TiO_2-Based Humidity Sensors with Different Dopants

Toshko Nenov

Abstract – **The paper presents results from the research of TiO_2-based humidity sensitive elements with different dopants, synthesized at various temperatures. The impact of dopants and sintering temperature on the parameters and characteristics of the sensing elements has been investigated. The results of the investigation of sensitivity, hysteresis of the characteristic and the reaction time are shown.**

Keywords – **Humidity sensors, ceramic, TiO_2, dopant.**

I. Introduction

Ambient air humidity or process gas is one of the important parameters determining the quality of outputs in many technological processes. Therefore, measuring gas humidity is very important and widely used in production and research. This requires development and testing of new and improvement of existing humidity sensors. One of the directions in the development of humidity sensors is the use of sensor elements based on ceramic materials. The use of ceramics for these purposes is determined by its following properties [1, 2]:

- easy adjustment of its microstructure by means of control of composition and conditions of synthesis;
- thermal stability and durability to environmental influences allowing for its use in high temperature processes;
- production using relatively simple operations;
- use of cheap materials in its production, which allows for obtaining relatively inexpensive sensors.

TiO_2 is of particular interest among the great variety of sensing element materials because of the possibility for easier control of the properties of sensing elements through dopants and the sintering temperature as well as its durability. TiO_2 easily forms titanates with dopants, which allows for modifying the parameters and characteristics of the sensing elements. It is relatively abundant and is used for other purposes in the electronics industry. It is also characterized with good durability.

In this respect, the present work describes the study of humidity sensing elements based on TiO_2 with different dopants, sintered at several temperatures.

II. Experiment

Table I contains the compositions of the studied experimental ceramic samples. In the study the dopant used are ZnO, SnO_2, Bi_2O_3, V_2O_5, PbO, CuO and $Na_2CO_3.10H_2O$. Apart from binary some ternarysamples have been investigated as well.

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The experimental samples are obtained using ceramic technology [1]. Homogenization is carried out in a planetary mill Pulverizete-5 in corundum pot for 4 hours. Grinding of oxides is carried out simultaneously with the homogenization. Distilled water is used as a medium for mixing and grinding. Granulation gives plasticity to the ceramics and provides better compression of the samples. Polyvinyl alcohol is used as a binder.

The samples are shaped as discs with a diameter of 20mm and thickness of 3mm. The sintering time is 2 hours but the sintering temperature varies for the different samples.

Mechanical processing of the ceramic samples is performed before applying the conductive electrodes after which the samples are cleaned in an ultrasonic bath. Electrodes are obtained after sintering the silver-palladium paste applied on the sample at a temperature of 850°C for 30min. Finally pins are soldered to the resulting electrodes. Figure 1 shows the appearance of investigated experimental samples.

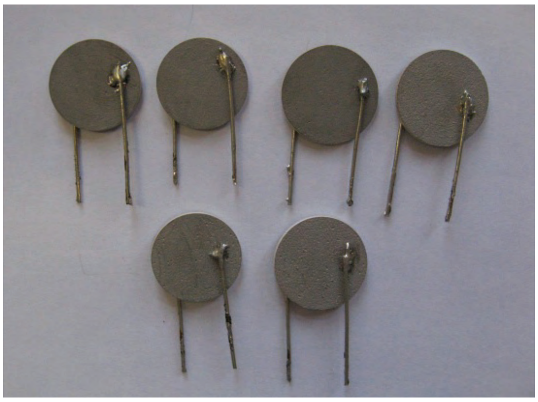

Fig.1. Experimental samples of humidity sensing elements

The humidity sensing characteristics of the samples were determined in conditions of controlled humidity through a relative humidity calibrator VAPORTRON H-100BL, product of BUCK RESEARCH INSTRUMENTS LLC [3]. The device supplies values of relative humidity in the range from 10 to 95%, with accuracyof 1.5%.

The active resistance and the impedance of the sensors, in the conditions of the humidity chamber were measured by an impedance analyzer Precision Impedance Analyzers 6505P product of Wayne Kerr Electronics Ltd. at a frequency of 1kHz and amplitude of 500 mV of the testing signal. The impedance analyzer permits evaluation of various parameters such as, phase angle, capacitance, resistance, inductance, and quality factor with a basic accuracy of 0,05% [4].

TABLE I
COMPOSITIONS OF THE STUDIED EXPERIMENTAL CERAMIC SAMPLES

Sample	Composition	Sintering temperature, °C
T1	$95mol\%TiO_2+5mol\%Bi_2O_3$	850, 950, 1050
T2	$90mol\%TiO_2+5mol\ \%ZnO+5mol\ \%Bi_2O_3$	850, 900, 950, 1050
T3	$90mol\%TiO_2+5mol\%Bi_2O_3\ +5mol\%SnO_2$	850, 950, 1050
T4	$50mol\%TiO_2+49mol\%SnO_2+1mol\ \%V_2O_5$	850, 950, 1050
T5	$50mol\%TiO_2+50mol\%ZnO$	850, 950, 1050
T6	$95mol\%TiO_2+5mol\%Na_2CO_3.10H_2O$	850, 900, 950, 1050
T7	$97,5mol\%TiO_2+2,5mol\%Na_2CO_3.10H_2O$	850, 950, 1050
T8	$33,3mol\%TiO_2+33,3mol\%ZnO+33,3mol\%SnO_2$	850, 950, 1050
T9	$95mol\%TiO_2+5mol\%PbO$	850, 950, 1050
T10	$95mol\%TiO_2+5mol\%CuO$	850, 900, 950, 1050

III. EXPERIMENTAL RESULTS

Based on the investigations made it is determined that dopants influence the ceramics sintering process. A higher concentration of $Na_2CO_3.10H_2O$ in the T6 sample improves sintering compared to T7. There is better sintering in the samples containing Bi_2O_3, PbO and CuO.

The results from the study of the dependence of resistivity of samples T1, T7, T9 and T10 on the change of relative humidity are shown in Figure2, Figure 3, Figure 4 and Figure 5.

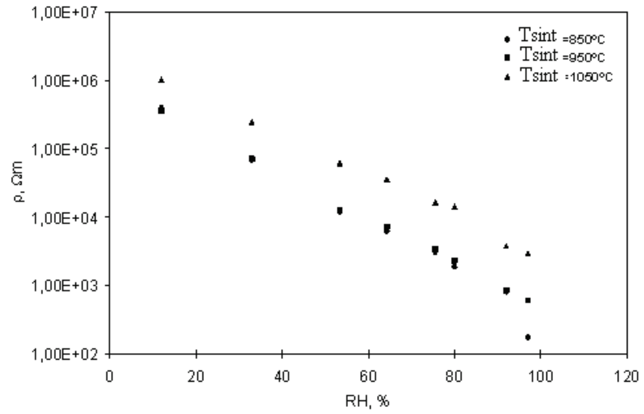

Fig.2. Resistivity dependence on humidity for sample T1

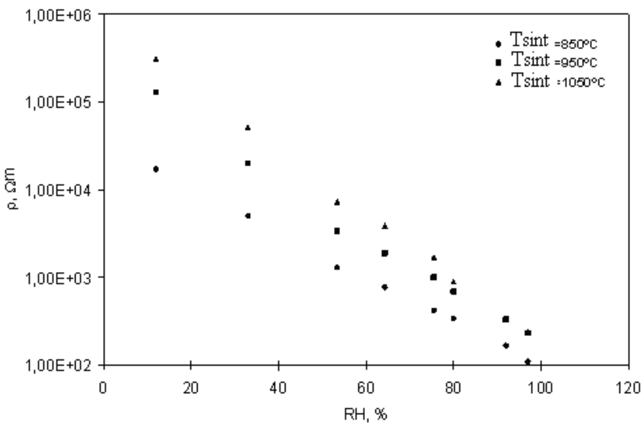

Fig.3. Resistivity dependence on humidity for sample T7

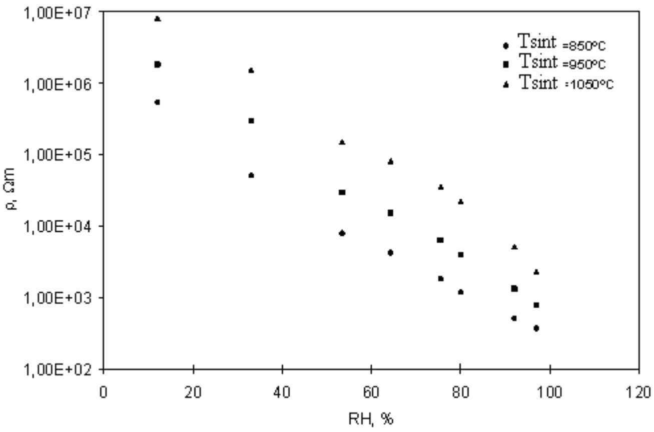

Fig.4. Resistivity dependence on humidity for sample T9

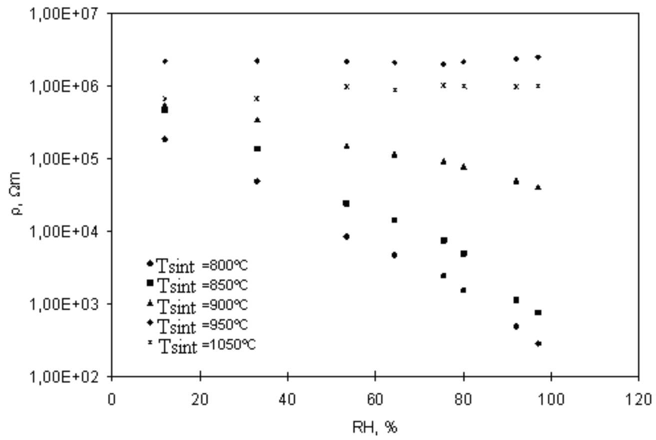

Fig.5. Resistivity dependence on humidity for sample T10

The characteristic function of ceramic humidity sensors with ionic conductivity can be approximated by the following dependence for a wide range of relative humidity:

$$\rho = \rho_0 \exp(-k_H RH) \ , \qquad (1)$$

where ρ_0 is the sensor resistivity at 0% relative humidity, RH is relative humidity in % and k_H is a sensitivity coefficient.

TABLE II
SENSITIVITY COEFFICIENTS FOR THE SAMPLES

Sample k_{Hi}	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
k_{H1}, x10^{-3} RH_1 = 10% RH_2 = 65%	76	57	72	83	92	61	85	78	92	66
k_{H2}, x10^{-3} RH_1 = 65% RH_2 = 95%	76	87	82	83	92	101	85	99	92	90

TABLE III
HYSTERESIS VALUES FOR THE STUDIED SAMPLES

Sample Hysteresis	T1	T2	T3	T4	T5	T6	T7	T8	T9	T10
F, %	1.3	1.4	1.3	0.6	1.9	11.7	1.6	1.2	1.5	1.7

To quantify the humidity sensitivity of the investigated samples the sensitivity coefficient k_H is used, which is determined by the dependence [1]

$$k_H = \frac{1}{RH_2 - RH_1}\ln\left(\frac{\rho_1}{\rho_2}\right) \quad , \qquad (2)$$

where ρ_1 and ρ_2 are the resistivities of the sensor at relative humidity RH_1 and RH_2 respectively ($RH_2 > RH_1$).

This coefficient allows for a comparative analysis of the characteristics of the studied samples. Since not all of the characteristics of the tested models are linear in a semi-logarithmic scale, they are divided into two linear segments - from 10 to 65% and 65 to 95% RH respectively. The sensitivity coefficients for these samples in both segments of their characteristic are shown in Table II.

All samples shown in Table II, are characterized with high sensitivity to relative humidity. Of particular interest are samples with linear characteristic in semi-logarithmic scale (T1, T4, T5, T7, T9). They have a constant sensitivity coefficient in the whole range of relative humidity.

For almost all sample the sintering temperature affects their resistivity. Only for samples T1 and T6 the sintering temperature in the ranges 850°C to 950°C and 900°C to 950°C, respectively, the sintering temperatures do not affect resistivity. This feature allows for good reproducibility of the characteristics of sensor elements based on T1 and T6.

Increasing the sintering temperature increases the resistivity of the samples. For some of them the characteristic changes from nonlinear to linear or it loses sensitivity to relative humidity. For example, for sample T2 raising the sintering temperature to 1050°C leads to loss of sensitivity. This also applies for sample T10 at sintering temperature above 900°C. For sample T3 increasing the sintering temperature leads to a reduction in the nonlinearity of the characteristic. Increasing the sintering temperature above 1050°C will lead to linearization of the characteristic. On the other hand, lowering the sintering temperature for sample T10 below 800°C has the same effect. Hence, by changing the sintering temperature of the studied samples one can control the type of dependence of resistivity on relative humidity. Additionally, this can be achieved by changing the percentage of dopant within certain bounds.

Hysteresis is found in the characteristics of all studied samples.

Hysteresis of the characteristic $\rho = f(RH)$ is defined as

$$F = \frac{\Delta\rho_{\max}}{\rho_{FS}} 100\,\%, \qquad (3)$$

where $\Delta\rho_{\max}$ is the maximum difference in resistivity of the sensor in the increase and decrease of relative humidity, and ρ_{FS} the range of change of resistivity to changes in relative humidity in the measurement range.

Hysteresis is similarly determined for the characteristics $R = f(RH)$. To study the hysteresis of sensor characteristics the resistance of the samples is first measured when relative humidity increases from 10 to 95%, and after that when it goes in the opposite direction. The hysteresis of the characteristic is determined in accordance with (3).Table III shows hysteresis values for the studied samples.

Figure 6 shows the hysteresis of the characteristic for sample T1 sintered at 850°C and Figure 7 shows the hysteresis of the characteristic for sample T7, also sintered at 850°C.

The change in resistance of the sensors during adsorption and desorption has been investigated as well.

The change in resistance during adsorption and desorption is used to determine the appropriate reaction time. This parameter determines the performance of the sensor, i.e. the time after which the change of humidity can be reliably reported.

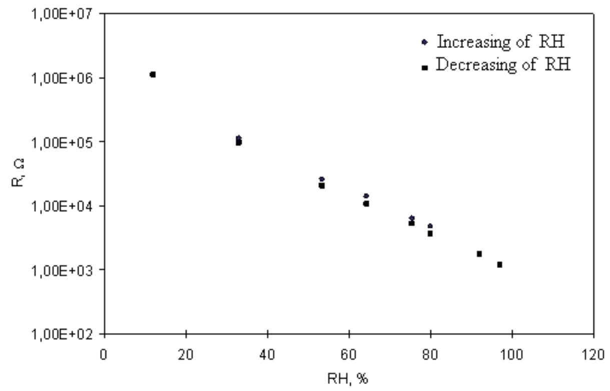

Fig.6. Hysteresis characteristic for sample T1 sintered at 850°C

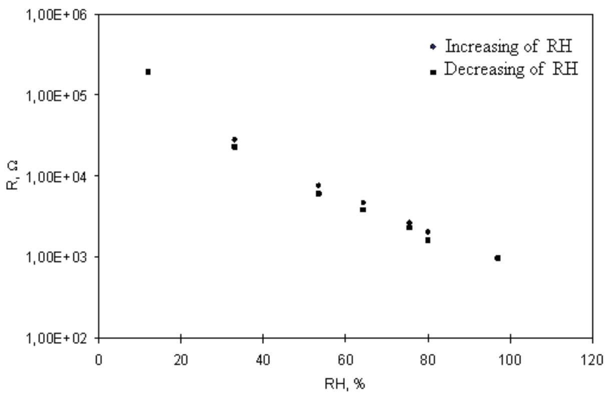

Fig.7. Hysteresis characteristic for sample T7 sintered at 850°C

Studying the change in sensor resistance during adsorption and desorption takes place at base relative humidity of 30% and 95%. Reaction time adsorption and desorption is defined as the time needed to reach $\left(R_{B1}+10\%R_{FS}\right)$ and $\left(R_{B2}-10\%R_{FS}\right)$, respectively, where R_{B1} and R_{B2} are the resistance values for the corresponding base humidities [5].

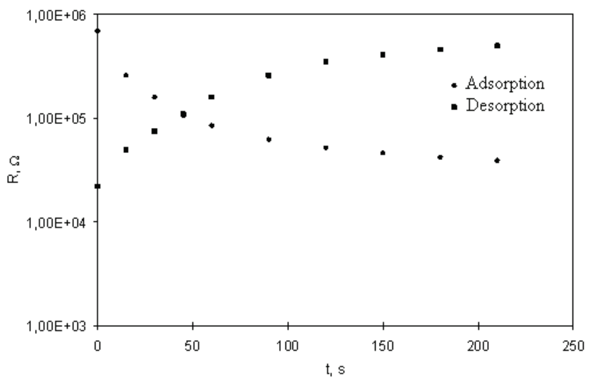

Fig.8. Resistance change for adsorption and desorption of sample T4, sintered at 1050°C

Figure 8 shows the resistance change for sample T4. The reaction time of the investigated sensors for adsorption is in the range 180…300s, and the reaction time for desorption is in the range 240…400s.

IV. Conclusion

Based on the investigations made on the influence of various dopants on the characteristics and parameters of the TiO_2-based ceramic humidity sensing elements the following conclusions can be drawn:

- Bi_2O_3, PbO, CuO and $Na_2CO_3.10H_2O$ have a significant impact on the sintering of the samples. One should expect similar influence of V_2O_5, but owing to its small concentration in the T4 sample, it is not clearly defined;

- The characteristics of the sensing elements with these dopants are linear in semi-logarithmic scale with the exception of samples with CuO;

- Samples with Bi_2O_3, PbO and $Na_2CO_3.10H_2O$ are characterized by high sensitivity for the range of change of relative humidity.

Acknowledgement

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