THIN LAYERS OF SnO$_2$ DEPOSITED BY SPRAY METHOD

Ing. Michal MACALÍK, Doctoral Degreee Programme (1)
Dept. of Electrical and Electronic Technology, FEEC, BUT
E-mail: xmacal01@stud.feec.vutbr.cz

Supervised by: Dr. Marie Sedlaříková

ABSTRACT

SnO$_2$ layers were prepared by spray deposition from SnCl$_4$ or SnCl$_2$ solutions. Physical and electrical properties of them were measured and compared with those prepared by sputtering process. In general, their structure corresponded to cassiterite. Doping by solutions of SbCl$_3$, NH$_4$F or both was performed, and in dependence of doping was investigated. Surface morphology, electrical conductivity, Hall effect and optical transmittance were investigated.

1   INTRODUCTION

In many branches of electrochemical research as well as in electronic technology, transparent electrodes deposited onto insulators have been used in quite many applications. They are based on tin dioxide, deposited as thin layers and containing additives or dopants, which increase their electric conductivity. Most frequent dopants are oxides of indium and/or antimony, and fluorine compounds. Correspondingly, they abbreviated names ITO, STO and FTO are used for them. The best way of their preparation in the laboratory is the sputtering from suitable targets which has become standard method. By this method, samples for the study of lithium electrochemical intercalation into ITO electrodes were prepared [1].

One of possible methods of preparation is the spray deposition onto glass or other substrate. This method was used for example by Tiburciosilver [2] who used addition of HF to the solution of SnCl$_4$ for its doping. Another study of spray deposited SnO$_2$ layers was performed by Singh [3]. Indium-doped layers were also prepared by the spray method [4].

The aim of this contribution is the use of that method for preparation of various SnO$_2$ layers with dopants and the description of their fundamental physical and electrical properties.

2   EXPERIMENTAL

Solution of SnCl$_4$ in methyl alcohol and dissolved SnCl$_2$ were deposited by a stream of air from an all-glass atomizer. For addition of NH$_4$F as dopant the compounds was dissolved in small quantity of water and then added to methanol. SbCl$_3$ was added directly to methanol solution.

Glass slides from SIMAX glass (similar to PYREX®) were used as substrates. They were laid on a hot plate heated to +300 °C before spraying of the solution. The size of the glass support was 25 x 20 mm.

Sputtered layers were used for comparison. The thickness of the layers was 75 nm.

2.1 THE PREPARATION OF LAYERS

Preparation from tetravalent tin compound: For deposition of the undoped layer, 3 ml of liquid $SnCl_4$ were added to 15 ml of methanol under agitation and cooling of the mixture. 100 mg of ammonium fluoride was dissolved in 1 ml of water and added to the same tin chloride solution in methanol. Similarly, 10 mg of antimony chloride $SbCl_3$ was used as the dopant for antimony doped layers. Both dopants were added to the same volume of $SnCl_4$ solution in methanol (doping by Sb + F).

Preparation from divalent tin compound: 20 g $SnCl_2.2H_2O$ and 7 ml concentrated HCl were mixed and heated. Then 3 ml of methanol and 70 ml of water were added. Resulting solution was divided into four equal volumes. One part was used as non – doped substance. 500 mg of ammonium fluoride was added to the second, 20 mg of $SbCl_3$ to the third part and a mixture of 500 mg NH_4F and 25 mg $SbCl_3$ to the last one.

Sputtered ITO layers were prepared using the Z550 r.f. magnetron sputtering plant. A high purity material (99.99 %) was used as the ITO target of 152 mm in diameter and 6 mm thick. The thickness of the layer was controlled by the deposition time at the known deposition rate.

2.2 PHYSICAL INVESTIGATIONS

The transmission spectra were measured on the PU 8720 UV – VIS spectrometer. The correction of the absorption by substrate glass was performed. The morphology and elemental composition were monitored by the scanning microscope enabled by an EDAX analyzer. Observations of the layer morphology were performed also by the optical microscope. The thickness and roughness were evaluated by means of Talystep profilometer.

2.3 CONDUCTIVITY AND HALL EFFECT

Resistance was measured on glass slices of dimensions 20 x 20 mm (approx.) in a four-point arrangement. The current leads were created as stripes of silver paint on opposite sides and the voltage probes as small dots between them. The same samples were also used for the estimation of Hall effect. The voltage probes were changed so that they were symmetrical on both sides of the probe. Magnetic field was supplied by the electromagnet from an EPR spectrometer Bruker E-540; its magnetic induction was varied between 0 and 1 T.

3 RESULTS AND DISCUSSION

3.1 MORPHOLOGY

A cross-section of the glass substrate with a deposited layer indicated that the layer is not completely homogenous and its average thickness is 300 to 400 nm. The non-homogeneity is caused by the spray method. The surface of spray deposited layers is not quite smooth as indicated on the profile recorded in fig. 1.
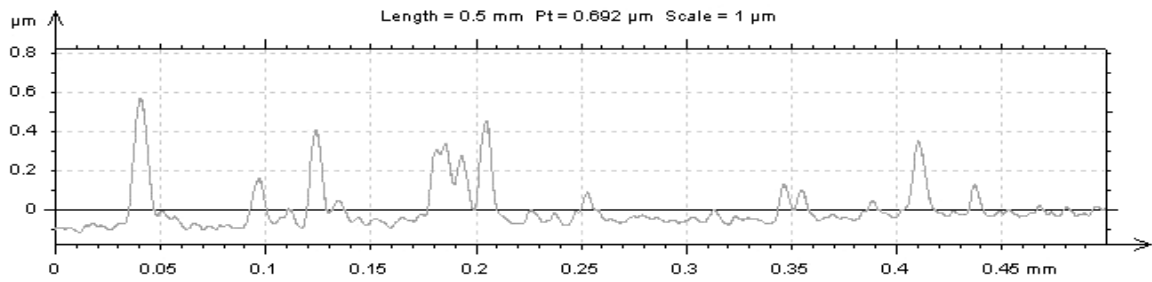
Fig. 1: *The profile of the spray deposited layer from the solution of SnCl₄*

It seems probable that the droplets of the solution evaporate immediately when they touch the substrate, as it is visible in fig. 2. The surface of the layer consists of small particles formed probably by rapid evaporation of the droplets. Its raduys (0.5 to 1 μm) corresponds to the size of roughness shown in fig. 1.
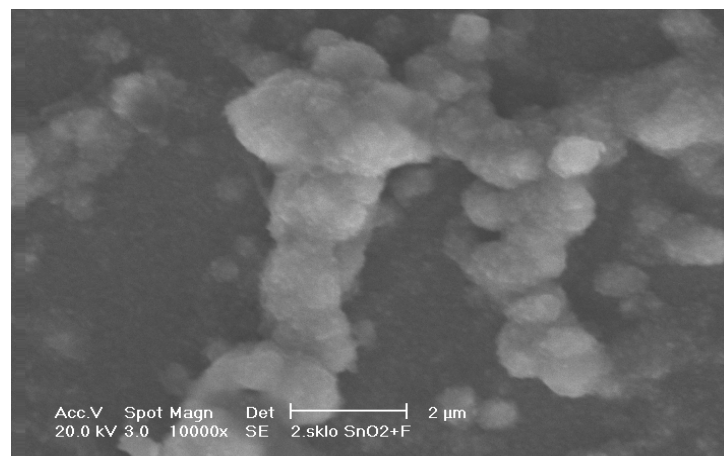

Fig. 2: *The surface of a spray deposited layer observed in scanning electron microscope*

3.2 UV/VIS

The optical absorbance of glasses coated by spray deposited oxide was measured between 300 and 900 nm for all. The data were corrected on the absorption of the substrate. The results are shown in figs. 3 and 4.
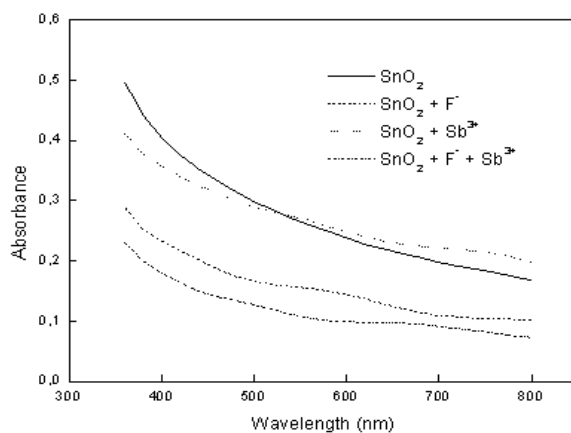

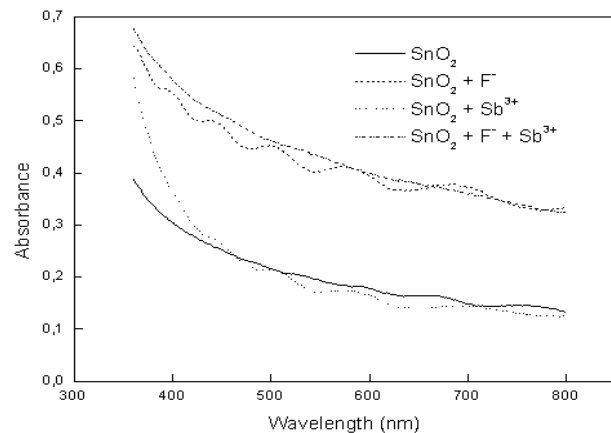**Fig. 3:** *Layers prepared from SnCl₂ (marked as SnO₂) and doped by F⁻, Sb³⁺ and/or their mixture*

Fig. 4: *Layers prepared from SnCl₄ (marked as SnO₂) and doped by F⁻, Sb³⁺ and/or their mixture*

For all samples, the non – doped one was the most transparent. Moreover, it looks like a spectrum of a semiconductor with a band gap corresponding to 3 eV approximately.

3.3   THERMAL DECOMPOSITION OF HYDROXYCOMPOUNDS

In order to explain how the tetravalent oxide is formed from divalent tin compounds, the corresponding hydroxides were prepared as follows: Ammonia solution was added to the solution of $SnCl_2$ or $SnCl_4$ chlorides and the precipitate was separated. Small amount of HCl was necessary to prevent the hydrolysis of $SnCl_2$ in the starting solution.
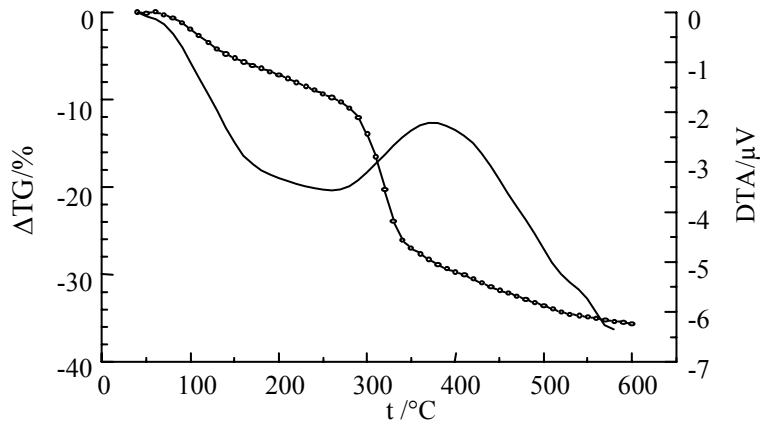

Fig. 5:   *DTA / TGA analysis of hydroxycompound prepared by hydrolysis of SnCl₂*

The products were dried at 90 to 100 °C and they were analyzed by DTA – TGA device NETZCH (differential thermal and thermogravimetric anayser). The results are given in fig. 5 where the thermogram of the sample prepared from $SnCl_2$ is shown. As we see, the substance looses some water between 100 and 200 °C. This decrease of mass is followed by opposite process, when the substance is gaining weight up to 400 °C. Apparently, this is connected with the oxidation of tin to Sn^{IV} by atmospheric oxygen. The thermogram of the samples of Sn hydroxide prepared from $SnCl_4$ is different. The liberation of water proceeds in two steps, each of them corresponding roughly to one molecule of water per one Sn and the whole curve sinks monotonously.

Temperature necessary for finishing both the loss of water and oxidation of divalent tin is up to 400 to 500 °C. The temperature 300 to 400 °C was used for the substrate in the process of spray deposition therefore as the glass substrate could not resist thermal shocks caused by the deposition of droplets on it.

3.4   ELECTRIC PROPERTIES

The electric conductivity varies in rather wide limits. The highest one was found for layers containing fluorine as a dopant of tetravalent tin chloride. The lowest conductivity was found for layers prepared from $SnCl_2$ solutions.

Marked difference was observed from Hall effect measurements. The layers prepared from $SnCl_2$ showed opposite type of conductivity than those prepared from $SnCl_4$. From the conductivity and Hall effect measurements, an apparent concentration of charge carriers was estimated in an usual way. The results are listed in tab. 1 as well. There is a rather rough

correlation between the carrier concentration and conductivity.

Precursor	Dopant	Resistivity ($\Omega/\square$)	Hall constant ($m^3A^{-1}s^{-1}$)	Concentration (m^{-3})	Type of conductivity
SnCl$_4$	-	20.92	2.14×10^{-8}	2.97×10^{26}	P
	F$^-$	0.203	5.91×10^{-9}	1.06×10^{27}	P
	Sb^{3+}	54.61	3.37×10^{-8}	1.85×10^{26}	P
	F$^-$ +Sb^{3+}	10.79	8.65×10^{-9}	7.22×10^{26}	N
SnCl$_2$	-	2090	2.26×10^{-7}	2.76×10^{25}	N
	F$^-$	251.8	3.08×10^{-8}	2.03×10^{26}	N
	Sb^{3+}	423.5	1.63×10^{-7}	3.84×10^{25}	N
	F$^-$ +Sb^{3+}	39.91	2.30×10^{-8}	2.72×10^{26}	P
Sputtered ITO	(In)	146	4.50×10^{-8}	1.39×10^{26}	P

Tab. 1: *Electric properties of various spray deposited layers of SnO$_2$*

The concentration and type of charge carriers will influence electrochemical properties of the layers undoubtedly.

4   CONCLUSION

The preparation of SnO$_2$ based layers by spray method seems interesting for the technology as no vacuum is necessary for it. The formation of tetravalent oxide from divalent compound was described and the difference in properties was shown. The layers are crystalline and far from being homogenous. Therefore the optical absorption is perhaps more influenced by macroscopic texture than by charge concentration. The correlation between electronic properties and electrochemical behavior will be investigated more thoroughly.

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