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The influence of glass surface preparation on electrical and optical properties of SnO_2 thin films obtained by spray pyrolysis technique

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SnO_2 conducting thin films were prepared by spray pyrolysis. Glass surface was prepared by etching in HF and acetic acid solutions. Sodium barrier coatings with different compositions were prepared by the sol–gel technique. The influence of the glass surface preparation on optical properties of SnO_2 was studied using reflectance spectroscopy. XPS was used as a tool to evaluate barrier properties of the coating. The morphology of the thin layer was studied by a scanning electron microscope. The results have shown that the titanium containing coating has the best sodium diffusion barrier property. The conductivity of SnO_2 film strongly depends on the glass surface preparation. The lowest conductivity was measured for clean glass but the highest for alumina containing barrier coating.

Keywords: spray pyrolysis, transparent conductive coating, optical and electrical properties.

1. Introduction

Transparent conducting oxide coatings are important element in a large number of applications, due to the unique combination of high electrical conductivity with good optical transmission in the visible range [1]. SnO_2 belongs to the important family of oxide materials that combines low electrical resistance with high optical transparency in the visible range of the electromagnetic spectrum [2]. Typical fields of applications for such coatings are, *e.g.*, the use as electrodes in displays, solar cells and heating elements or in the provision of electromagnetic shielding maintaining transparency, defrosting windows, low emissivity windows or antistatic properties [1–3]. SnO_2 is chemically inert, mechanically hard and can resist high temperature [4].

There are many techniques, including sputtering, evaporation and chemical vapour or spray deposition, by which the SnO_2 films may be deposited on glass substrates. In this study, tin oxide thin films were prepared by the spray pyrolysis technique [5]. The spray pyrolysis technique is particularly attractive because of its simplicity. It is fast, inexpensive, vacuumless and suitable for mass production [6].

The electrical and optical properties have been studied in detail for films deposited on glass substrates [7]. The fine mist of very small droplets of the aqueous solution containing the desired species is sprayed onto a preheated substrate. The thermal decomposition takes place on the hot substrate, giving rise to a continuous film. The tin oxide films prepared by the spray pyrolysis using $SnCl_4$ based solution as a source of tin are common although other precursors are also reported [8]. Very few reports are available using $SnCl_2$ as a precursor of tin [4, 5]. The advantages of the $SnCl_2$ are that it is cheaper than $SnCl_4$ and can be produced easily in a laboratory [4].

Various precursors ($SnCl_4$, $SnCl_2$, $SnCl_2{\cdot}2H_2O$) have been used to obtain tin oxide thin films and results are compared [5]. Different precursors used lead to differences in morphology, conductivity and growth rate of the films. It has been shown that physical properties of the tin films obtained by the spray pyrolysis method strongly depend on the form of a precursor. $SnCl_2$ leads to a higher rate of film formation with higher conductivity.

In this study we have tested the effect of different preparations of a glass substrate on optical and electrical properties of SnO_2 thin film obtained by the pneumatic spray pyrolysis.

2. Experimental procedure

Spray pyrolysis is based on the pyrolytic decomposition of a metallic compound dissolved in alcohol and sprayed onto a preheated (400–600 °C) substrate.

The processing stages applied in this study are outlined in Fig. 1. The thin layers were deposited on the soda-lime microscope glass slides (2×2 cm) which were chemically and ultrasonically cleaned. The cleaning process adopted was as follows: the glasses were washed in detergent solution for 5 minutes and then rinsed with distilled water for 1 minute in ultrasonic bath. Next they were treated in acid solution for 0.5 minute (5% hydrofluoric acid) or 3 minutes (10% acetic acid), then rinsed with distilled water for 1 minute in ultrasonic bath. Tin tetrachloride $SnCl_4$ (Fluka AG) was used as a tin precursor. $SnCl_4$ was dissolved in ethyl alcohol C_2H_5OH (POCH SA 95%) and HCl (37%) was added to prevent hydrolysis. The chemical composition of the sprayed solution was as follows: $SnCl_4$ – 4 ml, ethyl alcohol – 25 ml, hydrochloric acid – 0.5 ml.

Glass substrates with sodium diffusion barrier coating were prepared by the sol–gel method. The preparation procedure was described elsewhere [9]. SnO_2 layer deposition was performed by pneumatic spray of the solution on a preheated glass substrate (600 °C).

After deposition, the coated substrates were allowed to naturally cool down to room temperature before being taken out from the spray chamber.

In this paper, structural and morphological properties of tin films were investigated by scanning electron microscopy (Nova NanoSEM 200). Reflectance measurements were carried out using Konica Minolta spectrometer model CM-2600d/2500d. X-ray photoelectron spectroscopy (XPS) analyses were performed on “as made”

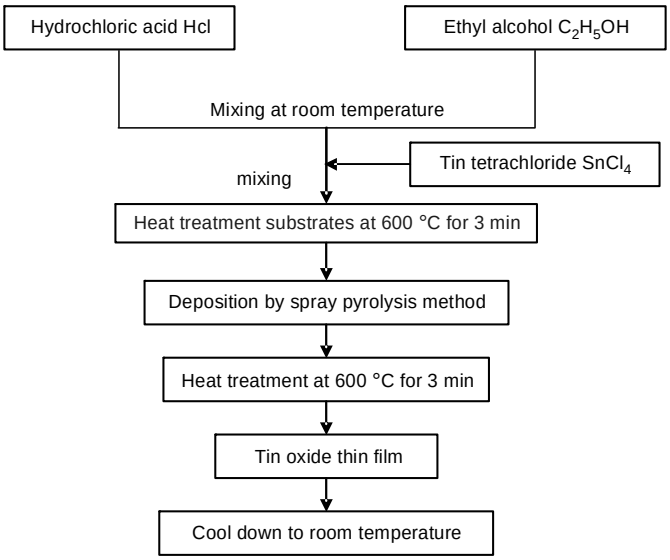

Fig. 1. Preparation procedure of a thin film by the spray pyrolysis process.

T a b l e 1. XPS spectra for differently prepared glasses.

	C 1*s*		O 1*s*		Na 1*s*	Si 2*p*	Sn 3*d*
	1	2	1	2	1	1	1
SAO2 (SiO_2–Al_2O_3 barrier coating)							
FWAM [eV]	1.7	4.0	1.8	1.7	1.8	2.7	1.9
Max [eV]	284.6	286.4	530.3	532.1	1071.2	102.7	486.6
Area	12299.4	2423.8	87953.6	14593.9	5362.8	963.4	642570.1
Content [%]	15.93		42.04		0.63	0.97	40.43
SMO2 (SiO_2 barrier coating)							
FWAM [eV]	1.6	3.0	1.9	1.7	1.8	2.6	2.0
Max [eV]	284.6	286.8	530.0	531.9	1071.0	102.1	486.1
Area	29311.4	3205.7	132155.2	24286.9	21078.0	2011.6	804353.5
Content [%]	22.79		41.53		1.61	1.31	32.77
STO1 (SiO_2–TiO_2 barrier coating)							
FWAM [eV]	1.8	3.2	2.0	2.1	—	2.0	2.1
Max [eV]	284.6	286.7	530.6	532.3	—	530.6	532.3
Area	21597.2	4225.6	47520.7	22449.4	—	47520.7	22449.4
Content [%]	36.77		37.74		—	1.23	24.26
Clean glass							
FWAM [eV]	2.0	2.8	2.8	2.2	2.4	2.4	—
Max [eV]	284.6	287.7	531.8	535.7	1071.5	103.0	—
Area	8141.07	1354.35	40156.88	3292.68	16787.32	3988.33	—
Content [%]	30.17		52.30		5.80	11.73	—

samples using VSW spectrometer with a hemispherical analysis. Spectra were obtained using Al Kα radiation source operated at 200 W and 10 kV. The electron energy analyzer was set to FAT mode with pass energy 20 eV. The shift of the binding energy due to the surface charging effect was calibrated by assuming binding energy of C 1*s* to be always 284.6 eV. Quantity analysis was carried out applying XPS sensitivity factors published by BRIGGS and SEAH [10].

3. Results and discussion

3.1. Photoelectron spectroscopy – XPS

Photoelectron spectroscopy was used to study the chemical composition of the layer and the diffusion of sodium from the glass to the top of the layer. The results of the study were shown in Tab. 1. The lowest value of sodium Na 1*s* peak was registered for the SnO_2 sample with titanium containing barrier coating in spite of a relatively thin layer of SnO_2. Alumina containing barrier coating (sample SA02) has also very good barrier properties. The comparison of sodium peak intensity for selected samples is shown in Fig. 2. SiO_2 barrier coating prepared from TEOS exhibits relatively poor barrier properties.

3.2. Optical properties – UV-VIS

Reflectance curves of the tin thin films deposited at 600 °C during 3 minutes are shown in Fig. 3. The thickness *d* of the layers deposited onto the glass plates was calculated from the following relation [11]:

$$2nd = \left(\frac{1}{\lambda_1} - \frac{1}{\lambda_2}\right)^{-1}$$

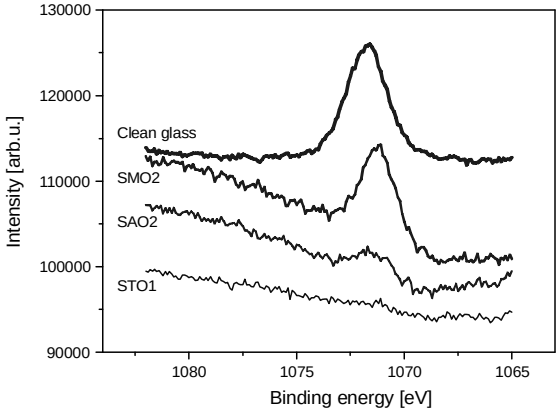

Fig. 2. XPS spectra – Na 1*s* region. Comparison of Na 1*s* peak for clean glass and SnO_2 coated samples.

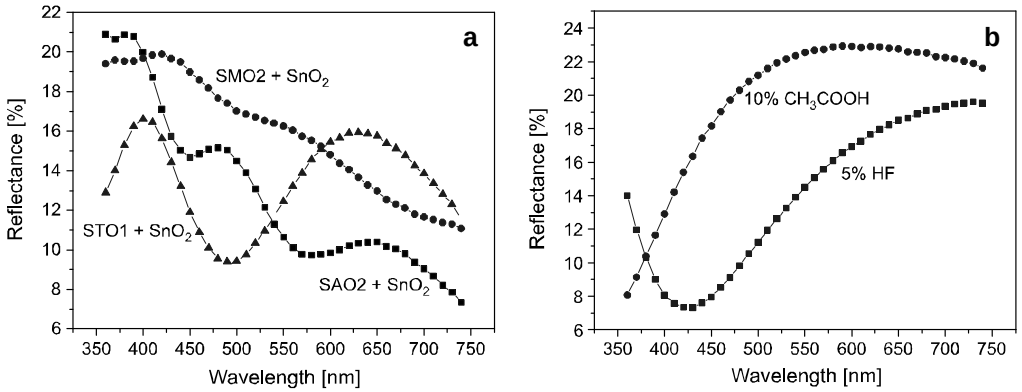

Fig. 3. Reflectance as a function of wavelength: **a** – SnO_2 thin film on glasses with different sodium diffusion barrier coatings, **b** – SnO_2 thin film on glasses treated in fluoric and acetic acid.

T a b l e 2. Thickness of the layer estimated from reflectance measurements.

Symbol	Thickness [nm]
STO1	423
SMO2	700
SAO2	814

where: λ_1, λ_2 – wavelength at the successive maxima, n – refractive index (assumed 2.0 for SnO_2 thin film). Results for the samples, where two evident maxima were registered, have been summarized in Tab. 2.

3.3. Microstructure observations – SEM

The SEM micrographs of the surface morphology of tin oxide thin films deposited at differently prepared substrates were shown in Fig. 4. The morphology of the SnO_2 film obtained on clean glass is affected by defects seen as holes in the layer – Fig. 4**a**. SnO_2 deposited on a substrate etched in hydrofluoric or acetic acid shows similar morphology – Figs. 4**b** and 4**c**. The layers are crystalline and homogeneous with uniform dimension crystals. The tin layer obtained on alumina containing diffusion barrier coating is less crystalline but homogeneous and uniform. Some defects are however visible. The morphology of SnO_2 thin film on titanium barrier coating is less crystalline than in the case of acid-treated glass substrates. The layer is crack- and defect-free, and homogeneous.

3.4. Resistance measurement

The resistance of the SnO_2 films was measured using the square method in a two-wire configuration. Results are shown in Tab. 3. The lowest value of resistance was

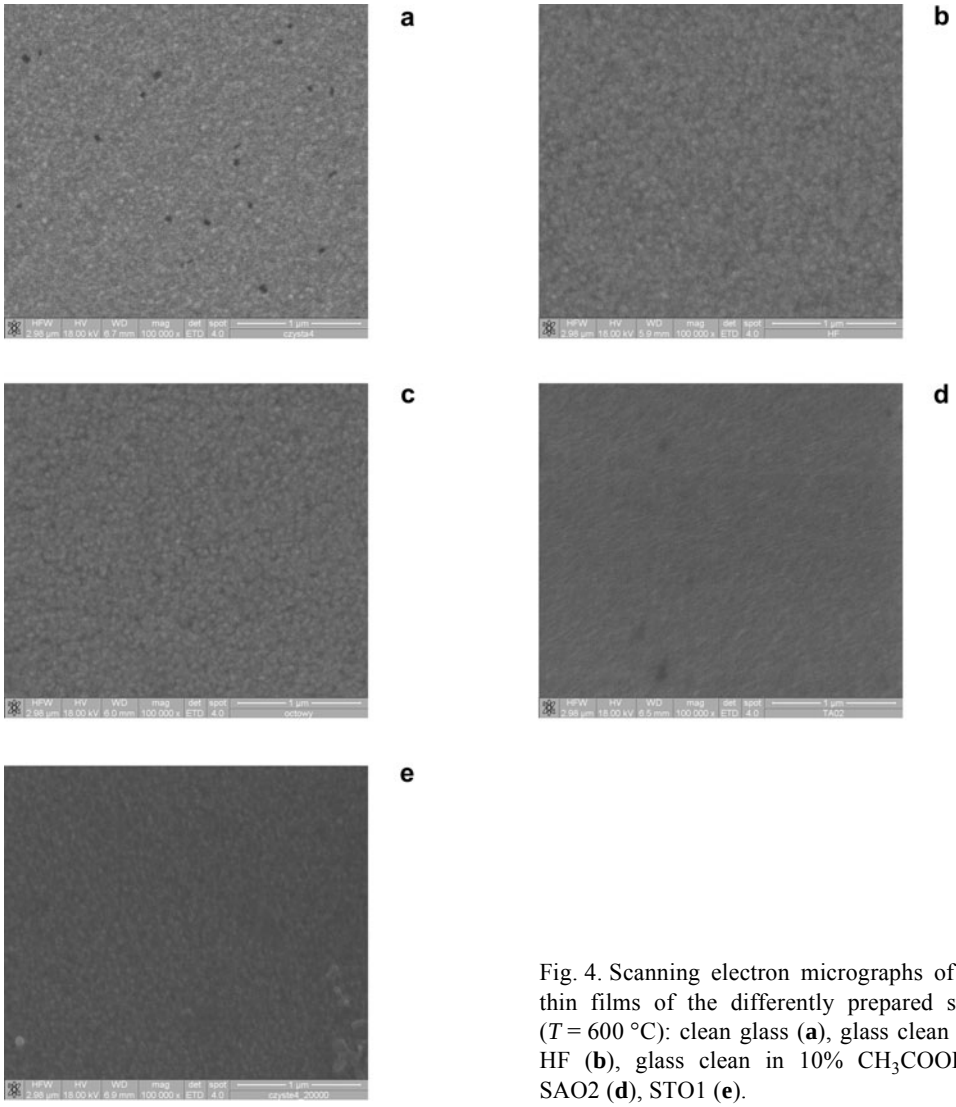

Fig. 4. Scanning electron micrographs of SnO_2 thin films of the differently prepared surface (T = 600 °C): clean glass (**a**), glass clean in 5% HF (**b**), glass clean in 10% CH_3COOH (**c**), SAO2 (**d**), STO1 (**e**).

measured for SnO_2 sprayed onto the clean glass substrate – 0.5 kΩ/□. The highest resistance was measured for the sample with SAO2 sodium diffusion barrier coating – 280 kΩ/□.

4. Conclusions

As far as the resistance is concerned, the best results have been obtained for a clean glass substrate without any preparation; however, an electron microscope revealed some defects in the tin film. Very similar resistance was measured for SnO_2 deposited on HF treated glass, but in the case of acetic acid treated glass, the resistance was much

T a b l e 3. Resistance of the tin films deposited on different substrates.

Sample	Resistance [kΩ/□]
STO1	1.4
SMO2	2.4
SAO2	280
Clean glass	0.5
Treated in 5% HF	0.9
Treated in 10% CH_3COOH	3.2

higher (almost 4 times higher) in spite of similar morphology. It suggests that the SnO_2 resistance is connected with the sodium content on the glass surface during pyrolysis (hydrofluoric acid does not remove sodium from the surface). Most probably sodium ions accelerate nucleation of SnO_2 crystals on the surface.

The highest value of resistance was recorded for SAO2 sample. Low conductivity of this sample should be connected with low crystallinity of the film. In the case of the pyrolysis technique of SnO_2 deposition, the best sodium diffusion barrier protection is offered by titanium barrier coating.

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