Development of sensing elements for humidity by deposition of Ce-doped SiO_2 films prepared via a sol-gel method

Z. Nenova, S. Kozhukharov, T. Nenov, N. Nedev, M. Machkova

Abstract: *Humidity sensing elements were elaborated by deposition of Ce-doped SiO_2 films on alumina ceramic substrates with silver-palladium electrodes, via sol-gel method. The obtained specimens were sintered either at 400°C, or at 800°C, in order to create durable and reliable sensors and to evaluate the impact of the thermal treatment on the features of the obtained sensing elements. The superficial morphology, and composition of the films, and the electrical characteristics of the respective sensors were investigated. The impedance spectra of the sensing elements were fitted to appropriate equivalent electric circuit. The results obtained show that both of the addition $Ce(NO_3)_3$ and the sintering at 400°C lead to remarkable improvement of the sensitivity of the SiO_2-based sensing elements.*

Key words: humidity, sensing elements, sol-gel method, silica, cerium-dopant

INTRODUCTION

The humidity affects various areas of human activities, revealing generally detrimental effect, causing corrosion [1, 2], or being appropriated medium for development of various microorganisms. They are able to deteriorate various nutrition [3] and pharmaceutical [4] products, or even to be harmful for the human health [5]. At last, the high levels of humidity favour destruction, so of electrical conductors [6], so of insulation materials [7], affecting branches as high voltage energy supply [8], microelectronics and communications [6]. Obviously, it damages the composition, structure and the properties of various hygroscopic materials, causing remarkable economic loses when such materials are employed.

Nevertheless, the humidity possesses beneficial effects in some cases, such as greenhouse agricultural [9, 10] and antibiotics production [11]. Some branches of chemical industry, as: the catalyzed steam-reforming of hydrocarbons [12], and storage of explosive materials [13, 14], also require elevated levels of humidity.

All of the mentioned above branches of human activity predetermine the tremendous importance of the humidity measurement and control. Various metallic oxides are available for preparation of sensor elements, as for instance: TiO_2, ZnO, Fe_2O_3, Al_2O_3, SnO_2, etc. [15].

In that means, the potentials for implementation of SiO_2 in humidity sensors are not investigated enough. Furthermore, the Si and Ce oxides are enough abundant in the nature [16, 17], and they are neither toxic, nor environmentally harmful [17, 18].

The aim of the present research work is to develop and assess the potential ability of Ce-doped silica films, obtained by sol-gel route for humidity sensing elements.

EXPERIMENTAL

2.1. Sample preparation

Initially, 60 ml. tetraethoxysilane (TEOS), produced by „Alfa Aesar"- Karlsruhe (Germany), were added to 40 ml. n-Buthanol (n-BuOH), preliminary heated up to 70°C in a covered beaker, by dripping for 30 minutes, while stirring by magnetic stirrer. Afterwards, 1.0056g cerous nitrate $Ce(NO_3)_3$ „Alfa Aesar"- Karlsruhe (Germany) and 2ml. concentrated HNO_3 was added to the obtained solution. It was left at 70 °C for 1 hour, while being stirred, and at last, cooled at room temperature for 20 min. The sol-gel system obtained by this way was left for one day at 5 °C, in covered vessel, in order to avoid whatever evaporation of its ingredients, during the polymerization process.

The film was deposited via a dip-coating procedure by triple dipping of alumina substrates with preliminary deposited silver-palladium electrodes. The procedure was performed by subsequent dipping of the substrates in the solution for 30 minutes at 70ºC, and drying at the same temperature. Finally, the samples were sintered for 30 min. either

at 400 ºC, or at 800 ºC. The samples are marked as: S_400 or S_800, respectively. The shape and size of the investigated sensors are identical to those of the used in previous works [19, 20].

2.2. Measurements

- Electrical characteristics and parameters: The measurement of the impedance of the obtained samples was performed by Precision Impedance Analyzer 6505P product of Wayne Kerr Electronics Ltd, at 1 kHz frequency and 500 mV signal amplitude. The influence of frequency was investigated in the range of 100 Hz to 1 MHz. The samples were inside "VAPORTRON H-100BL" humidity conditioning chamber, produced by BUCK RESEARCH INSTRUMENTS L.L.C., with accurate controlled humidity in a range of 15 to 95% with maximal deviation of up to 1.5% of relative humidity.

- Surface morphology Observations: They were performed by Scanning Electron Microscopy (SEM), in order to determine the morphological features of the respective surface films. They were done by Scanning Electron Microscope TESCAN, SEM/FIB LYRA I XMU.

RESULTS AND DISCUSSIONS

Electrical measurements

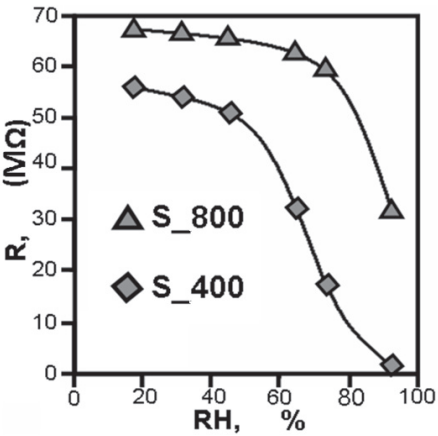

Fig. 1. Characteristics $R = f(RH)$ of samples S_400 and S_800 at a temperature of 25°C

The performance of the obtained humidity sensors was determined by impedance measurements, under controlled humidity and 25°C. Figure 1 presents the characteristics of samples S_400 and S_800, where R is their electric resistance and RH is relative humidity.

The sample S_400, sintered at temperature 400 ºC, reveal higher sensitivity of resistance, SR, to changes in relative humidity, RH, compared to the sample S_800, sintered at 800 ºC temperature. Sample S_400 has the highest sensitivity of about 1.7 MΩ / %RH in 40 - 82%RH range, and in the range of 15 - 40%RH and over 82%RH. This sensitivity is lower, being around 220 kΩ/%RH. Sample S_800 has relatively lower sensitivity compared to S_400. It is around150 kΩ/%RH in 15 - 80%RH range and there is also a sharp increase of its sensitivity at above 80%RH, reaching 1.8 MΩ/%RH.

The resistance of a sensor element decreases with an increase in the relative humidity due to the physical adsorption and condensation of water in the intercrystalline areas. During the initial stage of adsorption, there is chemical adsorption of water molecules on the surface of crystals. The active role in this process belongs to metallic atoms. They interact with the water molecules to form hydroxyl groups M-OH. In this way, the surface of crystals is covered by a monolayer of water molecules.

After the formation of the first chemically adsorbed layer, there is physical adsorption of water molecules on it. The physically adsorbed layer is more weakly connected to the surface of crystals. The process of condensation of water vapour depends on the size and distribution of the intercrystalline areas in the thin film. The filling of areas with smaller size starts at lower humidity, while the filling of areas with larger size happens at higher humidity levels.

Based on the structure of the samples from the SEM images in Fig. 4 (next section) and investigations of the electrical properties (Figure 1), it can be concluded that an increase in the sintering temperature increases the size of the intercrystalline areas, lowers the sensitivity of the elements at lower humidity, and vice versa. This correlation between intercrystalline area size and sensitivities corresponds to the water vapour adsorption mechanism described above.

Therefore, the samples sintered at 400°C, possess better properties, compared to those sintered at 800°C. On the basis of the characteristics obtained it can be concluded that the samples S_400 can be used as sensing elements in the range 15 - 93%RH, and samples S_800 are more appropriate as key-elements for humidity sensing.

The frequency-related characteristics of the samples were evaluated, as well. The characteristics z(f) and θ(f) for the samples S_400 at RH = 93% and a temperature of 25°C are shown in Figure 2.

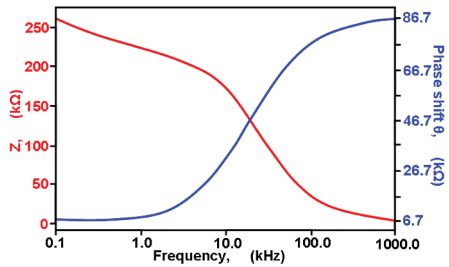

Fig. 2. Frequency characteristics of sample S_400
at *RH* = 97% and a temperature of 25°C

An increase in frequency leads to decrease in the impedance z, and increase of the phase angle of the sensor elements S_400.

Based on the parameters z(f) and θ(f), the dependence of reactive resistance on active resistance for sample S_400 at relative humidity of 97% and a temperature of 25°C has been obtained, as is shown in Figure 3. An equivalent electric circuit for the sensor element has also been determined. It is composed by parallel connection between resistor and capacitor.

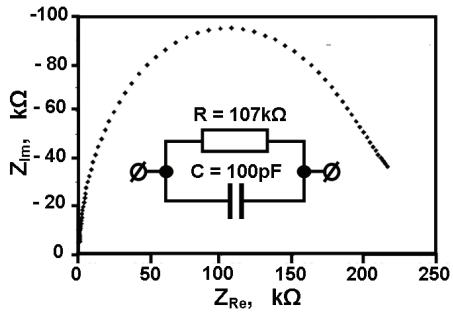

Fig.3. Dependence of reactive resistance on active resistance for sample S_400 at relative humidity of 97% and a temperature of 25°C

Scanning Electronic Microscopy

Figure 4 presents low magnification SEM–images of the surface of prepared samples S_400 and S_800. These images show that the sintering temperature affects the size of

the crystals and intercrystalline areas. It can be concluded that after sintering at 800°C, the respective crystals and intercrystalline areas have larger sizes than the sintered at 400 °C.

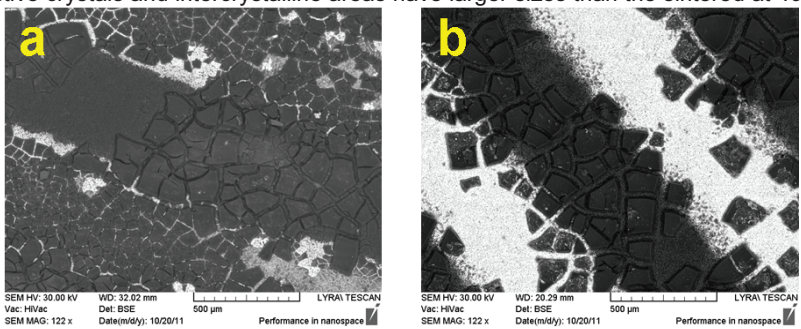

Fig. 4. SEM – images of samples: (a) S_400; (b) S_800

CONCLUSIONS

Humidity sensing elements were elaborated by deposition of SiO_2 films with additions of Ce-compounds, through sol-gel method, and posterior sintering. As a result, the impact both of the Ce-addition and the sintering temperature on the features and the behavior of the obtained sensors was evaluated. The results resemble that the increment of the sintering temperature from 400°C to 800°C increases the size of the crystals and intercrystalline areas, affecting significantly the sensor's electrical parameters.

Among the sensors studied, the best humidity sensing properties belong to the samples treated for 30 minutes in solution with $Ce(NO_3)_3$ and sintered at 400 **ºC**, whereas the samples, sintered at 800 °C, can be used as key-elements.

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The paper is reviewed.