Nanostructured Thin Sn-O-Te Films as Humidity and Ethanol Sensors†

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Abstract. Thermal co-deposition of Sn and TeO$_2$ in vacuum is used for preparing thin Sn-O-Te films, build-up of an oxide matrix and a finely dispersed phase of Te, Sn and/or SnTe. The method allows further doping with desired elements both in the microcrystallites and at their interfaces with the aim to obtain films with improved gas sensing properties.

The as-deposited films are amorphous and show very good characteristics as humidity sensors, operating at room temperature. Upon thermal treatment the structure and composition change and depending on the doping elements and the working temperature the observed nanocrystalline films show sensitivity to some reduction gases (ethanol, etc.). No cross-sensitivity of the crystalline films to water vapor is observed.

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1 Introduction

At present large-scale investigations are carried out worldwide on metal oxide nanocrystalline thin films mostly due to the possibilities of producing highly active catalysts and highly sensitive gas and humidity sensors. The sensing properties of the films are greatly dependent on the chemical composition and the microstructure and they, on their part, are critically determined by the method of preparation. Therefore, it is of intense interest to develop new preparation methods to control the morphology and the properties of the films. It is known, that SnO$_2$ films are sensitive to various reduction gases including humidity but their main disadvantage is the poor selectivity. To improve their parameters, the optimum working temperature and a suitable doping element have to be found. We developed a new method for preparing thin SnO$_2$ films by thermal vacuum co-evaporation of Sn and TeO$_2$ [1]. During the co-deposition, both substances react and nanograined amorphous SnO$_2$ films doped with a dispersed phase of Te, Sn, TeO$_2$ or SnTe (depending on the atomic ratio between Sn and Te – $R_{SnTe}$) are

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formed. Thermal treatment causes changes in the structure, surface morphology and composition.

The aim of this paper is to study the humidity and ethanol sensing properties of thin Sn-O-Te films obtained by the new method. To improve the sensitivity and selectivity towards ethanol, Sn-O-Te films are additionally doped with Pt.

2 Experimental

Films with thickness 60-80 nm and \( R_{\text{Sn/Te}} \approx 0.8 \) and 2.3 were prepared by co-evaporation of \( \text{TeO}_2 \) and Sn from independently heated Knudsen cells [1] under vacuum better than \( 10^{-4} \) Pa and on stationary substrates, held at ambient temperature. Condensation rates of both substances were controlled separately during the whole evaporation process by means of high frequency crystal monitors. The amount of both substances in the film, i.e. the \( R_{\text{Sn/Te}} \) values, and the thickness of the films were calculated on the base of the measured evaporation rates using computer programs as described in [2].

Thermal treatment up to 360°C (annealing step 40°C, 15 minutes at each temperature) was carried out on a heated plate, mounted in the test chamber and equipped with temperature controller. The doping with platinum was performed before the thermal treatment of the samples by vacuum evaporation in a separate vacuum cycle using a tungsten basket with a diameter of 0.8 mm. The chemical composition of the films and the amount of Pt were controlled by Energy Dispersive Spectrometry (EDS) in SEM. Transmission electron microscopy (TEM) and selected area electron diffraction (SAED) were used to observe the morphology, structure and composition of the films. Samples suitable for direct imaging in TEM were prepared on Cu grids by removing the films from the glass substrate and floating them off in water.

To test the films as gas sensors, Cr comb-like electrodes were patterned using a photolithographic technique [3]. The films 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 at elevated temperatures (up to 200°C) in the presence of ethanol vapors. The apparatus used was a multichannel ohmmeter, product of National Instruments. The data acquisition and processing, as well as the control of the ohmmeter were computerized, using Lab View software. As a measure of the sensitivity \( (S) \) towards ethanol the change in the electrical resistance of the thin films in the ethanol vapors \( (R_{\text{gas}}) \) as compared to dry air \( (R_{\text{air}}) \) was used.

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S[\%] = \frac{R_{\text{air}} - R_{\text{gas}}}{R_{\text{gas}}} \times 100 .
\]
3 Results and Discussion

3.1 Morphology and Composition

The as-deposited films with $R_{Sn/Te} \approx 0.3 \div 2.3$ are amorphous, with a fine-grained structure. The selected area electron diffraction does not indicate the presence of a crystalline phase. This is illustrated in Figure 1 with the TEM image and the SAED pattern of an as-deposited film with $R_{Sn/Te} \approx 0.8$.

Figure 1: TEM image and SAED pattern of an as-deposited film with $R_{Sn/Te} \approx 0.8$

The TEM micrograph of thermally treated SnO$_2$ films with $R_{Sn/Te} \approx 2.3$, Pt-doped before thermal treatment, is shown in Figure 2. It can be clearly seen that upon heating the films become crystalline. As ascertained by SAED they consist of a mixture of TeO$_2$ and Sn oxides. The composition of the films is given in Table 1. Auger analyses [4] also have shown that after thermal treatment above 250°C the films contain only oxide phases.

Figure 2: TEM image and SAED pattern of a film with $R_{Sn/Te} \approx 2.3$, Pt-doped before thermal treatment.
Table 1: Phases of thermally treated films doped with Pt

<table>
<thead>
<tr>
<th>Phase</th>
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<th>Sn Element</th>
<th>PDF Number</th>
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<td>41-1445</td>
<td></td>
<td>20-1293</td>
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<tr>
<td>Sn$_3$O$_4$</td>
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3.2 Humidity and Ethanol Sensing Properties

As the Sn-O-Te films obtained are of very low thickness, with nanosized structure and low density, respectively high specific area (the value of $\rho \approx 4 \text{ g/cm}^3$ is much lower than the respective values for the bulk materials TeO$_2$, Te, Sn and SnO$_2$ – 5.7 ÷ 7.3 g/cm$^3$ [2]) they were tested as humidity sensors. As shown in Figure 3, the response curve reveals a close exponential relationship between the sensor resistance and relative environmental humidity spanning 5 decades of resistance and can be linearized by taking the logarithm of the resistance. It is important to note that this high sensitivity is observed only at room temperature.

In the as-deposited amorphous state the films are not sensitive towards ethanol. The sensitivity of the nanocrystalline films (undoped and Pt-doped) in the presence of 2000 ppm ethanol vapors and at substrate temperature $T = 120^\circ C$ is presented in Figure 4. This temperature was chosen because, as revealed by the temperature dependence of the sensor response to ethanol, in the temperature range between room temperature and 200$^\circ$C the sensitivity exhibits a maximum at 120$^\circ$C. As it can be seen, the doping with Pt results in a substantial increase of the sensitivity. To check the cross sensitivity to environmental humidity of films with $R_{\text{Sn/Te}} \approx 2.3$ at the same substrate temperature the influence of RH [%] on the film resistance was followed. As shown in Figure 4-inset, no sensitivity towards humidity was observed at substrate temperature 120$^\circ$C. The lack of

Figure 3: $R$ [Ohm] as a function of RH [%] of amorphous Sn-O-Te films with $R_{\text{Sn/Te}} \approx 0.8$. 

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Figure 4: $S$ [%] of undoped and Pt-doped annealed Sn-O-Te films with $R_{\text{Sn/Te}} \approx 2.3$, at substrate temperature 120°C. Inset: $R$ [Ohm] of the film as a function of RH [%] at the same substrate temperature.

sensitivity to humidity at 120°C allows the development of Sn-O-Te-Pt sensors for selective detection of alcohol in the presence of moisture.

4 Conclusion

The new method for preparation of nanosized tin-oxide films described opens up new possibilities for developing sensors with improved characteristics. The as-deposited amorphous films with $R_{\text{Sn/Te}} \approx 0.8$ are very sensitive to ambient humidity at room temperature. The crystalline films with $R_{\text{Sn/Te}} \approx 2.3$ possess a high sensitivity towards ethanol and no cross sensitivity to relative humidity at substrate temperature 120°C. The conclusion could be drawn that the co-deposition of Sn and TeO$_2$ could find application for preparing sensor arrays which are able to distinguish between different ambient gases.

Acknowledgements

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References


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