

**X-RAY PHOTOEMISSION SPECTROSCOPY STUDY OF THE SURFACE
CHEMISTRY OF LASER-ASSISTED CHEMICAL VAPOUR DEPOSITION
SnO_x THIN FILMS AFTER EXPOSURE TO HYDROGEN¹**

M. Kwoka², G. Czempik, J. Szuber

Department of Microelectronics, Silesian University of Technology, 44-100 Gliwice, Poland

Received 11 February 2005, accepted 22 April 2005

In this paper we present the results of X-ray Photoemission Spectroscopy (XPS) study of the surface chemistry of Laser-assisted Chemical Vapour Deposition (L-CVD) deposited tin oxide SnO_x thin films before and after subsequent exposure to molecular hydrogen (hydrogenation) at room and elevated temperature up to 800 K. As-deposited L-CVD tin oxide thin films exhibited a nonstoichiometric composition with a relative concentration [O]/[Sn] equal to 1.29±0.05. After exposure to 10⁵ L of hydrogen at room temperature the relative concentration [O]/[Sn] was almost the same. After the same exposure to hydrogen at elevated temperature the relative concentration [O]/[Sn] decreases what confirms the effect of drastic reduction to the almost stoichiometric tin oxide SnO thin films. This evident reduction of L-CVD tin oxide thin films was confirmed by the shape analysis of corresponding XPS Sn3d_{5/2} and O1s peaks using the deconvolution procedure in which the different contribution of O-Sn²⁺ and O-Sn⁴⁺ bondings were determined.

PACS: 68.35 Dv, 68.55 a, 81.15 Gh, 81.65 Mq

1 Introduction

Tin dioxide (SnO₂), a wide band gap (3.6 eV) n-type semiconductor, is one of the most important material for gas sensors [1–3]. In general, the gas sensing mechanism of SnO₂ consists of significant changes of the surface electrical conductivity as a result variation of its stoichiometry after chemisorption and/or catalytic reactions in the presence of even low concentration of reducing gases (CO-50 ppm) and oxidising gases (NO_x –1ppm) [2, 3].

Since 30 years the commercial gas sensors devices based on SnO₂ are mainly fabricated using thick films of thickness of mm scale. Their fundamental limitation is a large power consumption. This limitation does not concern the thin solid film gas sensors. That's why in the last several years a great attention is given for elaboration of a good quality SnO₂ thin films which could be used in the gas sensors devices [1–3].

¹Presented at SSSI-IV (Solid State Surfaces and Interfaces IV) Conference, Smolenice, Slovakia, 8–11 Nov. 2004.

²E-mail address: Monika.Kwoka@polsl.pl

One of the most promising techniques in the preparation of high quality and almost stoichiometric tin dioxide thin films is the L-CVD technique, developed by the group of Larciprete [4–7]. Contrary to the commonly used deposition techniques for tin dioxide thin film recently reviewed in [1–3] the L-CVD method exhibits several advantages as low substrate temperature, high spatial resolution (the focused laser beam allows the growth of thin film patterned film with high lateral resolution), and a precise doping of the sample during deposition [4].

In early studies [4–7] the L-CVD SnO_x thin films were obtained in two step process, i.e. the thin Sn films were deposited on atomically clean Si substrates using the tetramethyltin $\text{Sn}(\text{CH}_3)_4$ (TMT) flux as precursor, irradiated by the ArF excimer laser, which subsequently were submitted to the oxidation process through an exposition to molecular oxygen up to 10^{12} L. The XPS studies showed that, in the as obtained thin films a relative concentration $[\text{O}]/[\text{Sn}]$ reached a maximal value of about 1.5 [6]. That's why, an another approach in L-CVD process for preparation of the SnO_x thin films has lately been developed defined as one step process, in which a mixture of two precursors, i.e. tetramethyltin $\text{Sn}(\text{CH}_3)_4$ (TMT) and molecular oxygen O_2 was used in the presence of ArF excimer laser [8, 9].

It has been shown by XPS studies that the such obtained L-CVD tin oxide thin films exhibit an evident nonstoichiometry because the relative concentration $[\text{O}]/[\text{Sn}]$ was at the level of about 1.4 [8, 9]. However, in these papers a simplified procedure of the determination of relative concentration $[\text{O}]/[\text{Sn}]$ was applied what gave us some evident inaccuracy.

In the recent paper [9] we presented the results of XPS studies of surface chemistry of the L-CVD deposited tin oxide thin films after their *in situ* additional oxidation. The relative concentration $[\text{O}]/[\text{Sn}]$ was equal to about 2.0, what evidently confirmed that after those procedures the obtained films are almost stoichiometric.

In this paper we present the XPS results of studies of the opposite effect, i.e. influence of reduction of the almost stoichiometric L-CVD SnO_2 thin films after subsequent *in situ* exposure to molecular hydrogen at room and elevated temperature. Basing on the area of XPS $\text{O}1s$ i $\text{Sn}3d_{5/2}$ spectral lines and using the procedure based on the atomic sensitivity factor [10], the relative concentration $[\text{O}]/[\text{Sn}]$ of L-CVD SnO_x thin films was determined. Moreover, from the shape analysis of corresponding XPS $\text{Sn}3d_{5/2}$ and $\text{O}1s$ peaks using the deconvolution procedure different bondings between Sn and O atoms were recognized.

2 Experimental

The preparation and XPS characterisation of the L-CVD SnO_x thin films was performed in ENEA (Ente Nazionale Energie Alternative) Centre, Frascati, Italy. The experimental set-up consists of a loading chamber, a deposition chamber (background pressure $\sim 10^{-7}$ Pa) for preparation of SnO_x thin films by the L-CVD technology using the ArF (193 nm) excimer laser (Lambda Physik, LPX 100 Model), connected via a gate valve to the analysis chamber (base pressure $\sim 10^{-8}$ Pa) equipped, among others, with the XPS spectrometer based on X-ray lamp (Al K_α 1486.6 eV) and a double-pass cylindrical mirror analyser (DPCMA) (PHI 255G Model) working at the constant resolution of 0.1 eV.

The SnO_x thin films were deposited on Si(100) substrates covered with a natural oxide, which were firstly cleaned by UHV (10^{-7} Pa) annealing at 940°C.

During a deposition TMT- O_2 mixture with 0.2 sccm and 5 sccm fluxes was used, respec-

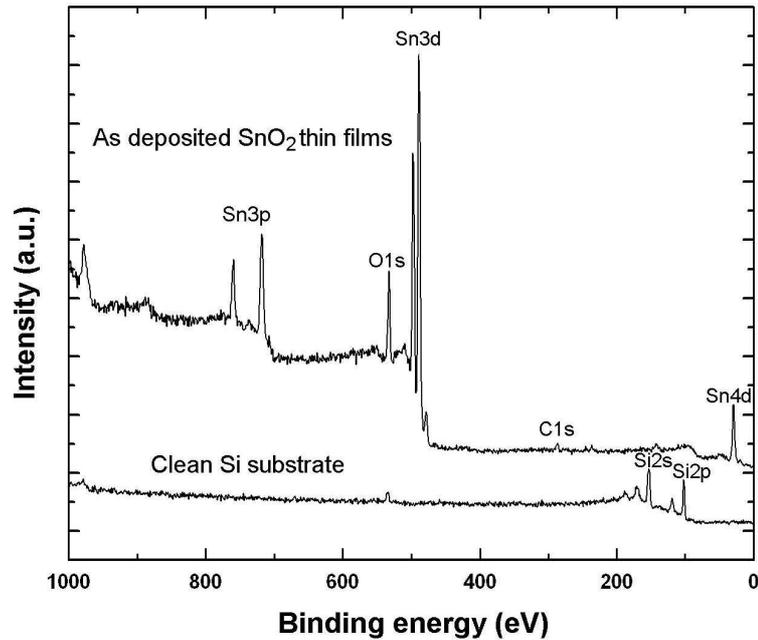


Fig. 1. XPS survey spectra of the as-deposited L-CVD SnO_x thin films on clean Si surface.

tively, with pulsed laser beam (5 Hz, 20 mJ/cm^2) set in a perpendicular geometry. The Si substrate was kept at room temperature. The thickness of deposited SnO_x thin films was about 20 nm after 60 min., as determined with a quartz crystal microbalance.

As-deposited samples were then exposed to the controlled doses of H_2 at different temperatures and then cooled down to room temperature for XPS measurements.

For XPS experiments the X-ray beam struck a sample at room temperature at an angle 70° with respect to normal, whereas the spectra have been recorded at take-off angle of 20° in order to enhance the surface sensitivity. All the reported binding energy (BE) data have been calibrated using C1s peak at 285.0 eV of residual carbon at the surface of SnO_x thin films. The analysis of the XPS data was performed using the XPS Peak Fitting Program version 4.1 elaborated by Kwok [11]. Background subtraction was done by Shirley method.

Other experimental details have been described elsewhere [7–10].

3 Results and discussion

Figure 1 shows the XPS survey spectrum of the as deposited L-CVD SnO_x thin films together with the reference XPS survey spectrum of the clean Si substrate [12]. One can easily note from the XPS survey spectrum that the as deposited L-CVD SnO_x thin films exhibit a good purity. Apart from a weak C1s peak at about 285 eV at the signal-to-noise ratio of about 2 (at the limit of detection), only Sn and O related core levels were detectable.

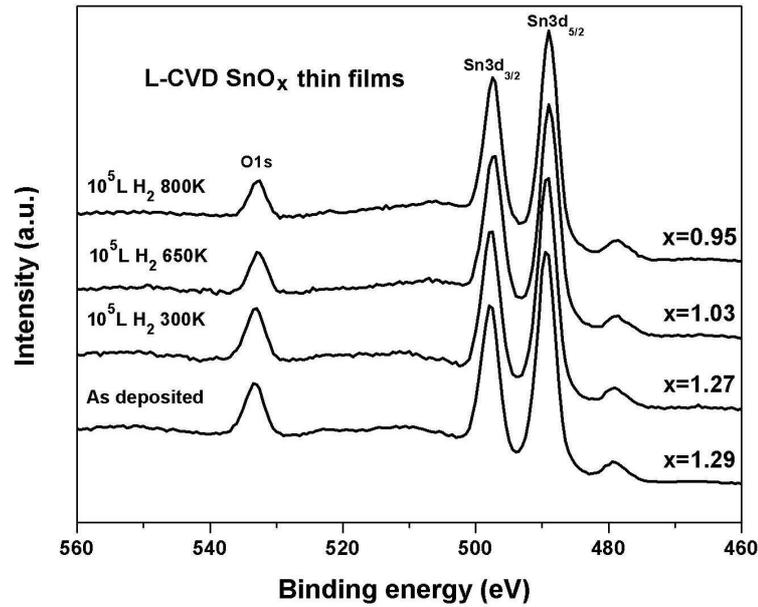


Fig. 2. XPS windows consisting the O1s and Sn3d peaks of the as-deposited L-CVD SnO_x thin films and after subsequent exposure to molecular hydrogen at room and elevated temperature. The X means the relative concentration [O]/[Sn].

Already our preliminary recent XPS experiments [8,9] showed that the stoichiometry of as freshly deposited L-CVD SnO_x thin films evidently changed after subsequent cycles of exposure to the molecular hydrogen H₂.

In this paper we focused on the detailed quantitative analysis of the surface chemistry of L-CVD SnO_x thin films of as-deposited and after subsequent exposure to molecular hydrogen of 10⁵ L (1 L = 10⁻⁴ Pa·s) at room and elevated temperature of 650K and 800K.

Figure 2 shows the corresponding XPS spectral windows of Sn3d and O1s peaks. From their areal intensities using the analytical procedure basing on the atomic sensitivity factor [10] we determined the relative concentration of [O]/[Sn]. The obtained values are shown on corresponding spectra in Fig. 2.

For the as-deposited L-CVD SnO_x thin films the relative concentration [O]/[Sn] was determined as equal to 1.29±0.05. This value shows an evident nonstoichiometry of the L-CVD SnO_x thin films, similarly as in our recent studies [8,9,13].

After exposure of as-deposited L-CVD SnO_x thin films to molecular hydrogen at room temperature the relative concentration [O]/[Sn] remains almost unchanged.

An evident decrease of the relative concentration [O]/[Sn] was only determined for the as-deposited L-CVD SnO_x thin films after subsequent exposure to molecular hydrogen at elevated temperature at 650 K. The relative concentration [O]/[Sn] = 1.03±0.05 evidently confirms the effect of reduction of as-deposited L-CVD SnO_x thin films to the form of tin oxide SnO.

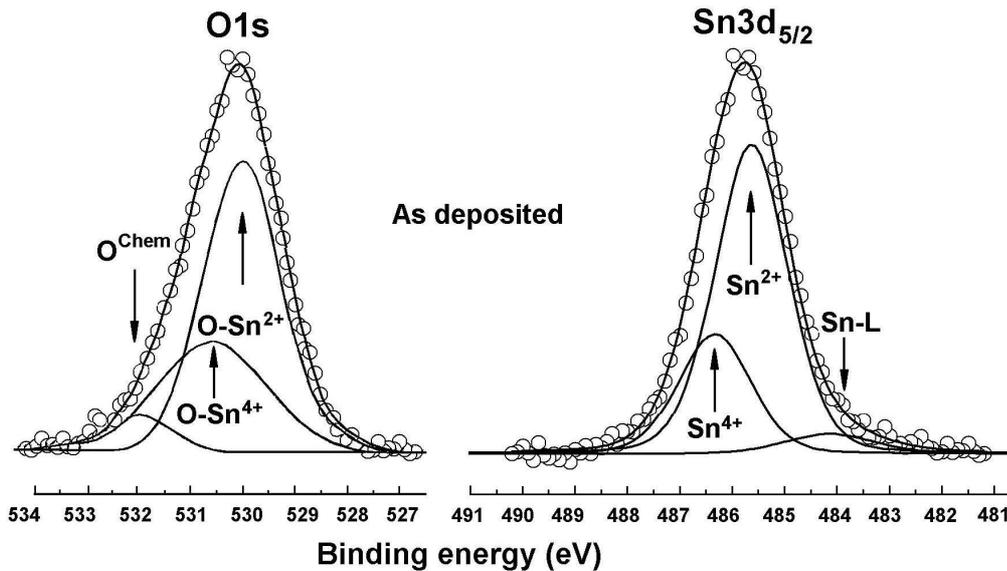


Fig. 3. Recorded XPS $\text{Sn}3d_{5/2}$ and $\text{O}1s$ peaks (in circles) and deconvoluted components (solid lines) of the as-deposited L-CVD SnO_x thin films.

A more evident effect was observed after exposure of L-CVD SnO_x thin films to molecular hydrogen at higher temperature of 800K. The relative concentration $[\text{O}]/[\text{Sn}]$ was determined as equal to 0.95 ± 0.05 . It means that after this last procedure the as-deposited L-CVD SnO_x thin films are reduced to stoichiometric tin oxide SnO .

This evident reduction of L-CVD SnO_x thin films was independently confirmed by the shape analysis of corresponding XPS $\text{Sn}3d_{5/2}$ and $\text{O}1s$ peaks using the deconvolution procedure.

In Fig. 3 (right side) the XPS $\text{Sn}3d_{5/2}$ line of as deposited L-CVD SnO_x thin films is presented. Already a simple observation indicates that it is asymmetrical. Thus, it is evident that it should contain the components corresponding to Sn atoms (ions) at various oxidizing states corresponding to the following BE values: Sn^0 (485.0 eV), Sn^{+2} (485.9 eV) and Sn^{+4} (486.6 eV) [9].

Accordingly, a procedure of deconvolution of XPS $\text{Sn}3d_{5/2}$ line has been performed assuming the presence of all these Sn components, corresponding to the three of Sn bonding just mentioned. The main parameters used in the applied fitting procedure as well as the best fitting parameters are summarized in Table 1.

The deconvolution of the $\text{Sn}3d_{5/2}$ peak of as-deposited L-CVD SnO_x thin films confirmed that it is built-up essentially as a mixture of three components. However, there are only two components corresponding to the Sn^{2+} and Sn^{4+} ions, respectively, separated by 0.7 eV (see Fig. 3). It means that the as-deposited L-CVD SnO_x thin films consist essentially of a mixture of tin oxide SnO and tin dioxide SnO_2 . No evidence from contribution of elemental Sn^0 atoms at BE of 485 eV was observed. The relative surface area of the both components independently

Tab. 1. The binding energy (at maximum), full width at half maximum (FWHM) and relative areal intensity of the main components of XPS Sn3d_{5/2} peak of as-deposited L-CVD SnO_x thin films.

XPS Sn3d _{5/2} peak parameters	Components		
	Sn-L(?)	Sn ²⁺	Sn ⁴⁺
Binding energy [eV]	484.0	485.9	486.6
FWHM [eV]	1.42	1.43	1.79
Relative areal intensity	0.05	0.68	0.27

Tab. 2. The binding energy (at maximum), full width at half maximum (FWHM) and relative areal intensity of the main components of XPS O1s peak of as-deposited L-CVD SnO_x thin films.

XPS O1s peak parameters	Components		
	O ^{chem} (?)	O-Sn ⁴⁺	O-Sn ²⁺
Binding energy [eV]	532.0	530.5	529.8
FWHM [eV]	1.25	2.08	1.31
Relative areal intensity	0.05	0.30	0.65

confirms a relative concentration of [O]/[Sn] ~1.3 of as-deposited L-CVD SnO_x thin films.

However, an additional third small component at BE about 484.0 eV was observed. A similar component in the Sn3d_{5/2} peak was recently observed by Larciprete et al. [6] for the two-step deposited L-CVD SnO₂ thin films and was attributed to ligand-type bonding of Sn atoms (Sn-L) with different fragments of residual TMT precursor Sn(CH₃)_n (where n=1-3) created during UV laser photolysis and incorporated in the deposited L-CVD SnO_x thin films. Our interpretation of the origin of this additional third small Sn3d component at BE about 484.0 eV confirms the fact that the relative amplitude of this component (Sn-L) with respect to Sn²⁺ and Sn⁴⁺ components is twice larger for the L-CVD SnO_x thin films prepared recently by Larciprete et al [6, 7] in two-step process for which the relative concentration [C]/[Sn] equal to 0.6 is also twice larger.

In Fig. 3 (left side) the XPS O1s line of as-deposited L-CVD SnO_x thin films is presented. Also in this case already a simple observation of XPS O1s peak shows that it is wide, asymmetrical, and exhibits an evident shoulder at the high BE side. Thus, it is evident that it should contain the components corresponding to O atoms (ions) in bonding with various Sn atoms (ions) at proper oxidizing states. The main parameters used in the applied fitting procedure as well as obtained parameters are summarized in Table 2.

The deconvolution of the XPS O1s peak of as-deposited L-CVD SnO_x thin films confirmed that it is built-up as a mixture of three components. Two components corresponding to the O-Sn²⁺ and O-Sn⁴⁺ bondings have easily been distinguished, respectively, separated by 0.7 eV, as shown in Fig. 3. The relative surface area of the two components independently confirms a relative concentration of [O]/[Sn] ~1.3 of as-deposited L-CVD SnO₂ thin films.

Moreover, an additional third small component at BE about 532 eV was observed. A similar

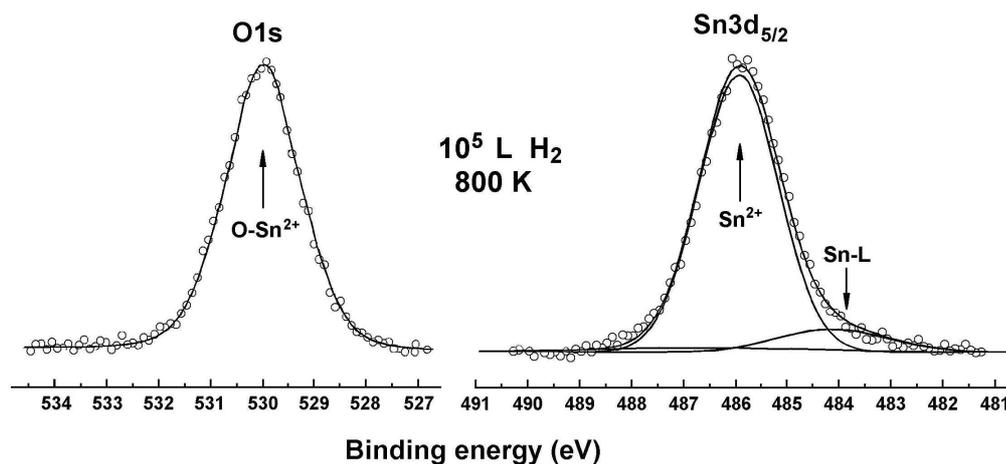


Fig. 4. Recorded XPS $\text{Sn}3d_{5/2}$ and $\text{O}1s$ peaks (in circles) and deconvoluted components (solid lines) of the as-deposited L-CVD SnO_x thin films after exposure to 10^5 L H_2 at 800 K.

components in the $\text{O}1s$ peak was recently observed in our recent paper [9] and was attributed to the additional oxygen atoms chemisorbed at the surface and defined as O^{chem} , what was in a good agreement with the recent observation of Mulla et al. [14] and Yea et al. [15], who propose the energetic position of this component close to 533.0 eV.

For the as-deposited L-CVD SnO_x thin films exposed to the molecular hydrogen H_2 the shape analysis have been performed only for the mostly reduced sample, i.e. after exposure to 10^5 L H_2 at 800 K.

In Fig. 4 (right side) the XPS $\text{Sn}3d_{5/2}$ line of as-deposited L-CVD SnO_x thin films after exposure to 10^5 L H_2 at 800 K is presented. Already a simple visual shape analysis showed that it is almost symmetrical. The deconvolution of $\text{Sn}3d_{5/2}$ peak confirmed that it is built-up by only one component Sn^{2+} which energetic position exactly corresponds to the centre of gravity of full peak at BE about 486 eV. As before for the as-deposited L-CVD SnO_x thin films no evidence from contribution of elemental Sn^0 atoms at BE about 485 eV was observed. It means that after H_2 exposure the almost all the tin Sn^{4+} ions become reduced to Sn^{2+} . This is also confirmed by a relative concentration of $[\text{O}]/[\text{Sn}] \sim 1.0$. However, there is still an additional component at BE about 484 eV corresponding to the ligand-type bondings of Sn atoms with different fragments of residual TMT precursor created during UV laser photolysis and incorporated in the deposited L-CVD SnO_x thin films.

Figure 4 (left side) shows the XPS $\text{O}1s$ line of as deposited L-CVD SnO_x thin films after exposure to 10^5 L H_2 at 800 K. Already a visual observation shows that the peak become narrow and symmetric. Its deconvolution confirmed that it is built-up by only one component O-Sn^{2+} which BE position exactly corresponds to the centre of gravity of all the peak at BE about 530 eV. It additionally confirms that after H_2 exposure almost all the tin Sn^{4+} ions become reduced to Sn^{2+} and finally the deposited thin films become the almost stoichiometric tin oxide SnO layer.

4 Conclusions

In this paper a detailed XPS studies of the SnO_x thin films of thickness of about 20 nm deposited by L-CVD technique and then subsequently exposed to the molecular hydrogen H₂ were performed. The influence of exposure to the molecular hydrogen H₂ on the stoichiometry of SnO_x thin films was determined.

Our studies that as deposited SnO_x thin films exhibit nonstoichiometric composition with a relative concentration [O]/[Sn] = 1.29±0.05, that corresponds to a mixture of tin oxide SnO and tin dioxide SnO₂. It was also confirmed by the shape analysis of XPS Sn3d and O1s peaks.

After subsequent hydrogenation the L-CVD SnO_x thin films have been reduced reaching after final hydrogen exposure 10⁵ L H₂ at 800 K a relative concentration [O]/[Sn] = 0.95±0.05 corresponding to the stoichiometric tin oxide SnO. It was also confirmed by the shape analysis of XPS Sn3d and O1s peaks.

These information on surface chemistry of the L-CVD SnO_x thin films will be a base for the interpretation of their electronic and sensing properties. Currently we are engaged in the depth profiling of L-CVD SnO_x thin films with XPS technique in order to get an information on their composition in subsurface region including the unknown origin of the Sn-L and O^{chem} components of XPS Sn3d and O1s peaks.

Acknowledgement: One of the author (G.C.) thanks for the fellowship within the EMSPS-TEMPUS Programme MJEP 08343-94 which allowed him to work in ENEA, Frascati, Italy, under direction of Dr. Rosanna Larciprete on the development of L-CVD technology for preparation of SnO₂ thin films for gas sensors application. The authors are also very grateful to Dr. P. De Padova and M. Nardelli for their indispensable scientific and technical assistance during experiments. This work was sponsored by the Polish State Committee for Scientific Research (KBN) within a research project 3 T11B 067 28. This work was performed within the V FPEC Project of Centre of Excellence in Physics and Technology of Semiconductor Interfaces and Sensors - CESIS, under the Contract: G6MA-CT-2002-04042.

References

- [1] K. Ihokura, J. Watson: *The Stannic Oxide Gas Sensor: Principles and Applications* CRC Press, Boca Raton, FL, 1994
- [2] W. Göpel, K.-D. Schierbaum: *Sensors and Actuators B* **26-27** (1995) 1
- [3] N. Barsan, M. Schweitzer-Barberich, W. Göpel: *Fresenius J. Anal. Chem.* **365** (1999) 287
- [4] R. Larciprete, E. Borsella, P. de Padova, M. Fanfoni, M. Mangiantini, P. Perfetti: *Appl. Surf. Sci.* **69** (1993) 59
- [5] R. Larciprete, E. Borsella, P. De Padova, M. Mangiantini, P. Perfetti, M. Fanfoni: *J. Vac. Sci. Technol. A* **11** (1993) 336
- [6] R. Larciprete, E. Borsella, P. De Padova, P. Perfetti, C. Crotti: *J. Vac. Sci. Technol. A* **15** (1997) 2492
- [7] R. Larciprete, E. Borsella, P. De Padova, P. Perfetti, G. Faglia, G. Sberveglieri: *Thin Solid Films* **323** (1998) 291
- [8] J. Szuber, G. Czempik, R. Larciprete, B. Adamowicz: *Sensors and Actuators B* **70** (2000) 177
- [9] J. Szuber, G. Czempik, R. Larciprete, D. Koziej, B. Adamowicz: *Thin Solid Films* **391** (2001) 198

- [10] C. D. Wagner, W. M. Riggs, L. E. Davis, J. F. Moulder, G. E. Mnilenberger: *Handbook of X-ray Photoelectron Spectroscopy*, Perkin-Elmer, Eden Prairie, MN 1979
- [11] R. W. M. Kwok: *XPS Peak Fitting Program for WIN95/98 XPSPEAK Version 4.1*, Department of Chemistry, The Chinese University of Hong Kong
- [12] M. Kwoka: *M.Sc. Thesis*, Silesian University of Technology, Gliwice, 2003 (in English)
- [13] M. Kwoka, L. Ottaviano, M. Passacantando, S. Santucci, G. Czempik, J. Szuber: *Thin Solid Films* (in press)
- [14] I. S. Mulla, V. J. Rao, H. S. Soni, S. Badrinarayanan, A. P. B. Sinha: *Surf. Coatings Technol.* **31** (1987) 77
- [15] B. Yea, H. Sasaki, T. Osaki, K. Sugihara, R. Konishi: *Jpn. J. Appl. Phys.* **38** (1999) 2103