Influence of the thickness and thermal treatment on the humidity and ethanol sensing properties of Sn-O-Te layers

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Abstract. Thin Sn-O-Te layers were prepared by thermal vacuum co-evaporation of Sn and TeO$_2$. Depending on the atomic ratio of Sn to Te ($R_{Sn/Te}$) and on the subsequent treatments, layers sensitive towards humidity or ethanol vapor were obtained. The as-deposited amorphous layers with $R_{Sn/Te} \approx 0.8$ and a thickness of 60 nm showed very good characteristics as humidity sensors operating at room temperature. Layers with $R_{Sn/Te} \approx 2.3$, additionally doped with Pt and crystallized by thermal treatment up to 360 ^{o}C, were found to be sensitive to ethanol vapor at 120 ^{o}C and 240 ^{o}C.

The $R_{Sn/Te}$ ratio in the films was estimated by EDS. The composition and structure of the thermally treated layers were studied by X-ray diffraction (XRD). The sensitivity to humidity and ethanol was determined on the basis of the electrical resistance changes in the presence of humidity and ethanol vapor. The influence was studied of the layer thickness and of the sequence of thermal treatment and Pt doping on the layer composition and gas sensing properties.

1. Introduction

The use of Sn-O-Te semiconductor thin films prepared by co-evaporation of Sn and TeO$_2$ as humidity and ethanol sensors is of substantial technological interest. It is known that the as-deposited amorphous layers with a thickness of 60 nm and $R_{Sn/Te} \approx 0.8$ exhibit high humidity sensitivities at room temperature [1]. Layers with the same thickness, but with $R_{Sn/Te} \approx 2.3$, thermally treated up to 360 ^{o}C and doped with Pt, are in turn sensitive to ethanol at 120 ^{o}C [2, 3]. Moreover, the processing sequence of the thermal treatment and Pt-doping affects the composition of the layers [3, 4].

In this paper, we present studies on the influence of the thickness of as-deposited amorphous Sn-O-Te layers with $R_{Sn/Te} \approx 0.8$ on their humidity sensing properties, as well as of the thickness and the sequence of the thermal treatment and Pt doping on the ethanol sensing properties of crystalline Sn-O-Te layers with $R_{Sn/Te} \approx 2.3$. The results obtained could lead to a better understanding of the relationship between structure, composition and sensing properties of Sn-O-Te layers.

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2. Experimental

Sn-O-Te layers with thicknesses of 60 nm and 200 nm and of $R_{Sn/Te} \approx 0.8$ and 2.3 were prepared by a method previously reported by us in [5]. The crystallization of the layers with $R_{Sn/Te} \approx 2.3$ was achieved by thermal treatment − non-isothermal up to 360 ^{o}C (with a step of 40 ^{o}C and a 15 minutes delay at each temperature) on a heated plate in the test chamber equipped with a temperature controller. Doping with Pt ($2 - 3$ at. %) was performed by thermal evaporation in a separate vacuum deposition process either before or after crystallization of the layers. Electron dispersive spectroscopy (EDS) in SEM was used for determining the atomic ratio ($R_{Sn/Te}$) and the Pt content in the samples. The layer thickness was established using a Talystep profilometer (Rank Taylor Hobson). The crystallographic structure and composition of the thermally treated layers with a thickness of 200 nm were investigated by X-ray diffraction (XRD). For these studies, the layers were evaporated on Si substrates. The results obtained by XRD were compared with those achieved for thin layers (60 nm) by selected area electron diffraction (SAED) [3, 4].

To test the layers as humidity and ethanol sensors, Cr comb-like electrodes were patterned using the photolithographic technique described in [6]. The layers were exposed to humidity and ethanol vapor in a test chamber equipped with temperature- and RH-controllers. The electrical resistance R [Ω] 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 280 ^{o}C) in the presence of ethanol vapor. For electrical measurements, a multichannel ohmmeter (National Instruments) was used. The data acquisition and processing, as well as the control of the ohmmeter, were computerized using Lab View. The sensitivity (S) to ethanol was calculated as the ratio of the difference between the electrical resistance of the layers in dry air (R_{air}) and in ethanol vapor (R_{gas}) to the electrical resistance of the layers in ethanol vapor (R_{gas}):

$$S[\%] = \frac{(R_{air} - R_{gas})}{R_{gas}} * 100 . \tag{1}$$

3. Results and discussion

3.1. Structure and composition

All as-deposited layers were amorphous, regardless of the value of $R_{Sn/Te}$. The selected area electron diffraction did not indicate the presence of any crystalline phase [7]. The thermal treatment of the layers led to crystallization processes and resulted in the formation of different crystalline Sn- and Te-oxide phases, depending on the temperature and the layer thickness.

Figure 1 illustrates the XRD pattern of a Sn-O-Te layer with a thickness of 200 nm thermally treated after doping with Pt. As is clearly seen, the layer is crystalline. The diffraction peaks can be indexed to SnO_2 and TeO_2 (since the layers were deposited on Si substrates and Pt-doped, there are peaks of Si and Pt as well). Differences in the composition are observed in the layers thermally treated in the same manner, but with a thickness of 60 nm [3, 4]. Moreover, the composition depends on the sequence of heating and Pt-doping. The phases are presented in table 1. Besides TeO_2 and SnO_2, the thinner layers contain non-stoichiometric Sn oxides, namely Sn_2O_3 and Sn_3O_4, if they have been doped with Pt before the thermal treatment on the one hand, and Sn_3O_4, if the doping has been conducted prior to the heating, on the other. As shown below, these differences in the composition correlate with differences in the sensitivity to ethanol.

3.2. Humidity and ethanol sensing properties

Figure 2 presents the resistance R [Ω] of an amorphous Sn-O-Te layer with $R_{Sn/Te} \approx 0.8$ and a thickness of 200 nm as a function of the relative humidity RH [%]. As seen, the layer is sensitive to humidity at RH [%] > 70 %. The inset shows the same dependence for samples with a thickness of 60 nm. The resistance change covers five decades when the relative humidity varies in the range of $30 - 100$ %.
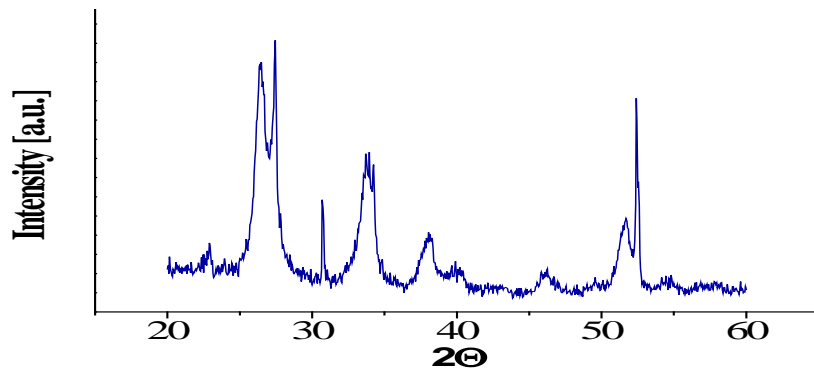
Figure 1. XRD spectra of a Sn-O-Te layer with a thickness of 200 nm.

Phases	PDF
SnO_2	77-0451
TeO_2	76-0680

Obviously, increasing the layer thickness leads to a decrease in the humidity sensitivity. This dependence has also been observed by other researchers [8].

Fgure 3 presents the sensitivity S (calculated by equation (1) to ethanol vapor as a function of the substrate temperature for layers with $R_{Sn/Te} \approx 2.3$ and a thickness of 60 nm doped with Pt before the thermal treatment. For comparison, in the same figure are also shown results for layers of the same composition and thickness, both doped and undoped with Pt after the thermally-induced crystallization. As it can be seen, the undoped layers are practically insensitive to ethanol. The Pt-doping results in a substantial sensitivity increase at 120 ^oC and 240 ^oC. Moreover, the sequence of doping and thermal heating plays an important role in improving the sensitivity; layers crystallized in the presence of Pt exhibit a higher sensitivity to ethanol than those doped after crystallization. As already shown, they differ in composition as well (see table 1).

Figure 4 presents the sensitivity of layers with a thickness of 200 nm that were non-isothermally treated and doped with Pt before the thermal treatment. They exhibit a significantly lower sensitivity to ethanol than similar layers with a thickness of only 60 nm. It should be noted that the thicker layers do not contain non-stoichiometric Sn-oxides, and there exists evidence that the latter could improve the sensitivity and selectivity of SnO_2 based sensors [9].

Table 1: Crystalline phases in non-isothermally treated layers with a thickness of 60 nm doped with Pt.

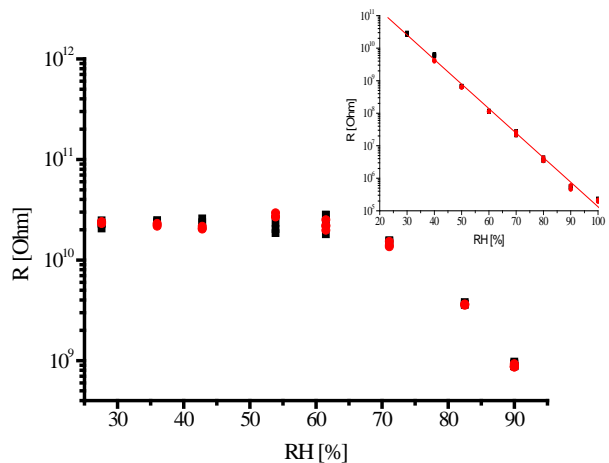| Doping with Pt	Phases	PDF
Before thermal treatment	TeO_2	Paratellurite 42-1365
	SnO_2	Cassiterite 41-1445
	Sn_2O_3	25-1259
	Sn_3O_4	20-1293
After thermal treatment	SnO_2	Cassiterite 41-1445
	TeO_2	Paratellurite 42-1365
	Sn_3O_4	20-1293

Figure 2. *R* [ohm] as a function of *RH* [%] of an as-deposited Sn-O-Te layer with $R_{Sn/Te} \approx 0.8$ and a thickness of 200 nm.
Inset: *R* [ohm] as a function of *RH* [%] of a sample with the same composition, but with a thickness of only 60 nm [1].

Investigations regarding the selectivity of the Sn-O-Te ethanol sensors showed no cross-sensitivity to humidity and ammonia at a substrate temperature of 120 ^oC.
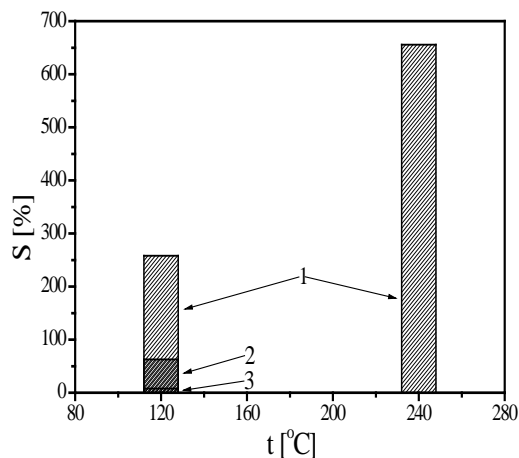
Figure 3. Ethanol sensitivity (S) of Sn-O-Te layers with $R_{Sn/Te} \approx 2.3$ and $d = 60$ nm as a function of the substrate temperature (t): (1) Pt-doped before and (2) after thermal treatment; (3) undoped layers.
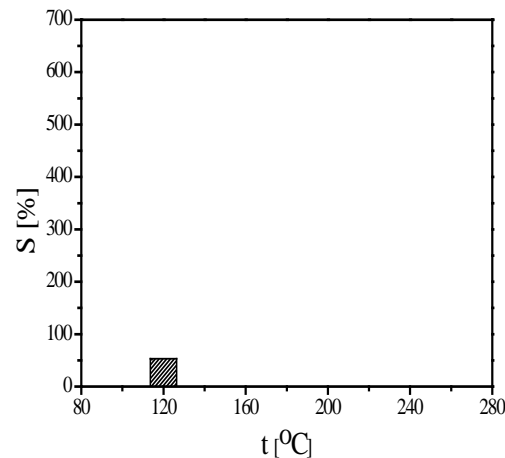
Figure 4. Ethanol sensitivity (S) of Sn-O-Te layers with $R_{Sn/Te} \approx 2.3$ doped with Pt before thermal treatment and $d = 200$ nm at 120 $^{\circ}$C.

4. Conclusions

Sn-O-Te layers prepared by co-evaporation of Sn and TeO$_2$ were investigated in view of applications as humidity and ethanol sensors. It is shown that the sensitivity depends on the layer thickness and (for ethanol sensors) on the sequence of Pt-doping and thermal treatment.

The as-deposited amorphous layers with $R_{Sn/Te} \approx 0.8$ show very good characteristics as humidity sensors operating at room temperature. Increasing the thickness leads to a decrease in sensitivity – layers with $d = 200$ nm are sensitive to humidity at $RH > 70$ %.

Layers with $R_{Sn/Te} \approx 2.3$ that were non-isothermally treated up to 360 $^{\circ}$C and doped with Pt are sensitive to ethanol at 120 $^{\circ}$C and 240 $^{\circ}$C. The layers' thickness affects the gas sensitivity – thinner layers of a thickness of about 60 nm have a gas sensitivity higher than that of thicker layers with $d = 200$ nm. Moreover, the sensitivity is significantly higher if doping precedes the thermal treatment.

Analysis of the crystallized layers revealed that their composition differs not only with the thickness but also with the sequence of Pt-doping and thermal treatment. Thinner layers doped after annealing contain non-stoichiometric Sn-oxide (Sn$_3$O$_4$), besides the stoichiometric SnO$_2$ and TeO$_2$. If the Pt-doping precedes annealing, a second non-stoichiometric Sn-oxide (Sn$_2$O$_3$) is detected in the layer. These results could explain the higher sensitivity of the thin layers and of the layers doped with Pt prior to the thermal treatment.

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