NANOSIZED TIN-OXIDE LAYERS - NEW METHOD OF PREPARATION AND HUMIDITY SENSING PROPERTIES

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Metal oxides in the form of thin films are finding an increasing application as resistive gas sensors, transparent conductors, in solar cells, etc. Among them SnO₂, doped or mixed with other metal oxides, is the most attractive material.

Investigations carried out in CLF on layers prepared by vacuum coevaporation of TeO₂ and Sn have shown that during the codeposition an oxidation-reduction process between both substances takes place. The layers obtained are amorphous, built up of a fine grained oxide matrix and a very finely dispersed phase (Fig. 1). The composition of the layers depends mainly on the relative amount of Sn, i.e. on the ratio Sn/Te (R_{Sn/Te}^{1,2}). As revealed by XPS and 119Sn-conversion electron Mössbauer spectroscopy the oxide matrix consists of TeO₂ and/or SnOₓ and the dispersed phase – of Te, Sn, and/or SnTe. In Fig.2 the relative amounts of TeO₂, Te and SnTe as a function of Sn content are given, calculated on the base of the XPS-data.

Upon subsequent thermal treatment, diffusion, segregation and crystallization processes occur. At a temperature about 125°C the dispersed tellurium phase starts to segregate and to crystallize on the free upper surface of the layer through diffusion from the bulk. At a higher temperature (about 250°C) the structure of the matrix begins to change from the amorphous into the crystalline state. Varying R_{Sn/Te} and the annealing conditions layers with desired composition and morphology can be achieved - amorphous or nano-sized microcrystalline layers of mixed Te- and Sn-oxides, SnOₓ or SnO₂, with a dispersed phase of Te, Sn and SnTe respectively.

Figure 3 shows as an example the TEM images and the SAED patterns of layers with R_{Sn/Te} 1.7 (in the as-deposited state) after annealing up to 350°C (Fig. 3a) and up to 400°C (Fig. 3b). As it can be seen from the SAED patterns the layers consist of a mixture of SnO₂ and TeO₂ (a) or of pure SnO₂ (b). The crystallite size is several nanometers. The corresponding EDS-analyses show a decrease of the Te content in the layer obviously due to diffusion to the surface and evaporation of the dispersed Te phase.

The method developed is applicable for the preparation of a variety of nanosized metal oxides and allows...
the introduction of very finely dispersed dopants both in the microcrystallites and at their interfaces. Moreover, it is compatible with the conventional microelectronics technologies.

Figure 3: TEM images and SAED patterns of layers with $R_{Sn/Te} = 1.76$ (in the as-deposited state) annealed up to: a) 350°C and b) 400°C

The as-deposited amorphous layers prepared by the coevaporation of TeO$_2$ and Sn show very good characteristics as humidity sensors operating at room temperature - high sensitivity, fast response and a very short recovery period. As shown by Fig. 4 the response curve reveals a close exponential relationship between the sensor resistance and relative environmental humidity spanning 5 decades of resistance (in the range of 20 – 90 % RH), and can be linearized by taking the logarithm of the resistance. Accelerated ageing tests have indicated that the layers exhibit a good long-term stability.

The method of layer preparation allows also coevaporation of different dopants, which are known to rise the sensitivity and selectivity of SnO$_2$-sensors in respect to a variety of reduction gases The results of these investigations are expected to be useful not only for the development of sensors with improved characteristics but also for the better understanding of the relationship between the preparation conditions, the specific structure and the properties of mixed oxide layers.

References:

2) G.Tyuliev, I.Podolesheva, X-Ray Photoelectron Spectroscopy of Thin Films, Obtained by Coevaporation of TeO$_2$ and Sn, to be published

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