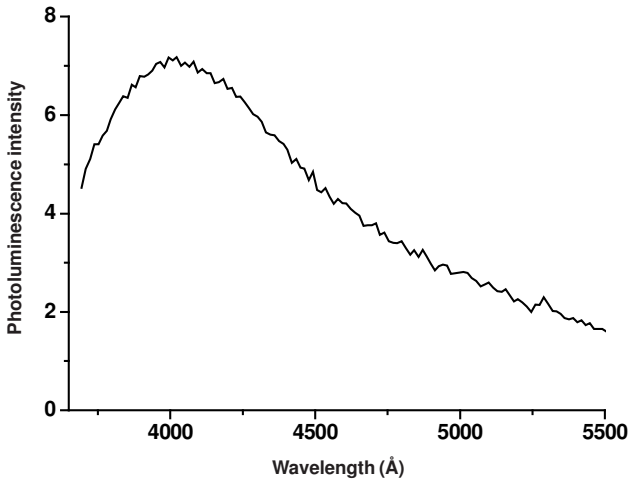


Fig. 5. Photoluminescence intensity plotted as a function of emission wavelengths ZnS thin film recorded at 300 K obtained by using chemical spray pyrolysis method

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