PREPARATION OF DOPED SnO_2 THIN LAYERS FROM $SnCl_2$ AND $SnCl_4$

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Introduction

SnO_2 layers are used in the technology of electrochromics, where they serve as conductive materials.
Electrochemical characteristics of SnO_2 layers prepared from $SnCl_2$ and $SnCl_4$ were studied. Prepared materials were doped by Sb^{3+} and F^- ions. Comparison of electrochemical properties of industrially produced layers and layers prepared by two different methods was done [1].

Experimental

Commercial product – indium tin oxide (ITO) electrodes were manufactured by sputtering in argon or argon – oxygen atmosphere.
Spray deposited layers were prepared by spraying of solutions containing tin compounds and NH_4F and/or $SbCl_3$ as dopants. Essentially, solutions of $SnCl_4$ in methanol and $SnCl_2$ in water – methanol mixture were used [2].
The electrochemical properties were studied in an aprotic solvent – propylene carbonate (PC) with 0.5 M $LiClO_4$ as a supporting electrolyte. Ferrocene (Fc) and ferrocenium tetrafluoroborate (Fc^+; 0.02 M solutions in PC both) as the electroactive species were used. Cyclic voltammetry was recorded by the usual way using Fc/Fc^+/Pt reference electrode in the same solution. Auxiliary electrode was made of platinum.
The sign and concentration of charge carriers were tested by a simple measurement of Hall effect by the d.c. method.

Results and discussion

XRD analysis has shown that sputtered layers are amorphous while spray deposited ones have the structure of kassiterite. Electric conductivity was measured at the room temperature and indicated rapid increase of conductivity with doping, both by fluoride and antimony [3]. The layers prepared from $SnCl_4$ exhibited N-type conductivity (with exception of Sb doped layers) while the properties of $SnCl_2$ based layers behaved in an opposite way (see Tab. 1).

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Table 1 *Properties of prepared thin layers (R□ ohmic resistivity)*

Coat – dopant		R□ (Ω/□)	charge carrier concentration (m^{-3})	conduction
$SnCl_4$	–	41.04	$2.97 . 10^{26}$	+
	F^-	0.431	$1.06 . 10^{26}$	-
	Sb^{3+}	107.12	$1.85 . 10^{26}$	+
	$F^- + Sb^{3+}$	19.65	$7.22 . 10^{26}$	-
$SnCl_2$	–	3331	$2.76 . 10^{25}$	-
	F^-	227.7	$2.03 . 10^{26}$	-
	Sb^{3+}	720	$3.84 . 10^{27}$	-
	$F^- + Sb^{3+}$	59.87	$2.72 . 10^{26}$	+
ITO – commercial product		266	$1.39 . 10^{26}$	+
ITO – no heat treatment		449.9	$9.09 . 10^{25}$	-
ITO – 270°C treatment		31.3	$5.27 . 10^{27}$	-
ITO – 320°C treatment		58.5	$1.87 . 10^{28}$	-

Three cyclic voltammograms are plotted in the Fig. 1. Voltammogram of Fc/Fc^+ couple measured on a smooth Pt electrode exhibits typical pair of anodic and cathodic peak of almost theoretical shape and size. On the contrary, voltammograms measured with doped layers of SnO_2 on glass show less reversible process.
Voltammogram measured on N-type layer (fluoride doped) prepared from $SnCl_4$ is typical for N-type semiconductors as the anodic peak is almost suppressed and its shape is distorted perhaps by the lateral resistivity of the thin layer.

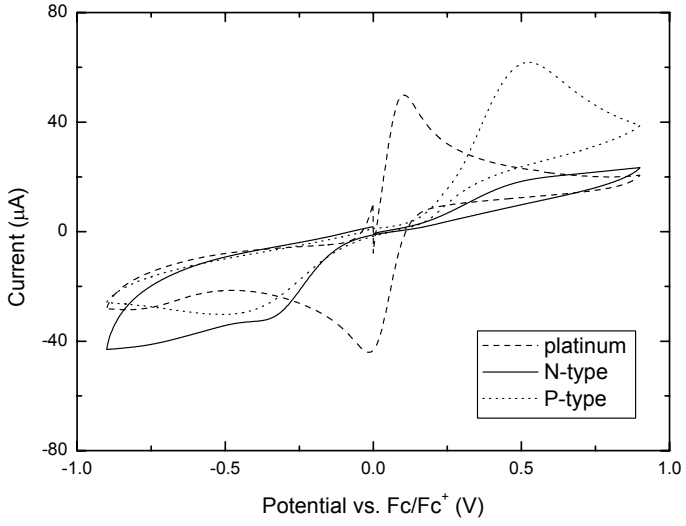

Fig. 1 *The voltammetry characteristics for different ITO layers (temperature 25°C, scan rate 0.01 V/s)*

Layer prepared from $SnCl_4$ is without doping and presents high P-type conductivity. Similar results were obtained with other samples. In general, they confirm the influence of doping both on the type of conductivity and kinetics of electrode reactions.

Conclusions

Thin layer electrodes based on SnO_2 were prepared by two methods (sputtering and spray deposition) and their electrical and electrochemical properties compared. Tin (IV) oxide was doped by fluoride or antimony ions and present N-type or P-type conductivity.

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