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SnO_2:F films synthesized by chemical vapour deposition technique using hydrofluoric acid as doping material

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Abstract. Highly transparent and highly conducting films of SnO_2:F were prepared by chemical vapour deposition technique. The films prepared at 350°C substrate temperature and 2·5 lit. min^{-1} flow rate of oxygen showed maximum figure of merit. The optimum doping concentration of fluorine was 1·02 wt%. The Hall experiment showed that the films prepared at optimum conditions had high carrier concentration and high mobility.

Keywords. Thin films; SnO_2:F; transparent conductors; chemical vapour deposition.

1. Introduction

SnO_2, In_2O_3, Cd_2SnO_4 etc are wide band gap semiconductors and have high carrier concentration when prepared under certain conditions (Haacke 1977). They are transparent to visible solar radiations and are reflecting to infrared radiations. These properties make them suitable for application in solar absorbers (Fan *et al* 1974), for they minimize emittance. The optical refractive indices of these coatings are such that they act as antireflection coatings for Si, GaAs and Ge (Chambouleyron and Saucedo 1979; Cheek *et al* 1979). Low resistive films of these transparent conductors are therefore suitable for use as top conducting layers in solar cells such as SnO_2/Si, ITO/Si etc. Transparent conducting coatings are also used to prevent the windscreens of vehicles from freezing and misting. These coatings are also used to control the internal environment of houses by their application to windows.

SnO_2 is an n-type material with a direct band gap of about 4·27 eV and an indirect band gap of about 2·73 eV (Bhardwaj *et al* 1981–82). The electron concentration in the conduction band arises due to non-stoichiometry produced by oxygen deficiency. The conductivity of these films can be increased by doping for instance with fluorine or antimony. Several processes such as spray pyrolysis (Bhardwaj *et al* 1981–82; Maudes and Rodriguez 1980; Pommier *et al* 1981), chemical vapour deposition (Muranoi and Furukoshi 1978; Kane *et al* 1975; Murty and Jawalekar 1983; Ghoshtagore 1978) and sputtering (Lehmann and Widmer 1975; Leja *et al* 1980) have been employed to deposit pure and doped SnO_2 onto semiconductor wafers and glass substrates. In the present paper we report the effect of substrate temperature, flow rate of oxygen and doping concentration of fluorine on SnO_2 films prepared by chemical vapour deposition (CVD) technique.

2. Experimental technique

Figure 1 shows the schematic diagram of the CVD apparatus, used for the deposition of SnO_2:F films. This consists of a 0·8 m long quartz furnace. A constant temperature

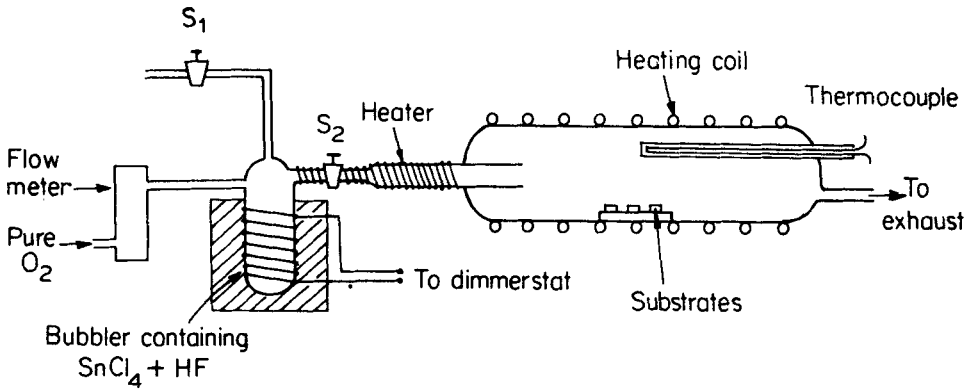

Figure 1. Schematic diagram of the experimental set-up used for the deposition of SnO_2 : F films.

zone of about 0·4 m in the middle of the furnace was maintained at a required temperature using electronic temperature controller (accuracy $\pm$ 5°C). Stannic chloride ($SnCl_4 \cdot 5H_2O$) was used as the source material and dilute HF was used as doping material. The glass apparatus was not affected by dilute HF during deposition. High purity oxygen gas was used as the carrier gas and oxidizing agent. Doping was done by mixing required amounts of HF in molten stannic chloride. The temperature of the bubbler containing the mixture of stannic chloride and HF was maintained at 200°C. The tubes connecting the bubbler and furnace were also maintained at 200°C to avoid condensation of vapours. The flow of oxygen was regulated by using a flow meter. After attaining the required temperature in the furnace cleaned glass substrates were loaded into the reaction zone. Stop cock S_2 was kept closed and after attaining the required temperature in the bubbler, oxygen gas was bubbled and initial vapours were allowed to escape through S_1. After adjusting the required flow rate S_1 was closed and S_2 was opened. Before establishing the optimum substrate temperature, films of various doping concentrations were deposited at a fixed substrate temperature (400°C) and a fixed flow rate of oxygen (2·0 lit. min^{-1}). For that optimum doping concentration, films were deposited at various substrate temperatures and different flow rates of oxygen. Then for optimum substrate temperature and flow rate of oxygen, doping concentration of fluorine was systematically changed.

The transmission spectra of the films were taken by putting a blank glass substrate in the reference beam of a spectrophotometer (Pye Unicam, SP 8–100). The Hall experiment was performed as described by Seeger (1973). Ohmic contacts were made by evaporating aluminium and thickness of the films was measured by Talystep instrument.

3. Results and discussion

SnO_2 : F films for fixed doping concentration of fluorine were deposited at various substrate temperatures and different flow rates of oxygen. The figure of merit F_t, defined by Jain and Kulshreshta (1981) which is independent of film thickness and depends only on the parameters of coating material and preparation technique is

given by:

$$F_t = R_{sh} \ln T$$

where R_{sh} is the sheet resistance and T is the transmission. The value of F_t was found maximum for the films deposited at substrate temperature of 350°C and oxygen flow rate of 2·5 lit. min^{-1}. Figure 2 shows the dependence of sheet resistance R_{sh}, transmission T and figure of merit F_t on doping level of fluorine. Figure 3 shows the dependence of carrier concentration and mobility on doping level of fluorine. At low doping level the carrier concentration is low; therefore the films are highly resistive. As we increase the doping level F_t becomes maximum ($-1{\cdot}11$) at 1·02 wt % of fluorine. A further increase in doping level reduces the carrier concentration because at higher doping level the fluorine atoms start compensating the effect of other fluorine atoms. The reduction in mobility at higher doping level is due to the deterioration in crystallinity (Saxena *et al* 1985). Therefore we conclude that the substrate temperature of 350°C, flow rate of oxygen of 2·5 lit. min^{-1} and doping level of fluorine of 1·02 wt % are the optimum conditions to deposit fluorine doped tin oxide films by CVD technique using HF as the doping material.

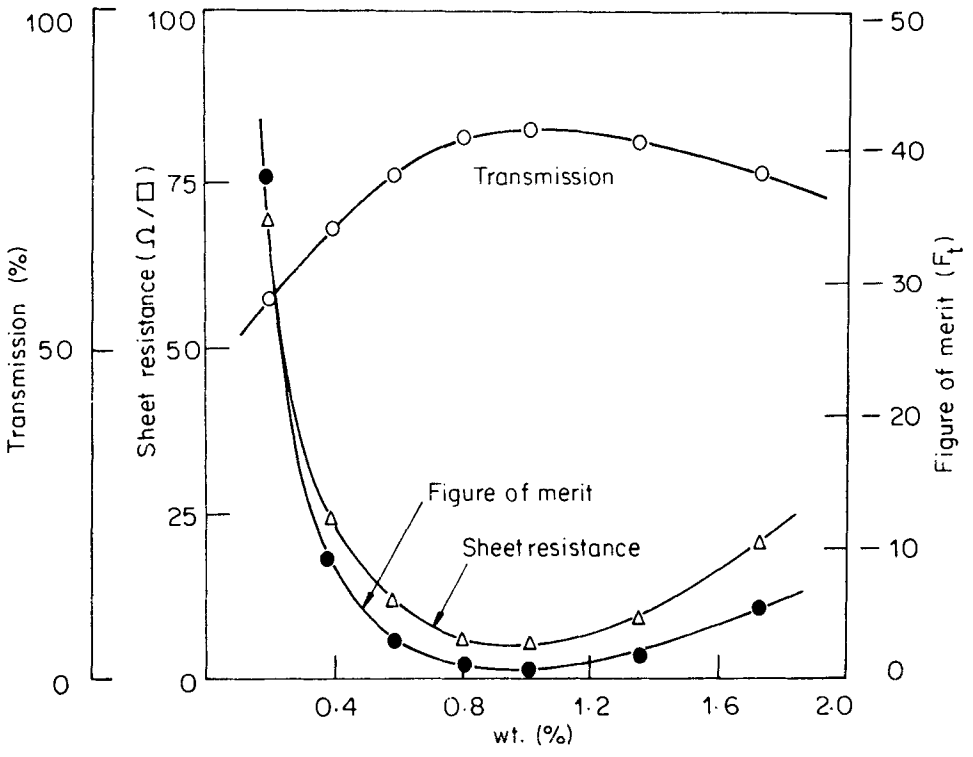

Figure 2. Dependence of sheet resistance, transmission and figure of merit on doping level of fluorine.

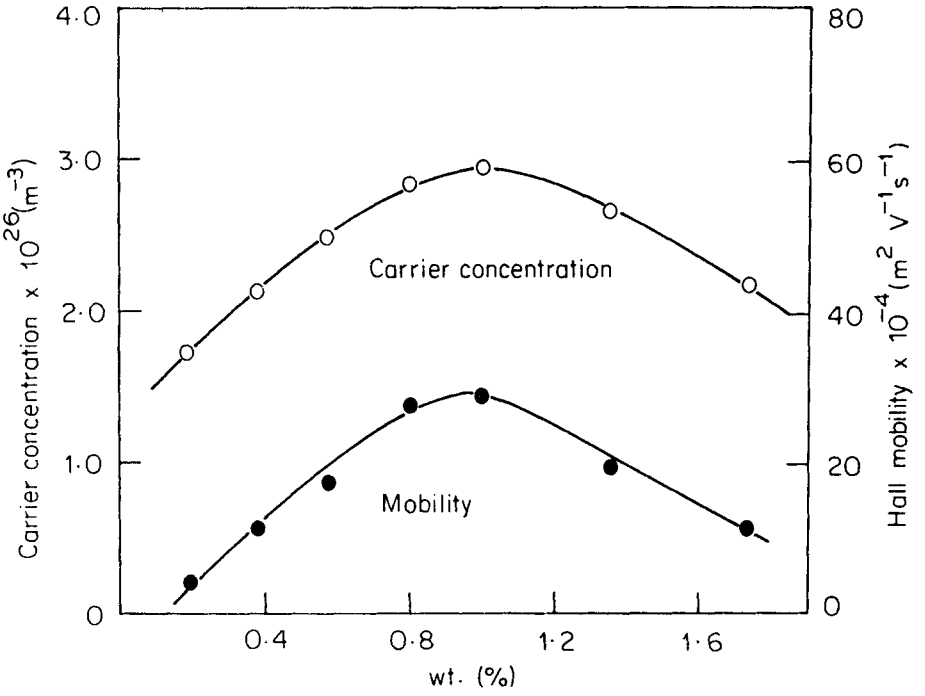

Figure 3. Dependence of carrier concentration and mobility on doping level of fluorine.

Acknowledgements

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References

Bhardwaj A, Gupta B K, Raza A, Sharma A K and Agnihotri O P 1981–82 *Solar Cells* **5** 39
Chambouleyron and Saucedo E 1979 *Sol. Energy Mater.* **1** 299
Cheek G, Genis A, DuBow J B and Verneker V R P 1979 *Appl. Phys. Lett.* **35** 495
Fan J C C, Reed T B and Goodenough J B 1974 *Proc. Ninth Intersociety Energy Conversion Engineering Conference*, San Fransisco, CA, Society of automotive engineers, New York, pp. 341–346
Ghoshtagore R N 1978 *J. Electrochem. Soc.* **125** 110
Haacke G 1977 *Annu. Rev. Mater. Sci.* **7** 73
Jain V K and Kulshreshta A P 1981 *Sol. Energy Mater.* **4** 151
Kane J, Schweizer H P and Kern W 1975 *J. Electrochem. Soc.* **122** 1144
Lehmann H W and Widmer R 1975 *Thin Solid Films* **27** 359
Leja E, Pisarkiewicz and Kolodziej A 1980 *Thin Solid Films* **67** 45
Maudes J S and Rodriguez T 1980 *Thin Solid Films* **69** 183
Muranoi T and Furukoshi M 1978 *Thin Solid Films* **48** 309
Murty N S and Jawalekar S R 1983 *Thin Solid Films* **108** 277
Pommier R, Gril C and Marucchi J 1981 *Thin Solid Films* **77** 91
Saxena A K, Thangaraj R, Singh S P and Agnihotri O P 1985 *Thin Solid Films* (accepted)
Seeger K 1973 *Semiconductor physics* (New York: Springer) p. 71