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Combined influence of titania and silica precursors on the properties of thin film humidity sensing elements prepared via a sol–gel method

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ABSTRACT

The present work deals with the comparative investigations of the combined influence of precursors of TiO_2 and SiO_2: Tetrabutyl orthotitanate, Tetraethoxysilane and (3-Glycidyloxypropyl)trimethoxysilane in the presence of Ce-ions on the properties of the respective thin film humidity sensing elements prepared via a sol–gel method and sintered at 400 °C. SEM, EDX and XRD analyses of the obtained samples have been carried out to study their surface morphology and structural composition. The electrical characteristics and parameters of the samples have been investigated by means of an impedance analyzer. It has been established that the type and proportions of the precursors substantially affect the structure of the films obtained and their humidity sensing properties. The combination of both types of precursors of TiO_2 and SiO_2 in all cases results in an enhancement of the sensor elements' response to humidity compared to the use of only one of these precursors. The change in resistance of the samples reaches about four orders of magnitude within the range from 15 to 93% relative humidity at a frequency of 20 Hz and at 25 °C.

1. Introduction

Modern industrial technological processes and operations require automatic control and regulation of the respective parameters and conditions. Automated systems for measurement, control and monitoring contain the respective sensors. Among the parameters to be controlled humidity appears to be one of the most important in the production, transportation and storage of various industrial and agricultural products. Other branches of humidity sensor implementation are the microclimate monitoring of office buildings, homes, industrial plants and agricultural nutrition plant growth, environmental monitoring, etc. This determines the need for continuous improvement of the parameters of humidity sensing elements including the search and examination of different materials and technologies for their manufacture so that these technologies are relatively less complicated and at lower cost.

Metal oxide materials as TiO_2, ZnO, Fe_2O_3, WO_3, SnO_2, etc. [1–10] are commonly used for preparing humidity sensing elements. TiO_2 among them is very widely used because the addition of various dopants to it and various sintering temperatures allow different titanates in the structure to be obtained which have different properties [11–16]. SiO_2 is also used as a basic material for preparing humidity sensing elements [17–24]. The joint use of these oxides is also of interest. The compositional modification of Si–Ti-oxide nanocomposites by Ni, Cu and Sn is described in [25,26].

On the other hand, the development of improved sensor elements requires good compositional and structural control of the synthesized material, related to the manufacturing process. In this connection, the sol–gel method is a versatile method that enables development of entire new generations of organic–inorganic hybrids and composite materials [27–35]. The technological potential of the sol–gel methods has been seriously investigated during the recent decades, when preparing humidity sensing elements including [17,36–38]. Ce-doped titania-silica thin film humidity sensing elements prepared via a sol–gel method with high response to humidity are presented in our previous work [39]. When preparing them as precursors of TiO_2 and SiO_2, respectively: Tetrabutyl orthotitanate (TBOT), and Polydimethylsiloxane, trimethylsiloxy-terminated (PDTS), have been used in the presence of Ce ions. Cerium compounds serve both as providers of Ce for doping and also as acid hydrolysis catalysts. Cerium oxide and other cerium compounds are used as ingredients of

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Table 1
Compositions of the precursor solutions and abbreviations of the respective samples.

Group 1	TB2TE8	TB4TE6	TB6TE4	TB8TE2	REF_TE[a]
TBOT:TEOS (ml:ml)	2:8	4:6	6:4	8:2	0:10
Group 2	TB2GP8	TB4GP6	TB6GP4	TB8GP2	REF_GP[a]
TBOT:GPTMS (ml:ml)	2:8	4:6	6:4	8:2	0:10

[a] An additional test tube was filled only with 10 ml of TBOT, which served as a first reference solution and the abbreviation of the respective samples is REF_TB.

sensor elements for oxygen [11], hydrogen and carbon monoxide [40], and relative humidity [41–43]. A beneficial effect of the Ce^{4+} ions on the polymerization processes in the sol–gel systems is described in [44]. In sol–gel methods the organic moieties have a strong effect on the structure formation of the oxide products resulting after sintering. Tetraethoxysilane (TEOS) and (3-Glycidyloxypropyl)trimethoxysilane (GPTMS) are often used as starting materials in preparing films for various applications [33,45–49]. Therefore the study of the influence of these compounds as silica precursors in combination with a titania precursor in the presence of Ce-providers in the sol–gel process on the structure and the response to the humidity of the obtained films is of interest.

Taking into account all the discussions above, the aim of the present work is the development of humidity sensing elements by a sol–gel method on the basis of TBOT:TEOS and TBOT:GPTMS as precursors of TiO_2 and SiO_2 respectively, in the presence of Ce ions. The combined influence of these precursors has been studied for different proportions on the surface morphology, structural composition and properties of the obtained Ce-doped titania-silica thin film humidity sensing elements. A comparative analysis has been conducted with reference elements prepared on the basis of only one of these precursors in order to summarize the positive effect of the joint application of providers of Ti and Si in the described sol–gel method on the response to the humidity of the obtained sensor elements.

2. Experimental

2.1. Sol–gel derived film deposition

In order to perform a complete evaluation research, the basic ingredients were mixed in different proportions by adding small (2 ml) portions of each one. This approach enabled to prepare two groups of initial Ti-Si containing precursor mixtures with a gradual variation of the precursor content. Tetrabutyl orthotitanate, product of "Alfa Aesar" – Karlsruhe (Germany) was used as Ti-source for both groups of precursor mixtures. Tetraethoxysilane, produced by "Alfa Aesar" – Karlsruhe (Germany) was used as Si-source for the mixtures in Group 1 and (3-Glycidyloxypropyl)trimethoxysilane "Alfa Aesar" – Karlsruhe (Germany) – in Group 2. These precursor mixtures are shown in Table 1.

The initial precursor mixtures were converted into sol–gel systems by hydrolysis/polymerization at 85 °C for 3 h in the presence of cerium containing hydrolytic solution. It was preliminary prepared by dissolution of anhydrous diammonium hexanitrocerate (FLUKA-Chemika, Switzerland) in isobutanol, until saturation at room temperature. This solution was used 24 h after its preparation.

The deposition solution was prepared by maturation in covered test tubes for 168 h at 5 °C.

The film deposition procedure was performed on preliminary cleaned alumina substrates with interdigitated silver–palladium electrodes by triple consecutive immersion/drying (30/30 min), performed at 85 °C, for both procedures. The substrate was cleaned before the film deposition by overnight exposition to Acetone:Ether – 1:1 mixture at room temperature.

Then the obtained samples were sintered at 400 °C for 30 min.

Fig. 1 shows a photograph of a sample prepared by the method described. The architecture of samples with interdigitated electrodes is frequently employed when preparing humidity sensing elements [50–52], gas sensors [53,54], etc. The resistance of sensitive films when using two parallel electrodes is most frequently high. The interdigitated electrode system allows decreasing this resistance since sensors can be considered as a circuit of individual elements connected in parallel [55]. This is of significance to the practical application of such elements.

2.2. Measurements and characterizations

2.2.1. Observations of the surface morphology and structural characterization

The samples underwent morphological observations by scanning electron microscopy (SEM), combined by elemental analysis, by TESCAN, SEM/FIB LYRA I XMU working at 30 kV. The map data analyses were carried out by energy dispersive X-ray spectroscopy (EDX) using Energy Dispersive Spectrometer (Quantax 200 of BRUKER detector). Structural characterization was performed by X-ray diffraction analysis (XRD) on powder materials from the respective gels, sintered at 400 °C. The measurements were taken by Philips PW 1050, supported by CuKα – X-ray emitter and monochromator of diffracted radiation. The conditions of the experiments were: angle range (2θ) from 8° to 90°, step of 0.05° and exposition of 2 s per step.

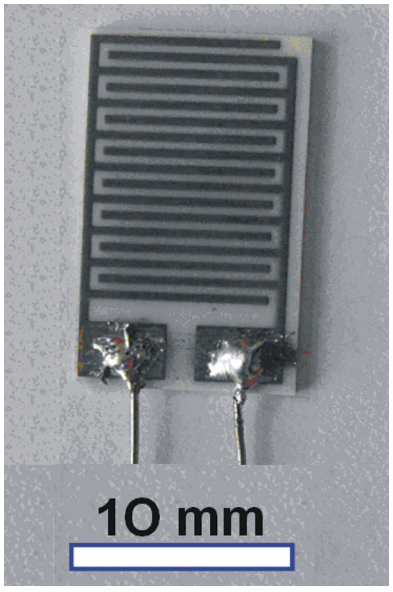

Fig. 1. Photograph of a sample.