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Original research article

Investigation on the structural, optical and electrical properties of mixed SnS_2—CdS thin films

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ABSTRACT

Mixed thin films of $(SnS_2)_x(CdS)_{1-x}$ $(0 \leq x \leq 1)$ were deposited by spray pyrolysis technique decomposition of aqueous solutions of Cadmium chloride ($CdCl_2$) and Tin chloride ($SnCl_2$) on glass substrates at a substrate temperature of 350 °C. Structural properties of the obtained films were studied by X-ray diffraction analysis. The surface morphology and elemental analysis of the films has been examined using scanning electron microscopy (SEM) and Energy-dispersive X-ray spectroscopy (EDX). Optical properties of the deposited films were obtained using transmittance measurements in the wavelength range [200–2500 nm].Some optical parameters such as, high frequency dielectric constant ε_∞, lattice high frequency dielectric constant ε_L and the dispersion parameters (oscillation energy E_0 and the dispersion energy E_d) were estimated by analyzing the refractive index data. The direct optical band gap value of these films varies from 2 to 2.41 eV. We have observed that $(SnS_2)_x$ $(CdS)_{1-x}$ thin films conductivity obeys the Meyer–Neldel rule (E_{MN} = 32 meV), which is interpreted as disorder parameter. The room temperature electrical resistivity of CdS (x = 0) films was found to be 2.22 10^{+4} Ω cm and it decreases when content of Sn in mixed films increases and reaches the optimum value of resistivity 2.32 10^{-2} Ω cm for the concentration x = 0.5. The carrier concentration was found to vary from −1.26 10^{+12} to −4.50 10^{+20} cm^{-3} and corresponding hall mobility varied from 6.51 10^{+1} to 2.64 10^{+1} cm^2/VS.

1. Introduction

In the past few decades, there has been an increasing interest in semiconducting chalcogenide (sulfides, selenides and tellurides. . ..) thin films, due to their wide range of applications in various fields of science and technology. Nanocrystalline binary and ternary semiconductors of Groups II–VI and IV–VI have potential applications in many technical fields, including solar cells, photovoltaic applications and optoelectronic devices [1–3].

Tin disulfide (SnS_2) is an n-type semiconductor with hexagonal cadmium iodide (CdI_2) structure. It is composed of sheets of tin atoms sandwiched between two close-packed sheets of sulfur atoms [4,5]. As an important member of the IV–VI group semiconductors. It is an n-type semiconductor having a wide optical band gap of about 0.8–2.88 eV [6,7]. It has many interesting properties related to electrical switching and conduction mechanism [8], and optical absorption in the visible region [9]. These properties suggest that this is a good material for solar cell and optoelectronic device applications [10].

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Cadmium Sulfide (CdS) is an important II–VI group chalcogenide semiconductor. CdS thin films is used as buffer material for high efficiency polycrystalline thin film solar cells, it is an n-type material with a band gap of 2.42 eV. CdS thin films were prepared by various methods such as sputtering [11], electrochemical deposition [12], vacuum deposition [13] and spray pyrolysis deposition [14].

In the recent years, interest on the preparation and study of physical properties of ternary chalcogenide compounds for their possible applications in solar cells, light emitting diodes and non-linear optical devices has increased [15,16], many reports were available on chemically deposited ternary composite thin films such as:$(CdS)_x$ $(PbS)_{1-x}$ [17], $Cd_{1-x}Ag_xS$ [18], $(Sn_2S_3)_x(Bi_2S_3)_{1-x}$ [19],$(CdS)_x(Bi_2S_3)_{1-x}$ [20],$Cd_{1-x}Cu_xS$ [21] $Cd_{1-x}Fe_xS$ [22], and suggested their applications in the area of energy conversion and solar energy utilization due to the modification in electrical and optical properties. However, there is no report on $(SnS_2)_x$ $(CdS)_{1-x}$ mixed thin films by spray pyrolysis method, as far as we know.

In the present work, for the first time, $(Sn\ S_2)_x(CdS)_{1-x}$ mixed thin films have been grown by spray pyrolysis method on the glass substrates at 350 °C, and the composition dependent structural, surface morphological, optical and electrical properties are discussed

2. Experimental details

The spray pyrolysis technique is employed to prepare mixed thin films of $(SnS_2)_x$ $(CdS)_{1-x}$ on microscope glasses of $(75 \times 25)mm^2$. The precursor solutions of tin chloride ($SnCl_2{\cdot}2H_2O$) and Thiouréa $CS(NH_2)_2$ were prepared using the solvent containing a mixture of deionized water and methanol in proper ratio, a few drops of HCl were also added for complete dissolutions to the solubility of $SnCl_2$. The prepared solutions of tin chloride and thiourea have been appropriately mixed to obtain a Sn:S proportion of 1:1. For the preparation of CdS, we followed the same procedure as before except that in this case the $CdCl_2$-$2H_2O$ powder was used instead of $SnCl_2$-$2H_2O$ and dissolved in deionized water only.

The substrates were first cleaned in a water bath, followed by dipping in con. HCl, acetone and ethanol successively. Finally the substrates were rinsed in deionized water and allowed to dry in a hot air oven. Compressed air at a pressure (2 bar) has been used as a carrier gas. In this preparation process, the following conditions have been used: substrate temperature 350 °C, solution flow of 8 ml/min, spray nozzle to heating plaque distance of 29 cm. One also notes that the prepared solutions were immediately sprayed to avoid any possible chemical changes with time.

In this paper we have described the preparation of mixed $(SnS_2)_x$ $(CdS)_{1-x}$ thin films by the spray pyrolysis method with variable composition (x = 1, 0.8, 0.5, 0.2 and 0). Structural characterization has been carried out at room temperature using a Philips 1830 X-ray diffractometer with a Cu Kα peak λ = 1.546 Å. Morphology was carried out by a Joel JSM 5800 scanning electron microscope. The optical transmittance was recorded from 200 to 2500 nm wavelength using an UV (Ultra-Violet) Visible JASCO type V-570 double beam spectrophotometer. The electrical properties were measured by ECOPIA HMS-5000 Hall Effect measurement at room temperature, and by the four-point probe method.

3. Results and discussion

3.1. Structural characterization

Multiple samples have been deposited and analyzed to ensure reproducibility of our results. The XRD patterns of mixed thin films $(SnS_2)_x$ $(CdS)_{1-x}$ deposited by spray pyrolysis technique at 350 °C on glass substrates for different *x* values (x = 1, 0.8,0.5,0.2 and 0) were shown in Fig. 1. The presence of sharp structural peaks in these XRD patterns confirmed the polycrystalline nature of the films, these films were not treated after deposition. The polycrystalline SnS_2 (x = 1) peaks in the patterns were identified as (001) and (101), while those of CdS (x = 0) were indexed as (100), (002), (101), (110), (103) and (112), respectively. These peaks are in agreement with the standard values of the JCPDS cards of SnS_2 (Card No. 23-0677) and CdS (Card No 41-1049). The XRD patterns of the as deposited films reveal the presence of hexagonal phase of both SnS_2 and CdS for x = 0.8, the XRD patterns clearly show three well defined peaks for CdS (100), (002), (101) correspond to 2θ = 24.98, 2θ = 26.68, 2θ = 28.36 respectively and one peak for SnS_2 (001) corresponds to 2θ = 14.95, This result clearly indicates that as deposited film $(SnS_2)_x$ $(CdS)_{1-x}$ (for x = 0.8) has a mixed phase of CdS and SnS_2. But for x = 0.5 and x = 0.2 we observed the presence of almost all intense CdS peaks and the extinction of all peaks of SnS_2. XRD results showed that no peaks of other phases like (SnO_2, SnS_2, Sn, CdSnS….).

CdS phase became dominant in these materials with the dominant peaks (002) and (101) reflection with a hexagonal structure, suggesting that the Sn becomes a dopant into thin films Cd_{1-x} Sn_xS. The absence of Sn in XRD results is also observed by Tulay Ozer [23]. From the XDR patterns (Fig. 1**)** it's also observed that the preferential orientation of the film for x = 0.2 changes from (002) to (101) with Sn incorporation. The shifts may be attributed to the stress effect, and structural disorder in the film.

The mean grain size (D) of the mixed thin films for the peak with highest intensity can be estimated by using the Debye-Scherrer formula [19,24,25]:

$$D = (0.9..\lambda) / \left(\beta.cos\theta\right). \quad (1)$$