Sintering temperature effect on the characteristics of Ce-doped Ti-Si-Zr-O surface layers of humidity sensing elements

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Abstract: *The monitoring and control of the ambient medium parameters demand appropriate and reliable sensors. The present work presents the development of humidity sensing elements based on Ce-doped Ti-Si-Zr-O surface layers. Since the sensor performance is entirely predetermined by the compositional, morphological and structural features of the composing materials, their dependence of the sintering temperature was evaluated by Scanning Electron Microscopy (SEM), and X-Ray Diffractometry (XRD) for morphological structural characterization. The dependency of these results and the impedance characteristics for the respective sensing elements was analyzed.*

Key words**:** *Humidity sensing elements, Ce-doped Ti-Si-Zr-O surface layers, SEM, EDX, electrical response analysis*

INTRODUCTION

The humidity affects almost all the fields of the human activities. The monitoring and control of humidity as parameter of different technological processes, in the agricultural plant growth, storage of production and in providing comfortable living environment require the development of efficient and reliable measurement systems with appropriate sensors.

Titanium dioxide is a very suitable material for various applications [1-3], including sensor element production [4, 5]. The experience has shown that the properties of TiO_2 can be easy modified by various dopants such as *Bi, Na, V* [4-6], *Zn* [7], etc. In this context, the beneficial effect of the cerium compounds addition regarding the resulting sensor characteristics has been evinced [8, 9]. Furthermore, a positive influence of cerium doping on SiO_2–based humidity sensors [10, 11] has been established. The mesoporous organically modified silicates have shown a great potential for elaboration of humidity and gas sensors and detectors, due to their considerable adsorption capability [12, 13]. All the advantages of the cerium, titanium and silicon oxides were successfully combined in recent research work [14]. Besides cerium, other lanthanides are proposed as glass-ceramic materials for environmental monitoring sensors [15].

On the other hand, the zirconium oxide stabilized by yttrium oxide is the basic material of entire class of engine exhaust gas sensors, known as “lambda sensors” [16]. In addition, Petkov et al. [17] have examined the suitability of the ZrO_2 - Ce_2O_3 - Y_2O_3 system as electrode materials for electrochemical synthesis of active chlorine via electrolysis. Besides the *Ce-Zr-O*, the ZrO_2 – SiO_2 system based ceramic materials encounter various applications, such as catalysts for combustion of volatile organic compounds [18], ceramic pigments [19-21], optical devices [22], etc. Especially, the applicability of *Ce-Zr-O* based materials for elaboration of gas sensors and detectors is evaluated by Arsent’ev et al. [23]. It is also worth to mention, that the structural and morphological characteristics, predetermined by the method and the conditions of their preparation, are so important to the properties and performance of the sensing elements produced, as their chemical composition [24, 25].

All these facts have motivated the investigations of the sintering temperature effect on the morphology and structure of the resulting *Ce-doped Ti-Si-Zr-O* surface layers, prepared via a sol-gel method, and on the electrical characteristics and performance of the respective humidity sensor elements, presented in this work.

EXPERIMENTAL

- Precursor solution preparation procedures - Titanium (IV) n-butoxide (TBOT) - 98%, Tetraethoxysilane (TEOS) - 99+ % and Zirconium *n*-butoxide (ZBO) - 80% *w/w* in 1-butanol, all products of “Alfa Aesar”-Germany were mixed in proportion 1 : 1 : 1 in volume parts. The volume of the ZBO addition was re-calculated, considering its lower

concentration.

In order to initiate the precursor hydrolysis, a saturated solution of diammonium hexanitrocerate (FLUKA-Chemika (Switzerland)) in isobutanol, was added to the initial precursor mixture, described above, again in proportion 1:1 in volume parts. Afterwards, precursor hydrolysis was performed at 85°C for 3 hours in covered vessel. Finally, the resulting sol was left in a refrigerator (5°C) for a week, for ensuring of gradual polymerization of the hydrolyzed precursors and homogenization.

Deposition procedure – It was performed on preliminary cleaned alumina substrates with interdigitated silver palladium electrodes and size dimensions, identical to the described in our previous works [12, 16]. The substrates were dip-coated by triple immersion in the above described solutions at 85ºC. Each cycle comprised 30 minutes of immersion, followed by 30 minutes of drying, in order to obtain higher level of uniformity and repeatability of the layer thickness. The resulting viscous sol-gel systems were put in Petri vessels and sintered at the same conditions as the specimens, as is described below. The obtained powders were further used for XRD analysis. The sol-gel coated substrates underwent final sintering at 400°C or 800°C, for 30 minutes.

Measurement and characterization procedures - The samples, prepared by the procedures described above, underwent electrical measurements of their resistance *R*, capacitance *C*, impedance *z* and phase θ 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 placed inside a humidity conditioning chamber VAPORTRON H-100BL, manufactured by BUCK RESEARCH INSTRUMENTS L.L.C., which provides conditioning of accurately controlled humidity with maximal deviation of up to ±1.5% of relative humidity. The *RH* levels used were in the range from 20% to 93%.

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 dispersion spectroscopy (EDX) using Energy Dispersion 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 and 800°C. The measurements were taken by Philips PW 1050, supported by CuKα - X-ray emitter within the angle range (2*θ)* from 8º to 90º with a step of 0.05º and exposition of 2 s per step.

RESULTS AND DISCUSSION

Electrical response characterization – Figure 1 represents the electrical response characteristics R = f(RH), C = f(RH), Z = f(RH) and Θ = f(RH) of the investigated specimens in accordance with *RH* variation at 20 Hz and 25°C.

One of the most important electrical response parameters is the relative ratio R_{max}/R_{min} of the electrical resistance, where R_{max} and R_{min} are the resistance values, related to the endpoints of the investigated *RH* range. In the case of sample TSZ_400, the electrical resistance *R* variation reaches about two orders of magnitude. For sample TSZ_800 this change is lower, but at the lowest *RH* levels its electrical resistance is by one order of magnitude lower compared to the sample, sintered at 400°C, which is important for the practical applications.

The relative variations of the capacitance C_{max}/C_{min} and the impedance z_{max}/z_{min} registered for the investigated samples are much lower than those of the resistance. Significant change is observed for the phase θ, which for TSZ_400 is from about 88° to 20°, whereas for TSZ_800 it is from about 82° to 38°.

Consequently, both the parameters *R* and θ can be considered as more informative regarding the detection of the *RH* variations, and they become more remarkable at *RH* levels over to 55%.

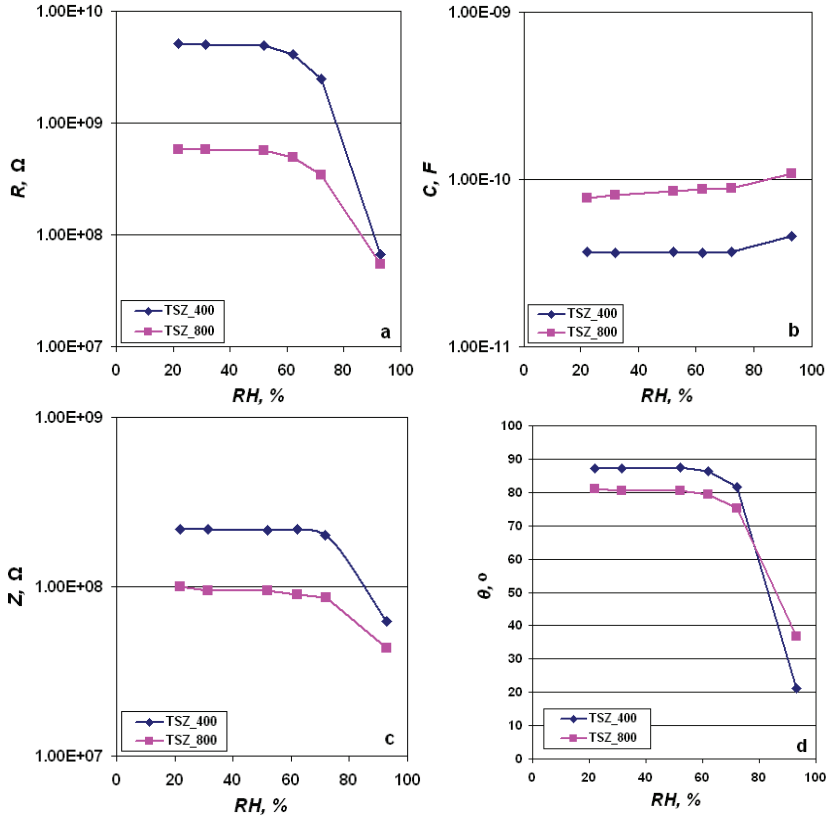

Fig. 1. Characteristics: a) R = f(RH), b) C = f(RH), c) Z = f(RH) and d) Θ = f(RH) of the investigated samples at 20 Hz and 25°C.

The sensitivity $S_R = \Delta R / \Delta RH$ was calculated for different segments of the R=f(RH) characteristic, where ΔR is the electrical resistance variation and ΔRH is the corresponding change of the relative humidity, registered for the respective segments. The maximal sensitivity $S_{R\,max}$ for sample TSZ_400 is about 160 MΩ/% *RH* and for sample TSZ_800 – about 15 M Ω/% *RH* in the range (60 - 70)% *RH.*

Surface layers morphology and structure – Figure *2a* and *b* shows SEM-images obtained for superficial topographies of both kinds of samples. For sample TSZ_400 clear aggregates of the deposited material, separated by channel-like spaces among them are observable. The specimen TSZ_800 possesses crystalline formations distinguishable at higher magnification rates (Fig. 2c).

The EDX maps (Fig. 3) confirm the presence of Ti, Si, Zr, Ce in the superficial layers of the sensing elements developed. The XRD analysis allows determining the impact of the sintering temperature on the structural features of the Ti-Si-Zr-Ce-O materials, composing the superficial layers deposited on the samples. The obtained XRD-patterns are shown in Fig 4.

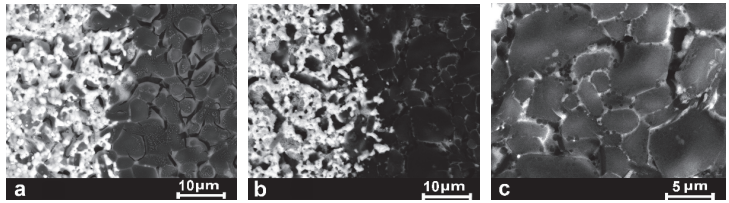

Fig. 2. SEM-images of the samples: a) TSZ_400, b) TSZ_800 with 5 kx and c) TSZ_800 with 10 kx magnification

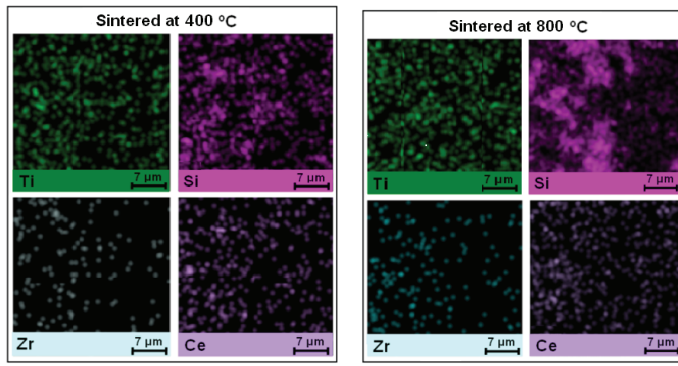

Fig. 3. EDX-images of the investigated samples

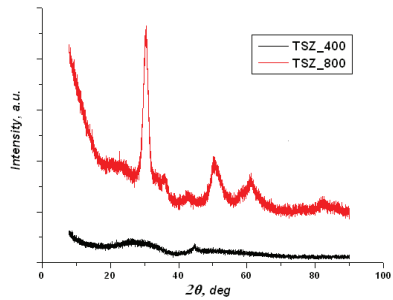

Fig. 4. XRD–patterns of the investigated surface layers materials

When sintering temperature of 400°C is used, the resulting structure is practically amorphous, whereas at 800°C of sintering, Srilankite phase with $ZrTiO_2$ composition is detected. The new compound formation of Srilankite crystal phase leads to a change in the resulting sensor properties, as it is shown in Fig. 1 as the positive effect is in a decrease of the resistance *R* at low humidity levels.

CONCLUSIONS

Humidity sensitive elements are elaborated via a sol-gel method, on the basis of TBOT, TEOS and ZBO at the presence of Ce-ions, and subsequent sintering at 400°C or 800°C.

The samples sintered at 400°C have amorphous structure of the superficial layer. The resistance R variation reaches about two orders of magnitude when the relative humidity changes from 20% to 93% at 20 Hz and 25°C.

The sintering at 800°C results in Srilankite phase formation, which causes changes in the superficial layer's properties. The sensitivity of the corresponding surface layer decreases, but a positive effect is a decrease of the resistance R at low humidity levels.

Beside the resistance R, significant changes in the phase θ are also registered, from about 88° to 20° for TSZ_400 and from about 82° to 38° for TSZ_800.

Both parameters R and θ can be efficiently used as informative parameters for various practical applications of the elaborated humidity sensor elements. At RH levels above 55% the sensitivity of the sensors developed increases significantly.

Further investigations on the Ti-Si-Zr-Ce-O system are very promising for studying the capabilities of this group of materials for development of advanced humidity sensor elements.

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