

Electrical conductivity of $(\text{PbO})_{1-x}(\text{SnO})_x$

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Abstract. Electrical conductivity of lead tin monoxide has been measured as a function of composition (x), temperature and electric field. Heat treatment of samples in vacuum produces an irreversible increase in conductivity and is probably due to chemisorption of oxygen. The thermal activation energies in screen printed layers have been found to be lower than that in pressed pellets and is considered to be due to more grain boundaries being present in the former. The non ohmic electrical conduction in pellets follows $J \propto V^n$ relationship where n ranges between 2 and 1.25 for different compositions and temperatures. The theory of space charge limited currents (SCLC) in defect insulators has been invoked to explain the observed results.

Keywords. Electrical conductivity; space charge limited currents; lead tin monoxide.

1. Introduction

Mixed lead tin monoxide layers are used as target material in Vidicon and Plumbicon tubes. The stable tetragonal tin monoxide is isomorphous with tetragonal lead monoxide. The physical properties of the mixed oxide crystals and layers have been studied by several workers (Czapla *et al* 1978; Takeuchi 1975; Vandenbroek and Netten 1970; Vandenbroek *et al* 1969). Studies of photo conductivity and reflection spectra (Vandenbroek *et al* 1969) on mixed oxide crystals, obtained by the chemical precipitation method show that the energy gap decreases from 1.94 to 0.62 eV with increase of SnO concentration. Similar optical studies have also been conducted on vacuum deposited films (Takeuchi 1975) and on sputtered layers (Czapla *et al* 1978). Electrical conductivity and dielectric properties of pure PbO (Kuznetsova *et al* 1977; Gasamov 1976; Malinova and Myasnikov 1976) and pure SnO (Agarwal and Saxena 1981, 1982a, b) thin films have been extensively studied. However, little work has been done on the dark electrical conductivity of mixed lead tin monoxide. This paper reports the results of experiments on electrical conductivity of $(\text{PbO})_{1-x}(\text{SnO})_x$ as a function of temperature, composition and electric field.

2. Experimental

Mixed lead tin monoxide layers (~ 2 to $5 \mu\text{m}$ thick) have been prepared by screen printing a paste of PbO (BDH 98% pure) and SnO (Burgoyne 98% pure) fine powders

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(grain size $\leq 5 \mu\text{m}$) in propylene glycol (binder) on to cleaned corning 7059 glass substrates supplied with semitransparent SnO_2 electrode using a circular mask having a diameter 1.5 cm. After drying and sintering the layers at 530 K for two hours in N_2 atmosphere, circular (dia. 1.0 cm) aluminium (Al) electrodes are deposited by vacuum evaporation at a pressure of 5×10^{-5} Torr to form $\text{SnO}_2/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ sandwich systems. Current through the specimen is measured by using an electrometer amplifier of range 10^{-12} – 10^{-6} amp. DC biasing was done by an electronically regulated power supply having regulation better than 0.01%. The temperature of the samples have been measured by precalibrated chromel-alumel thermocouples connected to a digital panel voltmeter of range (199 ± 0.01) mV. While taking observations at different voltages sufficient time was allowed for the specimen to attain a stable temperature. Finally electrical conductivity as a function of composition (x), temperature and electric field was studied. The observations were found to be reproducible.

$\text{Al}/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ systems have also been prepared by vacuum deposition of Al on the top and bottom surfaces of 2–3 mm thick pellets. The latter were obtained by pressing oxide mixtures at a pressure (P) of $(2\text{--}4.6) \times 10^7$ kg/m², sintering at 530 K in N_2 atmosphere for two hours and finally lapping off and polishing of the surfaces. Electrical conductivity, for different compositions, as a function of temperature (300–400 K) and electric field at 77 K and 300 K have been investigated.

3. Discussion

Figure 1 shows the variation of resistivity (ρ), of mixed oxide layers and pellets ($P = 4 \times 10^7$ kg/m²), with x at 300 K. For layers ρ decreases continuously from 2.1×10^{11} to 4.4×10^9 ohm m as x changes from 0 to 0.6 and for pellets it decreases from 1.3×10^9 to 5.6×10^5 ohm m as x changes from 0 to 1. The electric transport through inhomogeneous mixture $A_{1-x}B_x$ can be described by effective medium theory, EMT (Bruggeman 1935), which has been applied by different workers to calculate the composition dependence of resistivity (ρ) of $\text{As}_x\text{Te}_{1-x}$ films (Ast 1974), bulk chalcogenide glass (Shimakawa and Nitta 1978) and bismuth doped chalcogenide glass (Tichy *et al* 1985). According to this theory the compositional dependence of ρ of a mixture is given by

$$\rho = \frac{4\rho_1\rho_2}{\rho_1(3X_2 - 1) + \rho_2(3X_1 - 1) + \{[\rho_1(3X_2 - 1) + \rho_2(3X_1 - 1)]^2 + 8\rho_1\rho_2\}^{1/2}} \quad (1)$$

where ρ_1 and ρ_2 are the resistivities of components with volume fractions X_1 and X_2 respectively.

The observed resistivities of the pellets along with the calculated values using (1) have been inserted in table 1. Close agreement between the experimental and calculated values suggests that the variation in resistivity with composition for pellets can be explained by effective medium theory. Conductivity is found to increase linearly with the pressure ($P \leq 4.6 \times 10^7$ kg/m²) applied for preparing the pellets.

Figure 2 depicts the representative plots between $\log \sigma$ and $10^3/T$ for pellets ($P = 4 \times 10^7$ kg/m²) having $x = 0.2$ during heating-cooling cycles. It is evident from the graph that heat treatment of samples in vacuum (5×10^{-5} Torr pressure) and in air (1 atm) produces an irreversible increase in conductivity as temperature increases. On

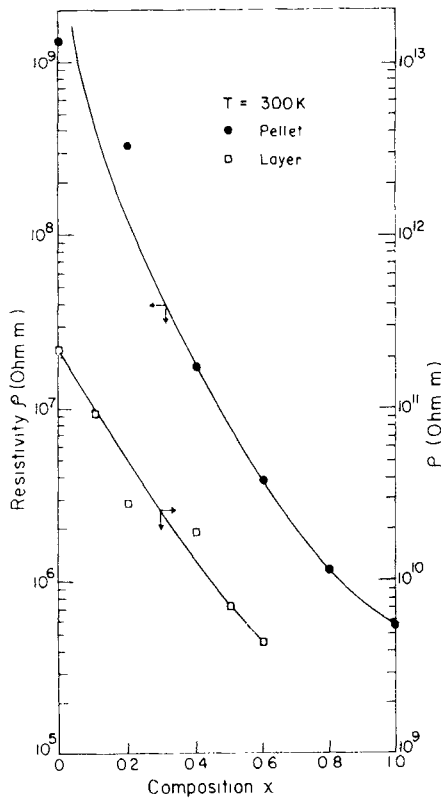


Figure 1. Variation of resistivity with composition at 300 K.

Table 1. Variation of E_a , σ_0 and ρ with x

| x | Layers | | Pellets | | | |
|-----|---------------|----------------------------------|----------------|----------------------------------|-------------------------|-------------------------|
| | E_a (eV) | σ_0 (ohm m) ⁻¹ | E_a (eV) | σ_0 (ohm m) ⁻¹ | σ_{exp} (ohm m) | ρ_{EMT} (ohm m) |
| 0 | 0.212 ± 0.015 | 1.468 × 10 ⁻⁵ | 0.384 ± 0.0007 | 2.609 × 10 ⁻⁵ | 1.313 × 10 ⁹ | 1.313 × 10 ⁹ |
| 0.1 | 0.274 ± 0.005 | 4.825 × 10 ⁻⁵ | — | — | — | — |
| 0.2 | 0.175 ± 0.013 | 1.235 × 10 ⁻⁶ | — | — | 3.268 × 10 ⁸ | 5.952 × 10 ⁸ |
| 0.3 | 0.224 ± 0.004 | 4.744 × 10 ⁻⁶ | — | — | — | — |
| 0.4 | 0.218 ± 0.003 | 4.067 × 10 ⁻⁶ | 0.327 ± 0.033 | 1.429 × 10 ⁻³ | 1.740 × 10 ⁷ | 9.108 × 10 ⁶ |
| 0.5 | 0.223 ± 0.003 | 4.996 × 10 ⁻⁶ | — | — | — | — |
| 0.6 | 0.116 ± 0.006 | 5.81 × 10 ⁻⁷ | 0.641 ± 0.047 | 5.199 × 10 ⁻³ | 3.827 × 10 ⁷ | 1.603 × 10 ⁶ |
| 0.8 | 0.103 ± 0.005 | 2.824 × 10 ⁻⁸ | 0.388 ± 0.01 | 1.224 × 10 ⁻² | 1.154 × 10 ⁶ | 8.553 × 10 ⁵ |
| 1.0 | — | — | 0.538 ± 0.007 | 1.283 × 10 ¹ | 5.747 × 10 ⁵ | 5.747 × 10 ⁵ |

cooling, the conductivity remains higher in vacuum and becomes lower than the initial value in air. These results are understandable on the basis that heat treatment in air leads to chemisorption of oxygen and further diffusion into grain boundaries and thus to an enhancement in barrier height, thereby lowering the conductivity. On the contrary, heat treatment in vacuum leads to a desorption of oxygen from grain

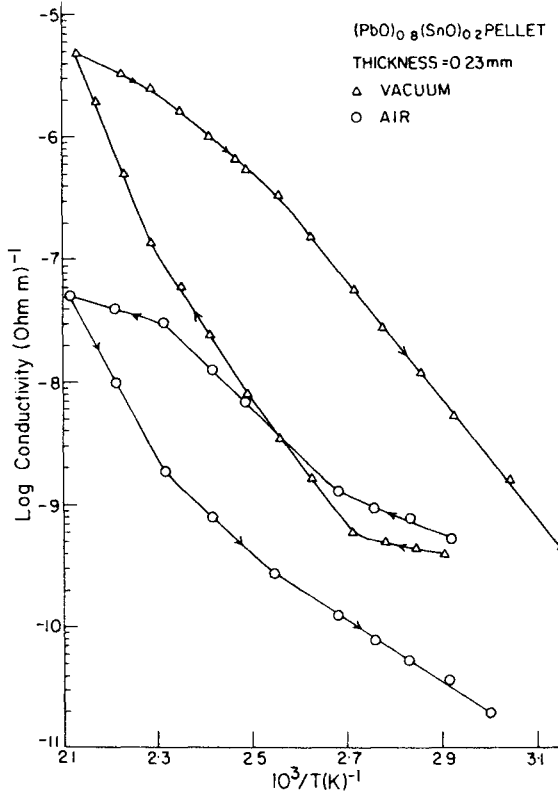


Figure 2. Variation of $\log \sigma$ with $10^3/T$ for $(\text{PbO})_{0.8}(\text{SnO})_{0.2}$ pellet.

boundaries resulting in a lowering of barrier height and increase in conductivity. Similar effects have been observed in tin oxide films (Shanthi *et al* 1980).

Observed data for temperature dependent conductivity (σ versus T) in the cooling mode have been used to estimate the thermal activation energy of electrical conduction which is given by the expression

$$\sigma = \sigma_0 \exp(-E_a/k_B T) \quad (2)$$

where σ is electrical conductivity, k_B the Boltzmann constant and T the temperature of the specimen. The values of E_a and σ_0 calculated by the least square fit method using (2) are given in table 1.

It can be seen that the values of σ_0 (table 1) change from 2.609×10^{-5} to 1.283×10^1 $(\text{ohm m})^{-1}$ in pellets and from 1.468×10^{-5} to 2.824×10^{-8} $(\text{ohm m})^{-1}$ in layers as x changes from 0 to 1. The observed increase in σ_0 with x in pellets may be attributed due to O_2 vacancies at grain boundaries and is supported by the fact that observed activation energies in the samples is about 0.38 eV which is in agreement with the value 0.32 eV for O_2 vacancies (Haskova 1973). The observed reverse trend in layers suggests the absence of O_2 vacancies and the decrease in σ_0 with x is possibly due to adsorption of O_2 at the grain boundaries which is in turn supported by the fact that observed E_a values are in general different from those for O_2 vacancies. It may be remarked here that

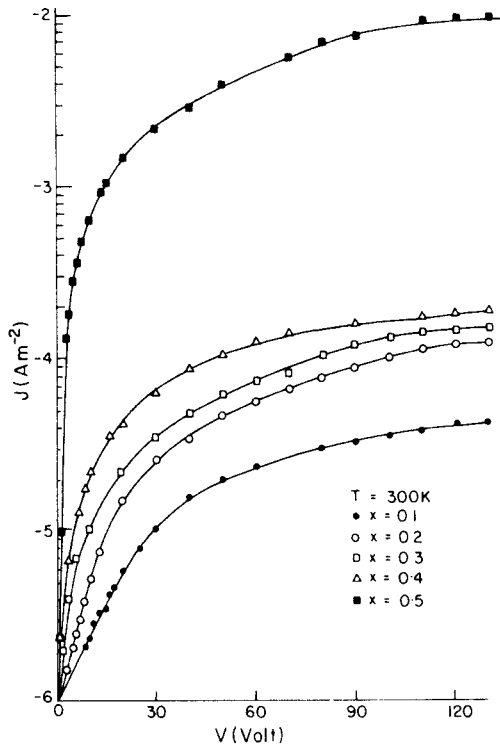


Figure 3. J - V characteristics of $\text{SnO}_2/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ layers at 300 K.

the present E_a values in screen printed mixed layers are close to those reported for vacuum evaporated SnO films (Agarwal and Saxena 1982a).

Figure 3 represents the J - V characteristics of $\text{SnO}_2/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ layers at 300 K for values of x varying between 0 and 0.5, on a semilog graph. The current first increases rapidly with increase of voltage and then saturates at about 100 volts. Such diode characteristics occur due to the presence of interparticle barriers (Slater 1956). A similar trend has been reported in vacuum evaporated PbO-PbS films (Kumar *et al* 1980) and chemically sprayed PbS films (Tyagi *et al* 1977).

Figure 4 depicts the J - V characteristics of $\text{Al}/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ pellets ($P = 4 \times 10^7 \text{ kg/m}^2$) at 77 K and 300 K. For low voltages the conduction is ohmic while for high voltages current density obeys $J \propto V^n$ dependence; the values of n are as given in table 2.

It may be noted that at 77 K the current density obeys square law dependence on voltage ($n \approx 2$) for all samples while at 300 K only samples with $x \leq 0.6$ obey this dependence.

To understand the mechanism involved in the observed $J \propto V^2$ dependence we first plotted $\log J/V^2$ versus $1/V$ and obtained nonlinear curves (not shown). It suggests that the observed behaviour can not be explained by the tunnel effect of the Fowler-Nordheim type. Similar attempts to explain the observed behaviour on the basis of Poole Frenkel effect [$\log(J - J_0)$ versus $V^{1/2}$] and exponential trap distribution

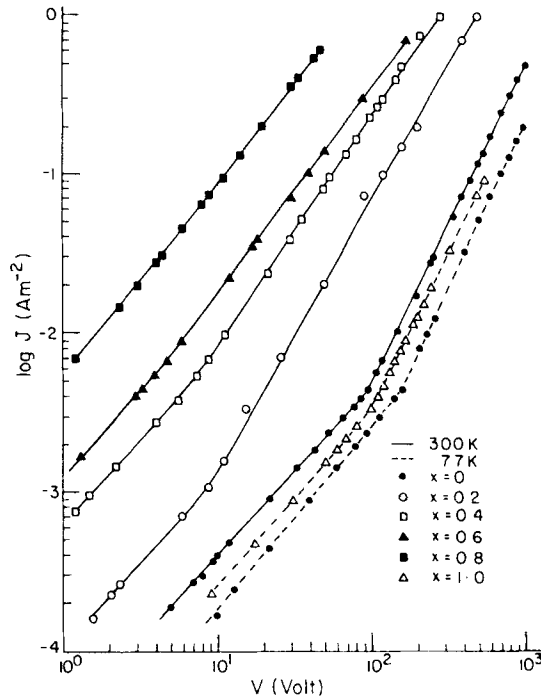


Figure 4. J - V characteristics of $\text{Al}/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ pellets.

Table 2. Values of n in $J \propto V^n$ dependence

| x | 0 | 0.2 | 0.4 | 0.6 | 0.8 | 1.0 |
|-------|------|------|------|------|------|------|
| 77 K | 2.05 | 1.80 | 1.73 | 1.80 | 1.80 | 1.88 |
| 300 K | 1.88 | 1.73 | 1.53 | 1.66 | 1.23 | — |

($\log J/V$ versus V) yielded negative results. Here J and J_0 are the total and ohmic current density respectively in the sample.

The other possibility to explain the observed J - V curves is on the basis of the shallow trap model (Rose 1955), according to which current density J is given by

$$J = \frac{9\mu\epsilon_r\epsilon_0\theta}{8s^3} V^2 \quad (3)$$

where μ is the mobility, ϵ_r the relative permittivity of medium, ϵ_0 the permittivity of free space, s the thickness of the pellet, V the applied voltage and θ the ratio of the free electrons to trapped electron density is given by

$$\theta = \frac{N_c}{N_t} \exp(-E_t/k_B T) \quad (4)$$

where N_c is the density of free carrier states in the conduction band, N_t is density of shallow traps positioned at an energy E_t below conduction band and K_B the Boltzmann constant. It was assumed that free space charge density is negligible in comparison to the trapped space charge density ($\theta \ll 1$).

The plots of $(J - J_0)$ and V^2 on log-log scale at different temperatures and for different compositions (Figure 5) are straight lines suggesting the suitability of the model. The slope of these straight lines (J/V^2) have been calculated using the least square fit method.

Using these values of slopes (J/V^2) and $\epsilon_0 = 8.85416 \times 10^{-12}$ F/m, $\mu = 1.2 \times 10^{-2}$ m²/V sec (Keezer *et al* 1968, assuming it to be independent of x), in (3), the values of θ have been calculated and are given in table 3. The relative permittivity of medium (ϵ_r) of the pellets are determined experimentally at 300 K and 10 kHz frequency, using an LCR bridge (Systronic make). The obtained values are given in table 3 and are fed into (3) to calculate θ . Transition voltage (V_T) at which ohmic conduction changes into non ohmic conduction (Lampert *et al* 1959) is given by

$$V_T = \frac{en_0 s^2}{\theta \epsilon_0 \epsilon_r}, \tag{5}$$

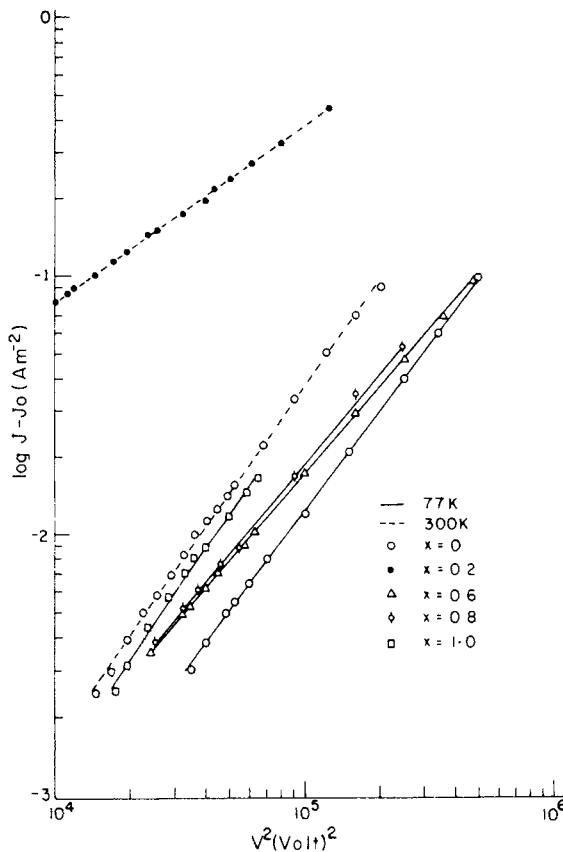


Figure 5. Variation of $(J - J_0)$ with V^2 for $\text{Al}/(\text{PbO})_{1-x}(\text{SnO})_x/\text{Al}$ pellets.

Table 3. The values of ϵ_r , V_T , θ and n_0

| x | ϵ_r at 300 K | T | V_T | θ | $n_0 \times 10^{-13} \text{ (m}^{-3}\text{)}$ |
|-----|-----------------------|-------|-------|-------------------------|---|
| 0 | 22.0 | 77 K | 160 V | 6.2973×10^{-4} | 3.0923 |
| | | 300 K | 96 V | 1.4113×10^{-3} | 4.1582 |
| 0.2 | 26.7 | 77 K | 130 V | 7.6644×10^{-4} | 2.7788 |
| | | 300 K | 9.0 V | 6.119×10^{-3} | 1.5359 |
| 0.4 | 38.5 | 77 K | 120 V | 5.7412×10^{-4} | 2.1998 |
| | | 300 K | 7.0 V | 6.0972×10^{-2} | 13.6046 |
| 0.6 | 37.4 | 77 K | 120 V | 2.0335×10^{-4} | 1.9447 |
| | | 300 K | 5.0 V | 9.7946×10^{-2} | 39.0406 |
| 0.8 | 32.8 | 77 K | 120 V | 4.8348×10^{-4} | 2.8743 |
| 1.0 | 23.9 | 77 K | 110 V | 1.2358×10^{-3} | 3.4686 |

where e is the electronic charge and n_0 the density of volume generated free carriers. The transition voltages obtained from J - V characteristics (figure 4) are fed into equation 5. The obtained values of V_T and n_0 are given in table 3. The observed increase in the value of n_0 for $x = 0.4$ and $x = 0.6$ may be attributed to the decrease in the band gap of mixtures (Vandenbroek *et al* 1969) as SnO concentration increases and the effect is enhanced with the increase in temperature. The ratio θ of density of free electrons (n_0) to trapped electrons (n_t) is very small ($\theta \ll 1$) in the samples (table 3) hence the observed J - V curves are explainable on the basis of a shallow trap model.

4. Conclusions

Chemisorption of oxygen is responsible for the decrease in electrical conductivity of lead tin monoxide during heating in air and desorption of O_2 increases the conductivity in vacuum. The thermal activation energies of screen printed layers are low in comparison to pressed pellets. Nonohmic conduction in pellets is explainable on the basis of the shallow trap model for SCLC in defect insulators.

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