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EFFECTS OF ANNEALING ON THE COMPOSITION AND PROPERTIES OF SnS THIN FILMS

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The effects of annealing in air, of chemically deposited thin films of SnS on glass plates are described. Short time annealing of the films at 280^{o} results in change of type of conductivity and increased conductivity. Long time annealing at the same temperature causes a change in the chemical composition and further increase of conductivity. Annealing of the films at 400^{o} leads to formation of SnO_2.

1. Introduction

SnS is one of several binary sulphides of tin, all of which are semiconductors. Thin films of SnS could be of practical interest for photovoltaic cells.

In an earlier work /1/, the effects of annealing have been studied on single crystals of SnS and it has been reported that no change in the composition occured in the temperature range between 230-500^{o}. In this work, the effects of annealing on the composition and electrochemical properties of chemically deposited SnS films were studied at 280^{o} and at 400^{o} in air. The films were deposited on glass plates, by successive immersions in aqueous solution. The technique has been described elsewhere /2/.

2. Experimental work and results

The x-ray diffraction spectrum of as deposited film is shown on Fig.1a. Such films are semiconductors of p-type and exhibit photoconductivity. After 30 minutes of annealing at 280^{o} no detectable change in composition is observed on the x-ray diffraction spectrum of such annealed film. However, the type of conductivity changes from p- to n and the conductivity increases for one order of magnitude. Such films no longer exhibit photoconductivity.

Atfer 6 h of annealing at 280°, a detectable chemical change takes place. Part of SnS disproportionates to SnS_2 (Fig.1b). The absence of the characteristic reflections of SnS_2, other than at d=5,90 Å reveals that during annealing prefered orientation of the crystals along the c-axis takes place. The conductivity of such films increases for one order of magnitude, remaining of n-type.

Further annealing at 280° slowly increases the SnS_2/SnS ratio, as well as the conductivity. On Fig. 1c, the x-ray diffraction spectrum of a 24 hours annealed film is shown. On such annealed films, the c-axis oriented crystals of SnS_2 are predominant over the small remains of SnS. The n-type conductivity of these films is four orders of magnitude higher in comparisson to the p-type conductivity of the corresponding non-annealed films.

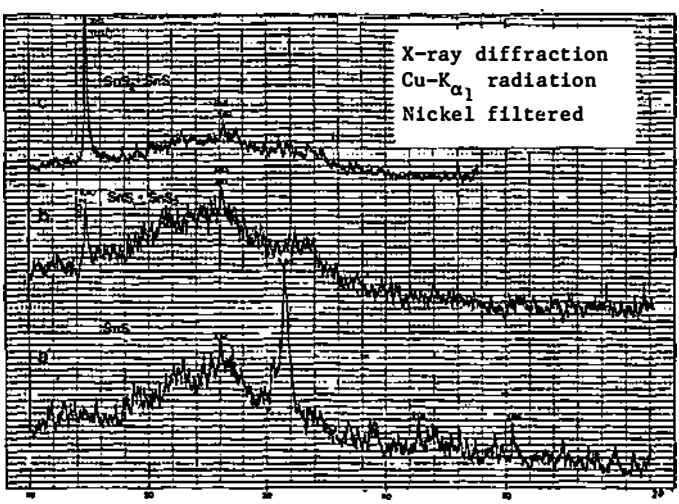

Fig. 1. X-ray diffraction spectra of SnS/SnS_2 thin films.
a) SnS as deposited; b) annealed for 6 h;
c) annealed for 24 h.

The temperature dependance of the resistivity for both the annealed and non-annealed films is shown in Fig. 2. The optical absorption spectra of non-annealed and annealed films are shown in Fig. 3. One can notice the obvious shift of the absorption edges towards lower wavelengths, during annealing.

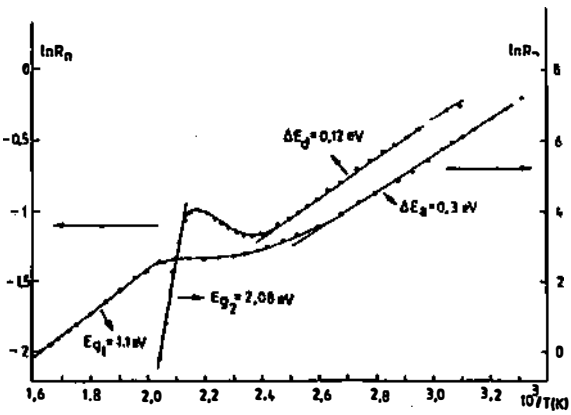

Fig. 2. The temperature dependance of the resistivity for SnS and SnS_2 films. R_p - resistance of p-type SnS; R_n - resistance of n-type SnS_2.

This is in accordance with the chemical change which occurs during annealing, since the optical band gap of SnS_2 (2.08 eV) is higher than that of SnS (1.1 eV).

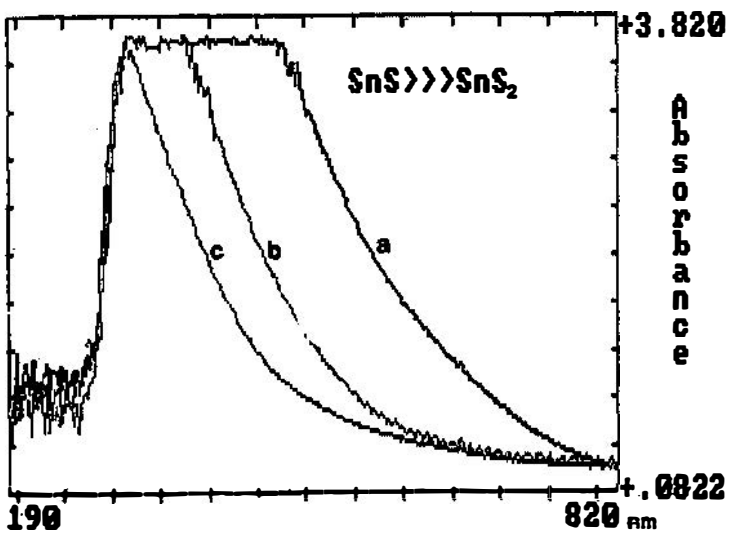

Fig. 3. Optical absorption spectra of non-annealed and annealed films.
a) Non-annealed SnS film; b) Annealed SnS film, for 6h at 280°;
c) Annealed SnS film, for 24h at 280°.

Annealing of the films at 400° causes a somewhat different chemical change, as shown in Fig. 4. Long time annealing of SnS thin films at this temperature leads to formation of

SnO_2. The conductivity of so annealed films was found to be lower than the one reported for SnO_2 obtained by spray pyrolysis /3/.

Fig. 4. X-ray diffraction spectra of films annealed at 400°.
a) SnS film, as deposited
b) Annealed for 6 h at 400°
c) Annealed for 10 h at 400°.

3. Conclusion

The results of this work show that annealing of thin SnS films in air, at 280°, causes changes in both, electrophysical properties and chemical composition of the films. The conductivity increases and the type of conductivity changes from p to n. A controlled transition of SnS into SnS_2 is possible. In this way, the electrophysical properties of the films can be adjusted as needed.

REFERENCES

1. W. Albers, C. Haas, H.J. Vink and J.D. Wasscher, J.Appl.Phys.Suppl., Vol. 32, No. 10 (1961) 2220.
2. M. Ristov, Gj. Sinadinovski, I. Grozdanov and M. Mitreski, Thin Solid Films, 172 (1989), in press.
3. G. Mavrodiev, M. Gajdardziska, N. Novkovski, Thin Solid Films, 113 (1984) 93.