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Influence of the Substrate on the Composition of Pd-Doped Tin Oxide Thin Films Studied by EPMA and SNMS

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Résumé. — Des couches minces d'oxyde d'étain ont été déposées sur silicium oxydé, sur alumine et sur Si_3N_4, en utilisant la pyrolyse d'un aérosol produit par pulvérisation à haute fréquence. La composition élémentaire a été étudiée par microanalyse par microsonde électronique (EPMA) et par spectrométrie de masse d'atomes neutres secondaires (SNMS). A cause de la pénétration du faisceau d'électron à l'intérieur du film et du substrat, les mesures de microanalyses X ont été traitées à l'aide d'un logiciel d'analyse de multicouches avec un modèle de correction basé sur une description de la répartition en profondeur $\varphi(\rho z)$ des ionisations. Les deux méthodes conduisent à des résultats concordants. La nature du substrat influence beaucoup la composition des couches. Dans le cas d'un substrat de type oxyde, une diffusion se produit entre le substrat et la couche, tandis qu'aucune diffusion n'est observée dans le cas du substrat de Si_3N_4.

Abstract. — Pd-doped tin oxide thin films were deposited on oxidized silicon, alumina and Si_3N_4, by using the pyrolysis of an aerosol produced by ultra-high frequency spraying. Elemental composition was studied by Electron Probe MicroAnalysis (EPMA) and Secondary Neutral Mass Spectroscopy (SNMS). Due to the penetration of the electron beam inside the film and the substrate, EPMA measurements were treated using a multilayer analysis software with thin film correction model based on the description of $\varphi(\rho z)$ depth distribution of ionisations. The two methods lead to similar results. The nature of the substrate greatly influences the film composition. In the case of an oxide type substrate, a diffusion occurs between the substrate and the films, whereas no diffusion is observed with Si_3N_4 substrate.

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1. Introduction

Semiconductor tin oxide is widely used as transparent electrode [1] and gas sensors [2, 3]. Devices based on thin film technologies are recently developed, owing to the possibility of miniaturization and low cost [4]. Gas sensor applications of tin oxide, based on its surface conductivity, require polycrystalline films and the electrical properties of these films strongly depend on the microstructure and the composition. By dispersing small metallic particles (palladium, platinum,...) on the surface of the SnO_2 grains, electrical properties are improved [5]. The elaboration process and thermal treatments can also induce an interaction and diffusion processes between the film and the substrate, leading to the formation of an intermediate layer and consequently to the decrease of the SnO_2 active layer thickness. Although the influence of the substrate on the film growth has not been often studied, this is a fundamental aspect of the multilayer analysis.

A detailed X-ray microanalysis (EPMA) associated with profile spectroscopy analysis of elements as Secondary Mass Spectroscopy (SNMS) is suitable for this kind of study. The analysis of three different structures based on palladium doped SnO_2 thin films are presented here: SnO_2(Pd)/SiO_2/[Si< 100 >substrate], SnO_2(Pd)/[Al_2O_3substrate] and SnO_2(Pd)/[Si_3N_4substrate].

2. Experimental Details

2.1 THIN FILM SYNTHESIS AND MICROSTRUCTURE. — The elaboration process has been reported elsewhere for SnO_2 [6] and also in connection with thin film synthesis of several types of oxides [7]. It is based on the pyrolysis of an aerosol produced by ultrahigh frequency spraying of an organometallic solution on a heated substrate. Dibutyltindiacetate and palladium acetylacetonate were dissolved in acetylacetone, and substrate temperature varied between 460 °C and 560 °C. Thermally oxidized silicon < 100 > was used for a large proportion of the samples, as well as single-crystalline alumina and Si_3N_4. Silicon was oxidized at 1000 °C for 15 hours under air. Some structures were annealed in sealed silica tube at 750 °C for 2 hours. Microstructure and

Table I. — *Treatment results of X-ray microanalysis: elaboration temperature T(°C), thickness z, composition and specific weight d of the SnO_2(Pd) and SiO_2 layers. z(SnO_2) was determined by SEM.*

T (°C)	z(SnO_2) (microns) ± 0.02	Pd %atom. *	d(SnO_2) (gr/cm^3) *	(Sn+Pd)/O (atom.) *	z(SiO_2) (microns) *	Si/O (atom.) *
460	0.85	3.1	3.40	0.56	0.54	0.06
480	0.95	2.2	2.65	0.56	0.38	0.03
500	1.00	1.5	3.25	0.51	0.40	0.03
500	0.90	1.5	3.95	0.51	0.48	0.05
520	0.87	1.4	4.70	0.50	0.59	0.03
540	1.00	1.2	5.60	0.50	0.31	0.11
560	1.00	1.2	6.40	0.50	0.38	0.11

* The accuracy of these parameters may be characterized by common relative error of *d* simulation no more than 10 %.

morphology were studied by X-ray diffraction and Scanning Electron Microscopy (SEM). The thickness (z) of SnO_2 films was determined by SEM (Tab. I).

2.2 ANALYSIS PROCEDURES. — Quantitative analysis of multilayer structures was performed by using electron probe microanalysis (CAMECA-SX50) with 4 different acceleration voltages (8, 12, 16 and 20 kV). Ten measurements were carried out on each sample at each voltage, using $K\alpha$-lines for oxygen and silicon and $L\alpha$-lines for tin and palladium. Palladium metal, silica and stoichiometric SnO_2 single-crystal were used as standards for the determination of the I/I(standard) ratios.The samples and standards (silica and SnO_2 single crystal) were identically coated with a carbon layer prior to testing. The relative errors of I/I(standard) ratios estimation after ZAF correction were no more than 5%. Owing to the penetration of the electron beam inside the substrate it is not possible to use conventional procedures suitable for bulky samples. Results were treated by using a software package which allows to study multilayer structures (SAMx-Strata). This software calculates the thickness distribution $\varphi(\rho z)$ of the X-ray intensities using Pouchou and Pichoir formulation [8]. An iterative sequence, applied to the 4 measurement series, minimizes the deviation d between calculated and measured K-ratios:

$$d = \left[\sum_i \left(\frac{K \text{ ratio (calculated)}}{K \text{ ratio (measured)}} - 1\right)^2\right]^{\frac{1}{2}}$$

For each layer the convergence of the sequence leads to the determination of two of three parameters: composition, thickness and specific weight. The thickness value of SnO_2 films was fixed according to SEM measurements, and the specific weight value of SiO_2 layers was assumed to be equal to 2.1 gr/cm^3 (silica glass). The accurcy of composition, thickness and specific weight estimation may be characterized by the common relative error for the magnitude of d simulation.

Secondary Neutral Mass Spectroscopy (INA-3, Leybold) was also performed on the three structures. Oxygen, silicon and tin profiles were determined by the same standards as used for X-ray microanalysis.

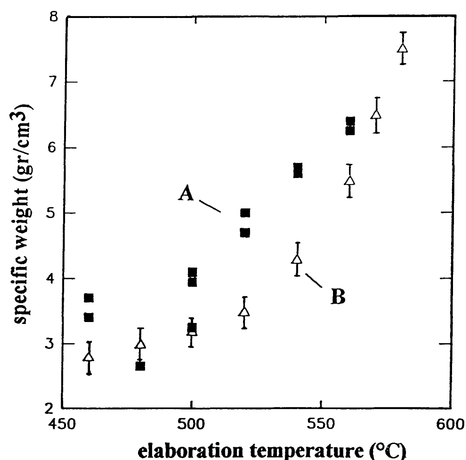


Fig. 1. — Evolution of the SnO_2 film specific weight as a function of elaboration temperature. A) results from X-ray microanalysis treatments; B) results from gravimetry on thicker layers.

3. Results and Discussions

3.1 SnO_2 FILM MICROSTRUCTURE. — When the deposition temperature increases from 460 °C to 560 °C the crystallite mean size of polycrystalline films (about 1 micron thickness) varies from 15 to 34 nm. Starting from atomic ratio Pd/Sn = 0.03 in the solution, co-deposition of Pd and SnO_2 leads to a fine dispersion of Pd particles (mean size < 10 nm) at the surface of the tin oxide grains inside all the layer. Pd clusters are probably partially oxidized due to sythesis conditions. This fine dispersion of very small Pd (or PdO) clusters between small SnO_2 grains can be treated for EPMA as an homogeneous material. This approximation leads to an error for quantitative results which can be omitted, owing to the specific weight and mean atomic number of (Pd, PdO) clusters compared with the one of SnO_2. The specific weight was measured by gravimetry on thicker layers ($\cong$ 5 microns) and increases from 2.8 gr/cm^3 to 7.5 gr/cm^3 (close to single crystal density) (Fig. 1).

3.2 ANALYTICAL STUDIES. — In the case of silicon substrate, the results were first treated considering a SnO_2(Pd)/[Si substrate] structure without SiO_2 layer. In that case the four measurement series lead to an unsatisfactory agreement between measured and calculated values, especially for of O, Sn and Si. Figure 2 reports the results of treatments for a film synthesized at 460 °C. When a complete structure was taken into account (SnO_2(Pd)/SiO_2/[Si-substrate]), a good agreement was obtained, except for the lower voltage (8 kV) (Fig. 3). A low penetration of the electron beam and metallization carbon coating (thickness: about 30 nm for both sample and standards) induce an important effect of the difference between the near surface composition for the films (Sn deficiency) and bulky standards. The results of the iterative sequences are reported in Table I for several elaboration temperatures. Pd content in SnO_2 layers decreases when the deposition temperature increases owing to the difference between the thermal decomposition mechanisms

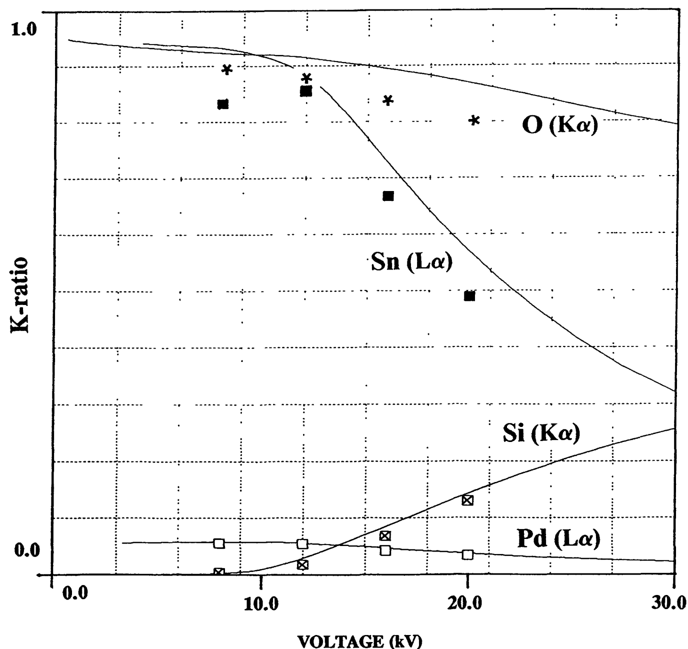


Fig. 2. — "K-ratio" results of the iterative sequence in the case of the SnO_2(Pd)/[Si substrate] model.

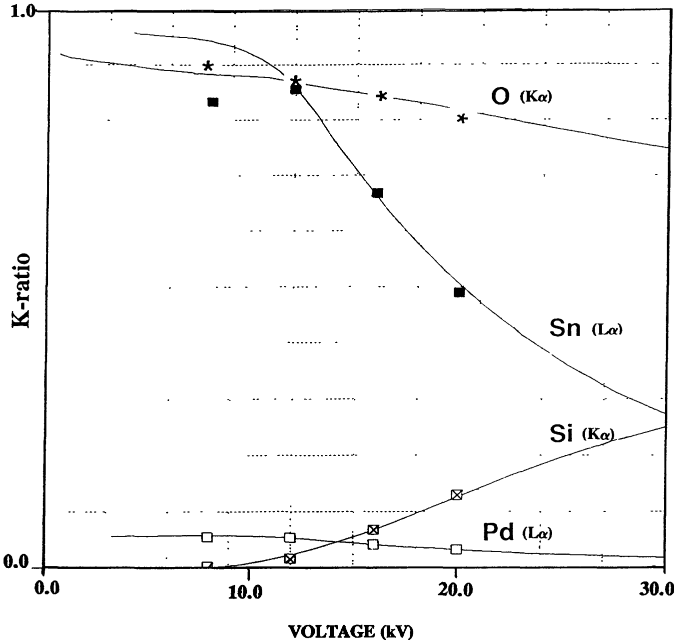


Fig. 3. — "K-ratio" results of the iterative sequence in the case of the SnO_2(Pd)/SiO_2/[Si substrate] model.

of the two Sn and Pd precursors [9]. The Sn/O ratio of all the SnO_2 samples is close to the stoichiometric SnO_2. The specific weight increases with the temperature and is consistent with gravity measurements carried out on thicker films (Fig. 1). In that case owing to the thicker deposited layer and the larger temperature gradient between the surface of the layer and the measured temperature inside the hot plate, the real deposition temperature is lower, leading to a lower specific weight as it can be observed on the data in Figure 1.

The SiO_2 thickness is consistent with the one expected after the thermal treatment of the silicon substrate. Nevertheless the Si content is lower than the one of stoichiometric SiO_2. This result can be explained by a partial diffusion of tin oxide in SiO_2 leading to the formation of an intermediate oxide layer (Sn, Si)O_2 which is not considered in the model of structure which has been choosed.

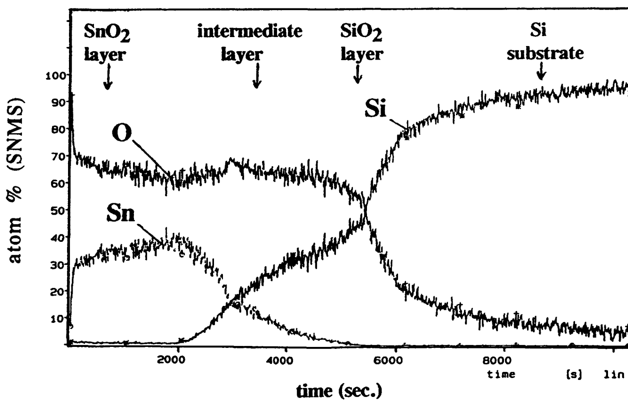


Fig. 4. — SNMS profile of the SnO_2/SiO_2/[Si substrate] structure.

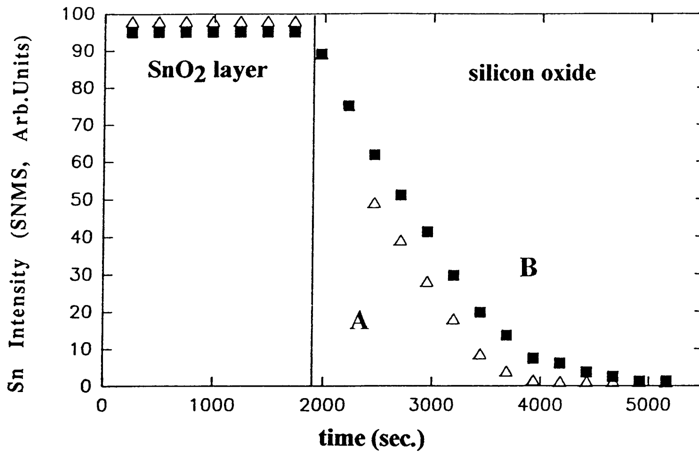
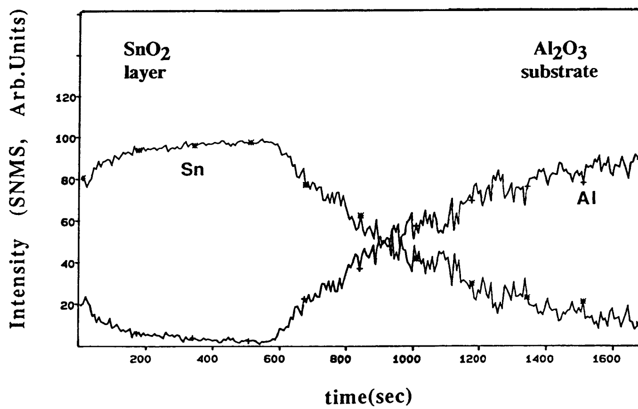


Fig. 5. — Evolution of the tin profile (SNMS) as a function of the thermal treatement at 750 °C for 2 hours. A) as received sample, B) after annealing.



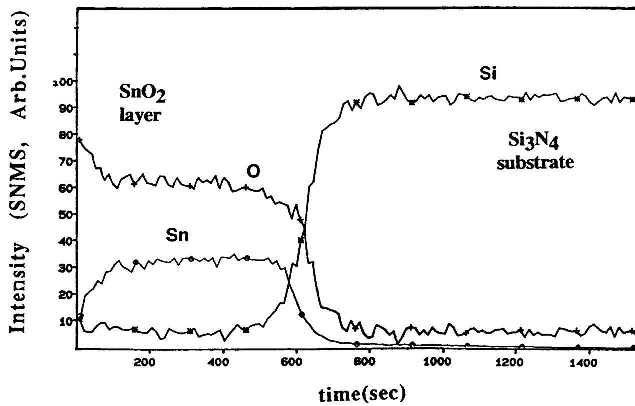


Fig. 6. — SNMS profiles of a) the SnO_2/[Al_2O_3 substrate] structure and b) SnO_2/[Si_3N_4 substrate] structure.

The phase diagram of the system SnO_2-SiO shows the possibility of the formation of a silicate stable up to 700 °C [10].

SNMS profile diagram (Sn, O and Si) confirmed this asumption, as showed Figure 4 as a function of the Ar plasma etching time on a sample synthesized at 460 °C. The first part (0 – 3000 s) is SnO_2 layer, with near stoichiometric composition up to 2000 s. Nevertheless silicon profile is not constant in the SiO_2 part and decreases continuously from silicon substrate to SnO_2 film, as well as the one of tin from SnO_2 to silicon substrate. On the other hand oxygen profile is constant up to silicon substrate. These results are in agreement with the presence of an intermediate oxide layer (Sn, Si)O_2 which takes place on a large part of the SiO_2 layer. The treatements of X-ray measurements were carried out considering only a silicon oxide layer and consequently give a low silicon content (Tab. I). This diffusion phenomenon increases after an annealing for 2 hours at 750 °C, as it can be observed on tin profile of the Figure 5.

SNMS studies were also carried out on SnO_2 films deposited on Al_2O_3 and Si_3N_4 substrates (Figs. 6a and 6b). An intermediate diffusion layer was also observed in the case of Al_2O_3 substrate. Nevertheless a sharp interface occurs with Si_3N_4 substrate. In that case a diffusion effect doesn't occur even after an annealing at 750 °C for 2 hours.

4. Conclusions

Tin oxide thin films were deposited on oxidized silicon and were studied by using both electron probe microanalysis and Secondary Neutral Mass Spectroscopy. Both results are in satisfactory agreement. SnO_2 films were also deposited on Al_2O_3 and Si_3N_4 and were studied by SNMS. All results show the important role of the substrate nature in the layer composition. In the case of oxide type substrates a diffusion between the substrate and the films takes place, and an intermediate layer appears, the thickness of which depends on the elaboration conditions and thermal treatments. The composition of this diffusion layer is not yet precisely defined. It can be a mixture of two phases SnO_2+SiO_2 and a partial formation of a silicate can occur. This interaction between the film and its substrate can lead to an important modification of the physical properties as the conductivity, particularly for thin films.

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