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Capacitive hygrometers based on natural organic compound

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In the present work, we have investigated the capacitive hygrometers fabricated by polymer, cellulose, using different electrodes. Polymer films were deposited by two different deposition methods: spin coater method and by placing the drop of cellulose suspension in distilled water on primarily deposited electrodes. The DC and AC (at frequency of 20 Hz) capacitances of the samples were evaluated in the relative humidity range of 30-90%. It was observed that the capacitance of the cellulose increases with increase in relative humidity level. Comparison of two different methods shows that the drop coasted films were more sensitive than the spin coated ones where as the response and recovery time of spin coated samples was much shorter than the drop coasted samples. The relative capacitance ratio to the relative humidity was found 1.5 and 7 for samples deposited by spin coating and drop method, respectively. Humidity dependent capacitive behavior of cellulose made it attractive for the development of humidity meter.

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Key words: Capacitive hygrometers, Cellulose, Drop method, Relative humidity level

1. Introduction

Investigations on organic materials have increased rapidly in recent years, due to low cost, simplicity, easiness in device fabrication, and interesting electrical and optical properties. No doubt, organic materials will find more suitable place among the electronic materials in near future and research on new organic materials is expected to prolong. Some of the organic materials (oligomers and polymers) are very sensitive to humidity [1, 2], temperature [3, 4], infra-red visible and ultraviolet radiation [5], and different types of gases [6]. The ambient conditions dependent properties of these materials made them very promising for the development of various types of sensors [1, 2].

Humidity is among the most commonly measured quantities in measurement science. The measurement of water vapors in atmosphere, which is called *hygrometry*, is very complex [7] and of the fact that no one solution will meet the entire requisite, all the time in all conditions [8]. Water hazes are the natural constituent of air and play a significant role in practical measurement. At present, different type of hygrometers are available in market and about 75% of these hygrometers are capacitive type [9, 10] and are very suitable for high temperature applications than the other types of humidity measuring instruments.

Currently, the most hygrometers have LiCl as active material [11, 12], in which a mixture of lithium chloride and carbon is used between the electrodes. Operating principle of this device is based on the ionic conductivity [7]. Ceramic materials such as Al_2O_3 are also used in many commercially available hygrometers [13] due to well established etching technology and temperature stability.

Some polymers show high sensitivity to humidity but these compounds dissolve in water [14, 15]. Organic materials that are insoluble in water such as cellulose acetate butyrate and polyimide have been used as humidity sensors [14]. Cellulose is also insoluble in water, so it is seem reasonable to investigate cellulose as a humidity sensor. Cellulose is one of the organic materials (polymers) that are found in nature. Cellulose is made of repeat units of the monomer glucose. It is the same glucose which our body needs in order to live. Cellulose is abundantly found in plants and is extracted from cotton or wood. It is a molecule consisting of 2000-14000 residues. Each residue is oriented at 180° to the next with the chain synthesized two residues at a time.

This paper reports the experimental results of investigation on humidity dependent properties of capacitive hygrometers, fabricated using a polymer (cellulose) films, deposited from spin coasting and drop methods. The aim of this research is to develop a cheap and reliable humidity sensing element for the assessment of relative humidity of the surrounding environment using polymer.

2. Device fabrication

Commercially available cellulose with molecular formula $(C_6H_{10}O_5)_n$ was used without further purification for the fabrication of the Metal/cellulose/Metal hygrometers. Density of the cellulose was 1.592 g/cm^3. Molecular structure of the cellulose is shown in Fig. 1. The suspension of cellulose 5 wt% was made in water. Glass substrates were cleaned for 10 min. using distilled water in ultrasonic cleaner and dried. Then the substrates were plasma cleaned for 5 min. The metallic electrodes on cleaned substrate were deposited, keeping the 50 μm gap between them by masking. The thickness of the electrodes was 100 nm where as the length of the gaps were 5 mm. Films of cellulose were deposited by spin coater method with angular rotation of 4000 RPM and by drop coasting method with thickness of 400 nm and 0.2 mm, respectively. The average diameter of all the film was 5-6 mm. The fabricated devices were kept at room temperature for one night to evaporate the moisture from the films. Top view of fabricated devices is shown in Fig. 2. Measurements were carried out in self made humidity measurement setup, which has been developed in our laboratory using conventional digital instruments and chamber. The CEM DT-8860 digital multimeter was used for *in situ* relative humidity level and temperature measurements.

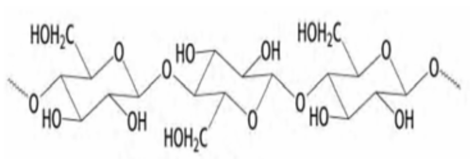
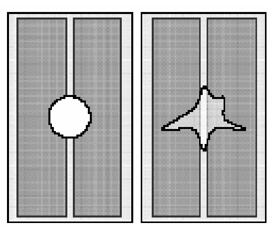


Fig. 1. Molecular structure of cellulose



(a) (b)

Fig. 2 Top views of fabricated devices: (a) Drop coasted method (b) Spin coating method.

3. Results and discussion

Conventional humidity sensors determine relative humidity level using capacitive technique. The element of these sensors is made of a thin film capacitor on substrates. The active material is used as dielectric which absorbs or releases water molecules and thus changes the capacitance of the capacitor. The capacitive humidity sensors, typically show a non linear response as a function of relative humidity [7, 16]. The capacitance depends upon the polarization [17], dielectric permittivity constant of the sensing material, gap between the electrodes and electrode geometry [18]. Polarization is caused by dipole, ionic and electronic polarizability. Dipoles and ions form due to charge transfer complexes and dissociation of molecules whereas electronic polarization arises due to relative displacement of electrons. The relation between dielectric constant and capacitance can be described by equation [7]

$$\frac{C_S}{C_0} = \left(\frac{\varepsilon_w}{\varepsilon_d}\right)^n \tag{1}$$

where ε_d , and ε_W are the permittivities of the dielectric at dry and wet states, respectively. The factor n is related to dielectric morphology. We consider an approximation, the metallic electrodes and gap between the electrodes with deposited cellulose as parallel plate capacitor (Fig. 2). Using this approximation the relative permittivity constant of cellulose can be calculated by following expression

$$C = \frac{\varepsilon_r \varepsilon_\circ A}{d} \tag{2}$$

where A is the area of plates and d is the distance between the plates.

Fig. 3 shows the capacitance-relative humidity relation of Al/cellulose/Al and Ag/cellulose/Ag surface type hygrometers deposited by spin coating method. These results can be explained as; the humidity level effects the concentration of ions, dipoles, electrons and holes and thus increases the polarization in cellulose. Water molecules effect the electrons and holes concentration only when they play a role of impurities. The increase in capacitance with relative humidity may also be due to the porous nature of thin film. Dielectric constant of cellulose increases with absorption of water molecules because the dielectric constant of water is greater than the cellulose dielectric constant. At higher relative humidity levels, variation in capacitance becomes less because the pores of film are being filled with water molecules and sensor sensitivity decrease [19]. This confirms that dielectric constant of cellulose increases with absorption of water molecules. Both the Al/cellulose/Al and Ag/cellulose/Ag hygrometers have almost same sensitivity. The value of capacitance at AC is less than the DC capacitance this is because the AC signals remove the parasitic capacitance and the samples shows only the real capacitance.

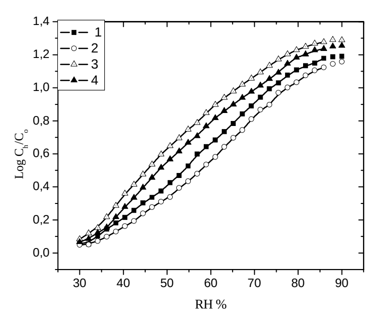


Fig. 3. Capacitance-Humidity relationship for spin coated samples (1) DC capacitance of sample with Al electrodes (2) AC capacitance of sample with Al electrodes (3) DC capacitance of sample with Ag electrodes (4) AC capacitance of sample with Ag electrodes.

Fig. 4 shows the relative capacitance-relative humidity relation for the Al/cellulose/Al and Ag/cellulose/Ag hygrometers, deposited by drop coasted method. In this case the cellulose films thickness is greater than the spin coated ones and hygrometers are more sensitive than the spin coated samples. This shows that the sensitivity increases with the increase in film thickness. One important thing is observed in all samples, the kind of electrodes has no significant effect on the sensitivity.

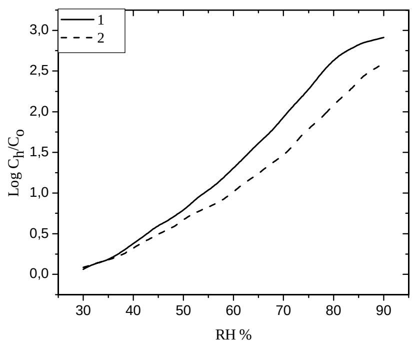


Fig. 4. *Capacitance-Humidity relations for samples fabricated by drop coasted method (1) Sample with Ag electrodes (2) Sample with Al electrodes.*

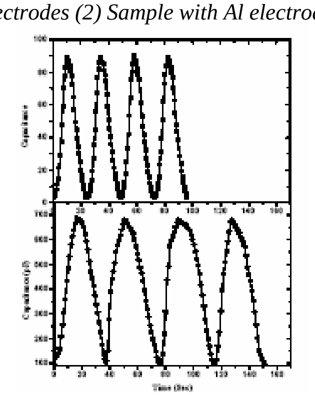


Fig. 5. Response and recovery time of hygrometers. Spin coated sample with Al electrodes (above). Drop coasted sample with Al electrodes (blow).

The capacitance verses time curve corresponding to absorption and desorption by changing the humidity rapidly from 30 to 90% and then decrease from 90 to 30% is shown in Fig. 4. It was found that the capacitive hygrometers with thin cellulose film are quick in response and recovery than the thicker ones. This is due to the fact that the diffusion and evaporation of water molecules take long time in thick samples. These results are obtained as, first we placed the sample in sealed glass with 30% RH and put it into chamber with 90%RH and suddenly removed the glass cover, the sample was introduced rapidly into ambient of humidity controlled chamber and similar method was adapted to measure the recovery time. The response time is shorter than the recovery time for all hygrometers. This time is including the equilibrium time inside the chamber, therefore real response and recovery time is shorter than the measured time. Repeated cycles between these two relative humidity levels gave almost same results as shown in the Figs. 5 (a) and (b).

The equivalent circuit diagram of surface type hygrometers is shown in Fig. 6.

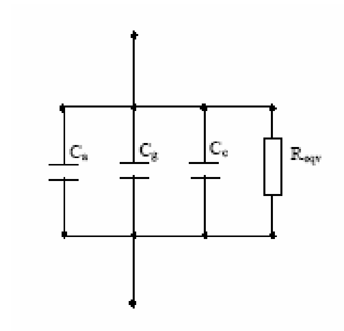


Fig. 6. Equivalent circuit diagram of the fabricated hygrometers.

In equivalent circuit diagram, there are shown three basic capacitances due to three kinds of dielectrics: air (C_a), cellulose (C_c) and glass (C_g). R_{eqv} is shunt or equivalent resistance of the hygrometers. Usually dielectric permittivity of organic semiconductor is larger than glass and air. Thus we can assume that $C_c >> C_a$ and C_g. Therefore we can neglect C_a and C_g.

4. Conclusions

The properties of the surface-type capacitive hygrometers were investigated. Equivalent circuit of the sensor was proposed that reflects the physical processes in cellulose. Results show that the capacitance of the hygrometer deposited by spin coater average increased by 16 times whiles the capacitance of drop coasted hygrometer average increased by 600 times. The change in capacitance is due to difference between the dielectric constants of cellulose and water molecules. From the response and recovery point of view the spin coasted samples are better while from the sensitivity point of view the drop coasted hygrometers show better results. The main feature of this device is its cost effectiveness. From technological point of view, it is very easy to make device from the solution processable organic compounds than the others.

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