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INDIUM OXIDE DEPOSITION ON GLASS BY AEROSOL PYROLYSIS (PYROSOL(R) PROCESS)

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The Pyrosol(R) process involves the pyrolysis of an aerosol generated by ultrasonic nebulisation from a solution of organic or inorganic compounds. This technique was used to deposit transparent n-conducting indium oxide films on glass. The electrical and optical properties of these films were studied as a function of the deposition temperature and doping (using tin or fluorine). A deposition temperature of 480°C and a Sn/In ratio of about 5% gave the best results. In this case, the transmission in the visible range was 92%, the infrared reflection 84% and the electrical resistivity 1.7×10^{-4} Ω. cm.

INTRODUCTION

In recent years, transparent conductive coating such as indium oxide on glass have become the object of a great deal of research. In fact, these oxides possess simultaneously a high optical transmission in the visible region of the spectrum, a good reflectivity in the infrared range and a low resistivity.

Glasses coated by thin films of tin oxide or indium oxide find a large number of different applications such as: heating glasses (used to de-ice the windshields of aircraft), distillation columns, conductive electrodes in liquid-crystal information display devices, antistatic coatings, thermal reflectors (glass panes capable of reflecting the infrared; solar energy captors).

These thin oxide films can be deposited by metal evaporation followed by oxidation (1) or by the sputtering technique (2-4) or by chemical vapor deposition (5-7) or, of course, by aerosol pyrolysis(8). The aim of the present work is to study the optical and electrical properties of doped or undoped indium oxide thin films deposited on glass by the Pyrosol(R) process (9). This process had initially been developped for the deposition of semi transparent iron oxide films (10).

EXPERIMENTAL CONDITIONS

OXIDE DEPOSITION

The Pyrosol(R) process consists principally of a low temperature pyrolysis (200°C to 500°C) of an aerosol, which in its turn has been obtained by ultrasonic treatment of a solution of a mineral salt or an organometallic compound of the metal to be deposited. This process presents a number of advantages, from the point view of technique, when compared with the standard method involving the nebulisation of the solution to be pyrolysed by the spraying technique. In fact, since for an identical gas flow the Pyrosol (R) process gives a finer and more homogeneous aerosol than that obtained by spraying, it can be considered as a very interesting technique. It has been used to produce aerosols which subsequently by pyrolysis, led to the formation of deposits of indium oxide. The main parts of the apparatus used to carry out this process are (figure 1):

- a furnace,
- a substrate holder which, to ensure a regular thickness of the film , rotates and simultaneously moves transversally,
- an ultrasonic atomizer,
- four nozzles to transfer the aerosol to the proximity of the substrate.

The various experimental parameters influencing the rate of growth and the properties of the deposits, for a given solution, are the following :

- nature and flow rate of the carrier gas,
- flow rate of the aerosol,
- nozzle temperature,
- substrate temperature ,
- nozzle-substrate distance ,
- speed of rotation and transverse movement of the substrate holder.

The thin films of indium oxide were obtained by treating a solution of indium acetylacetonate (decomposition temperature 280°C; sublimation temperature 260°C) in acetylacetone (boiling point : 136-140°C), the carrier gas being air.

The reaction which takes place is the following:

$$(C_5H_7O_2)_3\,In + 18\,O_2 \rightarrow \frac{1}{2}\,In_2O_3 + 15\,CO_2 + \frac{21}{2}\,H_2O$$

Thin or fluorine doped indium oxide thin films can be prepared by the addition in the solution to be atomized, either of dibutyltin diacetate or trifuoroacetic acid in known quantities.

DEPOSITED FILMS CHARACTERISATION

Deposited materials were identified by X-ray diffraction. The composition of the doped films were determined by an electron microprobe. The thickness of the deposits was measured by the stylus method (Talystep apparatus by Rank Xeros).

The surface resistances were measured by the in line four points method and the resestivities calculated from the formula : $\rho_{\Omega cm} = R_{\Omega} \times e_{cm}$ (R = surface resistance, e = thickness of the deposit).

The optical properties of these thin films were determined by measuring the optical transmission in the visible region of the spectrum and the infrared reflection.

RESULTS AND DISCUSSION

1 - INFLUENCE OF TEMPERATURE

The growth of these films has been studied as a function of temperature. The experimental conditions used were the following:

- solution concentration	0.05 mole.l^{-1}
- Flow rate of carrier gas	30. l. min^{-1}
- Flow rate of aerosol	80 cc. hr^{-1}
- Speed of rotation of substrate holder	8 revs. $min.^{-1}$
- Speed of transverse movement of substrate holder	1.3 mm. min^{-1}
- Distance between nozzle and substrate	20 mm
- Nozzle temperature	90°C

From figure 2, it can be seen that the growth rate is a linear function of temperature in the investigated range. From figure 3, which shows the effect of deposition temperature on resistivity, it can be seen that the resistivity of the deposited In_2O_3 decreases with an increase in temperature. However, above 480°C, the thin films take a frosty colour which reduces to a great extend the optical

transmission. The cause of this phenomenon is undoubtedly due to the formation of In_2O_3 in the vapor phase.

Measurements of the Hall effect show that the deposited indium oxide is a n-type conductor and that an increase of the deposition temperature has a greater effect on the free carrier density than on their mobility. This is well illustrated on figure 4. The departure from stoichiometry increases with the deposition temperature causing thus an increase of the number of free carriers, but their mobility remains constant above 450°C, probably as the result of a saturation of the scattering centers.

The influence of the deposition temperature on the optical properties of the thin films was also studied (table I). It was noticed that transmission in the visible region is practically independent of the deposition temperature in the range 440°C-480°C. On the contrary, beyond 480°C it falls sharply and the indium oxide thin films have a hazy appearance. This change can be attributed to the formation of In_2O_3, in the vapor phase, within the very close proximity of the substrate.

The infrared reflection, as well as the free carrier density, increases with the deposition temperature and this is illustrated on figure 5. This phenomenon is due to the influence of the conduction electrons on the optical characteristics in the near infrared (11).

2. DOPING EFFECT

The indium oxide thin film can be doped by elements having a valency either geater than indium or lower than oxygen. The consequence of this doping is an increase in the concentration of free carriers and hence a decrease in the resistivity.

The effect of doping indium oxide by tin and fluorine has been studied. The doping was carried out by means of an indium acetylacetonate solution in acetylacetone containing known quantities of dibutyltin diacetate. The temperature of deposition was 480°C, the experimental conditions being the same as those used for the preparation of undoped indium oxide films. A number of preliminary experiments showed that there exists a proportionality factor equal to 1.5 between the Sn/In ratio in the deposited material and in the solution to be nebulized (figure 6). Therefore, it would appear that the deposition rate of tin is greater than that of indium under the same experimental conditions.

The influence of the tin content on the film resistivity was also investigated. Figure 7 summarizes the results obtained and shows that the resistivity reaches a minimum ($\rho = 1.7 \times 10^{-4}$ Ω. cm) for Sn/In ≃ 5%.

The dependence of the concentration of free carriers and their mobility upon the Sn/In ratio is represented on figure 8. As this ratio increases from 0 to 8% the free carrier density simultaneously increases, reaching a maximum value of the order 7×10^{20} cm^{-3}. When the Sn/In ratio surpasses the 8% value the free carrier density diminishes while their mobility remains virtually constant.

A variation of free carrier density as a function of Sn/In ratio is always followed by variation of the infrared reflectivity as shown on figure 9. However, the transmission in the visible region remains unaffected.

So tin doping of indium oxide films prepared by the Pyrosol(R) process, improves their electrical and optical properties (table) The reflection curves for doped (Sn/In = 5%) and undoped indium oxide thin films can be seen on figure 10. Note the sharp cut-off at $\lambda \simeq 1.8\,\mu$ for the doped film. As for the pure In_2O_3 films, the tin doped indium oxide films are also stable up to 200°C. At higher temperature there is an increase in resistivity accompanied by a reduction of the reflectivity in the infrared region (table).

The experiments involving fluorine doping, which was introduced by the addition of trifluoroacetic acid to the solution to be nebulized, were negative. This means that doped films have always a greater resistivity than undoped films.

CONCLUSIONS

The sum of the results obtained by the Pyrosol(R) process demonstrate that glasses can be coated with indium oxide thin films, tin doped or undoped. The properties of these films are superior or, at least, equal to those obtain by other techniques (table) and their adherence to the substrate is excellent. From the above statements and from the fact that no vacuum equipment are required, the Pyrosol(R) process can be considered as an extremely useful technique which can be used for coating glass panes in continous production and internal tube surfaces. Actually, the above process is about to be used for the production of infrared reflector glasses and heater tubes of large dimensions.

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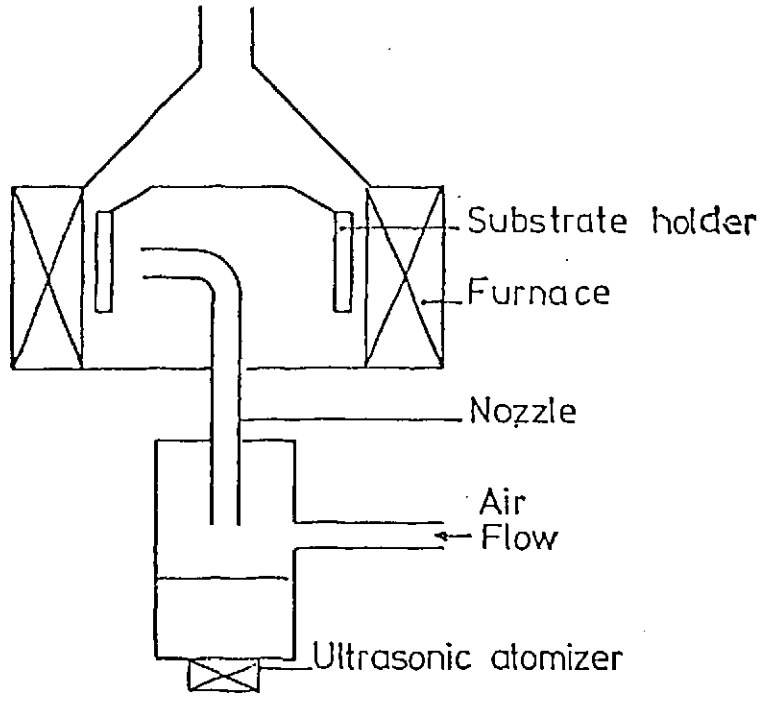

Figure 1 : Schematic diagram of Pyrosol$^{(R)}$ process.

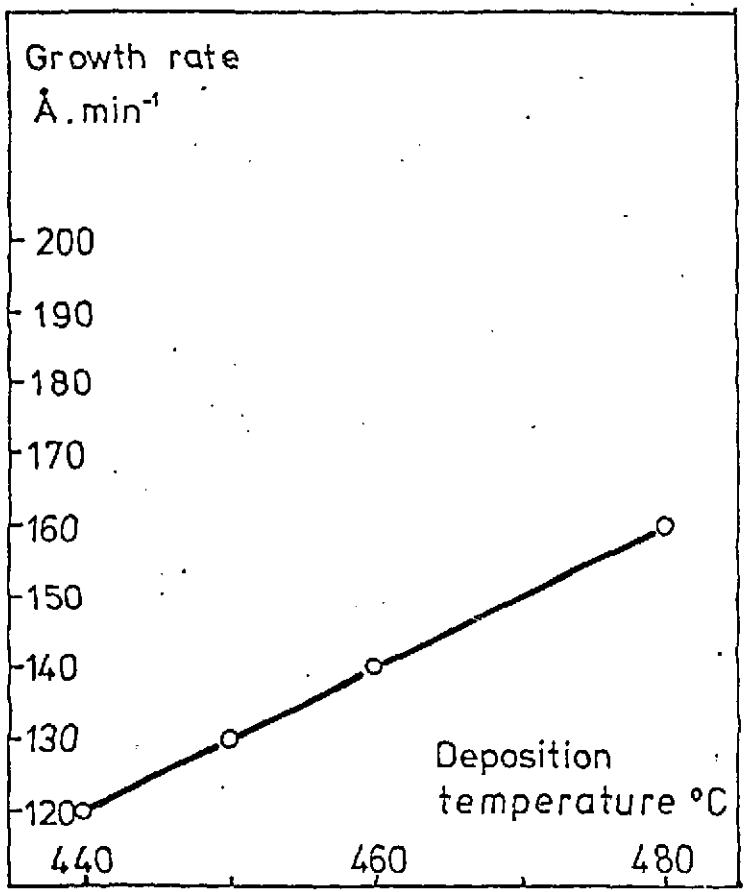

Figure 2: Effect of deposition temperature on growth rate.

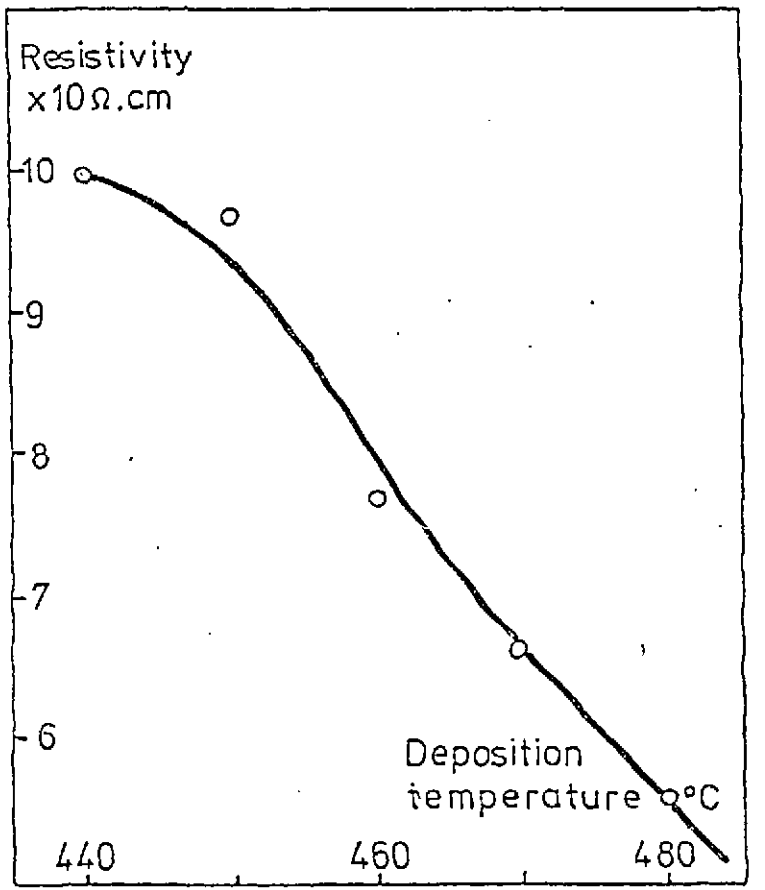

Figure 3: Resistivity as a function of deposition temperature.

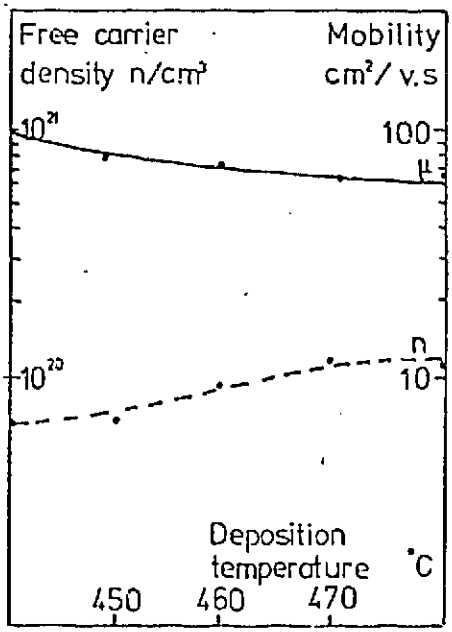

Figure 4

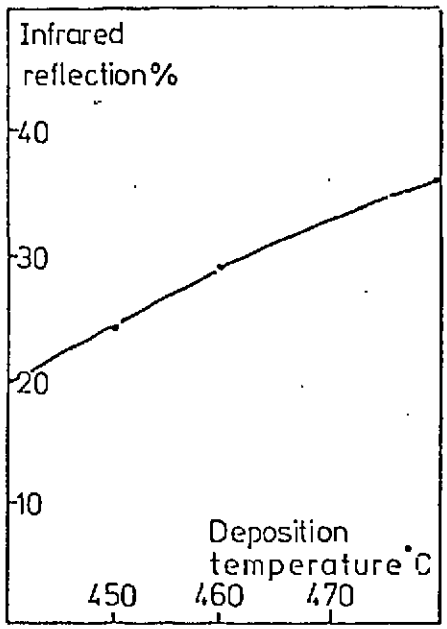

Figure 5

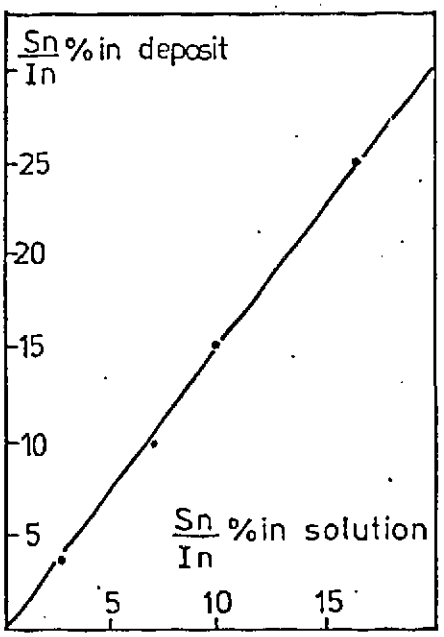

Figure 6

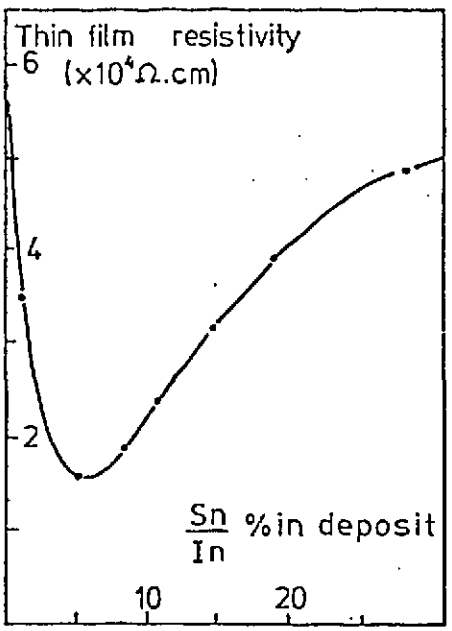

Figure 7

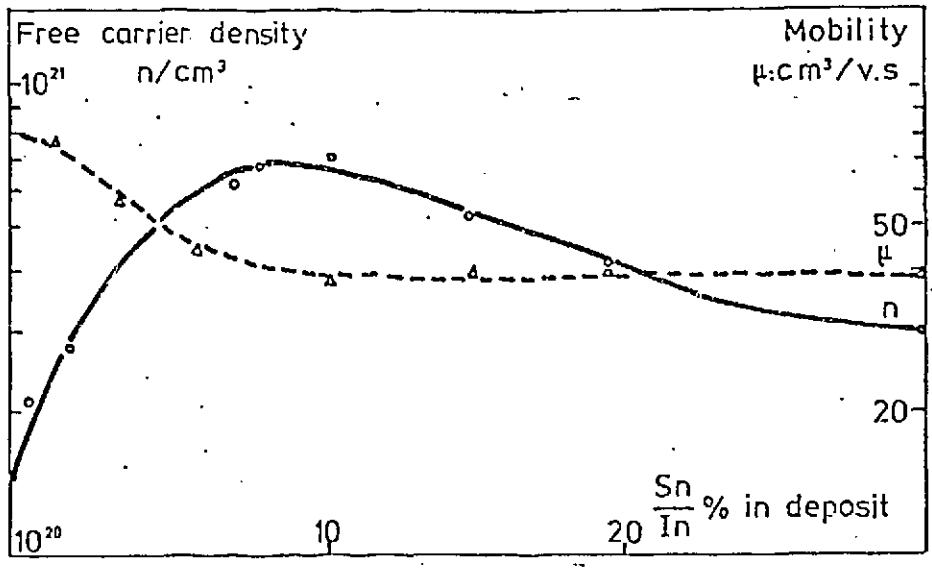

Figure 8 : Effect of Sn/In % in deposit on free carrier density and mobility.

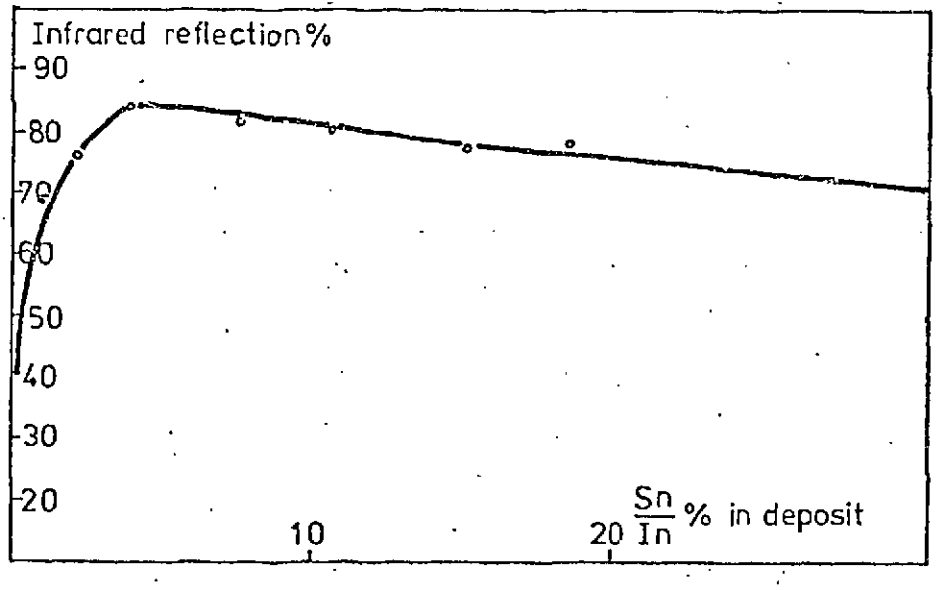

Figure 9: Effect of Sn/In % in deposit on infrared reflection.

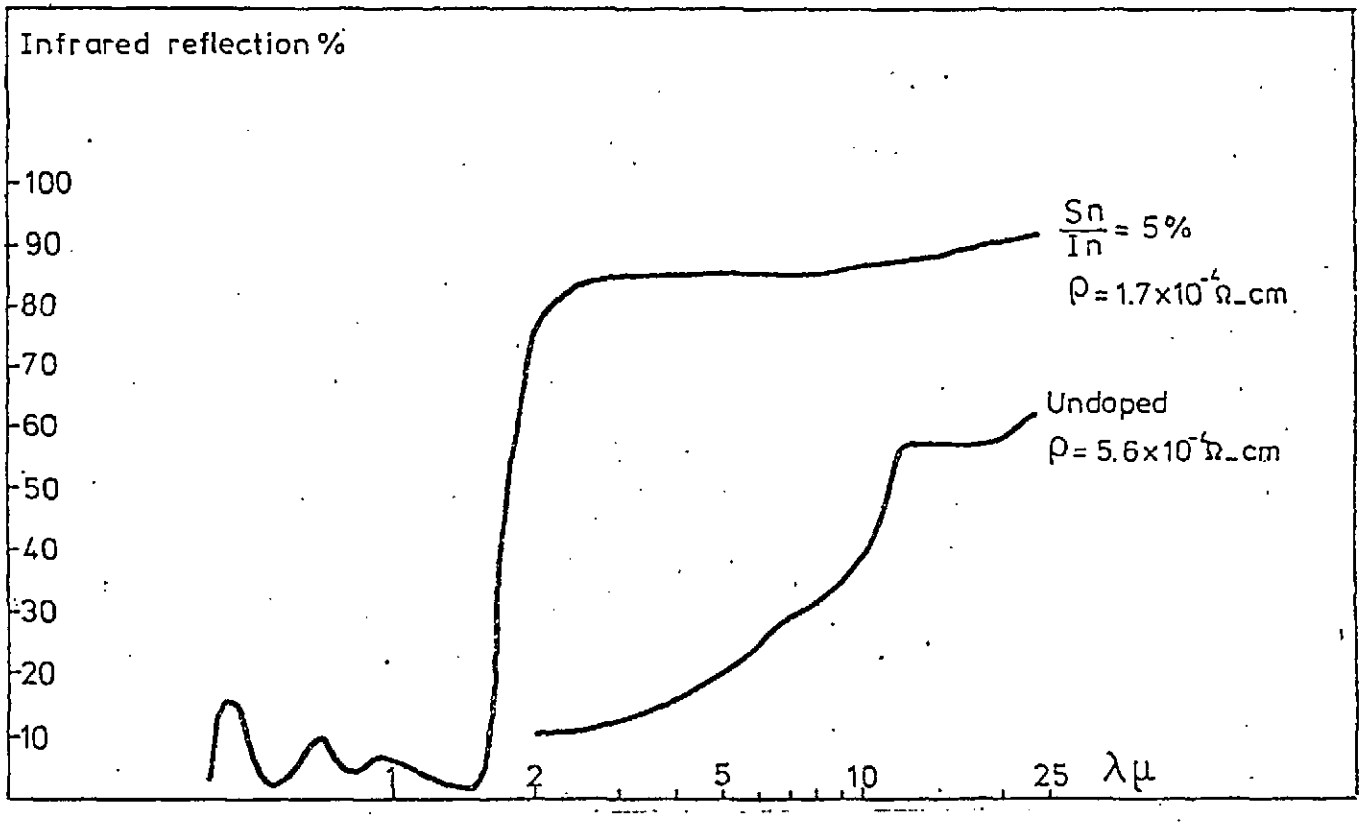

Figure 10 : Infrared reflection as a function of the wavelenght for doped and undoped indium oxide.

Table I

Deposition Temperature °C	Resistivity x 10^4 Ω. cm	Infrared reflection %				Optical transmission %		
		at λ=4μ	at λ=8μ	at λ=25μ	from λ=2.5μ to =25	at λ=5000 Å Å	at λ=6000 Å	from λ=4000 Å to λ=8000 Å
440	10.2	8	16	50	20	96	90	91
450	9.7	9	24	54	24	95	89	90
460	7.7	13	39	66	29	98	97	92
480	5.6	20	44	72	36	83	96	92

Table II

$\frac{Sn}{In}$ %	Resistivity x 10^4 Ω. cm	Infrared reflection %				Optical transmission %		
		at λ=4μ	at λ=8μ	at λ=25μ	from λ=2.5μ to λ=25 μ	at λ=5000 Å	at λ=6000 Å	from λ=4000 Å to λ=8000 Å
0	5.6	20	44	72	36	96	92	91
0.9	3.2	58	77	86	69	91	89	93
1.8	2.8	70	79	84	76	91	86	91
5	1.7	79	87	92	84	92	97	93
7.4	1.8	76	82	91	81	98	89	91
10.4	2.3	75	84	91	80.5	97	92	92
15	3.0	73	79	87	78	97	88	89
19.4	3.7	73	88	88	80	91	86	87
30	4.9	64	74	89	70	92	85	88

Table III

$\frac{Sn}{In}$ % in deposit		0	7
Thin films transmission in the visible region %	as deposited	91	91
	after annealing at 200°C for 60 hours	91	91
	after annealing at 400°C for 20 hours	92	91
Thin films infrared reflection %	as deposited	36	81
	after annealing at 200°C for 60 hours	36	81
	after annealing at 400°C for 20 hours	8	38
Resistivity $\times 10^4$ Ω. cm	as deposited	5.6	1.8
	after annealing at 200°C for 60 hours	5.6	1.8
	after annealing at 400°C for 20 hours	31	6.1

Table IV

Technique	Sputtering	Sputtering	Pyrosol	Sputtering	Sputtering	Sputtering	Spraying	Pyrosol
Références	3	12		3	13	2	8	
Treatment		Heat reducing treatment						
ρ Ω. cm	13×10^{-4}	$< 10^{-2}$	5.6×10^{-4}	1.77×10^{-4}	6.25×10^{-4}	3×10^{-4}	2.2×10^{-4}	1.7×10^{-4}
Transmission in the visible range %	77		92	79	93	86		92
$\frac{Sn}{In}$ %	0	0	0	18	target composition 20%		5.5	5