OPTICAL AND ELECTRICAL PROPERTIES OF SnO₂ THIN FILMS IN RELATION TO THEIR STOICHIOMETRIC DEVIATION AND THEIR CRYSTALLINE STRUCTURE

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Undoped SnO₂ film layers were prepared using two different methods. With the classical "spray" method, the absorption edge is found to be 3.7 eV and the structure is polycrystalline; the importance of any stoichiometric deviation in relation to the production of conductive layers is discussed; the minimum value ρ_{min} of the resistivity is about 5×10^{-3} Ω cm. Samples prepared using a vacuum evaporation method ("flash" samples) are much more resistive, with $\rho \approx 2 \times 10^5$ Ω cm; the structure is amorphous with an absorption edge $E_G \approx 2.4$ eV; stoichiometric deviations are important, and the high resistivity obtained is related to the highly disordered structure.

1. INTRODUCTION

Since 1942 when McMasters[1] synthesized transparent and conductive tin oxide thin films for the first time, SnO₂ has been studied extensively. Of most recent interest is the possibility of using it as an optical and conductive window in photocell technology. A sufficiently conductive SnO₂ layer could be used as a metallic electrode in a metal–semiconductor structure, thus making it unnecessary to use a collector grid.

Recently a sputtering method (r.f. sputtering or d.c. diode sputtering) using SnO₂/In₂O₃ targets[2,3] has been developed that leads to layers of exceptional quality: a resistivity $\rho = 2 \times 10^{-4}$ Ω cm and a sheet resistance $R_\square$ of a few ohms, corresponding to a transmission $T \approx 70\%$ at $\lambda = 0.5$ μm. Unfortunately this method is not easy to use.

The results we present here were obtained using the classical spraying method with an alcoholic tin chloride solution[1,4] (SnCl₄·5H₂O). The influence of the various preparation parameters has been studied recently[5]. However, the existing bibliography shows an important scatter in the values of the optical constants (refractive index n, extinction coefficient k, gap E_G etc.) and the electrical constants (resistivity ρ, carrier concentration n etc.); the exact physical properties of SnO₂ appear to be difficult to establish.

The results we present show that the optical and electrical properties of SnO₂ layers depend on (1) the stoichiometric deviation (SnO$_{2-x}$) and (2) the crystalline structure (polycrystalline, amorphous). In particular we shall show the relation that exists between the increase in conductivity and the stoichiometric deviation in

polycrystalline SnO_2 layers prepared by the "spray" technique. Moreover, we shall also give some results on the layers obtained by the vacuum flash evaporation technique. These layers have an amorphous structure and even though their stoichiometric deviation is greater their resistivity is higher by many orders of magnitude.

2. PREPARATION

The deposits were generally obtained on glass substrates of known refractive index but for some optical measurements we used quartz substrates.

2.1. *The spraying method*
Details of the procedure and of a systematic study of the layers formed can be found elsewhere[5]; the method involves spraying an alcoholic $SnCl_4$ solution through a preheating furnace at a temperature T_1, the glass substrate being at a temperature T_2. The principal preparation parameters are T_1, T_2, the gas flow rate F (N_2, Ar or CO_2) and the spraying time t. The synthesis reaction is

$$SnCl_4 + 2H_2O \longrightarrow SnO_2 + 4HCl$$
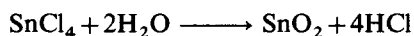
2.2. *The vacuum flash evaporation method*
SnO_2 powder* was first baked at 1200–1300 °C in a furnace under an inert atmosphere. This powder was then placed in the vacuum pumping unit and was projected into an alumina crucible which was heated to the sublimation temperature of SnO_2. The apparatus used was a flash evaporator type Balzers BSF 101.
The deposit formed on a glass substrate at temperature T_2. The pressure during evaporation was always less than 10^{-4} Torr.

3. EXPERIMENTAL RESULTS

The optical and electrical characteristics of typical samples are given in Table I.

TABLE I

CHARACTERISTIC PARAMETERS AT 300 K

Sample	Resistivity ρ (Ω cm)	Transmission T (%)	Thickness t (μm)	Sheet resistance $R_\square$ (Ω)
(a)	5×10^{-3}	80–90 ($\lambda = 0.4$–1.5 μm)	0.6	85
(b)	1.8×10^5	70–90 ($\lambda = 0.6$–3 μm)	2	—

(a) SnO_2 sample prepared by the spraying technique: $T_1 = 525$ °C; $T_2 = 475$ °C; $t = 3$ min; $F = 3$ l min^{-1}.
(b) SnO_2 sample prepared by the flash evaporation technique: $T_2 = 400$ °C; $t = 30$ min; pressure $= 8 \times 10^{-5}$ Torr.

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The SnO_2 sample prepared by evaporation was a light yellow colour; that prepared by spraying was transparent. The examination of the samples by electron diffraction confirmed the polycrystalline nature of the deposits obtained by the spraying technique; the presence of SnO and Sn was noted. In the case of samples obtained by vacuum evaporation the structure was amorphous; crystallization was beginning to occur for $T_2 > 600\,°C$.

3.1. Optical properties

The optical properties were studied by measuring the transmission T between $\lambda = 0.25\,\mu m$ and $\lambda = 3\,\mu m$ using a double-beam Beckman DK2A and Aminco DW-Z (UV–VIS) spectrophotometer.
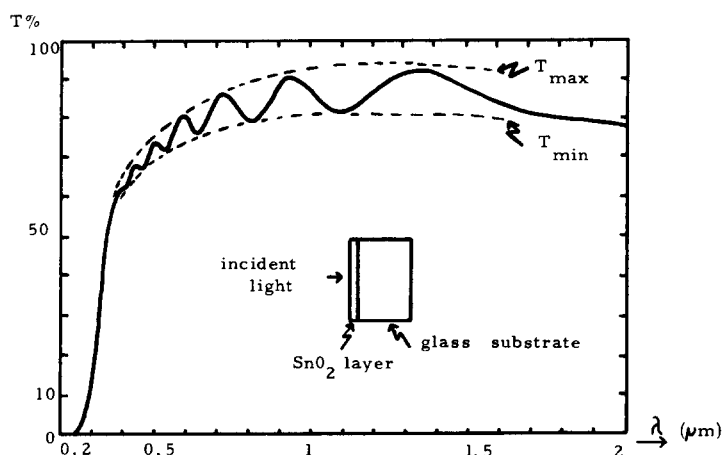

Fig. 1. The transmission spectrum at 300 K for an SnO_2 layer prepared using the spraying method: sample B370; fabrication parameters[5] $T_1 = 520\,°C$, $T_2 = 420\,°C$, $F = 3$ l min^{-1}, $t = 6$ min; $t = 0.90 \pm 0.04\,\mu m$.
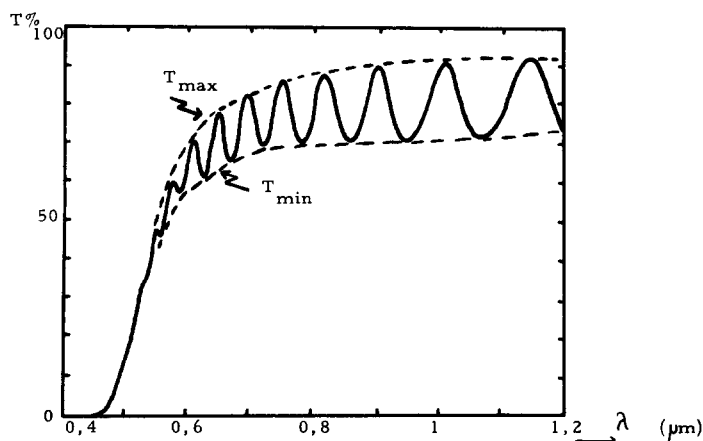

Fig. 2. The transmission spectrum at 300 K for an SnO_2 layer prepared using the flash evaporation method: sample 34; fabrication parameters[7] $T_2 = 400\,°C$, $t = 20$ min; $t = 2.03 \pm 0.08\,\mu m$.

Transmission spectra are given in Figs. 1 and 2 for the two types of samples. The optical constants were determined from the envelope curves T_{min} and T_{max} [6]. In the transparent region of these layers, between 0.4 and 1.5 µm for SnO_2 obtained by spraying and between 0.55 and 3 µm for SnO_2 obtained by vacuum evaporation, the variations of T are principally due to interference phenomena. We obtained [6]

$$n = \{N + (N^2 - n_0^2 n_1^2)^{1/2}\}^{1/2}$$

with

$$N = \frac{n_0^2 + n_1^2}{2} + 2n_0 n_1 \frac{T_{max} - T_{min}}{T_{max} \, T_{min}} \qquad (1)$$

$n_0 = 1$ is the refractive index of air and n_1 the refractive index of the glass substrate.

The thickness t of the layer can be calculated from two maxima or two minima using

$$t = \frac{M \lambda_1 \lambda_2}{2 \{n(\lambda_1)\lambda_2 - n(\lambda_2)\lambda_1\}} \qquad (2)$$

where M is the number of oscillations between the two extrema occurring for λ_1 and
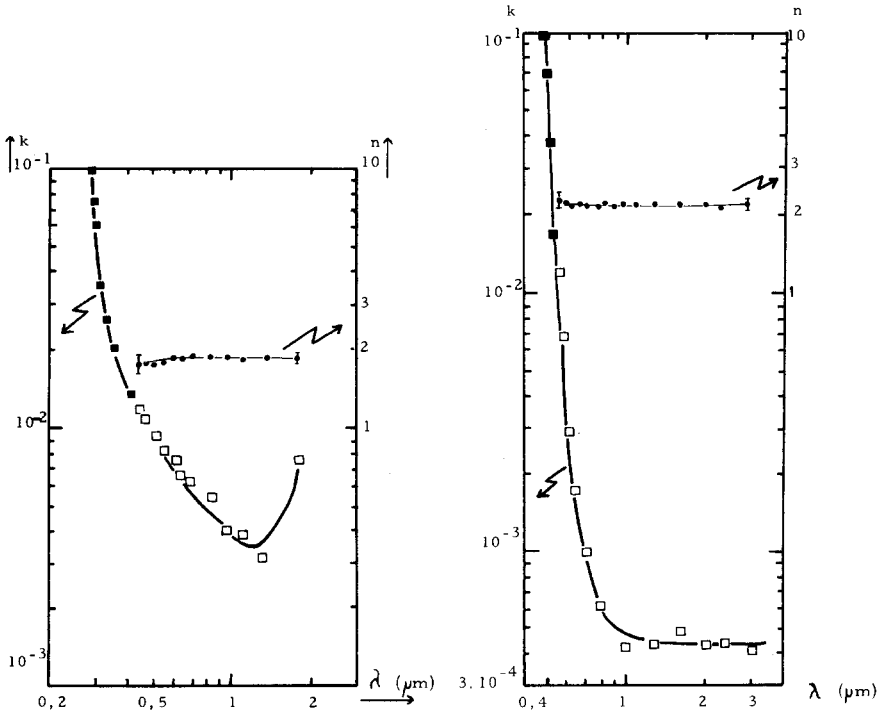
Fig. 3. The refractive index n and the extinction coefficient k *vs.* λ for a typical SnO_2 thin film (spraying method) at 300 K, sample B370: ■, values deduced from the fundamental absorption region, see eqn. (4); □, values deduced from the interference pattern, see Fig. 1.

Fig. 4. The refractive index n and the extinction coefficient k *vs.* λ for a typical SnO_2 thin film (flash evaporation method) at 300 K, sample 34: ■, values deduced from the fundamental absorption region, see eqn. (4); □, values deduced from the interference pattern, see Fig. 2.

λ_2, $n(\lambda_1)$ and $n(\lambda_2)$ being the corresponding refractive indices. Knowing t we can deduce[6] the value of the extinction coefficient k. Values of n and k are shown in Figs. 3 and 4 for an SnO$_2$ "spray" layer and an SnO$_2$ "flash" layer respectively. The relative error $\Delta n/n$ for these measurements does not exceed 4–5 %.

In the fundamental absorption region, the transmission T is given by

$$T = A \exp\left(-\frac{4\pi k t}{\lambda}\right) \tag{3}$$

with

$$A = \frac{16 n_0 n_1 (n^2 + k^2)}{\{(n_0 + n)^2 + k^2\}\{(n_1 + n)^2 + k^2\}}$$

for $k^2 \ll n^2$; the principal variation of T occurs in the exponential term, with $A \approx 1$. We obtained

$$T \approx \exp(-Kt) \tag{4}$$

and for the absorption coefficient K

$$K = 4\pi k/t$$

The value of the extinction coefficient k in the fundamental absorption region can be deduced; these values are in good agreement with those determined from the
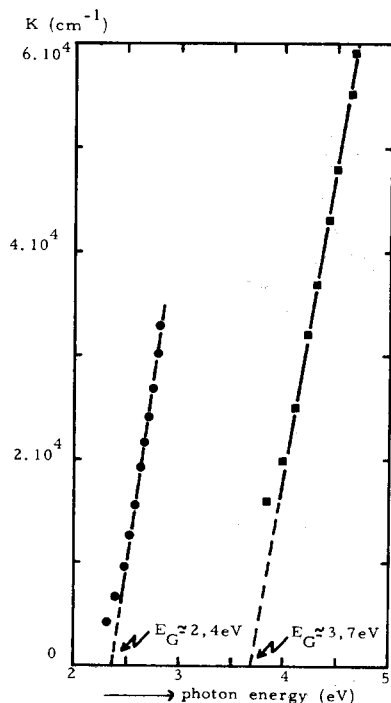

Fig. 5. The absorption coefficient K vs. the energy of the incident photons in the fundamental absorption region at 300 K: ■, sprayed SnO$_2$ sample B370; □, flash evaporated SnO$_2$ sample 34.

interference patterns (see Figs. 3 and 4). The variation of the absorption coefficient K with the energy of the incident light is shown in Fig. 5.

Thus we can deduce the absorption edge; it is found to be between 3.65 and 3.75 eV for "spray" samples[7] depending on the layer resistivity and between 2.3 and 2.5 eV for "flash" samples. It is difficult to correlate resistivity and optical gap for the "flash" samples, as was done by Arai[10] for the SnO_2 "spray" layer.

We report in Table II the values of these optical constants in the region of weak dispersion.

TABLE II

OPTICAL CONSTANTS AT 300 K

	n	k	E_G (eV)
SnO_2 "spray"	1.87 (0.8–1.8 μm)	Continuously variable	3.7
SnO_2 "flash"	2.15 (0.6–3 μm)	4×10^{-4} (0.8–3 μm)	2.4 ± 0.1

The increase of k (Fig. 3) observed for higher wavelengths ($\lambda > 1.2$–1.3 μm) is due to free carrier absorption. "Flash" SnO_2 is resistive enough to be studied by the capacitive method. Knowledge of the thickness t allows us to determine the value of the dielectric constant ε_r to be approximately 7–8; this value is slightly different from n^2 (≈ 5). The static dielectric constant of monocrystalline SnO_2 is strongly anisotropic for directions both parallel and perpendicular to the c axis; we find[8] that $\varepsilon_{r//} \approx 9$ and $\varepsilon_{r\perp} \approx 15$.

3.2. Electrical properties

The electrical properties of SnO_2 samples prepared by the same spraying method vary (see refs. 4, 5 and 9 and Table I). This is typical of the large number of parameters that are instrumental to the fabrication process. It should be noted that the resistivity *versus* temperature dependence varies very little between 77 K and 350 K; however, an irreversible evolution of ρ is observed for higher temperatures[9, 10].

For "flash" SnO_2, ρ was measured at 300 K (Table I) by studying sandwich and surface cells; the resistivity is very much greater for these samples.

4. STUDY OF THE STOICHIOMETRY OF THE SAMPLES IN RELATION TO THEIR RESISTIVITY

We tried to correlate the variation of ρ for "spray" SnO_2 to a stoichiometric deviation. It is well known that the high conductivity of tin layers is due to oxygen vacancies. We carried out tin dosimetry using a scanning electron microscope (SEM) and oxygen dosimetry by a nuclear reaction study; several layers of various resistivities were used.

4.1. SEM tin dosimetry

Measurements were made with a JEOL type JSMU3 SEM used as an X-ray analyser (beam intensity $I = 5 \times 10^{-9}$ A; accelerating voltage $V = 15$ keV). The same method could be used for oxygen but the light atomic mass of this element

leads to a very poor X-ray emission yield. As a reference, we used an SnO$_2$ crystal prepared using a gas phase transport method[11] (the high resistivity ($\rho \approx 10^{13}$–10^{14} Ω cm) of these crystals allowed us to assume a very good stoichiometry), or we used a tin substrate (99.995 %).

The results obtained show that there is an excess of tin in the layers compared with the theoretical stoichiometry:

$$\frac{\text{atomic mass of Sn}}{\text{molecular mass of SnO}_2} = \frac{118.7}{150.7} \approx 79\%$$

This excess cannot be evaluated precisely, however, because the thickness of the SnO$_2$ layers is less than the electron penetration given by eqn. (5)[12] for a tin substrate:

$$t(\mu m) = 0.033(E_0^{1.7} - E_K^{1.7})\frac{A}{Zd} \qquad (5)$$

where E_0 is the electron energy (15 keV), E_K the excitation level for Sn Lα_1 X-rays (4.445 keV), d the density (5.75 g cm^{-3}), Z the atomic number (50) and A the atomic mass (119 g). We find that $t \approx 1.2$ μm, but the thickness of the layers used was always less than 0.75 μm.

The stoichiometric deviation can be qualitatively accounted for, however, from the variation of the preparation parameters. The deviation is characterized by the variation of the tin concentration as evaluated by the ratio $\bar{c}$ of X-ray emission (X Sn Lα_1 counting rate) to the thickness of the layer.
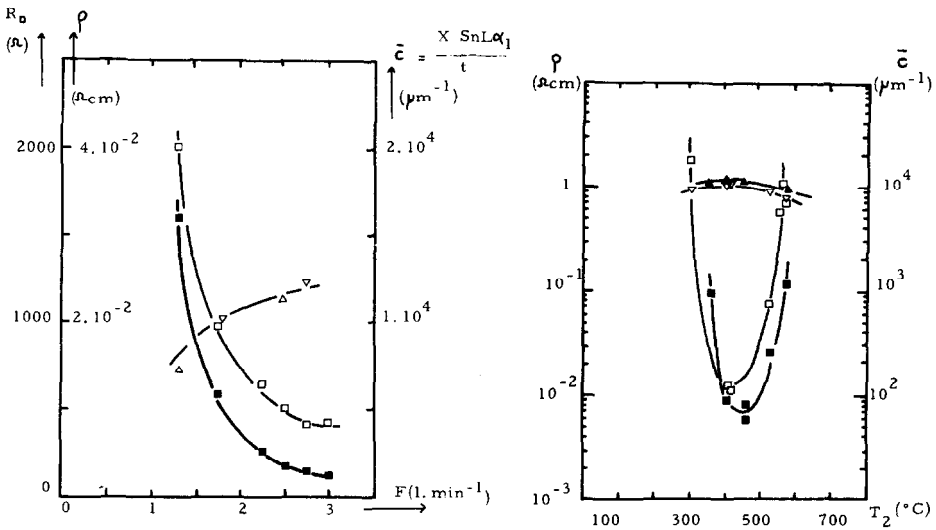

Fig. 6. The sheet resistance, resistivity and tin concentration *vs.* the gas flow rate F for an SnO$_2$ thin film (spraying method) at 300 K: ■, sheet resistance $R_\square$; □, resistivity ρ; △, concentration $\bar{c}$.

Fig. 7. The resistivity ρ and tin concentration $\bar{c}$ *vs.* the temperature T_2 of the substrate during preparation for an SnO$_2$ (spraying method) thin film at 300 K: □, resistivity for $F = 2.4 \pm 0.1$ l min^{-1}; ▽, tin concentration for $F = 2.4 \pm 0.1$ l min^{-1}; ■, resistivity for $F = 2.9 \pm 0.1$ l min^{-1}; ▲, tin concentration for $F = 2.9 \pm 0.1$ l min^{-1}; $T_1 = 500$–550 °C.

We show in Fig. 6 the variation of $R_{\square}$, ρ and $\bar{c}$ with gas flow rate[5], the other preparation parameters being kept constant. We note that a decrease in ρ corresponds to an increase in the tin concentration $\bar{c}$ and also that the X Sn Lα_1 counts number in the SnO_2 "flash" layers always corresponds to a concentration $\bar{c}$ which is greater than that of "spray" samples. The high resistivity observed must be related to an increase in the disorder of these films (amorphous structure).

4.2. *Dosimetry of oxygen by the direct observation of nuclear reactions*[13]

The method consists of the direct observation of nuclear reactions induced by charged particles impinging on oxygen nuclei. A beam of deuterons bombards the target under study; the reaction is

$$^{16}O + \text{incident deuteron} \longrightarrow {}^{17}O + \text{emitted proton}$$
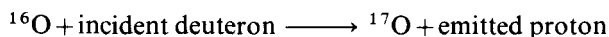
The number of protons emitted by the target are then counted. Using a reference target, with a known number of ^{16}O atoms per surface unit, we can deduce either the thickness of a stoichiometric oxide layer or the stoichiometric deviation if the thickness is known. It is not possible to use a similar method for counting the tin atoms because tin atoms are too heavy to contribute to nuclear reactions.

We used an SnO_2 layer deposited on a germanium substrate[7] for determining the oxygen counting rate because a glass substrate would have introduced spurious nuclear reactions.

The results obtained by this accurate method confirm the measurements carried out by SEM and show an important oxygen deficiency in the layers.

4.3. *Discussion*

We showed in Fig. 6 that the stoichiometric deviation corresponds to a tin excess and is closely correlated to an increase in the conductivity. Figure 7 shows the variation of ρ and the tin concentration $\bar{c}$ with the temperature T_2 of the substrate for two gas flow rates (2.4 l min^{-1} and 2.9 l min^{-1}). In both cases we observed that the minimum of the resistivity ρ shifted from $T_2 = 400\,°C$ ($F = 2.4$ l min^{-1}) to $T_2 = 450\,°C$ ($F = 2.9$ l min^{-1}). This minimum corresponds to a maximum in the tin concentration $\bar{c}$.

It should be noted that the variation of $\bar{c}$ corresponds to a drastic change in resistivity. It is difficult, however, to present quantitative results because foreign atoms such as chlorine are present in large quantities in the layer, as we have shown by SEM measurements. It is assumed here that a Cl$^-$ ion with a radius[14] $R_{Cl^-} = 1.81$ Å could substitute for an O^{2-} ion of radius $R_{O^2} = 1.46$ Å. Such a substitution would lead to an increase in conductivity.

5. CONCLUSION

We have studied SnO_2 layers prepared using two different methods. The essential characteristic of "spray" deposits is the polycrystalline structure; "flash" deposits have an amorphous structure.

Most of our experimental results were made on layers obtained using the spray method; for this case we verified that the resistivity decreases as the tin concentration increases. It is also certain that the order of the structure plays a

preponderant role since the high resistivity "flash" SnO$_2$ layers are associated with the greatest stoichiometric deviation. This can be related to our observations on SnO$_2$ "spray" doped layers (with Sb or F). The resistivity of these layers first decreases with dopant concentration; larger quantities of dopant correspond to an important increase in resistivity associated with an increase in disorder.

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