Influence of Ce(III)/Ce(IV) - supplements on the Characteristics of Humidity Sensors with TiO₂ Films Prepared via a Sol-gel Method

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Humidity sensors have been prepared via a sol-gel method to deposit TiO₂ films with additions of Ce-compounds on alumina substrates, with interdigitated silver palladium electrodes. Observations by scanning electron microscopy (SEM) were performed in order to determine the surface morphology of the respective layers. Structural and compositional characterization was done by X-ray diffraction analysis (XRD), and energy dispersive X-ray spectroscopy (EDX) for investigation of the relation between the film structures and the parameters of the respective sensors. The influence of Ce-compounds on the electrical characteristics of the samples as humidity sensing elements has been evaluated by an impedance analyzer.

Keywords: humidity sensors, sol-gel method, titania, cerium dopant.

Influencia de los suplementos de Ce(III)/(IV) sobre las características de los sensores de humedad con capas de TiO₂ preparadas mediante el método "sol-gel"

Los sensores de humedad han sido desarrollados mediante el método sol-gel para depositar películas superficiales basadas en TiO₂ con adiciones de compuestos de cerio sobre sustratos de corindón y electrodos de aleación de plata y paladio. Se han realizado observaciones mediante el Microscopio Electrónico de Barrido (MEB) para determinar la morfología superficial de las capas respectivas. Las caracterizaciones de la estructura y composición han sido realizadas mediante Difracción de Rayos X (DRX) y espectroscopía de dispersión energética de rayos X (EDERX), con el fin de investigar la relación entre la estructura de las capas y los parámetros de los sensores respectivos. La influencia de los compuestos de cerio sobre las características eléctricas de los sensores de humedad obtenidos se ha evaluado mediante el análisis de impedancia eléctrica.

Palabras clave: sensores de humedad, método sol-gel, titania, dotación de cerio.

1. INTRODUCTION

Humidity is a basic environmental operating condition of various devices and equipment, and therefore, it is a key factor that requires measurement and control during the production, storage, and transportation of a large variety of industrial and natural products.

On the other hand, the sol-gel method has been found to be a versatile way of preparation of entirely new generations of advanced materials for many applications [1]. It has been widely used for synthesis of various TiO₂-containing materials, such as: transparent, mesoporous anatase TiO₂ monoliths [2], nanomaterials of TiO₂ with controlled porosity [3, 4], thin dispersive powders [5], dense [6-9] or porous [10-13] thin film coatings, etc. Such nano-structured materials enable the development of a new generation of sensors with remarkably improved characteristics and parameters, compared to the state-of-the-art ceramic sensitive elements. Additionally, nano-materials allow size decrease and further integration in semiconductor systems. Therefore, the development and use of sensors, based on TiO₂ modified by various dopants, appears to be very promising [14 - 19].

The differences in the features of the TiO₂-based materials mentioned above originate from the variety of conditions applied during their syntheses. The correlation between the factors and conditions of synthesis, their structure, as well as the properties of the products obtained via a sol-gel method is described in [20]. The addition of various compounds can also lead to changes in the properties of the respective TiO₂-containing materials. For example, Zacharescu M, et al. [21] report successful synthesis of mono-component and binary phase TiO₂-CeO₂ ceramic nanometric powders via a sol-gel method. Ce⁴⁺ ions appear to have a beneficial effect on the polymerization of the respective sol-gel systems, when a Ce-compound is added to them [22]. The addition of cerium compounds also leads to the synthesis of advanced ceramics with high ionic and electron conductivity [23]. In particular, Ce-oxide [24, 25] and Ce-Ti-oxide films [26, 27] have electrical properties, which enable their application in various kinds of sensors, for example, in oxygen gas sensors, developed on the basis of Ti-oxide and Ce-Ti-oxide films [28]. Compared to other frequently used dopants for metal oxide humidity

sensors, the use of cerium as a dopant does not violate environmental regulations, which impose restrictions on the use of heavy metals [29, 30].

This paper presents an investigation in the humidity sensing properties of Ce-Ti-oxide films prepared via a sol-gel method. Humidity sensing elements are developed by deposition of TiO₂ films with additions of Ce-compounds on alumina substrates. The influence of several experimental parameters has been studied as follows: oxidation state of cerium in the additive compound, deposition time, and the temperature of the posterior sintering. The surface morphology, compositions, and electrical properties of the obtained samples are then investigated, comparing them to referent humidity sensing elements based on pure tetrabutylortotitanate (TBOT).

2. EXPERIMENTAL

2.1. Sample preparation

2.1.1. PREPARATION OF THE INITIAL SOLUTIONS

Solution 1: Initially, 0.58 grams of diammonium hexanitrocerate (NH₄)₂Ce(NO₃)₆ were added to 20 ml of n-butanol, preliminary heated up to 70°C in a covered beaker, to obtain a saturated solution of (NH₄)₂Ce(NO₃)₆. Afterwards, 30 ml of TBOT were added to the obtained solution by dripping for 30 minutes, under stirring. The solution was then left for 1 hour, while being stirred at the same temperature. The sol-gel system obtained was left for one week at 5°C. No acid was added to the solution, since in previous studies [31], it was established that the hexanitrocerate renders strong acidity to the liquid medium, after its dissolution, due to its hydrolysis.

Solution 2: Solution 2 was prepared by procedures, identical to solution 1: 0.54 grams of diammonium pentanitrocerate (NH₄)₂Ce(NO₃)₅ were added to 20ml of n-butanol, preliminary heated in a covered beaker (70°C).

Solution 3: 0.23ml. of 65% HNO₃ was added to the same volume of heated n-butanol. Tetrabutylortotitanate was added to the system following the procedure described above.

2.1.2. FILM DEPOSITION

The film was deposited via a dip-coating procedure [32] by triple dipping of alumina substrates with preliminary deposited interdigitated silver-palladium electrodes. The procedure was performed by subsequent dipping of the substrates into the solution for 30 or 60 minutes, depending on the sample, at 70°C, and drying at the same temperature. After that the samples were sintered at 400°C and 800°C, respectively, for 30 min. Figure 1 represents a schematic view and photograph of the obtained sensor elements.

Figure 1. Schematic view (a) and photograph (b) of sensor element.

The samples studied in the present paper are divided into the groups shown in Table 1.

TABLE 1. SAMPLES OBJECT OF INVESTIGATION

Solution N°	Exposure time (min)	Sintering temperature	
		400 °C	800 °C
Solution 1 (NH ₄) ₂ Ce(NO ₃) ₆	30	S1_400/1	S1_800/1
	60	S1_400/2	S1_800/2
Solution 2 (NH ₄) ₂ Ce(NO ₃) ₅	30	S2_400/1	S2_800/1
	60	S2_400/2	S2_800/2
Solution 3 (HNO ₃)	30	S3_400/1	S3_800/1
	60	S3_400/2	S3_800/2

2.2. Measurements

2.2.1. SURFACE MORPHOLOGY AND CHEMICAL CHARACTERIZATION

Comparative observations by Scanning Electron Microscopy, together with Energy Dispersive X-ray Spectroscopy were performed in order to determine the distinguishable features of the respective surface films. They were performed by Scanning Electron Microscope TESCAN, SEM/FIB LYRA I XMU working at 30 kV. The local compositions and map data analyses were studied, by Energy Dispersion Spectrometer (Quantax 200 of BRUKER detector).

The SEM observations were executed in the following sequence:

- Acquisition of SEM image at low resolution equal to 121 times of image magnification, in order to observe the difference between the surface Ce-Ti crystals on the Ag-Pd electrode surface and the alumina surface between the electrodes;
- Acquisition of divided SEM images at high magnification equal to 2160 times. It was done in order to obtain clearer image for the superficial morphology of the samples.

2.2.2. STRUCTURAL AND COMPOSITIONAL CHARACTERIZATION

It was performed on powder samples from the respective gels by XRD (X-ray diffractometry) and Rietveld analysis. The measurements were taken by DRON – 3, supported by CuKα - X-ray emitter at 3.0 kW (50kV, 60mA) and at angles ranging from 20° to 95°, at a step rate of 10 seconds per point. The structure was refined using FullProf program [33] by least square minimization of the weighted sum.

2.2.3. ELECTRICAL CHARACTERISTICS AND PARAMETERS

The measurement of the electrical resistance, capacitance, impedance and phase of the obtained samples was taken by Precision Impedance Analyzer 6505P product of Wayne Kerr Electronics Ltd, at a frequency of 1kHz and 500mV amplitude of the excitation signal. The influence of frequency was investigated in the range of 100Hz to 1MHz. The samples 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 in the range of 15 to 95% with maximal deviation of up to ±1.5% of relative humidity.

3. RESULTS AND DISCUSSIONS

3.1. Scanning Electron Microscopy

The observations were performed on all samples, in order to obtain images, which allow comparison of the surface morphologies with respect to: 1 - Ce-salt used for the preparation of the sol-gel system, 2 - the time of exposition of the substrates to the respective sol-gel system (i.e. solution); 3 - posterior sintering temperature.

The samples treated with solution 1 have somewhat different properties compared to the representatives of the other groups. The film has a weak adhesion to the alumina substrate, and is almost absent from the electrode surface. Additionally, during the deposition of this film, corrosion of the electrodes was observed due to the aggressive action of (NH₄)₂Ce(NO₃)₆. This substance acts both as a strong acid and as an oxidant, and in this way causes dissolution of the Ag-Pd alloy, leading to brownish-black corrosion products.

Figure 2 presents three low magnification SEM-images of samples treated in the respective solutions for 30 minutes, and sintered at 400°C.

Figure 2. SEM – images of samples treated in the respective solutions for 30 minutes, and sintered at 400 °C. a – treated in solution 1; b – treated in solution 2; c – treated in solution 3.

As can be seen in Figure 2, sample S1_400/1, treated with Ce(IV) compound (solution 1) has depositions of the surface film in sparse sections of the substrate, while both samples: S2_400/1 and S3_400/1, treated with solutions 2 and 3, have a better-defined surface film. Sample S2_400, treated with Ce(III) salt (solution 2) has deposited particle aggregates of primary crystals on the ceramic areas, and relatively smaller ones on the electrodes. Additionally, the deposited aggregates as well as the areas among them, obtained by film deposition from the third solution (S3_400/1), have larger sizes compared to those from the other Ce-containing solutions. The sintering temperature also affects both the size of the deposited aggregates and the width of the areas among them. From the results obtained (Figure 3) it can be concluded that after sintering at 800°C, the respective deposited aggregates and areas among them have larger sizes than after sintering at 400°C.

Also, Figure 3 reveals that the surfaces of samples S2_400/1, S2_800/1, exposed for 30 minutes were relatively more abundant in deposits compared to samples S2_400/2, S2_800/2, exposed for 60 minutes. In principle, it has been expected that the thickness of the deposited film increases with enlargement of the exposition of the substrates to the liquid sol-gel systems. However, the experiments show the opposite trend. After a longer exposure time, the thicknesses of the films reach a critical value, and at further expositions, film dissolution takes place.

Figure 3. SEM images of four samples treated by solution 2: a – exposed for 1 hour to the solution and sintered at 400°C; b - exposed for 1 hour to the solution and sintered at 800°C; c - exposed for one half hour to the solution and sintered at 400°C; d - exposed for one half hour to the solution and sintered at 800°C.

3.2. Energy Dispersive X-ray Analysis

The EDX chemical analysis for element distribution was performed only on the samples treated with solutions 1 and 2. Solution 3 does not contain any Ce-salt, and no Ce is expected on the sample surface. In this context, Figures 4 and 5 show selected EDX images for samples treated with solutions 1 and 2, respectively. It is seen from Figure 4, for the samples treated with solution 1, that Ce- and Ti- elements are relatively uniformly distributed. A comparison between both cations reveals that Ti-ions are better expressed with higher density in the samples. For the sample sintered at 800°C, it is clear that for both elements a homogeneous distribution exists. Additionally, the presence of smaller deposited particle aggregates of primary crystals with sizes of the order of 1

Figure 4. SEM – EDX high magnification images of the surfaces of samples, treated for 30 minutes by solution 1: a – SEM image, b - EDX image for Ce-distribution, c – Ti-distribution for sample S1_400/1, d – SEM image, e - EDX image for Ce-distribution, f – Ti-distribution for sample S1_800/1.

Figure 5. SEM – EDX high magnification map analyses of the surfaces of samples, treated for 30 minutes with solution 2:

a – SEM image, b - EDX image for Ce-distribution, c – Ti-distribution for sample S2_400/1, d – SEM image, e - EDX image for Ce-distribution, f – Ti-distribution for sample S2_800/1.

~ 2 microns are observed on the Ag-Pd metallic surfaces, according to high resolution SEM – EDX experiments carried out.

Figure 5 shows the Ce- and Ti- element distributions on the surface deposits for the cases of samples treated with solution 2. The EDX analysis data confirm the presence of Ce in the samples.

A point-quantitative analysis has been performed on the surfaces of selected deposits obtained from the sol-gel derived films. Figure 6 shows the compositions by elements of sample S2_400/1, sintered at 400°C (position a), and sample S2_800/1 sintered at 800°C (position b). The results obtained show that the obtained deposits are built from Ce, Ti, and oxygen. The additive presence of Al in position (b) reveals that the electron beam reaches the Al_2O_3 of the ceramic substrate, under the deposit.

Figure 6. Point-quantitative analysis for samples: (a) S2_400/1 and (b) S2_800/1.

3.3. X-ray Diffraction Analysis

In addition to the EDX analysis, carried out for element composition control and distribution, XRD analysis is performed as well. The aim is to determine the phase content in the samples, in order to clarify the structuring behavior as a solid solution formation, or whether they are rather polycrystalline agglomerates (clusters). For the purpose of the XRD analysis, powders obtained via the sol-gel method were subject to thermal treatment at 400 and 800°C, followed by XRD detection of the respective crystalline phases. It is known [34, 35] that TiO_2 exists in three main modifications: rutile, anatase, and more rarely, brookite. Anatase is the low-temperature modification of tetragonal TiO_2 with basic building units of TiO_6 octahedra. The Ti-Ti distances are

Figure 7. XRD diagrams of powder materials obtained from the three basic solutions. a – solution 1; b – solution 2; c – solution 3.

smaller in anatase than in rutile, while Ti-O distances are greater. The basic units of rutile are also TiO₆ octahedra. However, each octahedron is slightly distorted and forms a chain of edge-sharing octahedra with its neighbors [36]. At temperatures between 550 and about 1000°C, anatase is irreversibly converted into the equilibrium rutile phase. The temperature of this transformation depends on the impurities or dopants present, as well as on the morphology of the sample [37].

Figure 7 shows the XRD patterns obtained at a sintering temperature of 800°C. The diffraction peaks of the referent samples (Figure 7c) based on solution 3 (in the absence of Ce) are very sharp and narrow. The experiment and Rietveld analysis confirm that the sample can be indexed to 100% rutile phase only. The results obtained for the other two samples, Figure 7a and Figure 7b, based on solution 1 and solution 2, respectively, show that only partial conversion to rutile is registered. Another co-phase, which is registered in the samples, is a contribution from the anatase phase. Therefore, the presence of Ce in the samples stimulates poly-phase product (rutile and anatase) formation during the thermal treatment process at 800°C for 30 min. In other words, Ce-additives in the samples originating from solutions 1 and 2, prevent the completion of phase conversion of anatase to rutile at 800°C of sintering.

It is necessary to note that there are no diffraction peaks indexed for Ce₂O₃ and/or CeO₂ phases in the samples. This can be explained by observing that the respective Ce-additions have very low concentrations (less than 5% for X-ray phase detection).

3.4. Electrical measurements

Humidity sensing elements of metal oxide materials are characterized by electron and ionic conduction [38, 39]. As a result of ionic conduction, there are polarization effects during direct current measurements. Consequently, measurements have been taken with alternating current. The elements are normally represented by an equivalent circuit of resistors and capacitors connected in parallel [40].

Figures 8 and 9 present the characteristics $R = f(RH)$, $C = f(RH)$, $z = f(RH)$, $\theta = f(RH)$ of samples S1_400/1, S2_400/1 and S3_400/1, and of samples S1_800/1, S2_800/1 and S3_800/1, respectively, at a temperature of 25°C, where R , C , z and θ are their electric resistance, capacitance, impedance and phase, respectively, and RH is relative humidity. Electrical resistance, R , has the greatest change in the range from 15 to 95%RH. Therefore this parameter is considered to be the most informative and for that reason it is used to compare the sensitivity S_R of the different elements.

Sensitivity S_R has been determined for specific segments of the sensor characteristics, and is given by the slope of the characteristic of these segments [41]

$$S_R = |\Delta R / \Delta RH|, \quad (1)$$

where ΔR is the change in resistance given a change ΔRH in relative humidity for this segment.

To compare this parameter across samples, a statistical error analysis has been performed.

The deviation in resistance, R , for different samples is determined by taking measurements for 5 simultaneously

Figure 8. Characteristics: (a), (b), (c) and (d) of samples S1_400/1, S2_400/1 and S3_400/1 at a temperature of 25°C.

Figure 9. Characteristics: (a), (b), (c) and (d) of samples S1_800/1, S2_800/1 and S3_800/1 at a temperature of 25°C.

prepared samples of each type. Based on these measurements, for a given point on the characteristics, a mean

$$\bar{R} = \sum_{i=1}^n R_i / n, \quad (2)$$

and a standard error of the mean

$$s_{\bar{R}} = \sqrt{\sum_{i=1}^n (R_i - \bar{R})^2 / n(n-1)}, \quad (3)$$

have been computed, where R_i is the resistance at this point of samples' characteristics from given type, and n is their number ($n = 5$ in this case).

Based on these a 95% confidence interval has been determined [42]

$$J\{R\} = \bar{R} \pm 2 s_{\bar{R}} \quad (4)$$

The limits of this confidence interval are given by the vertical error bars in Figure 8a and Figure 9a. The relative errors for the mean of the resistance for the points of the characteristics are of the order of around $\pm 4\%$.

The error in RH, due to the error of the humidity chamber used, which is on the order of $\pm 1.5\%RH$, is given with horizontal error bars in Figure 8a and Figure 9a.

The obtained results show also that there is repeatability of sample characteristics within the indicated limits.

Based on the deviations in the experimental results, the minimum and maximum values of sensitivity, $S_{R \min}$ and $S_{R \max}$ [41] are obtained.

Sample S2_400/1 has the highest sensitivity. For this sample the range $S_{R \min}$ to $S_{R \max}$ is 530 to 640 k Ω /RH for the entire RH range of 15 to 95%RH. Sample S1_400/1 has sensitivity of 470 to 560 k Ω /RH for the range of 35 to 95%RH. The sensitivity of sample S1_400/1 in the range of 15 to 35%RH is smaller and changes from 95 to 380 k Ω /RH. The reference sample (the one coated by undoped TBOT sol-gel film) has the lowest sensitivity: from 50 to 210 k Ω /RH for the range of 15 to 75%RH. It increases to 470-850 k Ω /RH, between 75 and 95%RH. Therefore, the samples, prepared by Ce-compounds have higher sensitivity S_R in a wider range of relative humidity RH, compared to the reference sample. The latter has high sensitivity only at humidity over 75%. The best humidity sensing properties for the entire range of relative humidity are obtained when $(NH_4)_2Ce(NO_3)_6$ is used as a dopant for TBOT at a sintering temperature of 400°C.

Sample S2_800/1 has the sensitivity from 210 to 380 k Ω /RH in the range of 15 to 65%RH. For humidity above 65%RH this sensitivity decreases to 55/280 k Ω /RH. For the rest of the samples, S1_800/1 and S3_800/1, a relatively low sensitivity was obtained, of the order of 5 to 140 k Ω /RH for the range from 15 to 75%RH. At RH above 75%, their sensitivities sharply increase, reaching about 1.30 M Ω /RH. Therefore, samples S1_800 and S3_800 have characteristics of trigger switching threshold elements.

Based on the characteristics obtained, it can be concluded that samples sintered at 400°C, have better properties for humidity measurement, compared to those sintered at 800°C. Samples S1_800/1 and S3_800/1 can be used as detectors of high levels of humidity in automation devices that are turned on/off whenever a given humidity level is reached (in this case around 75%).

Humidity sensing elements of metal oxide materials are characterized by water adsorption and condensation [38]. The resistance of the investigated sensor elements, which are of metal oxide type, decreases with an increase in the relative humidity due to the chemical adsorption and physical adsorption and condensation of water molecules in the areas among particle aggregates in the thin film. The operating principle of such sensors is described in [43, 44]. In the initial stage of adsorption, there is chemical adsorption of water molecules on the surface of the respective sensors. The active

role in this process is played by metallic atoms, M. They interact with the water molecules to form hydroxyl groups M-OH. In this way the surface of crystals is covered by a monolayer of water molecules.

After the formation of the first chemically adsorbed layer there is physical adsorption of water molecules on it. The physically adsorbed layer is more weakly connected to the surface of crystals. The process of capillary condensation of water vapors depends on the size and distribution of the areas among particle aggregates in the obtained thin film in a manner consistent with Kelvin's equation [45, 46]. According to this equation, the filling of areas of smaller size starts at lower humidity, while the filling of areas of larger size happens at higher humidity.

The frequency characteristics of the samples were also investigated. These characteristics for the highest sensitivity sample, S2_400/1, at RH = 75% and a temperature of 25°C are shown in Figure 10. An increase in frequency leads to a decrease in resistance R and capacitance C, as well as impedance z of the sensor element. The frequency characteristics of the other sample behave similarly.

Figure 10. Frequency characteristics of sample S2_400/1 at RH = 75% and a temperature of 25°C.

Temperature affects the sensor elements (for humidity, gases, etc.) based on metal oxide materials [47]. Therefore its influence on the resistance of samples was investigated, as well. Figure 11 shows the results of the influence of temperature on the resistance of samples at a relative humidity of 75%. The change in resistance in the temperature range of 18 to 38°C is within 0.3 to 0.5 %/°C. This requires temperature compensation when the sensing elements are used in practice, in order to increase their precision. Various methods based

on interpolation, artificial neural networks, etc. [48-50], can be used for this compensation.

Figure 11. Temperature characteristics of the investigated samples at RH=75%.

3. CONCLUSIONS

Humidity sensing elements have been obtained based on TiO₂ films with additions of Ce-compounds using a sol-gel method. Among all the samples investigated in the present work, the samples treated for 30 minutes in solution with (NH₄)₂Ce(NO₃)₆ and sintered at 400°C and 800°C have the best surface films. Increasing the sintering temperature from 400°C to 800°C increases the size of the particle aggregates of primary crystals and the areas among them, which in turn leads to a change in the samples' electrical characteristics and parameters. Regarding the application of the obtained samples as humidity sensing elements, the introduction of Ce-compounds results in their improvement, by increasing their sensitivity and widening the measurement range for RH%, compared to the referent samples, prepared by pure TBOT. The sample treated by a solution with (NH₄)₂Ce(NO₃)₆ and sintered at 400°C, has the best humidity sensing properties among the samples investigated.

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REFERENCES

- G. Tsaneva, V. Kozhukharov, S. Kozhukharov, M. Ivanova, J. Gerwahn, M. Schem, T. Schmidt, "Functional Nanocomposite coatings for corrosion protection of aluminium alloy and steel", *J. Univ. Chem. Technol. Met.* **43** [2] 231-238 (2008).
- B. Yao, L. Zhang, "Preparation and characterization of mesoporous titania gel-monolith" *J. Mater. Sci.*, **34** 5983-5987 (1999).
- V. J. Nagpal, R. M. Davis, S. B. Desu, "Novel thin films of titanium dioxide particles synthesized by a sol-gel process", *J. Mater. Res.*, **10** [12] 3068-3078 (1996).
- H. Kochkar, M. Triki, K. Jabou, G. Berhault, A. Ghorbel, "Novel synthesis route to titanium oxides nanomaterials using soluble starch" *J. Sol-Gel Sci. Techn.* **42** 27-33 (2007).
- M. Jensen, P. Fuierer, "Low-temperature preparation of nanocrystalline anatase films through a sol-gel route", *J. Sol-Gel Sci. Techn.* **39** 229-233 (2006).
- V. Kozhukharov, Ch. Trapalis, B. Samuneva "Sol-gel processing of titanium-containing thin coatings. Part III properties" *Jour. Mater. Sci.* **28** 1283-1288 (1993).
- M. Mallak, M. Bockmeyer, P. Löbmann, "Liquid phase deposition of TiO₂ on glass: Systematic comparison to films prepared by sol-gel processing", *Thin Solid Films*, **515** 8072-8077 (2007).
- M-C. Carotta, M. Ferroni, V. Guidi, G. Martinelli, "Preparation and Characterization of Nanostructured Titania Thick Films" *Adv. Mater.* **11** [11] pp. 943-946 (1999).
- E. Cazzanelli, N. Scaramuzza, G. Strangi, C. Versace, R. Ceccato, G. Carturan, "Sol-Gel Synthesis and Characterization of TiO₂ and TiO₂-V₂O₅ films for Electrodes in Asymmetric Liquid Crystal Cells" *Proceed. "Meeting of the Italian Liquid Crystal Society"*, 24, 05, 2000 Calabria, (Italy); paper A. 372 (2002), pp. 305-320.
- I. Truijen, M. K. Van Bael, H. Van den Rul, J. D'Haen, J. Mullens, "Preparation of nanocrystalline titania films with different porosity by water-based chemical solution deposition", *J. Sol-Gel Sci. Technol.*, **43** 291-297 (2007).
- Z. Liu, Z. Jin, X. Liu, Y. FU, G. Liu, "Fabrication of Ordered TiO₂ Porous Thin Films by Sol-Dipping PS Template Method", *J. Sol-Gel Sci. Techn.* **38** 73-78 (2006).
- X. Liu, Z. Jin, S. Bu, T. Yin, "Influences of Solvent on Properties of TiO₂ Porous Films Prepared by a Sol-Gel Method from the System Containing PEG", *J. Sol-Gel Sci. Techn.*, **36** 103-111 (2005).
- G. Q. Liu, Z. G. Jin, X. X. Liu, T. Wang, Z. F. Liu, "Anatase TiO₂ porous thin films prepared by sol-gel method using CTAB surfactant", *J. Sol-Gel Sci. Techn.* **41** 49-55 (2007).
- W.-Y. Chang, Y.-C. Lin, W.-W. Ke, Y.-S. Hsieh, N.-H. Kuo, "Combined TiO₂/SnO₂ material with adding Pt by sol-gel technology for humidity sensor", *Mater. Sci. Forum*, **505-507** 397-402 (2006).
- Q. Qi, Y. Feng, T. Zhang, X. Zheng, G. Lu, "Influence of crystallographic structure on the humidity sensing properties of KCl-doped TiO₂ nanofibers", *Sensors and Actuators B*, **139** 611-617 (2009).
- M. L. Zhang, Z. H. Yuan, C. Zheng, "Fast response of undoped and Li-doped titania thick-films at low temperature", *Sensors and Actuators*, **B** **131** 680-686 (2008).
- K. P. Biju, M. K. Jain, "Effect of crystallization on humidity sensing properties of sol-gel derived nanocrystalline TiO₂ thin films" *Thin Solid Films*, **516** 2175-2180 (2008).
- B. C. Yadav, A. K. Srivastava, P. Sharma, "Resistance Based Humidity Sensing Properties of TiO₂" *Sensors & Transducers*, **81** [7] 1348-1353 (2007).
- P. M. Faia, A. J. Ferreira, C. S. Furtado, "Establishing and interpreting an electrical circuit representing a TiO₂-WO₃ series of humidity thick film sensors", *Sensors and Actuators B*, **140** 128-133 (2009).
- S. Kozhukharov, "Relationship between the Conditions of Preparation by the Sol-Gel Route and the Properties of the Obtained Products", *J. Univ. Chem. Technol. Met.*, **44** [2] 143-150 (2009).
- M. Zacharescu, A. Wittmar, V. Teodorescu, C. Andronescu, M. Wittmar, M. Veith, "TiO₂-CeO₂ Nanometric Powders Prepared by Sol-Gel Method", *Z. Anorg. Allg. Chem.*, **635** 1915-1924 (2009).
- P. Suegama, H. de Melo, A. Benedetti, I. Aoki, "Influence of cerium (IV) ions on the mechanism of organosilane polymerization and on improvement of its barrier properties" *Electrochim. Acta*, **54** [9] 2655-2662 (2009).
- C. E. Bamberger, T. J. Haverlock, S. S. Shoup, O. C. Kopp, N.A. Stump, "Compounds of cerium, titanium and oxygen", *J. Alloys Comp.* **204**, 101-107 (1994).
- O. Vasylyev, M. Brychevski, I. Brodnikovskiy, L. Dubyivskiy, V. Vereschak, V. Chedryk, R. Steinbrech, J. Malzbender, J. Irvine, C.-D. Savaniu, I. Kosacki, A. Smirnova, V. Sadykov "10Sc1CeSZ Powders, and their bulk and film electrolytes: mechanical, electric, and catalytic properties", *Proceed. "Second European Fuel Cell Technology Applications Conference, 2007, Rome, (Italy), EFC2007-39001*.
- N. F. Starodub, A. N. Shmiryeva, "Immune-Enzymatic Biosensors Based on the Cerium Isfets: Some Physical and Functional Characteristics at the Determination of Simazine and T2-Mycotoxin", *Proceed. "Sensor + Test Conference"* 7-9. 06. 2011, 2011 Nuernberg, (Germany), P1.3, pp. 680 - 685.
- P. Nikolopoulos, X. Mantzouris, F. Tietz, "Physical Characterization of Y₂O₃ - CeO₂ - TiO₂ (YCT) Mixed Oxides and Ni/YCT Cermets as Anode Electrodes in Solid Oxide Fuel Cells" *Proceed. "10th International Conference and Exhibition of the European Ceramic Society"* (ECerS-10), June 17-21, 2007 Berlin, (Germany).
- P. Nikolopoulos, X. Mantzouris, F. Tietz, "Physical Characterisation of Y-Ce-Ti Oxides as Mixed Conducting Anode Materials in Solid Oxide Fuel Cells", *Proceed. 7th European Solid Oxide Fuel Cell Forum*, 3-7 July 2006, Lucerne, (Switzerland) P. 0701-034.
- A. Trinchì, Y. X. Li, W. Wlodarsky, S. Kaciulis, L. Pandoufi, S. Viticoli, E. Comini, "Investigation of sol-gel prepared CeO₂-TiO₂ thin films for oxygen gas sensing", *Sensors and Actuators B*, **95** 145-150 (2003).
- EU Directive 2002/95/EC "Restriction of Hazardous Substances in Electrical and Electronic Equipment" (RoHS directive 2002); www.broadcom.com/docs/; www.chem.agilent.com/
- U.S. Department of Health and Human Services, Public Health Service, Agency for Toxic Substances and Disease Registry, (2008) Toxicological profile for Chromium. www.atsdr.cdc.gov/toxprofiles/tp7.pdf.

31. E. A. Matter, S. Kozhukharov, M. Machkova, V. Kozhukharov, "Electrochemical studies on the corrosion inhibition of AA2024 aluminium alloy by rare earth ammonium nitrates in 3.5 % NaCl solutions" *Proceed. "9th European Symposium on Electrochemical Engineering"* (9th ESEE) 19 – 23 June 2011, Chania (Greece).
32. C.J. Brinker, G.W. Scherer, "Sol-Gel Science: The Physical and Chemistry of Sol-Gel Processing", *Academic Press*, San Diego, (USA) 1990.
33. J. Rodriguez-Carvajal, "FULLPROF version 3.0. 0." Laboratoire Leon Brillouin, CEA-CNRS (2003).
34. "JCPDS Crystal Data Determinative Tables, Inorganic compounds", 3-rd Edition, Eds. H. Oudik, A. Mighell, , *US NSRDS Publ. Vol. 4* (1978), p. 17.
35. A. Linsebigler, G. Lu, J. Yates, "Photocatalysis on TiO₂ Surfaces: Principles, Mechanisms, and Selected Results", *Chem. Rev.* **95** 735-758 (1995).
36. R. DeVries, R. Roy, "A Phase Diagram for the System Ti-TiO₂. Constructed from Data in the Literature" *Bulletin Amer. Ceram. Soc.*, **33** 370-372 (1954).
37. A. H. Dorian, C. C. Sorrell, "Review of the anatase to rutile phase transformation", *J. Mater. Sci.*, **46** [4] 855-874 (2011).
38. T. Seiyama, N. Yamazoe, H. Arai, "Ceramic humidity sensors", *Sensors and Actuators*, **4** 85-96 (1983).
39. E. C. Dickey, O.K. Varghese, K.G. Ong, D.W. Gong, M. Paulose and C.A. Grimes, "Room temperature ammonia and humidity sensing using highly ordered nanoporous alumina films", *Sensors*, **2** (2002) 91-110.
40. M. K. Jain, M. C. Bhatnagar, G. L. Sharma, "Electric circuit model for MgO-doped ZrO₂-TiO₂ ceramic humidity sensor", *Appl. Phys. Lett.*, **73** 3854-3856 (1998).
41. Experimental Analysis 8/8/2006. (http://www.physics.usyd.edu.au/pdfs/current/jphys/lab/exp_analysis.pdf)
42. W. R. Leo, *Techniques for Nuclear and Particle Physics Experiments*, Springer-Verlag, 1992.
43. N. Yamazoe, T. Seiyama, "Humidity sensors: Principles and applications", *Sensors and Actuators*, **10** [3-4] 379-398 (1986).
44. T. Nenov, S. Yordanov, *Ceramic sensors: Technology and applications*, Technomic Publ. Co. Inc., Lancaster-Basel, 1996.
45. S. J. Gregg, K. S. W. Sing, *Adsorption, surface area and porosity*. 2nd edition, Academic Press Inc., London-New York, 1982.
46. Y. Shimizu, H. Arai, T. Seiyama, "Theoretical studies on the impedance - humidity characteristics of ceramic humidity sensors", *Sensors and Actuators*, **7** [1] 11-22 (1985).
47. E. Traversa, "Ceramic sensors for humidity detection: the state-of-the-art and future developments", *Sensors and Actuators B*, **23** 135-156 (1995).
48. T. Nenov, S. Ivanov, "Linearization of characteristic of relative humidity sensor and compensation of temperature impact", *Sensors and Materials*, **18** [2] 95-106 (2007).
49. T. Islam, H. Saha, "Study of long-term drift of a porous silicon humidity sensor and its compensation using ANN technique", *Sensors and Actuators A*, **133** [2] 472-479 (2007).
50. C.-Y. Lee, G.-B. Lee, "Micromachine-based humidity sensors with integrated temperature sensors for signal drift compensation", *J. Micromech. Microeng.*, **13** [5] 620 (2003).

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