Surface-type humidity sensor based on cellulose-PEPC for telemetry systems

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Abstract: Au/cellulose-PEPC/Au surface-type humidity sensors were fabricated by drop-casting cellulose and poly-N-epoxypropylcarbazole (PEPC) blend thin films. A blend of 2wt% of each cellulose and PEPC in benzol was used for the deposition of humidity sensing films. Blend films were deposited on glass substrates with preliminary deposited surface-type gold electrodes. Films of different thicknesses of cellulose and PEPC composite were deposited by drop-casting technique. A change in electrical resistance and capacitance of the fabricated devices was observed by increasing the relative humidity in the range of 0–95% RH. It was observed that the capacitances of the sensors increase, while their resistances decrease with increasing the relative humidity. The sensors were connected to op-amp square wave oscillators. It was observed that with increasing the relative humidity, the oscillator's frequencies were also increased in the range of 4.2–12.0 kHz for 65 μm thick film sample, 4.1–9.0 kHz for 88 μm thick film sample, and 4.2–9.0 kHz for 210 μm sample. Effects of film thickness on the oscillator's frequency with respect to humidity were also investigated. This polymer humidity sensor controlled oscillator can be used for short-range and long-range remote systems at environmental monitoring and assessment of the humidity level.

Key words: surface-type sensor; cellulose; poly-N-epoxypropylcarbazole; humidity sensor; controlled oscillator
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1. Introduction

There have been a great number of reports on investigations of organic semiconductors as humidity[1−4], temperature[5, 6], infrared, visible and ultra violet radiation[7], and different types of gases such as ammonia[8], sensitive materials. Therefore, the investigation of physical properties of organic semiconductors under different conditions is very promising field for development of the various types of sensors for humidity, temperature, light, radiation, strain, gases etc.

Numerous sensors based on different fabrication and detection techniques have been reported in Refs. [9–11]. Electrical detection is the most commonly used technique and is classified into two categories, which are the resistive type and capacitive type. At present, the most common material used in resistive sensors is lithium chloride[12, 13]. 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 sensor should be measured by applying AC to Wheatstone bridge or by combination of current and voltage measurements[12, 13]. DC voltage is not applied because it tends to breakdown the lithium chloride to its lithium and chlorine atoms. The resistive sensor must be operated either in constant temperature environment or temperature corrections must be incorporated. Resistance of the sensor changes from 10 kΩ to 10^3 MΩ as humidity changes from 100% RH to 0% RH. A thin film of polydimethylphosphazene and a membrane of polydimethylphosphazene (PDMP) have been used as resistive and capacitive humidity sensors, at low or at high humidity levels[14, 15] and a change in capacitance and resistance of about three orders of magnitude was reported with increasing RH from 0% to 100%. The orange dyes (OD) as a p-type organic semiconductor have potentially application for electronic devices[16, 17], and shows high sensitivity to the humidity as resistive sensor[18, 19].

A number of capacitive and resistive humidity sensors were fabricated and investigated on the base of porphyrin, phthalocyanine and poly-N-epoxypropylcarbazole[20−22]. These sensors showed good capacitive sensitivity at higher humidity and high resistive sensitivity at lower humidity levels. Investigation of the capacitive type humidity sensors fabricated by using cellulose and poly-N-epoxypropylcarbazole (PEPC) showed that the sensor is sensitive in the humidity range of 30%–95% RH and it became more sensitive when the humidity was above of 60% RH[23].

Poly-N-epoxypropylcarbazole (PEPC) is one of the well-studied organic semiconductors and widely used as photosensitive organic layer[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 PEPC thin 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 ℃). Recrystallization of PEPC layers obtained from organic solutions occurs at room temperature[20]. On the other hand, cellulose is one of many polymers found in nature. Wood, paper, and cotton all contain cellulose. Cellulose is an excel-

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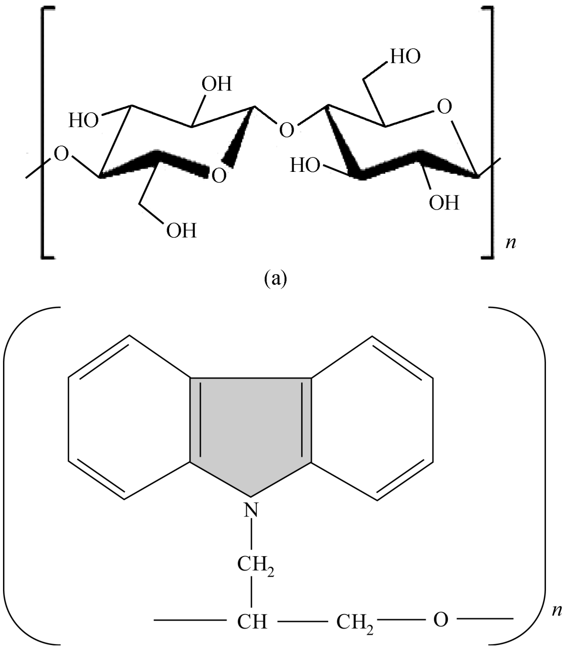


(a)

(b)

Fig. 1. Molecular structure of the (a) cellulose and (b) poly-N-epoxypropylcarbazole (PEPC).

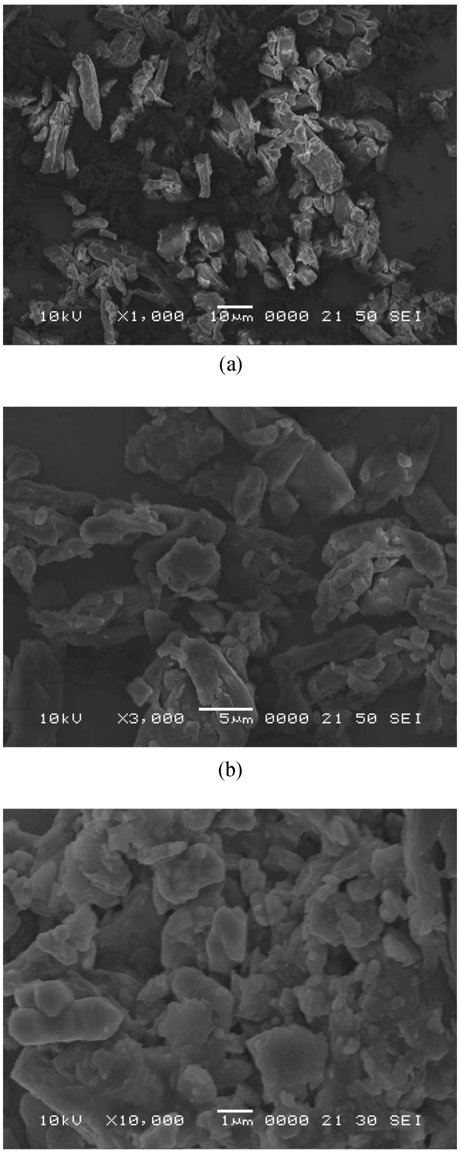
lent fiber. Cellulose is made of repeat units of the monomer glucose.

Normally, the humidity is measured by humidity meter at the spot. In some specific cases, there is a 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[24]. Response of sensor, which is converted to voltage, is in return 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[24]. The frequency modulation process can be simplified if the sensor directly modulates the frequency of oscillator.

In this paper we have described organic humidity sensor based on composites of cellulose and PEPC that can be used for the control of oscillator's frequency.

2. Experimental

Commercially available micro-powder of cellulose of sizes 15–25 μm with molecular formula $(C_6H_{10}O_5)_n$ and PEPC were used for the fabrication of the surface-type impedance sensor. Synthesis of PEPC has been described elsewhere[25]. Density of the cellulose was 1.592 g/cm^3. Molecular structures of the cellulose and PEPC are shown in Figs. 1(a) and 1(b).



(a)

(b)

(c)

Fig. 2. SEM images of the cellulose-PEPC composite film.

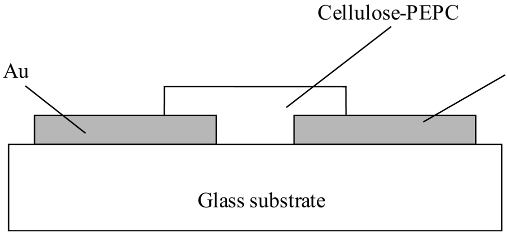


Fig. 3. Cross-sectional view of the fabricated Au/cellulose-PEPC/Au surface-type sensor.

The 2 wt% of cellulose and 2 wt% of PEPC were blended in benzol (unlike to PEPC the cellulose is not dissolved in benzol). Commercially available microscope glass slides were used as substrates. The substrates were cleaned for 10 min, using distilled water in ultrasonic cleaner and then dried in dust free environment. The substrates were also plasma cleaned for 5 min in thermal evaporator chamber. The surface-type gold electrodes were thermally deposited on cleaned substrates. Geometrical length and width of the semiconducting channel between metallic electrodes were equal to 50 μm and 5 mm, respectively. Edwards AUTO 306 vacuum coater having a diffusion pumping system was used for thermal evaporation. The thicknesses of the electrodes were 100 nm as measured by

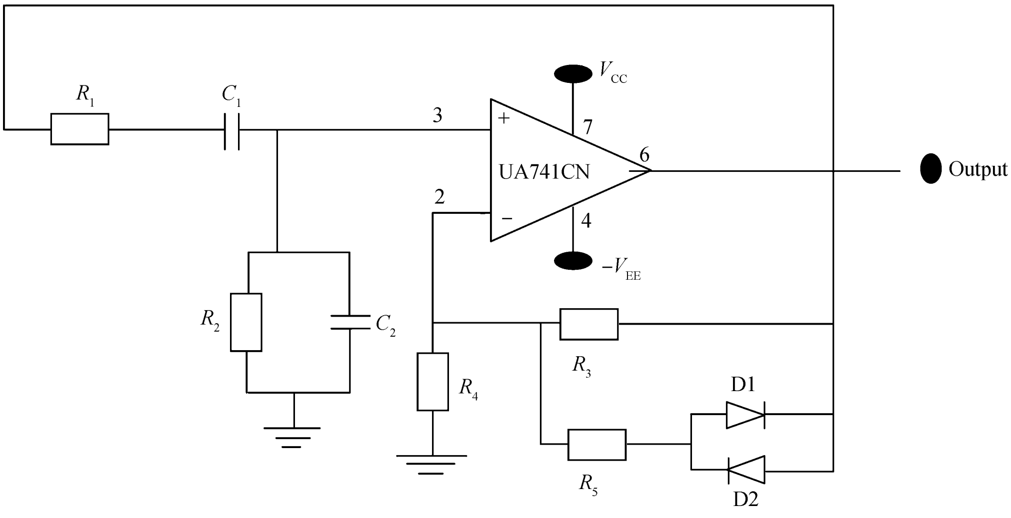


Fig. 4. Electric circuits of the organic humidity controlled oscillator with built in Au/cellulose-PEPC/Au surface-type sensor.

FTM5. The thermal evaporations were made under vacuum pressure of 5.5×10^{-3} Pa. Films of cellulose-PEPC composite were deposited by drop casting method with approximate thickness of 65, 88 and 210 μm, respectively. The fabricated sensors were kept overnight at room temperature to evaporate the moisture from the films. Figure 2 shows SEM images of the cellulose-PEPC composite film obtained by JEOL JSM-6460 at different magnifications.

Figure 3 shows the schematic diagram of the fabricated Au/cellulose-PEPC/Au surface-type sensor. Measurements were carried out in self made humidity measurement setup, which have been developed in our device testing laboratory. Resistance and capacitance of the sensors were measured by using ESCORT ELC-3133 A dual display LCR meter.

For frequency modulation, usually the voltage controlled oscillators (VCO), made on the base of IC technology, are used[26]. The sensor's resistance and capacitance depend on relative humidity and any kind of oscillator based on resistive and capacitive elements can be used for frequency modulation. We have selected one of the simplest[26], Wien bridge op-amp oscillator (Fig. 4), and replaced the capacitance (C_2) by the Au/cellulose-PEPC/Au sensor. In the op-amp oscillator circuit, $R_1 = R_2 = 47\ \text{k}\Omega, R_3 = R_5 = 300\ \text{k}\Omega, R_4 = 100\ \text{k}\Omega$, and $C_1 = 1$ nF. As seen from Fig. 4, the oscillator is controlled by built-in Au/cellulose-PEPC/Au sensor (C_2). The frequency of the oscillator is determined by[26]

$$f_0 = \frac{1}{2\pi\sqrt{R_1 C_1 R_2 C_2}}. \qquad (1)$$

Experimentally, the frequency was estimated by conventional cathode ray oscilloscope.

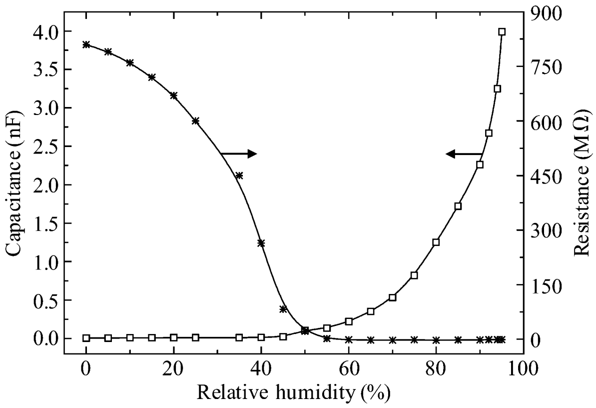


Fig. 5. Capacitance/resistance–humidity relationships for the Au/cellulose-PEPC/Au surface-type sensor at 100 Hz frequency for 88 μm sample.

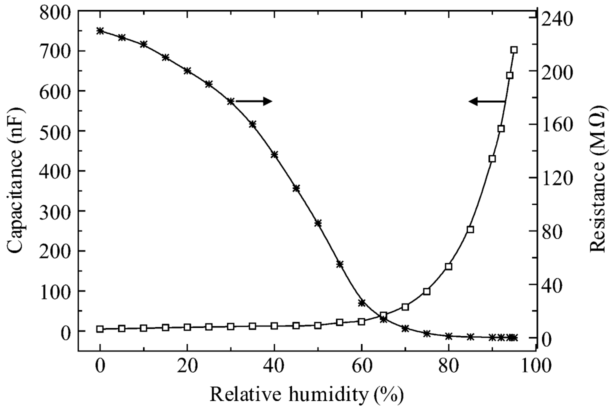


Fig. 6. Capacitance/resistance–humidity relationships for the Au/cellulose-PEPC/Au surface-type sensor at 1 kHz frequency for 65 μm sample.

3. Results and discussion

Figures 5 and 6 show capacitance (C) and resistance (R) with respect to relative humidity (RH) relationships for the Au/cellulose-PEPC/Au sensor at frequencies of 100 Hz and 1 kHz, respectively. It is seen that the resistance shows a very sharp decrease in the interval of 0–65% RH, and the capacitance shows large increase in the interval of 70%–95% RH. The changes of the sensor's resistance and capacitance in whole humidity interval (0–95% RH) are given in Table 1.

The equivalent circuit of the sensor can include both resistance and capacitance, connected parallel. As the frequency of

Table 1. Comparison of humidity sensing properties of the Au/cellulose-PEPC/Au sensors.

S. No	Frequency (kHz)	Thickness of film (μm)	$R_{(0\%)}/R_{(95\%)}$	$C_{(95\%)}/C_{(0\%)}$
1	0.1	65	2036	457
		88	3980	798
		210	471	41
2	1	65	2536	140
		88	2221	160
		210	1446	79
3	10	65	107	29
		88	53	10
		210	31	7

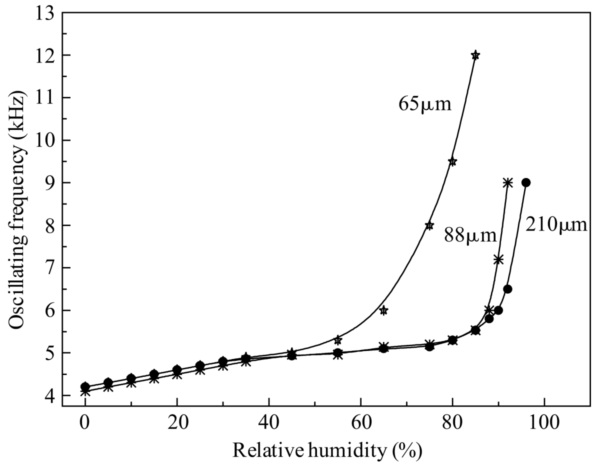


Fig. 7. Frequency–humidity relationships for the 65, 88 and 210 μm thick samples.

the oscillator is increasing with increase of the relative humidity, we can assume that the Au/cellulose-PEPC/Au sensor is mostly showing resistive properties in the oscillator circuit. For good frequency–capacitance response, we will use the sample of 88 μm at 100 Hz and if we want the better resistive response then we will select the 65 μm sample at 1 kHz.

The reason of the change in capacitance with humidity of the organic sensors was described earlier[20] and can be briefly explained by the following way. Low dielectric constant of the organic material ($\sim$4), increases due to absorption of water molecules, having higher dielectric constant value ($\sim$80), by surface, porous and bulk (in the case of diffusion of water molecules) of organic materials. The decrease of the resistance may be due to the presence of the displacement current caused by water molecules. Secondly, the 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 are described in detail with respect to some solids[27]. The high sensitivity of the cellulose-PEPC blend system to the humidity is due to the high sensitivity of cellulose and PEPC to humidity, and developed surface structure formed by cellulose micro-powder and covering it with thin PEPC film.

Figure 7 shows frequency–humidity relationships for the oscillator circuit. It is observed that the oscillator's frequency increases with humidity by 2.86, 2.20 and 2.14 times, respectively for 65, 88, 210 μm film thickness of the samples. As the oscillator's frequency is increasing with humidity, taking into account Eq. (1) and the resistance–humidity relationships (Figs. 5 and 6), where the resistance decreases with humidity, we can say that the effect of the sensor's resistance is dominating with respect to the effect of capacitance to the frequency of the oscillator. The increase of the oscillator's frequency with humidity is due to the decrease of the sensor's resistance with the increase of relative humidity. The average response and recovery times of the Au/cellulose-PEPC/Au sensors were in the range of 15–20 s and 40–50 s, respectively. The sensor showed repeatability (hysteresis) of ± 5%.

4. Conclusion

Cellulose and poly-N-epoxypropylcarbazole composite based humidity surface-type sensors were fabricated and their electrical properties were investigated. The resistances and capacitances of the samples were evaluated under the effect of humidity in the interval of 0–95% RH. It was observed that the capacitances of the sensors increase and their resistances decrease with increase of the relative humidity. The sensors were connected to the Wien bridge op-amp square wave oscillators. With the increase of humidity, the oscillator's frequency was increased in the range of 4.2–12.0 kHz for 65 μm, 4.1–9.0 kHz for 88 μm and 4.2–9.0 for 210 μm thick film samples depends on the sensor's resistance properties and oscillator's circuit elements. We can conclude that the 65 μm sample shows the best results with respect to oscillator frequency, so less thick sensors are preferred rather than the thicker ones, but it covers the shorter range of humidity interval i.e. 0–85% RH. To cover a wider humidity range, we can use thicker film sensors, as we observed that 88 μm sample cover the range of humidity from 0 to 90% RH and 210 μm sample cover 0–96% RH of humidity level. This 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.

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