TIN OXIDE HUMIDITY SENSORS OPERATING AT ROOM TEMPERATURE OBTAINED BY CO-EVAPORATION OF TeO$_2$ AND Sn$^\clubsuit$

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In this paper the humidity sensing properties of layers, prepared by a new method for obtaining doped tin oxide – the vacuum co-deposition of TeO$_2$ and Sn, are studied. The as-deposited layers are amorphous with great specific area and low density. They are built up of a fine grained matrix, consisting of oxides of Sn and Te, and a nanosized dispersed phase of Te, Sn and/or SnTe. The chemical composition of both the matrix and the nanosized particles depends on the ratio Sn/Te and the evaporation conditions. It is shown that as-deposited layers with Sn/Te-ratio ≈ 0.7 - 0.9 exhibit excellent characteristics as humidity sensors operating at room temperature – very high sensitivity, fast response and a very short recovery period. No hysteresis effects are observed. Accelerated ageing tests have shown that the layers possess a good long-term stability. The influence of a number of parameters (layer composition and thickness, thermal pre-treatment, material of the substrate and electrodes, etc.) is discussed.

1. Introduction

Tin oxide is the most studied gas sensing material in the last decades because of its capability to detect different gases. Its electrical resistance changes due to interaction with gas molecules of the surrounding atmosphere and serves as sensing signal. Many studies have shown that the sensing properties of tin oxide (conductivity, sensitivity and selectivity) depend strongly not only on the composition of the active layer and introduced dopants, but also on the preparation conditions and on the nature and geometry of the electrodes [1]. That is why the efforts of many researchers are directed towards improvement of existing preparation methods and development of new ones.

Recently, we have reported that the co-evaporation of TeO$_2$ and Sn represents a new method for obtaining doped tin oxide [2]. The aim of the present work is to study the humidity sensing properties of thin layers obtained by this method and the influence of various parameters (substrate, electrodes, thermal pre-treatment) and the chemical composition on these properties.

2. Experimental details

The mixed Sn-Te-oxide layers were obtained by deposition of TeO$_2$ and Sn from independently heated cells, under vacuum, better than 10^{-4} Pa. TeO$_2$ was evaporated from a Pt-crucible, and Sn – from a crucible made of glassy carbon, both of them enclosed, with small aperture (aperture / surface area of the evaporant ≈ 1: 40). The condensation rates of both substances were controlled separately during the whole evaporation process using quartz crystal monitors.

In order to ensure high homogeneity of the composition in the whole volume of the layer the evaporation was performed onto stationary substrates placed parallel to the emitting surfaces. Different materials were studied as substrates – glass plates; alumina; oxidized silicon; glass plates, precoated with vacuum evaporated polyimide [3]. They were held at ambient temperature.

The chemical composition, i.e. the amount of both substances in the layer (the atomic ratio $R_{Sn/Te}$) and the thickness of the layers were calculated on the base of the measured evaporation rates using computer programs as described in [4]. The data obtained for the composition were controlled by Energy Dispersive Spectrometry (EDS) in SEM (Philips 505 SEM, equipped with an EDAX 9100/60 analytical system) and for the thickness of the layer – by a profilometer Talystep (Rank Taylor Hobson).

The thermal treatment of the layers was performed in an oven; the layers were heated for different time at constant temperature (50-300 ^{o}C) under ambient atmosphere.

The structural characterization of the layers was carried out by transmission and scanning electron microscopy (TEM and SEM) and selected area electron diffraction (SAED) (Philips EM 420T). The samples intended for TEM studies in the as-deposited state were evaporated on glass plates with a water soluble PVA sublayer. The thickness of the layers (20 − 100 nm) was suitable for their direct imaging. In order to examine the growth morphology of the layers a SEM observation was carried out on fractured surfaces of samples with thickness 1 μm, covered with an arc deposited conductive carbon coating. To characterize the distribution of the elements in the samples X-ray mapping (EDS) was applied.

For electrical characterization, comb-like Au electrodes were used. As known, directly deposited gold (Ag, Pt) films do not show good adhesion to insulating substrates. For that reason a thin transition metal underlayer has to be vapour deposited first or the substrate has to be precoated with an insulating organic layer [5]. To enhance the adhesion of gold, in our investigations comb-like electrodes (width and distance between electrodes 20 μm) were formed in vacuum deposited thin Cr and Ni films by photolithography [6] and then electroplated with gold. Alternatively a thin vacuum evaporated polyimide layer was used as adhesive layer [3] and the comb-like gold electrodes were deposited in vacuum through masks (electrode width 0.8 mm, distance between electrodes 1 mm).

Sensor response to humidity was studied at 25 ^{o}C, at different values of relative environmental humidity (RH), in a test chamber equipped with temperature and RH controllers. The samples were placed in holders having two pressure contacts. The measurement of the resistance R of the samples as a function of RH was performed with a multi-channel ohmmeter, consisting of a resistor-connector-unit and a multi-channel analog-to-digital converter PCI 6024E (National Instruments). The DC resistance was measured using short electric pulses with alternate direction (± 10 V) thus keeping minimal polarization of the sample and precluding detrimental electrochemical migration. The control of the ohmmeter, the acquisition and processing of the data were computerized. The computer programs were created using LabView.

3. Results and discussion

A. Structure and composition of the layers, obtained by co-evaporation of TeO$_2$ and Sn

As shown in previous investigations [2], all as-deposited layers obtained by co-evaporation of TeO$_2$ and Sn are amorphous and exhibit a granular structure. The selected area electron diffraction does not indicate the presence of a crystalline phase. This is illustrated in Fig. 1 with the TEM image and the SAED pattern of an as-deposited layer with $R_{Sn/Te} \approx 0.8$. As seen from the SEM micrograph of the fractured surface of a layer with the same composition (Fig. 2), besides the granular structure it exhibits a columnar structure. This result, indicating a great free surface, agrees well with the very low density of the layers, established earlier by the weight method ($\rho \approx 4$ g/cm^3, much lower than the respective values for the bulk materials TeO$_2$, Te, Sn and SnO$_2$) [4].

The compositions of the matrix and the dispersed phase depend mainly on the value of $R_{Sn/Te}$ and on the preparation conditions. As shown by investigations on the thermally induced processes and confirmed by XPS and [119]Sn conversion electron Mössbauer spectroscopy studies, during the co-

evaporation of TeO$_2$ and Sn solid state reactions take place between both substances, resulting in the formation of tin oxide and atomic Te. [2, 7] At excessive amounts of Sn formation of SnTe also occurs. The subsequent thermal treatment leads to diffusion, segregation and crystallization processes. At about 250 ^{o}C the structure of the matrix begins to change from the amorphous into the crystalline state and at higher temperatures a pure crystalline SnO$_2$ layer is formed.
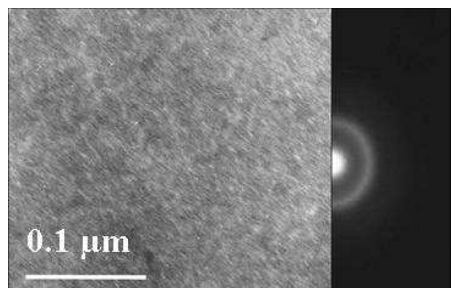

Fig. 1. TEM image and SAED pattern of 60 nm thick layer (R$_{Sn/Te}$ ≈ 0.8).
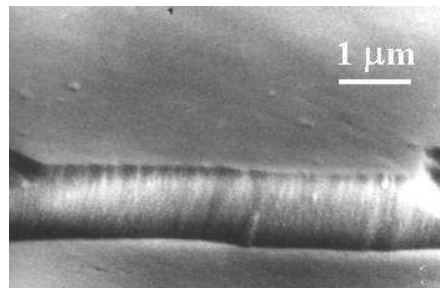
Fig. 2. SEM image of the growth profile of 1 µm thick layer (R$_{Sn/Te}$ ≈ 0.8).

B. Humidity sensing properties of the layers

To study the humidity sensing properties layers with R$_{Sn/Te}$ ranging from 0.5 to 2.0, in the as-deposited state and after thermal treatment up to 300 ^{o}C, were used. It was found that good sensitivity to humidity exhibit only the layers in the amorphous as-deposited state. That is why all further investigations were carried out with thermally untreated samples. The sensing properties depend strongly on the chemical composition of the layers. Best results were attained at R$_{Sn/Te}$ 0.7 – 0.9 and thickness < 100 nm. It has to be stressed however that at low relative humidity levels the electrical resistance of these layers is very high. This limits the choice of the substrates only to materials with resistance exceeding 10^{11} Ohm. Another requirement the substrate has to comply is a very smooth surface because of the small thickness of the sensing layer (50 - 60 nm). In the present investigation glass plates were used as substrates.

As mentioned above, to enhance the adhesion of the Au electrodes to the substrate, a layer of transition metal or an insulating organic underlayer have to be used. The transition metals we have studied are Ni and Cr. After they have been deposited in vacuum, the comb-like electrodes were formed by photolithography and then electroplated with gold. This method was chosen because literature data exist that if the Au electrodes are evaporated in vacuum and Cr, Ni and other metals are used as undercoating layers, problems related to diffusion of these metals along grain boundaries to the noble metal surface arise. This phenomenon leads to altering of surface properties of Au (Pt) and effects electron transfer [8, 9]. The results obtained with Au electrodes and Ni underlayer can be seen in Fig. 3. The figure shows the SEM image of sensors with Ni/Au electrodes (a) and Ni electrodes (c) after measurements of the electrical resistance as a function of RH have been performed. It has to be pointed that the samples exhibit a good stability even at elevated temperature if no current is applied. Electrical links between the electrodes are observed only in the presence of an electrical field (D.C. +/- 10 V) regardless of the alternation of the polarity (frequency > 0.2 Hz). The reason for the short-circuit is demonstrated in Figs. 3b and 3d with the Ni Kα X-ray mapping of the same areas of the samples, in Fig. 3e with the Te Lα X-Ray mapping and in Fig. 3f with the Sn Lα X-Ray mapping. It is clearly seen, that the formation of "bridges" between the electrodes is only due to electrodiffusion of Ni. Analogous results were observed with the Cr electrodes as well. The SEM image of a sensor with Cr electrodes (a) and the corresponding Cr Kα X-ray mapping (b) are given in Fig. 4. To overcome this problem at present the transition metal sublayer is replaced by a vacuum evaporated thin polyimide film.

The changes in the electrical resistance with relative environmental humidity (RH) of a 60 nm thick sensor with R$_{Sn/Te}$ ≈ 0.8, working at room temperature, are presented in Fig. 5. It can be seen that with increasing RH the resistance of the layer decreases. The response curve reveals a close exponential

relationship between the sensor resistance and RH spanning 5 decades of resistance and is linearized by taking the logarithm of the resistance. No hysteresis effects are observed. The recovery period of the sensor, measured in the test chamber, is very short - 3 to 4 seconds after being at 85 % RH. Accelerated ageing tests at 70 $^{\circ}$C and 90% RH have indicated that the layers exhibit a good long-term stability.
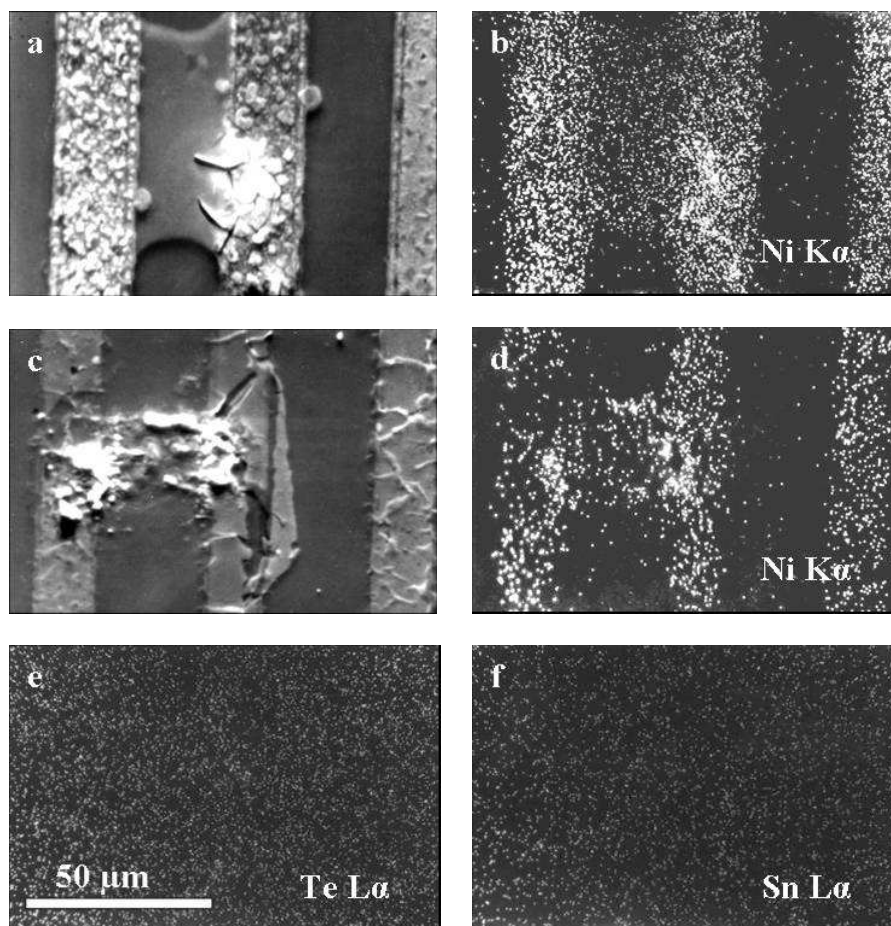

Fig. 3. SEM images of sensors ($R_{Sn/Te} \approx 0.8$) with (a) Ni/Au electrodes and (c) Ni electrodes. Corresponding Ni Kα X-ray mapping (EDS) (b) and (d) of the same samples; Te Lα X-Ray mapping (e) and Sn Lα X-Ray mapping (f) of sample (a).
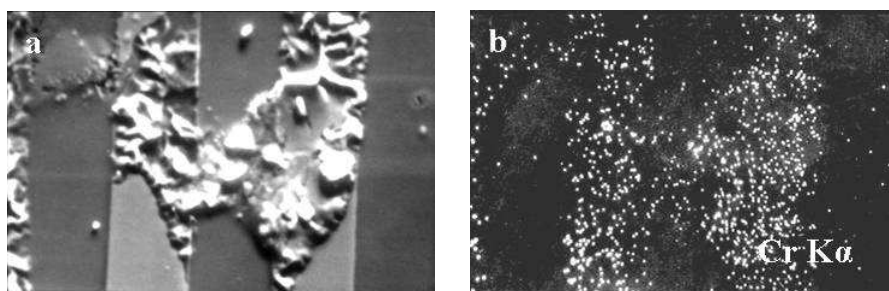

Fig. 4. SEM image of sensor with Cr electrodes (a) and Cr Kα X-ray mapping (b) of the same sample ($R_{Sn/Te} \approx 0.8$).

4. Conclusions

It has been shown that nanosized doped tin-oxide layers, obtained by co-evaporation of TeO$_2$ and Sn, offer promising possibilities for developing sensors with improved characteristics. The as-deposited thin amorphous Te-O-Sn layers with $R_{Sn/Te} \approx 0.8$ show excellent properties as humidity sensors. They are characterized by a very high sensitivity, working at room temperature – the resistance change covers 5 decades when the relative environmental humidity varies in the range of 20-90 %. No hysteresis effects are observed. The recovery period, measured in the test chamber, is very short - 3 to 4 seconds after 85 % RH. Accelerated ageing tests have indicated that the layers exhibit a good long-term stability.
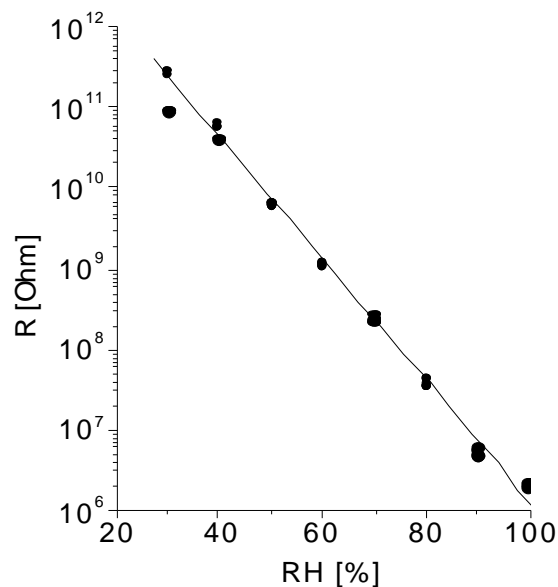

Fig. 5. Resistance change with relative humidity (RH) of sensors with $R_{Sn/Te} \approx 0.8$; glass substrate, Au comb-like electrodes.

The method is applicable for the production of a variety of nanosized metal oxides and allows the introduction of very finely dispersed dopants and mixing of the components at atomic level in desired proportions. It is compatible with the conventional microelectronic technology and allows the integration of the layer on the chip with field-effect transistors (enabling amplification of the current response for high-resistivity layers) or with entire subsystems for data processing (with possibility for development of "smart" sensors).

Acknowledgements

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