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XPS study of the surface chemistry of L-CVD SnO_2 thin films after oxidation

M. Kwoka[a,*], L. Ottaviano[b], M. Passacantando[b], S. Santucci[b], G. Czempik[a], J. Szuber[a]

[a] *Department of Microelectronics, Silesian University of Technology, 44-100 Gliwice, Poland*
[b] *CASTI-CNR Laboratory and Department of Physics, University of L'Aquila, Via Vetoio 10 I-67010 Coppito-L'Aquila, Italy*

Abstract

In this paper we present the results of XPS study of the surface chemistry of L-CVD SnO_2 thin films onto Si(100) before and after subsequent additional oxidation. Moreover, the ageing effect was also studied in order to check the influence of ambient oxidation. As-deposited L-CVD SnO_2 thin films exhibit evident nonstoichiometry with the relative concentration [O]/[Sn] equal to 1.29 ± 0.1. After in situ oxidation at high temperature (800 K) the relative concentration [O]/[Sn] increases to 1.95 ± 0.05 which corresponds to the almost stoichiometric SnO_2. Almost the same relative concentration [O]/[Sn] of L-CVD SnO_2 thin films has been obtained after long term exposure to air. The oxidation states of L-CVD SnO_2 thin films in both cases were confirmed by the shape analysis of corresponding XPS O1s and $Sn3d_{5/2}$ peaks using the decomposition procedure. For the as-deposited L-CVD SnO_2 thin films a mixture of SnO and SnO_2 was observed, while for the oxidized L-CVD SnO_2 thin films the domination of SnO_2 was determined.

Keywords: Tin dioxide; Thin films; Deposition; Oxidation

1. Introduction

In the last two decades tin dioxide (SnO_2), a wide band gap (3.6 eV) n-type semiconductor, has been an object of great attention in fundamental and applied research. In particular there has been a tremendous interest toward its gas sensing properties [1]. In general, the gas sensing mechanism of SnO_2 consists of significant changes of the surface electrical conductivity as a result of chemisorption and catalytic reactions in the presence of even low concentration of reducing gases like CO (50 ppm) and oxidising gases like NO_x (1 ppm) [1,2]. Up to date, commercial gas sensors devices based on SnO_2 have been fabricated with thick (about 1 mm) films, for which a fundamental limitation is a large power consumption. This limitation does not concern the thin solid film gas sensors [1–3].

One of the most promising techniques in the preparation of high quality SnO_2 thin films is the Laser-induced Chemical Vapour Deposition (L-CVD) technique, developed by the group of Larciprete [4–7]. Contrary to the commonly used SnO_2 thin film deposition techniques reviewed in [1] the L-CVD method exhibits several advantages as low substrate temperature, high spatial resolution (the focused laser beam allows the growth of thin patterned film with high lateral resolution), and a precise doping of the sample during deposition [4].

In the early studies the L-CVD SnO_2 thin films were obtained in a two-step process, i.e. the thin Sn films were deposited on atomically clean Si substrates using the tetramethyltin $Sn(CH_3)_4$ (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 for the as-obtained thin films a relative concentration [O]/[Sn] reached a value of about 1.5 [4].

Lately, a one-step L-CVD process for preparation of the SnO_2 thin films has been developed, in which a mixture of

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[*] Corresponding author. Tel./fax: +48 32 237 20 57.
E-mail address: Monika.Kwoka@polsl.pl (M. Kwoka).

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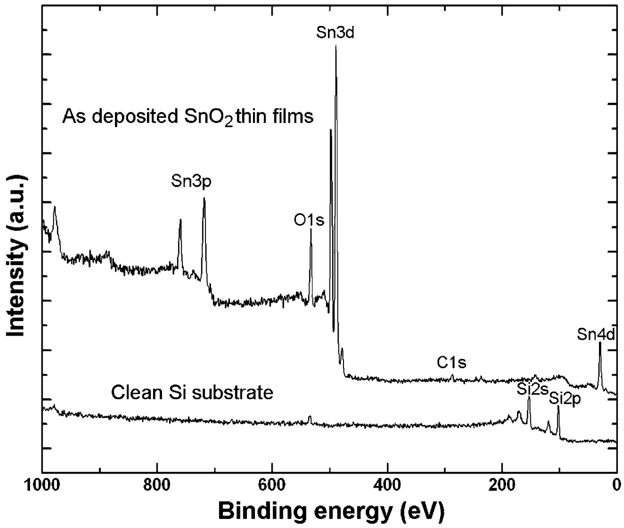

Fig. 1. XPS survey spectra of the as-deposited L-CVD SnO_2 thin films on clean Si surface.

two precursors, i.e. tetramethyltin $Sn(CH_3)_4$ (TMT) and molecular oxygen O_2 was used in the presence of ArF excimer laser [8,9]. The surface chemistry studies using XPS technique showed that in the such obtained thin films an evident nonstoichometry was observed because the relative concentration [O]/[Sn] was at the level of about 1.4 [8,9]. However, in these papers a simplified procedure of the determination of relative concentration [O]/[Sn] as well as a simplified procedure of shape analysis of XPS spectral lines was applied.

In this paper we present the results of XPS studies of surface chemistry of the L-CVD deposited SnO_2 thin films after their in situ additional oxidation, as well as after long term exposition to the atmospheric air.

2. Experimental

The preparation and XPS characterization of the L-CVD SnO_2 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_2 thin films by the L-CVD using the ArF (193 nm) excimer laser (Lambda Physik, LPX 100 Model), connected via a gate valve with an analysis chamber (base pressure $\sim 10^{-8}$ Pa) equipped, among other techniques, with an XPS spectrometer with the X-ray lamp (Al K_α 1486.6 eV) and a double-pass cylindrical mirror analyser (DPCMA) (PHI 255G Model) having a constant energy resolution of 0.1 eV.

The SnO_2 thin films were deposited on Si(100) substrates covered with natural oxide, which was firstly removed by UHV (10^{-7} Pa) annealing at 940 °C.

During a deposition TMT–O_2 mixtures with 0.2 sccm and 5 sccm fluxes were used, respectively, with pulsed laser beam (5 Hz) of 20 mJ/cm^2 flux density set in a perpendicular geometry. The Si substrate was kept at room temperature. The thickness of deposited SnO_2 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 O_2 at different temperatures and, after cooling down to room temperature, the XPS were measured.

Then the deposited L-CVD SnO_2 thin films samples were submitted to a long term exposition to dry atmospheric air in order to check the ageing effect. For these samples XPS data were taken at the CASTI (Center for the Scientific and Technological Assistance to Industries) Laboratory of the CNR and Department of Physics, University of L'Aquila, Italy.

The XPS spectrometer (PHI 5700 Model) (background pressure $\sim 10^{-7}$ Pa) used was equipped with an X-ray lamp (Al K_α 1486.6 eV) and a concentric hemispherical analyser (CHA) (PHI 10360 Model).

All the reported binding energy data have been calibrated using the residual carbon present on the surface of SnO_2 thin films, positioned at 285.0 eV. The analysis of XPS data was performed using the XPS Peak Fitting Programme version 4.1 [10].

Other experimental details have been described elsewhere [8,9,11].

3. Results and discussion

3.1. In situ XPS studies

Fig. 1 shows the XPS survey spectrum of the as-deposited L-CVD SnO_2 thin films of thickness at about 20 nm and the reference XPS survey spectrum of the clean Si substrate [8,9]. One can easy note that the XPS survey spectrum of the as-deposited L-CVD SnO_2 thin films exhibits a good purity. Apart from a weak C1s peak visible at about 285 eV at the signal-to-noise ratio of about 2 (that is at the limit of detection), only Sn and O related core levels are detectable in the spectrum. It was almost on the same level as on the Si substrate. Nevertheless, a quantitative analysis based on the area estimate of the XPS C1s and Sn3$d_{5/2}$ spectral lines (using the atomic sensitivity factor

Table 1
The relative concentration of different L-CVD SnO_2 thin films

L-CVD SnO_2 thin films	Relative concentration	
	[C]/[Sn]	[O]/[Sn]
As deposited	0.27±0.10	1.29±0.05
As deposited and then exposed to 10^8 L O_2 at 300K	0.25±0.10	1.30±0.05
As deposited and then exposed to 10^8 L O_2 at 800 K	0.25±0.10	1.95±6.05
As deposited after long term ageing	3.21±0.06	1.56±0.05
As deposited after ageing and UHV annealing at 670 K	2.55±0.06	1.21±0.05

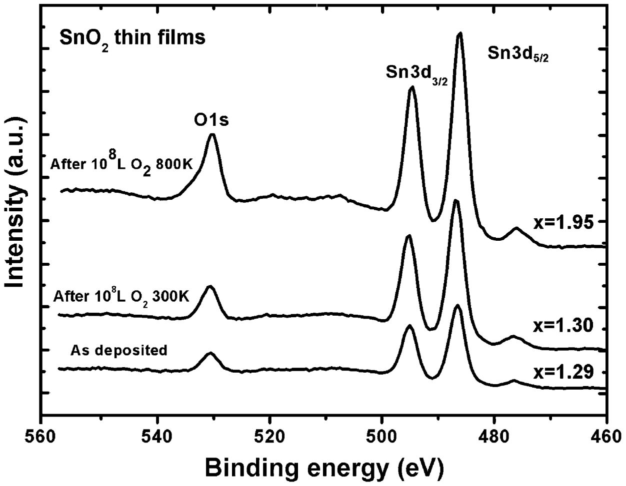

Fig. 2. XPS O1s and Sn3d spectral windows of the as-deposited L-CVD SnO_2 thin films, as well as after subsequent exposure to molecular oxygen O_2 at 300 K and 800 K, respectively. Parameter x indicates the relative concentration [O]/[Sn].

analytical procedure [12]) shows a [C]/[Sn] relative concentration of L-CVD SnO_2 thin films equal to 0.27±0.11. The same level of the [C]/[Sn] relative concentration was determined for the L-CVD SnO_2 thin films after their subsequent exposure to 10^8 L of molecular oxygen O_2 at 300 K and 800 K, as summarized in Table 1.

Our recent XPS experiments [8,9] already showed that the stoichiometry of as-deposited L-CVD SnO_2 thin films evidently changed after subsequent cycles of exposure to the molecular oxygen O_2. That's why a detailed analysis of the relative concentration [O]/[Sn] of L-CVD SnO_2 thin films submitted to molecular oxygen O_2 exposure has been performed in this work from a quantitative analysis of the XPS data shown in Fig. 2. There, the XPS Sn3d and O1s spectral windows of the 20 nm L-CVD SnO_2 thin films are shown for as-deposited samples and after subsequent oxidation at 300 K and 800 K.

For the as-deposited L-CVD SnO_2 thin films it was equal to 1.29±0.05. This value is almost 0.1 smaller than previously reported using a simplified analytical procedure [9]. Nevertheless, also this last value confirms an evident nonstoichiometry of the as-deposited L-CVD SnO_2 thin films [9].

The room temperature oxygen exposure of as-deposited L-CVD SnO_2 thin films does not affect the relative [O]/[Sn] concentration that remains substantially unaltered because measured ratio is equal to 1.30±0.05.

After the oxidation of as-deposited L-CVD SnO_2 thin films at 800 K the relative concentration [O]/[Sn] reaches a value of 1.95±0.05 corresponding to almost stoichiometric SnO_2 thin films (see the summary values reported in Table 1). However, it should be pointed out that this last value is almost 0.25 smaller than previously reported using a simplified analytical procedure [9].

This evident oxidation of as-deposited L-CVD SnO_2 thin films was independently confirmed by the shape analysis of corresponding XPS Sn3d$_{5/2}$ and O1s peaks using the decomposition procedure.

In Fig. 3 (right side) the XPS Sn3d$_{5/2}$ line of as-deposited L-CVD SnO_2 thin films is presented. Already a simple visual shape analysis indicates that it is wide and asymmetrical. Thus, it is evident that it should contain the components corresponding to Sn atoms (ions) at various oxidizing steps. Atoms of Sn in as-deposited L-CVD SnO_2 thin films can exist at three oxidizing steps corresponding to the following binding energy values: Sn^0 (485.0 eV), Sn^{+2} (485.9 eV) and Sn^{+4} (486.6 eV) as taken from NIST data base [13].

Accordingly, a procedure of decomposition of XPS Sn3d$_{5/2}$ line has been performed assuming the presence of all these Sn components, corresponding to three types of Sn

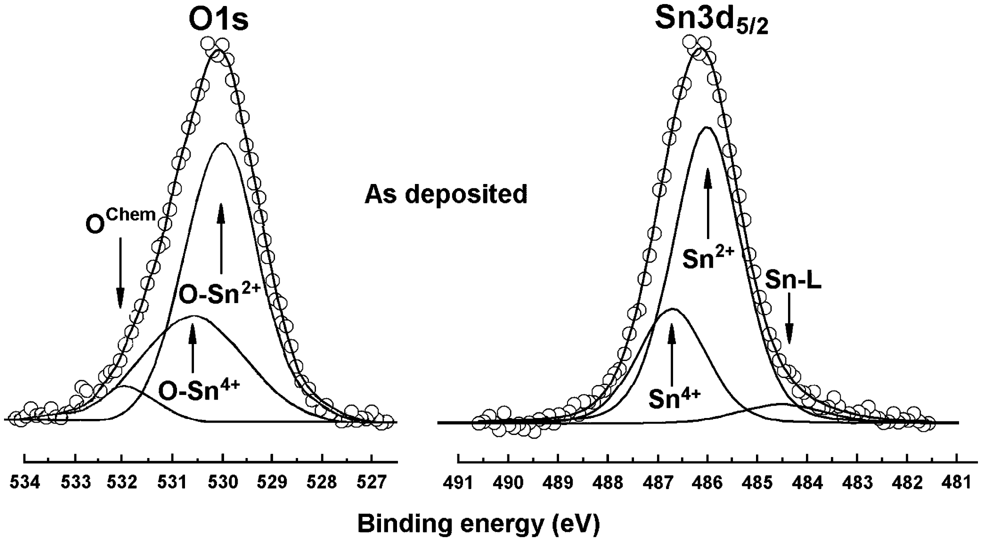

Fig. 3. Registered XPS Sn3d$_{5/2}$ and O1s peaks (in circles) and decomposited components (solid lines) of the as-deposited L-CVD SnO_2 thin films.

Table 2
The binding energy, full width at half maximum (FWHM) and relative peak areal intensity of main components of XPS $Sn3d_{5/2}$ and O1s peaks of as-deposited L-CVD SnO_2 thin films

XPS peak parameters	Sn $3d_{5/2}$			O1s		
Components	Sn–L(?)	Sn^{2+}	Sn^{4+}	O^{chem} (?)	O–Sn^{4+}	O–Sn^{2+}
Binding energy [eV]	484.0	485.9	486.6	532.0	530.5	529.8
FWHM [eV]	1.42	1.43	1.79	1.35	1.81	1.31
Relative peak areal intensity	0.05	0.68	0.27	0.05	0.30	0.65

bonding just mentioned. The main parameters used in the applied fitting procedure as well as the best fitting parameters are summarized in Table 2.

The decomposition of $Sn3d_{5/2}$ peak of as-deposited L-CVD SnO_2 thin films confirmed that it is built-up essentially as a mixture of two components, namely those 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_2 thin films consist only of a mixture of tin oxide SnO and tin dioxide SnO_2. No evidence from contribution of elemental Sn^0 atoms at BE about 485 eV was observed. The relative surface area of the both components independently confirms a relative concentration of [O]/[Sn] ~ 1.3 of as-deposited L-CVD SnO_2 thin films. This is in evident contradiction to the recently published analysis [9] of a relative surface area of Sn^{4+} and Sn^{4+} components which did not correlate with the relative concentration of [O]/[Sn].

Moreover, an additional third small component of BE at about 484.0 eV was observed, whose origin is still unknown. A similar component in the $Sn3d_{5/2}$ peak was recently observed by Larciprete et al. [7] for two-step deposited L-CVD SnO_2 thin films and was attributed to ligand-type bonding of Sn atoms with different fragments of residual TMT precursor created during UV laser photolysis and incorporated in the deposited L-CVD SnO_2 thin films. However, because an error analysis of the peak shape analysis has not been provided, the significance of this peak is rather small. But this does not affect the quantitative analysis, which has been performed on total intensities [14].

In Fig. 3 (left side) the XPS O1s line of as-deposited L-CVD SnO_2 thin films is presented. Also in this case already a simple visual shape analysis of XPS O1s peak shows that it is wide, asymmetrical, and exhibits an evident shoulder at the high binding energy side of the spectrum. 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 steps. The main parameters used in the applied fitting procedure as well as the obtained best fitting parameters are also summarized in Table 2.

The decomposition of XPS O1s peak of as-deposited L-CVD SnO_2 thin films confirmed that it is built-up as a mixture of three components. Two components corresponding to the O–Sn^{2+} and O–Sn^{4+} bonding 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 SnO_2 thin films. Moreover, an additional third small component of BE at about 532 eV was observed, whose origin is still unknown. A similar component in O1s peak was recently observed in our recent paper [7] and was attributed to the oxygen atoms chemisorbed at the surface, which was in a good agreement with the recent observation of Mulla et al. [15] and Yea et al. [16], who propose the energetic position of this component close to 533.0 eV.

Because the room temperature oxygen exposure of as-deposited L-CVD SnO_2 thin films to 10^8 L O_2 does not affect the relative [O]/[Sn] concentration (the relative concentration [O]/[Sn] was equal to 1.30 ± 0.05), the shape analysis have been performed only for the mostly oxidized sample, i.e. after exposure to 10^8 L O_2 at 800 K. The main parameters used in the applied fitting procedure as well as the obtained best fitting parameters are summarized in Table 3.

In Fig. 4 (right side) the XPS $Sn3d_{5/2}$ line of the above-mentioned L-CVD SnO_2 thin films. Already a simple visual shape analysis showed that it is narrow and even symmetrical, which was in contradiction to the as-deposited L-CVD SnO_2 case (Fig. 3).

Accordingly, a procedure of deconvolution of XPS $Sn3d_{5/2}$ line has been performed assuming the presence of only one component at about 486.6 eV. The main parameters used in the applied fitting procedure as well as the best fitting parameters are summarized in Table 3. The deconvolution procedure confirmed the existence of only

Table 3
The binding energy, full width at half maximum (FWHM) and relative peak areal intensity of main components of XPS $Sn3d_{5/2}$ and O1s peaks of as-deposited L-CVD SnO_2 thin films after high temperature oxidation (10^8 L O_2, 800 K)

XPS peak parameters	Sn $3d_{5/2}$			O1s		
Components	Sn–L(?)	Sn^{2+}	Sn^{4+}	O^{chem} (?)	O–Sn^{4+}	O–Sn^{2+}
Binding energy [eV]	484.0	485.9	486.6	532.0	530.5	529.8
FWHM [eV]	–	–	1.81	1.45	1.78	–
Relative peak areal intensity	–	–	1.00	0.05	0.95	–

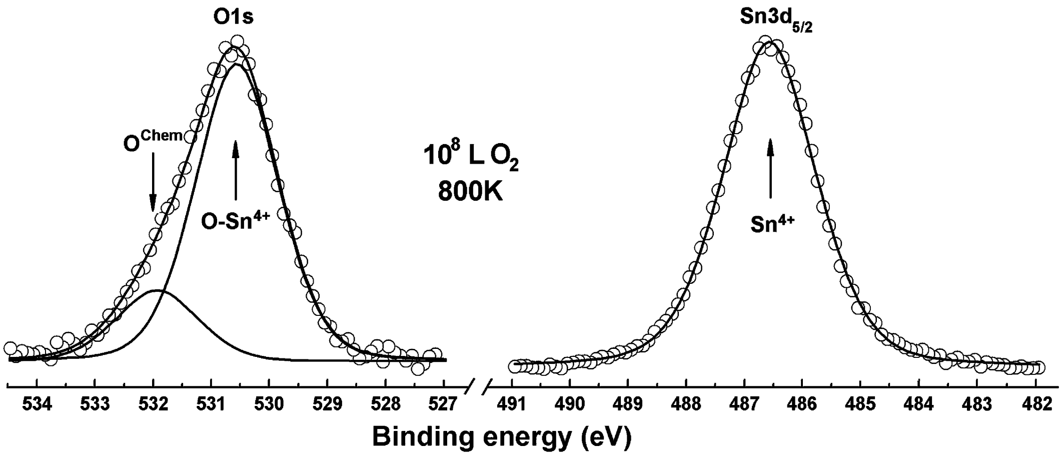

Fig. 4. Registered XPS Sn3d$_{5/2}$ and O1s peaks (in circles) and decomposited components (solid lines) of the as-deposited L-CVD SnO$_2$ thin films after exposure to 10^8 L in molecular oxygen at 800 K.

one above-mentioned component corresponding to Sn^{+4} having the same FWHM as for as-deposited samples. It really confirms that as-deposited L-CVD SnO$_2$ thin films after exposure to 10^8 L O$_2$ at 800 K contain mainly (98%) tin dioxide SnO$_2$. This is in a good correlation with a relative concentration of [O]/[Sn] ~1.95.

In Fig. 4 (left side) the XPS O1s line is presented. Also in this case already a simple visual shape analysis shows that it is slightly asymmetrical, and exhibits only a weak shoulder at the high binding energy side of the spectrum. Accordingly, in the decomposition procedure it has been taken into account that it is built-up as a mixture of two components. The main parameters used in the applied fitting procedure as well as the best fitting parameters are summarized in Table 3. The main component located at BE about 530.5 eV corresponds to the O–Sn^{4+} bonding, as taken from NIST data base [13]. What is important it has the same FWHM as for the as-deposited samples.

No evidence was observed from the O–Sn^{2+} bonding contribution. However, as in Fig. 3, an additional small component of BE at about 532 eV was observed of unknown origin as discussed earlier for as-deposited samples.

3.2. Ex situ XPS studies

Fig. 5 shows the XPS survey spectrum of the as-deposited L-CVD SnO$_2$ thin films of thickness at about 20 nm after long term ageing in dry air atmosphere at room temperature and then after UHV annealing at 670 K, according to the procedure by Maffeis et al. [17].

One can easily note that the XPS survey spectrum of the as-deposited L-CVD SnO$_2$ thin films after long term ageing in dry air atmosphere consists of well recognized Sn3p, O1s, C1s and double Sn3d and Sn4d XPS intrinsic peaks.

The relative [C]/[Sn] concentration of L-CVD SnO$_2$ thin films was determined as equal to about 3.2 (see Table 1), almost one order of magnitude larger than the corresponding value measured for the as-deposited L-CVD SnO$_2$ thin films. The increase of carbon contamination signal after ageing results from the adsorption of CO and CO$_2$ of the air atmosphere. From the depth profiling we determined that carbon is distributed only in the 3 topmost layers (1 nm) because after short ion sputtering it was completely removed from the surface. A more detailed information about the distribution of carbon in L-CVD SnO$_2$ thin films after ageing will be published elsewhere [18].

Fig. 6 shows the XPS Sn3d and O1s spectral windows of the as-deposited L-CVD SnO$_2$ thin films after long term ageing in air at room temperature and after UHV annealing at 670 K.

The relative [O]/[Sn] concentration of L-CVD SnO$_2$ thin films was also determined. For the long term ageing of as-deposited L-CVD SnO$_2$ thin films in air the relative concentration [O]/[Sn] was 1.56, as summarized in Table 1. It means that the as-deposited L-CVD SnO$_2$ thin films after exposure in air is more oxidised. However, it should be noted that the amount of carbon in these L-CVD SnO$_2$ thin

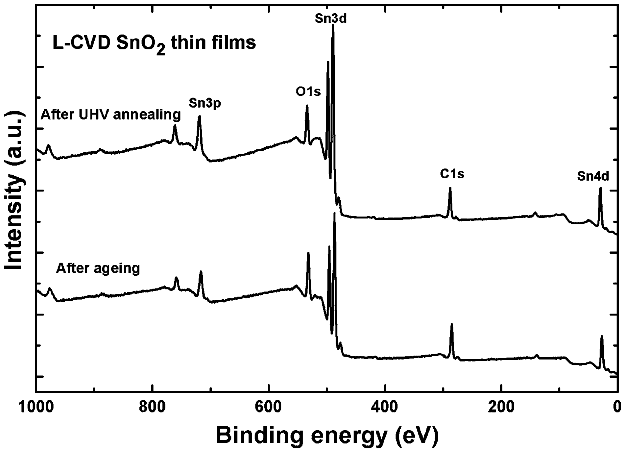

Fig. 5. XPS survey spectra of as-deposited L-CVD SnO$_2$ thin films after long term ageing in air and after UHV annealing at 670 K.

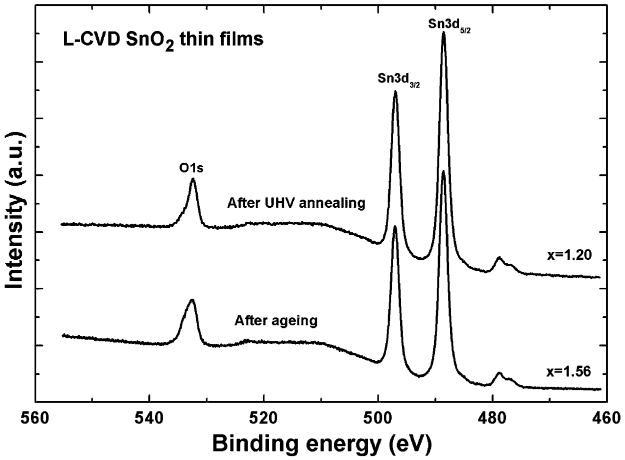

Fig. 6. XPS O1s and Sn3d spectral windows of the as-deposited L-CVD SnO_2 thin films after long term ageing in air and after UHV annealing at 670 K. Parameter x indicates the relative concentration [O]/[Sn].

films after air exposure is more than twice larger than oxygen.

This effect of oxidation of as-deposited L-CVD SnO_2 thin films after exposure to air was also confirmed by the shape analysis of corresponding XPS $Sn3d_{5/2}$ and O1s peaks using the decomposition procedure.

The decomposition of $Sn3d_{5/2}$ peak of as-deposited L-CVD SnO_2 thin films confirmed that it is built-up as a mixture of three components. Two components corresponding to the Sn^{2+} and Sn^{4+} ions, respectively, separated by 0.7 eV have almost the same area. It means that these L-CVD SnO_2 thin films consist of a mixture of tin oxide SnO and tin dioxide SnO_2. It is in good correlation with a relative concentration of [O]/[Sn] ~1.56. As before for the as-deposited samples, no evidence from contribution of elemental Sn^0 atoms at BE about 485 eV was observed. However, an additional third small component of BE at about 484.0 eV was observed as before for the as-deposited L-CVD SnO_2 thin films.

After subsequent UHV annealing of these L-CVD SnO_2 thin films atmosphere the XPS spectrum changed.

The relative concentration [C]/[Sn] of L-CVD SnO_2 thin films decreased to about 2.55 (see Table 1), about 20% of the value measured prior to the UHV annealing treatment. It indicates that this procedure is not useful for removal of surface carbon contaminants from L-CVD SnO_2 thin films after their long term ageing in dry air atmosphere. This is in contradiction with the observations of Maffeis et al. [17] by XPS method. In turn, the relative concentration [O]/[Sn] decreased to about 1.2, as summarized in Table 1. It means that the amount of oxygen in L-CVD SnO_2 thin films after long term ageing in air and subsequent UHV annealing decreased also by about 80%. It means that after this procedure the L-CVD SnO_2 thin films become even more nonstoichiometric. This is an evident limitation of these films in view of their application in construction of gas sensor structures.

4. Conclusions

Our XPS studies of L-CVD SnO_2 thin films showed that as-deposited samples exhibit nonstoichiometry with a relative concentration [O]/[Sn] = 1.29, which corresponds to a mixture of tin oxide SnO and tin dioxide SnO_2 in a 2:1 ratio. After subsequent in situ oxidation at 800 K the L-CVD SnO_2 thin films become almost stoichiometric with a relative concentration [O]/[Sn] = 1.95, which corresponds to about 98% of tin dioxide SnO_2.

After long term exposure in dry air the L-CVD SnO_2 thin films undergo an oxidation and the relative concentration [O]/[Sn] increases to about 1.55, which corresponds to a mixture of tin oxide SnO and tin dioxide SnO_2 in a 1:1 ratio. However, during this air exposure these films are covered with a large amount of carbon because the relative concentration [C]/[Sn] reaches a value of 3.2. It means that an amount of carbon is more than twice larger than oxygen.

After subsequent UHV annealing at 670 K the relative concentration [O]/[Sn] decreases to about 1.2. It means that after this procedure the L-CVD SnO_2 thin films become even more nonstoichiometric. At the same time the relative concentration [C]/[Sn] also decreases by about 20%.

These information on surface chemistry of the L-CVD SnO_2 thin films will be a base for the interpretation of their electronic and sensing properties, which are currently under investigation in our group.

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