Available online at www.sciencedirect.com

SciVerse ScienceDirect

Ceramics International 38 (2012) 2437–2441

CERAMICS INTERNATIONAL

www.elsevier.com/locate/ceramint

Electrospun titanium dioxide nanofiber humidity sensors with high sensitivity

Hira Jamil [a], Syeda Sitwat Batool [a], Zahid Imran [a], Muhammad Usman [a], M.A. Rafiq [a,*], M. Willander [b], M.M. Hassan [a]

[a] Micro and Nano Devices Group, Department of Metallurgy and Materials Engineering, Pakistan Institute of Engineering and Applied Sciences, Islamabad, Pakistan

[b] Department of Science and Technology, Campus Norrköping, Linköping University, SE-60174 Norrköping, Sweden

Received 5 October 2011; received in revised form 3 November 2011; accepted 3 November 2011
Available online 9 November 2011

Abstract

Titanium dioxide nanofibers were synthesized using electrospinning technique. The nanofibers were porous with an average diameter and length of ~150 nm and 200 μm, respectively. Humidity-sensing devices were fabricated by lithographically defined aluminum electrodes on top of the nanofibers deposited on silicon dioxide grown thermally on a silicon substrate. The performance of a TiO_2 nanofiber humidity sensor was tested by AC and DC electrical measurements at 40–90% relative humidity. The response and the recovery time were 1 s and 4 s, respectively, between 40% and 90% relative humidity. The sensitivity of the TiO_2 humidity sensor in the range of 40–90% RH was 150 MΩ/%RH and 20 MΩ/%RH at 10 Hz and 100 Hz, respectively. The excellent sensing characteristics are attributed to the porous nature and the small diameter of the nanofibers.

Keywords: C. Electrical properties; D. TiO_2; E. Sensors; Nanofibers

1. Introduction

In recent years, one-dimensional nanostructures, e.g., nanowires, nanotubes, and nanofibers, have been attracting much interest in physical, chemical, and biological sensor studies due to their unique properties such as small size and large surface-to-volume ratio [1–4]. Humidity sensors belong to chemical sensor category and have applications in semiconductor and automobile industries, pharmaceuticals, environmental control, food storage, and many other fields [5,6]. Among various materials, ceramic oxides (e.g., titanium dioxide) have also shown good sensing properties. Titanium dioxide (TiO_2) has also a variety of other applications in environmental cleaning and protection, photocatalysis, and solar cells [7]. Recently, a high-performance humidity sensor has been demonstrated using porous TiO_2 prepared by template-assisted sol–gel process [8]. Humidity sensing has also been reported using ZnO/TiO_2 double-layer nanofibers [9], TiO_2 nanotubes [10], ZnO/TiO_2 core shell nanorods [11], and TiO_2 films [12]. Mg^{2+} and Na^{+} doped rutile TiO_2 nanofibers have been used as antifogging humidity sensors as well [13].

In this work, we present a humidity-sensing device based on TiO_2 nanofibers prepared by electrospinning. Electrospinning is a simple, versatile, and relatively inexpensive technique for synthesis of nanofibers. Electrospinning has the advantage of synthesis of continuous, uniform nanofibers using different types of polymers and precursors [14,15]. Morphology of the nanofibers can be controlled well by viscosity, surface tension, and the density of net charges of the solution [14,15]. The nanofibers were prepared with an average diameter of ~150 nm and length of few hundred micrometers. The humidity sensor was tested at room temperature by varying the relative humidity from 40% to 90%. The TiO_2 nanofiber humidity sensor shows fast response and recovery time, and very good sensitivity. The sensitivity, response time and recovery time of the TiO_2 nanofiber sensor is comparable with previously reported TiO_2-based sensors discussed earlier. Further electrospinning is a simple technique to prepare nanofibers.

* Corresponding author.
E-mail address: fac221@pieas.edu.pk (M.A. Rafiq).

0272-8842/$36.00
doi:10.1016/j.ceramint.2011.11.010

2. Materials and methods

TiO_2 nanofibers were prepared by the electrospinning technique. The chemicals used in electrospinning (polyvinylpyrrolidone (PVP), titanium tetraisopropoxide, acetic acid, and ethanol) were purchased from Sigma–Aldrich. The chemicals were of analytical grade and used without further purification. The molecular weight of PVP was 1,300,000. Spin dope for electrospinning of TiO_2 nanofibers was prepared in the following manner. Solution 1 was prepared by adding 0.45 g of PVP in 7.5 ml of ethanol and stirred for 10 min. Then, solution 2 was prepared by mixing 1.5 ml of titanium tetraisopropoxide, 3 ml of ethanol and 3 ml of acetic acid in a glove box. Solution 2 was then poured dropwise in solution 1. The final solution was stirred for 1 h to get a homogenous solution of optimum viscosity.

Spin dope was then loaded in a plastic syringe with a stainless steel needle of 0.413-mm diameter. The copper collector plate was placed at distances of 7 cm, 8 cm, and 10 cm from the needle tip. High-voltage (10 kV) was supplied between anode (syringe) and cathode (copper plate). Composite (PVP/TiO_2) nanofibers were collected on an aluminum foil while the solvent evaporated during spinning. Uniform nanofibers with minimum beaded structure were obtained at an applied field of 1.25 kV/cm (i.e., when the distance between the needle and the collector was 8 cm). Pure TiO_2 nanofibers were obtained after heat treatment of as-spun PVP/TiO_2 composite nanofibers at 600 °C for 3 h in air. This resulted in removal of PVP from as-spun nanofibers. The nanofibers were characterized using scanning electron microscopy (SEM), energy dispersive spectroscopy (EDS), transmission electron microscopy (TEM), and X-ray diffraction (XRD).

To fabricate the humidity sensor, TiO_2 nanofibers were dissolved in iso-propanol by ultrasonic agitation. The nanofibers were then deposited on ~200-nm-thick SiO_2 grown thermally on the silicon substrate. Finally, aluminum electrodes were defined by lithography and thermal evaporation. Humidity-sensing devices with different separation between the aluminum electrodes were fabricated. Multiple nanofibers were present between the electrodes.

A home-made humidity measurement set-up was used for humidity measurements. Humidity-sensing devices were placed in a glass chamber. Probes for electrical measurements were fitted in the chamber. The DC and AC electrical measurements at different relative humidity (RH) were performed using a Keithley 2400 source meter and an Agilent E4980A LCR meter, respectively. Use of AC signal helps to avoid the polarization effects of adsorbed water [16]. However, in this case, the signal processing circuits are complicated. Therefore, sometimes, DC measurements are also used to evaluate the humidity sensors [16]. Saturated salt solutions were used to achieve required humidity levels. Saturated salt solutions of magnesium nitrate ($Mg(NO_3)_2$), sodium chloride (NaCl), and potassium chloride (KCl) were used to achieve 52%, 75%, and 86% RH, respectively at 24 °C [13]. Before AC and DC electrical measurements, each saturated salt solution was kept in the glass chamber for more than 24 h to attain the required RH. The RH values were confirmed by a commercial hygrometer before the electrical measurements.

3. Results and discussion

The XRD pattern of the TiO_2 nanofibers after heat treatment at 600 °C is shown in Fig. 1. It can be seen that anatase and rutile mixture phases are present. Fig. 2(a) shows the SEM image of the TiO_2 nanofibers after annealing at 600 °C. Fig. 2(b) shows the SEM image at a higher magnification. It can be seen that only the TiO_2 nanofibers are present. No other morphology such as beaded structure is observed. The nanofibers are very long (length in micrometers) and have diameters from ~30 nm to ~200 nm. EDS analysis of TiO_2 nanofibers shown in Fig. 2(c) reveals the presence of Ti and O in the atomic ratio of 1:2, indicating the formation of TiO_2. No other elements are present in the sample. This confirms that heat treatment at 600 °C removes PVP completely from the as-spun nanofibers. Fig. 3(a) shows a transmission electron microscope image of the TiO_2 nanofibers. The nanofibers are polycrystalline with average grain size of ~10 nm. The nanofibers have a porous structure. Lee et al. have reported that porosity depends on the calcination temperature [17]. They demonstrated that the nanofibers calcinated between 600 and 700 °C had porosity of 8% [17]. Because our nanofibers were prepared by the same technique and were calcined at 600 °C, we assume the nanofibers have similar porosity (not exactly 8%).

Fig. 3(b) shows the schematic diagram of the humidity-sensing device. Fig. 4(a) and (b) shows current voltage (*IV*) curves recorded at different relative humidity for devices A and B, respectively. The separation between two Al electrodes was ~200 μm for device A and 100 μm for device B. It is clear that the sensor responds to humidity change and current increases as the RH increases. This implies that the sensor offers low resistance at higher RH. These *IV* curves are nonlinear. Similar values of the current are observed for both devices, although the separation between the electrodes is different. The current flow in the nanofiber sensor depends on the distance between the

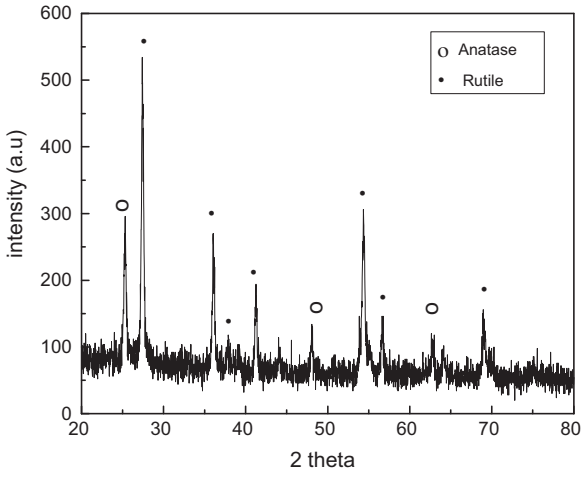

Fig. 1. X-ray diffraction pattern of the TiO_2 nanofibers.

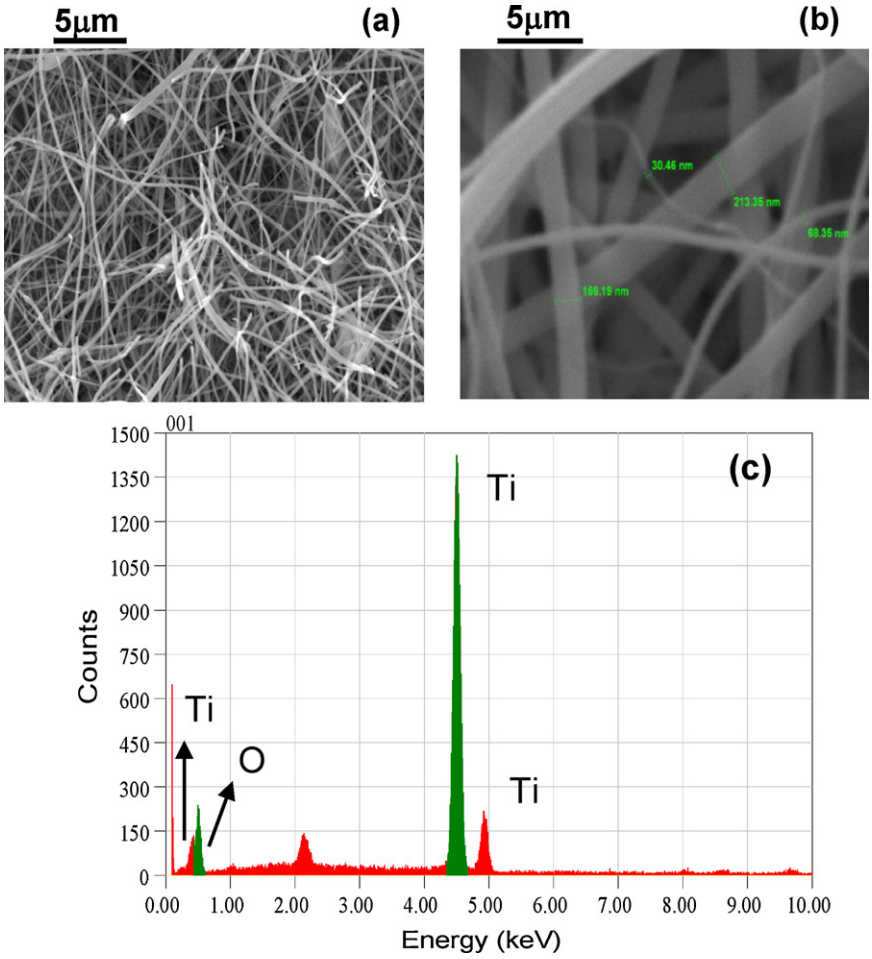

Fig. 2. (a and b) Scanning electron micrographs of the electrospun TiO_2 nanofibers and (c) EDS spectrum of the electrospun TiO_2 nanofibers.

electrodes and the number of nanofibers present between the electrodes. As the nanofibers were deposited randomly, therefore we believe that device B has more nanofibers between the electrodes as compared with the device A. Therefore, devices A and B have similar values of current in spite of the fact that the electrode separation is greater in device B than device A.

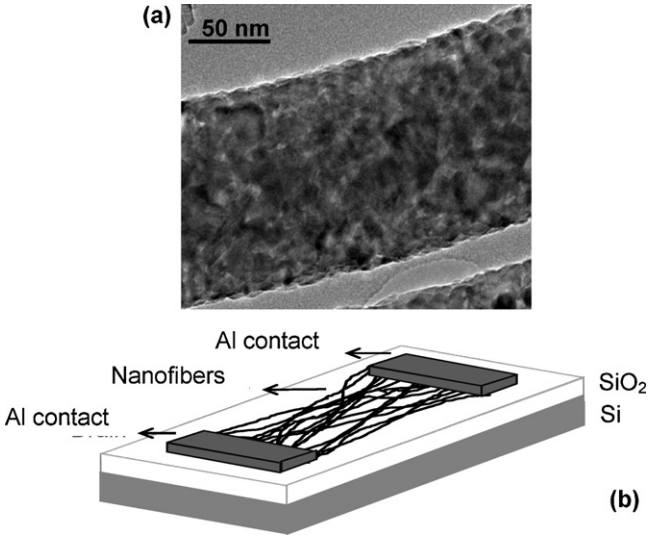

Fig. 3. (a) Transmission electron microscope images of the electrospun TiO_2 nanofibers and (b) schematic diagram of the TiO_2 nanofiber humidity sensor.

The performance of the nanofiber humidity sensor was also evaluated by impedance measurements at different relative humidity. Fig. 5 shows the relation between real and imaginary parts of impedance for device A at different relative humidity. AC measurements were carried out at 0.2 V in frequency range of 20 Hz–2 MHz. There is an increase in conductivity of the TiO_2 nanofibers with increase in relative humidity. Clear semicircles are formed at different RH. The intercept of semicircle with real axis gives the bulk resistance of the nanofibers. Fig. 5 shows clearly the decrease in bulk resistance as the RH increases. This response to RH is in accordance with the response during DC measurements.

Fig. 6 shows change in impedance with change in relative humidity at 10 Hz and 100 Hz for device C. The separation between the aluminum contacts was the same as for device A, i.e., 100 μm in this device. However, this was a different sample and was prepared at a different time. There was large humidity response at low frequency in contrast with the response at higher frequencies. The sensitivity of the TiO_2 sensor can be calculated from Fig. 6 and is given by the formula [18]:

$$\text{Sensitivity} = \frac{\Delta(\text{impedance})}{\Delta \text{RH}\%} \quad (1)$$

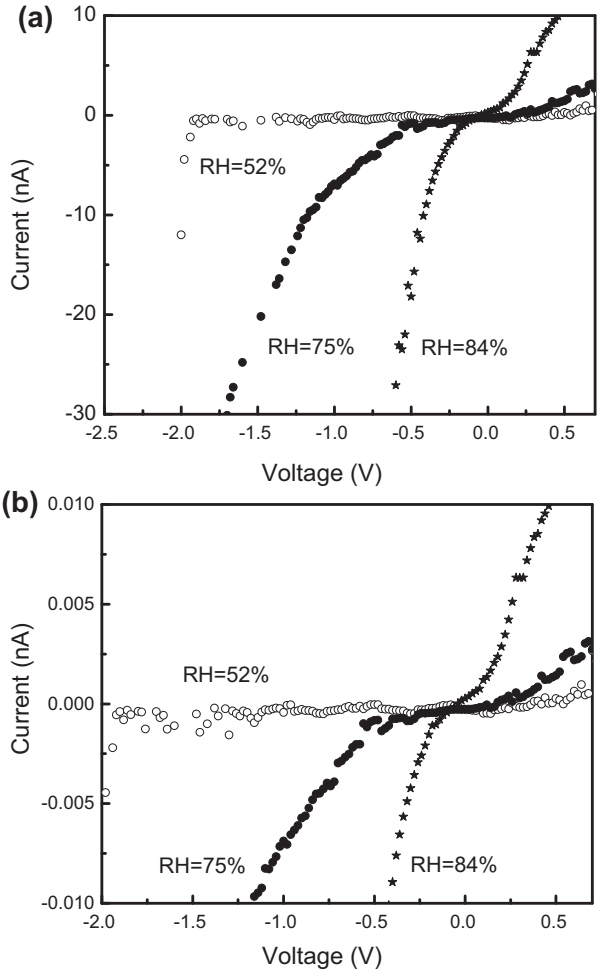

Fig. 4. Current–voltage characteristics of (a) device A and (b) device B at different relative humidity.

The sensitivity of the TiO_2 humidity sensor in the range of 40–90% RH was 150 MΩ/%RH and 20 MΩ/%RH at 10 Hz and 100 Hz, respectively.

The response and the recovery time are an important figure of merit of a humidity sensor. Fig. 7 shows the response–recovery characteristics of the TiO_2 nanofiber humidity-sensing device C. The response time measurements were performed by recording the impedance of the sensor at two different RH levels (AC voltage 1 V and $f = 100$ Hz). The time required to attain 90% of the total impedance change is referred to as the response time in the case of adsorption and recovery time in the case of desorption. The response time of TiO_2 nanofibers humidity sensor was 1 s as humidity changed from 40% to 90% and recovery time was 4 s as humidity changed from 90% to 40%.

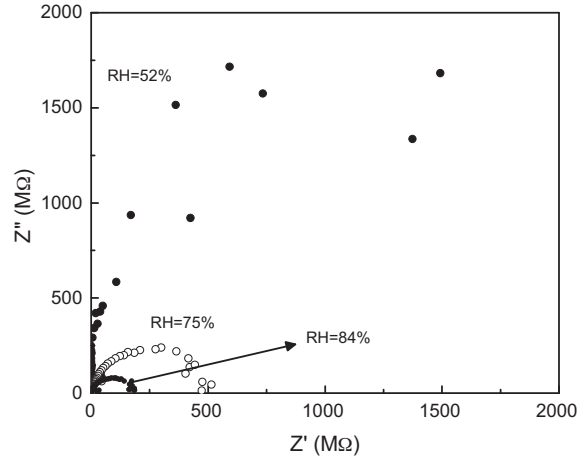

Fig. 5. Real part of impedance versus imaginary part of impedance for device A at 52%, 75%, and 84% RH.

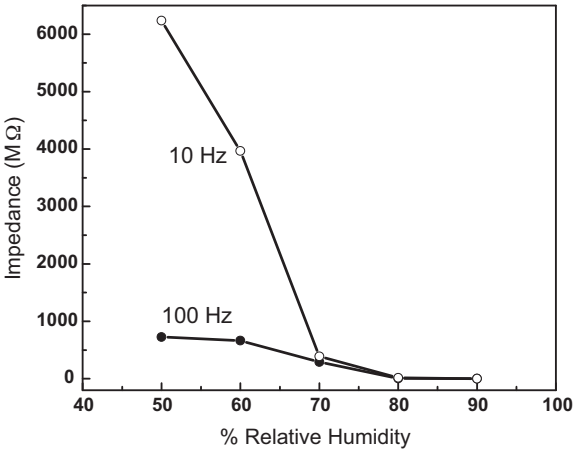

Fig. 6. Impedance versus RH humidity characteristics for device C at 10 Hz and 100 Hz.

Table 1 shows the comparison of the performance of our nanofiber sensor with a few recently reported metal oxide humidity sensors. The values suggest that response and recovery time of the TiO_2 nanofiber sensor is better or comparable with other sensors discussed in Table 1. However, the sensitivity is better than the sensors (discussed in Table 1) for which sensitivity data are available. Sensitivity for Mg^{2+}/Na^{+}-doped TiO_2 nanofibers (Fig. 3a in ref. [13]), ZnO/TiO_2 double-layer nanofibers (Fig. 5 in ref. [9]), and porous TiO_2 (Fig. 6 in ref. [8]) was determined by the authors using Eq. (1).

The excellent humidity characteristics of the TiO_2 nanofiber sensor are due to (i) small diameter of the nanofibers that increase the surface-to-volume ratio and (ii) presence of small

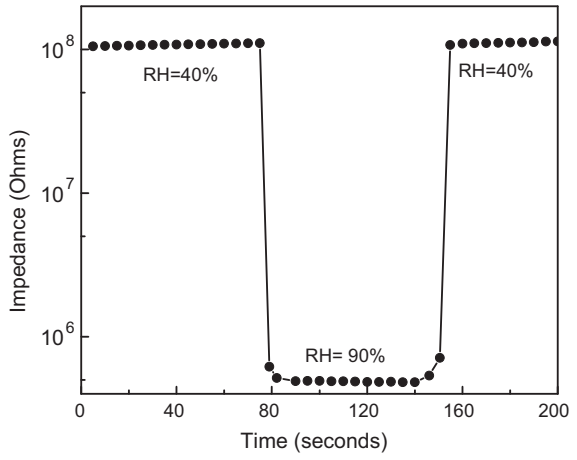

Fig. 7. Response and recovery characteristics of the TiO_2 nanofiber sensor.

Table 1
Comparison of the TiO_2 nanofiber humidity sensor with other metal oxide humidity sensors.

Material	Humidity range	Response time (s)	Recovery time (s)	Sensitivity	Reference
Porous TiO_2	11–95%	5	8	1.19 MΩ/%RH at 10 Hz	[8]
ZnO/TiO_2 double-layer nanofibers	11–95%	11	7	0.40 MΩ/%RH at 100 Hz	[9]
TiO_2 nanotubes	11–95%	100	190	–	[10]
ZnO/TiO_2 core shell nanorod arrays	11–95%	774.9	19.7	–	[11]
Mg^{2+}/Na^{+}-doped TiO_2	11–95%	2	1	0.47 MΩ/%RH at 100 Hz	[13]
ZnO thin film	6.3–84%	3	12	–	[20]
SnO_2 nanoparticles	5–95%	32	25	–	[21]
TiO_2 nanofibers (present work)	40–90%	1	4	150 MΩ/%RH at 10 Hz 20 MΩ/%RH at 100 Hz	

pores at the surface of the nanofibers that further increases the effective area of the TiO_2 nanofibers for the adsorption and desorption process due to possible diffusion in and out of humidity molecules through the pores and increases the sensitivity [8]. The humidity-sensing mechanism of the TiO_2 nanofibers is as follows [19]. First of all, water molecules are chemisorbed on active sites of the TiO_2 nanofibers by forming the hydroxyl ions. With increase in humidity, water molecules are physisorbed onto this hydroxyl layer by attaching with two neighboring hydroxyl groups through hydrogen double bonds. This layer is immobile due to the presence of the double bond. As humidity increases the number of physisorbed layers increases, the water molecules can form single bonds to a hydroxyl group, and the proton may have more freedom to move through the water layer. The conduction process is identical to the conduction in pure water. Capillary condensed water in small pores present in the TiO_2 nanofibers also reduces impedance in addition to earlier-mentioned process.

4. Conclusions

In conclusion, highly sensitive humidity-sensing devices with fast response and recovery time were fabricated. The response and the recovery time of the sensor were 1 s and 4 s, respectively. The sensor was highly sensitive to humidity having sensitivity as high as 150 MΩ/%RH at 10 Hz. The small size and the porous nature of the nanofibers facilitate the adsorption process of molecules and are a key factor due to which the sensor has excellent characteristics.

Acknowledgment

This work was financially supported by the Higher Education Commission, Islamabad, Pakistan through a research grant ''Electron Transport in Nanostructures''.

References

[1] J. Kong, N.R. Franklin, C.W. Zhou, M.G. Chapline, S. Peng, K.J. Cho, H.J. Dai, Nanotube molecular wires as chemical sensors, Science 187 (2000) 622–625.
[2] S. Chang, H. Hsueh, T. Hsueh, F. Hung, C. Hsu, B. Dai, Si nanowire-based humidity sensors prepared on glass substrate, IEEE Sens. J. (2011), doi:10.1109/jsen.2011.2156781.
[3] E. Comini, G. Sberveglieri, Metal oxide nanowires as chemical sensors, Mater. Today 13 (2010) 36–44.
[4] J.X. Huang, S. Virji, B.H. Weiller, R.B. Kaner, Polyaniline nanofibers: facile synthesis and chemical sensors, J. Am. Chem. Soc. 125 (2003) 314–315.
[5] E. Traversa, Ceramic sensors for humidity detection: the state-of-the-art and future developments, Sens. Actuators B: Chem. 23 (1995) 135–156.
[6] B. Patissier, Humidity sensors for automotive, appliances and consumer applications, Sens. Actuators B: Chem. 59 (1999) 231–234.
[7] D.V. Bavykin, J.M. Friedrich, F.C. Walsh, Protonated titanates and TiO_2 nanostructured materials: synthesis, properties, and applications, Adv. Mater. 18 (2006) 2807–2824.
[8] Z. Wang, L. Shi, F. Wu, S. Yaun, Y. Zhao, M. Zhang, The sol–gel template synthesis of porous TiO_2 for a high performance humidity sensor, Nanotechnology 22 (2011) 275502.
[9] X.J. Yue, T.S. Hong, X.U. Xing, Z. Li, High-performance humidity sensors based on double-layer ZnO–TiO_2 nanofibers via electrospinning, Chin. Phys. Lett. 28 (2011) 090701.
[10] Y. Zhang, W. Fu, H. Yang, Q. Qi, Y. Zeng, T. Zhang, R. Ge, G. Zou, Synthesis and characterization of TiO_2 nanotubes for humidity sensing, Appl. Surf. Sci. 254 (2008) 5545–5547.
[11] L. Gua, K. Zhenga, Y. Zhoub, J. Li, X. Moa, G.R. Patzkeb, G. Chena, Humidity sensors based on ZnO/TiO_2 core/shell nanorod arrays with enhanced sensitivity, Sens. Actuators 159 (2011) 1–7.
[12] J.J. Steelea, M.T. Taschuka, M.J. Brett, Response time of nanostructured relative humidity sensors, Sens. Actuators B 140 (2009) 610–615.
[13] H. Zhang, Z. Li, L. Liu, C. Wang, Y. Wei, A.G. Macdiarmid, Mg^{2+}/Na^{+}-doped rutile TiO_2 nanofiber mats for high-speed and anti-fogged humidity sensors, Talanta 79 (2009) 953958.
[14] W. Sigmund, W. Yuh, H. Park, V. Maneeratana, G. Pyrgiotakis, A. Daga, J. Taylor, J.C. Nino, Processing and structure relationships in electrospinning of ceramic fiber systems, J. Am. Ceram. Soc. (2006) 395–407.
[15] D. Li, J.T. McCann, Y. Xia, M. Marquez, Electrospinning: a simple and versatile technique for producing ceramic nanofibers and nanotubes, J. Am. Ceram. Soc. 89 (2006) 1861–1869.
[16] L. Wang, Y. He, J. Hu, Q. Qi, T. Zhang, DC humidity sensing properties of $BaTiO_3$ nanofiber sensor with different electrode materials, Sens. Actuators B 153 (2011) 460–464.
[17] J. Lee, Y. Lee, H. Song, D. Jang, Y. Choa, Synthesis and characterization of TiO_2 nanowires with controlled porosity and microstructure using electrospinning method, Curr. Appl. Phys. 11 (2011) S210–S214.
[18] N.K. Pandey, K. Tiwari, Morphological and relative humidity sensing properties of pure ZnO nanomaterial, Sens. Transducers 122 (2010) 9–19.
[19] Z. Chen, C. Lu, Humidity sensors a review of materials and mechanisms, Sens. Lett. 3 (2005) 274–295.
[20] P.K. Kannan, R. Saraswathi, J.B.B. Rayappan, A highly sensitive humidity sensor based on DC reactive magnetron sputtered zinc oxide thin film, Sens. Actuators A 164 (2010) 8–14.
[21] M. Parthibavarman, V. Hariharan, C. Sekar, High-sensitivity humidity sensor based on SnO_2 nanoparticles synthesized by microwave irradiation method, Mater. Sci. Eng. C 31 (2011) 840–844.