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INFLUENCE OF DEPOSITION ANGLE OF UPPER ELECTRODE ON RESPONSE TIME OF RELATIVE–HUMIDITY SENSORS

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Construction and testing of thin–film capacitive relative–humidity sensors, using a polymer film as dielectric, are presented. Methods of deposition of the upper electrode, which must have proper electrical conductivity and be porous to assure a quick response to changes of relative humidity in the environment, is discussed. The upper electrodes were deposited by vacuum evaporation of Ni, Cr and Ni–Cr alloy. The angle of incidence of evaporated material was varied with the aim to change porosity and, therefore, the response time.

1. *Introduction*

The measurement of relative humidity has always been a difficult and challenging task. Temperature, pressure and composition of gas influence the results of measurements, and stable and reliable sensors are lacking. There are three major types of humidity sensors, based on measurements of:

a. changes of mechanical properties of a film or filament,

b. changes of electrical property such as resistance or capacitance and

c. psychrometric properties of a gas, i.e. comparison of the latent heat of evaporation of a saturated environment to the environment in question.

The design, construction and testing of humidity sensors based on the change of the dielectic constant (capacitance) of a polymer thin–film are described. Problems of hysteresis, relative speed of response and sensitivity of the sensors were investigated.

With respect to rapid response and realiability, water–vapour absorbent organics are much better than inorganic materials. In this experiment, the capacity–type thin–film polymer humidity sensors with a rapid response were made by using spin–coated thin film as an absorbent of water vapour, with obliquely deposited metal electrodes [1–4]. Reliability and stability were improved by exposing the sensors to a moist and highly heated atmosphere. The primary characteristic of the sensors is a rapid response [5-8].

2. *Experimental*

Sandwich–type devices were prepared for the measurement of dielectric properties according to the following procedure. The polymer (cellulose acetate) was spread by a spin coating technique, about one μm thick, on a glass substrate that had two NiCr 80–20 electrodes deposited by the RF sputtering technique (about 100 nm thick). The thin film on the substrate was heated under various conditions. Formation of the upper electrode was made by vacuum evaporation using the oblique–deposition method. To make the upper electrode, the following materials were used: Ni, Cr and NiCr 80–20 alloy. For each of these materials, the influence of the angle of incidence upon the sensor on the sensors' response time was determined. The thin electrodes obtained show a high permeability to water vapour even when of μm thickness. They have columnar structure, growing in a certain direction, depending on the angle of incidence. Obliquely deposited films have porous structure, allowing the water vapour to diffuse easily into the film. Figure 1 shows the cross–section of a sensor.

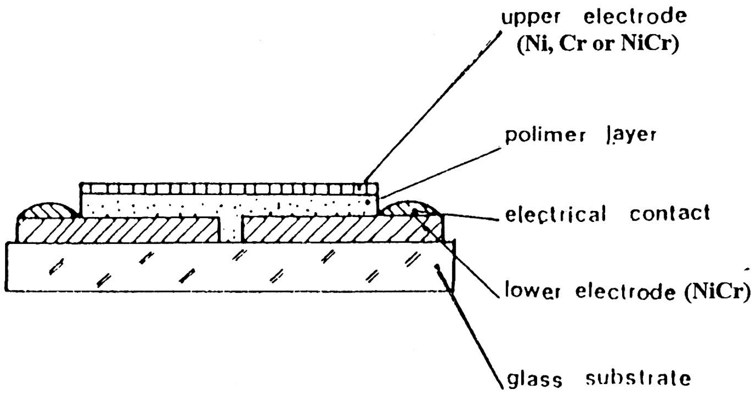


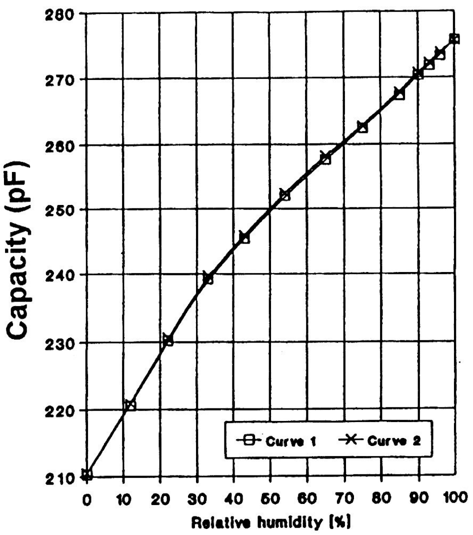
Fig. 1. Cross–section of the thin–film relative humidity sensor.

To examine the effects of sorbed water on the dielectric properties of the film, the devices were placed in a thermostat vessel in which water–vapour pressure was controlled by mixing dry and wet air. The electrical properties were measured by a LCR meter (Promax MZ-705) at various frequencies. A quartz crystal microbalance was used for accurate measuring of the mass change. It is useful for change–of–sorption observation in situ in the thin films.

The film thickness was measured with a mechanical surface–roughness analyzer (TENCOR Alpha Step 100).

3. Results and discussion

Figure 2 shows humidity characteristic of a sensor for 0 to 100% relative humidity (RH), made by using saturated salt solutions. This is a very useful method for producing known relative humidities, principally for testing and calibrating hygrometers at constant temperatures. Capacitance values of 220 picofarads, with a sensitivity of 3000 ppm/%RH, have been achieved with the sensor area of 28 mm^2. The capacity did not change even when increasing the temperature from 20 to 80 °C. Thus, these sensors show relative humidity characteristic of an accuracy that is typically less than ±2% RH.



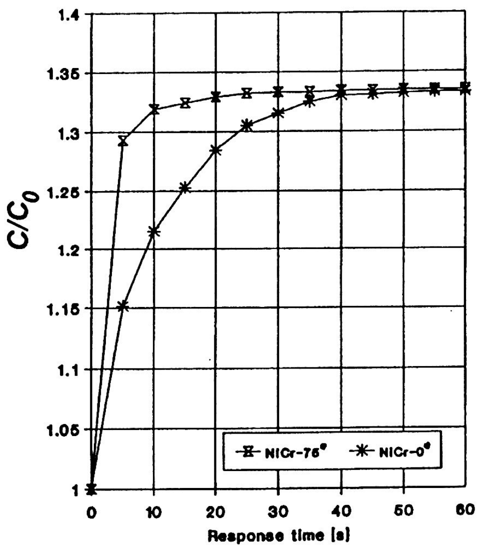
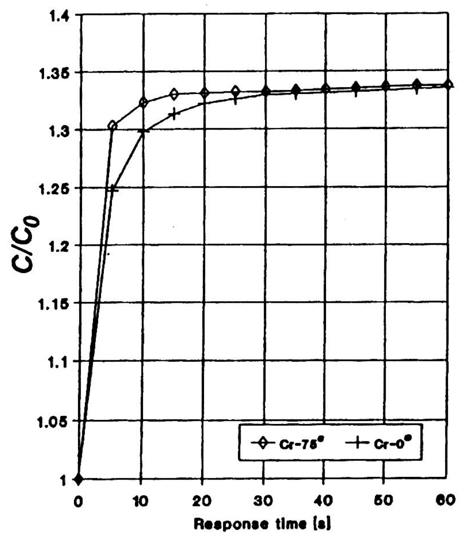


Fig. 2. The sensor's humidity characteristic for 0 to 100% RH measured by increasing (□) and decreasing (○) the humidity (determined by using saturated salt solutions).

Fig. 3. Curve (a) shows the response time of the sensor with permeable NiCr *alloy electrode deposited at normal incidence, and curve (b) the same for deposition at the angle of 75° (right).*

Figure 3, curve (a) shows the response time for the upper electrode of NiCr 80–20 alloy, deposited at normal incidence. The response time is found to be very slow (about 30 s). On the other hand, the sensor with the permeable electrode, deposited at the angle of 75°, responds fast (5 s) as shown in the same figure, curve (b). Figure 4, curve (a) shows the results for a chromium upper electrode deposited at normal incidence which has a shorter response time than the sensor with the NiCr electrode, and curve (b) shows the same for electrode deposited at 75° angle. This type of upper electrode shows a 5% shorter response time in the first 5 seconds. The response times for a nickel upper electrode evaporated at the incidence angles $\Theta = 0°$ and $\Theta = 75°$ showed similar rates as curves in Fig. 4. As the difference of the response times at the incidence angle $\Theta = 75°$ for used metals and 1000 nm polymer thickness is very small, we decided that the NiCr 80–20 alloy was the best solution, since this material had a small temperature coefficient of resistivity for temperatures between -20 and $+150$ °C.

Figure 5 shows the relationship of the response time and the thickness of the deposited electrode for different angles Θ. In the case of $\Theta = 0°$, the response time is longer in spite of the thinner electrode (< 10 nm). At $\Theta = 75°$ the response time is shortened to 5 s or less even though the electrode is 20 nm thick.



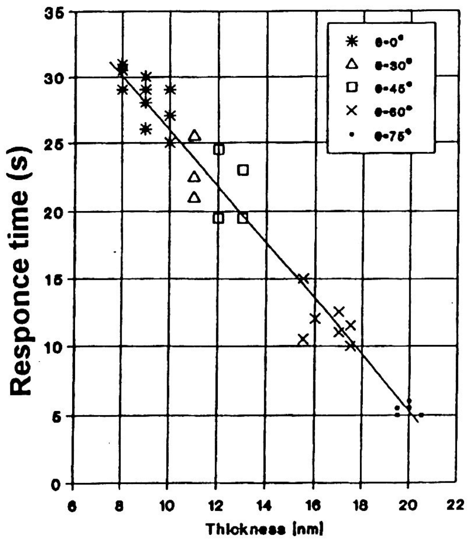


Fig. 4. Curve (a) shows the response time of the sensor with a Cr *upper electrode deposited at normal incidence and curve (b) the same for deposition at the angle of 75°. Essentially the same results were obtained by using the* Ni *upper electrode.*

Fig. 5. The relationship of the response time and the thickness of the deposited electrodes of NiCr *alloy for different angles of incidence.*

The second type of the porous electrode was obtained by chromium evaporation on a thin plastic film that was tensile stressed. The stresses generate a very large number of cracks in the polymer. The cracks, some 100 nm wide and spaced a few mm from each other, transform the polymer into many small islets, separated by thin films of metal. Permeability was achieved without impairing conductivity or mechanical strength, and the penetration rate of moisture is increased by several orders of magnitude, whatever the thickness of the metal (10 nm to 100 nm). Figure 6 shows this type of porous electrode.

We have used another type of the porous electrode on the polymer which has the surface shape generated by tensile stress, but has no cracks in the polymer. Figure 7 shows upper electrode without cracks obtained by vacuum deposition of NiCr alloy. In this way we have achieved the same rate of permeability, better conductivity and better response time. The other type of the electrode which produced cracks in the polymer showed a drift in the range +10% at 100% RH. The drift of sensors with electrode without cracks was found in the range $< 3\%$ at 100% RH. The severe environments chosen for these evaluations are not representative of typical applications envisioned for this device. However, even in these environments, the sensors' long–term and wet stability was typically less than $\pm 3\%$ RH. It is expected that under normal conditions, the long term and wet stability will be significantly better than $\pm 2\%$ RH.

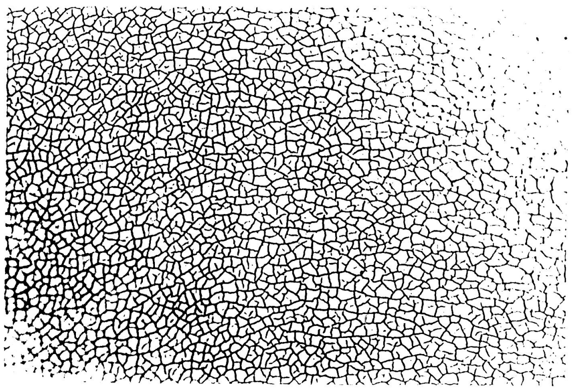


Fig. 6. The chromium porous–type electrode with a very large number of cracks.

The obliquely–deposited electrodes show higher water permeability. Therefore, the difference in density of the electrode deposited at the incidence angle $\Theta = 0°$ to that at $\Theta = 75°$ needs to be examined. NiCr alloy was deposited onto the glass substrate at various angles. To have the same surface mass density when evaporated at various angles, the deposition time (when evaporating at the same rate) must be changed. So, if deposition time at $\Theta = 0°$ is t_0, the deposition time at an angle is given by:

$$t(\Theta) = \frac{t_0}{\cos\Theta}. \qquad (1)$$

The constant rate of deposition was checked by using a quartz microbalance so that films on the glass substrates evaporated at various angles had the same surface mass density. The thickness of the films was measured by the surface roughness analyzer. The film thickness of the samples evaporated at various angles is presented in Table 1.

TABLE 1.
Thickness of the evaporated films of the same surface mass density (Θ is the angle of incidence).

Θ (°)	d (nm)
0	95
30	110
45	115
60	120
75	125

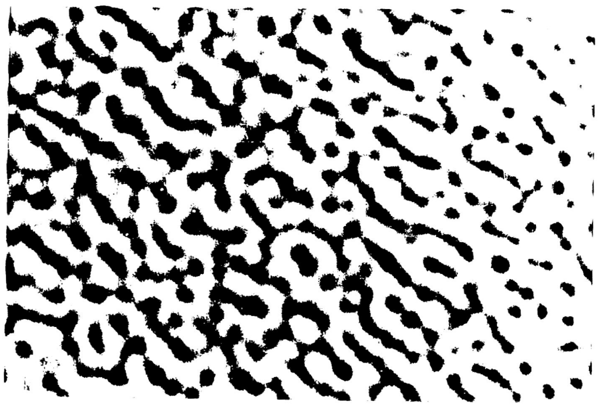


Fig. 7. The NiCr *porous–type electrode without cracks.*

The volume density of the film, having the same surface density is inversely proportional to its thickness. The results in Table 1 show a lower volume density of samples which were deposited obliquely. That causes larger porosity of the films deposited at large angles of incidence. The sensors were held for 8 h (4 cycles) in a vessel at the temperature of 80 °C and moist air of 97% RH. After this treatment, the change in (C(97% RH)-C(0% RH)/C(0% RH) is only 1–3% per year. This improved stability seems to indicate that the reaction of radicals and the association sites of water and the change of micro–voids by swelling expansion are stabilized.

4. Conclusion

Obliguely deposited water–permeable electrode and spin–coated polymerized cellulose acetate as the water–vapour absorbent are a practical solution to improve characteristics of relative–humidity sensors.

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UTJECAJ KUTA NAPARAVANJA GORNJE ELEKTRODE NA VRIJEME ODZIVA PROBA ZA MJERENJE RELATIVNE VLAŽNOSTI

Opisuje se gradnja i ispitivanje tankoslojnih kapacitivnih proba (senzora) za mjerenje relativne vlažnosti u kojima se primjenjuju tanki slojevi (listići) polimera. Gornja elektroda mora biti električki vodljiva i također porozna da bi odziv na promjene relativne vlažnosti bio brz. Gornje su elektrode načinjene vakuumskim naparavanjem Ni, Cr ili Ni–Cr legura pod raznim kutovima kako bi se postigla njihova povoljna poroznost.