AES study of Pt-doped thin Sn-O-Te films

G Spasov, B Georgieva and I Podolesheva

1 Technical University of Sofia, 8, Kliment Ohridski Blvd., 1000 Sofia, Bulgaria
2 Institute of Optical Materials and Technologies “Acad. J. Malinowski”, Bulgarian Academy of Sciences, Acad. G.Bonchev Str., Bl.109, 1113 Sofia, Bulgaria

E-mail: biliana@iomt.bas.bg

Abstract. Thin SnO$_2$-based films with Sn/Te ratio ($R_{Sn/Te}$) $\approx$ 2.1, prepared by thermal vacuum co-evaporation of Sn and TeO$_2$ and doped with Pt before or after thermal annealing, are studied by Auger electron spectroscopy (AES). Thermal annealing leads to changes in the chemical composition and structure (crystallization) of the amorphous as-deposited films. The depth profiling has revealed that the film composition is homogeneous and Pt is dispersed throughout the whole volume of the samples irrespective of their structure and the sequence of doping and thermal annealing. Information is obtained about the oxidation processes taking place during the preparation and thermal annealing of the films, about the influence of the substrate material and the correctness of the evaporation process modeling. It is shown that the significantly higher ethanol sensitivity of the films doped with Pt before annealing is not related to the Pt-distribution.

1. Introduction

Resistivity gas sensors on the base of metal oxide semiconductors, such as SnO$_2$, have been widely investigated during the last decades mostly due to their high sensitivity, fast response, small size and low power consumption [1]. To enhance their selectivity, doping with different additives like noble metals or other oxides is used [2]. The precise choice of the doping element and working temperature gives the possibility to improve the gas sensing properties, mainly the sensitivity and selectivity towards reducing gases.

The method developed in our Institute for obtaining doped SnO$_2$ by vacuum co-deposition of TeO$_2$ and Sn is described in detail elsewhere [3]. It allows preparing thin films with desired $R_{Sn/Te}$ which determines to a great extent the gas sensing properties. As-deposited amorphous films with $R_{Sn/Te}$ $\approx$ 0.8 have very good characteristics as humidity sensors operating at room temperature [4]. At a ratio of about 2.1, after additional Pt-doping and crystallization by thermal annealing, high sensitivity to ethanol is observed [5].

From previous investigations of films with $0 < R_{Sn/Te} < 2$ it is known that the as-deposited films are homogeneous in the whole compositional range and that in films with $R_{Sn/Te} > 2$ no segregation processes could be expected upon annealing at temperatures up to 200 °C [3]. In order to check this at higher temperatures and to find out if the in-depth distribution of Pt depends on whether the crystallization is carried out in the presence of Pt or not, a quantitative depth profiling had to be used. It turned out that dealing with a composite system with a low content of one of the components represents an interesting topic for Auger analysis.
2. Experimental
Sn-O-Te films with thickness \( d \) 40 – 60 nm and \( R_{\text{Sn/Te}} \approx 2.1 \) were prepared by thermal vacuum co-deposition of Sn and TeO\(_2\) using separate Knudsen type cells, under vacuum better than \( 10^{-4} \) Pa and on stationary substrates at room temperature. During the whole evaporation process the fluxes of both substances were controlled with quartz oscillators. The amount of each substance in the films was calculated on the base of the measured flux using computer programs [6] and was controlled by Energy Dispersed Spectroscopy in a scanning electron microscope (SEM/EDS). The thickness of the films was measured with a profilometer. The samples intended for SEM/EDS- and AES-analysis were deposited onto silica and carbon substrates. Doping with Pt was realized in a separate vacuum cycle using tungsten basket as a source. Before or after the Pt-doping the samples were crystallized by thermal annealing up to 360 °C with a step of 40 °C, for 15 min at each temperature.

To study the in-depth distribution of the main components (Te, Sn and O) and of the dopant (Pt) in as-deposited (amorphous) and thermally annealed (crystalline) films, Auger profiling was used. In the case of annealed films the influence of the doping/crystallization-sequence on the compositional distribution was investigated as well. The spectral Auger analysis was performed in the differential mode at primary electron energy \( E_p = 3 \) keV \( (I_p = 0.07 \, \mu\text{A}, V_{\text{mod}} = 4 \, V_{\text{pp}}, \Delta E/E = 0.3\%)\). The most intense Auger peaks of Sn \( (430-437 \, eV)\), Te \( (483-491 \, eV)\), O \( (510 \, eV)\), Pt \( (64 \, eV)\), C \( (272 \, eV)\) and Si \( (92 \, eV)\) were monitored.

The depth profiling was carried out by sputtering with an Ar\(^+\) ion beam with energy \( E_i = 3 \) keV and ion beam current \( I_i = 2 \, \mu\text{A}\), followed by AES analysis at each etching step.

3. Results and Discussion

3.1. Auger analysis data
The spectrum of a SnO\(_2\) standard sample with peaks of carbon, tin and oxygen, obtained in the energy window 205-555 eV, is shown in figure 1.

The data obtained during the depth profiling of an as-deposited Pt-doped Sn-O-Te film with \( R_{\text{Sn/Te}} \approx 2.1 \), presented as peak intensities vs. sputtering time, are displayed in figure 2.

![Figure 1. Spectrum from a SnO\(_2\) standard with peaks of carbon, tin and oxygen.](image1)

![Figure 2. Profile “intensities/sputtering time” from an as-deposited Pt-doped Sn-O-Te sample.](image2)

3.2. Quantification of the sputtering profiles

3.2.1. Calibration of the depth scale (x-axis of the profile). As it will be shown later, the profiling reveals that (i) the composition of the films is homogeneous over the entire thickness of the films and (ii) the distribution of Pt shows no peculiarities at the interface film/substrate, so the interface region needs no special attention and the detailed profiling can be limited to its beginning. The latter we have...
defined as the depth where the Auger signals from the film drop by 10%. Both experimental results have given us the reason not to perform detailed calibration of the x-axis. We have assumed that the distance between the film surface and the film/substrate-interface is equal to the film thickness measured with the profilometer and that the sputtered depth is proportional to the sputtering time.

3.2.2. Calibration of the concentration scale (y-axis of the profile). Here the analytical difficulties in the quantification are arising from the interference between the constitutive peaks of the doublets, leading to hard-to-evaluate changes in the intensity. One of the reasons for this interference (broadening of the peaks due to changes in the modulation energy or the energy resolution of the spectrometer) we eliminate using own standards. Of a greater importance are, however, the so-called “chemical changes” in the peaks (in this case due to oxidation of the analyzed element). They alter the linear dependence of the doublet intensity on the element content, which underlies the AES quantification. The “chemical changes” of an Auger peak manifest themselves in: (i) energetic shift, (ii) peak shape changes (as a rule causing changes in the elemental sensitivity) and (iii) a possible interference between the peaks of the element (due to (i)), if in the analyzed sample volume the element is present in more than one chemical state. The energetic shift itself does not influence the Auger quantification, that is why we are not going to discuss this problem; the analysis distinguishes between the elemental and oxidized state, regardless of the oxidation level (SnO and SnO$_2$) [7]. In the case of Sn we have studied the second and third effect experimentally. With the aim to examine whether the elemental sensitivity factor (ESF) changes with the chemical state, we have compared the Sn-signals from Sn (metal) and SnO$_2$ (figure 3). To the oxidized Sn we have applied matrix corrections for the electron backscattering [8], as well as for the atomic densities and IMFP (nonelastic mean free electrons path) [9], with the coefficient for oxides 0.55 [10]. As the normalized intensities differ within 20% – i.e. within this accuracy - it could be assumed that the elemental sensitivity factors for Sn (metal) and SnO$_2$ are identical [7,11,12]. Superposing both signals in different ratios we have modeled their interference (nanosized mixture “Sn-SnO$_2$” with prevailing dioxide). It turned out that the total Sn signal – up to the important for our investigations 25% – weakly depends on the relative amount of Sn in the mixture. That is why the relation between this intensity and the intensity of O (figure 4) changes much slower than predicted by the relation: $(1 + x)/(1 – x)$, that is valid for the case of two elements with constant ESF (according to this relation at 25% the relative intensity is 2.58). In figure 4 the maximal relative nonlinearity of the curve in the interval of interest is 1.9%. It should be stressed that, as stated in the literature, the value of the ratio $I_{SnO}(SnO)/I_{SnO}(SnO_2)$ – 1.32 [7,12] or 1.41 [13] – differs only by 4 to 10% from the value 1.27, obtained by replacing SnO with the mixture having the same composition (0.75 SnO$_2$, 0.25 Sn).

Figure 3. Auger spectra in the energy window 402-445 eV from the Ar$^+$ cleaned surface of SnO$_2$ and Sn standard (tenfold statistical accumulation).

Figure 4. Dependence of the intensity of the superposed Sn signal to the O one $I_{Sn}[xSn_{metal}+(1-x)Sn_{SnO_2}]$ $I_{O}(1-x)O_2$ from the nanosized mixture $[xSn_{metal}+(1–x)SnO_2]$ as a function of the $Sn_{metal}$ content $x$. 
As for the Te-doublet (.490 eV) an additional difficulty arises from its interference with the O-peak, so it is not possible to perform the classical Auger quantification. Thus we have calculated the local content of Te using the ratio $R_{SnTe}$, estimated by the SEM/EDS-analysis. The reason for applying this approach is based on the following two experimental results: (i) on the fact that $R_{SnTe}$ does not change upon heating up to 360 °C (2.1 before and 2.05 after the thermal annealing) and coincides well with the predetermined value (calculated by means of the computer programs [6]), and (ii) on the already mentioned in-depth film homogeneity (table 1). The latter gives us the reason to assume that Te follows the distribution of Sn, i.e. the integral SEM/EDS-result for $R_{SnTe}$ is valid for every point of the film. (In the quantification terminology, Te is determined using an external integral standard.).

Table 1. Characterization of the plateau in the Sn/O-dependence for the samples studied ("Film structure" – before Pt-doping, "Thermal annealing" – after Pt-doping)

| Sample No | Substrate | Film structure | Thermal annealing | Sn/O intensity | Error, Δ$I/I$, % |
|-----------|-----------|----------------|------------------|----------------|-----------------|
| 1         | Graphite  | crystalline    | No               | 1.085          | 0.5             |
| 2         | Graphite  | amorphous      | Yes              | 1.122          | 1.6             |
| 3         | Si        | amorphous      | No               | 1.638          | 1.3             |
| 4         | Si        | amorphous      | Yes              | 1.252          | 1.5             |

The calibration of the concentration axis (y) for Sn, O, Pt, Si, and C occurs according to the ESF method, as the Te content represents 1/2.1 of the Sn content. The standards used and the experimental ESF (relative to Si) are given in table 2. The statistical error of their determination does not exceed 0.8%. For Sn the value of ESF in the table is correct only in the case of compositions close to SnO$_2$.

Table 2. Experimental relative (to Si) element sensitivity factors

| Element | Si | O | Pt | Au | C | Sn |
|---------|----|---|----|----|---|----|
| Standard |    |   |    |    |   | SnO$_2$ |
| Rel. ESF | 1  | 1.03 | 0.87 | 0.70 | 0.31 | 3.23 |

3.2.3. Quantification and its verification. Knowing the mean relative content of Te, there are several ways of determining the homogenous Te profile. According to the procedure, chosen by us, first the mean ESF$_{Te}$ for the film was calculated (using the averaged relative intensity Sn/Te for the film, ESF$_{Sn}$ and ESF$_{Te}$ value obtained by SEM/EDS). Later on, at every point of the film the concentration of the components was determined using the standard ESF method. The profiles obtained are shown in figure 5. Table 3 summarizes the integral (averaged) concentrations of the elements in the film.

Table 3. Averaged concentrations of the film constituents (before and after excluding the carbon content) and concentration of Pt related to the total metal content (Pt/m, %)

| Sample No | Concentration, at.% | Conc. (– carbon), at% | Pt/m, % |
|-----------|---------------------|-----------------------|---------|
|           | Sn | O | Te | Pt | C | Sn | O | Te | Pt |                   |    |
| 1         | 17.0 | 50.8 | 8.4 | 5.7 | 18.1 | 20.8 | 62.0 | 10.2 | 7.0 | 18.4 |
| 2         | 19.1 | 57.4 | 9.5 | 5.7 | 8.3 | 20.9 | 62.7 | 10.3 | 6.2 | 16.6 |
| 3         | 23.5 | 45.5 | 11.4 | 7.9 | 11.5 | 26.6 | 51.5 | 12.9 | 9.0 | 18.6 |
| 4         | 22.1 | 56.8 | 10.6 | 5.9 | 4.6 | 23.2 | 59.6 | 11.1 | 6.2 | 15.2 |

Additionally, the measured by SEM/EDS content of Pt can be used to verify the quantification. It shows which (integral) part of the metal content represents Pt. The analogous parameter, calculated on the base of the Auger results (integrating along the depth of the film), reveals an average systematic increase of 39%. Taking into consideration the facts, that the Auger-signal of Pt is weak and that Pt is introduced into a “very thin” (for SEM-EDS analysis) film, the coincidence can be qualified as good.
Figure 5. Profiles “Elemental content vs. depth” from samples with $R_{Sn/Te} \approx 2.1$: a) as-deposited amorphous Pt-doped film, Si substrate; b) film, doped with Pt after crystallization, graphite substrate; c) and d) films, doped with Pt before crystallization, Si and graphite substrates, respectively.

A second method was applied to evaluate the oxygen content relative to the content of the elements in the substrate. It makes use of the direct relation of the signal intensities of the element $X$ from a sample and a standard with its corresponding concentration. Despite this relation reflects the essence of the Auger quantification, it is not used independently in the analytical practice, mainly because it does not take into account the inequality of the sample and the standard. If however two points of a profile are representing the sample and the standard, a big part of the problems is overcome. Additionally we have made the method more precise taking the corrections for the matrix differences. Relating the intensity of the substrate (C or Si) to that of oxygen the mean oxygen content (for the whole film) was determined. The results for the four samples differ from the corresponding values determined by means of the RESF-method on average by 10.6%. The small difference between the results, obtained using two independent methods, is indirect evidence that the quantification has been correctly carried out.

3.3. Conclusions from the Auger Analyses
The measured mean relative intensity Sn/O is approximately equal to that of SnO$_2$, i.e. the oxygen in the film is almost sufficient to oxidize Sn to SnO$_2$. This result could be expected due to the greater affinity of the oxygen towards Sn than towards Te [14]. So the amount of oxygen, which is not sufficient to oxidize the whole film, is predominantly bound to Sn. As Sn is present in the films mainly in the form of or close to SnO$_2$ it can be used as standard. On the other hand, the similarity between
the standard and the analyzed composition allows us to substitute ESF for Sn in the film with that for SnO$_2$. Thus, the quantification of Sn was performed – for simplicity and with an acceptable error – and not by the curve in figure 4. The other results obtained can be summarized as follows:

I. All films with $R_{Sn/Te} \approx 2.1$ (amorphous and crystalline) show a uniform in-depth composition.

II. The level of film oxidation depends on the film preparation and increases upon thermal annealing in air. In the as-deposited amorphous films the oxygen content is sufficient to oxidize almost all Sn to SnO$_2$. The oxidation of Te begins (if the oxidation process continues) after all Sn is oxidized. The end result is the total oxidation of Sn and Te.

III. The Pt nanoparticles penetrate the full depth of the film during the film doping. The distribution of Pt is slightly inhomogeneous (its content decreases towards the film-substrate interface) but it is not affected by thermal annealing.

IV. The type of the substrate does not influence the composition and the doping of the film (provided that it does not react with the film); this has been shown for graphite and Si (as well as for Au).

V. The film analysis confirms the correctness of the evaporation process modeling [6].

VI. The important experimental result that thermally annealed Pt-doped thin Sn-O-Te films with $R_{Sn/Te} \approx 2.1-2.3$ possess significantly higher ethanol sensitivity if the doping precedes the annealing is not related to differences in the in-depth-distribution of Pt. Perhaps it is due to differences in the morphology of films crystallized in the absence or presence of Pt.

4. Summary

Auger quantification of the system Sn-Te-O and Pt is proposed. The elemental sensitivity of Sn in the metal and oxidized state is studied and for the analysis the non-stoichiometric compound SnO$_x$ is modeled as a mixture of SnO$_2$ and Sn. The distribution of Te is supposed using the data from the SEM/EDS-analysis and the in-depth profiling.

Using Auger electron spectroscopy technique the distribution of the elements in as-deposited and thermally annealed films of one and the same composition ($R_{Sn/Te} \approx 2.1$) was studied. The depth profiling has revealed that the film is homogeneous and Pt is dispersed throughout the whole volume of the samples irrespective of their structure (amorphous or crystalline). Moreover, the in-depth distribution of Pt does not depend on the sequence of doping and thermal annealing.

Information is obtained about the oxidation processes taking place during the preparation and thermal annealing of the films, about the influence of the substrate material and the correctness of the evaporation process modeling. It has been shown that the significantly higher ethanol sensitivity of the films doped with Pt before the annealing is not related to the Pt-distribution.

References
[1] Yamazoe N, Sakai G, Shimanoe K 2003 Catalyst Surveys from Asia 7 63
[2] Rumyanceva M, Safonova O, Boulova M, Ryabova L and Gashkov A 2003 Russian Chem. Bulletin, International Edition 52 1217
[3] Podolesheva I, Dimov V, Tarassov M, Platikanova V and Konstantinov I 1998 J. Vac. Sci. Technol. A 16(4) 2608
[4] Georgieva B, Podolesheva I, Pirov J and Platikanova V 2005 J. Optoelectron. Adv. Mater. 7 2595
[5] Georgieva B, Podolesheva I, to be published
[6] Podolesheva I, Gushterova P, Platikanova and Konstantinov I 1998 J. Vac. Sci. Technol. A 16(2) 674
[7] de Kluizenaar E 1983 J. Vac. Sci. Technol. A 1 1480
[8] Ichimura S, Shimizu  and Langeron J P 1983 Surf. Sci. 124 L49
[9] Seah M P and Dench W A 1979 Surf. Interface Anal. 1 2
[10] Seah M P 1986 Surf. Interface Anal. 9 85
[11] Frankenthal R P and Siconolf D J 1980 J. Vac. Sci. Technol. 17 1315
[12] Powell R A 1979 Appl. Surf. Sci. 2 397
[13] Draudy J, Hoflund G, Gardner S, Yngvadottir E and Schryer D 1990 Surf. Interface Anal. 16 369

[14] CRC Handbook of Chemistry and Physics, 49th ed. (Chemical Rubber, Cleveland, 1969)