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Investigation of structural, optical and electrical properties of ZnS thin films prepared by ultrasonic spray technique for photovoltaic applications

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ABSTRACT

ZnS films have important applications in photovoltaic devices. In the current study, the ZnS films were deposited by ultrasonic spray method on heated glass substrate at temperature equal to 450 °C.

In this article, we report the effect of deposition time on the different structural, optical and electrical properties of ZnS. All the samples obtained were treated using X-ray diffraction (XRD), optical transmittance spectroscopy (UV-V) and four-point method. The results of X-rays diffraction showed that the deposited material was pure zinc sulfide having a cubic sphalerite structure with preferential orientation along the (111) direction. As well the grain size was around 38–102 nm, when the deposition time increases. The transmittance measurements exhibit an average optical transparency between 35 and 75% in the visible range (400–750 nm) for different deposition times. The direct band gap energy for all films was calculated and found to be from 3.48 to 3.92 eV. The films' thickness is increased with deposition time from 195 nm to 1756 nm. The electric resistivity of the deposited film varies also with the deposition time between 1.51×10^5 and 20.84×10^5 Ω.cm.

1. Introduction

ZnS compound is one of the most important semiconductor material, and it has been largely investigated in the recent years [1]. Due to the wide band gap (3.7 eV), non toxicity, safety to environment and high transparency [2] of ZnS, it can be useful for extensively applications in optoelectronic devices, such as light-emitting diode and laser diode from blue to ultraviolet band [3], fluorescence and electroluminescence thin film devices [4] and n-type window material in solar cell [5]. As well in comparison with CdS, the ZnS thin films are present better lattice matching to CIGS owing to the precedent advantages.

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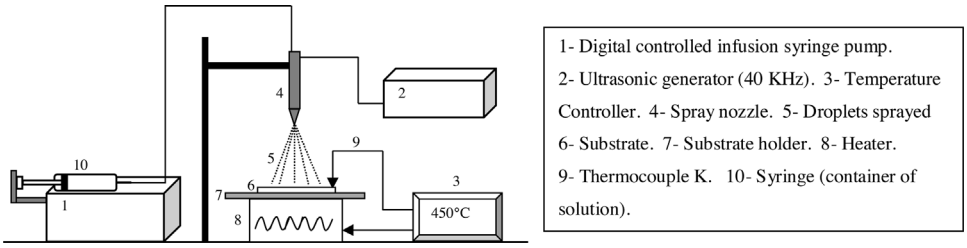

Fig. 1. The schematic experimental to used of deposition system.

Table 1
The deposition condition used to deposited of ZnS thin film.

Deposition condition	Corresponding values
Amount of solution	30 ml
Substrate – nozzle distance	50 mm
Substrate temperature	450 °C
Molarity of solution	0.1M
Deposition time	2 min, 4 min, 6 min, 8 min, 10 min
Spraying flow rate	50 ml/h

According to the literature, Zinc sulphide films can be deposit by several methods including reactive sputtering [6], electro-deposition [7], pulsed-laser deposition [8], chemical vapor deposition (CVD) [9], molecular beam epitaxy (MBE) [10], spray pyrolysis [11], chemical bath deposition (CBD) [12] and sol-gel process [13]. Among those methods, ultrasonic spray is the best one suited for the preparation of Zinc sulphide (ZnS) thin films because it is simplicity and do not cost an experimental requirement, ease of adding various doping materials, reproducibility, speed growth rate and mass production capability for uniform large area coatings [14].

In this paper, we attended zinc sulphide (ZnS) thin films on the glass substrate by ultrasonic spray technique. The aim of this work is to investigate the structural, electrical and optical properties of ZnS films as a function of deposition time. The obtained results are discussed and compared with other research results reported in the literature.

2. Experimental details

The deposition system has been prepared in the laboratory by the simple setup showed in (Fig. 1). Zinc sulphide thin films were deposited on glass substrates of the dimension (25×15) mm^2 using spray ultrasonic technique. These ZnS thin films exhibited good adherence to the substrate surfaces. The glass substrates were cleaned in acetone, ethanol, and distilled water respectively for 15 min, and then blowing dry with a compressed air. The starting solution was prepared by dissolving 0.1 M of Zinc Chloride ($ZnCl_2$) and thiourea ($SC(NH_2)_2$) in methanol. All the parameters were kept constant such as: the substrate temperature (450 °C), the flow rate solution (50 ml/h), the distance nozzle-substrate (50 mm). While, the deposition time changed from 2, 4, 6, 8, 10 min. In the Table 1, we summarized all the deposition condition.

Commonly when the solution droplets reach to the heated substrate surface, the following chemical reaction occurs:

$$ZnCl_2 + CS(NH_2)_2 + CH_3OH + \frac{3}{2}O_2 \rightarrow ZnS + 2NH_4Cl\,(gas) + 2CO_2\,(gas)$$

According to this reaction, a ZnS thin film should be formed on the glass substrate surface and the NH_4Cl, CO_2 leaves the system in gases form.

The structural, optical and electrical characteristics of these films have been studied extensively through several techniques. For the crystalline structure properties of the film was analyzed using X-ray diffracto-meter (D8 ADVANCED BRUKER) with Cu-Kα radiation (λ = 1.5418 Å) in 2θ range from 10° – 90°.

The optical properties have been recorded by using an ultraviolet-visible (UV-VIS) spectrophotometer (PerkinElmer LAMBDA25) between the wavelengths of 300 and 1100 nm. Moreover the electrical resistivity was determined using the four-point method at room temperature.

3. Results and discussion

3.1. Structural properties

According to the deposition process and experimental factors, Zinc sulphide films can be crystallized in two forms, cubic (Zinc blend) and hexagonal. The Fig. 2 shows XRD patterns of ZnS thin films deposited by ultrasonic spray at different deposition times. It was observed at different deposition time that there is a single one peak for all films with the preferred oriented growth along (111) plane at the diffraction angles of 28.7° and this is compatible with exhibited a zinc blende