FRI-21-P-CT(R)-07

HUMIDITY SENSING PROPERTIES OF SENSORS BASED ON Ti-Zr-Ce-O SURFACE LAYERS PREPARED VIA A SOL-GEL METHOD

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Abstract: *This paper presents humidity sensors prepared on the basis of Ti-Zr-Ce-O surface layers deposition via a sol-gel method and posterior sintering at 400□C and 800□C. The compositional, morphological and structural features of the composing materials have been investigated by means of scanning electron microscopy (SEM), energy dispersion spectroscopy (EDX) and X-ray diffractometry (XRD). The electrical characteristics of the obtained sensors have been evaluated with an impedance analyzer. The comparison of the characteristics of these sensors to the reference ones reveals the beneficial influence of Zr-doping, particularly after sintering at 800□C, when zirconium titanate is formed. The electrical resistance variation reaches two orders of magnitude within the range of 20% to 93% relative humidity and it is almost linear in semi-logarithmic scale.*

Key words: *Humidity sensing properties, sensors, sol-gel method, Titanium, Zirconium, Cerium*

INTRODUCTION

The humidity sensors are important part of the systems for environmental automatic measurement and control. This is the reason for the continuous development of new materials and methods for improvement of their properties. The sensors encounter application for environment monitoring in branches like agriculture, industrial sector, as well as for household and medical applications, etc.

Titanium dioxide is often used for sensing element preparation and its characteristics can be modified by dopants such as: *Zn* [1]*, Bi, Na, V* [2-6], *Ce* [7]*,* etc. Besides, appropriated sintering temperature enables the synthesis of different titanates with various compositions, structures and morphology for enhanced sensitivity to humidity. The sol-gel method is very useful for preparation of thin layers, because of the simplicity its employment and the necessary equipment [1, 8-12].

Basing on the above mentioned statements, the present study presents humidity sensor development on the basis of *Ti-Zr-Ce-O* surface layers deposition via a sol-gel method. The impact of the Zr-doping at presence of Ce-ions and of the sintering temperature on the superficial morphology and structure of the obtained sensitive layers and their humidity sensing properties is investigated. Comparative analysis with reference samples is performed, in order to show the beneficial effect of the Zr-doping.

EXPERIMENTAL

- Sensitive film preparation - It was performed in several consecutive stages:

Initial precursors mixing:Zirconium n-butoxide (ZBO)-80% and Titanium (IV)n-butoxide (TBOT) - 98% (both delivered by"Alfa Aesar"-Germany) were mixed in proportion 1.25:1 in volume parts, in order to compensate the lower concentration of the former precursor.

Hydrolytic solution preparation: Separately, another saturated (at room temperature) solution was prepared by dissolving of anhydrous diammonium hexanitrocerate $(NH_4)_2Ce(NO_3)_6$ (FLUKA-Chemika (Switzerland)) in isobutanol. Afterwards, both solutions were mixed in 1:1 in volume parts proportion.

Precursor hydrolysis regime: The precursor hydrolysis was performed at 85°C for 3 hours in covered vessel. The resulting sol was left in a refrigerator (5°C) for a week, for ensuring of gradual polymerization of the hydrolyzed precursors and homogenization.

Film deposition: The obtained viscous sol was deposited on preliminary cleaned alumina substrates with interdigitated silver palladium electrodes (size dimensions 18x10x0.5 mm), similar to the used in our previous works [13, 14]. The film deposition was performed by triple immersion in the sols at 85ºC in 30 min immersion/ 30 min drying at the same temperature. The sol-gel coated substrates were submitted to final sintering at 400°C or 800°C, for 30 minutes.

This approach enabled the preparation of thin layer sensors, and their sensitivity to humidity was investigated by the methods described below. The measured characteristics of these sensors were compared to those of reference sensors, prepared without of Zr precursor.

All resulting viscous sol-gel systems were also put in Petri vessels and sintered at the same conditions as the above described samples. The obtained powders were further used for XRD analysis.

- *Measurement* and characterization of the obtained humidity sensors

The surface layers of the obtained sensors were exposed to morphological observations by Scanning Electron Microscopy (SEM), and 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 acquired by Philips PW 1050, supported by CuKα - X-ray emitter within the angle range (2θ) from 8º to 90º with a step of 0.01º and exposition of 19 s per step.

The electrical characteristics of the obtained sensors were measured 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 values for sensor resistance R, capacitance C, impedance Z and phase θ were determined. The sensing elements were put 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 (RH). The *RH* levels used were in the range from 20% to 93%.

RESULTS AND DISCUSSION

- Surface layers morphology and structure – SEM and EDX images of the investigated samples are shown in Fig.1. The surface layers of the samples sintered at 400°C show clear aggregates of the deposited material, separated by channel-like spaces among them. The layers sintered at 800°C have much larger aggregates and narrower channel-like spaces among them.

The EDX maps confirm the presence of Ti, Zr, Ce in the superficial layers of the sensors developed.

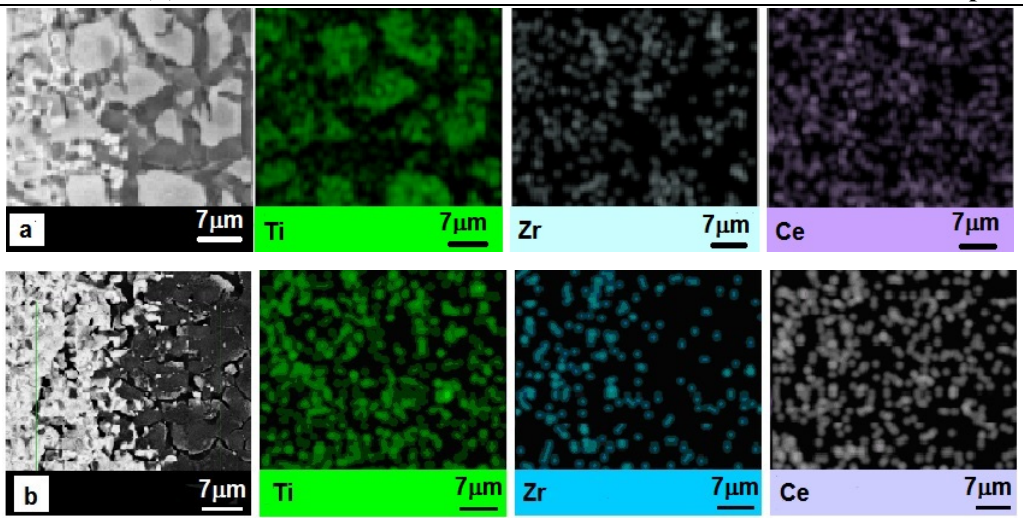

Fig. 1. SEM and EDX images of the samples: a) TZC_400, b) TZC_800

The XRD-patterns of the sensing layers materials are shown in Fig.2. According to the XRD-patterns acquired for the samples, treated at 400°C, the material is amorphous, and the maximum of the amorphous halo is near of 2θ=30°.

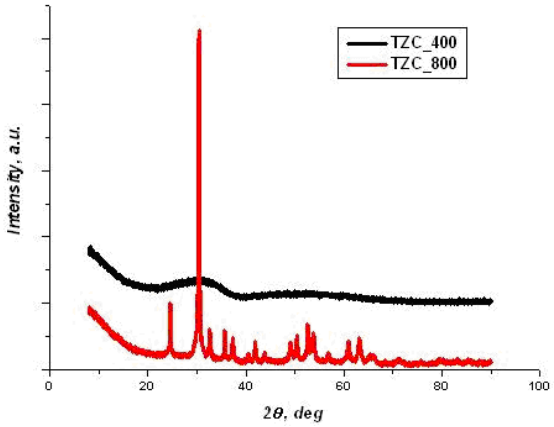

Fig. 2. XRD–patterns of the investigated surface layers materials

XRD-pattern for the material sintered at 800°C reveals occurrence of Zirconium Titanate ($ZrTiO_4$). The highest peak is near to 2θ=30° and corresponds with the maximum of the amorphous halo of the specimen, treated at 400°C. This coincidence reveals initiation of $ZrTiO_4$ formation, which at 800°C proceeds to complete zirconium titanate formation. Obviously, the morphological and structural differences should result in distinguishable variations in their characteristics.

- Electrical characteristics – The experimental characteristics $R=f(RH)$, $C=f(RH)$, $Z=f(RH)$ and $\theta=f(RH)$ of the investigated sensors TZC_400 and TZC_800, as well as those of the references T_Ref_400 and T_Ref_800 are acquired at *R*H-gradual elevation. The data measured at 20 Hz and 25°C is shown in Fig.3. The resistance, capacitance, impedance and phase are designated as *R*, C, *Z* and θ - respectively.

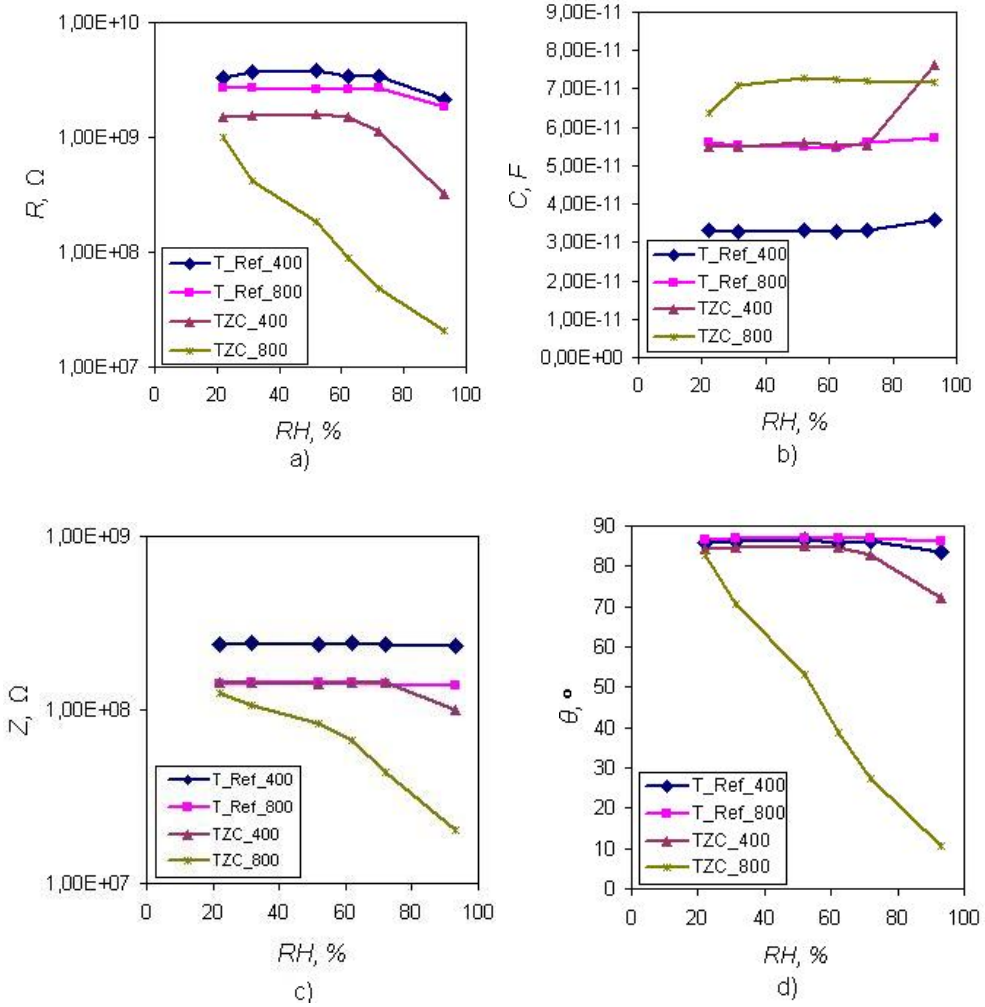

Fig. 3. Characteristics: a) $R=f(RH)$, b) $C=f(RH)$, c) $Z=f(RH)$ and d) $\theta=f(RH)$ of the investigated and reference samples at 20 Hz and 25°C.

The bigger variation of the sensors' parameters acquired for the samples doped with Zr in presence of Ce compared to the parameters' variation of the reference ones points the beneficial effect of the Zr-doping. The relative variation R_{max} / R_{min} is more significant in comparison to the relative variation of the rest parameters. The R decrement range at RH gradual increase from 20 to 93% registered for TZC_400 is about an order of magnitude, whereas for TZC_800 it achieves about two orders of magnitude. The phase θ for sample TZC_800 changes from about 83° to 11° being also informative parameter, which can be used for sensor connection to measurement circuits.

The occurrence of channel like spaces among the obtained aggregates promotes humidity penetration. The zirconium titanate formation at 800°C of sintering appears as beneficial regarding the humidity sensing properties of the sintered material and the respective sensors. Furthermore, the resistance variation of TZC_800 is almost linear at semi-logarithmic coordinates and this of θ is just proportional.

CONCLUSIONS

Humidity sensors were prepared based on TBOT and ZBO at the presence of Ce-ions by sol-gel method followed by sintering at 400°C or 800°C.

The samples sintered at 400°C have amorphous structure of the superficial layers and in those sintered at 800°C the process of zirconium titanate formation is conducted. The surfaces of both kinds of samples contain surface aggregates divided by channel-like spaces, promoting humidity penetration.

The Zr-doping leads to enhancement of the resulting humidity sensing properties of the

sensors, compared to the reference samples. The most significant variation is registered for the resistance of the sensors sintered at 800°C in the RH range from 20% to 93%, at 20 Hz and 25°C. It reaches around 2 orders of magnitude. In addition, this variation is almost linear in semi-logarithmic scale.

The humidity sensitivity enhancement for TZC_800 type of sensors originates from the $ZrTiO_4$ formation at 800°C. This fact confirms the possibility for enhancement of the capabilities of the surface layers, prepared by a sol-gel method, based on TBOT and an appropriate doping materials and sintering temperature.

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