Photoluminescence studies on Sb_2S_3 thin films prepared by vacuum evaporation and spray pyrolysis technique

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Antimony tri -sulphide (Sb_2S_3) thin films are deposited onto glass substrates by vacuum evaporation under the pressure of $2x10^{-5}$ Torr. The substrate to source distance is optimized and constant rate of evaporation is maintained. The samples are annealed at 473K and 523K. Similarly by using spray technology three different concentrations of Sb_2S_3 thin films are prepared by taking different molarities of antimony tri- chloride and thioacetimide by dissolving appropriate amounts of salts in acetic acid. The parameters such as temperature, spray rate and nozzle to substrate distance are optimized and the solution is sprayed onto hot glass substrate. The films obtained by both the methods are further investigated by photo luminescence studies. It is observed that variation of intensity of the luminescence is depending upon the annealing temperature and concentration.

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1. Introduction

Two distinct chemical formulations have been reported for the deposition of Sb_2S_3 thin films [1-3]. The one using antimony chloride and thiosulphate solution mixtures typically gives thin films of 200 nm thickness in about 4h at 2 to 10°C[1,2]. These films have been integrated into distinct photovoltaic structures with open circuit voltage (V_{oc}) of up to 640mV and conversion efficiency approaching1% [4,5]. The other formulation, using potassium antimony tartrate and thioacetamide solutions produce films of about 300 nm in thickness at deposition temperatures near 30°C [3]. The use of such films in hetrojunction solar cells has been demonstrated in 1994[6].Many binary and ternary semiconductors on a variety of substrates have been prepared by spray pyrolysis technique; the more important examples being CdS,CdSe,CdTe,$CuInS_2$, $CuInSe_2$,Bi_2 [7]. Vacuum evaporation techniques [8, 9] and Spray pyrolysis [10] have been reported for the preparation of thin film of Sb_2S_3.In this paper photoluminescence studies has been carried out for the films prepared by spray pyrolysis and vacuum evaporation technique.

2. Experimental details

2.1. Preparation of Sb_2S_3 thin films by vacuum evaporation method

The crystalline solid of Antimony Trisulfide [99.999% purity, Sigma Aldrich Company, India] is kept in the molybdenum boat (100 amps) and heated with high current by a transformer of supplying 150 amps at 20 volts used for the evaporation purposes. Prior to evaporation, the evaporant material is carefully degassed at lower temperature for about 45 minutes with the shutter closed. The current is slowly increased and the evaporation is started slowly. The pressure inside the chamber is found to be 2×10^{-5} Torr and the constant rate of evaporation 1Å/sec is maintained to evaporate the material completely. During the thermal evaporation Sb_2S_3 thin films are formed in brown in color. The adhesion of the film to the substrate is seemed to be poor. Hence, the substrate to source distance is varied and optimized to 14 cm inside the chamber. Good adherent thin films of thickness 2800Å are deposited and annealed at temperatures of 473K and 523K.The photoluminescence spectra measurements are carried out by using cary-50 spectrophotometer interfaced with computer for both the methods.

2.2. Preparation of Sb_2S_3 thin films from spray pyrolysis technique

0.1 M solution of antimony trichloride and (0.3 M, 0.45 M and 0.6M) thioacetamide are prepared by dissolving appropriate amounts of salts in acetic acid (20 ml). The different molarities of thioacetamide solutions are mixed with antimony trichloride in three beakers and the solutions are stirred for few minutes. A yellowish solution is obtained and the films are prepared by spraying the mixed solution (10 cc) onto hot glass substrates kept at an optimized temperature of 250 ^{o}C. The spray rate is maintained at 5 cc / min. The nozzle to substrate distance is 28 cm. The spray nozzle is moved to and fro over the substrate. The deposited films are brown in colour, uniform pinhole-free and well adherent to the glass substrate.

3. Results and discussion

3.1. Photoluminescence Study on the films prepared by vacuum evaporation method

Fig. 1 shows the photoluminescence spectra of Sb_2S_3 thin films of asdeposited and annealed films at thickness

of 2800A° and in the wavelength range of 250-500 nm respectively. The figure shows broad emission of a dominant peak at 361 nm for all films. The broad emission may be due to photon assisted transitions. Further large crystals tend to produce more defects than smaller one. The luminescence increases, when the temperature increases due to the increase in crystalline size of the films. The peak intensity in the case of annealed films is much higher compared to that of asdeposited films at room temperature. This could be due to shape effect and Sb atoms at S site. The shape of the materials has an important effect on the PL intensity [11]. Other peaks at 297 nm that are seemed to be associated to free electron to neutral acceptor transition. This also can be attributed to donor-acceptor pair transitions due to the presence of acceptor and native donor defects.

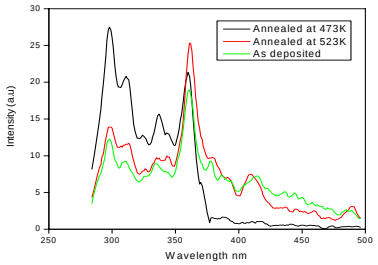

Fig. 1. Photoluminescence of Sb_2S_3 thin films at thickness 2800Å.

3.2. Photoluminescence study on the films prepared by spray pyrolysis method

The photoluminescence spectra of Sb_2S_3 films prepared by various molar ratios of Sb: S (a) 0.1: 0.3 M, (b) 0.1: 0.45 M and (c) 0.1: 0.6 M are depicted in Fig. 2. The effect of increase in molar concentrations on PL spectra can be seen by the increase in emission intensities. A peak at nearly 4.16 eV that seems to be associated to free electron to neutral acceptor transition or some LO phonon replicas that usually will be followed by free electron acceptor transition. This also can be attributed to donor – acceptor pair transitions due to the presence of acceptor and native donor defects [12, 13]. Figure also shows a broad emission with two dominant peaks at 3.42 eV for all molar concentrations and another at 3.008 eV occurs at higher molar concentrations.

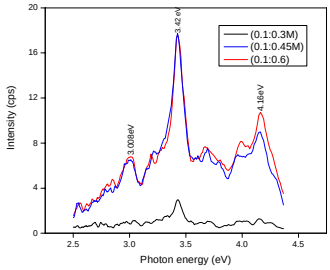

Fig. 2. Photoluminescence spectra of Sb_2S_3 for different molar ratio.

The deep level emission may be originated from a correlation that has been established with native defects such as Sb vacancy. Similar trend is observed by earlier reports of ZnO thin films [14, 15]. There is not much shift which can be observed in band edge emission of Sb_2S_3 with respect to sulphur concentration.

4. Conclusion

The Sb_2S_3 thin films of thickness 2800Å is prepared and annealed subsequently at 473 K and 523 K respectively by vacuum evaporation. The crystallinity of the film is improved by thermal annealing. The emission intensity peaks in the case of annealed films is much higher than that of the room temperature films due to shape effect. From the graph it is confirmed that donor-acceptor pair transitions is taking place due to the presence of emission peak, acceptor and native donor defects. The films obtained by spraying technology after PL investigation reveals that the intensity of the peaks gets increases with concentration. It also proves the presence of donor – acceptor pair transitions. There is no much shift observed in band edge emission of Sb_2S_3 with respect to sulphur concentration.

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