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Kazuhiro SUZUKI, Kyogo KOYAMA,* Yo-ichi NABETA*
and Tadao INUZUKA

Dept. of Electrical Engineering and Electronics, Aoyama Gakuin University, 6-16-1, Chitosedai, Setagaya-ku, Tokyo 157, Japan
**Kyoei Plastics Company, 3-17, Sakuragi, Chichibu-shi, Saitama 368, Japan*

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Hydrogenated carbon films containing oxygen are formed by RF plasma decomposition of amyl alcohol. It is found that the films obtained are applicable to humidity sensing. Then the change of the capacitance (C) and the mass of the absorbed water (m_{H_2O}) in the films by varying relative humidity (RH) has been measured simultaneously.

From the results of measurements, water molecules are absorbed in the film by physisorption and the temperature dependence can not be found in m_{H_2O}-RH characteristics. The hysteresis in m_{H_2O} versus RH and C versus RH characteristics is almost negligibly small (up to ±0.5%RH). The sensor is in a stable state even after kept in ethanol or acetone and/or water vapor (130°C≃100%RH).

§1. Introduction

Humidity control is required in a variety of field. The development of the humidity sensor, which has no hysteresis between electrical signal and relative humidity (RH), and works in a variety of circumstances, is desired.

The several kinds of humidity sensors using the change of electrical properties due to absorption and desorption of water molecules have been developed.[1,2] Especially, the humidity sensor using porous ceramics works even in a high temperature region, but it shows hysteresis (±3~±5%RH) between electrical signals and RH. The sensor using the polymer layer shows good response to humidity change. But the structure, texture and/or surface state of the polymer layer change irreversibly after kept in a high humidity atmosphere or dipped in organic solvents.

In this paper, the fablication process of a humidity sensor using the hydrogenated carbon film containing oxygen is described. This sensor can operate in a stable state after kept in organic solvent or in high humidity atmosphere (≃100%RH) at 130°C and has negligibly small hysteresis even in a high humidity region.

The moisture sensing mechanism of this humidity sensor is also discussed.

§2. Preparation of Hydrogenated Carbon Films Containing Oxygen

The experimental apparatus of RF plasma deposition[3-5] is shown in Fig. 1. schematically. Two glow-discharge electrodes (stainless steel; 170 mmφ) were installed parallel to each other in the center of the reactor 70 mm apart, and a substrate is fixed on the upper electrode.

After evacuation to 1×10^{-6} Torr using a diffusion pump, argon gas was introduced into the reaction chamber. To eliminate contamination adsorbed on the substrate surface, the substrate was exposed to argon plasma for 30 min. Then the system was evacuated to 1×10^{-6} Torr again, and amyl alcohol (n-$C_5H_{11}OH$: commercial grade) was introduced up to the pressure of 4×10^{-1} Torr through a mass flow controller, and RF power was supplied for starting glow discharge. The condition for film deposition is shown in Table 1.

§3. Simultaneous Measurement of m_{H_2O}-RH and C-RH

A structure of the humidity sensor which allows the simultaneous measurements of capacitance (C) and the mass of the absorbed water (m_{H_2O}) is shown in Fig. 2 schematically.

The measurements of m_{H_2O}-RH and C-RH characteristics have been done in the temperature range from 30°C to 60°C and also in the humidity range from 0% to 95%RH using a

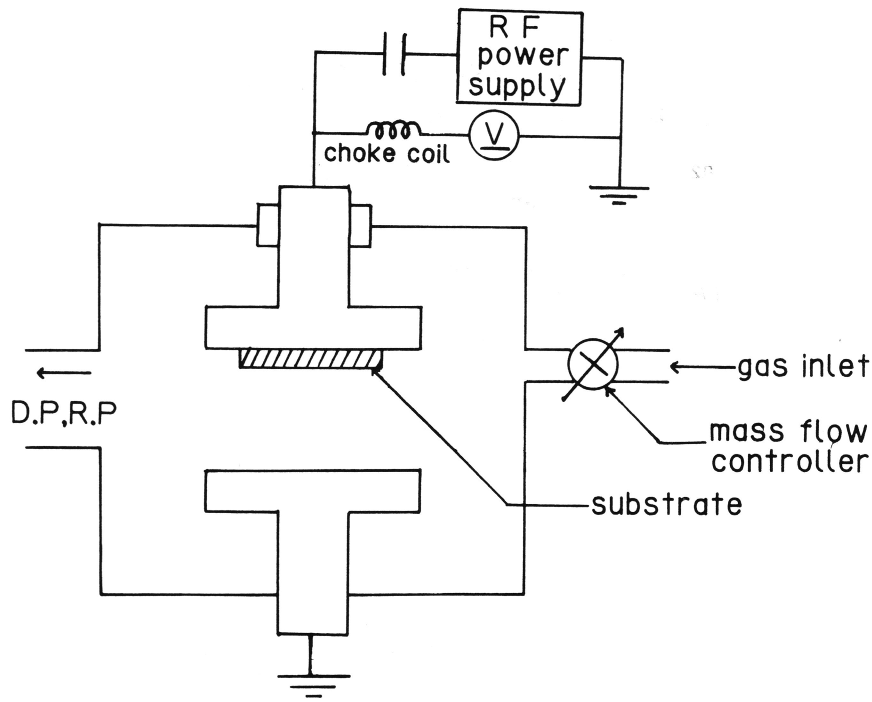

Fig. 1. Experimental apparatus for film deposition.

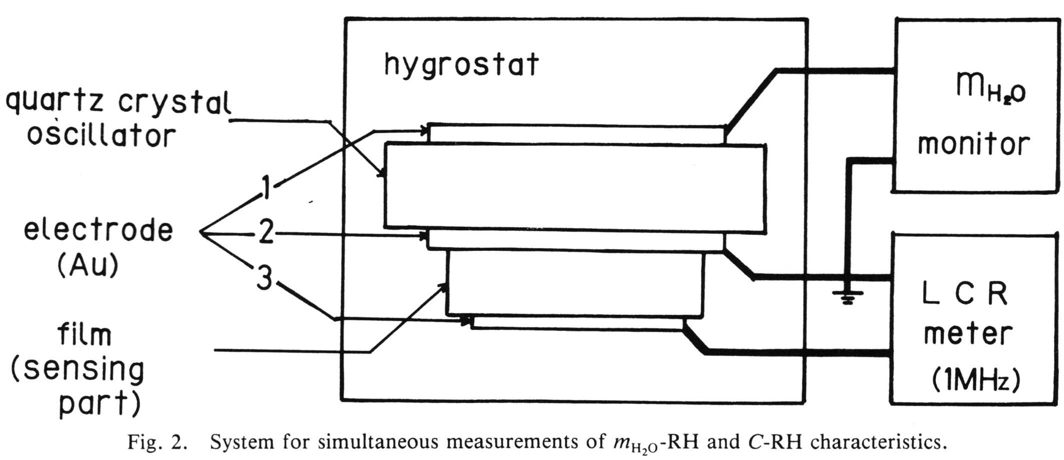

Fig. 2. System for simultaneous measurements of m_{H_2O}-RH and C-RH characteristics.

Table I. Typical experimental condition of film deposition.

Substrate	Quartz crystal
Reaction gas	$n\text{-}C_5H_{11}OH$
Gas pressure	4×10^{-1} Torr
Flow rate	10 SCCM
R.F. power	210 W
Reaction time	3 hours

divided flow humidity generator.† For the measurements of m_{H_2O} and C, a quartz crystal microbalance and an LCR meter operated at 1 MHz and 1 V were used respectively.

The electrodes 1 and 2 (1000 Å; Au) are deposited on a quartz crystal oscillator by conventional vacuum deposition. The thin electrode 3 (200 Å; Au) is formed by DC sputtering, since it is required to be permeable to water molecules. As the sensing part of the sen-

†SHINYEI KAISHA type SRH-1R135 (error ±1%RH)

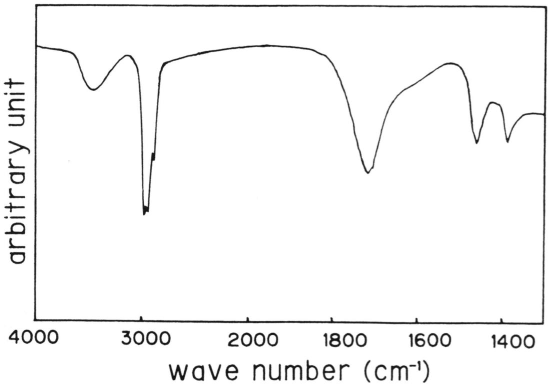

Fig. 3. Infrared spectrum of hydrogenated carbon film containing oxygen measured at $\simeq$0%RH and 10°C.

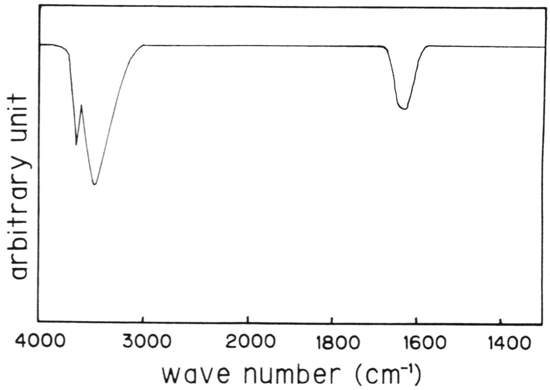

Fig. 4. Infrred spectrum for water molecules absored in a film at 75%RH.

sor, the hydrogenated carbon film containing oxygen ($\sim$8 μm) is prepared by RF plasma decomposition of amyl alcohol onto a substrate where the electrode 2 is previously deposited.

§4. Result and Discussion

A typical infrared spectrum ($\simeq$0%RH; 10°C) for the hydrogenated carbon film containing oxygen is shown in Fig. 3. In the spectrum, strong absorptions appear at 2960 cm^{-1} (CH_2), 2925 cm^{-1} (CH_3), 2850 cm^{-1} (CH_2), 1465 cm^{-1} (CH_3), 1455 cm^{-1} (CH_2, 1385 cm^{-1} (CH_3), 1715$\sim$1725 cm^{-1} (C=O) and 3500 cm^{-1} (OH). This spectrum indicates that the film consists of carbon, hydrogen and oxygen having chemical bond with each other. The infrared absorption spectra of the films for 75% RH and 0%RH are measured and the difference between these two spectra at the temperature of 10°C is plotted in Fig. 4. The shape of absorption peaks is quite alike to the spectrum of H_2O molecule, and is different from the spectrum of liquid water.

The results of m_{H_2O}-RH and C-RH measurements are shown in Fig. 5. It is observed that m_{H_2O} does not depend on temperature and C depends on temperature. When the humidity cycles between 0 and 95%RH were examined, it was found that the hysteresis between m_{H_2O} and RH is almost negligibly small (up to $\pm$0.5%). The m_{H_2O}-RH curve can be fitted to a BET equation in the range from 0%RH to 50% RH. It is known that water molecules absorbed in porous ceramics are in the form of liquid water due to capillary condensation because the surface of ceramics is almost hydrophilic radicals.

According to the Thomson's law, the capillary condensation makes it impossible to avoid the hysteresis of m_{H_2O} and electric output signals when the relative humidity is varied (generally in a case of ceramics, the values of hysteresis are $\pm 3 \sim \pm 5$%RH). The radius of a capillary where capillary condensation occurs is given by Kelvin's equation (4.1).

$$r \propto \frac{-1}{T \ln \dfrac{P}{P_0}}, \qquad (4.1)$$

where r is the radius of a capillary corresponding to m_{H_2O}, T is the absolute temperature and P/P_0 is the relative humidity.

If the capillary condensation occurs, it is evident from eq. (4.1) that m_{H_2O}-RH relationship depends on temperature. It is considered that the hydrogenated carbon film containing oxygen absorbs water molecules in the form of physisorption. The reasons are as follows: m_{H_2O}-RH relationship shows no temperature dependence, the shape of infrared spectrum is different from the spectrum of liquid water, and the hysteresis between m_{H_2O} and RH is almost negligibly small.

BET equation is given by the following equation,

$$\frac{v}{v_m} = \frac{c'x}{(1-x)(1-x+c'x)},$$
$$c' = e^{(E_1 - E_L)/RT},$$

where v/v_m is the coverage corresponding to m_{H_2O}, E_1 is heat of adsorption for 1st layer, E_L is heat of adsorption for L-th layer (L$\geqq$2), x is

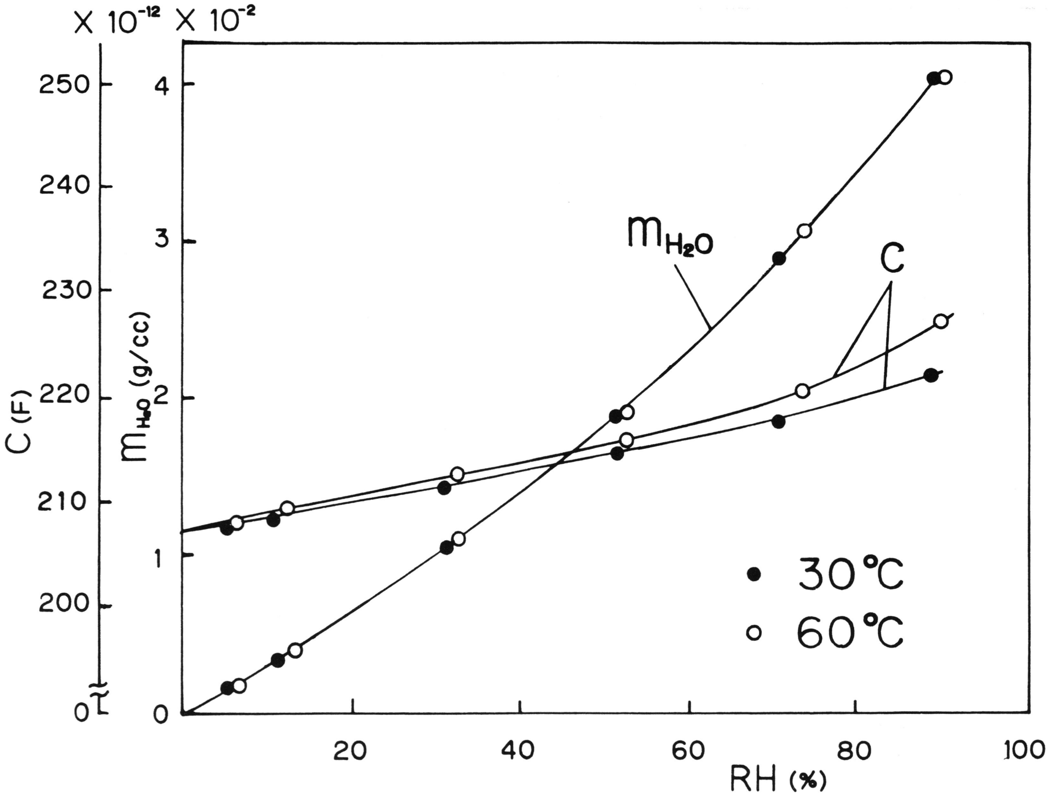

Fig. 5. m_{H_2O}-RH and C-RH characteristics.

the relative humidity and R is the gas constant. The value of c' in eq. (4.2) is the function of temperature except that $E_1 = E_L$. The reduction of the difference between the values of E_1 and E_L would be desirable to obtain a humidity sensor which can respond only to the change of relative humidity. Then, c' calculated from BET plots of Fig. 5 is 1.8 at 30°C. In a case of ceramics or polymer containing nitrogen, the value of c' is $50 \sim 1000$ because $E_1 \neq E_L$. The value of E_1/E_L of the carbon film is then estimated to be less than 1.03.† It is considered that the properties of hydroxyl groups bonding to carbon chains are different from that of hydroxyl groups chemisorbed on the ceramics or polymer containing nitrogen.

The value of C at 60°C against RH is larger than that of C at 20°C in Fig. 5. It is considered that the formation of ions such as H^+ and OH^- due to dissociation of water molecules contributes to C change. It is known that the dielectric constant of water molecules physisorbed at a hydrophilic radical surrounded with hydrophobic radicals does not change in the range from 20°C to 60°C.[6)]

In conclusion, a humidity sensor using the hydrogenated carbon film containing oxygen which has good durability and negligibly small hysteresis is prepared by RF plasma deposition. The sensor works stably in repeating humidity cycles even after kept in ethanol or acetone and/or water vapor (130°C; 100% RH) for 6 hours. And the mechanism of moisture sensing of capacitive humidity sensor is explained briefly.

The ideal characteristics of humidity sensor and a typical trend to realize the ideal characteristics are summarized below.

†E_L is estimated to be more than 44 kJ/mol by heat of condensation of water molecules.

Characteristics required for humidity sensor	To realize the characteristics
1. Hysteresis free	→ {Hydrophilic radicals are apart enough. (To avoid condensation)
2. Independence of *C* against temperature change {response of RH-m_{H_2O} and response of m_{H_2O}-C	→ {Use the hydroxyl groups bond to carbon chains as hydrophilic radicals. → {Surround a hydrophilic radical with hydrophobic radicals.
3. Quick response	→Use thin film for sensing part.
4. Good durability	→Bridge bonding.

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