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Room temperature humidity sensors based on co-evaporated TeO\textsubscript{2} and Sn

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Abstract. Thin layers prepared by vacuum co-deposition of TeO\textsubscript{2} and Sn are studied as humidity sensors working at room temperature. They are amorphous and, due to chemical interaction between the two substances, are built up of a mixed Sn- and Te-oxide matrix and a dispersed phase that at $R_{\text{Sn/Te}} < 2.0$ consists of elemental Te. The optimal composition of the layers is obtained by varying the atomic ratio $R_{\text{Sn/Te}}$. Auger analysis is used to follow the in-depth distribution of the components.

It is shown that the layers have a homogeneous composition over their entire depth. For $R_{\text{Sn/Te}} = 0.8 - 0.9$, they exhibit very high sensitivity to humidity – the electrical resistance changes by more than 4 decades in the range of 20 - 90% RH. The sensor response is very fast and the recovery period, very short. A very high long-term stability is observed as well.

1. Introduction

Over the past ten years, thin vacuum-deposited layers prepared by co-evaporation of Sn and TeO\textsubscript{2} \cite{1} have been the object of intensive investigation in our laboratory since they form the basis for the development of gas sensors, conductive layers, etc. The as-deposited layers are amorphous with high porosity and large specific area. They are built of a fine oxide (SnO\textsubscript{2}, SnO, and TeO\textsubscript{2}) matrix (grains with dimensions of several nm) and a dispersed phase (Te, Sn and/or SnTe) depending on the atomic ratio Sn/Te ($R_{\text{Sn/Te}}$). Upon thermal treatment, the layers become polycrystalline \cite{2}.

We have already reported that the amorphous layers exhibit very good characteristics as humidity sensors working at room temperature, namely, high sensitivity and selectivity \cite{2}.

In this paper we present results from a systematic study of the preparation reproducibility and the homogeneity of the amorphous layer deposited, as well as of the composition range where the layers possess high sensitivity to humidity. Data are also included about the sensor response and recovery time, the long-term stability, etc.

2. Experimental

The humidity sensing thin layers (50-60 nm) were prepared by thermal vacuum co-evaporation of Sn and TeO\textsubscript{2} from two independent Knudsen-type cells with different atomic ratios $R_{\text{Sn/Te}}$. The fluxes of both substances were controlled continuously during the evaporation process using quartz crystal monitors. The chemical composition, i.e. the amount of both substances (the ratio $R_{\text{Sn/Te}}$, respectively)

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and the thickness of the layers were calculated on the basis of the measured evaporation rates using computer programs as described in [3]. Analogous calculation procedures were used for selecting the experimental conditions necessary for obtaining the desired composition and thickness of the samples [3]. Polycrystalline layers were produced by thermal treatment up to 360 °C (15 min heating at each step of 40 °C). The layers’ chemical composition and $R_{\text{Sn/Te}}$ were controlled by energy dispersive spectrometry (EDS) in SEM. Auger electron spectrometry (AES) was used to determine the in-depth distribution of Sn, Te and O. The Auger spectra are derivative and obtained by a spectrometer with an energy resolution of ~0.3% (single-pass CMA and coaxial electron gun). Primary electron energy of 3 keV and modulation voltage of 4 Vpp were employed. The peak for O (510 eV) and the doublets for Sn and Te were monitored. The profiling was done by sputtering by 3 keV argon ions at a current of 2 μA. The quantification was made through a modified method of the elemental sensitivity factors. SnO$_2$ was used as own standard. The intensity of the tellurium doublet was measured from the maximum of the low-energy peak to the minimum of the high-energy peak.

Cr comb-like electrodes patterned by a photolithographic technique were used [4] to perform the electrical measurements at different temperatures and relative humidity (RH [%]). The sensor’s response to water vapor was studied as a function of the substrate temperature in a test chamber equipped with temperature and RH controllers. The measurement of the electrical resistance $R$ [Ohm] of the films was performed by a National Instruments multichannel ohmmeter. The data acquisition and processing, as well as the control of the ohmmeter, were computerized using Lab View software. The kinetic measurement was made with the same ohmmeter using saturated solutions that maintain constant relative humidity in the atmosphere over them – (NH$_4$)$_2$SO$_4$ keeps the humidity at 82% and NaOH, at 6% RH. The samples were hold above the solution and the change of $R$ [Ohm] was measured at intervals of 2 s.

3. Results and discussion

3.1 Preparation reproducibility and homogeneity of the layers

As it will be shown later, the sensing properties of the layers are strongly dependent on their composition. To check the reliability of the computer calculations described above and the preparation reproducibility, we compared the calculated $R_{\text{Sn/Te}}$ with the respective data obtained by the EDS-analyses in SEM. As seen in figure 1, the agreement is very good – the deviation is ~2%.

As already mentioned, we used AES profiling to investigate the homogeneity of the as-deposited layers, i.e. the elements’ depth distribution. Unfortunately, the direct application of the method is not possible because of the mobility of elemental Te upon heating and electron and ion beam bombardment, which could compromise the evaluation of its original distribution in the layer [1]. On the other hand, it is known that the other components of the layer do not exhibit mobility. Therefore, if the mobile Te atoms are removed from the layer by the electron beam prior to the AES - analysis, the distribution of the other components could be used to assess the homogeneity. The layers used for the analysis were with $R_{\text{Sn/Te}} \approx 0.8$ (confirmed by EDS analysis in SEM), i.e. they contained 20 parts of oxygen, 10 parts of Te and 8 parts of Sn (respectively 52.6, 26.3 and 21.1 at.%).
The solid-state reaction between TeO$_2$ and Sn during their co-deposition has resulted in 8 parts of SnO$_2$, 2 parts of TeO$_2$ and 8 parts of elemental Te. After removal of the elemental Te, the composition has become O:Te:Sn = 66.7:6.7:26.7. Their distribution should be homogeneous if the original as-deposited layer has been homogeneous. The dose used for removing the unbound Te exceeded by a factor of $5 \times 10^4$ the dose applied for EDS. As can be seen in figure 2, the profiles are quite homogeneous, the average plateau concentrations are O:Te:Sn = 61(±1):6.4(±0.4):28.6(±0.3). After correction accounting for the contamination with C (4%), the atomic concentration of O becomes approximately 64%.

3.2. Humidity sensing properties

In our previous investigations, we have shown that layers with $R_{Sn/Te} = 0.7$ - 0.8 exhibit excellent characteristics as humidity sensors. Figure 3 presents the sensor response kinetics under step-like changes in RH. As can be seen, the sharp rise in relative humidity (from 6% to 82%) causes a very fast response of the sensor, the recovery period being very short as well. This leads to the conclusion that the water molecules are physically adsorbed. Results from the ageing tests are demonstrated in figure 4. They indicate that measurements performed over a long period of time (2002-2011) do not show significant differences, i.e. the layers exhibit a very good long-term stability.

We studied the sensitivity of the layers to water vapor over a wide range of atomic ratios and, as seen in figure 5, the best humidity sensing properties are exhibited by layers with $R_{Sn/Te} \approx 0.4$ - 0.9. As shown in the same figure (inset), after crystallization (thermal treatment up to 360 °C), the layers with $R_{Sn/Te} = 0.7$ lose their sensing properties to water vapor.

3.3 Temperature dependence

Figure 6 presents the dependence of $R$ [Ohm] on the relative humidity measured at different temperatures – 25, 40, 60 and 80 °C. The sensor layers are practically not sensitive to water vapor above 40 °C. The cyan curve was obtained after heating the sample up to 80 °C (which does not lead to compositional and structural changes of the layers) and cooling
back to room temperature. It almost coincides with the black curve that was obtained before heating, with the as-deposited layer. This means that temperature variations in the range 20-80 °C do not result in changes in the sensing properties of the layers.

Figure 7 shows the dependence of $R$ [Ohm] on the temperature at different RH values. As seen, at low humidity values, the dependence is linear and the activation energy is 0.44 eV (figure 7 - inset). At high humidity values (80-85%), a maximum appears at about 50 °C, probably due to desorption of the water vapor off the layer’s surface.

**Conclusions**

Our investigation shows that reproducible and homogeneous thin layers are obtained using the method of co-evaporation of Sn and TeO$_2$. In the as-deposited state, the amorphous layers with $R_{Sn/Te} \approx 0.4÷0.9$ possess good humidity sensing properties at room temperature. No change in the sensing behavior is observed if the layers are heated up to 80 °C and cooled back to room temperature. If they are heated up to 360 °C, however, and become polycrystalline, they lose their humidity sensing ability. The amorphous sensing layers show fast response, short recovery time and very good long-term stability. The activation energy is calculated using the temperature dependence in low-humidity atmosphere. Based on the kinetics studies, the conclusion can be drawn that the water molecules are physically adsorbed on the layer’s surface.

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