Impedance characteristics of thin films humidity sensing elements based on Bi-doped TiO_2

Zvezditza Nenova, Toshko Nenov, Stephan Kozhukharov, Maria Machkova

Abstract: *The paper proposes results from the investigations of humidity sensing elements based on Bi-doped TiO_2 thin films, prepared by a sol-gel method. Titanium n-butoxide was used as a starting material for the preparation of the experimental samples, and bismuth acetate as doping compound. The samples were sintered at 400°C. Afterwards, the samples were placed into a calibrated humidity chamber and their electrical properties were investigated by a precision impedance analyzer in the frequency range of 20Hz – 5 MHz. The impedance characteristics, impedance spectra and equivalent electrical circuit of the investigated samples were obtained. The influence of Bi-dopant on the impedance characteristics of the samples has been compared with the respective characteristics of the referent samples based on pure TiO_2, prepared by the same method. The relation between the impedance spectra and the humidity sensing properties of the samples was also explained.*

Key words: *Impedance Characteristics, Humidity Sensing Elements, TiO_2, Bi-dopant, Sol-gel Method.*

INTRODUCTION

The detection and measurement of the humidity in gas mixtures and especially - of the ambient air is of extreme importance for the industrial practice and research activities in various scientific fields. This fact imposes demands for both of improvement of the nowadays existing and development of entirely new generations of humidity sensor elements. The metal-oxide materials have been widely used for the preparation of humidity sensors [1]. Among these materials, TiO_2 has a lot of applications because it is abundant in the nature, and possesses remarkable stability in chemically aggressive media, and significant mechanical and thermal strength. Furthermore, this material allows the formation of large variety of derivative solids with various modifying dopands, enabling achievement of sensor elements with improved characteristics [1, 2]. Recently, the interest to this compound has tremendously increased, because it combines optically dependent semiconductive properties [3]. Finally, it should be mentioned that TiO_2 finds application in entire new generations of energy supply devices, such as solid oxide fuel cells [4], dye sensitized solar cells [5-7], water splitting hydrogen generators [3, 7, 8], and etc.

The present paper deals to investigation of thin films sensor elements based on Bi-doped TiO_2, obtained via the sol-gel method. The electrical characteristics and the impedance spectra are obtained and compared with these of the referent samples based on undoped, pure TiO_2, prepared by the same approach. The relation between the complex impedance spectra, the type of conductivity and the sensitivity of the respective elements to the humidity is also discussed.

EXPERIMENTAL PROCEDURE

Sample preparation. The thin film humidity sensor elements based on Bi-doped TiO_2, marked as S1, were prepared by a sol-gel method, described in [9, 10]. Titanium n-butoxide is used as a starting material for the preparation of the experimental samples, and bismuth acetate as doping component. The samples were sintered at 400°C. Referent samples based on pure TiO_2, marked as S2 were also prepared by the same method for a comparison of the humidity sensing properties of the both types of samples. The sol-gel films were deposited on corundum substrates with Ag-Pd electrodes, with identical size dimensions, to these described in previous research works [9, 11].

Electrical measurements. The measurement of the impedance of the obtained samples was performed by Precision Impedance Analyzer 6505P product of Wayne Kerr Electronics Ltd, at 500 mVrms of the excitation signal. The influence of frequency was investigated in the range of 20 Hz to 1 MHz. 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 ±1.5% of relative humidity. The range of humidity used is from 15 to 93%.

RESULTS AND DISCUSSIONS

RH-characteristics

The characteristics $R = f(RH)$ and $C = f(RH)$ of the obtained humidity sensing elements S1 at different frequencies in the range of 20Hz to 1MHz and at the temperature of 25°C are shown in Fig.1, where *R* and *C* are their electric resistance and capacitance, respectively, and *RH* is relative humidity.

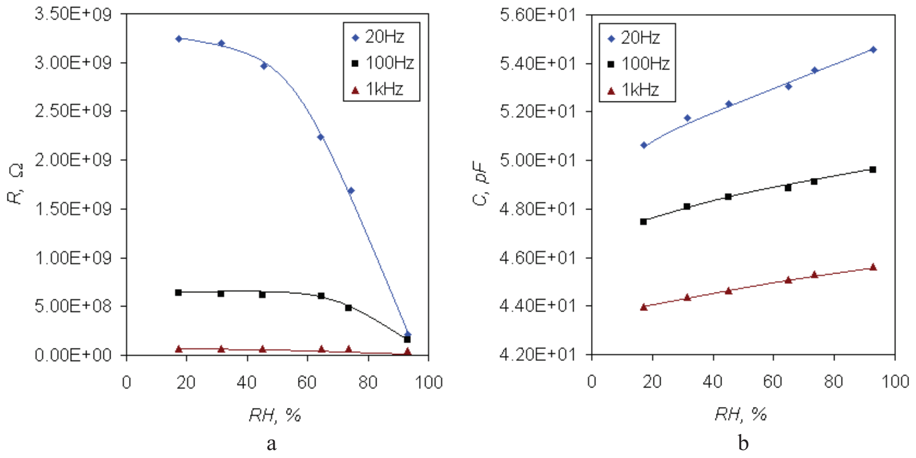

Fig.1. Characteristics: (a) $R = f(RH)$ and (b) $C = f(RH)$ of samples S1 at a temperature of 25°C and at different frequencies

The electrical resistance, *R,* has a higher relative change (R_{max}/R_{min}) in the range from 15 to 93%RH than the relative change (C_{max}/C_{min}). Therefore, this parameter is considered to be more informative.

The sensitivity S_R was determined for specific segments of the sensor characteristics, and is given by the slope of the characteristic, i.e. $S_R = |\Delta R/\Delta RH|$, where ΔR is the change in resistance, and ΔRH - the change in relative humidity for this segment.

The range of resistance change and the resistance sensitivity for the studied frequencies achieve the largest value at 20Hz and they decrease with a rise in frequency. They are insignificant above 100Hz.

Sensitivity to humidity is lower at low values of humidity and increases with the increment of the RH values. At a frequency of 20Hz and at temperature of 25°C, the sensitivity S_R reaches the maximum value of 77.1MΩ/%RH within the range of 75-93%RH. For comparison, Fig. 2 shows the characteristics $R = f(RH)$ for the samples S1 and S2 at 20Hz and 25°C.

As can be seen from Fig.2, the maximal sensitivity of the sample S2 is 50.6MΩ/%RH, being lower than this of S1. Besides, the range of variation of the electrical resistance *R* of the sample S1 is wider than this of the of the referent sample S2. Both these facts reveal the positive effect of the addition of Bi, as modifying element on the properties of the respective humidity sensors.

Impedance spectra

Humidity sensing elements of metal oxide materials are characterized by water adsorption and condensation. The resistance of these sensors decreases with an increase in the relative humidity due to the chemical adsorption and physical adsorption and condensation of water molecules [12]. At the initial stage of adsorption, there is chemical adsorption of water molecules on the surface of the respective sensors and prevailing type of electron conduction. After the formation of the first chemically adsorbed layer there is physical adsorption of water molecules on it and as result - an ionic conduction is appeared [1, 13]. The described mechanism of water adsorption is closely related to its effect on the impedance spectra of the samples. Based on frequency characteristics *z*(*f*) and *θ*(*f*), complex impedance characteristics (Nyquist plots of reactive resistances on active resistances) for samples S1 and S2 at various *RH* and a temperature of 25°C have been obtained. The impedance spectra and equivalent electric circuit at various *RH* for the sensor elements S1 and at 93%RH for the sensor elements S2, and at a temperature of 25°C within the frequency range of 20Hz to 5MHz are shown in Fig.3.

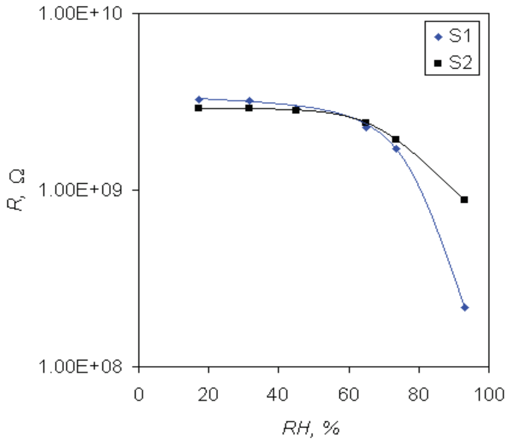

Fig. 2. Characteristics $R = f(RH)$ of samples S1 and S2 at a frequency of 20Hz and at a temperature of 25°C

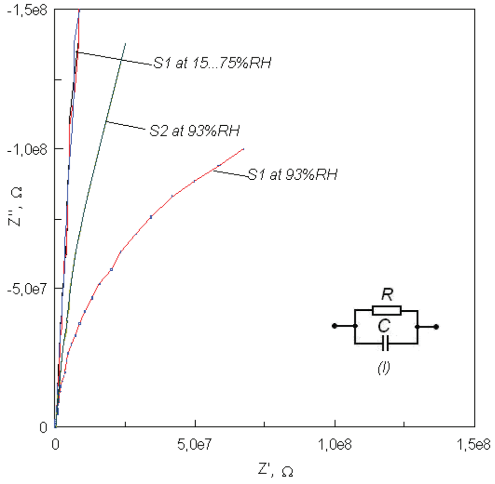

Fig.3. Nyquist plots and equivalent electrical circuit for samples S1 at various *RH* and for samples S2 at 93%RH and at a temperature of 25°C

The obtained plots, at low values of humidity, are close to a straight line which corresponds to Nyquist plots of the base sensing material [14]. When humidity rises complex impedance plots are arcs from semicircles of very large radii, and their equivalent circuit consists of resistance *R* and capacitance *C* connected in parallel, shown by circuit (I) in Fig.3. 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 above 75%RH the chemisorption enhancement and leakage current increment lead to growing the curvature of the arc. Simultaneously, a decrement in the sample impedance is observed related to the enhancement of this conduction. The comparison of the impedance spectrum for the sample S1 at 93%RH with this for S2 shows that both the lower impedance value and the higher curvature for S1, appears to be indicative consequence of its superior electron conductivity. This also corresponds to the resistance changes of the samples, illustrated in Fig 2, where the highest sensitivity S_R appears at values of RH, above 75%.

All these results reveal the direct relation between the presence of Bi-dopant in the composition of the TiO_2 films and electrical properties of the respective sensors

CONCLUSIONS

The obtained results for the investigated samples, prepared on the basis of TiO_2 modified, by Bismuth, reveal the possibility for their application as humidity sensors. The use of Bi as a doping component leads to improvement of the sensitivity of the respective humidity sensors at RH level above 73%. Furthermore, the range of variation of the electrical resistance of the Bi-modified sensors is enlarged, in comparison to the referent ones based on undoped TiO_2. The impedance spectra obtained, confirm the proposed mechanism of electrical conductivity, revealing predominance of the electronic conductivity compared to the ionic one. On the basis of the experimental impedance spectra, appropriated equivalent circuit is obtained. It is composed by one RC-group in parallel connection.

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ABOUT THE AUTHORS

Assoc.Prof. Zvezditza Nenova, PhD, Department of Fundamentals of Electrical and Power Engineering, Technical University of Gabrovo, Phone: +359 66 827 376, E-mail: z_nenova@yahoo.com

Prof. Toshko Nenov, PhD, Department of Automation, Information and Control Systems, Technical University of Gabrovo, Phone: +359 66 827 390, E-mail: thgnenov@gmail.com

Stephan Kozhukharov, PhD, LAMAR-Laboratory, University of Chemical Technology and Metallurgy - Sofia, E-mail: stephko1980@abv.bg

Prof. Maria Machkova, PhD, Department of Chemical Sciences, University of Chemical Technology and Metallurgy - Sofia, E-mail: marima4@abv.bg

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