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Humidity sensing elements based on cerium doped titania-silica thin films prepared via a sol–gel method

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ABSTRACT

This paper presents the studies of the characteristics and parameters of thin film humidity sensing elements, obtained by the deposition of Ti-Si-oxide films in the presence of a Ce-dopant via a sol–gel method using titanium (IV) n-butoxide and polydimethylsiloxane as basic precursors. The proportion between these precursors predetermines the mechanism of polymerization and subsequent gel-formation. As a result, this affects the structure and porosity of the obtained films after their sintering and also their response to humidity. The electrical characteristics of the respective samples were examined by an impedance analyzer. The sintered oxide films were observed by scanning electron microscopy, energy dispersive X-ray spectroscopy, and X-ray diffraction analysis. The sensing elements obtained are distinguished for their high response to humidity and the variation in their resistance reaches up to four orders within the range of 15–93% relative humidity at 20 Hz and 25 °C.

1. Introduction

Humidity sensors are widely used in various fields, including the production of household equipment and the automobile industry, for storage of agricultural products and food, in medicine, and in general in controlling the parameters of the surrounding environment. One of the directions in their development is the use and improvement of ceramic and thin film humidity sensing elements. The sol–gel technology is being increasingly used for their preparation and it allows the production of nanostructured films employing inexpensive equipment. In relation to the wide use of humidity measurement equipment and their continuous improvement there is a growing interest in discovering new materials for making these sensors.

One of the most widely investigated materials for preparation of ceramic humidity sensing elements is modified TiO_2 [1–12]. This oxide is also studied for gas sensors [13] and electronic components [14–16].

Another material of great importance for preparation of such elements is SiO_2, which is also known as the most widely spread oxide on Earth. This oxide is largely used for Metal-Oxide-Semiconductor (MOS) electronic elements and equipment [17,18]. The capabilities of silicon oxide films deposited on humidity sensors are widely investigated, as well [19–31]. In the majority of the papers mentioned, the authors preferred to use tetraethylorthosilicate (TEOS) as SiO_2 precursor. Besides the similar precursor compositions used, the authors investigated the impact of various additives of organic [20–22], or inorganic [23–26] origin and combinations of them [27–30]. The application of Si-providers, alternative to TEOS has a great potential for the synthesis of surface films, as demonstrated by Frignani et al. [31]. Furthermore, the addition of Si-alkoxides with different organic moieties, such as polydimethylsiloxane [32–38] results in obtaining porous structures.

As catalysts in sol–gel method for producing surface films, hydrochloric acid HCl or nitric acid H_2NO_3 are very frequently used. These hydrolysis catalysts can be successfully replaced by adding cerium nitrates to the sol and the beneficial effect of cerium addition to both TiO_2 and SiO_2 with respect to their properties as humidity sensing elements was shown in previous works [6,9,26,29]. Recently, the interest in the lanthanides, and especially in Cerium has increased [39], because it has been found that these elements are economically competitive [40], and especially cerium is as plentiful as copper [41]. Furthermore, it is established that these elements possess a low toxicity and their ingestion or inhalation is not considered harmful to health [42,43]. The

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

Abbreviations of the samples	TBOT:PDTS (ml:ml)
T2P8	2:8
T4P8	4:6
T6P4	6:4
T8P2	8:2
REF_T	10:0
REF_P	0:10

beneficial effect on the gel-formation processes, reported by Suegama et al. [44], combined with the improvement of the sensors' characteristics [6,9,26,29] give grounds to continue the investigations of Ce-doped Ti-Si-oxide thin films for humidity sensing.

In this sense, this paper presents investigations of the electrical, morphological and structural features of sol–gel deposited Ce-doped titania-silica thin film humidity sensor elements. Titanium (IV) n-butoxide (TBOT) and polydimethylsiloxane, trymetylsiloxy-terminated (PDTS) were used as basic precursors, whereas diammonium hexanitrocerate (CAN6) served as both acidic hydrolysis catalyst and Ce-dopant. The impact of the proportion between the basic precursors (TBOT and PDTS) in the presence of Ce-dopant on the properties of the humidity sensing elements obtained by the sol–gel method and sintered at 400 °C has been studied.

2. Experimental

2.1. Sample preparation

The preparation of the investigated samples was divided into two main stages: preparation of the sol–gel systems and film deposition.

2.1.1. Sol–gel systems preparation

The compositions of the respective solutions were prepared by subsequent additions of portions of the respective basic precursors in six test tubes, in the proportions given in Table 1. The source of titanium for the solutions, without the reference solution REF_P, was TBOT, produced by Alfa Aesar – Karlsruhe (Germany). The silicon was added to the solutions, without to the reference solution REF_T, in the form of PDTS, with 2000 molecular weight from the same manufacturer.

These precursor mixtures were prepared by multiple additions of 2 ml portions, thus obtaining different volume proportions, as it is given in Table 1.

Afterwards 10 ml of freshly prepared solution of CAN6, produced by FLUKA-Chemika (Switzerland) in isobutanol was added to each test-tube. The solution was prepared by addition of this cerium compound until saturation at room temperature.

The obtained mixtures were left at 85 °C for 3 h. Their preparation was finished after storage at 5 °C for a week.

2.1.2. Film deposition

Prior to the deposition process, the respective solutions were heated for 30 min at 85 °C. The deposition was performed on alumina substrates with symmetric interdigitated silver-palladium electrodes, preliminary cleaned by exposition to Acetone:Ether – 1:1 mixture. The films were deposited at 85 °C by triple dipping of the substrates – 30 min exposition to the respective solutions, and 30 min drying at the same temperature.

After depositing the gel the samples were sintered at 400 °C for 30 min. Schematic view and photography of some studied samples are shown in Fig. 1. The width of the electrodes and the spaces between them is 0.5 mm.

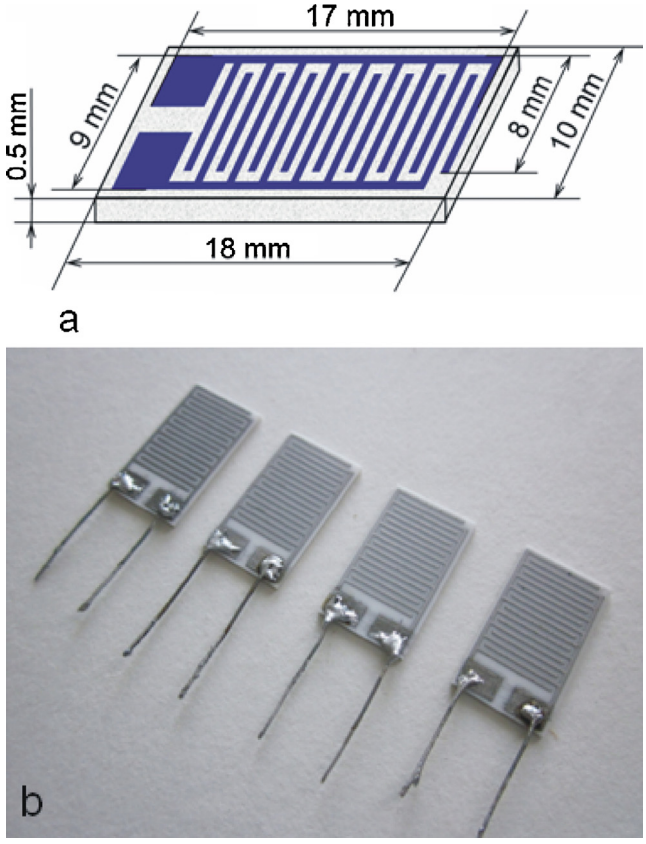

Fig. 1. Schematic view (a) and photography (b) of some studied samples.

In addition, after the deposition on ceramic substrates, the gels were put in Petri-vessels for turning them into powder substances, sintered at the same temperature as the samples in order to make a XRD analysis subsequently.

2.2. Measurements and characterizations

2.2.1. Electrical measurements

The measurements of the electrical resistance R, capacitance C, impedance Z and phase θ of the obtained samples were taken by Precision Impedance Analyzer 6505P product of Wayne Kerr Electronics Ltd., at a frequency of 20 Hz and 500 mV of the excitation signal. The samples were put inside a humidity/temperature conditioning chamber VAPORTRON H-100BL, manufactured by BUCK RESEARCH INSTRUMENTS L.L.C., which provides conditioning of accurately controlled humidity in the range of 15–93% with maximal deviation of up to ±1.5% of relative humidity at given temperature.

2.2.2. Surface morphology and structural characterization

Morphological observations were taken by scanning electron microscopy (SEM) by TESCAN, SEM/FIB LYRA I XMU working at 30 kV. The map data analyses were carry out by energy dispersion spectroscopy (EDX) using Quantax 200 of BRUKER detector. Structural and compositional 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. All the spectra were acquired within the angle range from $\theta = 10°$ to $\theta = 100°$, at scan rate $2\theta/\tau = 0.04°/s$, and 1 s exposition per step.