Cellulose and PEPC based humidity sensor for remote sensing

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In this study an investigation was made on properties of humidity sensor fabricated by using cellulose and poly-N-epoxypropyle carbazole (Au/Cellulose/PEPC/Au). The 2 wt. % of cellulose and 2 wt. % of PEPC was dissolved in benzol. Film of cellulose and PEPC deposited on glass substrates with preliminary deposited gold electrodes. The resistances and capacitances of the samples were evaluated under the effect of humidity which ranges from 30%-95%. It was observed that the capacitance of the sensor increases and resistance decreases with increase of the relative humidity. The sensor was connected to op-amp square wave oscillators. It was found that with increase of humidity the oscillator's frequency also increases in the range of 4.90-12.00 kHz for 65µm thick film sample and 4.80-9.00 kHz for 88µm thick film sample and for 210µm sample the oscillator frequency changes in the range of 4.86-9.00 KHz. This study also shows that how the film thickness effect the oscillator's frequency with respect of humidity. We can select the hygrometer film thickness according to its application so that more sensitive hygrometer can be designed. This organic humidity sensor controlled oscillator can be used for short-range and long-range telemetry system at environmental monitoring and assessment of the humidity level.

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1. Introduction

As is known some of organic semiconductors are very sensitive to humidity [1, 2], temperature [5, 6], IR, visible and UV radiation [7], and different types of gases such as ammonia [8]. Therefore, investigation of physical properties of organic semiconductors under different conditions is very promising field for development of the various sensors for humidity, temperature, light, radiation, strain, gases etc.

At present in resistive hygrometers, the most common material that is used is lithium chloride [9, 10]. The mixture of lithium chloride and carbon is put on insulating substrate between metal electrodes and forms bulk type sensor. Resistance of the element decreases with increase of humidity; it may be due to the formation of some energetic disorder in the element. Resistance of the hygrometer should be measured by applying AC to Wheatstone bridge or by combination of current and voltage measurements [9, 10]. DC voltage is not applied because it tends to breakdown the lithium chloride to its lithium and chlorine atoms. The resistive hygrometer must be operated either in constant temperature environment or temperature corrections must be incorporated. Response times are typically of the order of a few seconds [9, 10]. Resistance of hygrometer changes from 10 kΩ to 10^3 MΩ as humidity changes from 100% to 0%.

The orange dyes (OD) as a *p*-type organic semiconductor have potential application for electronic devices [11-12], first of all due to high sensitivity to the humidity as resistive hygrometer [13, 14].

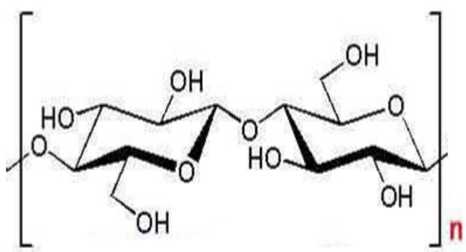
Poly-N-epoxypropyl carbazole (PEPC) is one of the well-studied organic photosensitive semiconductors [1, 2]. It has a high absorption coefficient over a wide spectrum and a high photo-electromagnetic sensitivity at low intensities of radiation. It is possible to deposit thin PEPC films simply, by vacuum sublimation. PEPC is very stable organic material and its purification is simple and economical as the sublimation occurs at relatively low temperatures (400–600°C). Recrystallization of PEPC layers obtained from organic solutions occurs at room temperature [17].

Last years a number of capacitive and resistive humidity sensors were fabricated and investigated on the base of porphyrin, copper phthalocyanine and poly epoxypropyle carbazol [15-17]. These sensors showed good capacitive sensitivity at higher humidity and high resistive sensitivity at lower humidity. Investigation of the capacitive type humidity sensors fabricated by using cellulose and poly epoxypropyle carbazol (PEPC) showed that the sensor is sensitive in the humidity range of 30%-95% and it will become more sensitive when the humidity is above of 60% [18]. The sensor fabricated on the base of cellulose only was less sensitive than sensor made with the mixture of cellulose and CuPc [18].

Practically in many cases the humidity is measured by meter at the spot. But in some specific cases there is need to measure humidity by means of short-range or long-range telemetry systems, where the sensor with transmitter is placed at one place and receiver is placed at a distance from the transmitter. Information is transferred by wireless communication means [19]. Sensor's response is converted into voltage and that applied to voltage controlled oscillator (VCO). The frequency of VCO is modulated by the voltage applied from sensor. In the receiver the frequency modulated (FM) signal is demodulated by the receiver and processed accordingly [19]. The frequency modulation process can be simplified if the sensor directly modulates the frequency of oscillator. In this paper we describe organic humidity sensor based on cellulose and PEPC that can be used for control of oscillator's frequency.

2. Experimental

Commercially available cellulose with molecular formula $(C_6H_{10}O_5)_n$ and PEPC synthesized in the laboratory and were used for the fabrication of humidity sensor. Density of the cellulose was 1.592 g/cm^3. Molecular structures of the cellulose and PEPC are shown in figure 1.a and figure 1.b.



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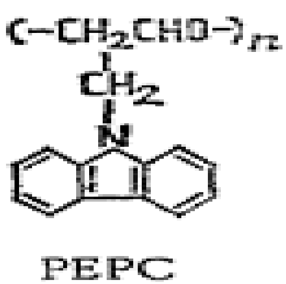

b

Fig..1(a) Molecular structure of the cellulose and (b) poly epoxypropyle carbazol (PEPC).

The 2 wt% of cellulose and 2 wt% of PEPC was mixed in benzol. Glass substrates were cleaned for 10 minutes using distilled water in ultrasonic cleaner and dried. Then the substrates were also plasma cleaned for 5 minutes. The gold electrodes on cleaned substrate were deposited, keeping the 50 µm gap between them. The thickness of the electrodes was 100 nm where as the gap lengths were 5 mm. Films of cellulose and PEPC were deposited by drop casting method with approximate thickness of 65 µm, 88 µm and 210 µm respectively. The fabricated sensors were kept at room temperature for one night to evaporate the moisture from the films. Figure 2 shows schematic diagrams of the fabricated Au/Cellulose/ PEPC/Au sensor. Measurements were carried out in self made humidity measurement setups, which have been developed in our device testing laboratory. Resistance and capacitance of the sensor were measured by using conventional digital instruments.

As is known the output frequency of the oscillators, including VCO, made on the base of IC technology containing external resistance ($R_1=R_2=51K\Omega$) and capacitance ($C_1=C_2=0.001\mu F$) elements is inverse proportional to the values of R and C [20]. We have selected Wien bridge op-amp oscillators and replaced the capacitance (C_2) by the organic Au/Cellulose/PEPC/Au sensor [20]. Figure 3 shows the electric circuit of the organic humidity controlled oscillators with built-in Au/Cellulose/PEPC/Au sensor. The frequency of the oscillator is determined by the following expression [20].

$$f_o = 1 / 2\pi \sqrt{R_1C_1R_2C_2} \qquad (1)$$

Experimentally the frequency was estimated by use of the conventional oscilloscope.

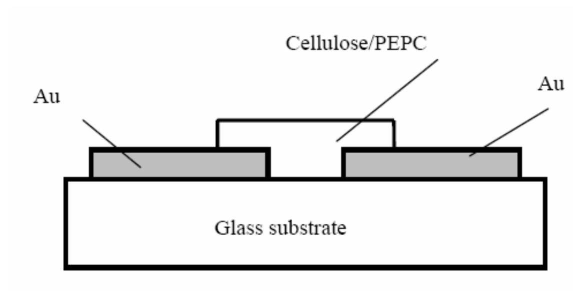

Fig..2. Cross-sectional view of the fabricated Au/Cellulose/PEPC/Au hygrometer.

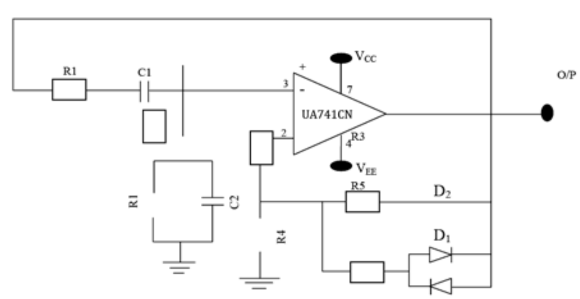

Fig. 3. Electric circuits of the organic humidity controlled oscillator with built in Au/Cellulose/PEPC/Au sensor.

3. Results and discussion

Fig..4 and Fig..5 show capacitance (C) and resistance (R) with respect to relative humidity (*H*) relationships for the Au/Cellulose/PEPC/Au sensor at frequency (*f*) equal to 100 Hz, 1 kHz and 10 KHz respectively. It is seen that the resistance shows very sharp decrease in the interval of humidity of 31% - 65% , and the capacitance shows large increase in the interval of humidity of 70%- 95 %. The change of the sensor's resistance and capacitance in whole humidity interval are shown in Table 1.

Table. 1 Comparison of humidity sensing properties of Au/Cellulose/PEPC/Au Hygrometer

S.No	Frequency	Thickness of Film µm	R_{max}/R_{min} (31%/95 %)	C_{max}/C_{min} (95%/30 %)
1	100 Hz	65 µm	347	190
		88 µm	1302	332
		210 µm	154	17
2	1 KHz	65 µm	1869	57
		88 µm	1637	65
		210 µm	1066	32
3	10 KHz	65 µm	79	12
		88 µm	39	4
		210 µm	23	3

From equivalent circuit of capacitor which includes both resistance and capacitance, we observe that our samples change both capacitances an resistance when we place them in the oscillator circuit. If we want the good capacitive response we will select the sample of 88 µm at 100 Hz and if we want the best resistive response then we will select the 65µm sample at 1 KHz.

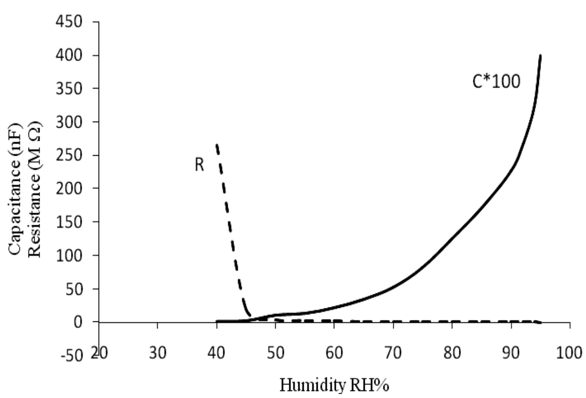

Fig. 4. Capacitance (C) and resistance (R) – relative humidity (RH%) relationships for the Au/Cellulose/PEPC/Au hygrometer at frequency (f) equal to 100 Hz for 88µm sample.

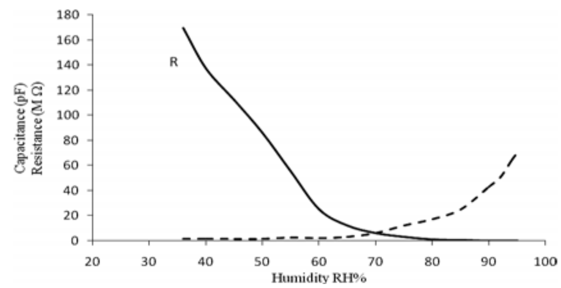

Fig. 5. Capacitance (C) and resistance (R) with relative humidity (H) relationship for the Au/Cellulose/PEPC/Au humidity sensor at frequency (f) equal to 1 kHz for 65µm sample.

The reason of the effect of the humidity to capacitance of the organic sensors was described earlier and can be briefly explained by the following way [17]. Firstly ,dielectric constant of the organic material increases due to absorption of water molecules, having higher dielectric constant value ,by surface , porous and bulk (in the case of diffusion of water molecules) of organic materials. The decrease of the resistance firstly may be due to presence of the displacement current caused by water molecules. Secondly, capacitance increases and resistance decreases due to possible doping of the organic material by the water molecules and increase of the polarizability and concentration of charges related to presence of the extra charge carriers. These mechanisms described in detail with respect of some solids [21]. The high sensitivity of the Cellulose/PEPC double layer system to humidity is due to high sensitivity of cellulose and PEPC to humidity, and to developed surface structure formed by cellulose powder and covering it with thin PEPC film.

Figure.6 shows frequency-humidity relationships for the oscillator circuit. It is seen that the oscillator's frequency increases with humidity at 2.45, 1.87 and 1.85 times accordingly for 65, 88, 210 µm film thickness of the samples. As the oscillator's frequency is increasing with humidity, taking into account the Equation (1) and the resistance-humidity relationship (Figure.4 and 5), where the resistance decreases with humidity, we can say that the effect of the sensor's resistance is dominating with respect of effect of capacitance to the frequency of the oscillator . The increase of the oscillators' frequency with humidity depends first of all from the decrease of the sensor's resistance with the increase of humidity, and secondly, the increase of sensor's capacitance at the increase of humidity.

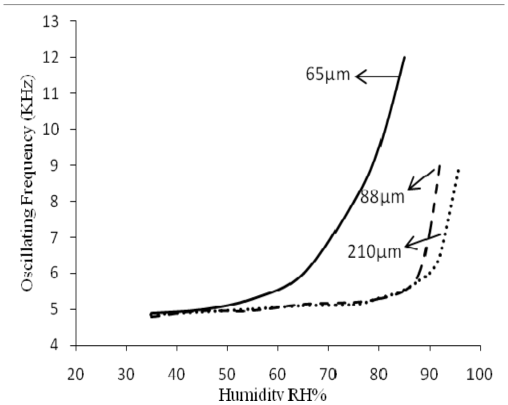

Fig..6 Frequency-humidity relationships for the 65, 88, 210 µm thick samples.

4. Conclusion

In this study it was fabricated and investigated the properties of humidity sensor based on cellulose and poly-N-epoxypropyl carbazole (Au/Cellulose/PEPC/Au). The resistances and capacitances of the samples were evaluated under the effect of humidity in the interval of 30%-95%. It was observed that the capacitance of the sensors increase and resistance decreases with increase of the relative humidity. The sensor was connected to the Wien bridge op-amp square wave oscillators. It was found that with increase of humidity the oscillator's frequency is increased in the range of 4.9-12.00 kHz for 65µm, 4.80-9.0 kHz for 88µm and 4.8-9.0 for 210µm thick sample depends on the sensor's resistance and capacitance properties and oscillator's circuit elements. From this we can conclude that 65µm sample shows the best results with respect of oscillator frequency so thin film humidity sensors, but it covers the shorter range of humidity interval from 35%-85%. To cover more humidity range we shall use thick samples, as we observed the 88µm sample cover the range of humidity from 35%-90% and 210µm sample cover 35%-96% of humidity level. These organic humidity sensor controlled oscillator can be used for short-range and long-range telemetry system for environmental monitoring and assessment of the humidity level.

Acknowledgments

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References

[1] F. Gutman, L. E. Lyons, Organic semiconductors, Part A, Krieger Robert E Publishing Company, Malabar, Florida, U.S.A, 1981, p.125.
[2] F. Gutman, H. Keyzer, L. E. Lyons, R. B. Somoano, Organic semiconductors, Part B Krieger Robert E Publishing Company, Malabar, Florida, U.S.A, 1983, p.35.
[3] E. Arnold, An introduction to molecular electronics, ed C M Petty, M R Bryce and D Bloor, St Edmundsbury Press Limited, London, 1995.
[4] T. Mikayama, H. Matsuoka, K. Uehara, A. Sugimoto, K. Mizuno, N. Inoue, Trans. IEE of Japan, **118**, 1435 (1998).
[5] Kh. S. Karimov, "Electric properties of tetra cyanoquino dimethane ion-radical salts crystals under hydrostatic pressure", PhD Thesis, A F Ioffe Physical Technical institute, St-Petersburg, Russia, 1982.
[6] Kh. S. Karimov, "Electric properties of organic materials at deformation" DSc Thesis, Department of Heat Physics, Academy of Sciences, Tashkent, Uzbekistan, 1994.
[7] Kh. S. Karimov, Kh. M. Akhmedov, A. A. Dzhuraev, M. N. Khan, S. M. Abrarov, M. I. Fiodorov, Eurasian Chem. Tech. Journal, **3-4**, 251 (2000).
[8] M. I. Fiodorov, "Gas sensor", Patent # 2124719, Moscow, Russia, (1999).
[9] U. Sinha, Electrical and electronics measurement and instrumentation, Smt Sumitra Handa, New Delhi, 1992, p.743.
[10] Colin D. Simpson. Industrial Electronics. Prentice Hall Inc., Englewood Cliffs, New Jersey, p. 134 (1996).
[11] Kh. S. Karimov, M. M. Ahmed, R. M. Gul, M. Mujahid, Kh. M. Akhmedov, J. Valiev Conference proceeding,Advanced Materials-2001, Published by Dr. A Q. Khan Research Laboratories Rawalpindi, Pakistan, 2002, p.329.
[12] M. M. Ahmed, Kh. S. Karimov, S. A. Moiz, IEEE transaction of Electron Devices **51,** 121, (2004).
[13] S. A. Moiz, Kh. S. Karimov, N. D. Gohar Eurasian Chem.Tech. Journal, No.6, 201 (2004).
[14] S. A. Moiz, M. M. Ahmed, Kh. S. Karimov, Japanese J. Applied Physiscs, **44** (3), 1199 (2005).
[15] M. Saleem, M. H. Sayyad, Kh. S. Karimov, M. Yaseen, M. Ali, J. Mater. Sci. **44**, 1192 (2009).
[16] M. Saleem, M. H. Sayyad, K. S. Karimov, Z. Ahmad, M. Shah,Y. Yaseen, I. Khokhar, M. Ali J. Optoelectron. Adv. Mater., **10**(6), 1468 (2008).
[17] Kh. S. Karimov, I. Qazi, P. H. Draper, F. A. Khalid, M. Mahroof Tahir, T. A. Khan, Environ. Monit. And Assess. **141**, 323 (2008).
[18] Zubair Ahmad, Muhammad H. Sayyad, Khasan S. Karimov, Journal of Ovonic Research **4**(5), 91 (2008).
[19] J. W. Dally, W. F. Riley, K G McConnell. Instrumentation for engineering measurements, John Willey & Sons, Inc., New York, 1993.
[20] R. L. Boylestad, L. Nashelsky, Electronic devices and circuit theory, 9th Edition, Prentice-Hall Inc., New Jersey, 2006.
[21] M. Ali Omar, Elementary Solid State Physics: Principles and Applications, Published by Pearson Education (Singapore) Pte.Ltd. 2002.

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