

# BENEFITS OF H<sub>2</sub>O<sub>2</sub> IN THIN FILM SnO<sub>2</sub> PREPARATION

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## ABSTRACT

Thin layers of tin dioxide were prepared by spraying of solution containing tin dichloride and hydrogen peroxide on glass substrates heated to 350 – 400°C. The action of peroxide is explained as formation of peroxytin compounds. The layers are crystalline, reasonably transparent and exhibit conductivity of N type as detected by voltammetric measurements of system ferrocene - ferricinium in propylene carbonate.

## 1. INTRODUCTION

Tin dioxide, SnO<sub>2</sub>, is a semiconductor exhibiting good electric conductivity, optical transparency and reflectivity in infrared irradiation. Good transparency is connected to the 3 eV width of the band gap. These properties can be modified easily by a variety of additives such as compounds of antimony, fluorides, metal salts and others. This material can be used in many applications, such as transparent electrodes for displays [1], solar cells [2, 3], semiconductor technology [4], gas sensors [5], heating elements or electromagnetic shielding and antistatic surfaces [6].

Various technologies for thin layer deposition are under investigation nowadays. Magnetron sputtering [7], electrodeposition [8], spray pyrolysis or deposition [2], methods based on CVD [9] or dip-coating [1] are among them. The spray deposition is rather cheap and does not require any sophisticated device.

## 2. EXPERIMENTAL

Tin dichloride dihydrate was used for preparation of starting solution. In the first set of samples, 1,5M SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved in 75ml of methanol. In the second set, 25,3g SnCl<sub>2</sub>·2H<sub>2</sub>O was dissolved by slowly added 10ml of H<sub>2</sub>O<sub>2</sub> solution under permanent agitation and finally methanol was added to total volume of 75ml. 10ml, 25ml a 40ml of each solution were used for spray deposition by means of a air – driven atomizer on pre-heated soda-lime glass substrate. The temperature of substrates was controlled by thermocouple.

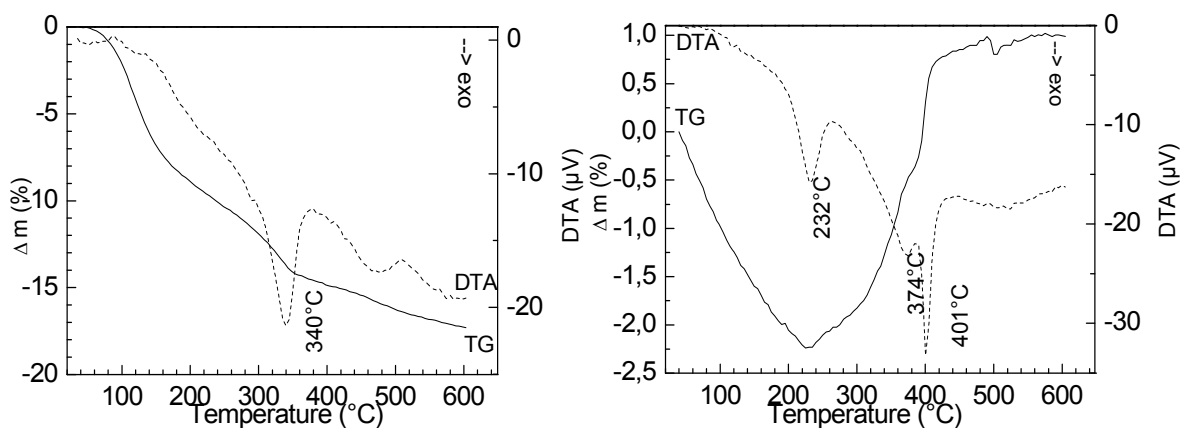
The surface morphology and thickness of the films were investigated by scanning electron microscope (Tescan VEGA 5135) and profilometer (Talysurf CLI 1000). Type of charge carrier, concentration and mobility were determined by room temperature Hall effect with standard Van der Pauw arrangement. Transmittance spectra of the films were measured be-

tween 325-900nm wavelength by spectrophotometer (Thermo Spectronic, Helios Delta). Differential thermal and thermogravimetric analysis were produced by DTA – TGA device (NETZSCH STA (QMS) 409 analyzer). Sheet resistance was measured by a linear four-probe type resistance meter (Jandel RM3). Temperature was controlled down to  $-50^{\circ}\text{C}$  in a cryogenic cell cooled by solid  $\text{CO}_2$ .

### 3. RESULTS AND DISCUSSION

#### 3.1. THERMOGRAVIMETRY ANALYSIS

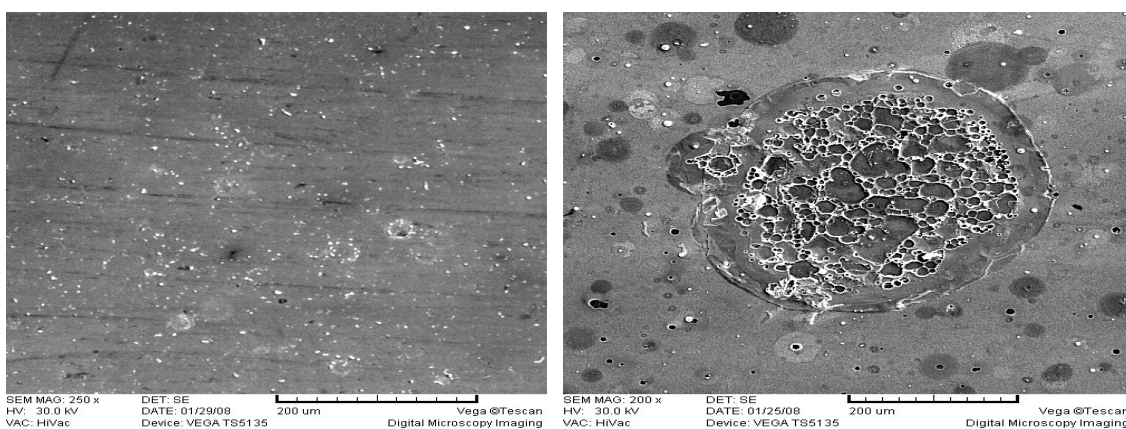
At first, the presence of hydrogen peroxide in prepared tin hydroxides was investigated. The heating of precipitated hydroxides is indicated in Fig. 1 on DTA curves. The peroxide treated sample just losses weight while the untreated one increases its mass between 200 and  $400^{\circ}\text{C}$ ; this is apparently accompanied by oxidation by atmospheric oxygen to  $\text{Sn}^{4+}$  species. Evidently, hydrogen peroxide contribute to tin oxidation and its valence change directly in starting solution.



**Fig. 1:** DTA curves of hydrogen peroxide treated (left) and untreated sample (right)

#### 3.2. MORPHOLOGY AND OPTICAL PROPERTIES

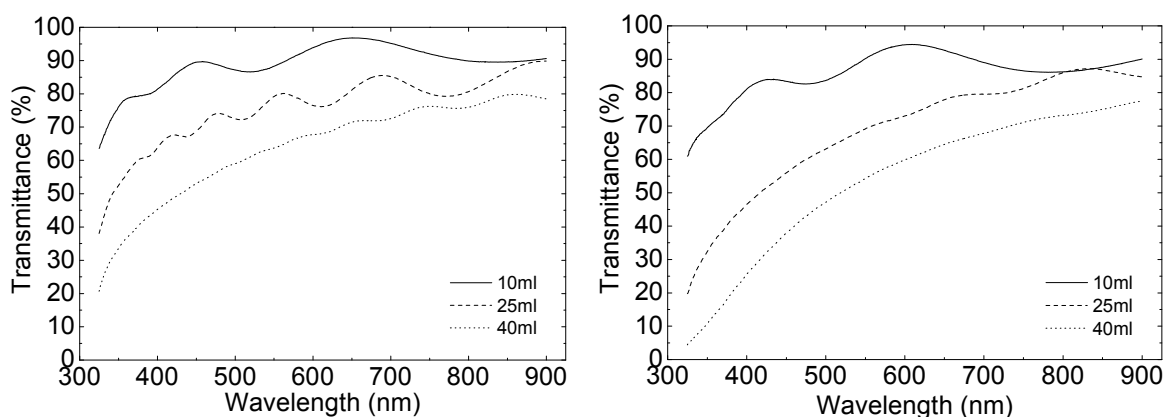
The microphotographs of both type of layers are shown in Fig. 2. Better homogeneity of the layer is visible there.



**Fig. 2:** SEM images of hydrogen peroxide treated (left) and untreated (right) samples prepared from 25ml solution

The surface of the layer consists of small particles formed probably by rapid evaporation of the solution droplets.

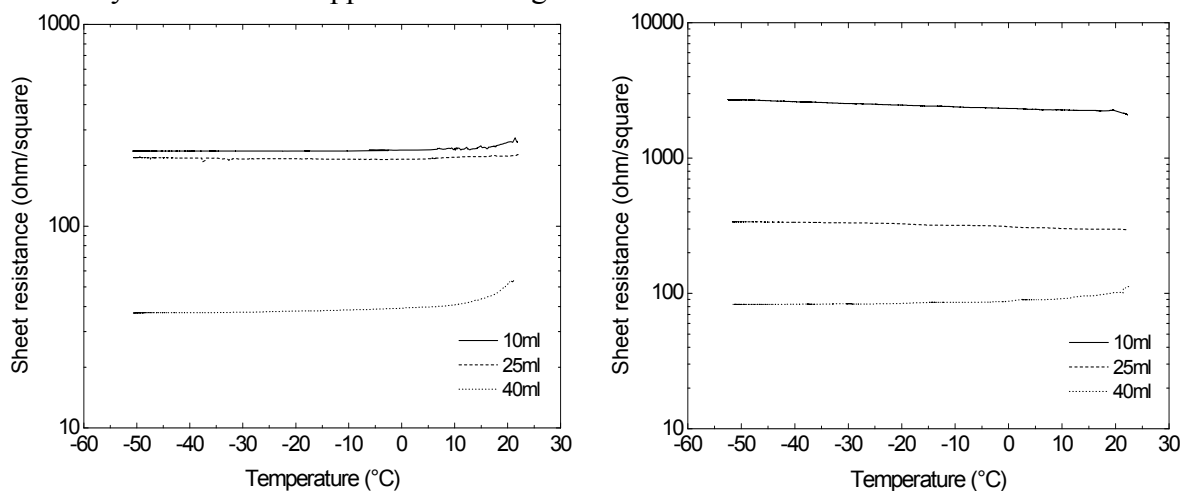
Thin films of  $\text{SnO}_2$  prepared by spray pyrolysis method from  $\text{SnCl}_2$  precursor without hydrogen peroxide using are darker and brownish than almost clear and colourless films prepared from solution with adding  $\text{H}_2\text{O}_2$ . It is in good agreement with colouring of precipitated hydroxides from previous paragraph. Optical transmission curves from prepared samples measured in the range of wavelength 325 – 900nm are depicted in figure 3. Peroxide treated samples are more transparent than untreated samples.



**Fig. 3:** Transmission spectra of hydrogen peroxide treated (left) and untreated sample (right)

### 3.3. ELECTRICAL AND ELECTROCHEMICAL PROPERTIES

The resistance dependence on temperature is shown in Fig. 4. In general, no behavior typical for a semiconductor was observed. At temperatures over zero, the resistivity increases with increasing temperature, while it is almost constant below that limit. We suppose that the material should be described as a highly doped or degenerated semiconductor in which the conductivity is controlled by numerous defects in the crystal lattice and by the mean free path of charge carriers. On the other hand, the improvement of charge carrier mobility by the peroxide addition is clearly visible. Also the decrease of resistivity with increasing of the layer thickness is apparent from Figs. 4.



**Fig. 4:** Temperature dependence of sheet resistance (peroxide treated left, untreated right)

Hall effect measurement on SnO<sub>2</sub> thin films on glass substrates from the 40ml solution in room temperature show again the hydrogen peroxide contributes to lowering electrical resistivity due to increased concentration and mobility of charge carriers.

Sample	Thickness (μm)	R <sub>□</sub> (Ω/□)	ρ, 10 <sup>-5</sup> (Ωm)	n, 10 <sup>25</sup> (m <sup>-3</sup> )	μ <sub>H</sub> , 10 <sup>-3</sup> (m <sup>2</sup> V <sup>-1</sup> s <sup>-1</sup> )	Cond. type	% of ionization
without H <sub>2</sub> O <sub>2</sub>	1.23	64.79	7.97	4.82	1.62	N	1.7×10 <sup>-1</sup>
with H <sub>2</sub> O <sub>2</sub>	1.35	29.18	3.94	7.56	2.10	N	2.7×10 <sup>-1</sup>

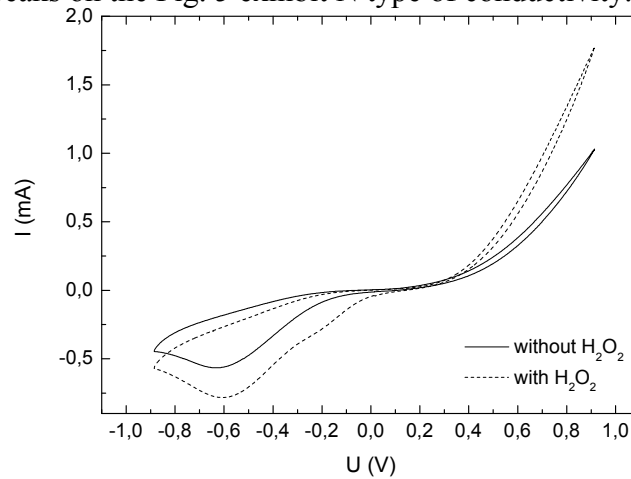
**Tab. 1:** Sheet resistance and Hall effect measurement of 40ml solution samples

A good criterion to define the quality of highly transparent and conductive thin film is through the introduction of a figure of merit calculated using Haacke's equation  $\Phi = T^{10}/R_{\square}$  (Ω<sup>-1</sup>).

Sample	T (%) at λ = 550nm	R <sub>□</sub> (Ω/□)	Figure of merit, Φ (Ω <sup>-1</sup> )
without H <sub>2</sub> O <sub>2</sub>	10ml	90.2	1.7931×10 <sup>-4</sup>
	25ml	69.2	5.9406×10 <sup>-5</sup>
	40ml	54.3	3.4161×10 <sup>-5</sup>
with H <sub>2</sub> O <sub>2</sub>	10ml	88.3	8.8947×10 <sup>-4</sup>
	25ml	79.2	4.3711×10 <sup>-4</sup>
	40ml	63.7	3.8156×10 <sup>-4</sup>

**Tab. 2:** Quality classification of samples

For determination of type of semiconductor conductivity can be used cyclic voltammetry measurement. Sample is measured in redox system ferrocene-ferricinium in propylene carbonate. Cathodic peaks on the Fig. 5 exhibit N type of conductivity.



**Fig. 5:** Cyclic voltammetry measurement of 40ml samples in ferrocene-ferricinium system

#### 4. CONCLUSION

The action of hydrogen peroxide in the precursor for SnO<sub>2</sub> deposition by spray method seems to be based on two factors. First it is the oxidation of divalent tin to tetravalent one before the spraying process. Second, we must not forget the formation of peroxyanions which are well soluble and which are undoubtedly present in the precursor. Both these effects yield in the formation of smooth, almost transparent and well conductive layer of tin dioxide. Essentially, the oxidation of the precursor by hydrogen peroxide yields in material with better transparency, lower coloration and higher conductivity. All these benefits are probably caused by better stoichiometry and lower concentration of structural defects in the peroxide treated material. This precursor is predominant over SnCl<sub>4</sub> precursor in technology because it does not irritate people and is non – corrosive.

#### ACKNOWLEDGEMENT

This work was supported by the Ministry of Education, Youth and Sports (project MSM 0021630516).

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