

Characterization of In_2S_3 films obtained by slurry painting

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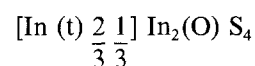
Layers of In_2S_3 were prepared by a slurry painting method from powder of the respective semiconductor, followed by annealing in nitrogen and hydrogen. The layers were characterized by X-ray powder diffraction, surface analysis, optical properties and for their photoelectrochemical behaviour. Incorporation of the flux model InCl_3 into the layers produces recrystallization and growth of large grains and it can also act as a dopant for the semiconductor.

1. Introduction

Coating and sintering is a convenient and economical method for mass production of materials in the form of thin films on substrates [1]. The method consists in the dispersion of a powder of the chosen material in liquid to obtain a slurry. The slurry is painted on to a conducting substrate and dried. Subsequently it is annealed at higher temperature and after cooling a well-adhering polycrystalline layer can be obtained. In the case of In_2S_3 the uniformity of the sintered films depends on the particle size and volume per cent of In_2S_3 powder in the slurry, as well as the temperature for sintering. The In_2S_3 powder can be mixed with a suitable fluxing material and dispersed in liquid. The fluxing agent has a dual role in the formation of the layers. Primarily, by dissolving the outer layer of the semiconductor grains, and subsequently vaporizing, it binds the grains together and thus imparts structural coherence to the layer. It also promotes recrystallization and growth of large grains. In addition, it can act as a dopant for the semiconductor. This method is versatile and low-cost for preparing semiconductor films. It has been used for preparation of a number of different semiconductor films, in particular those of the II-VI family.

$\beta\text{-In}_2\text{S}_3$ belongs to $\text{A}_2^{\text{II}}\text{B}_3^{\text{VI}}$ compounds which represent an interesting case of solids with a large concentration of vacancies and yet with completely satisfied chemical bonds. The majority of these compounds crystallize to a defect zincblende structure [2]. In_2S_3 is an exception in this family due to the fact that it crystallizes in a spinel-like structure and exists in three crystallographic modifications α , β and γ [3]. The room-temperature phase, $\beta\text{-In}_2\text{S}_3$, stable up to 420°C , crystallizes in a defect spinel lattice. Under certain preparation conditions [4] a high degree of vacancy ordering at tetrahedral cation sites takes place. This ordering leads to a tetragonal [5] super cell containing three spinel blocks along the c -axis. The ordered modification can therefore be interpreted as a quasi-ternary compound consisting of indium, sulphur and

vacancies. The chemical formula can be written as



where the symbols (t), (O) and () represent tetrahedral, octahedral and vacant sites, respectively.

In this paper we report the results of a detailed investigation of uniformity and properties of such sintered films as a function of the amount of fluxing material and sintering temperature.

2. Experimental procedure

Commercial In_2S_3 and anhydrous InCl_3 were used in the present investigation. A number of slurries consisting of In_2S_3 powder with various amounts of InCl_3 were prepared by mixing and dispersing. Distilled water was used for the preparation of films presented in this paper. Each slurry was coated on glass, SnO_2 and stainless steel and dried in air to obtain dried films with thickness of 20 to $50\ \mu\text{m}$. A dried In_2S_3 film was then placed in a nitrogen or hydrogen atmosphere using a tube furnace with quartz tube. The furnace was flushed with nitrogen or hydrogen for 30 min before sintering and a flow of nitrogen or hydrogen was used during sintering.

The crystal structure and texture of sintered film were analysed using an X-ray diffractometer. Surface photographs were taken for each sample before and after sintering with a scanning electron microscope (SEM). Energy dispersive analysis (EDAX) was performed to determine the composition of the sintered films.

Determination of the absorption coefficient was based on the transmittance and reflectance measurements of the films, which were carried out using a Hitachi, 150-20 spectrophotometer.

The electrochemical and photoelectrochemical measurements were carried out in a conventional single-compartment cell with a flat pyrex glass window for illumination of the semiconductor electrode. A saturated calomel electrode (SCE) and a large area

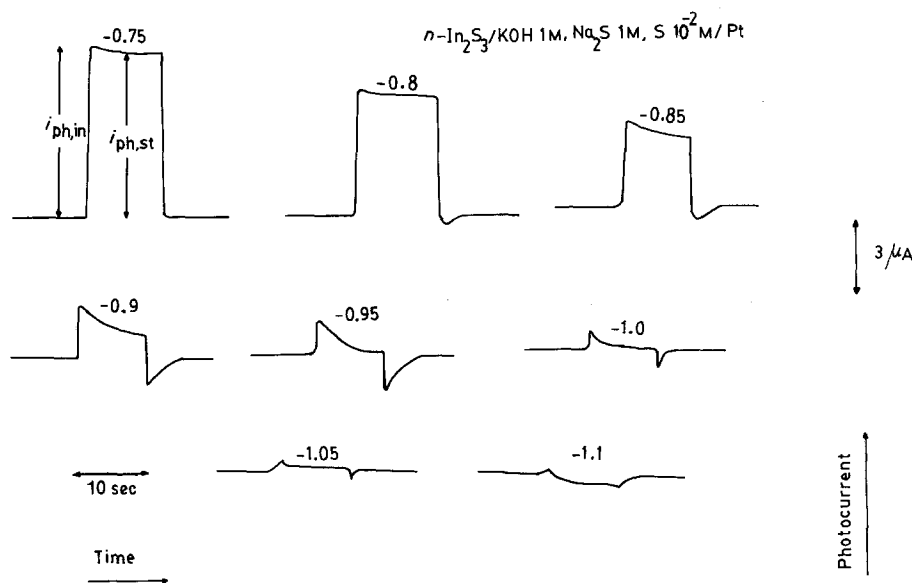


Figure 1 Photocurrent-time transient behaviour of In_2S_3 in a polysulphide couple under polychromatic illumination at different potentials.

platinum gauze electrode were used as reference and counter electrodes, respectively. A 150 W halogen-tungsten lamp served as the light source in polychromatic illumination experiments.

3. Results and discussion

The photocurrent-time transients have been used for determination of the flatband potential of the In_2S_3 films in different electrolytes. The V_{fb} is the potential where the stationary current disappears or changes.

Figs 1 and 2 show the evolution of the photocurrent in solutions containing sulphur/sulphide and sulphite/sulphate when the electrodes were illuminated with polychromatic light. It is possible to observe that an initial photocurrent spike, $i_{ph,in}$ is obtained when the light is switched on, and a few seconds after that, a stationary photocurrent is reached, $i_{ph,st}$. When the illumination is switched off the current returns to the initial level. Fig. 3 shows the plot of the ratio $i_{ph,st}/i_{ph,in}$ against potential. We can observe that at high potentials of polarization, the ratio between the initial and stationary photocurrent values is close to 1, but it

begins to decrease when the polarization potential is changed to cathodic values. This is attributed to the apparition of a cathodic reaction that competes with the process of photo-oxidation of the redox couple. In agreement with Wilson [6] a surface recombination process due to an ineffective separation of the electron-hole pairs at low band bending occurs. In the flatband situation, holes recombine with the electrons before they can be transferred to the redox couple, and $i_{ph,in} = 0$. The V_{fb} values obtained are -1.1 and -0.95 V versus (SCE) in the interfaces In_2S_3 / polysulphide and In_2S_3 /sulphite-sulphate, respectively. Although we found some variation from sample to sample, the values of V_{fb} are within an error of ± 25 mV.

It can be observed that the flatband potential is different according to the redox potential of the couple in the solution. This shift of the V_{fb} can be due to the different strength of adsorption of the S^2 and SO_3^{2-} on the semiconductor surface [7]. Other authors studied V_{fb} in CdS [8] and they observed that SO_3^{2-} ions were mainly physisorbed and S^{2-} ions are largely

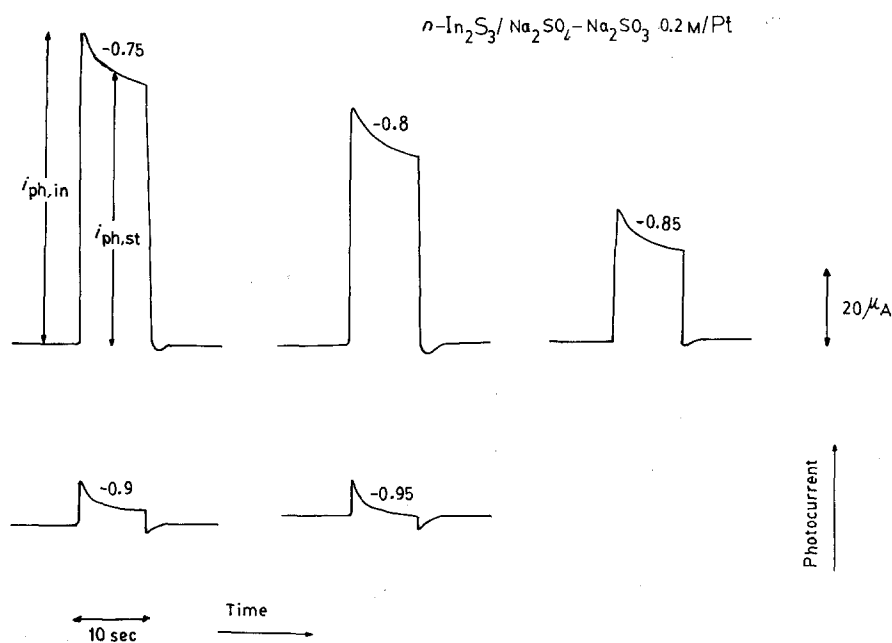


Figure 2 Photocurrent-time transient behaviour of In_2S_3 in a sulphite/sulphate couple under polychromatic illumination at different potentials.

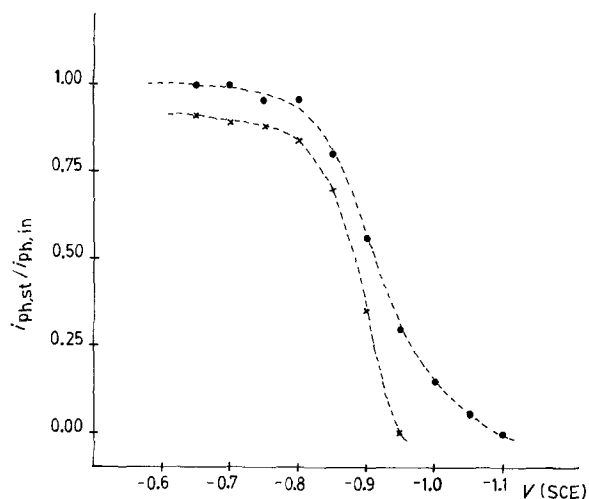


Figure 3 Plot of the ratio $I_{ph,st}/I_{ph,in}$ against potential.

chemisorbed on the surface. This difference can explain our values of V_{fb} in both solutions, because S^{2-} ions in the solution cause a shift in the V_{fb} to more negative values.

Figs 4 and 5 show the behaviour of In_2S_3 semiconductor under AM1 chopped-light illumination. Fig. 4 shows the $I-V$ response obtained when the electrode was prepared without thermal treatment and Fig. 5 corresponds to an electrode sintered at $400^\circ C$. We observe that sintering of the film produces a diminution of the cathodic current in the dark, but does not have any effect on the anodic wave. This decrease can be due to the formation of a protective layer that prevents the corrosion of the semiconductor. This layer is In_2O_3 [9] formed by the treatment.

3.1. Optical properties

The band gap of the semiconductors was calculated from the dependence of the adsorption coefficient on the incident photon wavelength. The experimental points fit quite well to a straight line of α^2 -photon energy, $h\nu$. By extrapolating down to $\alpha^2 = 0$, we obtain the energy gap for each temperature. Fig. 6 shows the temperature dependence of E_g for samples

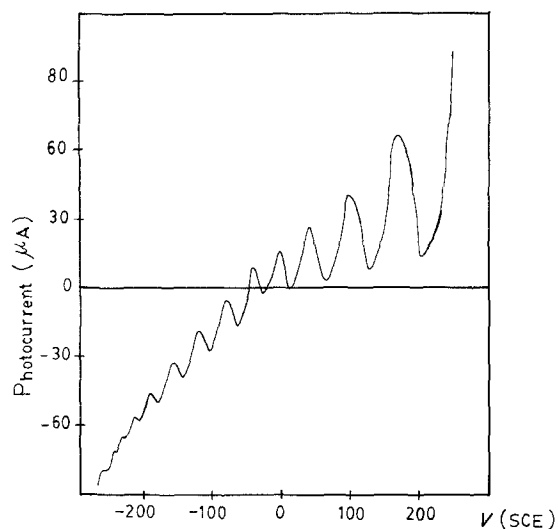


Figure 4 $I-V$ plot under AM1 chopped light illumination. Solution In_2S_3 electrode without treatment.

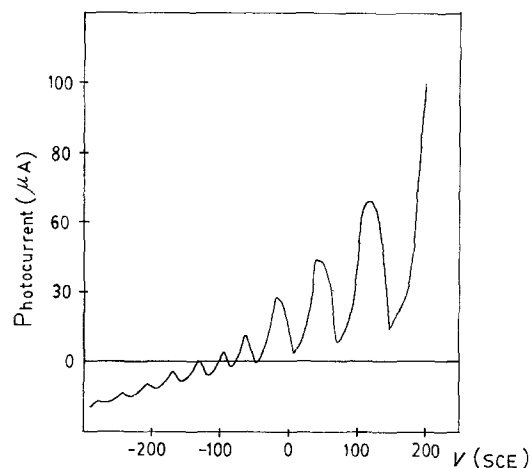


Figure 5 $I-V$ under AM1 chopped light illumination. Solution In_2S_3 electrode after treatment in a nitrogen atmosphere at $400^\circ C$.

not coated with Cl_3In . We can observe that the energy gap decreases slowly as the temperature increases, and then increases from $500^\circ C$. Starting from $600^\circ C$ the energy gap remains constant. This is attributed to the presence of oxygen (> 100 p.p.m.) in the atmosphere which produces the oxidation of In_2S_3 to O_3In_2 . The band gap of O_3In_2 is obtained at temperatures of $600^\circ C$ and above. These results are not obtained in samples sintered with small amounts of oxygen. Fig. 7 shows the variation of the energy gap with the temperature when the sintering atmosphere contains 20 p.p.m. oxygen. We observe that the value of the band gap is constant at all temperatures studied.

The largest decrease in the energy gap is obtained when the coating contains Cl_3In ; samples were obtained with 20% Cl_3In and then annealed. Fig. 8 shows the variation of band gap of these samples. A progressive diminution occurs until $600^\circ C$. It is observed this can be due to Cl_3In , which prevents the rapid evaporation of sulphur when the temperature is high. The Cl_3In fluxing agent can produce greater crystallization and growth of the grains, and on the other hand, can act as a dopant for the semiconductor, thus facilitating the diminution of the energy gap.

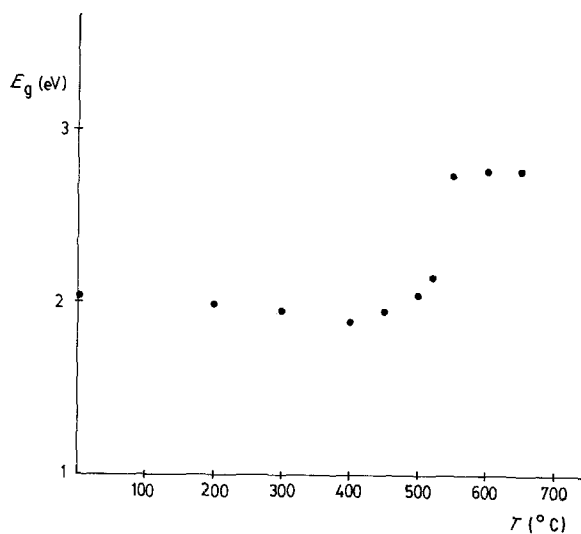


Figure 6 Temperature dependence of the energy gap in In_2S_3 electrode with thermal treatment in a nitrogen atmosphere.

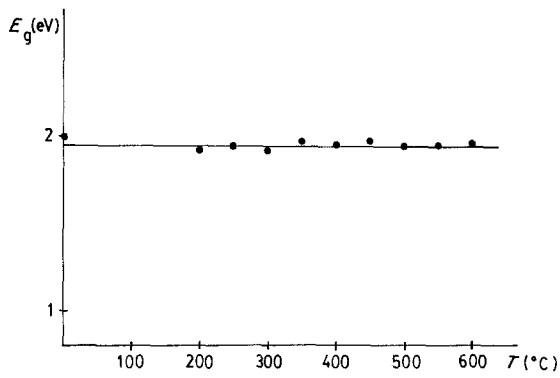


Figure 7 Temperature dependence of the energy gap in In_2S_3 electrode with thermal treatment in a hydrogen atmosphere.

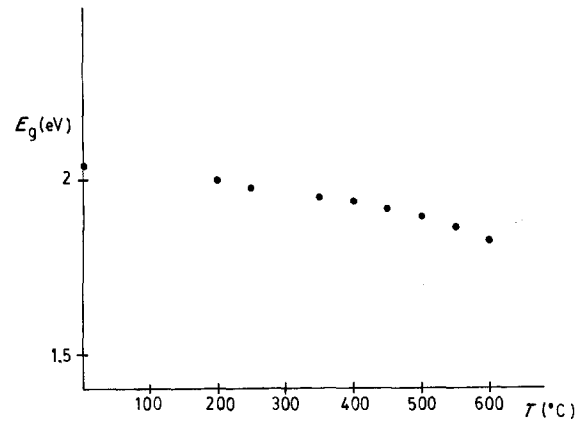


Figure 8 Temperature dependence of the energy gap in In_2S_3 electrode obtained with 20% InCl_3 in the slurry paint and with thermal treatment in a nitrogen atmosphere.

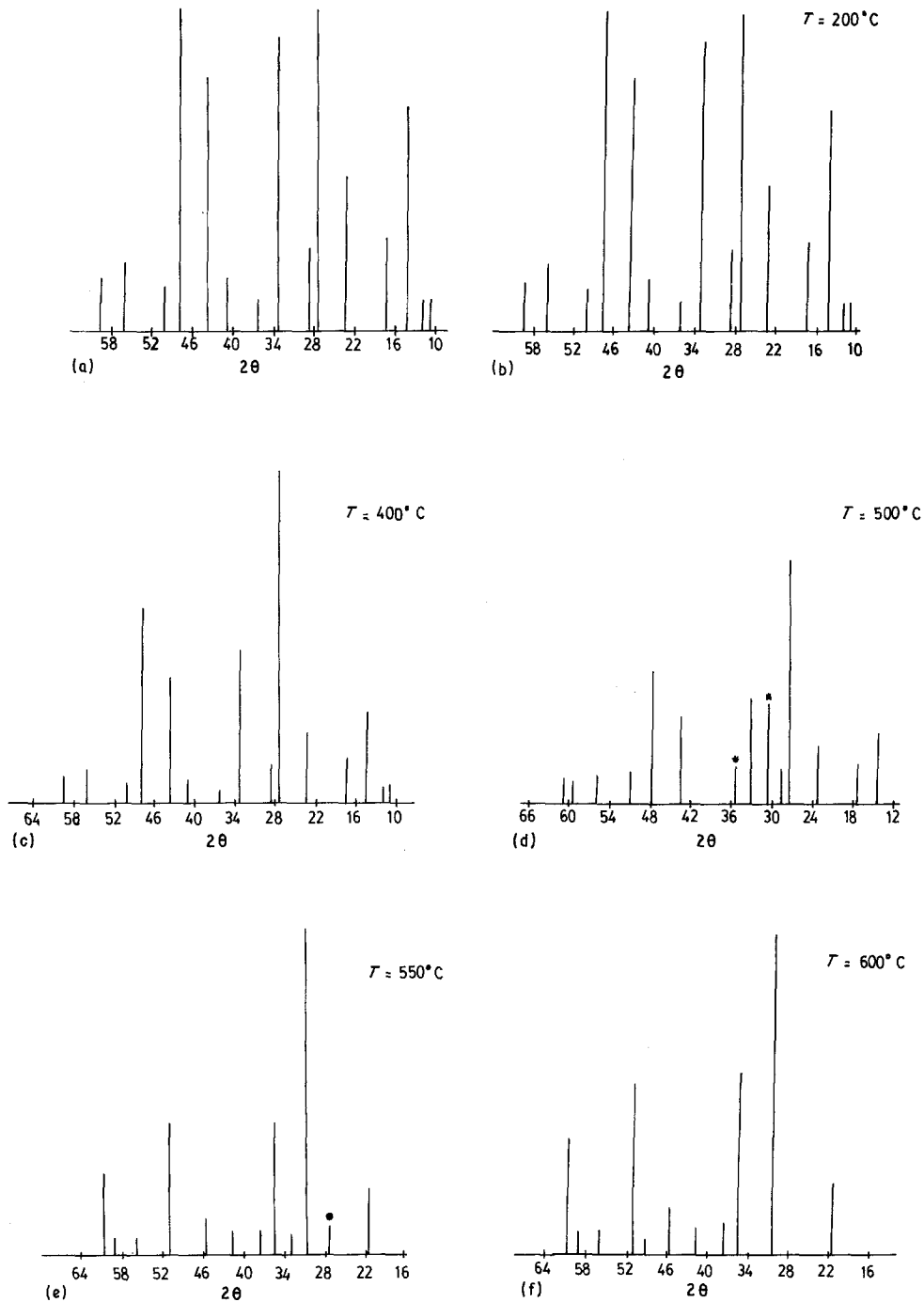


Figure 9 X-ray diffraction patterns for In_2S_3 electrodes obtained without InCl_3 in the slurry paint at different temperatures.

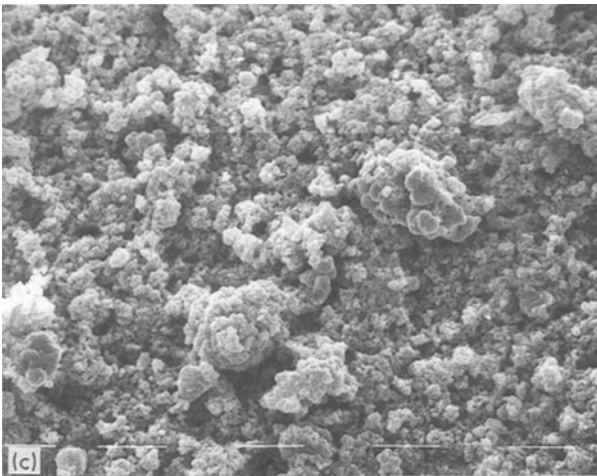
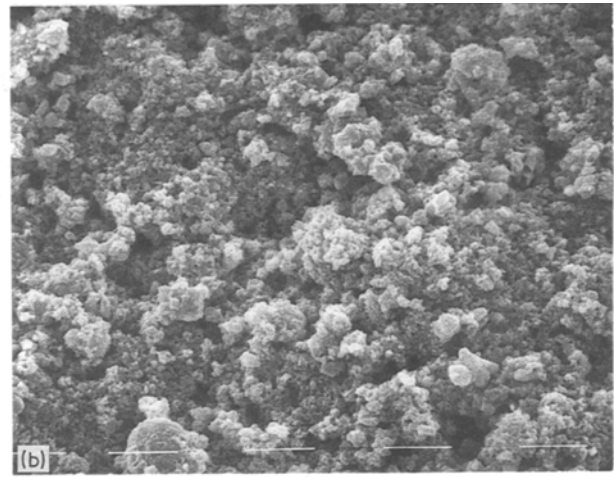
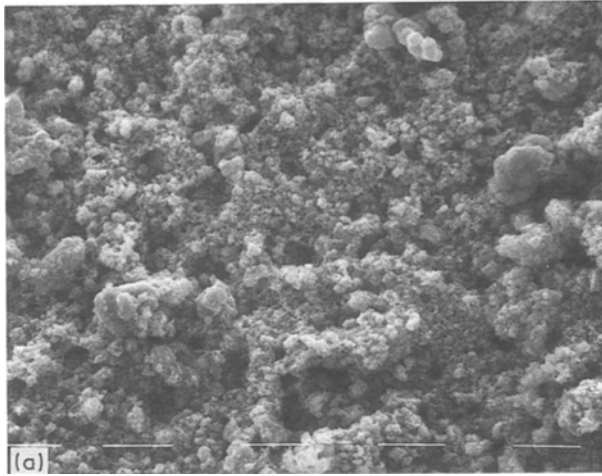


Figure 10 Photographs of In_2S_3 , obtained without InCl_3 in the slurry paint at different temperatures; (a) 200°C, (b) 520°C, (c) 600°C. $\times 875$.

nitrogen atmosphere with 20 p.p.m. oxygen, the diffractograms are not altered, i.e. the intensity of the peaks does not diminish. If the treatment is carried out in a hydrogen atmosphere, the diffractograms show a diminution in the intensity of the peaks corresponding to $\beta\text{-In}_2\text{S}_3$, but this diminution is smaller than in the preceding case. This is due to the reducing character of the hydrogen atmosphere.

The samples prepared with InCl_3 in the coating show a diffractogram without variation. The only difference is that recrystallization is more pronounced when the temperature is increased, using the same treatments.

3.2. Structure

Fig. 9a shows the X-ray diffraction patterns corresponding to $\beta\text{-In}_2\text{S}_3$ without thermal treatment. The diffractogram shows all peaks of this phase. Annealing of the samples in a nitrogen atmosphere with 100 p.p.m. oxygen substantially modifies the diffractograms. Figs 9b, c, d, e and f show that the intensity of all peaks decreases with temperature. At 500°C the peaks with an asterisk correspond to indium oxide. At 550°C only one peak (●) corresponded to the $\beta\text{-In}_2\text{S}_3$ phase. This change is also observed because the colour of the samples changes from intense orange to clear grey. When the thermal treatment is performed in a

3.3. Microstructure

The surface morphology of the samples prepared at different temperatures was investigated by SEM techniques. Fig. 10 shows photographs of the surface of these films. The sintered In_2S_3 films have a dense microstructure. However, the porosity increases and the thickness of the films decreases with temperature. Figs 10a to c are obtained from films treated in a nitrogen atmosphere with 100 p.p.m. O_2 . When the temperature is increased, the grain size also increases, but analysis by EDAX shows that these samples have a considerable diminution in the amount of sulphur.

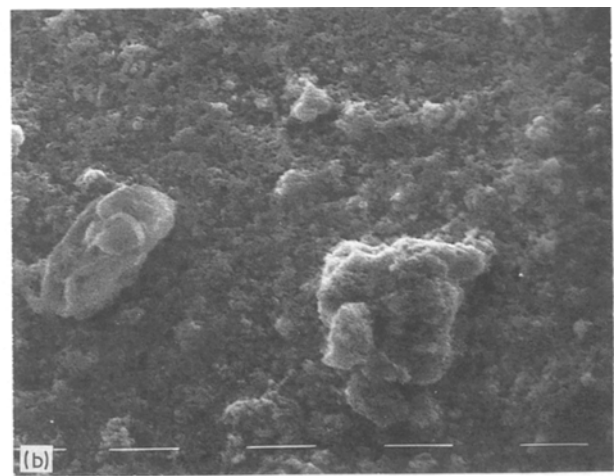
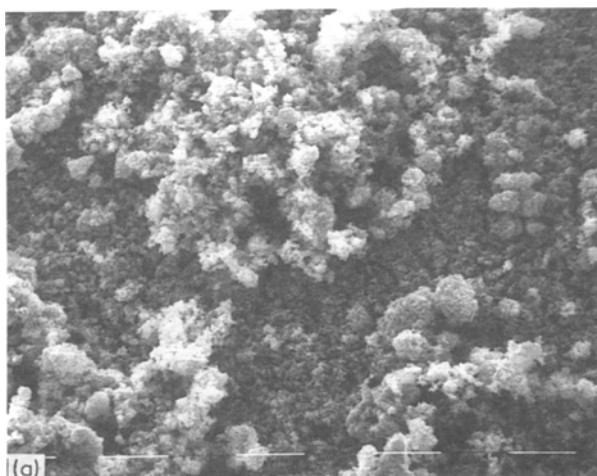


Figure 11 Photographs of In_2S_3 , obtained with InCl_3 in the slurry paint at 350°C; (a) 5% InCl_3 , (b) 20% InCl_3 . $\times 875$.

For example, one sample annealed to 300°C has 62.2% In and 37.8% S while another annealed at 500°C has 82.2% In and 17.8% S. On the other hand, the samples with Cl₃In in the coating do not show variations in the percentages of indium and sulphur with increasing temperature. The microstructure of these films is more compact and the grain size is greater, when Cl₃In is included in the slurry, as can be seen in Figs 11a and b.

4. Conclusions

The production of thin film semiconductors of In₂S₃ by a coating and sintering method is economical and simple. The properties of these films improve substantially when Cl₃In is used in the slurry painting. Cl₃In prevents excessive evaporation of sulphur when the sintering temperature is high.

The films obtained by this method show good photoelectrochemical properties and the values of the flatband potential and energy gap are in agreement with those in the literature for the same films obtained by other methods.

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