Orange dye–polyaniline composite based impedance humidity sensors

Muhammad Tariq Saeed Chani[a)b)†], Kh. S. Karimov[a)c)], F. A. Khalid[a)], S. Z. Abbas[a)], and M. B. Bhatty[a)]

[a)] *GIK Institute of Engineering Sciences and Technology, Topi* 23640, *Khyber Pakhtunkhwa, Pakistan*

[b)] *Center of Excellence for Advanced Materials Research (CEAMR), King Abdulaziz University, Jeddah* 21589, *P.O. Box* 80203, *Saudi Arabia*

[c)] *Physical Technical Institute, Aini St.* 299/1, *Dushanbe*, 734063, *Tajikistan*

(Received 5 January 2012; revised manuscript received 28 February 2012)

This study presents the fabrication and investigation of humidity sensors based on orange dye (OD) and polyaniline (PANI) composite films. A blend of 3 wt.% OD with 1 wt.% PANI was prepared in 1 ml water. The composite films were deposited on glass substrates between pre-deposited silver electrodes. The gap between the electrodes was 45 μm. The sensing mechanism was based on the impedance and capacitance variations due to the absorption/desorption of water vapor. It was observed that with the increase in relative humidity (RH) from 30% to 90%, the impedance decreases by 5.2×10^4 and 8.8×10^3 times for the frequencies of 120 Hz and 1 kHz, respectively. The impedance–humidity relationship showed a more uniform change compared to the capacitance–humidity relationship in the RH range of 30% to 90%. The consequence of annealing, measuring frequency, response and recovery time, and absorption–desorption behavior of the humidity sensor were also discussed in detail. The annealing resulted in an increase in sensitivity of up to 2.5 times, while the measured response time and recovery time were 34 s and 450 s, respectively. The impedance–humidity relationship was simulated.

Keywords: organic–organic composite, humidity sensor, polyaniline, orange dye

PACS: 07.07.Df, 07.07.Vx, 72.80.Le, 84.37.+q **DOI:** 10.1088/1674-1056/22/1/010701

1. Introduction

The measurement and control of humidity are very important not only for human comfort but also for manufacturing processes and industrial products.[1,2] The use of humidity sensors for environmental monitoring, safety, building air conditioning, civil engineering, and in the semiconductor, automobile, medicine, pharmacy, healthcare, textile, paper, agriculture, and food industry is well known.[2–4]

Conventional sensing materials like alumina, ceramics, and electrolytic metal oxides are used for the fabrication of commercially available humidity sensors.[3] To make the sensor suitable for commercialization, a wide range, sensitivity, linear response, small hysteresis, short response and recovery time, low cost, low power, and long term physical and chemical stability are required.[5,6] Depending upon the nature of materials, commercially available sensors may be expensive or require high operational power/temperature and have a high maintenance cost.[4,7] Due to their low cost, light weight, flexibility, large surface area, and simple technology, organic materials are very promising for their use in humidity sensors. Depending on the basic sensing principle, those humidity sensors are classified as capacitive and resistive type sensors.[2] In the last few decades, a lot of research on polymer based humidity sensors has been done and applied in industry.[3] As a result of extensive investigations, polymers like polypyrole, polythiophene, and polyaniline have gained significant attention as humidity sensing materials.[3,7,8] The humidity sensing mechanisms of most conducting polymers are the same. The formation of hydrogen bonds takes place as a result of the interaction between the water molecules and the nitrogen centers of the polymer backbone, which results in the increase of the charge carriers.[7] These charge carriers decrease the resistance and increase the conductivity of the material.[7–9]

Due to its wide range of applications[3] and salient features like simple preparation and doping, easy polymerization, excellent chemical stability, relatively high levels of conductivity, and low-cost, polyaniline (PANI) has become the most attractive polymer for researchers.[3,9,10] PANI and its derivatives are famous humidity sensing materials, but their responses are low (the change in conductivity is only one order of magnitude[2]) due to their weak hygroscopicity. One of the methods to improve the humidity sensing properties of PANI is blending it with hygroscopic polymeric materials.[3,11]

For the measurement of humidity and temperature, a polyaniline/tungsten oxide was synthesized through an *in situ* deposition technique by Parvatikar *et al*.[12] In this study, the pellets (3 mm thick and 10 mm diameter) of composites (having 10–50 wt.% tungsten oxide) were characterized for humidity and temperature sensing. The changes in resistivity for various compositions of PANI–tungsten oxide composite were measured for change in humidity from 10% to 95%. Pandey *et al*. investigated the resistance–humidity behavior of polyaniline pellets (0.55–0.89 mm thick and 13 mm diameter), which

†Corresponding author. E-mail: tariq_chani@yahoo.com

© 2013 Chinese Physical Society and IOP Publishing Ltd

were pressed using a 7 ton hydraulic press.[13] The change in resistance for a change in humidity from 15% to 90% was reported to be from 5.8 GΩ to 13.9 MΩ, while the response and recovery time for a 30% change in humidity was 60 s.

In this work, we fabricate and investigate Ag/OD–PANI /Ag humidity sensors based on a blend of orange dye (OD) and PANI. The orange dye is a p-type semiconductor, and its properties such as high purity, a well defined chemical structure, its harmless nature, normal condition stability, and good light absorption in the visible spectrum make it a possible entrant for use in electronic devices.[14] It is also highly sensitive to humidity.[15] In earlier studies, our group has investigated OD for different semiconducting devices.[14–17]

2. Experiment

Laboratory synthesized orange dye ($C_{17}H_{17}N_5O_2$)[16] and commercially available emeraldine base (EB) polyaniline (PANI) (C_{24} $H_{20}N_4$) were used for the fabrication of the humidity sensors. The density of orange dye is 0.9 g·cm^{-3} and its molecular weight is 323, while the molecular weight of PANI is ∼ 20000. Figures 1(a) and 1(b) show the molecular structures of orange dye and PANI, respectively.

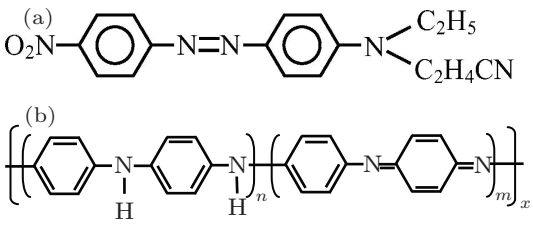


Fig. 1. Molecular structures of (a) orange dye and (b) polyaniline, where $n = m = 0.5$.

The solution was prepared by mixing 3 wt.% OD and 1 wt.% PANI powder in 1 ml water and stirring at room temperature. Before the deposition of metallic electrodes, the glass substrates were cleaned for 10 min in an ultrasonic cleaner by dipping in acetone and then dried. The dry substrates were plasma cleaned for 5 min in a thermal evaporator. The 50 nm thick silver electrodes were deposited on the cleaned substrates by vacuum evaporation, and there was a 45 μm gap between the two electrodes. The gap length was kept at 10 mm. The OD–PANI composite films of thicknesses 50–170 μm were deposited by drop-casting the OD–PANI solution onto the silver electrodes. Figure 2 shows a schematic diagram of an Ag/OD–PANI/Ag sample. The fabricated devices were dried at room temperature for two weeks. After drying, the films showed very good adhesion with glass substrate. The samples were annealed at 100 °C for 1 h in an oven. For the microstructural analysis of the films, optical and scanning electron microscopes were used.

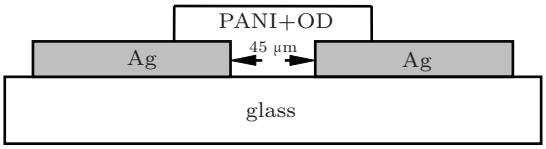


Fig. 2. Schematic diagram of an Ag/OD–PANI/Ag humidity sensor.

The sensors were tested in an indigenously made humidity chamber, which has been fabricated in our device testing laboratory. It consisted of a closed chamber with inlet and outlet valves for gas. To create humidity in the chamber, nitrogen gas was passed through water and then injected into the chamber. The Fisher scientific digital hygrometer was used to measure the humidity, while the ESCORT ELC-132A LCR meter was used to measure capacitance C and dissipation D at three different frequencies. The resistance R and impedance Z are calculated by the following expressions:[18]

$$R = 1/(2\pi fCD), \tag{1}$$

$$Z = 1/Y = 1/[(1/R^2) + (2\pi fC)^2]^{1/2}, \tag{2}$$

where f is the frequency and Y is the admittance. Here the impedance of the hygrometer is considered as an impedance of parallel connected resistance and capacitance. The experiments were conducted at least four times to ensure the repeatability of the results.

3. Results and discussion

Figures 3 (optical micrograph) and 4 (SEM image) show the surface morphology of a polyaniline thin film in as fabricated condition. It is evident from the micrograph that the OD–PANI composite forms a two-phase structure, which consists of a granular matrix and a network of microtubes. This structure is different from the pure polyamine film structure, which was fabricated by us using the same solvent and deposition method. These results reveal that the orange dye causes a better dispersion of polyaniline powder and also the nucleation and growth of microtubes. These microtubes improve the electrical properties of the composite.[19] Due to the presence of polyaniline particles, the surface of the film develops, i.e., the surface area increases, which combined with the orange dye makes the film very sensitive to humidity. In addition to better performance, the orange dye results in a better adhesion of film with substrate, which in turn enhances the life of the sensor.

Figure 5 shows the relationships of capacitance and impedance with humidity (during absorption) for the Ag/OD–PANI/Ag sensor at 120 Hz. The film (OD–PANI composite) thickness is 170 μm. It can be seen that the impedance shows a consistent change with the change in humidity, while the change in capacitance is not uniform. The plot of the

impedance–humidity relationship on a semi-logarithmic scale is more linear as compared to that of the capacitance–humidity relationship in the humidity range of 30–90%. The changes in capacitance and impedance of sensors over the whole humidity interval are 1.5×10^4 and 5.2×10^4 times, respectively.

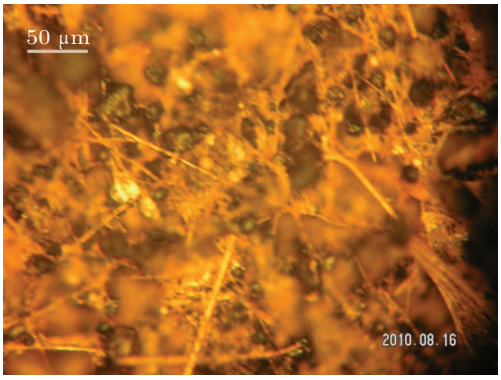


Fig. 3. (color online) Optical micrograph of the OD–PANI film's surface.

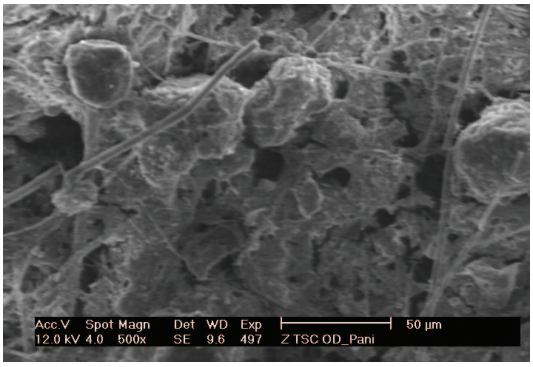


Fig. 4. SEM image of the OD–PANI film's surface.

These results depict that with the increase in humidity, the resistance of the material reduces. It is also believed that the absorbed water molecules dissociate into protons (H^+) and hydroxyl ions (OH^-). The migration of a positive charge in PANI increases its conductivity, which is called the proton effect.[7] The oxidized and reduced (non-oxidized) forms of emeraldine base PANI (Fig. 2) can be protonated due to the unbonded electron pair on the nitrogen atom[12] such as –NH– → $-NH_2^+$ and –N= → $-NH^+=$. These protonated sites are named as charged sites and H-bond accepting/donating sites, Zeng *et al*. explained how these sites contribute in the conduction mechanism of PANI.[7] It is also believed that the H^+ ions produced as a result of the dissociation of water molecules react with the orange dye and generate holes[17]

$$2H^+ + \frac{1}{2}O_2 + 2(C_{17}H_{17}N_5O_2) \rightarrow H_2O + 2(C_{17}H_{17}N_5O_2)^+,$$
$$(C_{17}H_{17}N_5O_2)^+ \rightarrow (C_{17}H_{17}N_5O_2) + h^+.$$

The generation of these holes also increases the conductivity of the composite. The impedance–humidity relationship during absorption and desorption of humidity is shown in Fig. 6, where the values are taken at room temperature at a frequency of 120 Hz. The sensor with a relatively thick film (170 μm) shows a hysteresis, while the absorption and desorption curves of a thin film (50 μm) sensor (shown in the inset of Fig. 6) coincided within the experimental error of ±2%. This means that with the increase of the film thickness, the hysteresis increases, the reason for this may be the differences in the rates of absorption and desorption of water vapor. Another cause for the hysteresis is the porosity of the film, which facilitates the absorption process due to a large surface area and the capillary effect, but it makes the desorption process slightly difficult.[1,20] It also reveals that it may not be the humidity memory effect described earlier in doped PANI and PANI with 5-formyl-2-furansulfonic acid.[11,21] Those materials showed irreversible changes of their sheet resistance and capacitance under the effect of humidity. As a result of the irreversible dedoping process under the effect of humidity, the phase separation and the crystallization of a hydrated form of its protonating agent took place.

The effect of annealing on the humidity sensing properties of the OD–PANI composite is shown in Table 1. The an-

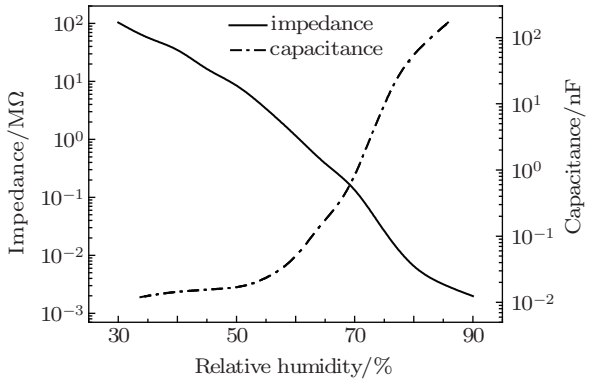


Fig. 5. Capacitance and impedance humidity relationships for the Ag/OD–PANI/Ag sensor at 120 Hz.

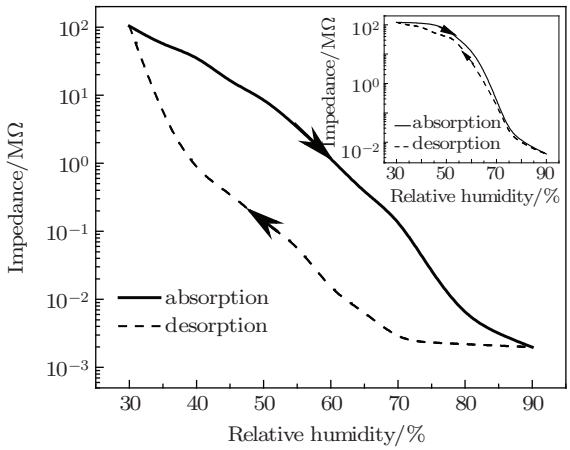


Fig. 6. Impedance–humidity relationship for a thick film (170 μm) Ag/OD–PANI/Ag sensor at 120 Hz during absorption and desorption of humidity; inset shows the impedance–humidity relationship for a thin film (50 μm) Ag/OD–PANI/Ag sensor.

Table 1. Humidity sensing properties of sensor.

Thickness/μm	Frequency/Hz	$C_{90\%}/C_{30\%}$		$Z_{30\%}/Z_{90\%}$	
		As-fabricated	Annealed	As-fabricated	Annealed
170	120	$1.5\text{x}10^4$	$2.6\text{x}10^4$	$5.2\text{x}10^4$	$1.3\text{x}10^5$
	1000	$1.7\text{x}10^3$	$2.7\text{x}10^3$	$8.8\text{x}10^3$	$1.98\text{x}10^4$

nealing results in the improvements of capacitance–humidity and impedance–humidity sensitivities up to 1.7 and 2.5 times, respectively. The change in sensitivity can be attributed to the structural changes, which take place due to the annealing.[22] The annealing increases the porosity, therefore the sensitivity increases. The comparison of relative impedance–humidity relationship before and after annealing is given in Fig. 7.

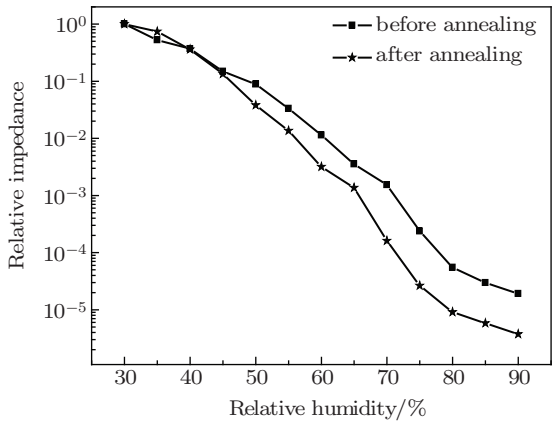


Fig. 7. Comparison of the relative impedance–humidity relationship before and after annealing.

The impedance–humidity relationships for frequencies of 120 Hz and 1 kHz are shown in Fig. 8. From Fig. 8, it is evident that with the increase in frequency at a specific humidity level, the sensor's impedance decreases. The increase in humidity also results in a consistent decrease in impedance. The results also reveal that the sensitivity of the sensors decreases with an increase in frequency. This can be explained by the dependences of dielectric permittivity,[23] the mobility of ions (firstly) and electrons (secondly), and the transit time of charge transfer on the frequency.[24]

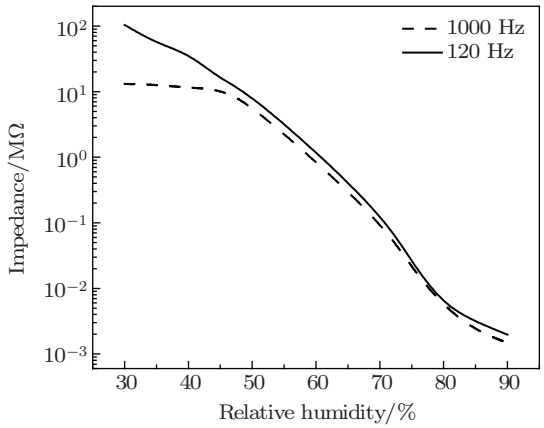


Fig. 8. Impedance–humidity relationships for the Ag/OD–PANI/Ag sensor at 120 Hz and 1 kHz.

More consistent changes can be observed in impedance–humidity relationship in the range of 30–90% as compared to the capacitance–humidity relationship, and it is imperative for the design of a humidity sensor on the base of investigated materials. The reason behind the uniformity of impedance–humidity relationship as compared to the resistance and capacitance is that the impedance depends on both resistance and capacitance changes (Eq. (2)). It is obvious that the effect of resistance to impedance is dominating with respect to the effect of capacitance. The change in impedance with the change in humidity takes place in the same manner as that in resistance of the sensor. The decreases in impedance for frequencies of 120 Hz and 1 kHz when the humidity changes from 30% to 90% are 5.2×10^4 and 8.8×10^3 times, respectively.

For the simulation of the experimental results of the impedance–humidity relationship shown in Fig. 5, the following exponential function[25] is used:

$$f(x) = \mathrm{e}^{-x}, \tag{3}$$

which for the present experiment can be represented in the following form:

$$Z/Z_{\mathrm{o}} = \mathrm{e}^{-(H/H\mathrm{m})\Delta HK}, \tag{4}$$

where ΔH is the change in humidity ($\Delta H = H - H_{\mathrm{o}}$), H_{m} is the maximum humidity, K is the humidity factor, Z and Z_{o} are the impedances at different humidities and a humidity of 30%, respectively. From the experimental data shown in Fig. 5, the humidity factor K is determined ($K = 0.117$ /%) for the 90% RH. The comparison of normalized experimental impedance–humidity relationships (from Fig. 5) and simulated (by Eq. (4))is shown in Fig. 9. It is evident that the deviation of the simulated curve from the experimental one is in a reasonable range.

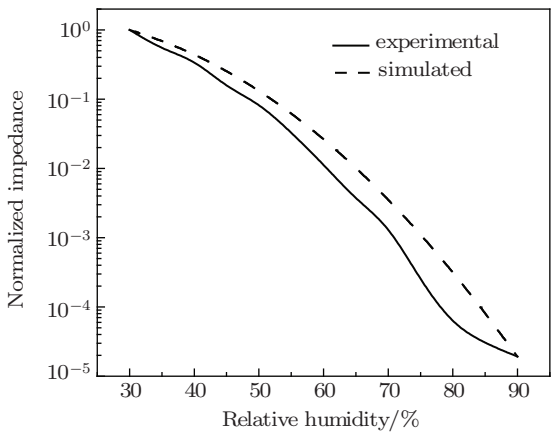


Fig. 9. Normalized experimental and simulated impedance–humidity relationships for the Ag/OD–PANI/Ag sensor at 120 Hz.

The experimental impedance–humidity curve actually follows the exponential function, and the curve is not exactly linear for the utilization of the sample as a humidity sensor. For linearization, electronic circuits like a logarithmic amplifier are used.[26]

The response and recovery time is defined as the time required by the sensor to measure 90% of the total impedance change.[6] The curves for the response time τ_{res} and recovery time τ_{rec} of the Ag/OD–PANI/Ag sensor are obtained by suddenly changing the humidity from 30% to 90% and from 90% to 30% as shown in Fig. 10. It is evident from the curves that τ_{res} and τ_{rec} are 34 s and 450 s, respectively.

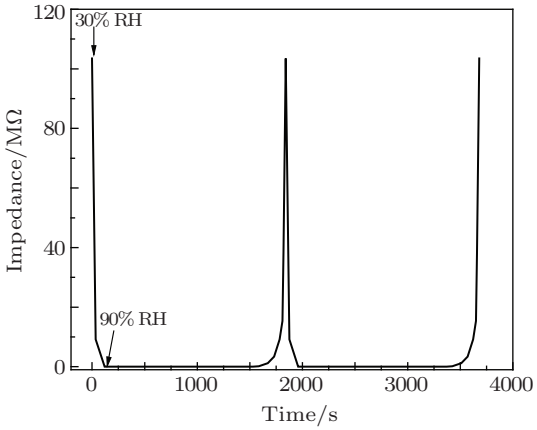


Fig. 10. Response time τ_{res} and recovery time τ_{rec} of the Ag/OD–PANI/Ag sensor.

The material's polarizability governs its capacitance.[23] Three basic sources of polarizability are dipolar polarizability α_{dip}, ionic polarizability α_i, and electronic polarizability α_e. Due to the presence of dipoles (H_2O absorbed by the OD–PANI composite). The dipolar polarizability α_{dip} may play a dominant role in the present case. The electronic polarizability is universal and arises due to the relative displacements of the orbital electrons. The OD–PANI composite in the presence of water molecules may form charge-transfer complexes, and it can be assumed that the ionic polarization takes place in this material. Amy *et al*.[27] and Iwamoto *et al*.[28] investigated the polarizability due to the transfer of charge carriers such as electrons and holes that are presented in organic materials in normal conditions.

With the increase in humidity, the capacitance increases due to the diffusion of water molecules into the OD–PANI composite film through the surface. The high dielectric permittivity of water molecules causes the increase of the dielectric permittivity of the OD–PANI composite. As the presence of displacement current caused by water molecules is the main reason for the increase in capacitance and decrease in resistance; the doping of the composite material by water molecules, the concentration of charge related to the presence of extra charge carriers, and the raise in polarizability of the OD–PANI composite also play important roles. Boguslavsky *et al*.[29] described these mechanisms in detail with respect to some solids. For the simulation of the physical processes concerned with the capacitance–humidity relationship, the same approach can be used as described in Ref. [30].

The results reveal that for the investigation of humidity response of sensors, the measurements of resistance and capacitance are complimentary, which can be replaced by an impedance measurement. The high diffusivity of water molecules into the OD–PANI composite and the interactions between water molecules and the OD–PANI composite are two main reasons for the high sensitivity of the OD–PANI composite films to humidity. The interactions between water molecules and the OD–PANI composite result in the formation of charge-transfer complexes and accordingly increase the concentration of the charge carriers (electrons and holes).

4. Conclusion

The humidity sensors have been fabricated by the deposition of OD–PANI composite films from a blend of orange dye and PANI in distilled water. The capacitance and the impedance of the sensors are evaluated at room temperature under a humidity of 30–90%. It is observed that with the increase in humidity, the impedance of the sensor decreases, and the capacitance increases. In the humidity interval of 30–90%, the impedance–humidity relationship shows more uniform changes with respect to the capacitance–humidity relationship. It is observed that the resistance plays a dominating role as compared to the capacitance in the impedance. It is also found that annealing increases the sensor's sensitivity to humidity by up to 2.5 times. Due to the difference in the diffusion rates during absorption and desorption, a hysteresis is observed in sensors with thicker films. For the design of an OD–PANI composite based humidity meter, impedance–humidity measurements are sufficient. It is found that the impedance–humidity relationship actually follows an exponential function. It can be linearized by using op-amp electronic circuits. The humidity dependent impedance of this sensor makes it attractive for use in an impedance humidity meter. The impedance humidity meter may be used in the instruments for environmental monitoring and assessment of humidity.

Acknowledgment

Authors are thankful to the GIK Institute of Engineering Science and Technology for the support extended to this work. Mr. Muhammad Tariq Saeed would like to acknowledge the Higher Education Commission of Pakistan for providing the financial support.

References

[1] Fuke M V, Kanitkar P, Kulkarni M, Kale B B and Aiyer R C 2010 *Talanta* **81** 320

[2] Chen Z and Lu C 2005 *Sens. Letters* **3** 274

[3] Ramaprasad A T and Rao V 2010 *Sensor and Actuators* B **148** 117

[4] Nohria R, Khillan R K, Su Y, Dikshit R, Lvov Y and Varahramyan K 2006 *Sensor and Actuators* B **114** 218

[5] Huang J R, Li M Q, Huang Z Y and Liu J H 2007 *Sensor and Actuators* A **133** 467

[6] Ahmad Z, Sayyad M H, Saleem M, Karimov K S and Shah M 2008 *Physica* E **41** 18

[7] Zeng F W, Liu X X, Diamond D and Lau K T 2010 *Sensor and Actuators* B **143** 530

[8] Matsuguchi M, Okamoto A and Sakai Y 2003 *Sensor and Actuators* B **94** 46

[9] Palaniappan S and John A 2008 *Prog. Polym. Sci.* **33** 732

[10] Huang L M, Chen C H, Wen T C and Gopalan A 2006 *Electrochimica Acta* **51** 2756

[11] Li Y, Ying B, Hong L and Yang M 2010 *Synth. Met.* **160** 455

[12] Parvatikar N, Jain S, Khasim S, Revansiddappa M, Bhoraskar S V and Prasad M V N A 2006 *Sensor and Actuators* B **114** 599

[13] Pandey M, Srivastava A, Srivastava A and Shukla R K 2010 *Sensors & Transducers Journal* **119-2** 33

[14] Karimov K S, Sayyad M H, Ali M, Khan M N, Moiz S A, Khan K B, Farah H and Karieva Z M 2006 *J. Power Sources.* **155** 475

[15] Karimov K S, Sayyad M H, Ahmed M M, Khan M N, Karieva Z M, Moiz S A, Shah M, Zakaullah K and Turaeva M A 2004 *Euras. Chem. Tech. J.* **6** 145

[16] Ahmed M M, Karimov K S and Moiz S A 2008 *Thin Solid Films* **516** 7822

[17] Moiz S A, Ahmed M M and Karimov K S 2005 *Jpn. J. App. Phys.* **44-3** 1199

[18] Irwin J D 1999 Basic Engineering Circuit Analysis (6th edn.) (New York: John Wiley & Sons)

[19] Wan M, Huang J and Shen Y 1999 *Synth. Met.* **101** 708

[20] Sun A, Li Z, Wei T, Li Y and Cui P 2009 *Sensor and Actuators* B **142** 197

[21] Vilkman M, Lehtinen K, Makela T, Rannou P and Ikkala O 2010 *Org. Electron.* **11** 472

[22] Sze S M 1985 *Semiconductor Devices*: *Physics and Technology* (New York: Wiley)

[23] Omar M A 2002 *Elementary Solid State Physics*: *Principles and Applications* (Singapore: Pearson Education Pte. Ltd.)

[24] Neamen D A 1992 *Semiconductor Physics and Devices*: *Basic Principles* (Boston: Richard D. Irwin Inc.)

[25] Croft A, Davison R and Hargreaves M 1993 *Engineering Mathematics, A Modern Foundation for Electronic, Electrical and Control Engineers* (London: Addison-Wesley Publishing Company)

[26] Irvine R G 1994 Operational Amplifiers Characteristics and Applications (3rd edn.) (New Jersey: Prentice Hall)

[27] Amy F, Chan C and Kahn A 2005 *Org. Electron.* **6** 85

[28] Iwamoto M and Manaka T 2005 *Proc. Int. Symp. IPAP Conf. Series* **6** 63

[29] Boguslavsky S N and Vannikov V V 1968 *Organic Semiconductors* (Moscow: V.A. Kargin, Nauka)

[30] Karimov K S, Akhmedov K, Qazi I and Khan T A 2007 *J. Optoelectron. Advanced Materials* **9** 2867