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PHYSICAL AND ELECTRICAL PROPERTIES OF $\text{In}_2\text{O}_3 : \text{Sn}$ FILMS. APPLICATIONS TO OPTOELECTRONIC DEVICES

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Résumé. — Des dépôts conducteurs et transparents d'oxyde d'indium dopé à l'étain ($\text{In}_2\text{O}_3 : \text{Sn}$) préparés par une simple méthode *spray* ont été caractérisés.

Les concentrations de dopants ont été déterminées par une méthode de microanalyse X adaptée, et comparées avec les concentrations dans la solution.

Les propriétés électriques ont été reliées aux résultats physiques de façon à contrôler le processus de fabrication en vue d'applications optoélectroniques.

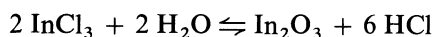
Abstract. — Transparent highly conductive layers of tin doped indium oxide, $\text{In}_2\text{O}_3 : \text{Sn}$, prepared by a simple spraying method have been characterized. Stoichiometry and dopant concentrations of the layers, determined by an adapted method of X-ray microanalysis have been compared with concentrations in the solution. Electrical properties are related to the physical results in order to control the process for optoelectronic applications.

1. Introduction. — Recent interest in the fabrication of Schottky or heterojunction (H.T.J.) diodes is directly motivated by the greater facility of preparation, a lower cost than p-n⁺ Silicon junction diodes.

Prepared using a vapor transport method (spray), tin-oxide (SnO_2) and indium oxide (In_2O_3) with dopant in thin layers are degenerate semi-conductors n-type ($n = 10^{20}$ to 10^{21} cm^{-3}) and have a high transparency across the visible to near infrared (IR) spectrum [1]. They can be used as transparent and protective electrodes in the fabrication of solar cell structures. Moreover, they could be used on polycrystalline silicon substrates in future technology (due to the low-temperature processing). They have also a high reflectivity in the I.R. So they can be used in flat plate collectors technology as spectral selective windows with large transmission for solar radiation and high reflection for thermal I.R. thus increasing the efficiency of the black-body collector.

We present here results concerning thin films of In_2O_3 with tin dopant on glass and silicon substrates.

2. Thin films experimental preparation. — As reported elsewhere [2], an aerosol stream containing an alcoholic solution of SnCl_4 or InCl_3 and an additional dopant is sprayed through a preheating furnace onto a heated substrate. The method of hydrolysis is based on the reversible endothermic reaction



which appears at 350 °C. The best results have been obtained for doping by adding stannic chlorine hydrated ($\text{SnCl}_4, 5 \text{H}_2\text{O}$).

A gas flow (nitrogen) is used as a carrier with a typical rate of about 31/min. The deposition rate can vary from 2 000 Å to 4 000 Å/min. The typical layer thickness is 2 000 Å on a heated substrate at 500 °C.

The value of the transparency (up to 85 %) can be easily optimized. The R_{\square} value is reported on the figure 1 as function of the atomic ratio Sn/In in the solution (for a preheating furnace temperature T_1 and

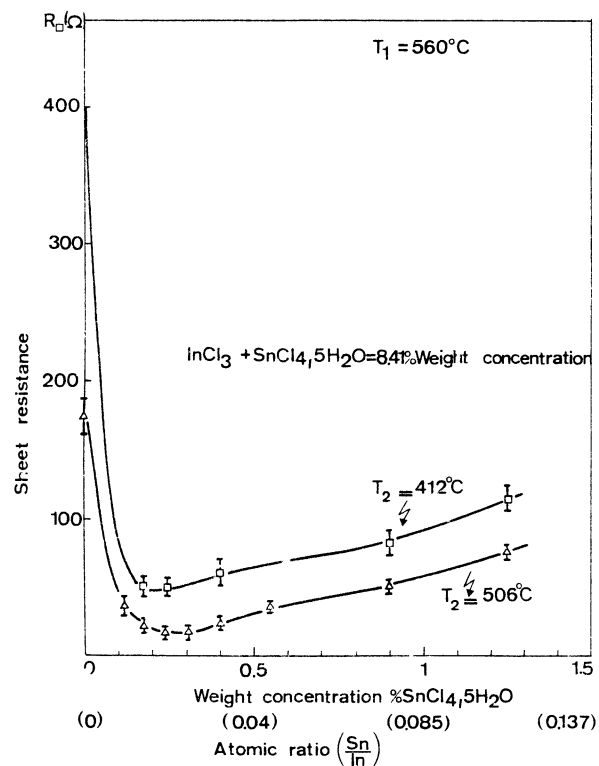


FIG. 1. — Sheet resistance R_{\square} versus $\text{SnCl}_4 \cdot 5 \text{H}_2\text{O}$ weight concentration. The Sn/In atomic ratio is also indicated.

two different substrate temperatures T_2). Moreover, parameters such as substrate temperature during deposition or Sn/In atomic ratio in the layers can be of critical importance for the open circuit voltage V_{oc} of the solar cell. It has been shown recently [3] that conversion efficiency around 10 % for Si(n)- In_2O_3 : Sn structures under AM1 illumination can be obtained with lower substrate temperature (430-450 °C) and higher Sn/In atomic ratio than the ones corresponding to the minimum sheet resistance reported on the figure 1. So, the knowledge of Sn/In atomic ratio is needed for these applications.

3. Characterization of the films. — As needed for a better knowledge of layer composition, quantitative dosimetry (element In, Sn, Cl, O) have been performed using an X-ray microanalyser. Qualitative analysis have been made using secondary ion mass spectroscopy (S.I.M.S.) in order to obtain ion mass spectrum and concentration profiles in the layer depth.

3.1 S.I.M.S. MEASUREMENTS. — A positive ion mass spectrum is shown in figure 2 for a film deposited on borosilicate glass slide. Many impurities appear in this spectrum (K, Na, Si, Al, B, Cl, F).

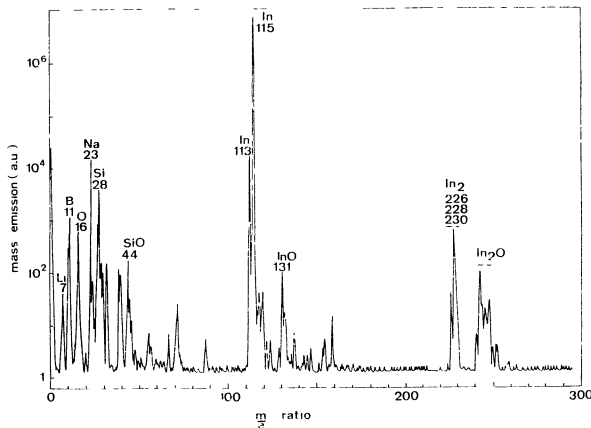


FIG. 2. — Dynamic positive secondary ion mass spectrum on an In_2O_3 : Sn layer (Borosilicate glass substrate).

An example of profiling by S.I.M.S. for the same In_2O_3 : Sn layer obtained by monitoring the intensity of appropriate masses, for a large area under continuous ion bombardement is shown in figure 3.

The accumulation at the interface of alkali ions and silicon can be noted, the borosilicate glass acting as a diffusion source for these elements.

The profiles show that the concentrations of major elements in the film (In, Sn, O) are practically constant.

3.2 ELECTRON PROBE MICROANALYSIS. — Quantitative dosimetry have been made on many thin layers of In_2O_3 : Sn which thickness varies from 1 000 Å to 4 000 Å.

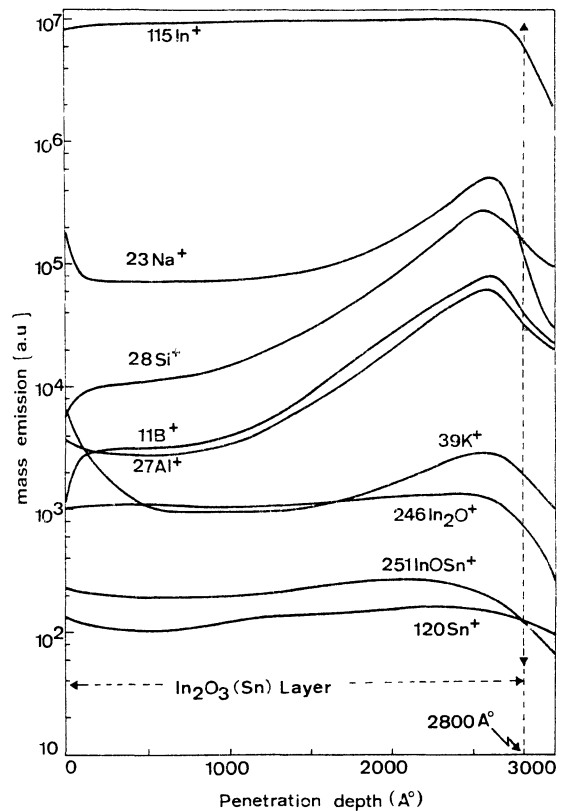


FIG. 3. — Depth profiling for an In_2O_3 : Sn layer. Positive ion mass spectra (Borosilicate glass substrate).

The quantitative use of X-ray microanalysis on thin films involves specific problems, that we try to solve by an appropriate solution [4]. We essentially take into account :

- of the electron penetration larger than the layer thickness,
- of the mean energy of electrons passing through the layer, which is bigger than the excitation energy of the characteristic emission of the elements being in the layer,
- of the mean energy of the backscattered electrons coming from the substrate.

A conventional method for corrections can be adapted to this new situation, only the measurements corresponding to an element present in the substrate (silicon in our case) and eventually the layer thickness are needed.

All the measurements need a standard for each analysed element and assume that the concentration of the elements determined by the analysis are constant in depth.

The concentration of the elements Sn, In, Cl have been tested to be constant in depth by S.I.M.S. profiles and are determined on a CAMECA microprobe using compound standards, oxygen have been determined by difference.

The stoichiometry and the atomic ratio Sn/In and Cl/In can be determined with an accuracy better than 5 %. Some examples of physical and electrical results are reported on the table I.

TABLE I

Sample	n cm^{-3}	ρ $10^{-4} \Omega \text{ cm}$	$\frac{\text{Cl}}{\text{In}}$ Solution	$\frac{\text{Cl}}{\text{In}}$ layer	$\frac{\text{Sn}}{\text{In}}$ Solution	$\frac{\text{Sn}}{\text{In}}$ layer	Thickness (\AA)
412	7.8×10^{19}	26.6	14.0	0.006	0.0	0.001	1 400
415	3.2×10^{20}	7.6	14.0	0.033 6	0.004 5	0.007	1 600
434	7.4×10^{20}	5.2	14.5	0.009	0.023	0.040	4 800
224	4.2×10^{20}	14.8	15.6	0.008 5	0.076	0.20	2 000
527	5.2×10^{20}	11.2	16.2	0.017 5	0.105	0.159	2 700
525	4.1×10^{20}	51.6	19.4	0.025	0.25	0.26	1 220

The Sn/In atomic ratio have been compared for the initial solution and the deposited layers, for the two types of substrates. The figure 4 reports the results obtained on borosilicate glass and the figure 5 compares some results obtained on glass and silicon substrates. Using this two curves, a linear relation can be established which corresponds to a slope of 1.6, so a more important quantity of the dopant exists in the layer than in the solution.

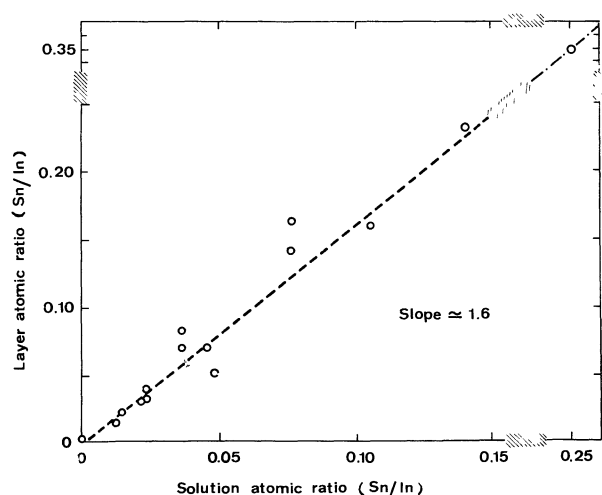


FIG. 4. — Sn/In atomic ratio in the $\text{In}_2\text{O}_3 : \text{Sn}$ layers versus Sn/In atomic ratio in the solution determined by X-ray microanalysis (Borosilicate glass substrate).

Such a curve can be plotted for the chlorine quantity. The figure 6 represents the atomic Cl/In ratio versus Sn/In atomic ratio, where a linear variation can be also investigated. The initial chlorine concentration (for Sn/In = 0) is still important, due to the presence of InCl_3 and HCl in the solution.

4. Electrical properties. — Hall measurements permit the determination of the value of the carrier concentration n and the mobility μ_H . The properties of some typical films with the lowest sheet resistance and highest optical transparency are listed in the table I. A free electron density of $n \approx 10^{21} \text{ cm}^{-3}$ can

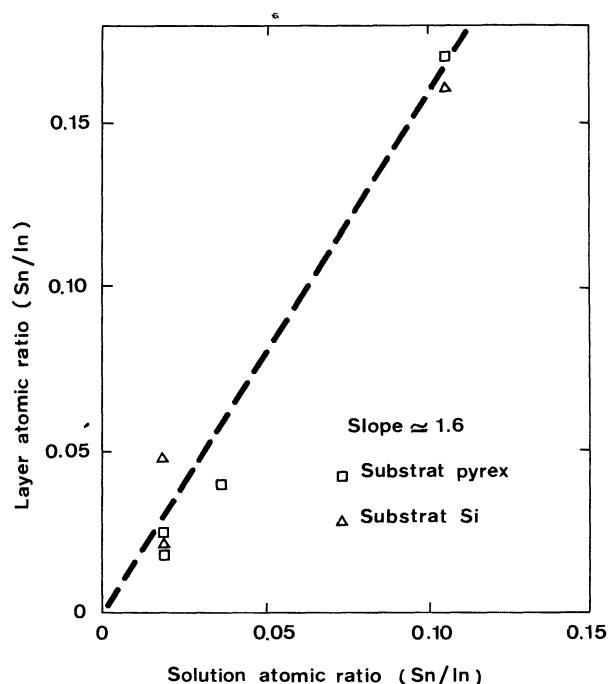


FIG. 5. — Sn/In atomic ratio in layers versus Sn/In atomic ratio in the solution for pyrex and silicon substrates.

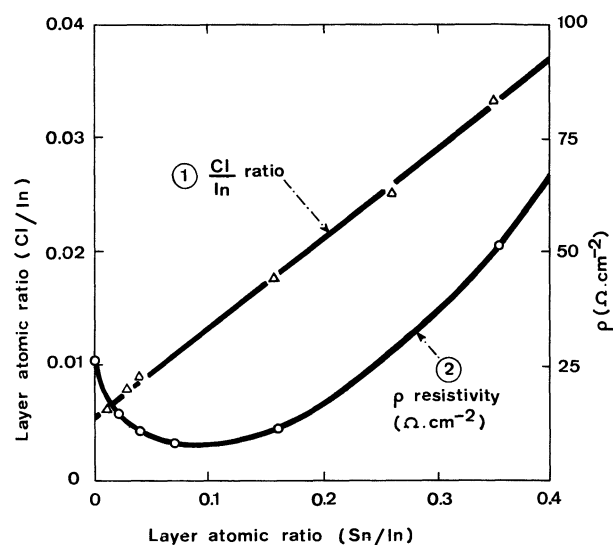


FIG. 6. — Cl/In atomic ratio and resistivity of the layers versus atomic ratio Sn/In in the solution.

be achieved corresponding to a strongly degenerate semi-conductor.

The variation of the resistivity as function of the atomic ratio Sn/In is also plotted on the figure 6.

A maximum is observed in the carrier concentration, which corresponds to a minimum of the resistivity, for an atomic ratio Sn/In = 0.04 in the layer.

The contribution to the conductivity of the ionized donors and the stoichiometry deviation has to be taken into account to explain the variation of the free carrier density with Sn/In. The heat treatment results are in good accordance with this analysis. After annealing under inert ambient (Ar) a decrease in the sheet resistance is observed even for highly doped samples corresponding to the creation of oxygen vacancies [5].

The difference in crystalline quality according to the various methods of preparation could easily explain the scattering in the Sn/In atomic ratio found to give the lower resistivity films.

5. Conclusion. — In_2O_3 : Sn layers prepared using a very simple and cheap *spray* method have been characterized from the point of view of physical and electrical properties. In spite of a certain spread in the results, a good correlation can be obtained between electrical properties and the physical parameters, as dopant concentration determined by X-ray micro-analysis and S.I.M.S. The choice of good experimental conditions of fabrications would permit to optimize the optical and the electrical properties.

These layers which have figure of merit of the same order of magnitude than those obtained by the best deposition technique, can be made easily with a high production rate necessary to industrial applications. They have also a good adherence and stability.

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