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SnS THIN FILMS PRREPARED BY ENCAPSULATED SULFURIZATION

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ABSTRACT

Tin sulphide (SnS) thin films were grown using a method called encapsulated sulfurization from the Sn/S stacked layers previously coated on a glass substrate at pressure 10^{-5} mbar and film thickness ratios; Sn:S=1:1, 1:2 and 1:3. In this technique the samples were placed in a carbon block and annealed in argon gas at temperatures between 260-450°C for three hours to allow the formation of SnS thin films by chemical reaction which took place in the Sn/S bilayer. In the early stage (260°C) Sn was sulfurized gradually into mix compositions of SnS, Sn and S, and a further increase of temperatures between 300-400°C changed the process rapidly and dominantly into SnS. XRD and SEM results confirmed the existence of stoichimetric SnS with improved crystallinity. The measured resistivities were found to be between 0.65-2.92 Sm^{-1} over the range of substrate temperature concerned.

INTRODUCTION

A polycrystalline of SnS thin film has a great importance as a material for the photovoltaic generation in the future with regard to its electrical and light absorbing properties[1]. Earlier investigators have reported energy gap of SnS thin films in the range 1.1-1.3 eV and exhibited p-type conductivity[2,3]. Rhombohedrally-structured SnS belongs to the space group symetry D^{16}_{2h} comprises of four molecules, with lattice parameters a = 0.398 mm, b = 0.433 mm and c = 1.118 mm[4]. Among the preparation techniques used were evaporation[5] and chemical methods[6].

Encapsulated sulfurization is a new effective method for producing SnS thin films and has the potential to produce a large volume of low-cost and large area photovoltaic cells. Originally, it was applied to selenization process of Cu/In/Se stacked layers for the formation of $CuInSe_2$ films[7,8]. Similar technique was developed in this investigation to study the sulfurization and selenization processes of SnSe[9] and SnS thin films, respectively. This work describes some initial results of SnS thin films prepared by encapsulated sulfurization with emphasis given on structural analysis and electrical resistivity measurements.

EXPERIMENTAL

Evaporated Sn and S films were prepared on glass substrates at thickness ratios 1:1, 1:2 and 1:3, forming Sn/S stacked layers. Experimentally, these ratios were Sn:Se=200:200 nm, 200:400 nm and 200:600 nm. The samples were then placed in a high gred carbon block of dimension 6 cm x 4 cm x 1 cm and the contents were annealed in running argon gas inside a furnace between 260-450°C for three hours at a pressure about 0.1 mbar. It is expected that, at this range of temperature, S is easily evaporated if compared to Sn due to its low degree of volatility. The excessive content of S vapour can be prevented from desorption losses by means of encapsulation for effective reaction between Sn-S. Typical encapsulated sulfurization technique is shown in Figure 1. The stages in the formation of SnS were studied using X-ray analysis and SEM; both annealing temperatures and thickness ratios were the factors considered in this investigation.

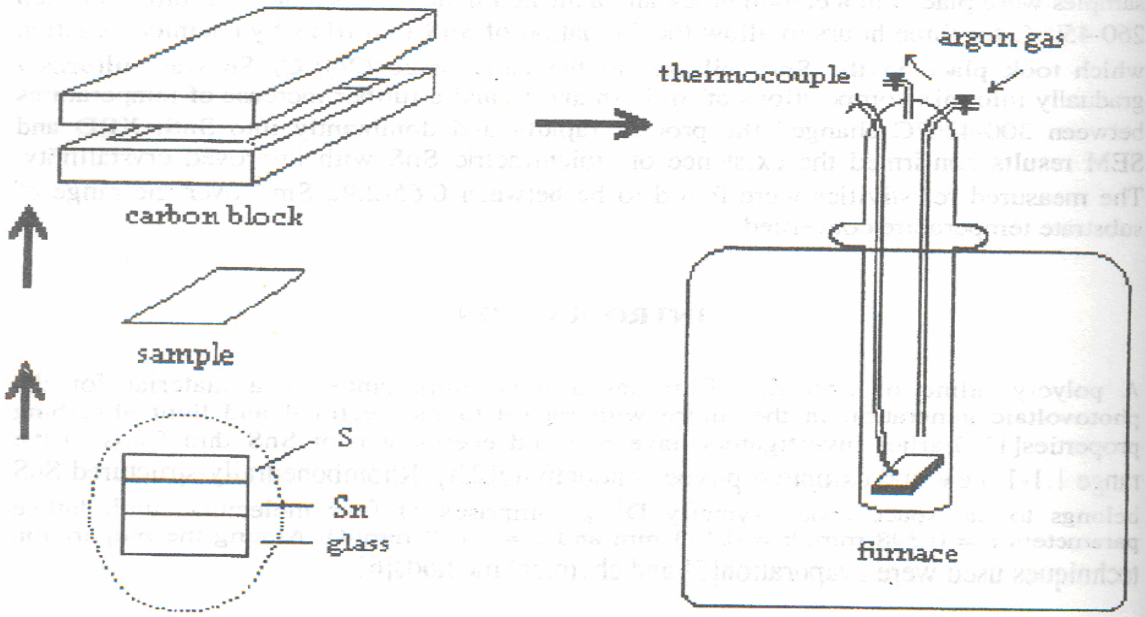

Figure 1. Encapsulated sulfurization of Sn/S stacked layers to form stoichiometric SnS.

RESULTS AND DISCUSSION

Figure 2 shows X-ray diffraction spectrums of the grown SnS films at temperatures 350°C, 400°C and 420°C. The sulfurization process is expected to be initiated at 260°C (not shown) by the presence of a single (040) peak along with the dominant Sn and S peaks in the composition. Rapid selenizing reaction occured in all the Sn/S bilayer at higher annealing temperatures, and eventually reached the conditions where most of the SnS orientation emerged as strong peaks, mainly at annealing temperature 350°C. The preferred orientations of the sample prepared at 400°C were found to be optimum, comprising of (120), (021), (101) (111), (040), (131), (141), (151), (042) and (080) strong reflections which corresponded closely to ASTM data file. This trend changed with an increase of annealing temperature up to 420°C by the presence of weak Sn (220) and (211) peaks. The results suggested optimum annealing temperature for the growth of SnS which lied just around 400°C; this temperature was higher than those of SnSe thin films prepared using similar technique and conditions[8].

The effect of thickness ratio on the structural properties of SnS thin films is shown in Figure 3. X-ray spectrums were obtained from the samples prepared at a fixed annealing temperature 380°C and varying ratio of Sn:S. It is obvious that, from the analysis, the spectrums obtained from Sn:S=1:1 resembles exactly to that shown in Figure 2(b), while the spectrums for Sn:S=1:2 and Sn:S=1:3 indicate the existence of mixed SnS and SnS_2 compositions. Figure 4 shows typical SEM micrographs of the sample surfaces, showing the appearance of polycrystal structures. The analysis gave the grain sizes of 0.4 μm and 0.2 μm for the thickness ratios Sn:S=1:1 and both Sn:S=1:2 and Sn:S=1:3, respectively. The results showed an improvement in the stoichiometric formation of SnS thin films if compared to those reported earlier[3] using evaporation technique.

The dark electrical conductivity measurements gave σ which increased rapidly from 0.65-2.30 Sm^{-1} over the 260-380°C range, and a further gradual rise up to 2.92 Sm^{-1} leading to 450°C. See Figure 5. Lower values of σ was attributed to the existence of metallic Sn found in the composition which contributed to electrical conduction and σ varied almost linearly with annealing temperature. However, the slope of this variation reduced at 380°C in association with the formation of dominant SnS, and a further change of σ at higher annealing temperatures was likely governed by its semiconducting properties. Deraman et al.[4] have reported the range of σ between 0.6-2.0 Sm^{-1} and showed σ dependency on substrate temperatures.

CONCLUSIONS

Encapsulated sulfurization technique is capable of producing stoichiometric SnS thin films with better crystallinity. It was found that the optimum conditions for SnS thin films

were annealing temperature of about 400°C (for three hours) and thickness ratio, Sn:S=1:1. The grown films exhibited lower electrical resistivity of the order 2 Sm^{-1}.

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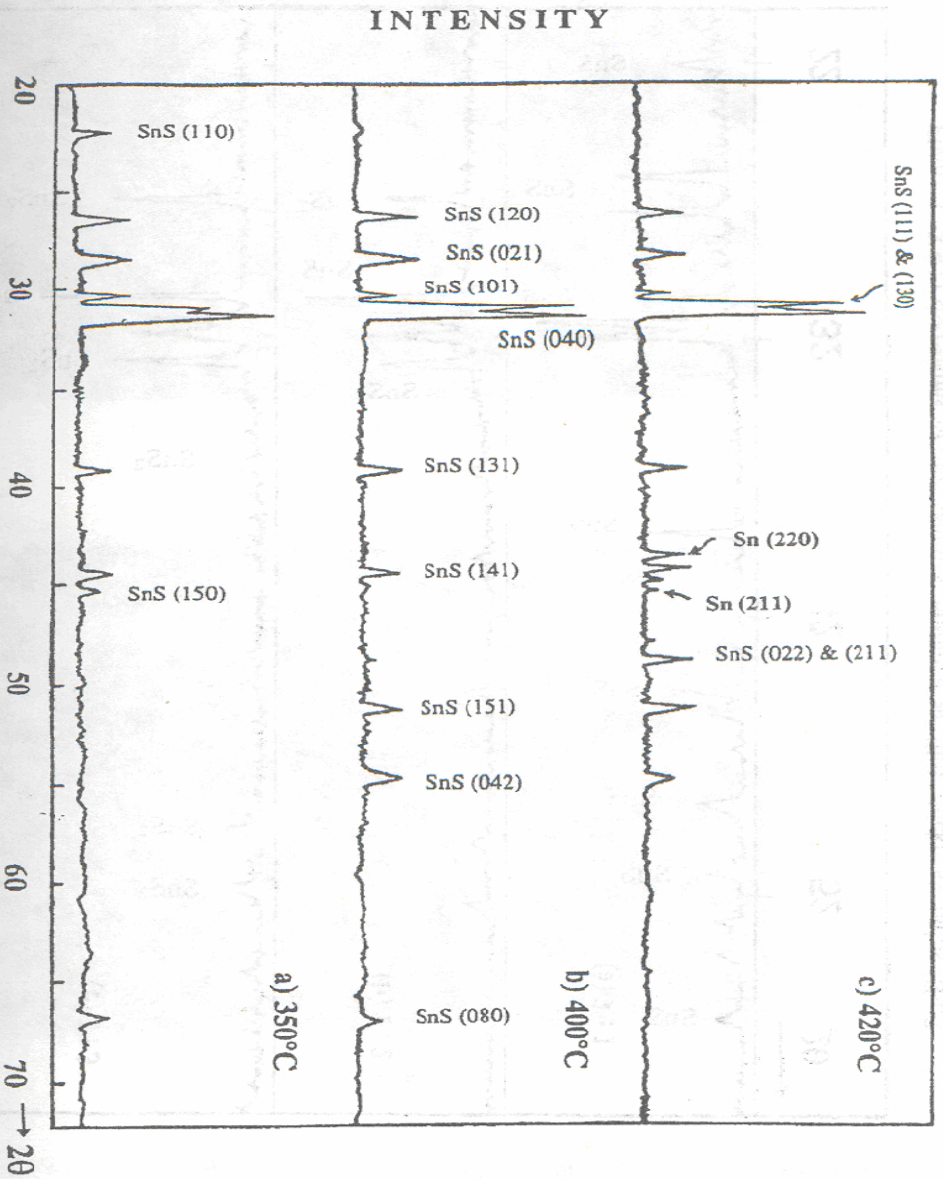


Figure 2. XRD spectrums showing progress in the formation of SnS thin films at different annealing temperatures of a) 350°C, b) 400°C and c) 420°C (film thickness ratio of Sn:S = 1:1, annealing period = 3 hours).

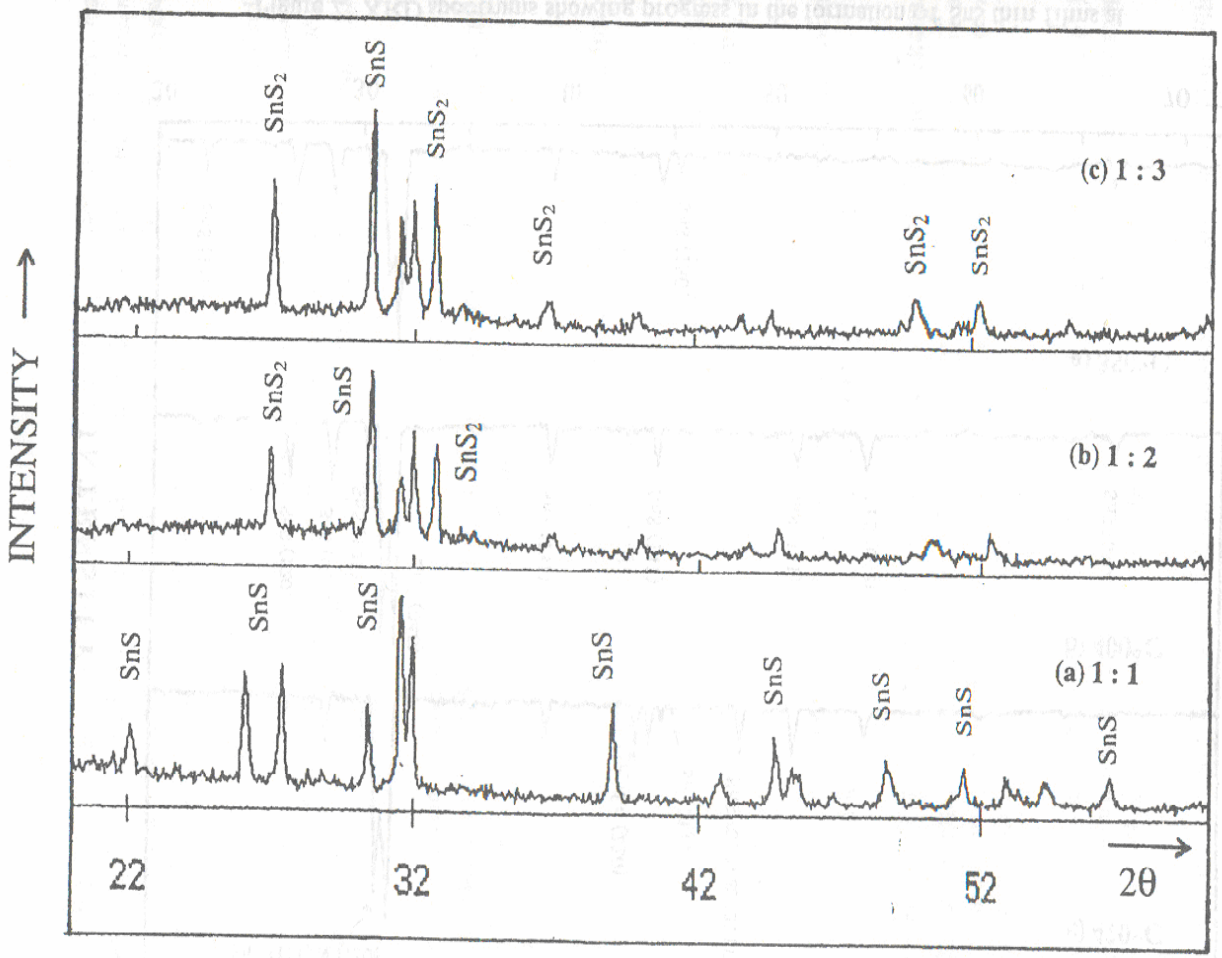
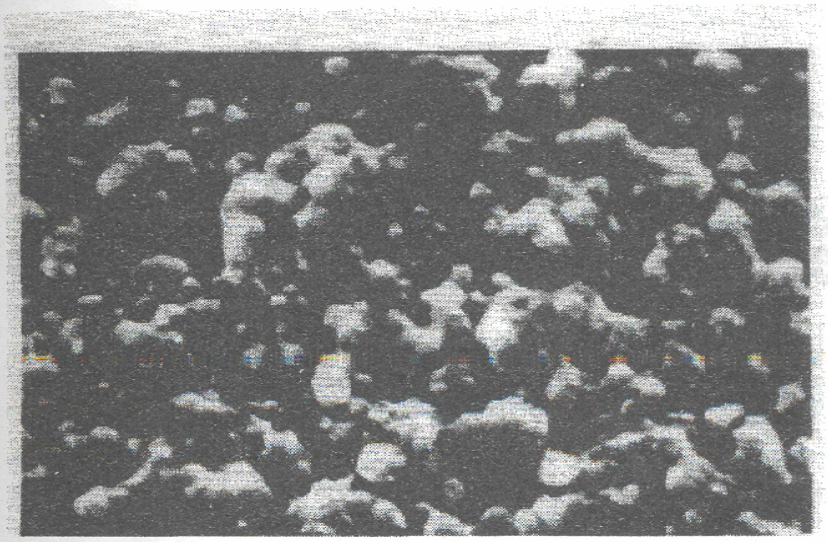
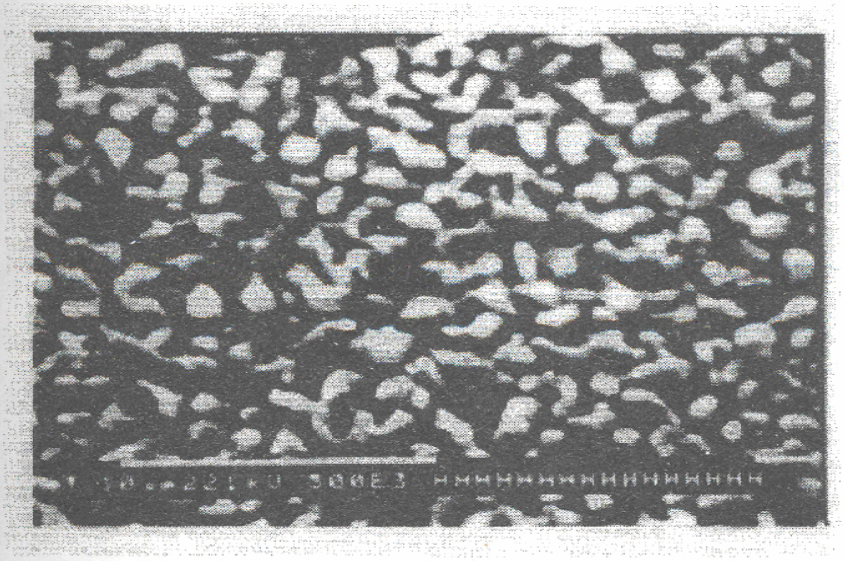


Figure 3. XRD spectrums of the samples prepared at film thickness ratios, Sn:S equivalents to (a) 1:1, (b) 1:2 and (c) 1:3. Annealing condition was 380 °C for three hours.



(a) Sn : S = 1 : 1



(b) Sn : S = 1 : 2

Figure 4. SEM micrographs of the samples prepared at diffrent thickness ratio

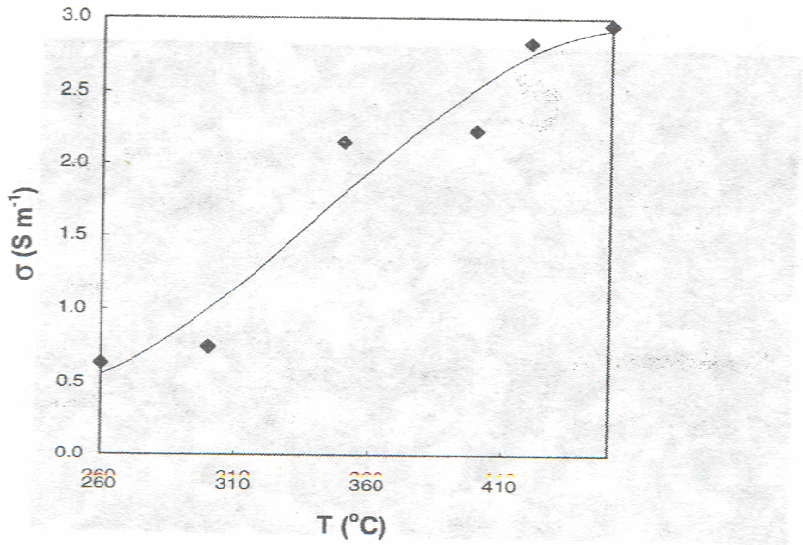


Figure 5. Electrical conductivity versus annealing temperature for SnS thin films (Sn:S=1:1)