

# REPRODUCIBILITY OF PROPERTIES OF $\text{SnO}_x$ THIN FILMS PREPARED BY REACTIVE SPUTTERING

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The preparation of tin dioxide films by low energy reactive sputtering of tin and tin-antimony (1–10% wt. Sb) in an oxygen — argon atmosphere is described. The dependences of oxygen content in the range from 0 to 50%, target compositions, substrate temperature of 300 K–573 K on minimum resistivity at satisfactory transmittance and on reproducibility are discussed. The correlation between the electrical and optical properties and the microstructure of the films is shown.

## 1. INTRODUCTION

Methods of preparation of conductive transparent thin films based on doped tin and indium oxides have been developed in connection with the technology of optoelectronic devices. The oxide films can be obtained usually either by chemical or sputtering methods<sup>1,2,3</sup>. The tin oxide films are the conductive electrodes in the devices and for this a low resistivity and high transparenence with good stability of these parameters is required. The production method used must give good reproducibility of the film parameters. It is difficult by chemical methods to obtain sufficiently low resistivity. Because of the high substrate temperature and presence of chemically active products the use of chemical methods as a first step in the production of such devices presents technological difficulties.

More flexible methods are vacuum deposition, particularly sputtering,<sup>4,12</sup> because of the low substrate temperature during condensation. Sputtering from an oxide target and reactive sputtering from a metal target can both be used.

The reproducibility of the resistivity of sputtered films is the essential problem. The nonreproducibility of the film resistivity is a result of their semiconducting properties<sup>1,2</sup>. Conductivity of  $\text{SnO}_x$  films is generally attributed to oxygen vacancies, tin interstitials and the type and quantity of the dopants. These factors are connected with technological parameters such as composition and nature of gaseous atmosphere, composition of target, substrate temperature and sputtering efficiency.

In this paper the method of tin dioxide film preparation by reactive low energy sputtering from metallic targets of tin and tin-antimony alloys in an argon-oxygen atmosphere is reported. The sputtering conditions for obtaining the minimal resistivity and good transmittance are described. The dependence of oxygen content in a gaseous mixture, target composition, and substrate temperature on a minimum of resistivity and on reproducibility are analysed. With regard to the reactive sputtering the phenomena on the target surfaces and their influence on the film properties are discussed in detail.

## 2. EXPERIMENTAL

The tin dioxide thin films were prepared by reactive sputtering of tin and tin-(1–10% wt.)

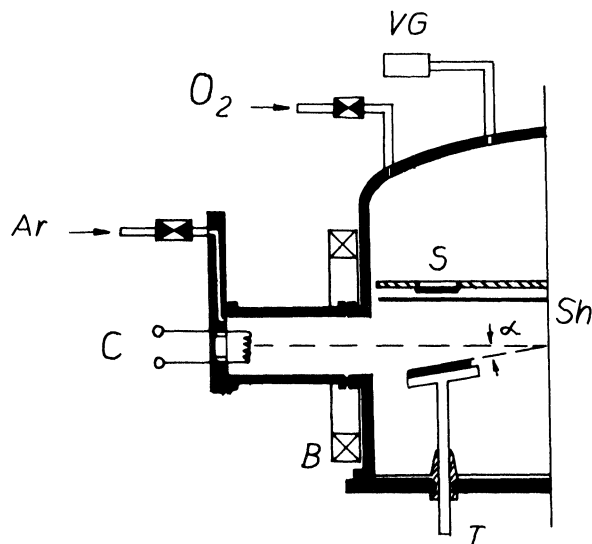


FIGURE 1 The ion sputtering system: C — hot cathode, T — target, B — magnetic coil, O<sub>2</sub> and Ar gas inlet, VG — vacuum gauge, S — substrate, Sh — shutter.

antimony alloys targets in an oxygen-argon atmosphere. A d.c. triode low energy device was used.<sup>13</sup> The fundamental part of the device (Figure 1) is an ion sputtering system mounted in a commercial vacuum system. Positive gaseous ions are produced in an arc discharge plasma. The target is placed on the axis of the ion beam and negatively polarized. The target surface is bombarded by ions with energy due to the potential difference between the plasma and the target. The influence of the magnetic field applies over the whole space of the discharge. This construction permits us to obtain a relatively high sputtering efficiency at a relatively low voltage of ion extraction from the plasma (around one hundred volts).

Sputtering parameters were as follows: arc discharge voltage  $U_{AC} = 18\text{--}50\text{V}$ ; arc discharge current  $I_{AC} = 6\text{A}$ ; the magnetic coil current  $I_{MC} = 7\text{A}$  (magnetic induction about 76 Ga); the total gas pressure was  $p_t = 5 \cdot 10^{-4}$  Torr. The residual pressure was  $p_r = 2 \cdot 10^{-6}$  Torr. The oxygen content in the gaseous mixture, K, was defined as the ratio of oxygen partial pressure to total pressure.

The targets were in disc form with a diameter of 78 mm and thickness about 5 mm. They were prepared by two methods. In the first method tin or tin alloy layers coated the copper discs which were set up inside the target holder. In the second method tin alloys were prepared in disc form. The construction described had various heat transfer conditions because tin has a heat conductivity six times lower than copper.

The extraction voltages of ions from plasma were fixed experimentally at the level from  $-200\text{V}$  to  $-150\text{V}$ , a figure necessitated by the low melting point of tin and the target cooling properties. The  $\text{SnO}_x$  films were condensed on amorphous substrates (Corning 7059 glass) at a temperature of  $300\text{--}573\text{K}$ . The thin film properties were defined on the basis of the measurement of thickness, resistance and resistance changes with temperature, and transmittance in the range of  $330\text{--}850\text{ nm}$  wavelength. The film structure was investigated by X-ray diffraction analysis. The values of the temperature coefficient of resistivity (TCR) were defined for the linear and reversible resistance changes in the temperature range from  $300\text{ K}$  to  $400\text{ K}$ .

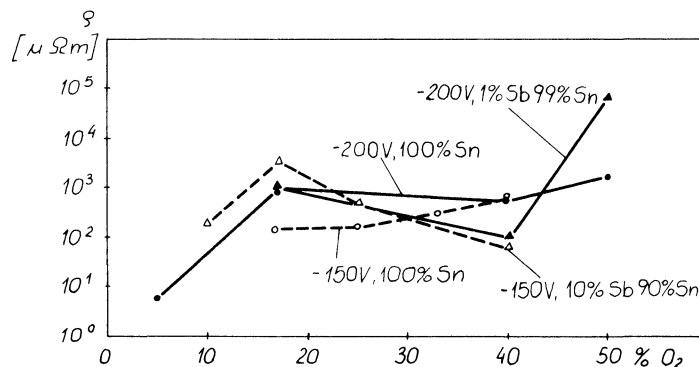


FIGURE 2 Resistivity,  $\rho$ , as a function of oxygen doping for films sputtered from Sn, 1%Sb99%Sn and 10%Sb90%Sn targets (copper disc). Sputtering time 10 min,  $T_s = 473$  K.

### 3. RESULTS

Transmittance as well as resistivity are important in assessing the use of SnO<sub>x</sub> films for various applications. These properties are connected in such a way that with increasing oxygen deficiency the films become more conductive and at the same time they become less transparent. Obtaining low resistivity and high transmittance simultaneously requires the close control of sputtering conditions.

In Figure 2 the resistivity  $\rho$ , as a function of oxygen doping for films sputtered from different targets is shown. In the range from 16% O<sub>2</sub> to 40% O<sub>2</sub> a minimum in resistivity at a satisfactory transparency is achieved depending on the alloy composition and on the target voltage. In comparison with the undoped tin the lowest resistivity of about 50  $\mu\Omega\text{m}$  is obtained for films prepared by sputtering from a 10%Sb-90%Sn target in a 40% O<sub>2</sub> atmosphere. In Figure 3 the transparency as a function of light wavelength, for films produced from Sn (Figure 3a) and 1%Sb-99%Sn (Figure 3b) targets at different oxygen concentration is shown. In spite of the significant resistance differences, about one order of magnitude, the transmittance changed only from 85% to almost 100% for

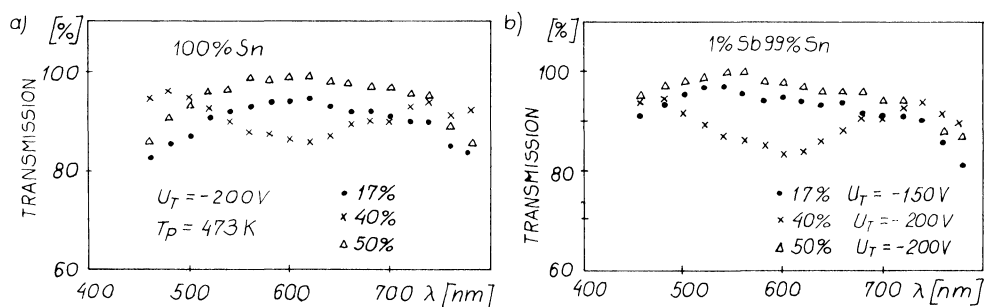


FIGURE 3 Transmittance as a function of light wavelength for the films produced from (a) Sn and (b) 1%Sb99%Sn targets (copper disc). Thickness of films about 200 nm.

oxygen concentration in the range from 17%  $O_2$  to 50%  $O_2$ . The increase of film thickness from 100 to 300 nm caused a decrease of transmittance by 5 to 10% depending on the wavelength. At a satisfactory transmittance value the place of the minimum of the resistivity depends on the target composition and oxygen doping level. However the oxygen doping level depends on such technological parameters as oxygen concentration in the gaseous atmosphere, the substrate temperature and the sputtering efficiency.

In the case of the Sb doped films the minimum of resistivity appears at about 40% oxygen. However for undoped films the minimum of resistivity requires more oxygen deficiencies and it appears at a lower oxygen concentration in a gaseous atmosphere of about 17%  $O_2$ . The substrate temperature has a similar influence on oxygen deficiency in the films. For example, for undoped films the minimum of resistivity was obtained at 33% of oxygen concentration for a substrate temperature of 523 K, while for a substrate temperature of 423 K the minimum of resistivity appeared at about 15% of oxygen.<sup>14</sup>

The undoped films with the minimum of resistivity contained the  $SnO_2$  phase together with a large amount of amorphous phase (Figure 4). Figure 4 also shows the

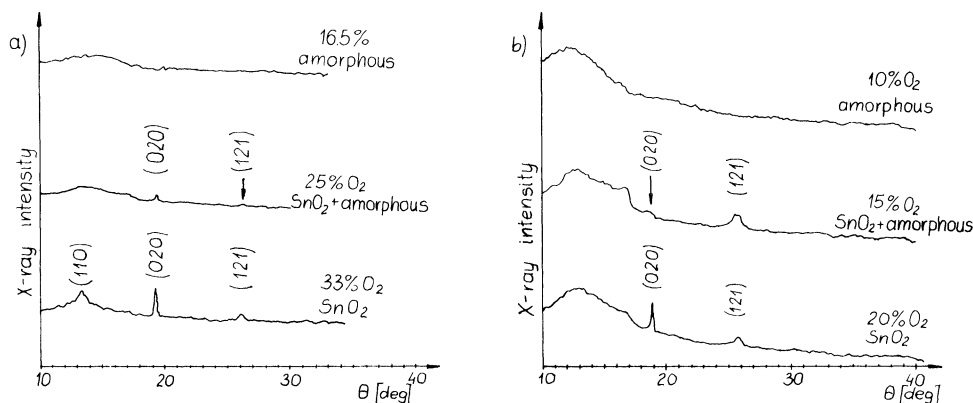


FIGURE 4 Parts of the diffraction patterns of films with resistance about the minimum: (a) substrate temperature of  $T_s = 523$  K; (b) substrate temperature of  $T_s = 423$  K. Thickness of films about 300 nm. 100% Sn on copper disc.

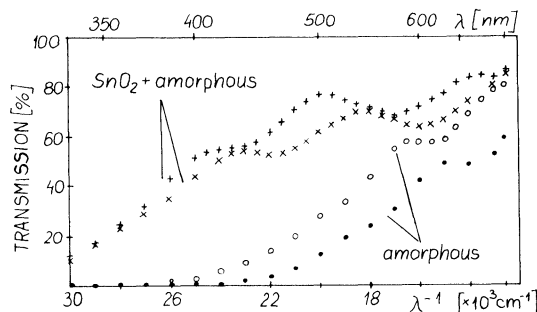


FIGURE 5 Transmittance as a function of the light wavelength for films with resistance about minimum ( $T_s = 423$  K, thickness of films about 400 nm, 100% Sn on copper disc).

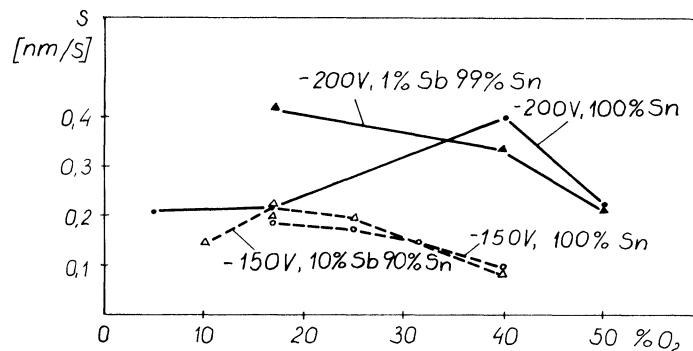


FIGURE 6 Deposition rate,  $S$ , as a function of oxygen doping for different target compositions. Sputtering time 10 min, copper discs  $T_s = 423$  K.

effect of substrate temperature, Figure 4a referring to a substrate temperature of 523 K and Figure 4b to a value of 423 K. The samples with about the minimum resistance were characterized by a small increase of conductivity within an increase of temperature in the range of 40–400 K. The TCR defined in the temperature range between 300 K and 400 K was negative and about  $(100-500) \times 10^{-6}/\text{K}$ . The amorphous films were less transparent than those with a small amount of a polycrystalline SnO<sub>2</sub> as can be seen in Figure 5.

During bombardment by oxygen and argon ions the target surface was covered with the  $\text{Me}^+ - \text{O}^-$  reaction product. Sputtering efficiency as well as condensation rate is the result of an equilibrium condition being obtained between the creation rate of the oxide layer on the target surface and the ion etching rate. An additional effect of bombardment is target heating despite intensive water cooling.

For all other parameters constant, the increase of oxygen concentration caused changes in the deposition rate of the sputtered films as shown in Figure 6. For high oxygen concentration (40–50%) a considerable decrease of deposition rate was obtained.

The deposition rate and film resistivity as a function of oxygen concentration is shown in Figure 7. The influence of the target preparation on the characteristics is

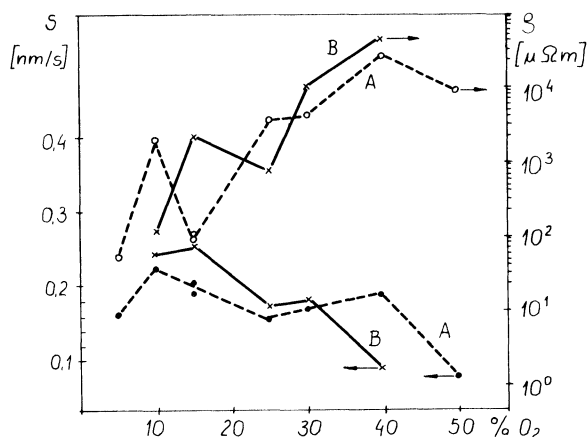


FIGURE 7 Deposition rate and resistivity as a function of oxygen concentration for two types of targets (A-Sn on Cu; B-Sn). Substrate temperature  $T_s = 423$  K, target voltage  $U_T = -150$  V, sputtering - time -30 min.

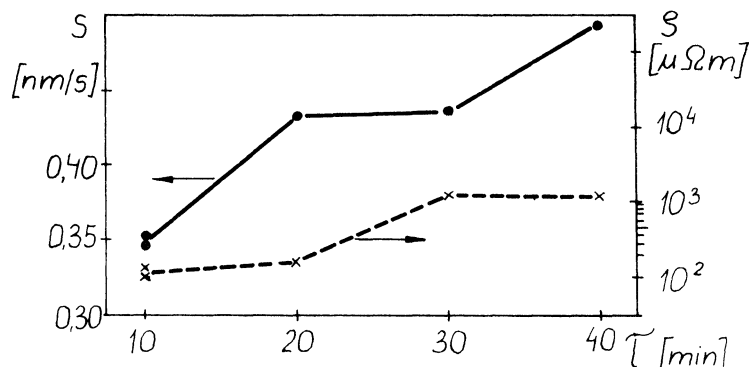


FIGURE 8 Average deposition rate,  $S$ , and resistivity,  $\rho$ , as a function of target sputtering time,  $\tau$ . Sputtering conditions:  $U_T = -200$  V,  $T_s = 473$  K,  $K = 40\%$ . Measured samples were deposited in groups of four separately with 10 minute intervals (Sn on copper disc).

apparent. In the case of a low thermal conductivity target (tin disc — curves B) for low and medium oxygen concentrations, a higher deposition rate is obtained in comparison with the rate for a target prepared in the form of Sn on a copper disc (curves A). For the tin disc target a rapid decrease of deposition rate is observed at lower oxygen concentrations. At the same time the minima of resistivity are displaced towards higher oxygen concentration for the films sputtered from the target with lower thermal conductivity. The phenomena of decrease of sputtering efficiency occurred on the target due to the creation of an oxide layer caused by sputtering induced by the ion bombardment. The increase of target temperature also caused permanent changes in sputtering efficiency. In consequence the changes of deposition rate and non-reproducibility of film properties were observed as shown in Figure 8.

It can be seen in Figure 8 that prolonged bombardment caused a considerable increase of deposition rate and the film resistivity,  $\rho$ . The effect of the prolonged bombardment is an increase of the target temperature up to the Sn melting point (target of Sn on Cu disc), which caused changes of sputtering efficiency with time. Also the wide spread of TCR values (Figure 9) and transmittance (Figure 10) for these films can be observed.

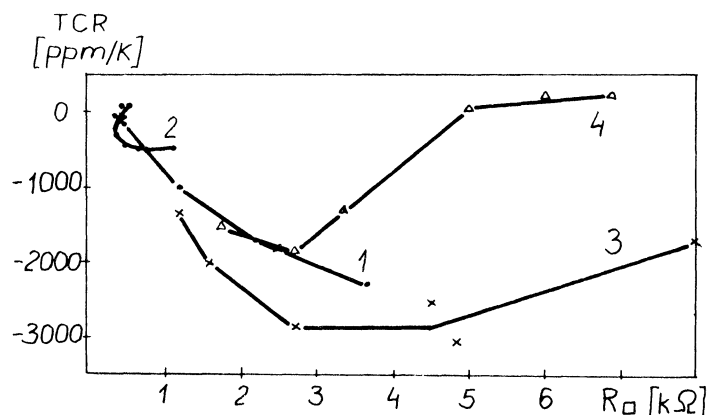


FIGURE 9 Correlation between TCR and sheet resistance  $R_{\square}$  for tin oxide films sputtered in four sequential processes. Sputtering conditions as in Fig. 8. Film thickness: 1–200 nm, 2–260 nm, 3–250 nm, 4–300 nm.

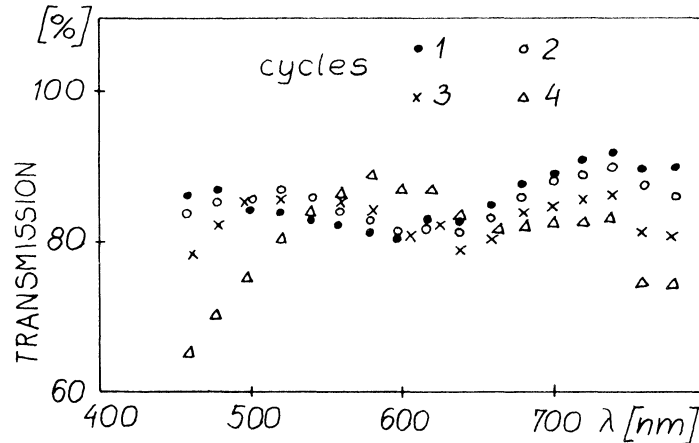


FIGURE 10 Transmission as a function of light wavelength for SnO<sub>x</sub> films sputtered in four sequential processes. Sputtering conditions as in Fig. 8.

On the basis of the presented results it is seen that besides the oxygen doping, the history of the target and its temperature influence the dispersion of thin SnO<sub>x</sub> film properties prepared by the described method.

For the purpose of reduction of the target temperature the target voltage was decreased to -150 V. However the dispersion of the film properties decreased unsatisfactorily.

The dependence of  $TCR = f(R_{\square})$  for 12 different sputtering processes (Figure 11) was similar to that shown in Figure 9.

Initial target preparation based on argon ion bombardment for 10 min was examined. The initial target preparation stabilized the film deposition rate over the whole range of substrate temperature, which is illustrated in Figure 12.

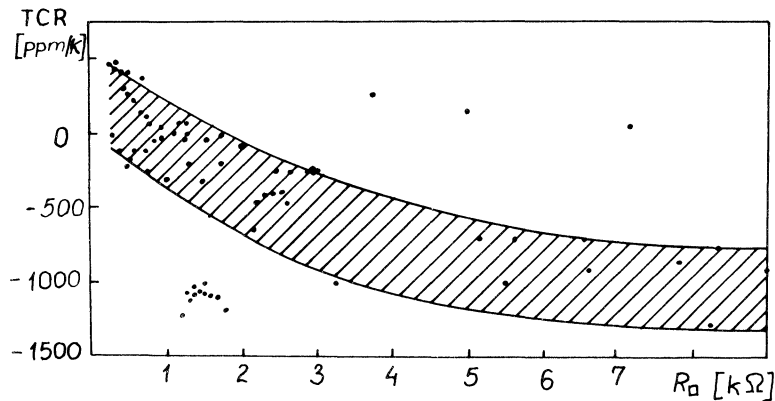


FIGURE 11 Correlation between TCR and  $R$  for tin oxide films obtained in 12 different sputtering processes. Sputtering conditions:  $K = 30\%$ ,  $U_T = -150$  V,  $T_s = 523$  K. Film thickness about 100 nm.

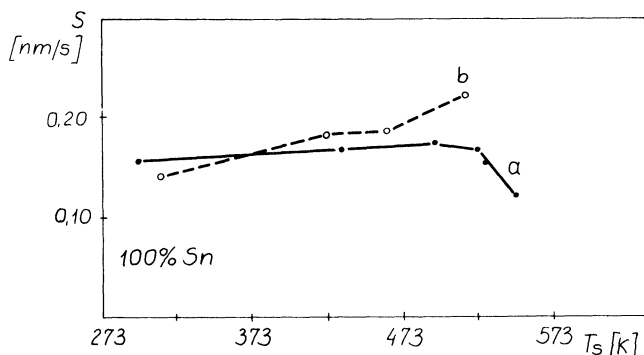


FIGURE 12 Deposition rate as a function of substrate temperature during sputtering for: (a) applied initial target preparation, (b) without preparation ( $U_T = -150$  V,  $K = 33\%$ ,  $d = 100$  nm).

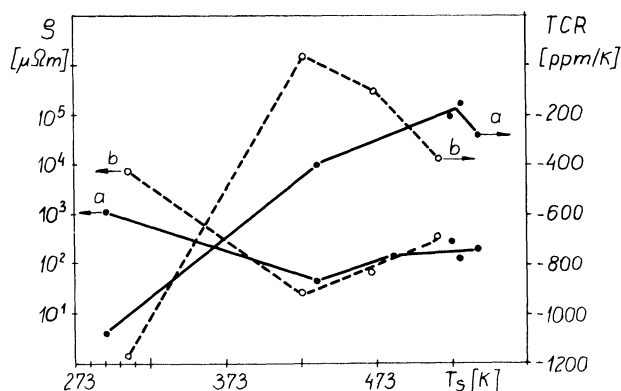


FIGURE 13 Resistivity,  $\rho$ , and TCR as a function of substrate temperature during sputtering for: (a) applied initial target preparation, (d) without preparation ( $U_T = -150$  V,  $K = 33\%$ ,  $d = 100$  nm).

In Figure 13 it will be seen that a minimum of resistivity occurred at a substrate temperature of about 423 K. However a minimum in TCR was obtained at a substrate temperature of about  $T_s = 523$  K. For the initially prepared target the characteristics obtained for  $\rho$  and TCR versus substrate temperature  $T_s$  showed less variation than those for the non initially prepared target. The parameters of the films sputtered at the substrate temperature of 423 K were satisfactorily stable. For such fixed sputtering parameters ( $U_T = -150$  V,  $T_s = 423$  K and 10 min of initial preparation of the Sn on Cu targets) the minimum of resistivity as a function of oxygen concentration,  $\rho = f(K)$ , was remeasured. Assuming the satisfactory transparency of the films, the minimum of resistivity was obtained at an oxygen concentration of about 15%. For these films the dispersion of the properties decreases significantly (Figure 14).

#### 4. CONCLUSION

The results presented establish that it is possible to produce thin transparent conductive films of doped tin oxide by the low energy reactive d.c. triode sputtering method. The advantages of this method are the low voltage of ion extraction from the plasma (target voltage), lower gaseous pressure during sputtering than in the d.c. diode



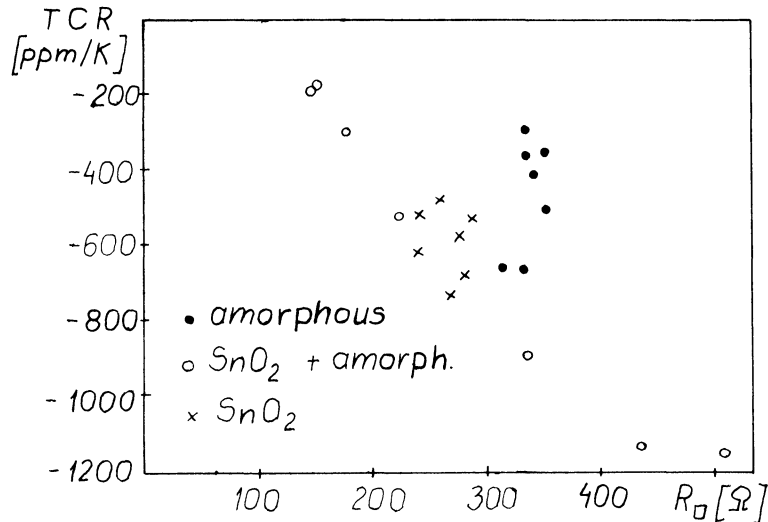


FIGURE 14 TCR versus sheet resistance for  $\text{SnO}_x$  films sputtered at  $U_T = -150$  V,  $T_s = 423$  K,  $K = 10\%$ – $15\%$ .

sputtering method and the low substrate temperature compared with other sputtering methods. For these reasons the use of this method in optoelectronic device preparation is a useful possibility.

The film parameters were comparable with parameters noted by other investigators. The strong dependences of thin film properties such as resistivity, transmittance and structure on oxygen doping level during sputtering have been discussed.

The compromise between low resistivity and high transparency discussed in a previous paper<sup>1</sup> was obtained in non-doped films. In these films the minimum of resistivity appeared in the range of transition from amorphous to polycrystalline  $\text{SnO}_2$  phases. The minimum of resistivity for antimony doped films occurred in the range of high oxygen concentration (existence of  $\text{SnO}_2$  phase), where the transparency is less sensitive to oxygen doping. (Figure 14 shows the effect of structure on the sheet resistance and TCR).

The reproducibility of the properties of thin  $\text{SnO}_x$  films prepared by sputtering depends on sputtering parameters having time stability. As a result of the reactive nature of the process it is difficult to keep the sputtering parameters, especially the sputtering efficiency, constant. It was apparent that the sputtering efficiency depended in great part on non-controlled parameters as follows: changes in target temperature, creation of an oxide layer on the target surface, and connected with it, changes in plasma parameters and, finally, target history. The target temperature which is relative to ion bombardment depends on the thermal conditions. The target construction has a direct influence on these conditions. It is very important in the case of tin and tin alloys, in relation to their low melting point and low thermal conductance. If the target surface melted, the sputtering parameters changed and evaporation was possible. The oxygen layer formed on the target surface influenced the changes of sputtering efficiency, in particular at high oxygen concentration. This phenomenon is responsible for the influence of target history on the reproducibility of sputtering parameters.

In this paper the dependences of these factors on the dispersion of thin tin oxide film parameters has been shown. The procedure which limited the effect of these factors on reproducibility of the film properties has been suggested.

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