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Structural and optical properties of $Cd_{1-x}Sn_xS$ semiconductor films produced by the ultrasonic spray pyrolysis method

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ABSTRACT

$Cd_{1-x}Sn_xS$ semiconductor films have been produced onto glass substrates at 573 K substrate temperature by the ultrasonic spray pyrolysis (USP) method using an aqueous solution with varying tin concentrations. The thicknesses of the films have been calculated to be in the range of 1–4 μm. The films have been characterized to evaluate the structure, morphology, composition and optical energy band gap. X-ray diffraction (XRD) studies show that the films are polycrystalline with hexagonal, tetragonal and orthorhombic structures. The morphological and compositional properties of the films have been investigated using scanning electron microscopy (SEM) and energy dispersive spectroscopy (EDS). Sn concentrations in the films have been varied from 0% to 84% as determined from energy dispersive analysis. The optical band gap energies and types of optical transition of the films have been determined from the optical transmittance spectra. The optical band gap energy values of the films decrease from 2.43 to 1.21 eV as the Sn concentration increases.

1. Introduction

In recent years, there has been considerable interest in the field of transparent semiconducting materials such as CdS, ZnS, etc. for use in a variety of applications, including architectural windows, solar cells, heat reflectors, light transparent electrodes, thin-film photovoltaic devices and many other optoelectronic devices [1–5]. CdS and SnS are both promising materials for solar cells. CdS, which belongs to II–VI compound semiconductors, is one of the promising materials. It is very desirable for a window layer in many photovoltaic solar cells. It is an important transparent conductive semiconductor for many optoelectronic devices due to its optical and electrical properties [2,6,7]. CdS is a well-known n-type direct band gap semiconductor (E_g=2.4 eV) [8,9], which has been used as the traditional partner for CdTe and CIS ($CuInSe_2$) solar cells [10]. SnS has attracted considerable attention in recent years due to the possibility of its application in photovoltaic devices as it is a non-toxic material that is abundant in nature. SnS, as one of the important IV–VI compound semiconductors, is usually a p-type semiconducting material with an orthorhombic crystal structure. Direct and indirect band gap energies of SnS films were reported to be 1.2–1.5 eV [11–15] and 0.9–1.3 eV [14,16–18], respectively. $Cd_{1-x}Sn_xS$ ternary alloy compounds are also promising materials for a variety of optical device applications, such as the top layer of solar cells [19]. The reason for using the ternary compound is the possibility of tailoring its semiconductor properties between values corresponding to the pure binaries. This fact allows one to adopt the material properties to the device requirements [20]. $Cd_{1-x}Sn_xS$ semiconductor films are both conductive and optically transparent in the visible region. Optical transparency in the visible region depends on the band gap of the alloy.

Various methods employed for depositing CdS and SnS films are chemical bath deposition [15,21], chemical vapour deposition [22], electrochemical deposition [23–26], rf sputtering [27,28], vacuum evaporation [29] and spray pyrolysis method [30–33]. Amongst all the deposition methods, spray pyrolysis (SP) method is a simple, convenient and low-cost method for large area deposition of many binary, ternary and quaternary semiconducting films with varying anion and cation concentrations. The SP method is an effective production method, leading to short production time, homogeneous particle composition and a one-step production method [34]. In the SP method, ideal conditions of deposition are obtained when the droplet approaches the substrate just as the solvent is completely vaporized. When a non-uniform droplet size is generated, the consequence is a change in thermal behaviour depending on mass of droplets. The deposition process is then affected by differences in size of droplets (the decomposition temperature depends on droplet size) [35]. In the USP method, the droplets of the solution generated by ultrasonic waves can be

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transported by the carrier gas to a heated surface of the substrate, where several reactions such as solvent evaporation and atomic rearrangement take place successively [34]. The USP method is a versatile method for producing various materials in a wide range of composition, size and morphology. Compared with other deposition methods, the USP method possesses the advantages of simplicity, good thickness uniformity over a large area and homogeneous particle composition with controlled particle size [36].

It is noted that so far there are a few reports in the literature on the physical properties of $Cd_{1-x}Sn_xS$ semiconductor films. In this work, the structural and optical properties of the $Cd_{1-x}Sn_xS$ semiconductor films in relation to composition x produced by the USP method have been reported and discussed.

2. Experimental details

$Cd_{1-x}Sn_xS$ semiconductor films were produced on glass substrates at 573 K substrate temperature by the USP method using aqueous solutions. A schematic diagram of the USP system used in this work is given in Fig. 1 [30]. The spray solution is usually made by dissolving salts of the constituent atoms of desired compound in an aqueous medium. The spray solution consisted of a 1:1 mixture (by volume) of 0.05 M cadmium chloride ($CdCl_2 \cdot H_2O$), thiourea (H_2NCSNH_2) and 0.05 M tin chloride ($SnCl_2 \cdot 2H_2O$) solutions. The composition of $Cd_{1-x}Sn_xS$ films changed from pure CdS to pure SnS (x=0.4, 0.6, 0.8 and 1.0). The glass substrates ($13 \times 26 \times 1$ mm^3) were boiled with detergent, soaked in chromic acid, cleaned in isopropyl alcohol, rinsed in distilled water at each step and dried in air. The ultrasonic spray-head-to-substrate distance was fixed approximately at 30 cm. The solution flow rate during spraying was adjusted to be about 5 ml min^{-1} by a flowmeter. Nitrogen was used as the carrier gas (0.2 kg cm^{-2}) during spraying. The glass substrates were heated by an electrical heater and control of substrate temperature was done by means of a chromel–alumel thermocouple. The deposition time was about 40 min. The thicknesses of the $Cd_{1-x}Sn_xS$ semiconductor films were determined using an Elcometer 345 Model Digital Coating Thickness Gauge. The thicknesses of the $Cd_{1-x}Sn_xS$ samples (x=0, 0.4, 0.6, 0.8 and 1.0) have been determined to be 4.0, 1.5, 1.0, 1.0 and 2.0 μm, respectively. Conductivity of the $Cd_{1-x}Sn_xS$ alloy films has been determined to be of n-type by the hot probe method. Structural properties of the films were studied using XRD analysis and it was performed by a Rigaku X-ray diffractometer system using CuK_α radiation with the wavelength of λ=1.5406 Å. Morphological properties of the films were investigated using a Jeol SEM 5600 LV system. Compositional properties of the films were determined using a Noran Voyager EDS 3050 system. Optical transmittance spectra of the films were carried out using a Lambda 2S Model Perkin Elmer UV/VIS Spectrometer system covering the spectral range from 200 to 1100 nm.

3. Results and discussion

The structural properties of the $Cd_{1-x}Sn_xS$ films have been investigated by XRD patterns. The XRD patterns of the samples are given in Fig. 2. The spectra have been obtained by scanning angle 2θ in the range from 20° to 60°. The existence of multiple diffraction peaks, and sulphide and oxide phases in the diffraction patterns indicates the polycrystalline nature of the $Cd_{1-x}Sn_xS$ samples. It is seen that crystallinity of the CdS film is better than that of other films. It should be noted that the XRD patterns exhibit clear dependence on Sn concentration. The CdS film has been crystallized in a hexagonal structure (JCPDS Card no.: 41-1049)

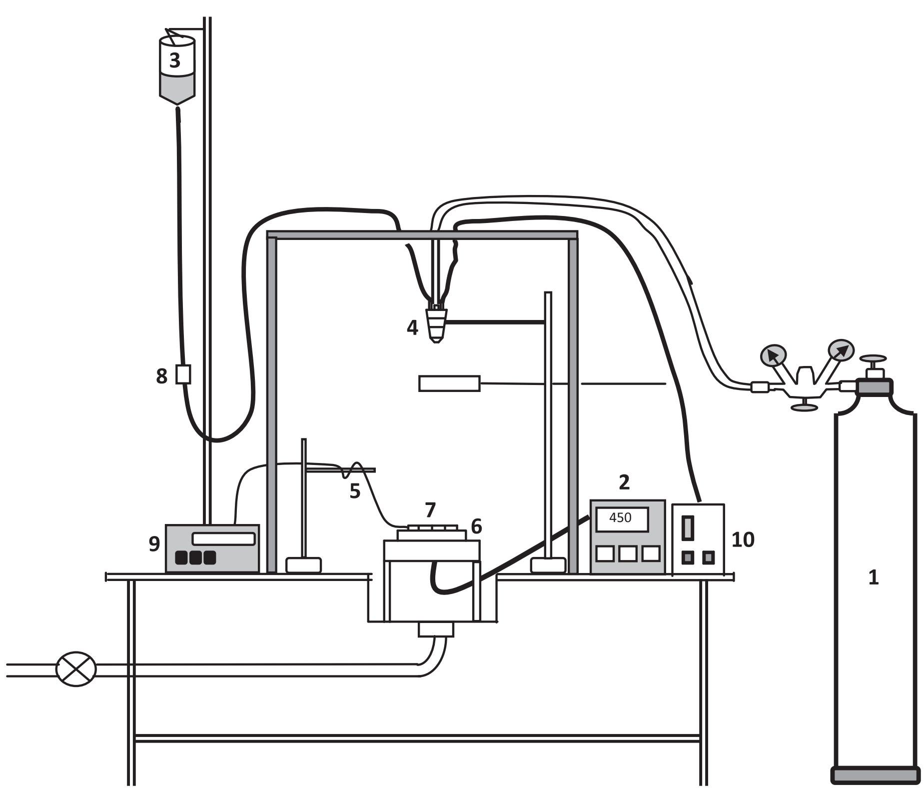

Fig. 1. Schematic diagram of the USP system: (1) nitrogen gas tank, (2) variable current source, (3) spraying solution, (4) ultrasonic spray head, (5) thermocouple, (6) heater bronze block, (7) glass substrates, (8) flowmeter, (9) voltmeter for thermocouple and (10) ultrasonic generator.