

## Characterization of humidity sensors with Ce-modified silica films prepared via sol-gel method

Z.P.Nenova<sup>1\*</sup>, S.V.Kozhukharov<sup>2</sup>, T.G.Nenov<sup>1</sup>, N.D.Nedev<sup>1</sup>, M.S.Machkova<sup>2</sup>

<sup>1</sup> Technical University of Gabrovo, 4 H.Dimitar Str., 5300 Gabrovo (Bulgaria)

<sup>2</sup> University of Chemical Technology and Metallurgy, 8 Kliment Ohridski Blvd., 1756 Sofia (Bulgaria)

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Silica films modified by Ce-compounds have been deposited on corundum substrates with silver-palladium electrodes. The depositions have been performed through dip-coating procedure of the substrates into sol-gel systems composed by tetraethyl orthosilicate (TEOS) and cerous nitrate ( $\text{Ce}(\text{NO}_3)_3$ ) as Si and Ce providers, respectively. After posterior sintering of the obtained sensors at 400°C and 800°C, their electrical properties have been characterized by means of precision impedance analyzer, in a humidity conditioning chamber. The respective superficial films have been observed by scanning electron microscopy (SEM). As a result, the relation between the surface morphology and electrical characteristics, as well as the properties of the investigated samples and their performance as humidity sensing elements have been determined.

**Key words:** humidity sensors, sol-gel method, silica, cerium-dopant, impedance spectroscopy

### INTRODUCTION

Humidity sensors are widely used in industry, agriculture, medicine, for storage and transportation of various products and raw materials, pieces of art, etc. Various types of humidity sensors are known. Ceramic and film elements based on metal oxide materials, such as:  $\text{Al}_2\text{O}_3$ ,  $\text{TiO}_2$ ,  $\text{SiO}_2$ ,  $\text{SnO}_2$ , and  $\text{ZnO}$  also belong to this group. They possess numerous advantages, as a comparatively easy manner of manufacturing, stability in aggressive media, relatively low cost, etc. [1, 2].

One of the directions in the preparation of thin film humidity sensing elements based on oxide materials is by a sol-gel method [3, 4]. This method makes possible the synthesis of nanostructured ceramic films. The specific features of nanostructured materials should lead to humidity sensing elements with improved parameters and characteristics.

Humidity sensing elements based on  $\text{SiO}_2$  are less studied. Their application to the preparation of humidity sensing elements with nanostructure is promising, since it enables their integration with other elements in the semi-conductor technology. Previous studies [5-7] have investigated  $\text{SiO}_2$ -based sensor elements obtained by the sol-gel method, using tetraethyl orthosilicate (TEOS) as a precursor. The influence of humidity on sol-gel derived  $\text{SiO}_2$ -based films, doped with  $\text{Fe}_2\text{O}_3$  has also been

studied [8, 9]. Cerium as an additive ingredient for metal oxide humidity sensors excels other frequently used dopants, because it corresponds to the environmental regulations which impose severe restrictions on the use of heavy metals [10, 11].

This paper proposes thin film humidity sensing elements based on silica films, doped with Ce-compound and prepared by a sol-gel method. The characteristics and parameters of the sensing elements obtained at different sintering temperatures have been investigated. Their impedance characteristics and equivalent electric circuits have also been determined.

### EXPERIMENTAL

#### *Sol-gel procedure*

The initial sol was composed of 60 ml of TEOS, „Alfa Aesar“- Karlsruhe (Germany), and 40 ml of n-Butanol (n-BuOH), preliminary heated up to 70°C in a covered beaker. The hydrolysis-polymerization process was induced by the addition of 2 ml of saturated solution (at room temperature) of  $\text{Ce}(\text{NO}_3)_3$  „Alfa Aesar“- Karlsruhe (Germany) in concentrated  $\text{HNO}_3$ . The sol-gel process was performed at 70°C for 1 hour, on magnetic stirrer. Finally, it was cooled at room temperature for 20 min. The sol-gel system obtained in this way was left for one day at 5°C, in a covered vessel, in order to avoid any evaporation of its ingredients, during the polymerization process.

\* To whom all correspondence should be sent:  
E-mail: z\_nenova@yahoo.com

### Film deposition

The film was deposited by a dip-coating procedure by triple dipping of alumina substrates with Ag-Pd electrodes. The sizes of the substrates are 18x10x0.5mm, identical to those, used in previous investigations [12, 13]. The procedure was performed by subsequent dipping of the substrates in the solution for 30 minutes at 70°C, and drying at the same temperature. Finally, the samples were sintered for 30 min, either at 400°C, or at 800°C. The samples are marked as: S\_400 or S\_800, respectively. Photograph of a sample, prepared as a humidity sensor, is shown in Fig.1.

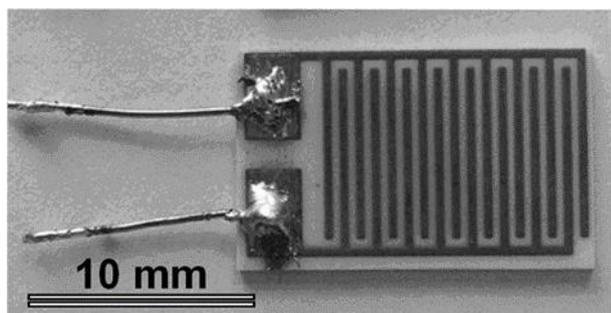


Fig. 1. Photograph of an investigated sample

### Measurements

- *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 taken by scanning electron microscope TESCAN, SEM/FIB LYRA I XMU.

- *Electrical characteristics and parameters:* The measurement of the impedance of the obtained samples was taken by Precision Impedance Analyzer 6505P, produced by Wayne Kerr Electronics Ltd, at 500 mV of the excitation signal. The influence of frequency was investigated in the range from 20Hz to 1MHz. The investigated samples were placed inside a humidity generator VAPORTRON H-100BL, produced by BUCK RESEARCH INSTRUMENTS L.L.C., which provides conditioning of accurately controlled humidity with maximal deviation of up to  $\pm 1.5\%$  of relative humidity (RH). The range of relative humidity used is from 30 to 93%.

## RESULTS AND DISCUSSION

### Scanning electron microscopy

Fig.2 presents low magnification SEM-images of the surface of prepared samples S\_400 and S\_800, sintered at 400°C or 800°C, respectively. These images show that the sintering temperature

affects the size of the deposited aggregates of primary crystals and the areas between them. The size of these aggregates and areas between them increases with the rise of sintering temperature.

Quartz, tridymite and cristobalite are the three basic crystalline phases of pure SiO<sub>2</sub>. According to [14], the phase transition of silica from quartz to tridymite takes place at 870°C, whereas transformation to cristobalite proceeds at a temperature of 1470°C. Both sintering temperatures used for the present research are lower than these temperatures. Consequently, there are no phase transitions of these types.

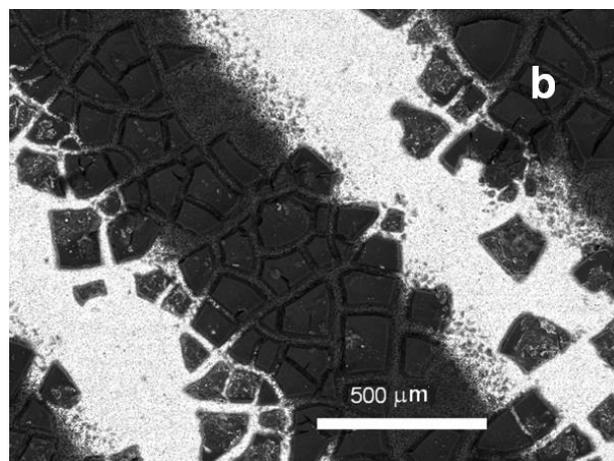
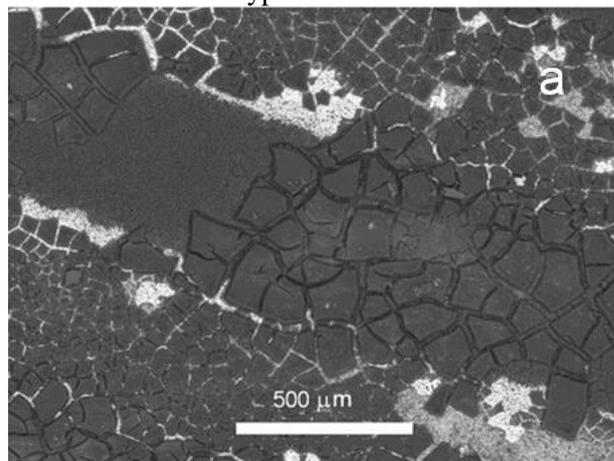


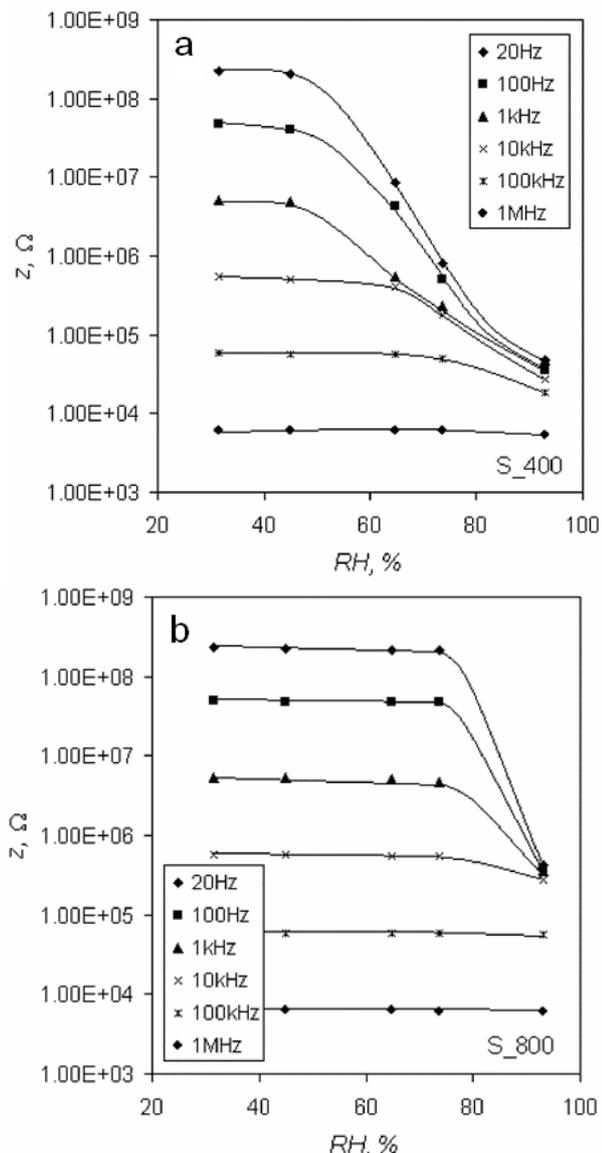
Fig.2. SEM – images of samples: (a) S\_400; (b) S\_800

### Electrical measurements

#### RH-impedance characteristics

The most widely used measure for humidity determination is relative humidity (RH). It can be defined as the percentage ratio of the measured partial pressure of water vapours to the saturated water vapours for given temperature [2]. The performance of the obtained humidity sensors was determined by impedance measurements at various humidity levels and at 25°C. Fig.3 presents the characteristics of samples S\_400 and S\_800 at

different frequencies in the range from 20Hz to 1MHz and at a temperature of 25°C, where  $z$  is the impedance and RH is the relative humidity.



**Fig. 3.** Characteristics of samples: (a) S\_400 and (b) S\_800 at a temperature of 25°C

The figures are similar for both samples – when frequency increases, electric resistance decreases but at the same time, to our regret, sensitivity to humidity also decreases for both samples.

Sample S\_400, sintered at a temperature of 400°C, exhibits higher sensitivity of impedance to relative humidity in the range of 40-93 %RH. The maximal sensitivity value is 7.0 MΩ/%RH, 1.4 MΩ/%RH and 166.5 kΩ/%RH for 20Hz, 100Hz and 1kHz, respectively. Sample S\_800 has exhibited practically a constant value of the impedance for the 30-75%RH range, while at RH higher than 75%, its impedance abruptly drops, accompanied by enhancing its sensitivity, reaching

10.8 MΩ/%RH, 2.4 MΩ/%RH and 222.9kΩ/%RH for 20Hz, 100Hz and 1kHz, respectively. Thus, its characteristics are of switching type.

The impedance of the samples decreases with an increase in the relative humidity due to the chemical and physical adsorption and condensation of water in the areas between the deposited aggregates. In the initial stage of adsorption there is chemical adsorption of water molecules on the surface of crystals [2]. 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 a second stage of physical adsorption of water molecules on it. During this stage, physical adsorption of water molecules proceeds on the formed layer [2]. The physically adsorbed layer is more weakly bonded to the surface of crystals, only by intermolecular interactions. The process of condensation of water vapour depends on the size and distribution of the areas between the deposited aggregates in the thin film. The filling of areas of smaller size starts at lower humidity, while the filling of areas of larger size happens at higher humidity levels.

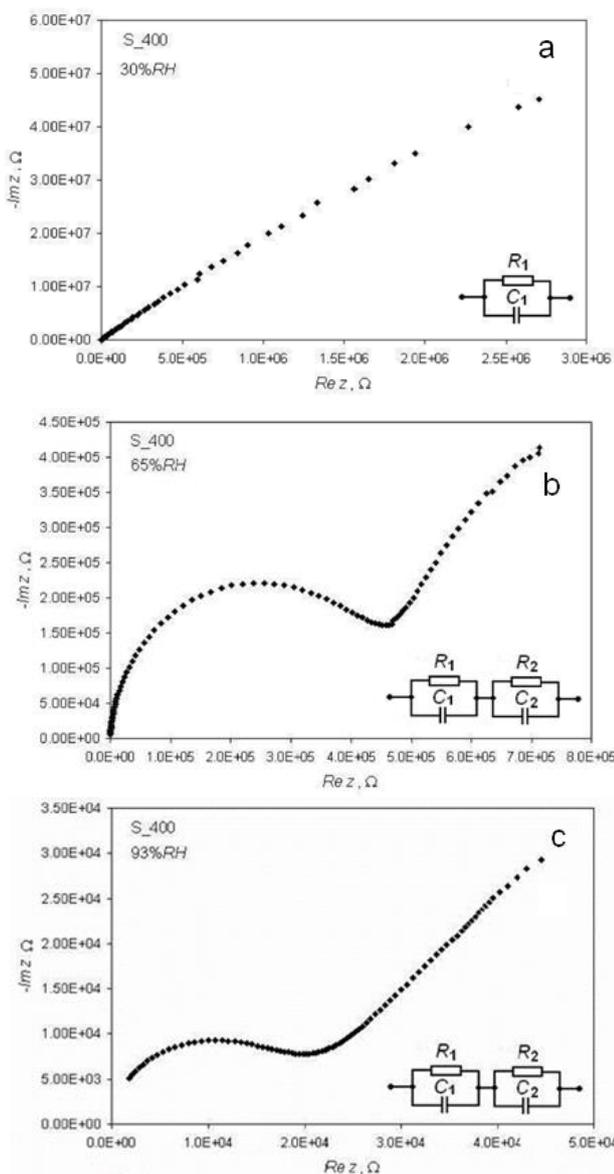
Based on the topographies of the samples from the SEM images in Fig.2 and the investigations on their electrical properties (Fig.3), it can be concluded that an increase in the sintering temperature causes enlargement of the size of the areas between the deposited aggregates, lowers the sensitivity of the elements at lower humidity, and vice versa. This correlation of the size of areas between deposited aggregates with the sensitivities corresponds to the water vapour adsorption mechanism described above.

#### Impedance spectra

The frequency characteristics  $z(f)$  and  $\theta(f)$  of the samples have also been studied, where  $z$  is the impedance, and  $\theta$  is the angle, which change with the change in frequency. Based on these characteristics, the Nyquist plots of reactive resistances on active resistances for samples S\_400 and S\_800 at various RH and a temperature of 25°C have been obtained. Impedance spectra and equivalent electric circuits for the sensor elements are shown in Fig.4 and Fig.5.

In the absence of humidity, these plots are close to a straight line which corresponds to Nyquist plots of the initial films [15]. At lower levels of humidity (in the case of 30% - Fig.4a and Fig.5a)

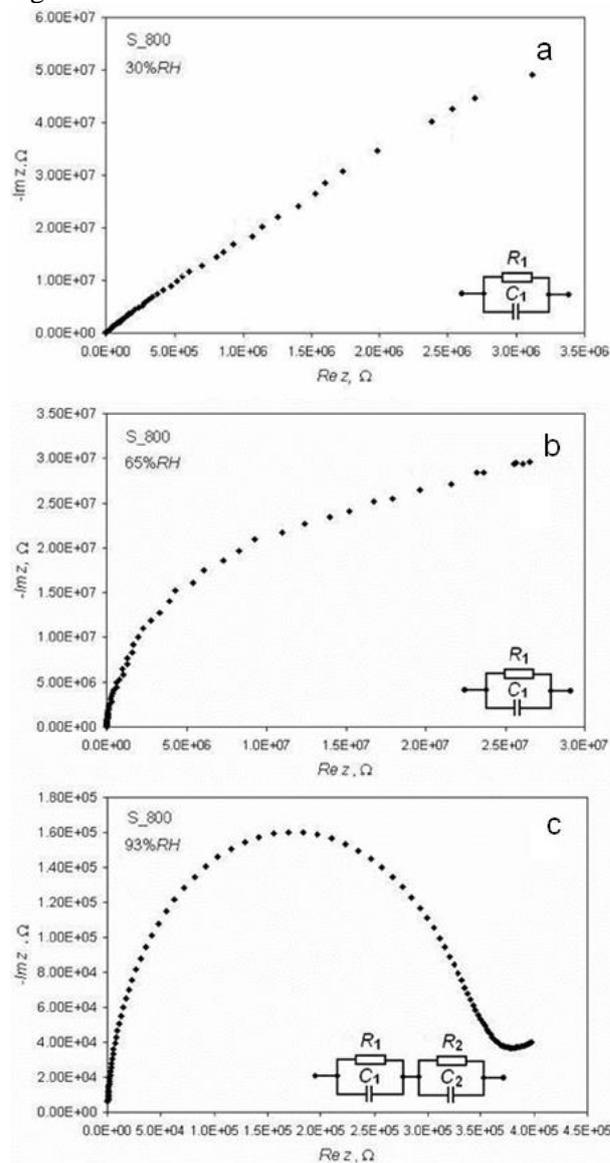
Nyquist plots are arcs from semicircles of very large radii, and their equivalent circuit consists of a resistance  $R_1$  and capacitance  $C_1$  connected in parallel.



**Fig.4.** Nyquist plots and equivalent electric circuits for sample S\_400 at a temperature of 25°C and at relative humidity of: (a) 30%; (b) 65 % and (c) 93%

This type of impedance spectra can be explained by the prevailing type of electron conduction through the base material and the adsorbed water in the stage of chemical adsorption [15]. With an increasing RH (Fig.5b – 65%RH for S\_800) the chemisorption enhancement and leakage current increment lead to growing the curvature of the arc and it gradually approximates a complete semicircle. For sample S\_400 this transition occurs at humidity lower than 65%. Simultaneously, a decrement in the sample impedance is observed

related to the enhancement of this conduction. For sample S\_400 at 65%RH (Fig.4b), the equivalent circuit is composed of two groups of resistance and capacitance with parallel connection. The second group of  $R_2C_2$  is explained by the appearance of ionic type of conduction, as a consequence of the presence of physical adsorption as well. Therefore, the entire conduction mechanism is a combined action of both electron conduction and ionic conduction [15, 16]. In the Nyquist plots this is shown with the initiation of a second semicircle with a very large radius. For sample S\_800 this type of equivalent circuit and conduction is observed at higher level of humidity of 93% (Fig.5c) where the electron conduction still remains significant.



**Fig.5.** Nyquist plots and equivalent electric circuits for sample S\_800 at a temperature of 25°C and at relative humidity of: (a) 30%; (b) 65 % and (c) 93%

For sample S-400 at higher level of relative humidity of 93% (Fig.4c) the ionic conduction is higher compared to electron conduction, which is illustrated by extending the predominance of the second semicircle which turns into a nearly straight line. The appearance of ionic conduction results in sharp decrease in sample impedance. For sample S\_400 this happens at lower levels of humidity (at humidity levels below 65%RH – Fig.4b). This correlates also with the lower impedances of this sample at lower levels of humidity (Fig.3). On the basis of the impedance characteristics and spectra, it can be concluded that the samples sintered at 400°C, possess better sensing properties to humidity, compared to those sintered at 800°C. Therefore, it can be concluded that samples S\_400 can be used as humidity sensing elements within the range from 45 to 93%RH, and samples S\_800 can be used as trigger switching elements for humidity sensing.

### CONCLUSION

Humidity sensing elements have been obtained by deposition of SiO<sub>2</sub> films with the addition of Ce-compound by a sol-gel method. Among the samples investigated in the present work, increasing the sintering temperature from 400°C to 800°C increases the size of the deposited aggregates of primary crystals and the areas between them, leading to changes in the samples' electrical characteristics and parameters. Regarding the application of the obtained samples as humidity sensing elements, the best humidity sensing properties belong to the samples treated for 30 minutes in solution with Ce(NO<sub>3</sub>)<sub>3</sub> and sintered at 400°C. The samples, sintered at 800°C, can be used as trigger switching elements for humidity sensing.

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## ОХАРАКТЕРИЗИРАНЕ НА СЕНЗОРИ ЗА ВЛАЖНОСТ С Се-ЛЕГИРАНИ СИЛИЦИЕВО-ДИОКСИДНИ СЛОЕВЕ, ИЗГОТВЕНИ ПО ЗОЛ-ГЕЛ МЕТОД

З. П. Ненова<sup>1</sup>, С. В. Кожухаров<sup>2</sup>, Т. Г. Ненов<sup>1</sup>, Н. Д. Недев<sup>1</sup>, М. С. Мачкова<sup>2</sup>

<sup>1</sup> Технически университет – Габрово, ул. "Хаджи Димитър" 4, 5300 Габрово (България)

<sup>2</sup> Химикотехнологичен и металургичен университет, бул. "Климент Охридски" 8, 1756 София (България)

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(Резюме)

Получени са тънки слоеве от силициев диоксид, легиран с Се, върху подложки от двуалуминиев триоксид с предварително нанесени сребърно-паладиеви електроди. Отлагането на слоевете е извършено чрез метода на потапяне на подложките в зол-гел система от тетраетил ортосиликат (TEOS) и цериев нитрат ( $\text{Ce}(\text{NO}_3)_3$ ). След последващо синтероване на получените образци при 400°C и 800°C, са изследвани техните електрическите свойства с помощта на прецизен импедансен анализатор като те са поставяни в калибрираща камера за влажност. Получените слоеве са наблюдавани чрез сканиращ електронен микроскоп (SEM). Като резултат е определена връзката между структурната морфология и електрическите характеристики на изследваните образци, както и техните свойства и възможности за използване като чувствителни елементи за влажност.