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by Thin Film Humidity Sensor**

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The simultaneous measurement of capacitance and resistance of a sensor, and also mass of absorbed water in a sensor has been done using a newly designed humidity sensor. As the sensing part of the sensor, CaF_2 , Al_2O_3 and cellulosic polymer films are used.

In polymer films, water molecules are absorbed in the form of physically adsorbed water and the humidity characteristics do not depend on temperature.

In CaF_2 and Al_2O_3 films, water molecules are absorbed in the form of liquid water, so called capillary condensation, and it is found that the change of capacitance and resistance relates to the electrolysis process of water molecules.

The sensing mechanism of relative humidity is discussed in connection with the results of BET plots and infrared spectra.

§1. Introduction

Recently, the requirements of humidity measurement and control have motivated the development of various types of humidity sensors which give the electric signal. These are classified by the measuring principles as follows: 1) resistance (R) change, 2) capacitance (C) change, 3) mass ($m_{\text{H}_2\text{O}}$) change due to absorption of water. The change of R, C and $m_{\text{H}_2\text{O}}$ due to relative humidity (RH) depends on temperature in almost all sensing materials except the well treated polymers.¹⁻³⁾ There are few reports concerning the absorption states of water molecules in a sensing part and also the detection mechanism of RH.

This paper reports the mechanism of moisture sensing using a newly designed sensor which allows the simultaneous measurement of C, R and $m_{\text{H}_2\text{O}}$, in connection with the results of BET and infrared spectroscopy.⁴⁻⁶⁾ The origin of C changes due to RH is discussed in the sense of the absorption state of water molecules.

§2. Experimentals

As the sensing part of the sensors, the thin films of Al_2O_3 (thickness $t \sim 5 \mu\text{m}$) and CaF_2 ($\sim 5 \mu\text{m}$) are formed by conventional vacuum deposition and also the cellulosic polymer films ($\sim 12 \mu\text{m}$) are prepared by dip-coating.

2.1 Simultaneous measurements of $\text{RH} \cdot m_{\text{H}_2\text{O}} \cdot C \cdot R$

These films are formed on a quartz crystal microbalance (QCM) measuring the mass of water ($m_{\text{H}_2\text{O}}$) and the very thin film of Au ($\sim 150 \text{Å}$) permeable to water molecules are deposited on these films as an electrode for C and R measurements. This system is shown in Fig. 1 schematically. The measurements of humidity characteristics have been done in the temperature range from 20°C to 60°C and also in the humidity range from 0% to 90% RH using a commercial humidity chamber calibrated by the dew point method.

2.2 Measurements of infrared spectra

For the measurement of the infrared spectra for water molecules, polished CaF_2 plates are used as substrates, since the infrared absorption of CaF_2 is extremely low and flat ($1400 \sim 4000 \text{cm}^{-1}$). The films of Al_2O_3 , CaF_2 and polymer are formed on CaF_2 substrates. The experimental system is shown in Fig. 2. The sample is set in the chamber which is under control of temperature from room temperature to 100°C , and heated dry air can be flowed to desiccate the system.

In this system, the constant humidity circumstance is produced by the dry air for $\sim 0\%$ RH* and the saturated-salt-solution method

*This condition is prepared by flowing dry air for 15 hours.

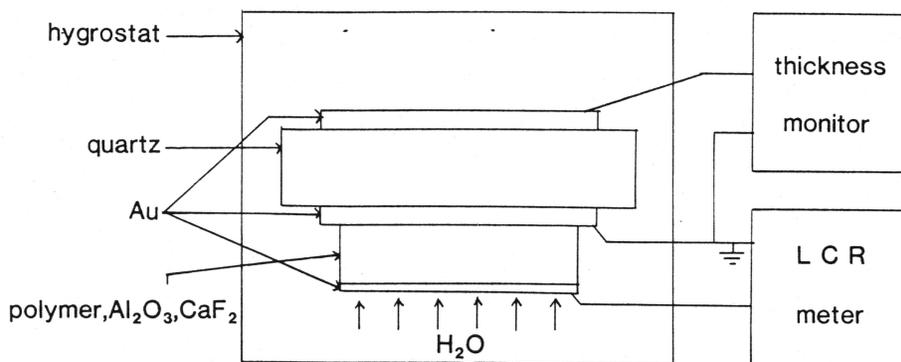


Fig. 1. System of simultaneous measurement of $RH \cdot m_{H_2O} \cdot C \cdot R$.

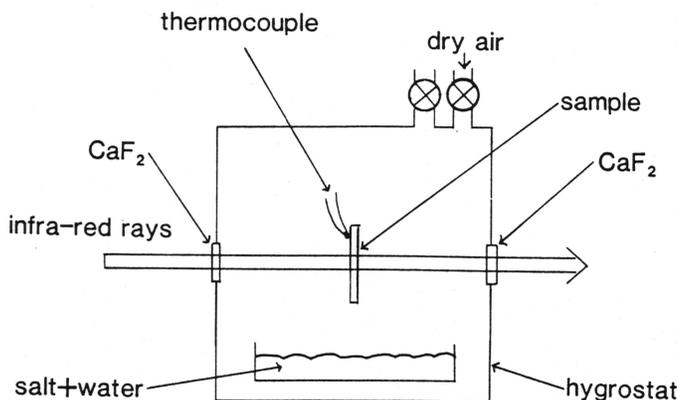


Fig. 2. System of measuring infrared spectra.

such as LiCl (~11% RH) and NaCl (~75% RH) in the temperature range from 10°C to 50°C.

§3. Results

3.1 $RH \cdot m_{H_2O} \cdot C \cdot R$ characteristics

The results of $RH \cdot m_{H_2O} \cdot C \cdot R$ characteristic measurements for CaF₂ and polymer films are shown in Figs. 3 and 4, respectively. In these figures, mass of water (m_{H_2O}) is converted to the mean thickness of water (d_{H_2O}).

It is observed in Figs. 3 and 4 that, in the case of CaF₂ thin films, d_{H_2O} at 60°C decreases incomparably with d_{H_2O} at 20°C and, in the case of polymer films, d_{H_2O} doesn't depend on temperature. In the case of CaF₂ thin films, C increases at 60°C but d_{H_2O} decreases at constant RH and, in the case of polymer films, C change doesn't depend on temperature. For Al₂O₃ thin films, the results are quite similar to that of CaF₂. In RH range of 20~70%, d_{H_2O} for CaF₂, Al₂O₃ and polymer films are in the

range of 100~240 Å per 1 μm of thickness for each films.

3.2 Infrared spectrum

The infrared spectra for CaF₂ thin films, the absorption spectra for 75%RH and 0%RH are measured and the difference of these spectra is plotted in Fig. 5 at the temperature of 10°C and 50°C. At the higher temperature, the intensity of infrared absorption decreases. This coincides with the decrease of d_{H_2O} by increasing temperature.

It is considered by comparing Fig. 5 with the data for the infrared spectra or liquid water, that water molecules absorbed in CaF₂ thin films are in the form of liquid water. For Al₂O₃ thin films, similar results are obtained. The infrared spectrum plotted by the similar process as Fig. 5 for polymer films is shown in Fig. 6.

The shape of absorption peaks is different from that in Fig. 5. This result suggests that the water molecules are absorbed in the

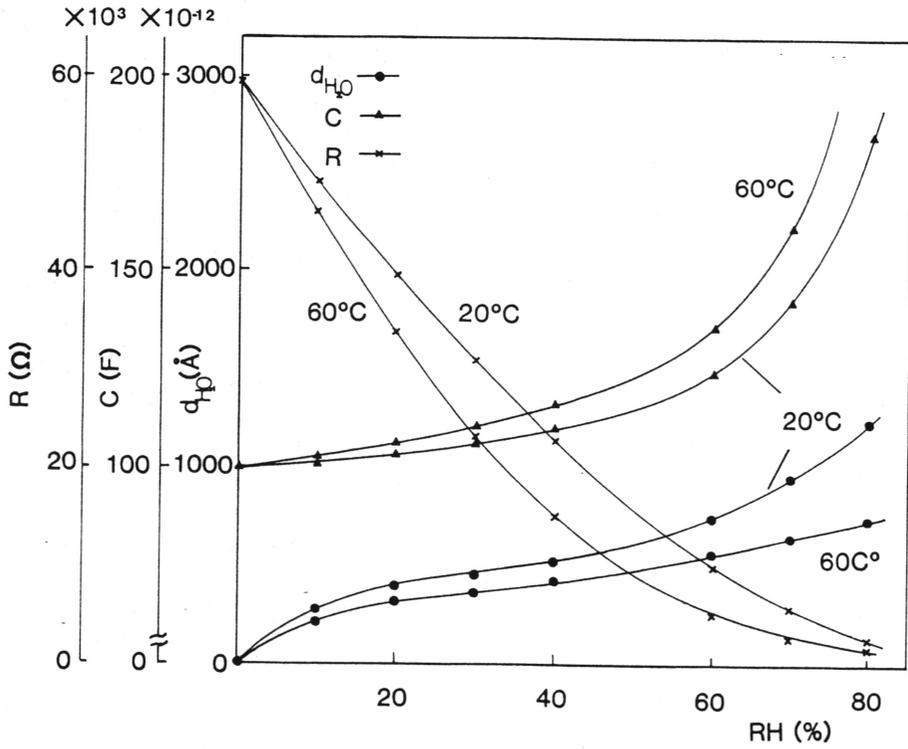


Fig. 3. RH-d_{H₂O}·C·R characteristics of the sensor using CaF₂ thin films.

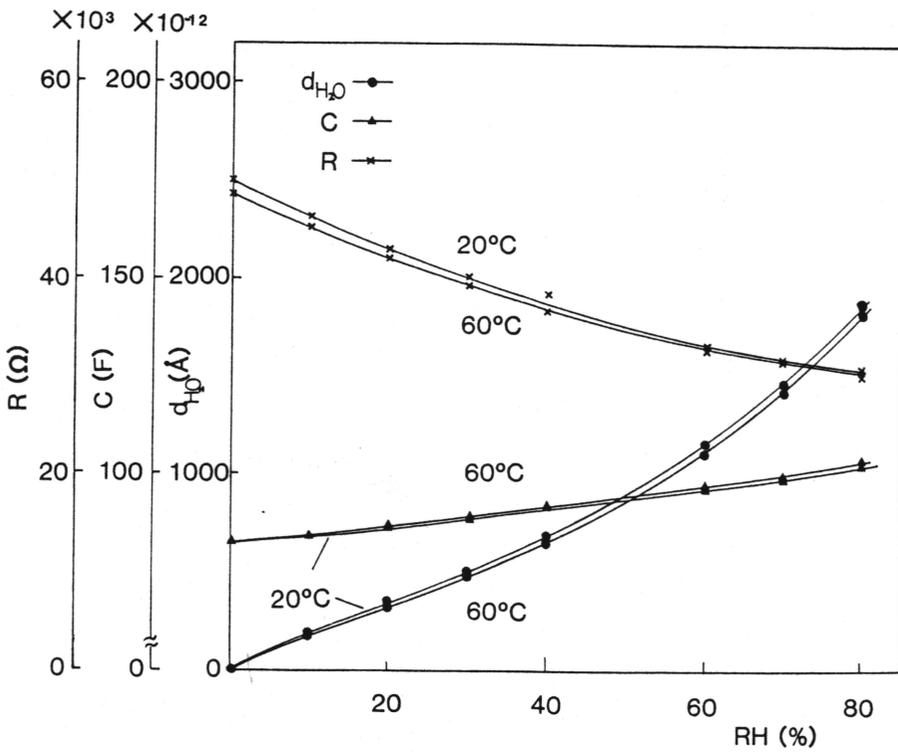


Fig. 4. RH-d_{H₂O}·C·R characteristics of the sensor using polymer films.

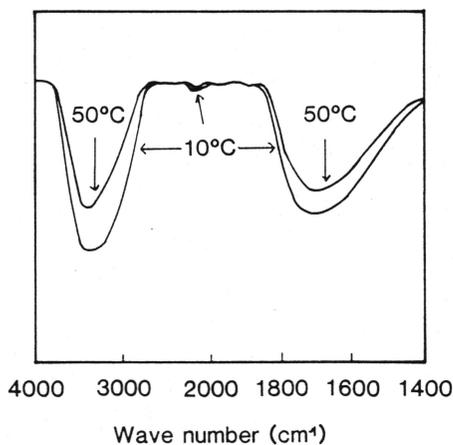


Fig. 5. Infrared spectra for CaF_2 thin films at temperature of 10°C and 50°C .

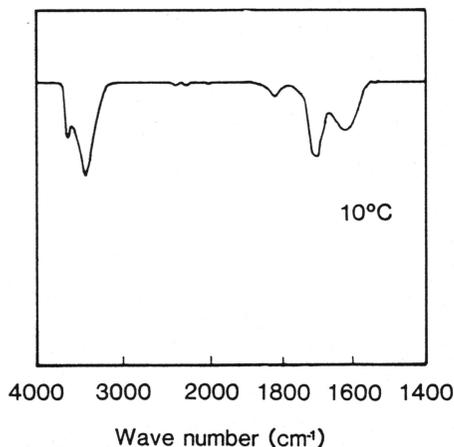


Fig. 6. Infrared spectrum for polymer films.

different form compared with the case of CaF_2 and Al_2O_3 thin films.

§4. Discussion

It is revealed from the result of the infrared spectrum that the water molecules absorbed in CaF_2 and Al_2O_3 thin films are in the form of liquid water. This is considered to be due to the capillary condensation in thin films. The radius of capillary where the capillary condensation occurs is given by Kelvin's eq. as follows:

$$r \propto \frac{1}{T \ln \frac{P}{P_0}} \quad (4.1)$$

where r : radius of capillary

T : absolute temperature

P/P_0 : RH

If the capillary condensation occurs, it is found from (4.1) that RH- $d_{\text{H}_2\text{O}}$ relationship depends on temperature. This coincides qualitatively with the results of infrared spectra.

For polymer films, the existence of the other form of water is found, since RH- $d_{\text{H}_2\text{O}}$ relationship shows no temperature dependence as shown in Fig. 4, and the shape of infrared spectrum peaks is different from that of liquid water. As the form of water included in the films, liquid water, physically adsorbed water, OH^- and H^+ are considered. Generally, the mechanism of R change in humidity sensors is explained by the electric conduction of H^+ formed by the surface ionization. In the case of CaF_2 , lowering of R is relatively large, but the change of R is quite small for polymer films. Then, in polymer films, the water molecules cannot exist in the form of H^+ and OH^- but are in the form of the physically adsorbed state even at higher RH (Fig. 6).

The BET equation for the polymer-water system⁷⁾ is given by

$$\frac{v}{v_m} = cx \quad (4.2)$$

$$\begin{cases} c = e^{(E_1 - E_L)/RT} \\ x = AP e^{E_L/RT} = \frac{P}{P_0} \end{cases}$$

where

v : volume of adsorbed gas

v_m : volume of adsorbed monolayer

E_1 : heat of adsorption for 1st layer

E_L : heat of adsorption for L th layer

c in eq. (4.2) is the function of temperature except $E_1=0$ or $E_1=E_L$. In practical, $E_1=0$ is impossible. Then, c calculated from the BET plots of Fig. 4 (polymer films) is 1.76 at 60°C and $E_1 - E_L$ is obtained (E_L is known in the table). E_1/E_L is estimated to be less than 1.03. This leads to the results of $E_1 \approx E_L$ in the case of polymer films.

The dielectric constant of liquid water⁸⁾ changes as $\epsilon_s \propto T^{-1}$. However the dielectric constant of physically adsorbed water does not de-

pend on temperature from 20°C to 60°C as shown in Fig. 4. In polymer films, it is considered that the physical adsorption of water molecules will take place at OH groups** on polymer surfaces and this is the reason that the dielectric constant does not change even if temperature varies.

In the case of CaF₂ and Al₂O₃ thin films, increasing temperature, $d_{\text{H}_2\text{O}}$ decreases by the change of dielectric constant with temperature change ($\epsilon_s \propto T^{-1}$) and it is considered that the formation of ions such as H⁺, OH⁻ due to dissociation of water molecules mainly contributes to C change.

§5. Conclusion

① In the range of 10~75% RH, water molecules are in the form of liquid water for Al₂O₃ and CaF₂ thin films and are in the form of physically adsorbed water for polymer films.

**This is confirmed by the infrared spectrum.

② In the case of the well treated polymer films, the relationship between the amount of physically adsorbed water and RH slightly depends on temperature.

③ In the temperature range from 20 to 60°C, the dielectric constant of physically adsorbed water unchanges.

④ In the case of CaF₂ and Al₂O₃ thin films, the formation of ions due to dissociation of water molecules is the main factor for C change.

References

- 1) T. Usui: *Sensor Technology* **1** 28 (1981) (in Japanese).
- 2) T. Nitta: *Ionics* **12** 7 (1981) (in Japanese).
- 3) S. Takeda: *Jpn. J. Appl. Phys.* **20** 1219 (1981).
- 4) M. Primet, P. Pichat and M. V. Mathieu: *J. Phys. Chem.* **75** 1216 (1971).
- 5) B. A. Morrow and I. A. Cody: *J. Phys. Chem.* **77** 1465 (1973).
- 6) Y. Sadaoka and Y. Sasaki: *Denkikagaku* **50** 172 (1982) (in Japanese).
- 7) M. Dole: *J. Chem. Phys.* **16** 25 (1948).
- 8) J. G. Kirkwood: *J. Chem. Phys.* **7** 911 (1938).