



Polyaniline based impedance humidity sensors

M. Tariq Saeed Chani^{a,b,*}, Kh.S. Karimov^{a,c}, F. Ahmad Khalid^a, S. Abdul Moiz^d

^a GIK Institute of Engineering Sciences and Technology, Topi 23640, Swabi, 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

^d Department of Electrical Engineering, College of Engineering and Islamic Architecture, Umm Al-Qura University, Makkah, Saudi Arabia

ARTICLE INFO

Article history:

Received 6 December 2011

Received in revised form

22 November 2012

Accepted 14 January 2013

Available online 26 January 2013

Keywords:

Humidity sensor

Conducting polymer

Polyaniline

Dielectric permittivity

Simulation

ABSTRACT

In this study, the fabrication and sensing response of humidity sensor based on the polyaniline (PANI) thin film have been studied. PANI thin films with 30–70 μm thickness were deposited on glass substrates between pre-deposited silver and gold electrodes. It was found that the sensing mechanism is based on the impedance and capacitance variations. For change in Relative Humidity (RH) from 36 to 90%, the change in sensor's capacitance and impedance is 167 and 471 times, respectively. The impedance–humidity relationship is more uniform as compared to capacitance–humidity relationship for this range of humidity. It is also observed that annealing enhanced the sensitivity of the sensor by two times. The consequence of measuring frequency and absorption–desorption behavior of the humidity sensor are also discussed in detail. Response (τ_{res}) and recovery (τ_{rec}) times are 8 and 27 s respectively. Results are examined by simulation and found in good agreement with experimental data.

© 2013 Elsevier Masson SAS. All rights reserved.

1. Introduction

Investigation and modification of electrical, optical and photo-voltaic response [1–5] of organic semiconductors reveal their potential for a variety of applications. Organic materials are very sensitive to humidity [1,2,6], temperature [5,7], radiations [8] and different types of gases etc [9–11].

Measurement and control of humidity is very important not only for human comfort but also for manufacturing processes and industrial products [12] because of universal existence of water, which affects the human health and physical properties of materials [13]. Humidity sensors are widely used in semiconductor, automobile, medical, pharmaceutical, health caring, textile, paper, agriculture and food industry [14,15].

Commercially available humidity sensors are fabricated by conventional sensing materials like alumina, ceramics and electrolytic metal oxides [14]. Depending upon the nature of materials these sensors may be expansive or require high operational power/temperature and high cost of maintenance [6,15]. Organic materials due to light weight, flexibility, simple technology, low cost and

large surface area have developed great interest for their use in humidity sensors. The humidity sensors based on organic sensing materials are classified in to capacitive, resistive [14] oscillating, mechanical [16], and thermoelemental [17] type sensors depending upon basic sensing principle. Based on its unique advantages each type of sensor has specific applications. To make the sensor suitable for commercialization; the wide range sensitivity, linear response, small hysteresis, short response and recovery time, low cost and low power along with long term physical and chemical stability are the required characteristics [16,17].

The polyaniline (PANI) is one of the most interesting polymers due to its good stability, easy preparation and its potential for fabrication of different microelectronic devices [18–21]. The tailoring of conductivity of PANI by doping level of oxidation and protonation makes it unique among such other polymers. The existence of oxidation states in PANI provides basis for its sensitivity to water [22].

The change in resistance of polyaniline with change in relative humidity was studied by Ref. [23]. In this study 0.55–0.89 mm thick pellets of polyaniline with 13 mm diameter were prepared by using 7 ton hydraulic press. The change in resistance from 5.8 G Ω to 13.9 M Ω is reported for change in humidity from 15 to 90% RH, while response and recovery time was 1 min for 30% change in humidity. A rapid response humidity sensor based on ultra thin film layer by layer (LBL) assembly of poly(anilinesulfonic acid) (SPANI) were fabricated by Ref. [15] and compared with SPANI based

* Corresponding author. Faculty of Materials Sciences and Engineering (FMSE), GIK Institute of Engineering Sciences and Technology, Topi 23640, District Swabi, Pakistan. Tel.: +92 938 271 858x2669; fax: +92 938 271868.

E-mail addresses: tariq_chani@yahoo.com, tariqchani1@gmail.com (M.T.S. Chani).

sensors fabricated by spin coating. For LBL and spin coated structure the reported sensitivity is 11% and 6% respectively for 5% change in relative humidity. The response time is 15 s and 27 s respectively for LBL and Spin coated sensors, while the overall recovery time is 60 s. In Ref. [24] the synthesis of polyaniline/tungsten oxide composite by in situ deposition technique and the fabrication of pellets having thickness 3 mm and diameter 10 mm and their electrical characterization for the measurement of temperature and humidity is reported. In the range of 10–95% RH, the pellets of composite show linear resistance–humidity behavior.

In continuation of the research done in fabrication and investigation of the humidity sensors based on organic materials by our group, here we present the investigation of humidity sensing properties of Au/PANI/Ag sensor. Simple technique has been used for the fabrication of sensors and these sensors showed higher sensitivity and faster response and recovery times as compared to some previously reported sensors based on PANI or PANI based composites [15,23].

2. Experimental

A commercially available polyaniline (PANI) emeraldine base (EB) with molecular weight $\sim 20,000$ and formula ($C_{24}H_{20}N_4$) was purchased from Sigma Aldrich and was used for preparation of samples. A molecular structure of the polyaniline is shown in Fig. 1.

The solution was prepared by mixing 1 wt% PANI powder in a mixture of 90 wt% water and 10 wt% alcohol, and stirred at room temperature. Glass substrates were cleaned for 10 min using acetone in ultrasonic cleaner and dried. Then the substrates were also plasma cleaned for 5 min. The Au and Ag thin film electrodes were deposited by vacuum evaporation on cleaned substrates, keeping a gap of 50 μm between them. The thickness of the Au and Ag electrodes was 100 nm and the gap length was kept 10 mm. Polyaniline films having thickness of 30–70 μm were deposited at room temperature from solution by drop-casting on to the Au and Ag electrodes which were preliminary deposited on glass substrates. Fig. 2 shows schematic diagram of the Au/PANI/Ag samples.

Two different metals are used to enhance the sensitivity of sensors. As different metals with different work functions create the electric field in inter-electrodes space [25] and the depletion region accordingly where, the concentration of charges is usually less in comparison with the same materials. If intrinsic concentration of charges became less the sensor is more sensitive to the effect of extrinsic charges.

The fabricated devices were kept at room temperature for 72 h to let the moisture evaporate from the films. Fig. 3 shows SEM images of polyaniline thin film. It can be seen that the polyaniline film's surface structure is porous and non-uniform; it also contains clusters of particles and the size of clusters are in the range of 5–15 μm . The samples were annealed at 100 $^{\circ}\text{C}$ for 1 h.

The sensors were tested in indigenously made humidity chamber, which has been developed in our device testing laboratory. It is a closed chamber with inlet and outlet valves for gas. To create humidity in the chamber, nitrogen gas is passed through the water and then injected in to the chamber. The humidity is measured by Fisher Scientific Digital Hygrometer. The capacitance (C) and dissipation (D) are measured by using ESCORT ELC-132 A LCR

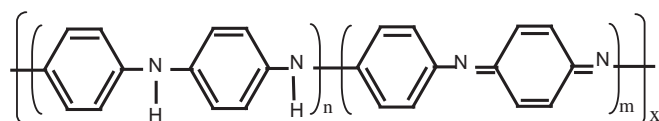


Fig. 1. Molecular structure of the polyaniline, where $n = m = 0.5$.

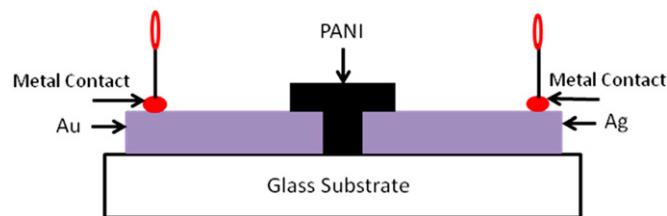


Fig. 2. Schematic diagram of the Au/PANI/Ag humidity sensor.

meter at different frequencies, while the parasitic capacitance is deducted from the data. The resistance (R) and impedance (Z) are calculated by the following expressions [26]:

$$R = 1/(\pi f C D) \quad (1)$$

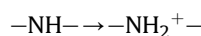
and

$$Z = 1/Y = 1/\left[\left(1/R^2\right) + (2\pi f C)^2\right]^{1/2} \quad (2)$$

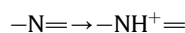
where f is frequency and Y is admittance. Here the impedance of the hygrometer was considered as an impedance of parallel connected resistance and capacitance.

3. Results and discussion

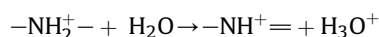
Fig. 4 shows the relationships of capacitance and impedance with relative humidity for the Au/PANI/Ag sensor at 120 Hz. It can be seen that the capacitance shows enormous increase in the intervals of 70–90% RH, while change in impedance with increase in humidity is more uniform in the range of 36–90% RH. The change of the sensor's capacitance and impedance over whole humidity interval are 167 and 471 times respectively. This change in the electrical properties of PANI due to change in relative humidity is because of firstly, adsorption (chemisorptions and physisorption) and absorption of water molecules and secondly, increase of charges concentration due to doping of PANI and formation of charge transfer complexes (CTC) [22]. The emeraldine base PANI structure is comprised of oxidized and reduced (non-oxidized) forms of structures (Fig. 1). These both forms can be protonated due to the un-bonded electron pair on the nitrogen atom as Ref. [27]



and



The buildup model explains that when water content in PANI reaches 0.1% (mole ratio) the hopping is the dominant conduction process [28]. In this process electron is transferred from the protonated reduced form ($=\text{NH}_2^+=$) to the protonated oxidized form ($-\text{NH}^+=$). In the conduction process water plays a vital role and reaction by which proton is transferred to the water is the following [15,27]



The electron hopping assisted by proton exchange makes PANI sensitive to water vapors. Hence it may be considered that electronic and ionic conduction take place during humidity sensing process [27].

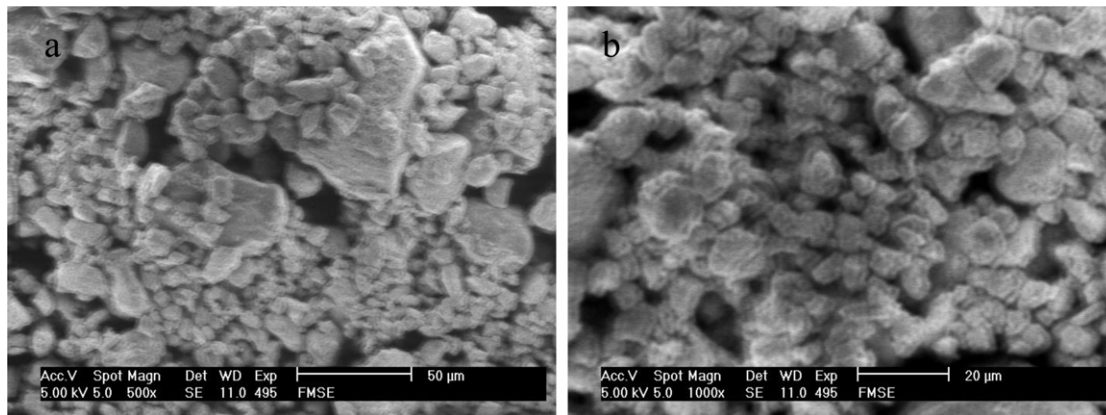


Fig. 3. Surface morphology of PANI film at low (a) high (b) magnification.

Fig. 5 shows impedance–relative humidity relationship for frequencies of 120 Hz and 1 kHz respectively. From Fig. 5 it can be seen that the calculated values of the sample's impedance decrease uniformly with increase of humidity. The values of the impedance also decrease with the increase of frequency on any relative humidity level. Dependence of the impedance on the frequency can be explained by the dependence of dielectric permittivity [29], mobility of ions (firstly) and electrons (secondly) and transit time of charges transfer on the frequency [30].

Fig. 6 shows impedance–humidity relationship during absorption and desorption of humidity where the values are taken at room temperature at a frequency of 120 Hz. It can be seen that the absorption and desorption curves are coincided within the experimental error of $\pm 2\%$. It means that hysteresis is small and the humidity memory effect is not like that was observed in PANI and PANI doped with 5-formyl-2-furansulfonic acid [31,32] earlier. Table 1 shows the humidity sensing properties of the PANI.

Simulation of the data is done as described in number of papers and books [33]. For simulation, first of all, such a mathematical function is selected that could describe the experimental results in a better way (in this case selected function is exponential function (Eq. (3))). Secondly, the function is replaced by relative value (Eq. (4)). Thirdly, the fitting parameter “K”, i.e. humidity factor is introduced and its value is found by using the values of impedance

at lowest and highest humidity levels which is further use for the calculation of impedance at different humidity levels.

For simulation of the experimental results of impedance–humidity relationship shown in Fig. 4, the following exponential function [34] is used:

$$f(x) = e^{-x} \quad (3)$$

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

$$Z/Z_0 = e^{-(2H/(H_m+H))\Delta HK} \quad (4)$$

where ΔH is change in relative humidity ($\Delta H = H - H_0$), H_m is maximum humidity ($H_m = 90\%$), K is humidity factor, Z and Z_0 are impedances at different humidity and humidity of 36% respectively.

From experimental data shown in Fig. 4 the humidity factor K is determined ($K = 0.114/\%$) for the $H = 90\%$. Fig. 7 shows normalized (Z/Z_0) experimental (from Fig. 4) and simulated (by Eq. (4)) impedance–humidity relationship. It can be seen that the deviation of the simulated curve from experimental is in the reasonable range. Fig. 7 shows that experimental impedance–humidity curve

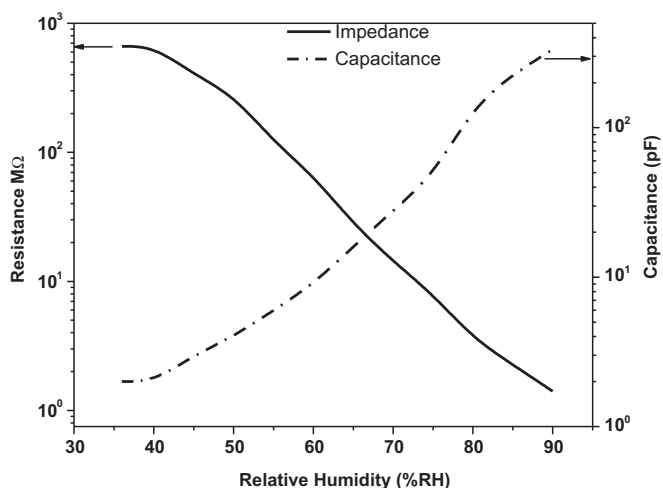


Fig. 4. Capacitance and impedance–relative humidity (RH) relationships for the Au/PANI/Ag sensor at 120 Hz.

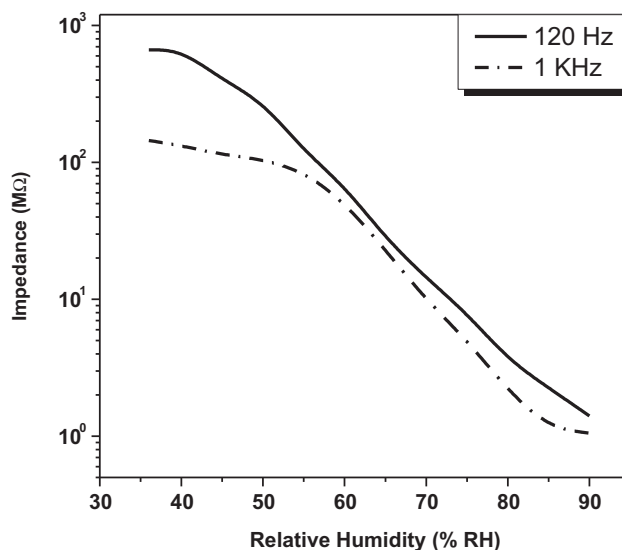


Fig. 5. Impedance–relative humidity (RH) relationships for the Au/PANI/Ag sensor at 120 Hz and 1 kHz.

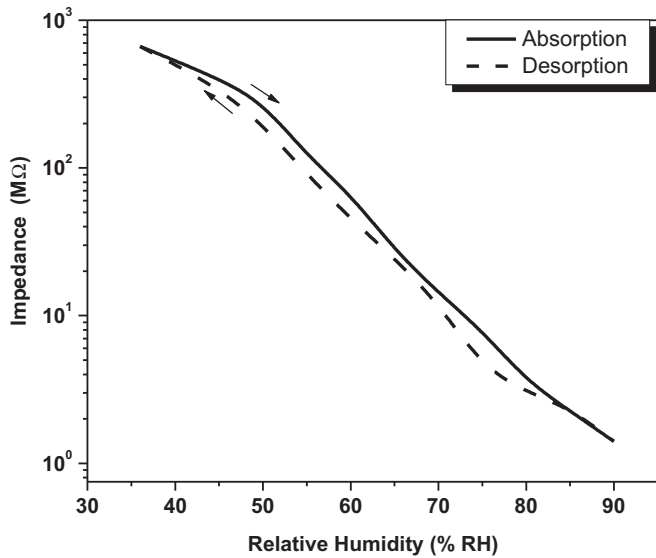


Fig. 6. Impedance–relative humidity (RH) relationships for the Au/PANI/Ag sensor at 120 Hz during absorption and desorption of humidity.

actually follows to exponential function. As this curve is not exact linear for utilization of the samples as a humidity sensor, the linearization circuit should be used. Practically the linearization can be made by logarithmic amplifier (Fig. 8) [35]. The log diode, for example 1N914 diode, in this circuit is operating in forward-bias region. As diode is temperature-dependent element, so the diode and amplifier should be kept in a temperature-controlled chamber [35].

Table 1 shows the comparison of humidity sensing properties of sensor in as fabricated and annealed conditions. It can be observed that annealing has improved the sensitivity of the samples by two times. The change in properties, particularly impedance humidity sensitivity as a result of annealing can be attributed to the structural changes which take place due to annealing [36].

The obtained experimental results reveal that impedance–humidity relationship shows more consistent changes over wide range of the humidity (36–90%) as compared to the capacitance–humidity relationship that is important for the design of humidity sensor on the base of investigated materials. The impedance depends on both resistance and capacitance changes (Eq. (2)) this is a reason that the impedance–humidity relationship is uniform as compared to the relationships of the resistance and capacitance. At the same time the impedance decreases with increase in humidity, in principle, in the same manner as the resistance of the sensor. It is obvious that the effect of the resistance to impedance is dominating with respect to the effect of the capacitance. The decrease in impedance for frequency of 120 Hz and 1 kHz when humidity changes from 36% to 90% is 471 and 137 times, respectively.

Fig. 9 shows the response (τ_{res}) and recovery (τ_{rec}) times of the Au/PANI/Ag samples. The response and recovery time is the time required by the sensor to measure the 90% of the total impedance change [17]. It can be seen that τ_{res} and τ_{rec} are equal to 8 and 27 s

Table 1
Humidity sensing properties of sensor.

Thickness (μm)	Frequency (Hz)	C (90%)/C (36%)		Z (36%)/Z (90%)	
		As-fabricated	Annealed	As-fabricated	Annealed
70	120	167	324	471	727
	1000	42	59	137	161

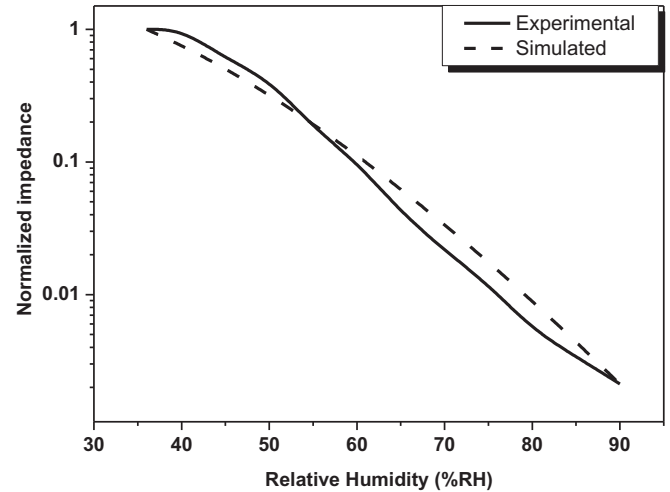


Fig. 7. Normalized experimental and simulated impedance–relative humidity (RH) relationships for the Au/PANI/Ag sensor at 120 Hz.

respectively. These curves are obtained by suddenly changing relative humidity from 36 to 90% and 90 to 36%.

It is well-known that the value of the capacitance depends on the polarizability of the material, which has several basic sources i.e. dipolar α_{dip} , ionic α_i and electronic α_e polarizability [29]. In this case the dipolar (α_{dip}) polarizability due to the presence of dipoles (H_2O) absorbed by the polyaniline seems to play a very important role. Electronic polarizability is universal and arises due to relative displacement of the orbital electrons. Polyaniline may comprise charge-transfer complexes with water molecules; it can be assumed that ionic polarization takes place as well in this organic material. The polarizability due to the transfer (α_t) of charge carriers such as electrons and holes that are present at normal conditions in the organic material was investigated by Refs. [37–39].

The increase in capacitance with increase in humidity can be explained by the following way. The dielectric permittivity of the polyaniline increases due to absorption of water molecules, having higher dielectric permittivity value, by diffusion through the surface of the PANI. The decrease in resistance and increase in capacitance firstly may be due to the presence of displacement current caused by water molecule, and secondly may be due to possible doping of the polyaniline by the water molecules and increase of the polarizability and concentration of charges related

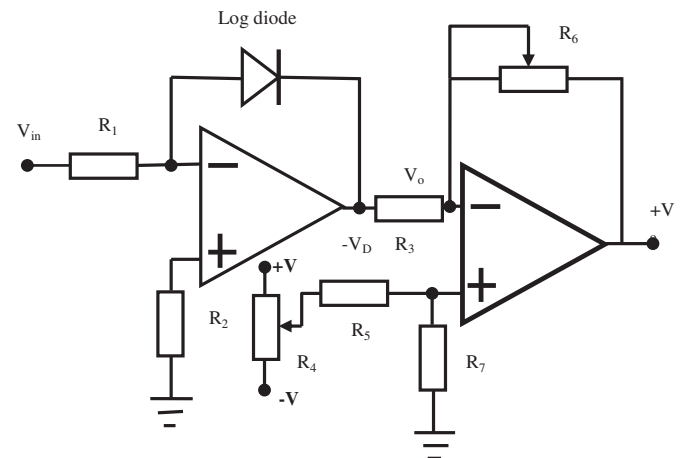


Fig. 8. Circuit diagram of op-amp logarithmic amplifier.

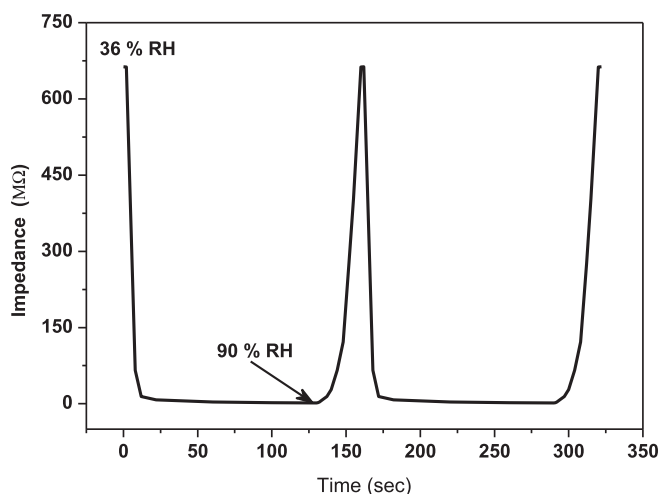


Fig. 9. The response (τ_{res}) and recovery (τ_{rec}) times of the Au/PANI/Ag sensor.

to presence of the extra charge carriers. These mechanisms have been described in detail with respect to some solids [37].

The results show that with the increase in frequency, the sensitivity of the samples decreases. It may be due to comparability of the relaxation time of the related processes with period of applied measuring AC voltage [29].

The simulation of the physical processes concerned with impedance–humidity relationship can be easily done by the use of the Eq. (4) and approaches for simulation of the capacitance used by the same authors earlier for organic semiconductor poly-N-epoxypropylcarbazole complexes photo-capacitive detectors [40].

The results also showed that the resistance and capacitance measurements for investigation of the humidity response of the samples are complimentary and can be replaced by impedance measurement only. The high sensitivity of the polyaniline to humidity is first of all due to high diffusivity of the water molecules in the polyaniline. Secondly, it is due to molecular interactions between water molecules and polyaniline which resulted in the formation of charge-transfer complexes and accordingly increased the concentration of the charge carriers as electrons and holes.

4. Conclusions

The humidity sensing properties of the polyaniline films deposited by drop casting were investigated. The capacitance and impedance of the samples were evaluated under the effect of humidity in the range of 36%–90% RH. It was observed that the capacitance of the sensor increases and impedance decreases with increase of the relative humidity. It was found that impedance–humidity relationship shows more uniform changes in the interval of 36%–90% RH with respect to capacitance–humidity relationship that show less consistent changes in this interval. It was observed that resistance contribution in the impedance was dominated with respect to the capacitance. It was also found that annealing increases sensors sensitivity to humidity for two times. Only impedance–humidity measurements are sufficient for design of the polyaniline based humidity meter. It was found that the impedance–humidity relationships actually follow to exponential function. It can be discussed by op-amp electronic circuit for linearization of the impedance–humidity relationships. Humidity dependent impedance of this sensor makes it attractive for use in impedance humidity meter. The impedance humidity meter may be used in the instruments for environmental monitoring and assessment of humidity.

Acknowledgments

We are thankful to GIK Institute of Engineering Science and Technology for the support extended to this work. The authors also acknowledge the enabling role of Higher Education Commission (HEC) of Pakistan and appreciate the financial support through indigenous PhD fellowship program.

References

- [1] U. Lange, N.V. Roznyatovskaya, V.M. Mirsky, *Anal. Chim. Acta* 614 (2008) 1–26.
- [2] B. Adhikari, S. Majumdar, *Polymers in sensor applications*, *Prog. Polym. Sci.* 29 (2004) 699–766.
- [3] S.A. Moiz, M.M. Ahmed, Kh. S. Karimov, *Jpn. J. Appl. Phys.* 44 (2005) 1199–1203.
- [4] T. Mikayama, H. Matsuoka, K. Uehara, A. Sugimoto, K. Mizuno, N. Inoue, *Trans. IEEE, Jpn.* 118 (1998) 1435–1442.
- [5] M.M. Ahmed, Kh.S. Karimov, S.A. Moiz, *Thin Solid Films* 516 (2008) 7822–7827.
- [6] F.W. Zeng, X.X. Liu, D. Diamond, K.T. Lau, *Sens. Actuators B* 143 (2010) 530–534.
- [7] Kh.S. Karimov, *Electric Properties of Organic Materials at Deformation*, D.Sc. thesis, Department of Heat Physics, Academy of Sciences, Tashkent, Uzbekistan, 1994.
- [8] Kh.S. Karimov, Kh.M. Akhmedov, A.A. Dzhruev, M.N. Khan, S.M. Abrarov, M.I. Fiodorov, *Eur. Chem. Tech. J.* 3–4 (2000) 251–256.
- [9] M. Matsuguchi, A. Okamoto, Y. Sakai, *Sens. Actuators B* 94 (2003) 46–52.
- [10] M.I. Fiodorov, *Gas Sensor Patent # 2124719*, Moscow, Russia, 1999.
- [11] S.C.K. Misra, P. Mathur, B.K. Srivastava, *Sens. Actuators A* 114 (2004) 30–35.
- [12] M.V. Fuke, P. Kanitkar, M. Kulkarni, B.B. Kale, R.C. Aiyer, *Talanta* 81 (2010) 320–326.
- [13] N. Camaioni, G.C. Micelia, Y. Li, M.J. Yang, A. Zanelli, *Sens. Actuators B* 134 (2008) 230–233.
- [14] A.T. Ramaprasad, V. Rao, *Sens. Actuators B* 148 (2010) 117–125.
- [15] R. Nohria, R.K. Khillan, Y. Su, R. Dikshit, Y. Lvov, K. Varahramyan, *Sens. Actuators B* 114 (2006) 218–222.
- [16] J.R. Huang, M.Q. Li, Z.Y. Huang, J.H. Liu, *Sens. Actuators A* 133 (2007) 467–471.
- [17] Z. Ahmad, M.H. Sayyad, M. Saleem, Kh.S. Karimov, M. Shah, *Physica E* 41 (2008) 18–22.
- [18] S. Palaniappan, A. John, *Prog. Polym. Sci.* 33 (2008) 732–758.
- [19] S. Bhadra, D. Khastgir, N.K. Singha, J.H. Lee, *Prog. Polym. Sci.* 34 (2009) 783–810.
- [20] H. Bejbouji, L. Vignau, J.L. Miane, M.T. Dang, E.M. Oualim, M. Harmouchi, A. Mouhsen, *Sol. Energy Mater. Sol. Cells* 94 (2010) 176–181.
- [21] K. Mallick, M. Witcomb, R. Erasmus, A. Strydom, *J. Appl. Polym. Sci.* 116 (2010) 1587–1592.
- [22] M.V. Fuke, A. Vijayan, M. Kulkarni, R. Hawaldar, R.C. Aiyer, *Talanta* 76 (2008) 1035–1040.
- [23] M. Pandey, At. Srivastava, An. Srivastava, R.K. Shukla, *Sens. Transducers J.* 113–2 (2010) 33–40.
- [24] N. Parvatikar, S. Jain, S. Khasim, M. Revansiddappa, S.V. Bhoraskar, M.V.N.A. Prasad, *Sens. Actuators B* 114 (2006) 599–603.
- [25] C.J. Brabec, V.D. Yakonov, J. Parisi, N.S. Sariciftci, *Organic Photovoltaics. Concepts and Realization*, Springer-Verlag, Berlin, Heidelberg, 2003.
- [26] J.D. Irwin, *Basic Engineering Circuit Analysis*, sixth ed., John Wiley & Sons, New York, 1999.
- [27] Z. Chen, C. Lu, *Sens. Lett.* 3 (2005) 274–295.
- [28] J.P. Travers, M. Nechtschein, *Synth. Met.* 21 (1987) 135–141.
- [29] M.A. Omar, *Elementary Solid State Physics: Principles and Applications*, Pearson Education Pte.Ltd, Singapore, 2002.
- [30] D.A. Neamen, *Semiconductor Physics and Devices: Basic Principles*, Richard D. Irwin Inc., Boston, USA, 1992.
- [31] Y. Li, B. Ying, L. Hong, M. Yang, *Synth. Met.* 160 (2010) 455–461.
- [32] M. Vilkman, K. Lehtinen, T. Makela, P. Rannou, O. Ikkala, *Org. Electron.* 11 (2010) 472–478.
- [33] J.W. Dally, W.F. Riley, K.G. McConnell, *Instrumentation for Engineering Measurements*, second ed., John Wiley & Sons, Inc, New York, 1993.
- [34] A. Croft, R. Davison, M. Hargreaves, *Engineering Mathematics, a Modern Foundation for Electronic, Electrical and Control Engineers*, Addison-Wesley Publishing Company, Great Britain, 1993.
- [35] R.G. Irvine, *Operational Amplifiers Characteristics and Applications*, third ed., Prentice Hall, NJ, 1994.
- [36] S.M. Sze, *Semiconductor Devices: Physics and Technology*, Wiley, New York, USA, 1985.
- [37] S.N. Boguslavsky, V.V. Vannikov, *Organic Semiconductors*, V.A. Kargin, Nauka, Moscow, 1968.
- [38] M. Iwamoto, T. Manaka, *Proc. Int. Symp. Super-functionality Organic Devices: IPAP Conf. Series*, vol. 6, 2005, pp. 63–68.
- [39] F. Amy, C. Chan, A. Kahn, *Org. Electron.* 6 (2005) 85–91.
- [40] Kh.S. Karimov, Kh. Akhmedov, I. Qazi, T.A. Khan, *J. Optoelectron. Adv. Mater.* 9 (2007) 2867–2872.