

S.p.33. PALSON, T.I.—Investigations on the Preparation and Properties of Reactivity Evaporated Lead Sulphide and Tin Telluride Thin Films—1987—Dr. Joy George.

IV-VI compounds such as sulphides, selenides and tellurides of lead and tin and their alloys have attracted much attention for a long time. Suitably prepared polycrystalline films of lead salts have been used as photoconductive detectors in the near infrared. More recently solid solutions of SnTe in PbTe, and SnSe in PbSe have been used to construct photoconductive and photovoltaic detectors for longer wavelengths. The construction of p-n junction injection lasers of lead salts, and of solid solutions with their tin analogs has been an important technological development.

The work reported in this thesis is the preparation and the structural, electrical and optical properties of reactivity evaporated lead sulphide and tin telluride thin films. The three temperature method had been used for the preparation of these semi conductor thin films. In this preparation technique constituent elements are evaporated from separate sources with the substrate kept at a particular temperature. When one of the constituent element is a gas near room temperature, the method is often called reactive evaporation. It has been found for many materials that a stoichiometric interval exists with a limited range of flux and

substrate temperature. Usually this technique is used for the preparation of thin films of high melting point compounds or of materials which decompose during evaporation. Tin telluride and lead sulphide are neither high melting point materials nor do they decompose on melting. But even then reactive evaporation offers the possibility of changing the ratios of the flux of the constituent elements within a wide range and studying its effect on the properties of the films.

A variety of physical and chemical deposition techniques have been developed for the deposition of thin films of lead sulphide. Nobody has yet reported the preparation of PbS thin films by the reactive evaporation technique. Stoichiometric as well as sulphur rich films can be prepared by this technique. To get stoichiometric films the sulphur source was baffled, so that the sulphur vapour beam did not strike the substrate as such. The number of sulphur molecules striking the substrate surface per unit area in unit time in this case will be that due to the partial pressure of the sulphur vapour in the chamber. In the case of sulphur rich films, the sulphur source was not baffled and more sulphur molecules will strike the substrate surface.

It has been found that the following parameters give good stoichiometric films of PbS:

Pb atom flux : 1.3×10^{15} to 2.6×10^{15} atoms $\text{cm}^{-2}\text{S}^{-1}$

S_2 molecule flux : 2.2×10^{16} to 1.1×10^{17} molecules $\text{cm}^{-2}\text{S}^{-1}$

Substrate temperature : 300 - 650 K.

Unless otherwise stated lead sulphide films refer hereafter to stoichiometric lead sulphid films. X-ray diffraction studies of the PbS films indicated that films prepared below the substrate temperature of 325K were amorphous in nature. As the substrate temperature was increased polycrystalline PbS films were obtained. Further increase in the substrate temperature gave a preferred orientation to the grains with (100) planes parallel to the substrate surface.

Electrical measurements were made and d.c. conductivity, Hall mobility, carrier concentration and thermoelectric power were studied in the temperature range 100 - 400 K on polycrystalline films prepared at different substrate temperatures. Hall effect measurements showed that the films obtained were p-type. A typical PbS film prepared at 400 K had a carrier concentration of $6 \times 10^{17} \text{cm}^{-3}$ and Hall mobility of $30 \text{cm}^2 \text{V}^{-1}\text{S}^{-1}$ at 300 K. Thermoelectric power was high as 500 V/K at 300 K. This is around 1.7 times the single crystal value. Films prepared at substrate temperature 600 K gave a maximum mobility of $125 \text{cm}^2\text{V}^{-1}\text{S}^{-1}$ at 300 K.

Amorphous films of PbS had been characterised optically and electrically. Optical characterisation showed that amorphous PbS films had an optical band gap of 1.6 eV and a refractive index of 2.5. Crystalline PbS is having a band gap of 0.39 eV and refractive index of 4.5. This large deviation was explained in terms of the difference in coordination of the amorphous and crystalline environments. Sulphur rich amorphous PbS films had a still higher optical band gap of 1.8 eV and show no optical absorption before the onset of band to band transitions, whereas stoichiometric amorphous PbS films show an absorption which was decreasing with the photon energy before the onset of band to band transition.

Electrical measurements of amorphous PbS films showed a room temperature resistivity of 1.7×10^4 ohm cm. The films crystallised when heated beyond 330 K and the resistivity of the films decreased by three orders of magnitude. sulphur rich amorphous films were more resistive (4×10^6 ohm cm) and these films

crystallised at around 330 K and resistivity decreased by five orders of magnitude.

SnTe films were usually prepared from p-type SnTe ingots prepared by fusing stoichiometric proportions of Sn and Te. In the work reported here, SnTe thin films were prepared for the first time by the three temperature method to avoid incongruent evaporation from a single source and the consequent lack of stoichiometry.

It had been found that good stoichiometric films of SnTe were obtained with the following parameters:

tin flux = 4.1×10^{14} to 2.4×10^{15} atoms $\text{cm}^{-2}\text{S}^{-1}$

tellurium flux = 7.4×10^{15} to 2.2×10^{16} atoms $\text{cm}^{-2}\text{S}^{-1}$ substrate temperature = 568 - 598 K.

The structural characterisation of these films were done by x-ray diffraction technique. These films had grains oriented such that (111) planes were parallel to the substrate surface. Optical micrographs of the films before and after annealing showed that annealing at the preparation temperature had no effect on the grain size. The temperature dependences of the electrical conductivity, the Hall coefficient and Hall mobility of these films were studied in the temperature range 100 - 450 K. As prepared thin films of SnTe, had got the following electrical characteristics at room temperature:

Conductivity 6.5×10^3 (ohm cm)⁻¹

Hall coefficient 1.55×10^{-2} cm^{-3} coulomb⁻¹

Hall mobility $100 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$

The effect of annealing on the electrical properties had also been investigated. The carrier concentration and conductivity decreased after annealing whereas the Hall mobility increased.

Due to the low chemical diffusion constant of tin, which results in the freezing of the equilibrium tin vacancy concentration, SnTe is always a p-type extrinsic semiconductor. Because of the heavy carrier concentration and the consequent repulsion between the carriers the mobility of charge carriers in SnTe films are low. The mobility can be increased by reducing the carrier concentration. This can be achieved by filling the tin vacancies by an appropriate cation which is having a high mobility in the SnTe matrix. It has been possible to obtain mobilities better than $1000 \text{ cm}^2\text{V}^{-1}\text{S}^{-1}$ at room temperature by doping SnTe films with germanium.

A setup for testing IR detectors had been fabricated and is also reported in this thesis. A cell which could be evacuated and cooled to LN₂ temperature with provisions for detector mounting and illumination had been fabricated as part of this setup. A light chopper also was designed and fabricated in house, for this purpose. This chopper can produce light pulses from 10 Hz to 2000 Hz using two chopping blades and had an accuracy better than 0.1% and negligible temperature drift.