

## Effect of impurities on TCR of tin oxide thin films

V A JANI and D B GHARE

*Department of High Voltage Engineering, Indian Institute of Science,  
Bangalore-560012*

(Received 7 June 1976, revised 2 June 1977)

Iron, copper and sulphur ion impurities were introduced in the lattice of heavily antimony doped tin oxide thin films, deposited by the chemical vapour deposition technique. The effect of the presence of these additional impurities on the temperature coefficient of resistance (TCR) of such films was studied. It was found that the TCR increased in magnitude in case of the introduction of iron ions, and tended to become negative in case of the introduction of copper ions, while the introduction of sulphur ions seemed to make it more positive.

### 1. INTRODUCTION

Thin films of semiconducting tin oxide are known to have numerous applications in various technologies (Kuznetsov 1960, Dodd 1956) such as high stability resistors (Burket 1961), Transparent electrodes for semiconductor and liquid crystal devices (Ranney 1969, Bosnell & Waghorne 1973), Transparent heating elements for aeroplane and automobile windshields (Raymond & Dennison 1952, Young 1955, Marriot *et al* 1958 and Thomas 1958) as well as Chemical and industrial glass/ceramic wares (Kuznetsov *et al* 1956, 1957, Little 1953), Transparent abrasion resistant coatings (Ward 1975), Electron tubes (Selmdt & Robert 1958, RCA Corp 1973), Phosphors (Otam & Hasegawa 1957, Gaiser 1959, Compagnie des Lampes 1954), Printed Circuits (Saunders 1956), etc

Thin films of semiconducting tin oxide can be deposited on glass and ceramic substrates by pyrohydrolysis of tin chloride solutions on hot substrates (Gomer 1953, Imai 1960, Arai 1960) or by Vacuum sputtering techniques (Sinclair *et al* 1965, Vossen *et al* 1971, 1972)

In case of certain applications such as high stability resistors (Burrkett 1961) and low temperature thermometry (Lyon & Geballe 1950); the temperature coefficient of resistance of such films play an important role. We have studied the effect of introduction of iron, copper and sulphur impurities on the temperature coefficient of resistance of such films.

+ Presently with Gujarat Electricity Board, Uka, Gujarat.

## 2. EXPERIMENTAL

Thin films of semiconducting tin oxide were deposited on glass samples by the chemical vapour deposition technique as described earlier (Ramamujam & Ghare 1974, 1976). Cleaned glass samples were heated in an electric furnace to desired substrate temperature ( $550^{\circ}\text{C}$ ). The hot substrates were then sprayed with the desired tin chloride solution, when a thin film of tin oxide gets deposited on the surface of the substrate by the hydrolysis of tin chloride on the hot surface (Aitchison 1954, Kim & Laitinen 1975). Samples with identical film composition but with wide variations in surface resistivity values were prepared by controlling the film thickness of the deposited film. A solution of stannous chloride (A.R.) in hydrochloric acid and doped with 2 At. percent of antimony was used as the parent solution to which any other desired impurities were added in appropriate concentrations. Iron and copper ions were introduced by doping the parent solution with appropriate amounts of their chlorides while sulphur ions were introduced through dilute sulphuric acid.

After deposition, the samples were annealed in an electric oven at  $150 \pm 1^{\circ}\text{C}$  for 75 hours for stabilisation of the resistivity of such films by thermal annealing (Ramamujam & Ghare 1974). Contacts were then made by electroplating nickel at desired positions and the leads were then soldered on to this nickel. The measurements of temperature coefficient of resistance of the film samples were carried out in the temperature range from room temperature to  $110^{\circ}\text{C}$  with the help of a OSAW Wheatstone bridge and a constant temperature oil bath thermostat.

## 3. RESULTS AND DISCUSSION

The plots of the Temperature Coefficient of Resistance (TCR) of the tin oxide films as a function of surface resistivity for various compositions are shown in figures 1 to 3.

It can be seen from figure 1 that in case of the presence of iron as the impurity ions, the TCR of almost all the films have very high magnitude (irrespective of its sign). Such high magnitudes of TCR are detrimental in certain applications such as high stability low TCR resistors. However, in case of certain other applications such as the low temperature thermometry, the higher magnitudes of TCR might prove to be useful.

In case of copper as the impurity ions (figure 2), and at 0.01 per cent impurity ion concentration, the TCR is positive in magnitude in most cases, even upto a surface resistivity value of about  $1500 \Omega/\text{sq}$ . However, when the impurity ion concentration is increased to 1 per cent, almost all samples with surface resistivity values higher than even about  $200 \Omega/\text{sq}$ . have exhibited negative TCR. The presence of copper impurity ions therefore seems to influence the TCR to become

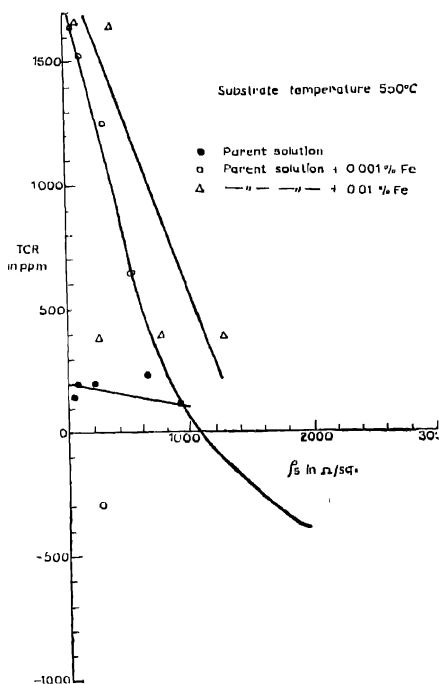


Fig. 1. Variations in Temperature Coefficient of Resistance as a function of surface resistivity for iron as the impurity ions.

negative even at low surface resistivity values. Further, it may also be noted here that at 1 per cent copper ion impurity concentration and at surface resistivity values lower than about 200  $\Omega/\text{sq}$ , the magnitude of TCR for all our samples is very small ( $\sim 100$  ppm/°C) and positive.

In case of sulphur as the impurity ions, it can be seen from figure 3 that at 0.01 per cent impurity ion concentration, the TCR of all the samples (with a spread in surface resistivity value from 50 to 2000  $\Omega/\text{sq}$ ) is very small in magnitude (30-150 ppm/°C). However, as the concentration of the sulphur impurity ions is increased to 0.1 per cent, the magnitude of TCR also increased substantially (200 to 500 ppm/°C) and its sign became distinctly positive.

Tin oxide is known to be a broad band semiconductor. When the material is doped with pentavalent donor impurity ions it becomes an *n* type semiconductor. Now since all the donor impurity ions are expected to have donated their

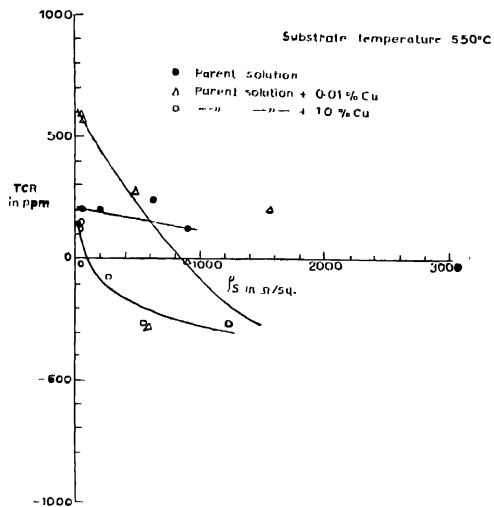


Fig. 2. Variations in Temperature Coefficient of Resistance as a function of surface resistivity for copper as the impurity ions.

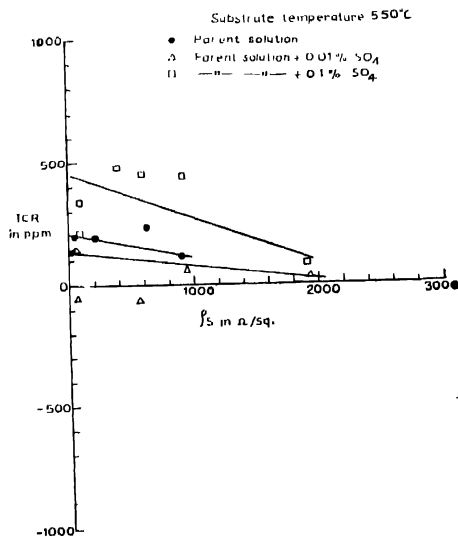


Fig. 3. Variations in Temperature Coefficient of Resistance as a function of surface resistivity for sulphur as the impurity ions.

extra electrons at room temperature and if the material is heavily doped, the number of charge carriers is expected to be independent of temperature (around RT). The material is therefore expected to exhibit a small positive TCR arising from the scattering of the charge carriers as a result of increased lattice vibrations at higher temperatures. Such a behaviour is indeed exhibited by thick semiconducting tin oxide thin films. Therefore, when the material is heavily doped with pentavalent antimony ions, a small number of additional impurity ions (as in our present case) acting as additional donor, acceptor or trap centres are not expected to have such a marked influence on the TCR of the material as has been experimentally evidenced (figures 1, 2, 3).

However, tin oxide thin films of any given doping concentration are known to exhibit both negative and positive TCR depending upon the thickness of such films. The films exhibit negative TCR at lower film thickness and positive TCR at higher film thickness even though the impurity doping concentration is maintained constant. Ramanujam & Ghare (1974, 1976) have studied the effect of variation in various process parameters on the conductivity of such films. They have suggested that the variation in the electrical properties of the tin oxide thin films as a function of film thickness are due to the associated variation in the lattice defect density during the deposition process. The films are initially associated with higher lattice defect density which gradually decrease with the increase in the film thickness. These variations in the lattice defect density are reflected in the electrical properties such as  $\rho$ ,  $\rho_s$ ,  $\sigma$ , TCR, etc. Jani & Ghare (to be published) have found that the presence of Fe, Cu and S as small additional impurity ions have an influence on the lattice defect density profile during the deposition of such tin oxide thin films. The effect of the presence of some foreign ions on the lattice defect profiles have also been reported by some previous workers (Wagner 1950, 1952, Wagner 1974). It is therefore suggested that the influence of these small additional impurity ions on the TCR of the heavily antimony doped tin oxide thin films reported in this article might have its origin in their influence on the film lattice in addition to their behaviour as additional donor, acceptor or trap centres.

#### 4 CONCLUSIONS

The presence of iron ions in minute quantities leads to an increase in the magnitude of Temperature Coefficient of Resistance of heavily antimony doped tin oxide thin films. The presence of copper ions tends to make the TCR negative in magnitude while the presence of sulphur ions tends to make it positive. It is suggested that such marked influence on the TCR of such heavily doped tin oxide thin films as a result of minor additional impurity doping concentrations is perhaps a consequence of the influence of these foreign ions on the lattice defect density profile during the deposition of such films.

## ACKNOWLEDGMENTS

The authors are thankful to Professor R. S. N. Rau for his kind encouragement and support.

## REFERENCES

- Atchison A. E. 1954 *Aust. J. Appl. Sci.*, **5**, 10.  
 Arai T, 1960 *J. Phys. Soc. Japan* **15**, 916.  
 Bosnell J. R. & Waghorn R. 1973 *Thin Solid Films* **15**, 141.  
 Burket R. H. W. 1961 *J. Brit., I. R. N.* **21**, 301.  
 Compagno dos Lamos 1954 *Fr. Pat.*, 1.062.791.  
 Dordis S, M, 1956 *Materials and Methods* **44**, 108.  
 Gaiser R, A. 1959 *W. S. Pat.*, 2.919 212  
 Gomer R. 1953 *Rev., Sci., Instrum.*, **24**, 993.  
 Immi T. 1960 *J. Phys., Soc., Japan*, **15** 937,  
 Jani V. A. & Ghare D. B. *Trans., Indian Ceram. Soc.*, (Commented).  
 Kuznetsov A. Ya. 1960 *Sovt, Physics—Solid State* **2**, 30,  
 Kuznetsov A, Ya., Kruglova A, V, & Kryzhanovskii 1956 *Zavodskaya Lab*, **22** 993,  
 Kuznetsov A, Ya, 1957 *Zavodskaya Lab*, **23** 90,  
 Kim H. & Laitinen H. A. 1975 *J. Amer., Ceram., Soc.*, **58**, 23,  
 Lyon D, N, & Gebale T, H, 1950 *Rev, Sci, Instrum*, **21** 769,  
 Lytle Wm., O. 1953 *U.S. Pat.*, 2.648.754,  
 Marriott J. G. Felt R. M. Boicoy J. H, & Ryan J D. 1958 *Ger. Pat* , 1 045.612,  
 Otani S. & Hasogawa Y. 1957 *Jap., Pat.*, 4852,  
 RCA Corp. 1973 *W.S. Pat.*, 3.713.884,  
 Ramanujam M. A. & Ghare D. B. 1974 *J. Instrum , Soc., India* **4** 17,  
 Ramanujam M A & Ghare D. B. 1976 *J. I.T Sc* , **58**, 254,  
 Ranney M. W. 1969 *Solar Cells*. Noyes Data Corp.  
 Raymond R, F. & Donnison B. J. 1952 *W. S. Pat.*, 2.617 745,  
 Saunders A E. 1956 *W.S. Pat.*, 2.762 725 and 2.762 726.  
 Schmidt W. & Robert L. 1958 *Ger, Pat*, 1.030 471.  
 Sinclair W. R . Peter F. G . Stallinger D. W & Koonco S E. 1965 *J Electrochem, Soc* **112** 1006.  
 Thomas L. D. 1958 *Ger., Pat.*, 1.045.613.  
 Vossion J. L. 1971 *RCA Review* **32**, 289.  
 Vossion J. L. & Pollniak E. S. 1972 *Thin Solid Films* **13**, 281.  
 Wagner C. 1950 *J. Chem, Phys.* **18** 62.  
 Wagner C. 1952 *J. Electrochem. Soc.* **99**, 346c.  
 Wagner J B 1974 *Electrical Conductivity in Ceramics and Glass* Part B. Ed, by N. M. Tallan.  
 Marcel Dekker Inc.  
 Ward J. B. 1975 *Glass Technol.* **16**, 68.  
 Young T. K. 1955 *U.S. Pat.* 2.703.767.