A capacitive humidity sensor using cross-linked cellulose acetate butyrate

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Abstract

This paper reports on the fabrication of a new capacitive humidity sensor having good characteristics and being robust enough to be considered as a component in industrial processes. This sensor is manufactured using a mixture of three cellulose acetate butyrates cross-linked by a melamine formaldehyde resin as sensing material. Details of the fabrication process and sensor characteristics such as linearity, sensitivity, hysteresis, response time, maximum operating temperature or physical and chemical stresses influence are included.

Keywords: Humidity sensors; Capacitive sensors; Cellulose acetate butyrate; Water structure

1. Introduction

Many kinds of capacitive humidity sensors have been developed for the last years. However the fact that many of the sensors available on the market were not robust enough has discouraged many potential candidates from including a humidity measurement system in high demanding applications.

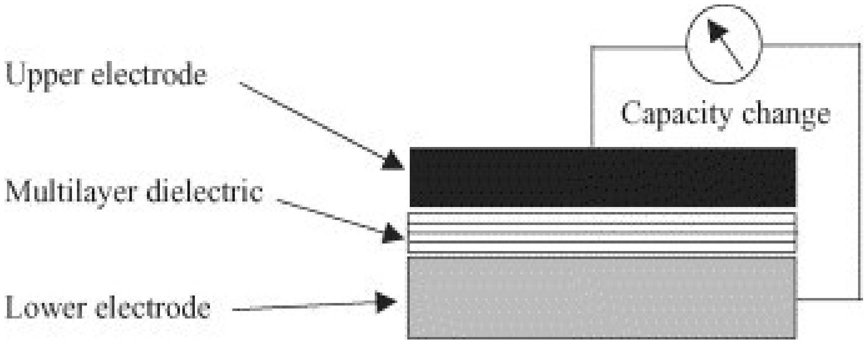
Thus the challenge is to design a capacitive humidity sensor having good characteristics (e.g. high sensitivity, small hysteresis, good linearity, low temperature coefficient, short response time and long-term stability, etc.) and being robust enough to bear automatic insertion, wave soldering and high operating temperature, as well as to be washable and to have a good chemical resistance.

This paper describes a sensor for which a cross-linked cellulose acetate butyrate was used as sensing material which meets these requirements.

2. Structure of the sensor

The sensor is made of three basic elements as shown in Fig. 1. The lower electrode (100 µm substrate) must not create a variable serial resistance with respect to humidity, time or chemical atmosphere and also not trap water molecules. The performances of the sensor depend on the nature of the multilayer dielectric which thickness must be as homogeneous as possible. A polymer upper electrode (4 mm × 3 mm × 100 µm) fabricated from phthalic resin is permeable to humidity providing a short response time to humidity changes (3 s, 33–75% RH, still air at 63%).

Fig. 1. Structure of the sensor.



As shown in the following equation, the sensor capacity varies with the polymer dielectric constant which changes according to the water adsorption and desorption [1].

$$C_p = \frac{\varepsilon_r \varepsilon_0 S}{t}$$

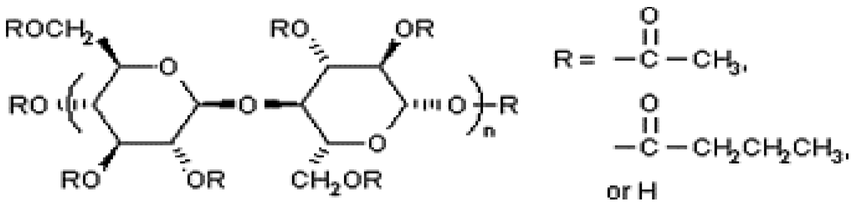
where C_p is the sensor capacity, ε_r the dielectric constant, ε_0 the vaccum dielectric constant, S the electrode surface area and t the thickness of dielectric polymer.

3. Materials and fabrication

3.1. Materials

Polymers such as polyimide (PI) [2], [3], [4] and [5], polymethyl metacrylate (PMMA) [6], [7] and [8], polyethylene terephthalate (PET) [9] and polysulfone (PSF) [5], [10] and [11] are some of the materials employed in capacitive humidity sensors but the material used most of the time in industrial applications is cellulose acetate butyrate (CAB). Indeed, CABs have been known for several years to be suitable polymers for capacitive humidity sensors [6], [10] and [12]. However several problems such as large hysteresis, bad linearity, too short durability on exposure to some kinds of organics vapours and questionable long-term stability still remain to be solved. The CAB chemical structure is shown in Fig. 2.

Fig. 2. Cellulose acetate butyrate chemical structure.



Five different CABs manufactured by various suppliers have been tested as dielectric polymer. Table 1 summarizes the main differences between these five polymers.

Table 1.

Type of cellulose acetate butyrate

Type CAB	**% Acetyl**	**% Butyryl**	M_w	T_g (°C)
CAB52	3	52	16000	105
CAB38	13	38	20000	125
CAB37	14	37	70000	140
CAB46	2	46	20000	140
CAB17	30	17	200000	155

3.2. Fabrication

The dielectric polymer is dissolved in a mixture of solvents and is then spin-coated onto a wafer. Several layers are successively spin-coated to improve the homogeneity and the reproducibility of the dielectric film. Indeed, a study shown in Fig. 3 on the CAB37 dielectric shows that a thickness plateau exists from six layers spin-coated. This process allows the control of the dielectric deposition and thus the achievement of a thickness homogeneity of 3 ± 0.05 µm across the wafer.

Fig. 3. Thickness change of CAB37 film according to the number of layers and the viscosity (V_1–V_5) of the polymers.

4. Experimental results and discussion

4.1. Initial performances of the sensors

The capacity of each sensors is measured with a LCR meter at a frequency of 10 kHz and a voltage of 1 V. Humidity range from 10 to 95% RH at 25 °C is generated with a SECASI climate chamber.

The evolution of the normalized capacity of each sensors according to the relative humidity is shown in Fig. 4. Table 2 summarizes the fundamental characteristics of these sensors: maximum operating temperature, normalized sensitivity, linearity and maximum hysteresis. The linearity is defined as being the maximum error between the RH–*C* curve and the least squares line calculated in the humidity range from 10 to 95% RH. The maximum hysteresis is defined being the maximum difference between the first capacity values obtained in humidity cycle and those obtained after 2 h at 95% RH.

Fig. 4. Normalized capacity of the sensors according to the relative humidity.

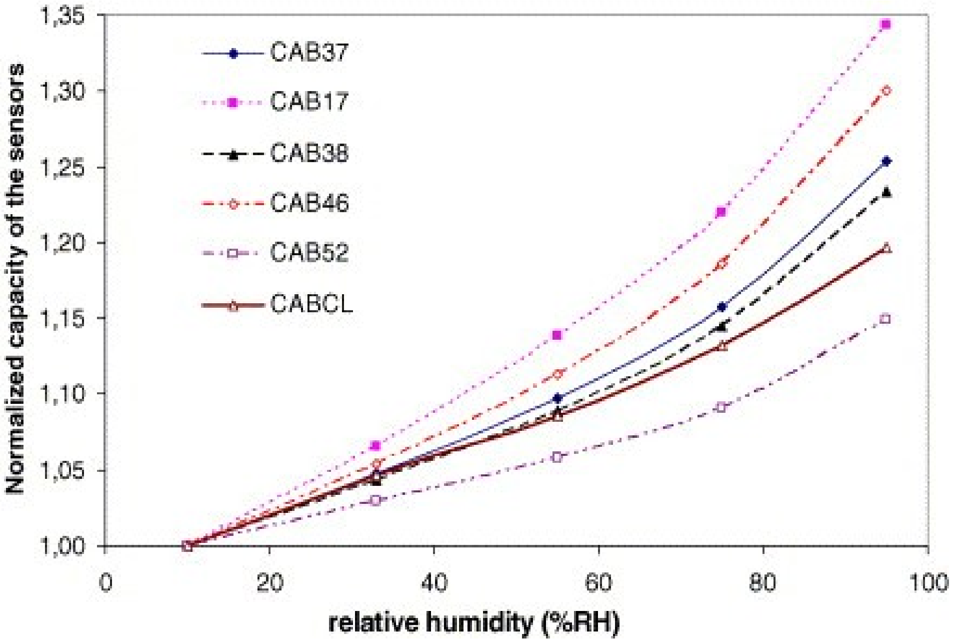


Table 2.

Fundamental characteristics of the sensors

Type CAB	Maximum operating temperature (°C)	10–95% RH		
		Normalized sensitivity	Maximum hysteresis (% RH)	Linearity (% RH)
CAB52	105	1.15	2.1	±2.8
CAB38	125	1.23	3.8	±4.3
CAB37	140	1.25	3.7	±4.4
CAB46	140	1.30	6.6	±5.5
CAB17	155	1.34	4.3	±4.9
CABCL	130	1.20	2.9	±3.5

The differences that are shown in Table 2 are due to the fact that according to the % acetyl group, the % butyl group and the polymer molecular weight (M_w), polymers absorbs varying amounts of water in different forms (free water, bonded water, clusters of water) [13]. These different forms of water induce different behaviours (Henry's law, Langmuir's law or Clustering law). For example the reason for hysteresis or increase of sensitivity at high humidity is the formation of water molecule clusters [14].

To sum up Table 2, the sensor using the CAB52 has the best characteristics of linearity and hysteresis. However its sensitivity and particularly its maximum operating temperature are too low to permit it to be used in many industrial applications.

4.2. Final characteristics of the sensor

In order to achieve all the requirements, the idea has been conceived to mix three CAB formulations (50% of CAB52 mixed with 25% of CAB17 and 25% of CAB37). Thanks to this, the sensitivity increases and the new sensor (called CABCL) can bear the operating temperatures met in industrial applications. As shown in Table 2 and Fig. 4, the hysteresis increases slightly and the linearity is a bit worse. In spite of that, these characteristics are a good compromise solution.

The last problem then remaining to be solved is the improvement of the sensor chemical resistance. The way chosen to do it is to add a CAB compatible cross-linker to the selected mixture of CAB. The cross-linker used is a melamine formaldehyde resin. The chemical structure of this resin is shown in Fig. 5. In order not to modify the sensor characteristics the concentration of this cross-linker in the mixture must be low (less than 3 wt.%). As shown in Fig. 6, this melamine cross-linker (M) reacts to the hydroxyl group of the CABs and a reticulated film forms [7] and [15]. This film is resistant to the chemical attacks commonly occurring within the framework of industrial applications. Thus, as shown in Table 3, the CABCL sensor is resistant to the physical and chemical stresses mentioned and its characteristics remain particularly good. Relative humidity measurements are referred to a VAISALA transmitter under metrology control. Measurement accuracy in relative humidity is ±2% RH.

Fig. 5. Melamine formaldehyde resin chemical structure

Fig. 6. Cross-linked cellulose chemical structure.

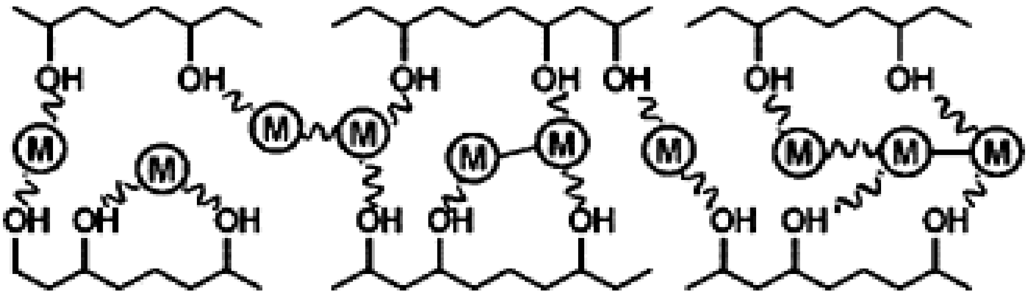


Table 3.

Physical and chemical stresses influence

Test	Description	Sensor output shift at 55% RH/23 °C
Wave soldering	Wave soldering at 233 °C + DI water clean at 25 °C	±2% RH
Vibration	Variable frequency (100–2000 Hz); fixed frequency (35 Hz)	±2% RH
Thermal shocks	−40 °C(1 h)/85 °C(1 h), 100 cycles	±2% RH
Electrostatic discharge	HBM at 2000 V & MM	±2% RH
Salt atmosphere	96 h, 5% salty	±2.5% RH
Water immersion	720 h	±3% RH
Methanol	Satured atmosphere of C_2H_5O, 500 h	±3.5% RH

Test	Description	Sensor output shift at 55% RH/23 °C
Acetic acid	Satured atmosphere of C_2H_4O, 1000 h	±3% RH
Nitric, sulfuric and chlohydric acids	Satured atmosphere of a mixture of these three acids (HCl, H_2SO_4, HNO_3), 500 h	±4% RH
Chlorinated solvents	Satured atmosphere of CH_2Cl_2 and $C_2H_3Cl_3$, 1 h	±4% RH
Cigarette smoke	Smoke of 10 cigarettes in 1 l container, 24 h	±3% RH
Plasticizer, glass cleaner	Immersion in plasticizer and glass cleaner, 24 h	±2% RH

4.3. Long-term stability

The long-term stability of CABCL sensors was evaluated in various harsh environments. Indeed, one of problems of CAB sensors is commonly instabilities in the sensor RH characteristics if the sensor is left in a high temperature and high humidity environment for extended periods [16].

The long-term stability of the sensor without stress at 25 °C is 0.5% RH per year. After 1000 cycles at low/high humidity (10% RH/90% RH) and at a temperature of 40 °C the results confirm good stability of the sensors: reversible increase of 3–5% RH and no cumulative hysteresis effect. This sensor performance under hot and humid conditions is superior to that of most commercially available capacitive sensors fabricated with cellulose acetate butyrate.

5. Conclusion

In order to meet precise requirements, a new capacitive humidity sensor has been fabricated. It is made of a mixture of three CAB cross-linked by a melamine formaldehyde resin. This sensor works effectively from 0 to 100% RH and from −40 to 120 °C. Furthermore it is robust enough to be used in many applications such as industrial processes. The work in progress on the sensor behaviour according to water molecules forms (Henry, Langmuir and clustering laws) will allow a better understanding of the physical sensor model.

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