ISSN 1726-5479

SENSORS & TRANSDUCERS

7 vol. 142 /12

Sensor Networks and Wireless Sensor Networks

International Frequency Sensor Association Publishing

Sensors & Transducers

Volume 142, Issue 7, July 2012 www.sensorsportal.com ISSN 1726-5479

Sensors & Transducers Journal

Contents

Volume 142
Issue 7
July 2012

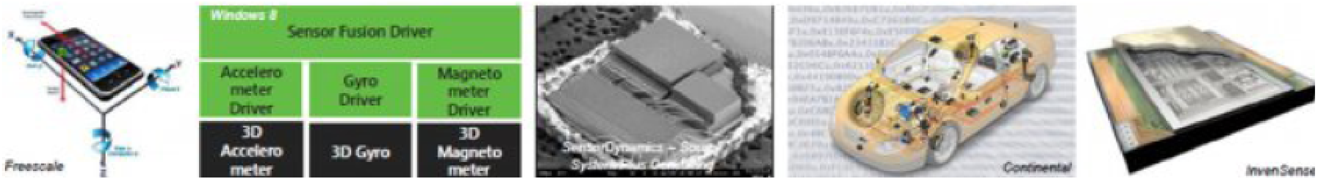
www.sensorsportal.com

ISSN 1726-5479

Research Articles

Authors are encouraged to submit article in MS Word (doc) and Acrobat (pdf) formats by e-mail: editor@sensorsportal.com
Please visit journal's webpage with preparation instructions: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm

International Frequency Sensor Association (IFSA).



Sensors & Transducers Journal, Vol. 142, Issue 7, July 2012, pp. 143-149

Sensors & Transducers

ISSN 1726-5479

TiO_2 Thin Film Capacitive Humidity Sensor Based on Sol-gel Technique

[*] Manju Pandey, [**] Debdulal Saha, [*] K. Sengupta, *S. S. Islam, [*]M. P. Singh

*Nano-Sensor Research Laboratory, F/O Engineering and Technology,
Jamia Millia Islamia (Central University), New Delhi, India
[**] Sensors and Actuators Division, Central Glass & Ceramic Research Institute,
196 Raja S. C. Mullick Road, Kolkata-700032, India
E-mail: kamalendusengupta@yahoo.co.in, manju.pandey22@yahoo.com

Received: 5 May 2012 /Accepted: 23 July 2012 /Published: 31 July 2012

Abstract: A new approach for humidity sensing is reported. The sensor is based on ordered nanoporous titanium dioxide (TiO_2) thin film over silver palladium coated nonporous alumina substrate. Porous TiO_2 thin films were prepared by emulsification-gelation technology using hydrolysis and reflux process. Coating optimization was achieved and hydrophilicity of the TiO_2 thin film was determined. SEM results revealed that pores were distributed uniformly throughout the sample, which enhanced the adsorption of water molecule over the film. Raman study clearly confirmed the anatase and rutile phase of TiO_2 thin film. Electrical sensing response was calculated using impedance measurement. It was found that at an optimized coating thickness the sensitivity of our humidity sensor was suitable for commercial applications. *Copyright © 2012 IFSA.*

Keywords: Humidity sensor, TiO_2, Thin films, Sol-Gel, Raman spectroscopy.

1. Introduction

Thin film technology is found to be in many applications including microelectronics, optics, magnetic, hard and corrosion resistant coating, micro-mechanics etc [1-7]. Progress in each of these areas depends upon the ability to selectivity and controllability on deposited thin film thickness ranging from tens of angstroms to micro meter with specified physical properties. This, in turn, requires control often at the atomic level of film microstructure and microchemistry. There are a vast number of deposition methods available and in use today [8-10]. Titanium dioxide(TiO_2) is being used in a great variety of applications. It has been investigated for humidity and gas-sensing behavior. It has three different crystallographic forms: brookite, anatase and rutile. Anatase is metastable and converted irreversibly into rutile at high temperature. Its preparation is fundamental to obtain properties suitable for gas-sensing applications such as: structural stability, porosity and high surface-to-volume ratio in order to emphasize surface effects. The sensing properties of TiO_2 films are based on surface interactions of reducing or oxidizing species, which affect the conductivity of the films. TiO_2 films have been made by a variety of techniques such as e-beam evaporation, magnetron sputtering technique, anodization, chemical vapour deposition (CVD) and sol-gel technique. Among the different methods for the preparation of thin TiO_2 film, sol-gel method has many advantages, particularly the possibility of producing large surface. The films are generally deposited by dip-coating, but may also be deposited using spin coating, the sol-gel processes are particularly efficient in producing thin, transparent layers on various substrate. Numerous literature reports on the fabrication of TiO_2 thin films by sol-gel dip coating technique using many types of titanium alkoxides as precursors. In this work, we report the fabrication of TiO_2 nanostructured films from sol–gel technique and their application as humidity sensors. The impedance spectroscopy technique was used in order to evaluate the electrical behavior of the samples under different atmospheres and temperatures.

2. Experimental

2.1. Development of Porous Titania Sensor

For making capacitive type humidity sensor, films are developed on a silver palladium coated α-Alumina Substrate of size (20 mm × 20 mm × 1 mm). Second electrode is formed on film coated substrates. It is then finally fired at 900 ^{o}C for curing the electrodes (Fig-1). The film on the silver palladium surface is used as transducing layer for sensing the ambient trace moisture. The effective dielectric of the porous layer undergoes a large change when water vapour diffuses to the inner regions of the pore structure and absorbs on the porous layer. The capacitive sensor developed in this work consists of a non porous substrate coated with silver palladium on which the thin films are deposited of thickness 120-150 nm. It is covered by another porous electrode of silver palladium. Contacts are taken from the two parallel silver palladium electrodes. The water vapour is free to diffuse through the porous electrodes to the porous titania film shows increase in capacitance.

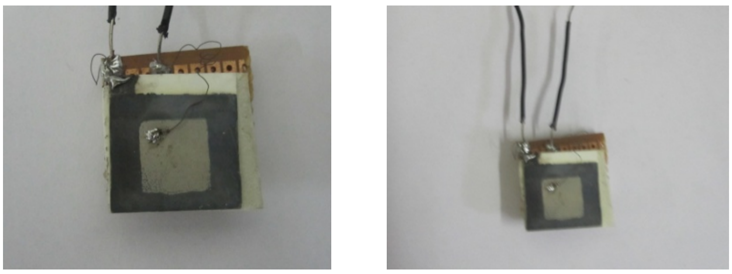


Fig. 1. TiO_2 humidity sensors.

2.2. Preparation of TiO_2 Thin Film

Fig. 2 shows the flow chart of the preparation of TiO_2 thin film using sol-gel method. TiO_2 was synthesized with titanium (IV) isopropoxide(TIP) as its precursor. TiO_2 sol was prepared by adding appropriate amount of isopropanol to a 50 ml beaker containing 3.6 ml of TIP. This mixture was stirred vigorously for 10 min using a magnetic stirrer. Subsequently, 1N HCl was added after adding DI water(Millipore, USA) and the mixture was rigorously stirred for 2 hr with the flask sealed with

Parafilm to avoid any loss of isopropanol and/or water by evaporation during mixing . This mixture has a molar ratio of TIP: isopropanol: H_2O: HCl of 1:27:5:20. The hydrolysis and the polycondensation of titanium alkoxides proceed according to the following scheme,

$$Ti(OR)_4 + H_2O \longrightarrow Ti(OR)_3(OH) + ROH$$

$$Ti(OR)_4 + Ti(OR)_3(OH) \longrightarrow Ti_2O(OR)_6 + ROH$$

$$Ti(OR)_4 + 2H_2O \longrightarrow TiO_2 + 4ROH$$

A TiO_2 film was formed on the silver palladium coated alumina substrate by dipping it into the solution and pulling it up at a constant rate by a dip coater machine. This process is optimal for producing highly uniform coatings, by simple control of the thickness through control of the speed of withdrawal from the coating solution. The dip coated alumina substrate along with first electrode was therefore left to dry at ambient temperature followed by heating at 60 ^oC. The dried films were further heated in a muffle furnace to 450 ^oC at a heating rate of 100 ^oC/hr and maintained at this temperature for 1 hour. Then, the films were cooled down to room temperature at similar cooling rate.

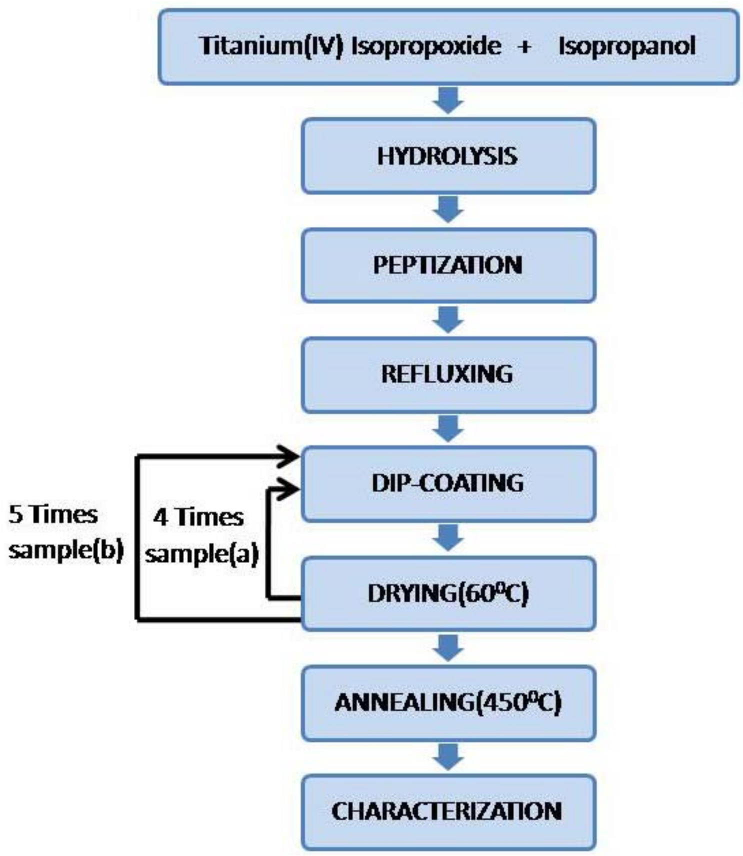


Fig. 2. Flow chart for the preparation of TiO_2 thin films.

2.3. Coating Optimization

The repeated direct sol-gel coating tends to crack due to the presence of large strain upon heat treatment and densification. So optimization in coating process is an essential factor for developing a rigid, uniform and crack free thin films. We have made two samples with different number of coating for optimization.

3. Results and Discussion

3.1. Morphologies of Coatings

The morphologies of TiO_2 thin film coatings are shown in Fig. 3. It can be seen from Fig. 3 ((i), (ii)) that the sample (a), which has four times coatings has uniformity and no obvious cracks appear. It showed the successful preparation of porous TiO_2 thin films with uniform and interconnected pore distribution throughout the entire sample. From Fig. 3 ((iii), (iv)) shows the sample which have five times coatings, and it was observed that the films was dense and smooth surface but full of cracks exist in the coating. These results reveal that for making uniform and crack free thin film of TiO_2, times of coating should not exceed more than four, and this is confirmed by repeating the said experiment several times.

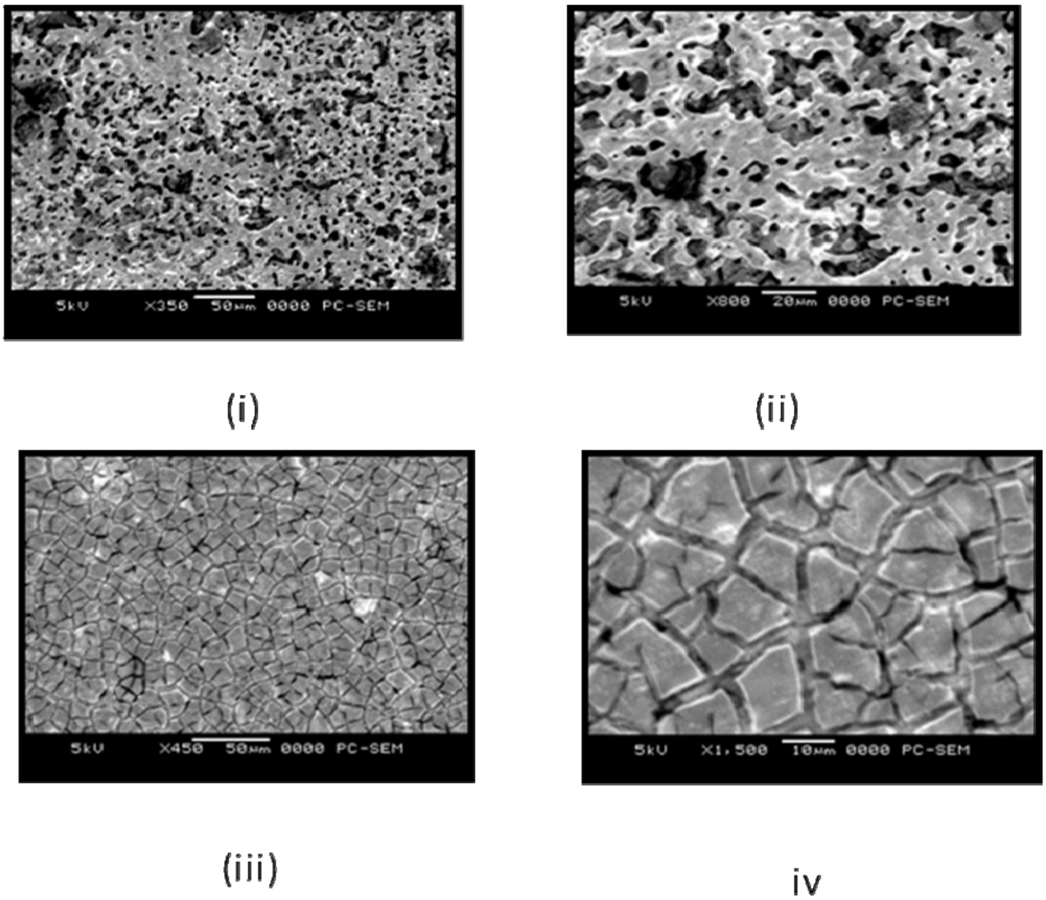
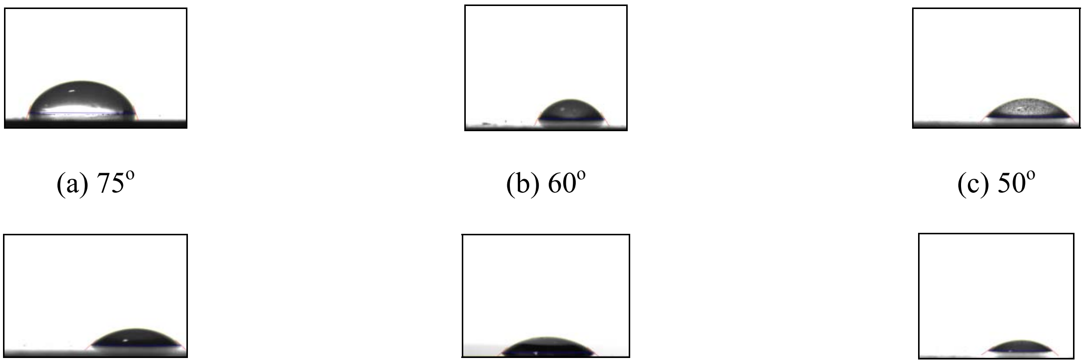


Fig. 3. SEM images of TiO_2 thin film annealed at 900 ^{0}C of sample (a) ((i), (ii)), and sample(b) ((iii), (iv)).

3.2. The Analysis of Contact Angle

Contact angle measurements (Fig. 4) were carried out to detect the surface nature of the TiO_2 thin films which in turn showed the affinity towards the selective target. In measurement, a water droplet is placed on the surface and adjusts its objective for the horizontal direction to make eyepiece cross thread parallel to substrate surface. Table 1 shows that the water contact angles decreased with the number of TiO_2 coating of film (Fig. 5). The reason was that in corporation of TiO_2 thin film on siver-palladium coated alumina substrate decreased the roughness of the surface and increased the surface free energy.



(a) 75° (b) 60° (c) 50°

(d) 45° (e) 40° (f) 35°

Fig. 4. Variation of contact angle with different surface (a) alumina substrate, (b) silver Palladium coated alumina substrate, (c)first coating of TiO_2, (d)second coating of TiO_2, (e)third coating of TiO_2, and (f)fourth coating of TiO_2.

Table 1. Coating thickness dependent contact angle study.

	Surface	No. of Coating	Contact Angle(θ)
(a)	Alumina Substrate	Nil	75°
(b)	Alumina Substrate + Silver Palladium (1st Electrode)	Nil	60°
(c)	Alumina Substrate + Silver Palladium (1st Electrode)	One	50°
(d)	Alumina Substrate + Silver Palladium (1st Electrode)	Two	45°
(e)	Alumina Substrate + Silver Palladium (1st Electrode)	Three	40°
(f)	Alumina Substrate + Silver Palladium (1st Electrode)	Four	35°

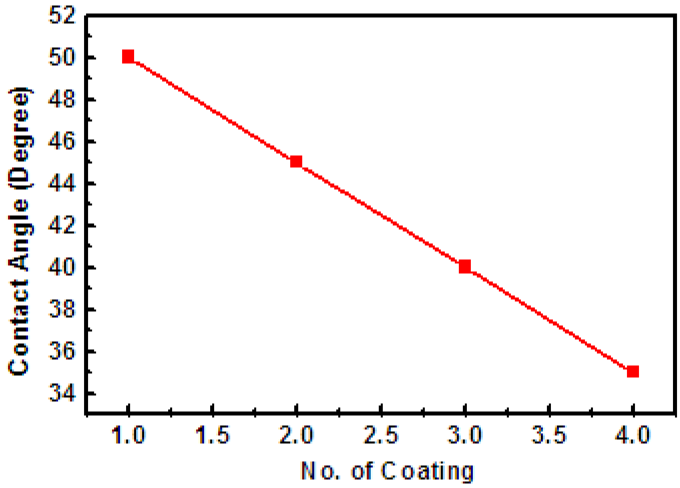


Fig. 5. Variation of contact angle with no. of coatings.

3.3. Raman Spectra of TiO_2 Thin Film

Among the various techniques to characterize TiO_2, Raman spectroscopy has certain unique advantages, as it is very sensitive to nanocrystallinity of anatase and rutile TiO_2.

The Raman spectrum between 100 and 1000 cm^{-1} of TiO_2 is shown in Fig. 6. As it can be seen, a well-defined Raman peak is located at 141.57 cm^{-1} which clearly corresponds to anatase phase. The spectrum of TiO_2 rutile, prepared from a xerogel and calcined at high temperatures, showed two main peaks at 446.04 and 609.41 cm^{-1}. It is observed that both the phases coexist even after the annealing process.

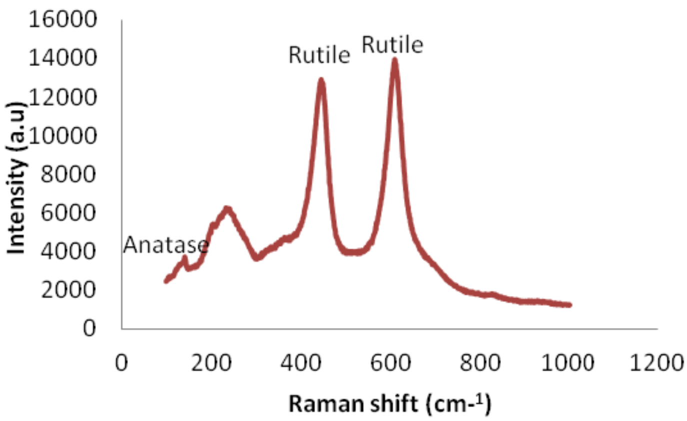


Fig. 6. Raman spectra of TiO_2 thin film.

3.4. Sensing

The sensor was characterized in a controlled chamber with temperature maintained at 30 ^{0}C. The ppm vs. moisture inside the chamber was varied from 20 RH%-90 RH% in a controlled manner with the help of needle valve which controls the moisture level. The corresponding change in capacitance was measured by Keithley 4200 model. For calibration, commercial moisture sensor (SHAW, UK) was used in parallel with the controlled chamber.

Fig. 7 showed that the capacitance of the sample increases almost linearly with relative humidity. This is due to the absorption property of the dielectric film whose ionic conductivity increases due to the water content in the pores of the film. Once the pores are being filled with water content, the dielectric property will be predominant over the conductivity of water [11].

4. Conclusions

In this work TiO_2 based humidity sensor was fabricated. Thin film TiO_2 humidity sensor was fabricated using dip coating technique. The sample showed a good variation in its capacitance with variation in the relative humidity which can be translated into voltage or current as desired. Hydrophilic surface was created by measuring contact angle after each coating that increase the surface energy. A sophisticated electronic system was developed using these films as sensing element, which could successfully detect low level RH% of moisture at room temperature.

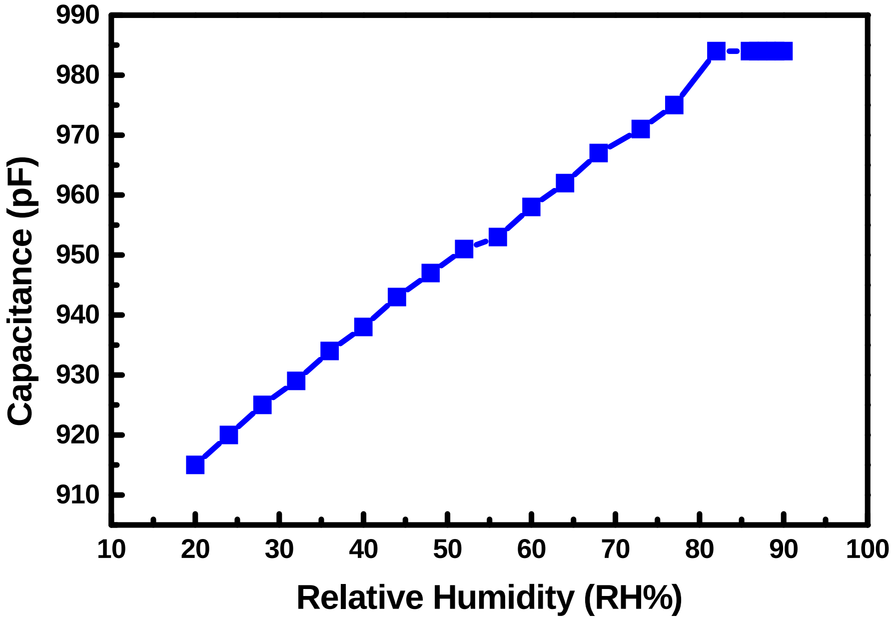


Fig. 7. Variation of capacitance with relative humidity.

References

[1]. I. Strawbridge, P. F. James, Thin silica films prepared by dip coating, *J. Non-Cryst. Solids*, 82, 1986, pp. 366-372.

[2]. C. J. Brinker, A. J. Hurd, K. J. Ward in Ultrastructure Processing of Advanced Ceramics, eds. J. D. Mackenzie and D. R Ulrich, *Wiley*, New York, 1988, p. 223.

[3]. H. Schroder, Physics of Thin Films, *Academic Press*, New York-London, Vol. 5, 1969, pp. 87-141.

[4]. H. Dislich, Sol-gel: Science, processes and products, *J. Non-Cryst. Solids*, 80, 1986, pp. 115-121.

[5]. C. J. Brinker, G. W. Scherer, Sol-Gel Science, *Academic Press Inc*., 1990, p. 236.

[6]. O. Yamamoto, T. Sasamoto, M. Inagaki, Indium tin oxide thin films prepared by thermal decomposition of ethylene glycol solution**,** *J. Mater. Res*., 7, 1992, p. 2488.

[7]. A. Maddalena, R. Del Machio, S. Dire, A Raccanelli, Electrical conductivity of tin oxide films prepared by the sol-gel method, *J. Non-Cryst. Solids,* 121, 1990, p. 365.

[8]. Q. Fu. C. B. Cao, H. S. Zhu, Preparation of alumina films from a new sol-gel route, *Thin Solid Films*, 348, 1999, pp. 99-102.

[9]. T. Ogikara, Alumina Coating on Glass Fibers by Sol-Gel Method and Mechanical Property of GRC, *J. Soc. Mater. Sci*., 49, 2000, pp. 200-203.

[10]. T. Olding, M. Sayer, D. Barrow, Ceramic sol–gel composite coatings for electrical insulation, *Thin Solid Films*, 398/399, 2001, pp. 581-586.

[11]. Lit Ho Chong, Kanad Mallik, C H de Groot and Reinhard Kersting, The structural and electrical properties of thermally grown TiO2 thin films, *J. Phys.: Condens. Matter*, 2006, 18 645–657.

___

Guide for Contributors

Aims and Scope

Sensors & Transducers Journal (ISSN 1726-5479) provides an advanced forum for the science and technology of physical, chemical sensors and biosensors. It publishes state-of-the-art reviews, regular research and application specific papers, short notes, letters to Editor and sensors related books reviews as well as academic, practical and commercial information of interest to its readership. Because of it is a peer reviewed international journal, papers rapidly published in *Sensors & Transducers Journal* will receive a very high publicity. The journal is published monthly as twelve issues per year by International Frequency Sensor Association (IFSA). In additional, some special sponsored and conference issues published annually. *Sensors & Transducers Journal* is indexed and abstracted very quickly by Chemical Abstracts, IndexCopernicus Journals Master List, Open J-Gate, Google Scholar, etc. Since 2011 the journal is covered and indexed (including a Scopus, Embase, Engineering Village and Reaxys) in Elsevier products.

Topics Covered

Contributions are invited on all aspects of research, development and application of the science and technology of sensors, transducers and sensor instrumentations. Topics include, but are not restricted to:

- Physical, chemical and biosensors;
- Digital, frequency, period, duty-cycle, time interval, PWM, pulse number output sensors and transducers;
- Theory, principles, effects, design, standardization and modeling;
- Smart sensors and systems;
- Sensor instrumentation;
- Virtual instruments;
- Sensors interfaces, buses and networks;
- Signal processing;
- Frequency (period, duty-cycle)-to-digital converters, ADC;
- Technologies and materials;
- Nanosensors;
- Microsystems;
- Applications.

Submission of papers

Articles should be written in English. Authors are invited to submit by e-mail editor@sensorsportal.com 8-14 pages article (including abstract, illustrations (color or grayscale), photos and references) in both: MS Word (doc) and Acrobat (pdf) formats. Detailed preparation instructions, paper example and template of manuscript are available from the journal's webpage: http://www.sensorsportal.com/HTML/DIGEST/Submition.htm Authors must follow the instructions strictly when submitting their manuscripts.

Advertising Information

Advertising orders and enquires may be sent to sales@sensorsportal.com Please download also our media kit: http://www.sensorsportal.com/DOWNLOADS/Media_Kit_2012.pdf