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Carrier transport and predominant scattering mode in pyrolytic indium oxide thin film

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Electrical transport properties have been studied of polycrystalline thin films of In_2O_3 and In_2O_3:Sn prepared by a chemical spray technique on a glass substrate. Dominant carrier scattering processes have been discussed critically by studying the Hall mobility and Seebeck coefficient. It has been observed that the Hall mobility in these films is mostly limited either by the optical mode of lattice scattering or by the acoustic mode of scattering, and there is a critical level of the carrier concentration at which one is masked by the other. The position and nature of the Fermi levels were also determined for these degenerate semiconductor samples.

1. Introduction

Transparent conducting coatings like tin-doped indium oxide (In_2O_3:Sn) or ITO are very important for their various applications in optoelectronic device technology. Because of their good spectral selectivity properties these coatings are useful in preparing transparent infrared reflectors [1], multi-layer electrochromic coatings [2] for "smart windows" and many other devices where energy efficiency is concerned. In preparing thin film hetrojunction solar cells these coatings have potential application either as a window material or as an anti-reflection coating material for the device [3].

There are various methods by which these films may be prepared. One of the common processes is the so called pyrosol process, and we have used here a modified spray system [4] to prepare the experimental samples pyrolytically. These transparent conducting films were prepared with a view to using them as transparent conducting electrodes in our laboratory while fabricating heterojunction solar cells [5]. The present paper is a report on the study of Hall measurement, thermopower and carrier scattering characteristic of some of these samples. Obviously the prepared samples were all polycrystalline in structure and were optically very transparent in the visible range of the spectrum.

2. Experimental procedure

Solution of $InCl_3$ of concentration about 0.2–0.4 M in equal volumes of H_2O and C_2H_5OH was taken as the working liquid for preparing undoped In_2O_3 film. For Sn-doped films $SnCl_4$ was added to the working liquid at a different mole percentage of $InCl_3$ to obtain films of different conductivity, Hall mobility and carrier concentration. Spraying was performed at an average rate of 0.8 ml min^{-1} through a pneumatic spray gun using compressed air as the carrier gas. A constant substrate temperature of 400° C was maintained during the film deposition period. The details of the technique may be obtained from our previous paper [4]. All the experimental samples were prepared on glass substrate supplied by the Corning Glass Works (USA). After deposition the substrate with the film was cooled down to room temperature and was kept in a desiccator.

For the measurement of thermopower and Hall mobility samples of different shapes and size are required. Fig. 1 shows the shape of the various samples. At each run two samples were obtained on the same substrate for these measurements. Van der Pauw's method [6] was used to measure the Hall mobility and conductivity and therefore a clover leaf shaped sample B was adequate. On the other hand the integral method [7] was used to measure the Seebeck coefficient so the shape C′AC was appropriate for the samples. Here A is the test material and C and C′ are the reference metal film (lead) deposited on the same substrate by vacuum evaporation of pure metallic lead. The details of the sample preparation and measuring technique may be obtained elsewhere [8].

The thickness of the samples was determined by an interferometric method. The thickness of the test samples was about 0.2 μm and was kept unchanged for the present investigation. Digital multimeters (Hewlett Packard 3465A (USA)) were used for the electrical measurements. The magnetic field for the Hall measurements was provided by an electromagnet (Newport Type A).

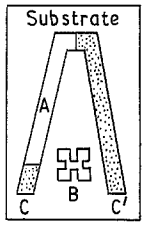

Figure 1 The shape of the experimental sample for the measurement of conductivity, Hall effect and thermopower.

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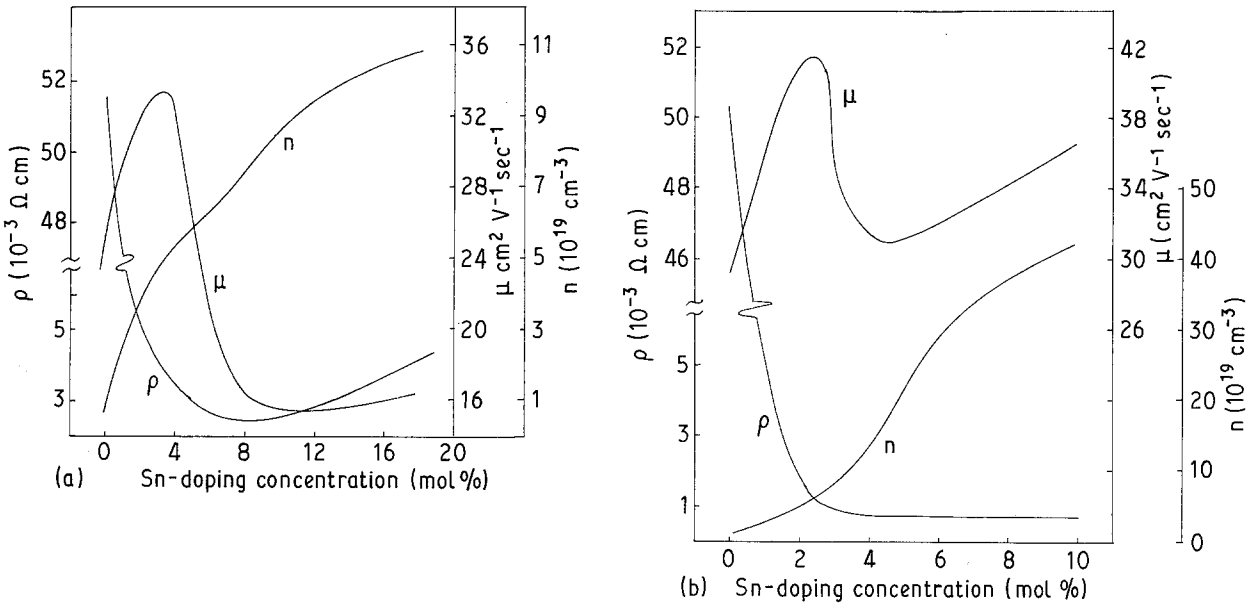

Figure 2 (a) Variation of resistivity ϱ, Hall mobility μ, and carrier concentration n of In_2O_3:Sn film with the Sn-doping concentration when the working solution concentration is 0.2 M in equal volumes of water and alcohol. (b) The same variation when the working solution concentration is 0.4 M.

3. Results and discussion

3.1. Effect of Sn-doping on the Hall mobility

The effect of Sn-doping on the electrical properties of In_2O_3:Sn film is shown by the two sets of typical curves in Figs 2a and 2b for two different concentrations of the working liquid, 0.2 and 0.4 M respectively.

It is observed that the nature of variation of resistivity ϱ, Hall mobility μ and carrier concentration n on the films with the Sn-doping concentrations are very similar in the two cases, and about 2 to 3 mol % of Sn can produce higher Hall mobility. A minimum in these curves is found near ~4.5 mol % of Sn-doping in the case of 0.4 M solution and at about 9 mol % of Sn-doping in the case of 0.2 M solution. It is however clear that films with higher mobility and conductivity can be obtained from 0.4 M solution rather than from 0.2 M solution at similar doping levels. Undoped films always have lower Hall mobility than doped films. The working solution concentration is thus a valuable parameter for In_2O_3:Sn film in controlling the Hall mobility and needs precise optimization if higher mobility is required.

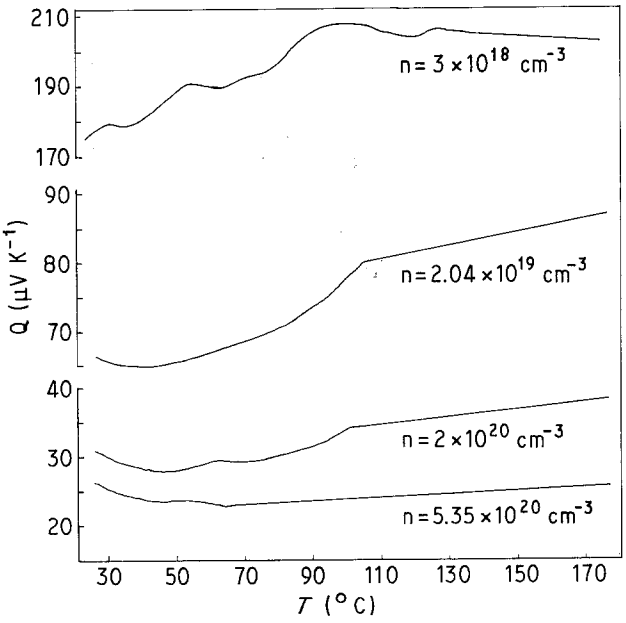

Figure 3 Variation of the thermoelectric power Q with temperature T. The different curves are for samples of different carrier concentrations n as indicated under each curve.

3.2. The thermoelectric power

The thermoelectric power Q of several doped and undoped samples with different carrier concentrations was measured. The measured values are shown in Fig. 3 where Q has been plotted as a function of temperature T for four typical samples of different carrier concentrations. The general pattern of variation is very similar for all the samples. From 30 to ~100° C the TEP increases nonlinearly, but above 100° C it rises very slowly but linearly with temperature. From this figure it is also clear that with the increase of free carrier concentration of the samples the TEP values decrease very rapidly. We have studied samples with carrier concentration ranging from $\sim 10^{18}$ to $\sim 10^{21}$ cm^{-3} and observed that the corresponding TEP values at room temperature run from ~200 to 16 μV K^{-1} in this range.

From this study of Seebeck coefficients the position of Fermi level E_F with respect to the conduction band edge E_c have been determined for the samples following the procedure used by R. W. Wright [9] for degenerate semiconductor. The variation in the position of E_F as a function of carrier concentration n is shown in Fig. 4. It is noticed that the value of E_F gradually increases with the increase of n up to about 5×10^{20} cm^{-3}, and then it decreases a little. At decreasing carrier concentration on the other hand the Fermi levels tend to become almost temperature independent, which is however indicative of the gradual pinning mode of the Fermi levels in this region [8]. The seats of the Fermi levels are found always inside the conduction band and all the

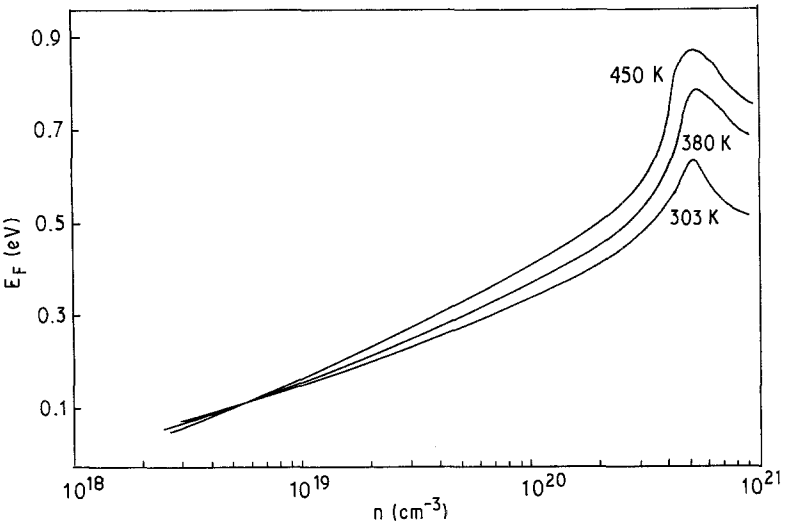

Figure 4 Variation of Fermi energy E_F with the carrier concentration n at three different temperatures.

investigated samples were therefore degenerate at room temperature.

3.3. The carrier scattering process

In all our polycrystalline indium oxide thin film samples the maximum Hall mobility obtained was $\sim 42\,cm^2\,V^{-1}\,sec^{-1}$ for the Sn-doped variety. Clearly this value is very small in comparison with the value of $100\,cm^2\,V^{-1}\,sec^{-1}$ for the single crystal of In_2O_3:Sn samples [10]. In thin film samples however various scattering processes are responsible for the low value of Hall mobility. From the knowledge of the thermoelectric power we may have some valuable information about the dominant scattering process in the sample. For this purpose the various thermopower data can be handled with the help of a well known thermopower theory [11] for degenerate n-type crystalline semiconductor which gives

$$dV/dT = Q = -(\pi^2 k_B/e)\,(k_B T/E_F)\,(\tfrac{1}{2} - \tfrac{1}{3}r) \quad (1)$$

where Q is the measured thermopower of the samples at temperature T and r is the carrier scattering index and is related to the relaxation time τ by $\tau = \tau_0 E^{-r}$. In a very small temperature region T_1 to T where E_F and r may be considered to be sensibly constant, integration of the above equation gives

$$V - V_1 = -(\pi^2 k_B^2/2eE_F)\,(\tfrac{1}{2} - \tfrac{1}{3}r)\,(T^2 - T_1^2)$$

where V_1 is the thermo-e.m.f. corresponding to a reference temperature T_1 and V is the thermo-e.m.f. at any higher temperature T. Therefore we have

$$-(V - V_1)/(T + T_1) = (\pi^2 k_B^2/2eE_F)\,(\tfrac{1}{2} - \tfrac{1}{3}r) \times (T - T_1)$$

Taking T_1 as the room temperature 303 K the various thermo-e.m.f. data for the samples are plotted in terms of $-(V - V_1)/(T + T_1)$ against $(T - T_1)$ in Fig. 5. We see that the polycrystalline experimental data are in good agreement with the crystalline theory. Therefore using the values of E_F and Q at room temperature in Equation 1 the values of r may be obtained. In Table I some of the calculated values of r for the samples have been given corresponding to their different carrier concentrations. Since $r = \frac{1}{2}$ corresponds to optical mode scattering [12], we may infer at this point that in spray-deposited In_2O_3:Sn film having carrier concentrations $n \geqslant 10^{19}\,cm^{-3}$, optical mode lattice scattering is predominant. On the other hand in undoped In_2O_3 films, which generally have carrier concentration of the order of $\sim 10^{18}\,cm^{-3}$, acoustic mode [12] scattering may predominate at room temperature. It may be noted here that with the present technique of film deposition we have obtained good quality transparent conducting films, but they are all of the Sn-doped variety and have carrier concentration always $\geqslant 1 \times 10^{19}\,cm^{-3}$; undoped films however have a lower carrier concentration but they have lower figures of merit for use as transparent conducting electrodes.

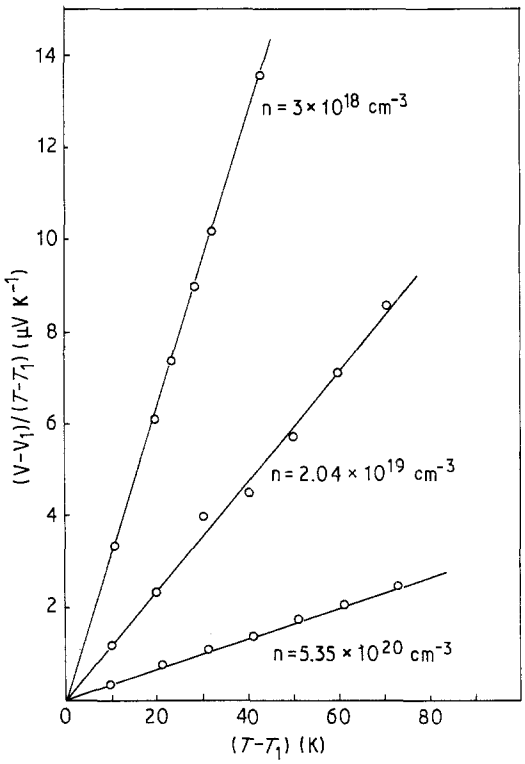

Figure 5 Thermopower plotted in terms of $-(V - V_1)/(T + T_1)$ against $(T - T_1)$ for samples of indium oxide of different carrier concentrations.

4. Conclusions

Carrier transport at room temperature in spray-

TABLE I r at different carrier concentrations

Carrier concentration (cm^{-3})	1.3×10^{18}	3×10^{18}	2.04×10^{19}	2×10^{20}	5.35×10^{20}	7.48×10^{20}
Scattering index r	+ 0.48	+ 0.26	− 0.41	− 0.46	− 0.45	− 0.47

deposited polycrystalline In_2O_3:Sn film may be influenced by various scattering processes of which optical mode lattice scattering predominantly limits the Hall mobility values when the carrier concentration in the sample exceeds $1 \times 10^{19} cm^{-3}$. At lower carrier concentrations and mostly in undoped In_2O_3 film however acoustic mode scattering may be important. Sn-doping concentration and the working solution concentrations have also a remarkable effect in controlling the Hall mobility. To obtain higher mobility of carriers precise control over the deposition process is required. For use as transparent electrodes Sn-doped films should be preferred. Seebeck coefficients in these films are of the order of 16 to $200 \mu V deg^{-1}$ and they slightly increase with the increase of temperature up to 175° C. All the tested samples were degererate in nature with their Fermi levels well inside the conduction band. These levels may also have a gradual pinning mode near the conduction band edge at decreasing carrier concentration.

References

1. J. C. MANIFACIER, *Thin Solid Films* **90** (1982) 297.
2. J. S. E. M. SVENSSON and C. G. GRANQVIST, *Solar Energy Mater.* **12** (1985) 391.
3. J. C. C. FAN and F. J. BACHNER, *J. Appl. Optics* **15** (1976) 1012.
4. M. N. ISLAM and M. O. HAKIM, *J. Phys. Chem. Solids* **46** (3) (1985) 339.
5. M. N. ISLAM and M. A. HAQUE, *Thin Solid Films* **94** (1982) 15.
6. L. J. VAN DER PAUW, *Philips Res. Rep.* **13** (1958) 1.
7. A. BOYER, D. DESCHACHT and E. GROUBERT, *Thin Solid Films* **76** (1981) 119.
8. M. N. ISLAM and M. O. HAKIM, *J. Phys. D, Appl. Phys.* **18** (1985) 71.
9. R. W. WRIGHT, *Proc. R. Soc. A* **64** (1951) 350.
10. Y. KANAI, *Jpn. J. Appl. Phys.* **23** (1) (1984) 127.
11. R. A. SMITH, "Semiconductors" (Cambridge University Press, 1959) p. 173.
12. E. H. PUTLEY, "The Hall Effect and Related Phenomena" (Butterworths, London, 1960) p. 146.

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