Research Journal of Applied Sciences, Engineering and Technology 9(9): 715-721, 2015
DOI:10.19026/rjaset.9.2616
ISSN: 2040-7459; e-ISSN: 2040-7467

Submitted: August 31, 2014 Accepted: October 12, 2014 Published: March 25, 2015

Research Article

Tapered Optical Fiber Humidity Sensor Coated with Nano-crystalline ZnO Doped with KCI

[1]Sivacoumar Rajalingam, [1]Z.C. Alex and [2]Elizabeth Rufus
[1]School of Electronics Engineering, VIT University, Vellore, Tamil Nadu, India
[2]Department of Electronics and Communication Engineering, Middle East College, Knowledge Oasis, Al Rusayl Muscat, Sultanate of Oman

Abstract: In this research study we have targeted to fabricate a tapered optical fiber coated with zinc oxide doped with KCl to improve the humidity sensing capability of zinc oxide. The optical fiber was tapered through chemical etching method by HF acid (49.5%). The nano-crystalline Zinc Oxide (ZnO) was synthesized using single molecular precursor method doped with KCl. The resulting material was characterized with Fourier Transform Infrared spectroscopy (FTIR), X-Ray Diffractometry (XRD) and Scanning Electron Microscopy (SEM). The sensing mechanism of this sensor is based on the change of the optical properties of the coating when the relative humidity increases. The humidity sensing characteristic has been estimated by measuring the Optical Permeability (OP) as a function of percentage of Relative Humidity (%RH) in the ranging from 5 to 98% inside a closed chamber. The tapered optical fiber tested with an overlay coating at the optimal working point achieves better sensitivity. The experimental results show that the 5.7 wt% KCl doped ZnO nano-fibers hold super-rapid response and recovery than normal ZnO coating.

Keywords: Chemical etching (HF), evanescent field sensors, KCl nanocrystals, tapered fiber sensor, Zno

INTRODUCTION

A wide range of optical fiber humidity sensors have been reported in the literature. Most of these fiber optic humidity sensors work on the basis of a hygroscopic material coated over the optical fiber to modulate the light propagating through the fiber. In general, sensitive elements are needed for efficient fibre-optic sensing, which amplify the chemical interaction of analytes and convert it into a measurable optical response as signal (Ueda *et al*., 2007). Current research in the field of optical fibre sensors is focusing on the creation and development of new sensitive elements which can expand an application area and increase the number and range of the analytes that can be utilized by fibre-optic sensors.

The Humidity sensors have been gained much attention of scientists because of their demand for the monitoring of humidity in the environment and also in various industrial processes including food, electronics, textile and pharmaceuticals (Li Lijuan and Minchai, 1998). It is found that most of the existing humidity sensors are based on the modulation of their electrical parameters like resistance, capacitance or conductance however; they are expensive, large in size and sometimes cannot operate at room temperature. Thus much attention has been paid lately to the development of compact, low-priced sensors that can detect humidity in real time at room temperature.

The use of nano-materials to fabricate sensors is one of the most exciting approaches because nano-materials have a unique structure and high surface-to-volume ratio (Muto *et al*., 2003). Many attempts have been made to fabricate nano-crystalline ZnO of unique properties for versatile applications in the area of transparent electronics, light emitting diodes, piezoelectric devices, spin electronics and chemical sensors (Shukla *et al*., 2009; Kersey, 1996). Further KCl doped nano-crystalline ZnO has stable structure with good chemical stability and favorable properties that are suitable for device fabrications (Qi *et al*., 2008). In the past few years, many reports have been published on the fabrication of ZnO films of different surface morphologies such as single and multi-dimensional nano-structural shapes like nano-wire, nano-tube, nano-ring and nano-tetrapods (Yang *et al*., 2007; Correia *et al*., 2012) using various film deposition techniques for example chemical vapor deposition, thermal evaporation, electro-deposition (Sakai *et al*., 1996).

In this study, we demonstrate a simple route for the synthesis of Potassium doped ZnO nano-fibers with super-rapid response (about 2 sec) and recovery (about 1 sec) to humidity. ZnO has been chosen as the

Corresponding Author: Sivacoumar Rajalingam, School of Electronics Engineering, VIT University, Vellore, Tamil Nadu, India

functional material for its high sensing performance (Qi *et al*., 2009; Xiaofeng *et al*., 2007). At the same time, the addition of potassium ions (K+) is used to increase the carrier concentration, thereby resulting in the improvement of the humidity sensing performance (Li and Minchai, 2010; Qi *et al*., 2008; Shukla *et al*., 2009). The advantageous features of the present sensor include low price tag, ease of fabricated, sufficiently larger operational range, good stability and sensitivity.

METHODOLOGY

Selection of chemicals: Zinc acetate dihydrate Zn $(OAc)_2 \cdot 2H_2O$, 99%, Sigma-Aldrich), Potassium Chloride (KCl), ethanol (99.5%, E. Merck), methanol (99.8%, E. Merck) and benzene (99.8%, Sigma-Aldrich) were used without further purifications.

Synthesis of precursor: To prepare the precursor solution, 50 mM of Zn $(OAc)_2 \cdot 2H_2O$ and an appropriate amount of KCl was dissolved in a 25 mL of anhydrous ethanol. Next, the resulting mixture was stirred for 2 h at room temperature until the Zn $(OAc)_2 \cdot 2H_2O$ flakes were completely dissolved. In the obtained homogeneous solution, added 5 mL of anhydrous benzene and again stirred at 60°C for 24 h. The solution is then kept at standing for 72 h to ensure hydrolytic stability against any sort of precipitation, coagulation or suspension. The prepared precursor solution was used further for the fabrication of nano-crystalline ZnO films using Dip Coating Method (Shukla *et al*., 2004; Gupta, 2006).

Characterization: The film prepared by the above process has been characterized using FTIR, XRD and SEM techniques are show.

Fabrication of tapered fiber: One of the simplest ways to create tapers is to use HF as the etching agent. As the fiber is etched, the conditions governing the propagation of light inside the fiber change with the decrease in fiber diameter (Gupta, 2006; Murray and Dutcher, 2006). To monitor the progress of etching, it is desirable that the fabrication method incorporates a means to measure the light coming in at the output end of the fiber. This will allow the precise control of the etching process and consequently, the management of the diameter of the tapered region.

During the etching process, the diameter of the fiber declines in the region exposed to HF. HF reacts with silica according to the following reactions, with the second reaction dominating at high HF concentration:

$$SiO_2+4HF \rightarrow SiF_4+2H_2O \quad (1)$$

$$SiO_2+6HF \rightarrow H_2SiF_6+2H_2O \quad (2)$$

Etching was stopped at different times by the procedure described above and the resulting fiber diameter was measured using an optical microscope (model IMT-2, Olympus, Japan) equipped with a video camera linked to a computer. SCION IMAGE software (Scion Corp.) was used to acquire the microscope images from the camera. With large experimental trials, it became clear that the length of the etching time needed at room temperature was in the order of about 12 from 125 to 61 μm for a multimode fiber (125/62.5 μm).

In the experiments conducted the exposed core region is 6.4 mm. The fiber is surrounded by 49.5% (w/w) HF uniformly. Total volume of HF solution added to the chamber is 200 mL. The total amount of fiber material that can potentially react and dissolve in HF is 0.72 mmol and the amount of HF present in the etching chamber is 5000 mmol (Mehdi *et al*., 1997).

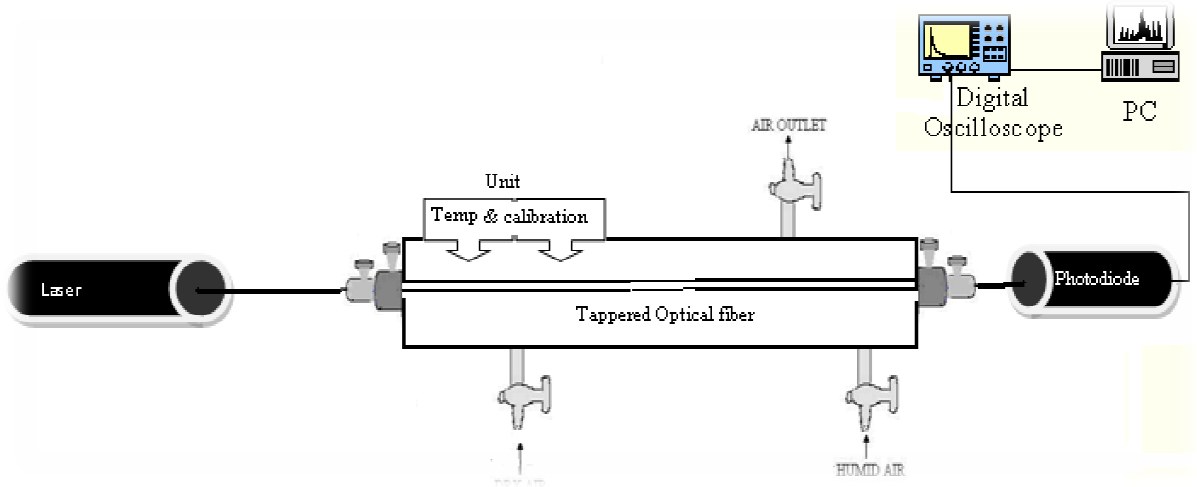

Fig. 1: Schematic illustration of optical fiber based humidity sensor using nano-crystalline ZnO film as a sensing element in a device assembly

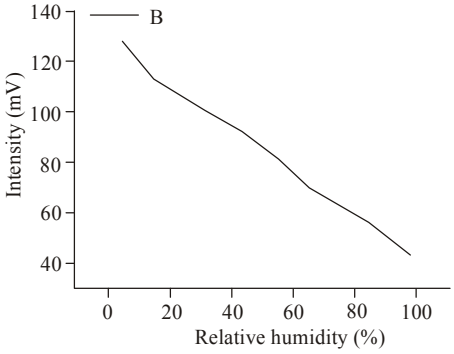

Fig. 2: Linear relationship between optical output and % relative humidity of KCl doped nano-crystalline ZnO

Table 1: Relative humidity of saturated salts at room temperature

Saturated salts	Relative humidity
Lithium chloride	11.30
Potassium acetate	23.11
Magnesium chloride	33.07
Potassium carbonate	43.16
Magnesium nitrate	52.89
Sodium chloride	75.29
Potassium chloride	84.34
Potassium nitrate	93.58
Potassium sulfate	97.30

Total HF consumed by the dissolution reaction (2), is less than 0.5%.

Device fabrication, assembly and sensing measurements: The Potassium doped nano-sized ZnO coated with tapered optical fiber was fixed inside a glass chamber via a mid-hole. The resulting arm of fiber were projected outside and coupled with normal optical fiber. And the other whole present near the inlet side is to send the humidity content inside the closed chamber which should be passed using different chemicals which has a standard value of moisture content (Bariain *et al*., 1998). This vapour (moisture) content of chemicals should be passed such that the chemicals should be poured in a beaker which has one inlet and one outlet so that one is for sending the vapour content inside while the air is pumped through a pump and the other is to send the vapour content inside the closed chamber which is as shown in the Fig. 1 (Corres *et al*., 2006a). The optical fiber was a standard multimode optical fiber with core and cladding diameters of 68 and 125 μm, respectively. The unpolarized laser light from He-Ne laser source (2 mW) was passed from one end of the fiber and the output intensity was measured at the other end of the optical fiber.

During our experimental observations setup, the relative humidity inside the sensing chamber was variably controlled up to 95%. To increase the humidity inside the chamber a beaker filled with the phosphorous pentoxide (P_2O_5) which has 5% of moisture content which is standard value was placed in a bottle which has two connected pipes of which one end is connected to the glass chamber and the other end is connected to the pressure pump so that the humidity inside the chamber increases to 5% and with respect to that the intensity change is noted as output as shown in Fig. 2 and Table 1 (Bariáin *et al*., 2000). The same process is continued to increase the moisture content inside the chamber with the saturated salt solutions such as LiCl, $MgCl_2$, Mg $(NO_3)_2$, NaCl, KCl and KNO_3 and their corresponding RH values were 11, 33, 54, 75, 85 and 95%, respectively. A thermometer with least count of 0.1°C was also positioned together for monitoring the temperature inside the chamber.

The complete experimental setup is shown in Fig. 1. All experiments were conducted at room temperature (25°C), with the same sensor used for each set of measurements. Prior to each measurement the sensor was heated in vacuum at 100°C for 2 h to completely remove the adsorbed moisture. All measurements were carried out at 25°C.

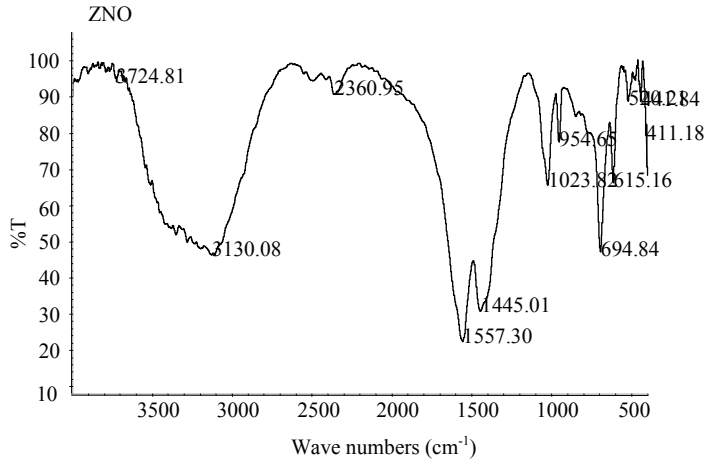

Fig. 3: FTIR spectra of the ZnO film prepared at 25°C

RESULTS

The tapered optical fiber was employed as a candidate to act as a prospective waveguide when carefully clad with KCl doped nano-crystalline ZnO film with a desired thickness as homogenous cast as possible (Corres *et al*., 2006b; Gaston *et al*., 2003).

FTIR spectra: The soluble form of the precursor, coated on the glass substrate at room temperature issubjected to FTIR investigation in the region from 500 to 4000/cm. The spectrum given in Fig. 3 clearly shows a broad strong band cantered around 3130/cm possibly due to the presence of -OH stretching vibrations contributed by the surrounding solvent molecules. The two bands appearing at 1554 and 1440/cm may attribute to the presence of anti-symmetric and symmetric C-O stretching vibrations, respectively which confirm the presence of acetate group in the precursor.

Similarly, the bands appearing in the FTIR analysis of nano-crystalline ZnO doped potassium which is as shown in Fig. 4, indicates the presence of anti-symmetric and symmetric C-O stretching vibrations, which confirms the acetate group in precursor and the narrow band at 3435.11/cm indicates the presence of dopant potassium ions.

XRD spectra: The ZnO precursor film without dopant (KCl) and with dopant (KCl) (Zhuyi *et al*., 2007), after heating at 500°C has been examined by XRD and the diffraction pattern is shown in Fig. 5 and 6 respectively. The Observed peaks in XRD of Fig. 5 are matching with the reported diffraction peaks for ZnO for wurtzite hexagonal structure. In Fig. 5 the XRD pattern ZnO film shows the sharp X-ray reflection at 2θ = 31° (1 0 0), 34° (0 0 2), 36° (1 0 1), 47° (1 0 2), 56° (1 1 0), 62° (1 0 3), 66° (2 0 0), 67° (1 1 2), 69° (2 0 1), 72° (0 0 4) and 76° (2 0 2). And similarly in Fig. 6 which is with KCl doped nano-crystalline ZnO the peaks of X-ray

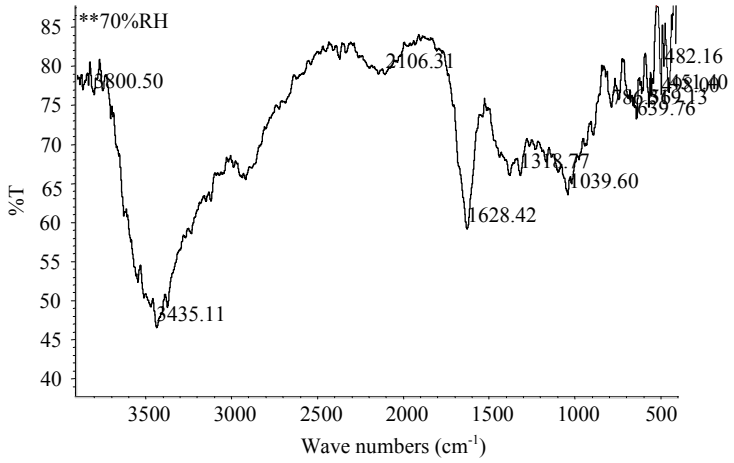

Fig. 4: FTIR spectra of the potassium doped ZnO

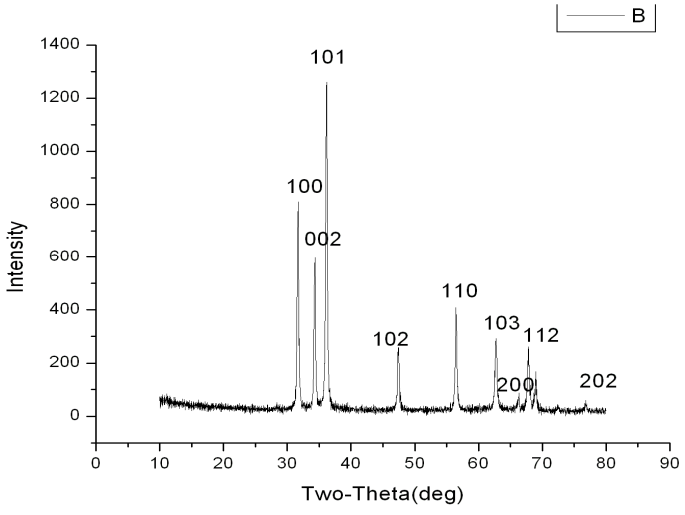

Fig. 5: XRD spectra of the ZnO film after heat treatment at 500°C

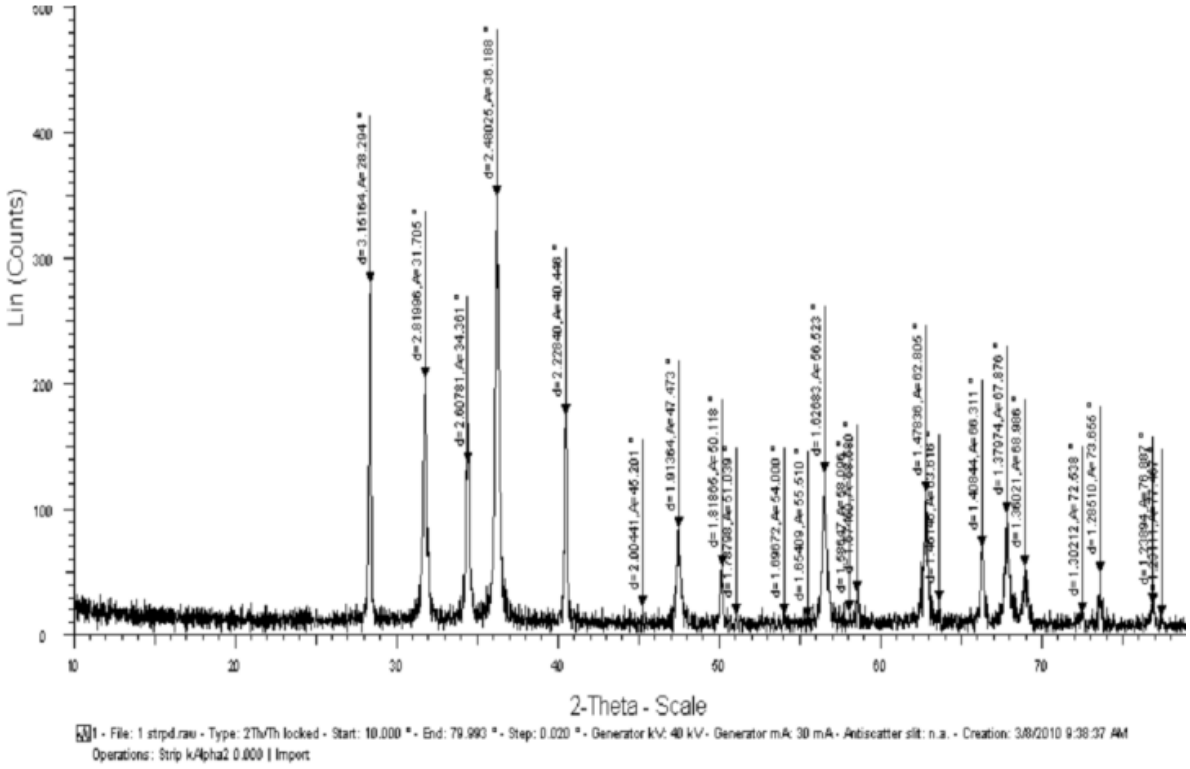

Fig. 6: XRD spectra of the KCl doped nano-crystalline ZnO film after heat treatment at 500ºC

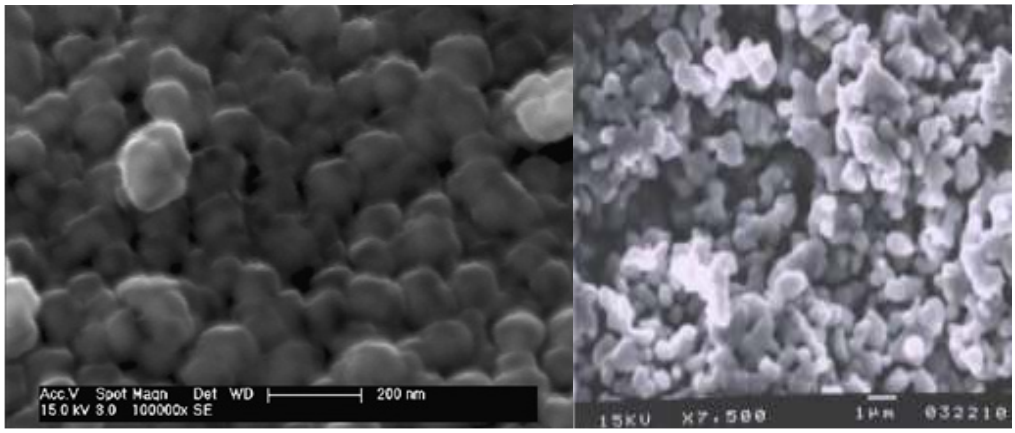

Fig. 7: SEM micrograph of the nano-crystalline ZnO film (a) without K+ heat treatment at 500°C (b) with K+ doped after heat treatment at 500°C

reflection has been shown. These peaks correspond to nano-crystalline ZnO. The crystallite size of ZnO nano-particles was calculated using the Scherer's equation and was found to be in the range of 70-80 nm.

SEM studies: SEM image of the ZnO film (after heat treatment at 500°C) is shown in Fig. 7. The microstructure of ZnO film illustrates a homogeneous distribution of globular particles in a porous film surface. The estimated value of ZnO particles in the film was measured in a range of ~70-80 nm. It appeared that some of the ZnO particles visualized bigger. It may happen due to agglomeration of neighbouring ZnO particles. In this context, the dip coated precursor of ZnO film can be converted into nano-crystalline ZnO film.

Humidity sensing behavior: The Humidity sensing behaviour of nano-crystalline ZnO of potassium doped film is evaluated with the change in optical permeability of the sensing probe as a function of % RH and time was recorded in a closed chamber at room temperature. A very convenient method to calibrate humidity sensors is the use of saturated salt solutions.

The saturated salt solution, made up as a slushy mixture with distilled water and chemically pure salt, is enclosed in a sealed chamber. We have prepared various salt mixers like lithium chloride, potassium acetate, magnesium chloride, Potassium carbonate, magnesium nitrate sodium chloride, potassium nitrate and potassium sulfate at room temperature. The output intensity decreases with an increase in time that is with respect to relative humidity ranging from 5 to 98%.

CONCLUSION

The sol-gel deposited KCl doped ZnO film has been prepared with ZnO particles size 70-80 nm size, was coated on optical fiber which is sensitive for humidity adsorption application. It would be utilized for monitoring the change in humidity in the environment and can be employed safely in many possible applications. Also, KCl doped nano-crystalline ZnO film was deposited on the etched optical fiber, where the change in optical output power corresponds to change in humidity as shown in Fig. 2. This can be calibrated as a humidity sensor element and are more convenient than the conventional humidity sensors. In conclusion, as the humidity around the cladding is increasing, output power is decreasing because the change in refractive index. This, perfectly, is in agreement with our experimental results and can be an underlying principle for humidity detecting devices.

ACKNOWLEDGMENT

This study is supported by the Department of Science and Technology, under the scheme Fund for Improvement of Science and Technology Infrastructure in Higher Educational Institutions (FIST) (SR/FST/ETI -288/2011).

REFERENCES

Bariain, C., I.R. Matias, F.J. Arregui and M. Lopez-Amo, 1998. Experimental results toward development of humidity sensors by using a hygroscopic material on biconically tapered optical fiber. Proceeding of the SPIE 3555 Optical and Fiber Optic Sensor Systems, Vol. 95.

Bariáin, C., I.R. Matías, F.J. Arregui and M. López-Amo, 2000. Optical fiber humidity sensor based on a tapered fiber coated with agarose gel. Sensor. Actuat. B-Chem., 69(1/2): 127-131.

Corres, J.M., J. Bravo and I.R. Matias, 2006a. Sensitivity optimization of tapered optical fiber humidity sensors by means of tuning the thickness of nanostructured sensitive coatings. Sensor. Actuat. B-Chem., 122(2): 442-449.

Corres, J.M., F.J. Arregui and I.R. Matias, 2006b. Design of humidity sensors based on tapered optical fibers. J. Lightwave Technol., 24(11): 4329-4336.

Correia, S.F.H., P. Antunes, E. Pecoraro, P.P. Lima, H. Varum, L.D. Carlos, R.A.S. Ferreira and P.S. André, 2012. Optical fiber relative humidity sensor based on a FBG with a Di-ureasil coating. Sensors, 12: 8847-8860.

Gaston, A., I. Lozano, F. Perez, F. Auza and J. Sevilla, 2003. Evanescent wave optical-fiber sensing (temperature, relative humidity, and pH sensors). IEEE Sens. J., 3(6): 806-811.

Gupta, B.D., 2006. Fiber Optic Sensors Principles and applications. New India Publishing Agency, India.

Kersey, A.D., 1996. A review of recent developments in fiber optics sensor technology. Opt. Fiber Technol., 2(3): 291-317.

Li Lijuan, S. and H. Minchai, 1998. Laser Assisted Microtechnology. In: Osgood, R.M. Jr. (Ed.), 2nd Edn., Springer-Verlag, Berlin, Germany.

Li, L. and H. Minchai, 2010. The mathematical model of food storage safety monitoring and control system. Proceeding of the International Conference on Computer Application and System Modeling (ICCASM, 2010), pp: V13-591-V13-594.

Mehdi, S., M. Juan, G. Fernando and T. David, 1997. Sensing ammonia with ferrocene-based polymer coated tapered optical fibers. Fiber Integrated Opt., 16(1): 115-122.

Murray, C.A. and J.R. Dutcher, 2006. Effect of changes in relative humidity and temperature on ultrathin chitosan films. Biomacromolecules, 7: 3460-3465.

Muto, S., S. Osamu and A. Takashi, 2003. Plastic optical fibre sensor for real-time humidity monitoring. Meas. Sci. Technol., 14: 746.

Qi, Q., Z. Tong and W. Lijie, 2008. Improved and excellent humidity sensitivities based on KCl-doped TiO2 electrospun nanofibers. Appl. Phys. Lett., 93: 023105.

Qi, Q., Z. Tong, W. Shujuan and Z. Xuejun, 2009. Humidity sensing properties of KCl-doped ZnO nanofibers with super-rapid response and recovery. Sensor. Actuat. B-Chem., 137(2): 649-655.

Sakai, Y., Y. Sadaoka and M. Matsuguchi, 1996. Humidity sensors based on polymer thin films. Sensor. Actuat. B-Chem., 35(1/3): 85.

Shukla, S.K., A. Tiwari, G.K. Parashar, G.C. Dubey and A.P. Mishra, 2009. Exploring fiber optic approach to sense humid environment over nano-crystalline zinc oxide film. Talanta, 80(2): 565-571.

Shukla, S.K., G.K. Parashar, A.P. Mishra, M. Puneet, B.C. Yadav, R.K. Shukla, L.M. Bali and G.C. Dubey, 2004. Nano-like magnesium oxide films and its significance in optical fiber humidity sensor. Sensor. Actuat. B-Chem., 98: 5-11.

Ueda, M., H. Kita, K. Nakamure, K. Okamoto and K. Tanaka, 2007. Water-resistant humidity sensors based on sulfonated polyimides. Sensor. Actuat. B-Chem., 127(2): 15.

Xiaofeng, Z., J. Tao, Z. Jian and Z. Zhu, 2007. Humidity sensor based on quartz tuning fork coated with sol-gel-derived nano-crystalline zinc oxide thin film. Sensor. Actuat. B-Chem., 123(1): 299-305.

Yang, B.Z., B. Aksak, Q. Lin and M. Sitti, 2007. Low-cost humidity sensors using nano-porous polymer membranes. Nanotechnology, 18: 465501-465507.

Zhuyi, W., C. Cheng, Z. Tong, G. Hailing, Z. Bo and W. Rui, 2007. Humidity sensitive properties of K+-doped nanocrystalline $LaCo_{0.3}Fe_{0.7}O_3$. Sensor. Actuat. B-Chem., 126(2): 678-683.