ELUCIDATION OF THE CONTRIBUTION OF MODIFIED TITANIA FILMS OVER THE PERFORMANCE OF THIN FILM HUMIDITY SENSORS

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ABSTRACT

The present research focuses on comparative measurements of the influence of complex additives on the sensitivity of humidity sensors, prepared by the sol-gel method. Three different dopants were added to the primary mixture in order to improve the properties of the films, expressed in water uptake capability, as follows: Bismuth acetate (CH₃COO)₃Bi, Vanadium-2,4 pentadionate (C₁₅H₂₁O₆V), and Sodium tert-butoxide (CH₃)₂CONa. The properties of the obtained sensors were evaluated by determination of their electrical resistances in a chamber with controlled humidity. As a result, it was experimentally established that the most significant positive effect over both the increase of sensitivity and the measurement range enlargement come from V(III)-2,4 pentadionate with Sodium tert-butoxide.

Keywords: sol-gel method, sensitive elements, dopants, comparative measurements.

INTRODUCTION

Humidity, together with pressure, temperature and chemical composition of the atmospheric environment are some of the basic environmental operating conditions for various kinds of devices and equipment. In other words, the humidity is one of the key factors which should be measured and controlled during industrial production, storage, and transportation of a large variety of industrial and natural products. Generally, relatively high levels of humidity have a detrimental effect upon the quality of the respective products. The detrimental impact of humidity affects many aspects of human activities, as for instance:

- Industry and transport: atmospheric corrosion of various metal constructions [1].
- Transport and energy systems: change of the regime of combustion for various kinds of fuels in internal combustion engines and Solid Oxide Fuel Cells (SOFC) [2]. The ageing of the anodic materials of SOFC, due to water content (moisture) in the gaseous fuel supply has been described in the literature [3]. Similar undesirable phenomena related to the presence of moisture [4] are observed for the Polymer Electrolyte Membrane Fuel Cells (PEMFC), as well.
- Architectonics: destruction of buildings, because of water uptake of the limestone constructive materials [5].
- Electronics: corrosion of the conductive materials [6], as well as deterioration of the electric insulations [7]. In addition, the relatively higher levels of moisture increase the probability for direct damage of electronic and electric devices, especially high voltage energy supply installations [8]. The increase of the relative humidity (RH) enhances the probability for water condensation. The condensed water forms undesirable conductive pathways, which enable the occurrence of short connections in the electric circuits. In the case of fine electronic devices, the distances between the conductive elements are usually very short. Consequently, even an insignificant quantity of condensed water could cause irreversible damages. In addition, moisture in high voltage energy supply systems represents even potential danger for the human life.
- Automatics: Damage of various kinds of sensors, caused by the humidity, for example potassium
bromide IR detectors [9], which are widely used in IR spectroscopy.

- Biotechnologies: High level of moisture provides a convenient environment for growth of undesirable microbial species, which could cause considerable damage of the respective products, and even could be harmful for the human health [10].
- Chemical industry: deterioration of hygroscopic raw materials and products, and severe corrosive attack when acidic gases are represented.

Nevertheless, there are some cases, when the high levels of RH are rather desirable, as in antibiotics and agricultural production. In some branches of the chemical industry, a hot water steam is used as basic precursor. Particularly, the catalyzed steam-reforming of hydrocarbons is a key process for generating synthesis gas or hydrogen for many different industrial applications including the production of fertilizers, chemicals, synthetic fuels, and oils [11]. In these cases, the measurement of the humidity of the produced synthesis gas could provide valuable information for the chemical conversion rate, which enables the control of the parameters of the chemical processes, like temperature, pressure, and flows of the water steam, and the respective hydrocarbons. All of the mentioned above aspects of the impacts of humidity on the human activities reveal the importance and necessity for its measurement and control, which call for development of humidity sensors with improved characteristics.

The sol-gel route was found to be a versatile method for development of new generations of advanced materials for various applications [12]. This method is widely used for synthesis of various TiO$_2$-containing materials for different applications. Typical examples include: transparent, mesoporous anatase TiO$_2$ monoliths [13], Nanomaterials of TiO$_2$ with controlled porosity [14], thin dispersive powders [15], dense [16 - 18] or porous [19, 20] thin films and coatings.

In addition to its versatility, the sol-gel route enables the synthesis of various materials which cannot be obtained via other technologies [21]. Furthermore, the properties of the respective products could be designed by addition of various dopants to the sol-gel system, during their synthesis.

The general purpose of the present research is to compare the influence of different dopants to the sensitivity of sensor elements, prepared by the sol-gel approach, expressed by change of their resistance with respect to the humidity of the surrounding environment.

**EXPERIMENTAL**

**Preparation and deposition of superficial coatings**

Three solutions were prepared by mixing of 40 ml. butanol and 60 ml. Tetrabutyloxititanate - TBOT. After their heating up to 70°C, the respective dopants and the catalyst were added. For the former two cases, the Bismuth acetate (BA), and the Vanadium (III)-2,4 pentadionate (VP) were dissolved in the catalyst, in proportion about 1g. per 2ml. of concentrated HNO$_3$, in order to obtain saturated solutions at room temperature. The third solution was prepared by subsequent addition of 2ml. of the acid, and 1g Sodium tert-butoxide (SB).

Afterwards, the obtained sol-gel systems were deposited by triple dipping, on ceramic substrates, with Ag-Pd electrodes. The procedure is described in detail in previous works [22, 23]. All sensor elements have identical geometric features (i.e: shape and size) as is presented in Fig. 1.

The specimens are divided into two groups. The first one is represented by singular dopants, whereas the second one is prepared by mixtures of dopants. The
respective symbols for the specimens of the first group are, as follows: S1 - with BA; S2 - with VP, S3 - with SB.

Afterwards, in order to investigate the coincident influences of the dopants, the above described solutions were mixed together in equal volume parts to prepare the second group of specimens. The following symbols were used for them: S4 – with BA + VP; S5 – with BA + SB; S6 - with VP + SB, and finally S7 – which includes all of the dopants together.

Measurement of the sample parameters

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 L.L.C. [24]. This device provides precisely controlled relative humidity in the range from 10 to 95%, with precision of 1.5 %. The active resistances R in the conditions of the humidity chamber were measured by Precision Impedance Analyzer 6505P product of Wayne Kerr Electronics Ltd. at a frequency of 1 kHz 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 % [25].

RESULTS AND DISCUSSION

Singular dopants: The characteristics \( R = f(RH) \) of the respective specimens from the first group are represented in Fig. 2, where the relative humidity is designated by RH. The comparison among them shows various impacts of the dopants on the sensitivity of the samples, in different ranges of RH.

The highest sensitivity for the entire RH range (i.e. from 15 % to 95 %), was shown by S2, doped by VP. In addition, it was more pronounced at RH values, lower than 40 %RH. The S3 specimens, doped by SB revealed its sensitivity in a shorter RH range, between 30 % and 95 % of RH. The shortest sensitivity range belongs to S1 samples, prepared by addition of BA. They reveal distinguishable sensitivity only at RH-values, higher than 75 %. Consequently, samples S2 and S3 can be used as sensors for the respective RH-ranges, whereas S1 – can be applied as key-switch elements.

From the above comments, it can be concluded that the chemical nature of the dopants predetermines significant differences in the behaviour of the representatives of the first group.

Mixed (combined) dopants: The characteristics \( R = f(RH) \) of the experimental samples prepared by combined dopants S4 (BA+VP), S5 (BA+SB), S6 (VA+SB) and S7 (BA+VA+SB) were also determined. These samples were prepared by additions of combinations of dopants. Their characteristics are shown in Fig. 3.
The results reveal that generally, the addition of VP to the sol-gel system, either alone, or with other dopants, always leads to increase of the sensitivity of the respective sensors (i.e. samples S4, S6, S7), in the range 15 – 60 %. Among them, the specimens doped with the combination of VP and BA (S4), revealed a relatively lower sensitivity in the range enclosed between 30 and 60 %. The highest sensitivity was shown by the samples, prepared by simultaneous addition of VP and SB (samples S6 and S7). In the cases of the specimens with doping of BA and SB, enlargement of the range of sensitivity, from 55 to 93 % was detected, in comparison to the samples doped only by BA (S1). The specimens, prepared only by VP (S2), possessed higher sensitivity at lower RH range (i.e. 15 to 30 %RH).

CONCLUSIONS

It was established that there is a significant influence of each dopant on the behaviour of the respective specimen. The dopants influence both the sensibility of the respective sensitive elements, and the RH range of maximal detection. The addition of VP, for all cases, causes a rise of their sensitivity at lower humidity values. Among them, the specimens prepared with VP as unique dopant reveal their highest sensitivity at 15 to 30 % of RH. When VP is combined with SB, a significant increase in the sensitivity of the respective samples in the range between 30 and 60 %, reaching values which are higher than these of the samples prepared with only one of them. In contrast, BA decreases the sensitivity of the respective samples in the lower RH range. In combination with another doping agent (either VP, or SB), the range of sensitivity is considerably larger, compared to these with BA, as unique dopant. The latter possesses key-switch type characteristics. The combined use of BA and SB enables increase of the sensitivity in the range of higher RH values, from 55 to 93 %. The experiments performed reveal the possibility for control of the sensitivity and the measurement range of sensor elements, prepared by the sol-gel method, with different kinds of dopants, and various combinations between them.

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REFERENCES


