Morphology and gas sensing properties of as-deposited and thermally treated doped thin SnO$_x$ layers

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Abstract. Thin layers intended for gas sensors are prepared by vacuum co-evaporation of TeO$_2$ and Sn. The as-deposited layers consist of a nanosized oxide matrix and finely dispersed dopants (Te, Sn, TeO$_2$ or SnTe, depending on the atomic ratio R$_{Sn/Te}$). In order to improve the characteristics of the layers they are additionally doped with platinum. The gas sensing properties are strongly dependent on the atomic ratio R$_{Sn/Te}$, as well as on the structure, composition and surface morphology. The as-deposited layers with R$_{Sn/Te} < 0.8$ are highly sensitive humidity sensors working at room temperature. Thermally treated Pt-doped layers with R$_{Sn/Te} > 2.3$ are promising as ethanol sensors.

With the aim of obtaining more detailed knowledge about the surface morphology, structure and composition of layers sensitive to different environments, various techniques - TEM, SAED, SEM, EDS in SEM and white light interferometry (WLI), are applied. It is shown that all layers with 1.0 > R$_{Sn/Te}$ > 2, as-deposited and thermally treated, exhibit a columnar structure and a very smooth surface along with the nanograinated matrix. The thermal treatment causes changes in the structure and composition of the layers. The ethanol-sensitive layers consist of nanosized polycrystalline phases of SnO$_2$, Sn$_2$O$_3$, Sn$_3$O$_4$ and TeO$_2$. This knowledge could help us understand better the behaviour and govern the characteristics of layers obtained by co-evaporation of Sn and TeO$_2$.

1. Introduction

Resistive gas sensors based of metal oxide semiconductors, such as SnO$_2$, have been widely studied during the last decades mostly due to their high sensitivity, fast response, small size, low cost and low power consumption [1]. To resolve the problem with their low selectivity, doping with different additives, such as noble metals or other oxides, have been used [2]. Since the morphological and electrical parameters of the sensors are strongly affected by the preparation conditions, different methods have been investigated for their preparation with the aim to improve further their characteristics.

We developed a method for preparing thin SnO$_2$ layers by thermal vacuum co-evaporation of Sn and TeO$_2$ [3]. During the co-deposition, both substances react and nanograinated amorphous SnO$_2$ layers doped with a dispersed phase of Te, Sn, TeO$_2$ or SnTe (depending on the atomic ratio R$_{Sn/Te}$) are formed. Thermal treatment causes changes in the structure, surface morphology and composition. As we have

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already reported, at $R_{\text{Sn/Te}} = 0.8$, the as-deposited layers possess good humidity sensing properties at room temperature [4]. At higher $R_{\text{Sn/Te}}$ values (2.3), and after thermal treatment and Pt-doping, the layers show high sensitivity towards ethanol vapors at substrate temperatures 120 and 240 °C [5].

The aim of our work was to use different techniques (WLI, TEM, SAED, SEM and EDS in SEM) to obtain more detailed information about the surface morphology, structure and composition of the humidity- and ethanol-sensitive layers, as well as about the changes the Pt-doped layers with $R_{\text{Sn/Te}} = 2.3$ undergo upon thermal treatment which makes them sensitive to ethanol. This knowledge could help us manage the characteristics of layers obtained by co-evaporation of Sn and TeO$_2$.

2. Experimental

Tin oxide layers were deposited under vacuum ($10^4$ Pa) on stationary substrates using thermal vacuum co-evaporation of Sn and TeO$_2$ from independent Knudsen-type cells. During the co-evaporation, the condensation rate of each substance was controlled by a quartz oscillator. The additional doping element (Pt) was deposited on the sensing layers in a separate vacuum cycle. The atomic ratio $R_{\text{Sn/Te}}$ of the humidity sensitive layers was $\approx 0.8$, and that of the ethanol-sensitive, $\approx 2.3$. Thermal treatment was carried out up to 360 °C with a step of 40 °C with a 15-min delay at each temperature, before or after doping with platinum.

The layer thickness was controlled by a Talystep profilometer (Rank Taylor Hobson), and the $R_{\text{Sn/Te}}$, by EDS in SEM. Transmission electron microscopy (bright and dark field) and SAED were used to observe the morphology and structure of the layers and SEM, to study their growth profile. The samples intended for SEM were evaporated on glass substrates to a thickness of about 800 nm. Samples suitable for direct imaging in TEM were prepared on Cu grids by removing the layers from the glass substrate using vapor-phase hydrogen fluoride (HF) treatment and floating off in water. WLI (White Light Interferometric Profiler MicroXAM S/N 8038) was used to determine the surface roughness. The resolution of the interferometer was 1–2 nm in vertical (z) and 1-3 µm in lateral (x, y) direction. For this investigation, the as-deposited amorphous ($R_{\text{Sn/Te}} = 0.8$) and the thermally treated ($R_{\text{Sn/Te}} = 2.3$) Pt-doped layers were prepared on glass substrates.

To test the layers as gas sensors, Cr comb-like electrodes were patterned using a photolithographic technique [6]. The layers were exposed to humidity and ethanol vapors in a test chamber equipped with temperature- and RH-controllers. The electrical resistance $R$ [Ohm] of undoped and Pt-doped samples was measured at room temperature as a function of the relative humidity (RH [%]) or as a function of the substrate temperature in the presence of ethanol vapours. The apparatus used was a multichannel ohmmeter (consisting of a resistor-connector-unit and a multichannel analog-to-digital converter PCI 6024E), product of National Instruments. The data acquisition and processing, as well as the control of the ohmmeter were computerized, using Lab View software.

3. Results and Discussion

3.1. Structure and composition

Figure 1 shows the profile of as-deposited (a) and thermally treated (b) layers with thickness $d = 800$ nm and $R_{\text{Sn/Te}} = 2.3$. As it could be seen, the amorphous as-deposited layer exhibits a columnar structure. After thermal treatment, the shape of the columns changes, obviously due to structural transformations of the layer. Along with the nanograined matrix, this columnar structure indicates a large free surface which is important for the gas sensing properties. Analogous results have been obtained earlier for layers with $R_{\text{Sn/Te}} < 1$.

The surface profile morphology of as-deposited (a) and thermally treated Pt-doped (b and c) layers is shown in figure 2. The root-mean-square (rms) values for as-deposited amorphous layers with $R_{\text{Sn/Te}} = 0.8$ and for layers with $R_{\text{Sn/Te}} = 2.3$, doped with Pt before or after the thermal treatment respectively, are given in the same figure. Regardless of the difference between the rms-values of layers doped with Pt before and after thermal treatment, the surfaces of both as-deposited amorphous and thermally treated samples are generally very smooth.
Figure 1. SEM images of the growth profile of as-deposited (a) and thermally treated (b) layers with $R_{\text{Sn/Te}} = 2.3$ and $d = 800$ nm.

Figure 2. Surface profile obtained using a WLI surface profiler of: a) as-deposited amorphous layers with $R_{\text{Sn/Te}} = 0.8$; b) layers with $R_{\text{Sn/Te}} = 2.3$, Pt-doped before thermal treatment and c) layers with $R_{\text{Sn/Te}} = 2.3$, Pt-doped after thermal treatment.

The TEM micrographs of thermally treated SnO$_2$ layers with $R_{\text{Sn/Te}} = 2.3$, Pt-doped before thermal treatment, are shown in figure 3. It can be clearly seen that upon heating the layers become crystalline and consist of a mixture of Sn oxides and TeO$_2$. It should be noted that the crystalline layers do not show sensitivity to humidity; this is why we do not comment the changes layers with $R_{\text{Sn/Te}} < 1$ undergo upon thermal treatment.

Phases:
- TeO$_2$: Paratellurit PDF 42-1365
- SnO$_2$: Cassiterite PDF 41-1445
- Sn$_2$O$_3$: PDF 25-1259
- Sn$_3$O$_4$: PDF 20-1293

Figure 3. TEM images: a- bright field; b- dark field and SAED pattern of a layer with $R_{\text{Sn/Te}} = 2.3$, Pt-doped before thermal treatment.

3.2. Gas sensing properties

3.2.1. Humidity sensing properties. In our previous investigations [4], we have shown that the amorphous layers with $R_{\text{Sn/Te}} \approx 0.8$ are very sensitive to the ambient relative humidity at room temperature. The response is very fast, the recovery period, very short and no hysteresis effects are observed. Accelerated ageing tests have shown that the layers exhibit a good long-term stability. However, at low humidity levels the resistance of the sensing layers is too high. One of the ways to overcome this problem is additional doping, e.g. with some metals (in our case with Pt). The effect of 2-3 at.% Pt on the response curve is shown in figure 4. As it could be seen, doping with platinum leads to a decrease of the resistance with one order of magnitude compared with the undoped layers. Therefore, a substantial resistance decrease, without any changes in sensitivity, could be attained through optimal doping.
3.2.2. Ethanol sensing properties. Without Pt-doping, the crystalline layers with \( R_{\text{Sn/Te}} \approx 2.3 \) show no sensitivity to ethanol, while introduction of Pt makes them sensitive to ethanol vapors. The sensitivity depends on the layer preparation conditions, on the substrate temperature, etc. Since, however, these results will be the object of another publication they will not be discussed further here.

4. Conclusions
Using a method developed in our laboratory, doped SnO\(_2\) thin layers were synthesized with desired composition and structure which govern the sensing properties. The as-deposited amorphous layers with \( R_{\text{Sn/Te}} \approx 0.8 \) are very sensitive to ambient humidity at room temperature but at low humidity levels their resistance is too high. It was shown that this problem could be overcome through Pt-doping. The study of the morphology and composition by various techniques revealed that, along with the nanograined matrix, the layers exhibit a columnar structure indicating a large free surface and that the surface of all layers is very smooth. Furthermore, it was shown that the thermal treatment of the layers with \( R_{\text{Sn/Te}} \approx 2.3 \) leads to the formation of nanocrystalline phases of SnO\(_2\), Sn\(_2\)O\(_3\), Sn\(_3\)O\(_4\) and TeO\(_2\). These layers, additionally doped with Pt, possess good sensing properties to ethanol.

As the layer preparation method is compatible with the conventional microelectronics technologies, after optimisation the sensors can be integrated on one chip with field-effect transistors or with entire subsystems for data processing.

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