Electrical conductivity measurements in evaporated tin sulphide thin films

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Tin sulphide (SnS) has been evaporated on to substrates maintained at fixed temperatures in the range 50–300°C. X-ray diffraction measurements have shown that the films deposited at the lower substrate temperatures are non-stoichiometric, containing higher sulphides of tin, but that those deposited at 300°C consist essentially only of SnS. Film conductivity increased in the range $0.5–2.0\,\mathrm{S\,m^{-1}}$ as the substrate temperature during deposition increased from 50°C to 250°C, this effect being attributed to the changing film composition. Films deposited at 50°C and 150°C showed thermally activated conductivity at temperatures above 220–250 K, with activation energies E_a of $0.12\,\mathrm{eV}$ and $0.14\,\mathrm{eV}$, respectively. At lower temperatures both conductivity and activation energy were considerably lower, consistent with hopping via localized states. The conductivity is modified after prolonged cooling to 160 K, although the mechanism of this process is not understood.

1. Introduction

Thin film studies of IV–VI tin compounds have previously focused on tin oxide (SnO_2) (Muranaka *et al.* 1981, Manifacier 1982, Deraman 1987), which is transparent and highly conductive and thus useful in the fabrication of optoelectronic devices. Few studies have been performed on the various sulphides of tin, although SnS has potential uses in solar cell fabrication, since its optical bandgap of $1.08\,\mathrm{eV}$ is similar to that of silicon (Ristov *et al.* 1989, Albers *et al.* 1961). Among the investigations that have been performed to date, the majority of workers have developed chemical deposition methods (Nair and Nair 1991, Grozdanov *et al.* 1989, Engelken *et al.* 1987) with the exception of Goswami and Mitra (1975) who used evaporation. The main properties investigated include the effects of annealing on film composition (Grozdanov *et al.* 1989) and the basic optical properties (Elkorashy 1990).

This work describes some initial results of van der Pauw conductivity measurements in evaporated tin sulphide films and their correlation with the structural properties (Deraman *et al.* 1992).

2. Experimental method

Tin sulphide films were prepared from granules (purity 6N) supplied by High Purity Chemetals (Japan). The material was thermally evaporated on to previously cleaned glass substrates at a pressure of less than $7 \times 10^{-4}\,\mathrm{Pa}$ and at a deposition rate of $0.02\,\mathrm{nm\,s^{-1}}$. During the deposition, substrate temperatures were maintained

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at a stable value in the range 50–250°C and film thickness was carefully monitored using a conventional quartz crystal monitor. After deposition the thickness was confirmed using a Planer Surfometer stylus instrument, with all films in the range 330–420 nm. Some of the films deposited at substrate temperatures of 100°C, 200°C and 300°C were studied using a Philips PW 3710 X-ray diffractometer.

Electrical conductivity was measured using the van der Pauw technique and deduced from the slope of current–voltage curves and the thickness of the planar samples. The samples were circular, of diameter 10 mm, and were contacted by four symmetrically-placed evaporated aluminium electrodes of thickness 100 nm. The measurements were performed in a vacuum cryostat at a pressure of approximately 5×10^{-3} Pa at temperatures in the range 160–300 K, which were measured using a Cole-Parmer digital thermometer. A regulated DC constant-current power supply was used in conjunction with a Keithley 617 electrometer for the electrical measurements. Conductivity measurements were also performed on some samples after prolonged thermal treatment at a reduced temperature of 160 K.

3. Results and discussion

Figure 1 shows X-ray diffractometer traces for films deposited at different substrate temperatures. For the film deposited at 100°C there are major peaks at $2\theta = 14\cdot4°$ and $17\cdot3°$, corresponding to interplanar spacings $d_{hkl} = 0\cdot61$ nm and $0\cdot51$ nm, respectively. A further minor peak is also visible at $2\theta = 32\cdot5°$ ($d_{hkl} = 0\cdot28$ nm). The major peaks are both broad, with the first extending from approximately 13–15° and the second from 15–18°.

Within these ranges the ASTM data file contains no reflections from the compound SnS. However, strong reflections are expected from the compounds Sn_2S_3 at 14·8°, SnS_2 at 15·03° and 16·23°, and Sn_3S_4 at 16·09°; elemental S has a reflection at 19·6°. We tentatively suggest that the first peak is composed of reflections characteristic of Sn_2S_3 and SnS_2, while the second derives from SnS_2 and Sn_3S_4 (and possibly S). The minor peak may be identified with the (040) reflection of SnS.

For the film deposited at 200°C the (040) SnS peak becomes significantly more intense, with a second (080) SnS peak appearing at $2\theta = 67\cdot4°$ ($d_{hkl} = 0\cdot14$ nm). For the film deposited at 300°C the intensities of the first two peaks are drastically reduced, while the (040) SnS peak becomes even more significant.

Thus, films deposited at 100°C consist mainly of SnS_2, Sn_2S_3 and Sn_3S_4, while at 300°C the composition is almost entirely SnS, preferentially oriented in the [040] direction. It may also be seen from Fig. 1 that the peaks (particularly the SnS (040) peak) become sharper with increasing temperature, indicating a tendency towards better crystalline perfection with increasing mean grain size.

In Fig. 2 the dependence of conductivity σ at room temperature is shown as a function of the substrate temperature T_s during deposition for a typical set of samples. It is clear that, in general, σ increases with T_s over the temperature range studied, with the most rapid increases occurring over the T_s ranges of 50–100°C and 200–250°C. This variation is thought to be due to structural and compositional effects, as the composition changes from primarily higher sulphides of tin to SnS with increasing T_s. Higher conductivity is also expected to be related to the better crystallinity of the films as discussed above and elsewhere (Deraman et al. 1992) for our films and also for SnS_2 films (George and Joseph 1983).

In Fig. 3 the dependence of conductivity on inverse temperature is shown. Curves A and B relate to films deposited with T_s values of 50°C and 150°C, respectively. In the higher temperature range both of these curves show a linear dependence of $\log \sigma$ on $1/T$ and thus the behaviour may be described in terms of a thermally-activated process according to the expression

$$\sigma = \sigma_0 \exp\left(-\frac{E_a}{kT}\right) \tag{1}$$

where σ_0 is a pre-exponential factor and E_a is an activation energy. Below a particular temperature the thermal activation appears to be less well defined with considerable curvature in the plots. For $T_s = 50°C$ this transition temperature is approximately 250 K, while for $T_s = 150°C$ it is approximately 220 K. Similar transitional behaviour has been observed in SnS_2 by Kawano *et al.* (1989). Activation energies in the higher temperature regions were 0·12 eV ($T_s = 50°C$) and
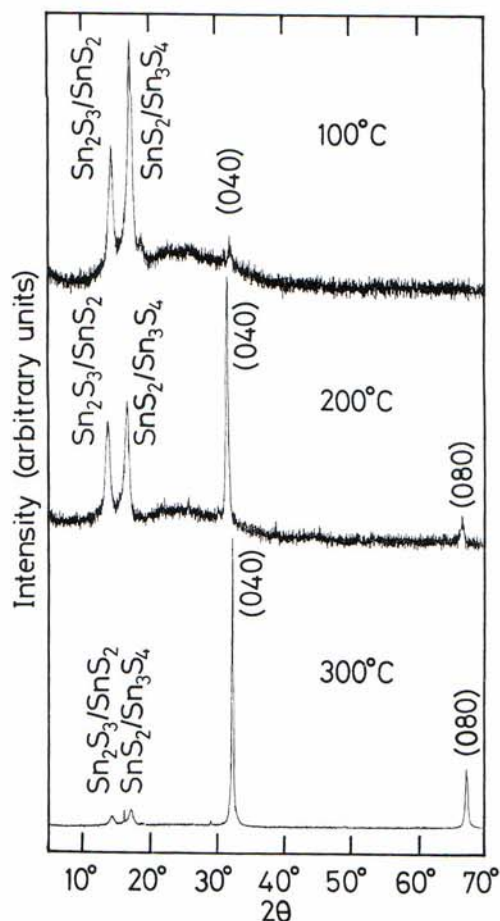

Figure 1. X-ray diffractometer traces obtained for films deposited at different substrate temperatures, showing the emergence of stoichiometric SnS and the disappearance of higher sulphides of tin with increasing temperature.

0·14 eV ($T_s = 150°C$). These values are somewhat lower than the values of 0·3 eV (Ristov *et al.* 1989) and 0·44 eV (Nair and Nair 1991) measured previously for chemically deposited films, but nevertheless indicate a free band conductivity originating from levels within the bandgap. The origin of such levels remains somewhat speculative, but is most probably related to the existence of the non-stoichiometric components Sn_2S_3, SnS_2 and Sn_3S_4, particularly in the films deposited at the lower temperature. Ristov *et al.* (1989) have suggested that E_a corresponds to acceptor levels created from Sn^{2+} vacancies during film deposition.

At low temperatures the slopes are less and thus the corresponding activation energies are also lower. For example, values of E_a calculated from the slopes of the curves at the lowest temperatures are 0·026 eV ($T_s = 50°C$) and 0·049 eV ($T_s = 150°C$). It would thus appear that below the transition temperature free band conduction is replaced by a different mechanism. It is well known that hopping between localized levels may occur at low temperatures, although the activation energies associated with this process are usually even less than those quoted above. We suggest that the behaviour observed in our lower temperature range represents the effects of a transitional region between free band and hopping conductivity, and that further reductions in temperature might allow the unequivocable observation of hopping behaviour as described by Gould and Ismail (1992) for CdTe films.

Finally curve C in Fig. 3 shows measurements on the same sample as in curve B, but after thermal treatment at a reduced temperature of 160 K. There is a reduction in overall conductivity and in the activation energies, with a high temperature E_a value of 0·09 eV and a low temperature value of 0·03 eV. The effects of cooling are similar in this respect to those of annealing, after which a value of 0·1 eV has been
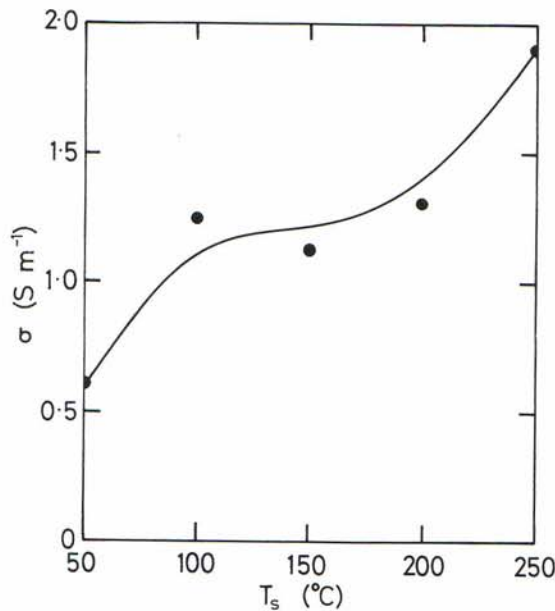

Figure 2. Dependence of room temperature film conductivity on substrate temperature during deposition.
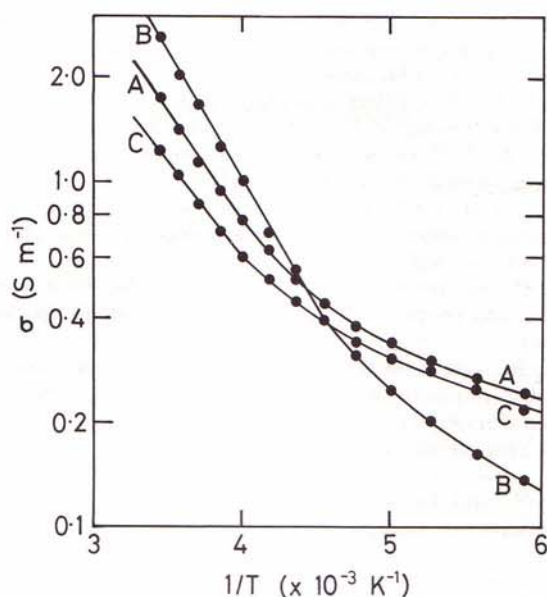
Figure 3. Dependence of film conductivity on inverse temperature for films deposited at 50°C (curve A) and 150°C (curve B), and for the latter film after prolonged cooling at 160 K (curve C).

reported (Ristov *et al.* 1989). At present this effect is not understood, and further studies are still in progress which will be reported elsewhere.

4. Summary and conclusions

X-ray diffraction measurements have shown that evaporated films prepared from SnS at a substrate temperature T_s of 300°C are primarily SnS. However, those prepared at lower temperatures have significant proportions of Sn_2S_3, SnS_2 and Sn_3S_4. Film conductivity increased from approximately $0.5\,S\,m^{-1}$ to $2\,S\,m^{-1}$ when the value of T_s increased from 50°C to 250°C. Non-stoichiometric films deposited at lower temperatures showed free band conduction at temperatures above about 220 K, with hopping suggested at lower temperatures. Prolonged cooling of samples tended to decrease both the overall conductivity and the activation energies. Further work is required into the effects of low temperature cooling and on conduction processes at low temperatures.

REFERENCES

ALBERS, W., HAAS, C., VINK, H. J., and WASSCHER, J. D., 1961, Investigations on SnS. *Journal of Applied Physics*, **32**, 2220–2225.
DERAMAN, K., 1987, Structural, optical and electrical properties of SnO₂ films. M.Sc. thesis, National University of Malaysia.
DERAMAN, K., ISMAIL, B., SAKRANI, S., and GOULD, R. D., 1992, Structural and optical properties of evaporated tin sulfide films. *Annual Seminar on Solid-State Science and Technology, Malaysia*.
ELKORASHY, A. M., 1990, Optical constants of tin sulphide single crystals measured by the interference method. *Physica Status Solidi (b)*, **159**, 903–915.

ENGELKEN, R. D., MCCLOUD, H. E., LEE, C., SLAYTON, M., and GHOREISHI, H., 1987, Low temperature chemical precipitation and vapor deposition of Sn_xS thin films. *Journal of the Electrochemical Society*, **134**, 2696–2707.

GEORGE, J., and JOSEPH, K. S., 1983, Effect of heating on the electrical and optical properties of tin disulphide films. *Journal of Physics D: Applied Physics*, **16**, 33–38.

GOSWAMI, A., and MITRA, A., 1975, Optical properties of vacuum-deposited SnS films. *Indian Journal of Pure and Applied Physics*, **13**, 508–511.

GOULD, R. D., and ISMAIL, B. B., 1992, Observations of low temperature hopping conduction in evaporated cadmium telluride thin films using current-temperature measurements. *Physica Status Solidi (a)*, **134**, K65–K68.

GROZDANOV, I., RISTOV, M., SINADINOVSKI, GJ., and MITRESKI, M., 1989, Effects of annealing on the composition and properties of SnS thin films. *Fizika* (Yugoslavia), **21** (supplement 1), 320–323.

KAWANO, K., NAKATA, R., and SUMITA, M., 1989, Effects of substrate temperature on absorption edge and photocurrent in evaporated amorphous SnS_2 films. *Journal of Physics D: Applied Physics*, **22**, 136–141.

MANIFACIER, J. C., 1982, Thin metallic oxides as transparent conductors. *Thin Solid Films*, **90**, 297–308.

MURANAKA, S., BANDO, Y., and TAKADA, T., 1981, Preparation by reactive deposition and some physical properties of amorphous tin oxide films and crystalline SnO_2 films. *Thin Solid Films*, **86**, 11–19.

NAIR, P. K., and NAIR, M. T. S., 1991, Chemically deposited $SnS-Cu_xS$ thin films with high solar absorptance: new approach to all-glass tubular solar collectors. *Journal of Physics D: Applied Physics*, **24**, 83–87.

RISTOV, M., SINADINOVSKI, GJ., GROZDANOV, I., and MITRESKI, M., 1989, Chemical deposition of tin (II) sulphide thin films. *Thin Solid Films*, **173**, 53–58.