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Original research article

Influence of post-deposition annealing on the structural and optical properties of γ-MnS thin film

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ABSTRACT

γ-MnS thin film was deposited at 40 °C temperature on glass substrate by Chemical Bath Deposition (CBD) method that has superior advantageous in terms of fast and cheap production. MnS thin film was annealed in nitrogen atmosphere at temperatures 100, 200, 300, 400, 500 °C for an hour. The effect of annealing temperature on structural and optical properties have been investigated. X-ray diffraction (XRD) analysis revealed that gamma-MnS thin film had the phase change and oxidized at 400, 500 °C annealing temperature. The grain size of the annealed film was calculated between 241 and 280 Å as a function of annealing temperature. It was observed that optical transmission values decreased at wavelength of 400–700 nm (visible region) after annealing at temperatures 400 and 500 °C. Increasing annealing temperature induces reduction in energy band gap values from 3.89 eV down to 3.46 eV. Refractive index (n) values were calculated by envelope method. Refractive index values at visible region increased from 2.03 to 2.54 with increasing annealing temperature.

1. Introduction

In recent years there has been intense research activities on semiconductor thin films due to utilization them in electronic, optic and magnetic memory devices [1]. MnS that is consisted of group of VIIB-VIA compounds is categoried as magnetic material VIIB-VIA groups [2]. The energy band gap of MnS thin films is $E_g \sim 3.7$ eV and are used for optoelectronic devices, supercapacitors [3], solar cells, fotoconductivity and optical memory devices [4]. MnS is crystallized into three forms as rock-salt (α-MnS), zinc blend (β-MnS) and wurzite (γ-MnS) [5]. In those structures, β and γ are formed at low temperature and shifts α form which is regular at temperature 100–400 °C [6].

MnS thin films are prepared by using following techniques; spray pyrolysis [7], silar [8], rf-sputtering [9], molecular epitaxy [10], hydrothermal synthesis [11], solvothermal [12], electro-deposition [13], chemical vapor deposition [14], thermal vacuum evaporation [15] and chemical bath deposition [16–18]. The chemical bath deposition technique is based on slow deposition of solution ions on the suitable substrates to produce films. The method does not require any expensive experimental set-up and low vacuum. Morever, it is considered one of the most preferable techniques due to providing adjustment of the film thickness and dimensions as function of solution concentration, pH and temperature. Using the technique low

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cost thin films can be produced on a very wide surface. Considering all those advantegous given above gamma-MnS thin films were deposited by chemical bath deposition.

In this study, gamma-MnS this film was produced by chemical bath deposition at 40 °C temperature followed by 100, 200, 300, 400 and 500 °C annealing process in nitrogen atmosphere for an hour. The effect of annealing temperature on structural and optical properties was investigated as well as the reasons of effects. To our best of knowledge, there has been no detailed investigation in the literature on the annealing of gamma-MnS in nitrogen atmosphere.

2. Experimental details

MnS thin film was produced on the glass substrate (76 mm × 26 mm × 1 mm dimensions) The cleaning of substrate is crucial for good quality of films. For this reason, detailed cleaning procedures was used for cleaning of the substrate as followings; firstly, it was washed with hot detergent water and rinsed with deionized water followed by washing with diluted chromic acid and rinsed by deionized water. Then, it was kept into the isopropil alcohol approximately 3 min, after that it was washed with deionized water and kept in the oven at 100 °C to dry up. All the chemicals and reagents used for the deposition were analytical grade. The solutions were prepared in deionized water (Purelab flex 3, water purity: 18.2 MΩ at 25 °C). To prepare MnS films; 1 M mangan acetate [$Mn(CH_3COO)_2$], 1 M thioacetamide [(CH_3CSNH_2)], 3.75 M triethanolamine [$N(CH_2CH_2OH)_3$], ammonia/ammonium chloride buffer solution [(NH_3/NH_4Cl) (pH = 10.6)] and deionized water were used. In this reaction, the function of trietanolamin is to provide complex with manganese and release Mn^{2+} from formed manganese complex. However, the duty of NH_3 is to form hydroxyl ions at water enviroment to release from tiyoasetamit S^{2-} ions. The released S^{2-} ions Mn^{2+} ions get together to form manganese sulfate on glass substrate. The reactions of producing gamma-MnS thin films are as below,

$$Mn(CH_3COO)_2 + TEA \rightarrow [Mn(TEA)]^{2+} + 2CH_3COO^- \quad (1)$$

$$CH_3CSNH_2 + 3OH^- \rightarrow C_2H_3COO^- + NH_3 + S^{2-} + H_2O \quad (2)$$

$$Mn(TEA)^{2+} + CH_3CSNH_2 + 2OH^- \rightarrow MnS + TEA + CH_3CONH_2 + H \quad (3)$$

The total solution, which was formed to film, put into the beaker and mixed until homogeneously distributed. The obtained solution was poured into the 20 ml volume beaker. The cleaned glass substrates were immersed vertically in the beaker. As a result, due to precipitation of irregular particles, high film quality was provided. The procedure was carried out in 20 ml beaker at a temperature of 40 °C and held for 3 h for each immersion. A new solution was prepared after each immersion procedure and repeated 3 times for each. The results of the procedure revealed that an adequate deposition of the film was obtained and there was adhesion between the glass substrate and the deposited film. The film was then cleaned with diluted acid solution followed by a drying procedure in order to carry out gamma-MnS characterization techniques on the samples. X-ray diffraction characterization of the samples were obtained using the Rigaku RadB diffractormeter system (Cu-Kα_1, 1.5406 Å, 30 kV, 15 mA, scanning rate 3°/min), Optical transmission measuremnts were achieved using Perkin Elmer UV–vis Lamda 2S spectrophotometer (λ = 190–1100 nm).

3. Results and discussion

3.1. Structural properties

The gamma-MnS films of this study were obtained at 40 °C using the chemical deposition method followed by an annealing procedure for 1 h in a nitrogen atmosphere at different temperatures (100, 200, 300, 400, 500 °C). Fig. 1 shows the X-ray diffraction patterns of different samples obtained by this method at different annealing temperatures.

The figure shows the peak intensity in *y*-axis and the Bragg diffraction angle in the *x*-axis as 2θ. The Fig. 1(a) illustrates the X-ray diffraction pattern of samples that were obtained at 40 °C. It can be seen that there is a sharp peak around $2\theta = 27.87°$ that gives rise to the d-interplanar spacing calculated to be 3.1974 Å. The results revealed that MnS thin film was grown on *c*-axis (002) phase in the crystal hexagonal phase according to the standard PDF card (No.: 40-1289) of gamma-MnS. The similar studies in the literature reported that the film prepared at temperature at 27 and 30 °C was formed as amorphous [19,20], polycrystal [21] and single phase [22]. X-ray diffraction pattern of MnS thin film annealed at temperature of 100 °C for an hour is given in the Fig. 1(b). As a result of annealing the film at 100 °C temperature, a peak is observed at $2\theta = 27.88°$ and the distance of the atomic planes which is responsible for the observed peak *d*-interplanar spacing is calculated as 3.1976 Å. MnS thin film was grown on *c*-axis (002) planes in the crystal structure. The intensity of X-ray diffraction peaks enhances for MnS thin film annealed at 100 °C temperature compared to as grown one. The X-ray diffraction pattern of MnS thin film annealed at 200 °C for an hour is given in the Fig. 1(c). It was observed that MnS thin film had two peaks at $2\theta = 27.97°$ and $2\theta = 50.3°$. The peak at $2\theta = 27.97°$ is much stronger than the $2\theta = 50.3°$ The distance between atomic planes (*d*-interplanar spacing) were calculated as 3.1872 Å and 1.8123 Å, respectively. The small increase was observed in peak intensity of the film. Beside having the *c*-axis (002) plane hexagonal structure orientation, the low intensity (103) plane peak is seen. Fig. 1(d) showed the MnS thin film X-ray diffraction pattern at annealed 300 °C temperature for an hour. There was no significant change was observed with annealing temperature. The diffraction pattern of gamma-MnS thin film annealed at 400 °C for an hour is given in Fig. 1(e). Additionally, a weak peak at $2\theta = 34.36°$ which was attributed to the cubic phase of MnS was observed as