Reprinted from
PROCEEDINGS OF THE 2ND SENSOR SYMPOSIUM, 1982. pp. 61～65

Fabrication and Characteristics of Thin Film Humidity Sensor

Kazuhiro SUZUKI, Yo-ichi NABETA and Tadao INUZUKA

Dept. of Electric Engineering and Electronics
Aoyama Gakuin University, Setagaya-ku, Tokyo

PROCEEDINGS OF THE 2ND SENSOR SYMPOSIUM, 1982. pp. 61 ~ 65

Fabrication and Characteristics of Thin Film Humidity Sensor

Kazuhiro SUZUKI,* Yo-ichi NABETA and Tadao INUZUKA

Dept. of Electric Engineering and Electronics
Aoyama Gakuin University, Setagaya-ku, Tokyo

A capacitive humidity sensor utilizing an aluminum-oxide thin film formed by reactive ion plating is fabricated and the characteristic of the sensor is measured by a newly designed humidity test chamber.

It is found that the sensor fabricated in this experiment works in quite stable states with a high reproducibility, especially in the high humidity region, and it is also revealed that the structure of the aluminum-oxide film suitable for the humidity sensor is "amorphous like" one. The capacitance of the sensor varies proportionally to the change of relative humidity between 10 and 80%, and a similar behavior is observed on the mass measurement of absorbed water molecules.

It is considered that the absorbed water molecules will form a condensed phase (liquid water) in micro-capillaries in an aluminum-oxide film. A simple model for water absorption in the film is given and a mechanism of condensation to liquid water will be discussed briefly relating to the capacitance change of the film.

§1. Introduction

Humidity control is required in a variety of fields and the development of the humidity sensor functionable in a wide range of relative humidity and in a variety of circumstances is desired.

The principle of humidity sensor developed until now is to use the change of mechanical or electrical properties of material due to absorption or desorption of water molecules. The humidity sensor using the change of electrical properties is classified as follows;

1) Resistance change [1-6]
2) Capacitance change[7]
3) Absorption of electro-magnetic wave[8]
4) Electro-motive-force change[9]
5) CFT (Charge-Flow Transistor)[10]

and the several kinds of sensors have been developed using the measuring principle of 1) and 2). Especially for the capacitive sensor, a metal oxide layer formed by a sintering[11] or an anodic oxidation method[12] and a polymer layer formed by a dip-coating method are used as a sensing part of a sensor. The structure, texture and/or surface state of these layers change irreversibly, if the sensors are kept in high humidity circumstances. These undesired change of the sensing part is due to the "porosity" in the case of sintered or anodized layers, and "stickiness" in the case of polymer layers. It is considered that the less-porous film compared with the sintered or anodized layer will be formed, if the films are grown from the vapor phase. In this paper, the fabrication process of a capacitive humidity sensor which can operate in a high humidity region (RH ~90%) and the characteristics of the sensor measured by using a newly designed humidity test chamber are described. The relationship between the amount of water molecules occluded in a metal oxide film (aluminum-oxide film) and the change of the capacitance will also be discussed.

§2. Structure and Formation of a Capacitive Humidity Sensor

A structure of the humidity sensor fabricated in this experiment is shown in Fig. 1 schematically and Fig. 2. The interdigital lower electrode (1000 Å; Pd, Au, etc.) is deposited by ion plating

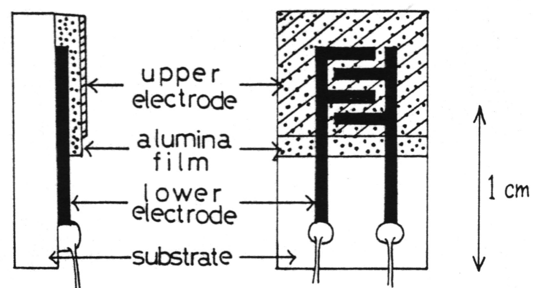

Fig. 1. Structure of humidity sensor.

*Present adress: Phoenix Int. Corp.

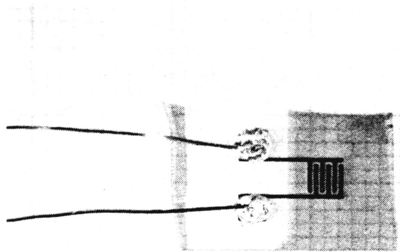

Fig. 2. Photograph of humidity sensor.

method on a cleaned substrate such as Boro-Silicate glass or sapphire and the thin upper electrode (100～200 Å; Pd, Au) is formed by a conventional vacuum deposition method, since it is required to be permeable to water molecules. Electron micrographs of the very thin deposits on NaCl (100) surface are shown in Fig. 3. These photographs depict the change of thin film structure caused by varying the mean thickness of deposits as a) 20 Å, b) 60 Å, and c) 120 Å. The films having the mean thickness of about 120 Å are available for the upper electrode, because the films give an electric conduction and are also permeable to water molecules. These two electrodes form a capacitor (C).

A dielectric film (aluminum-oxide film; 1 μm) is prepared by Reactive Ion Plating (RIP) onto a substrate where the lower electrode is previously deposited. The system of RIP is shown in Fig. 4.

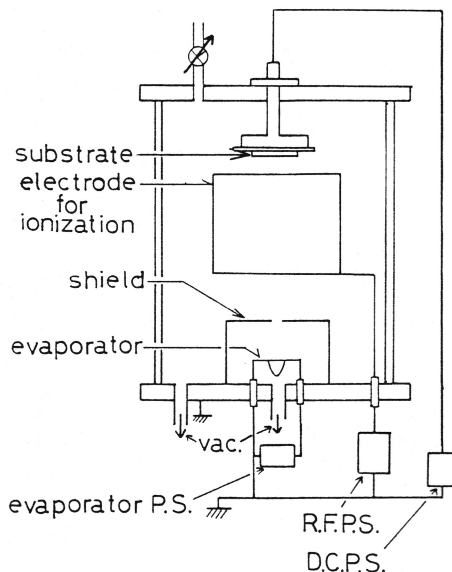

Fig. 4. System of reactive ion plating.

As a RIP chamber, a conventional vacuum deposition apparatus is used with the addition of an electrode for ionization of O_2 and Al and a variable leak valve for O_2 import.

As an evaporator of Al, an alumina-coated W basket is used considering impurity contamination. In order to prevent the oxidation of the evaporator, the evaporator is covered, as shown in Fig. 4, by an earthed stainless-steel box with a small hole (a few mmϕ) to pass the evaporated vapor, and the box is evacuated by another vacuum system to 10^{-4} Torr. To attach

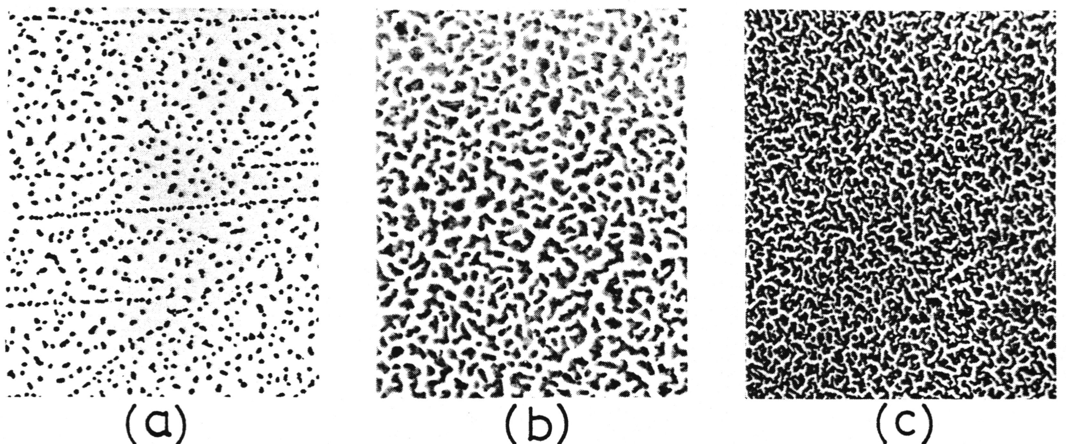

Fig. 3. Electron micrographs of Au thin films.
Mean thickness: a) 20 Å
b) 60 Å
c) 120 Å.

the cover to the evaporator, the control of O_2 gas pressure becomes easy during deposition.

The formation process of aluminum-oxide films is as follows, after evacuation to 10^{-6} Torr, O_2 gas is introduced to the pressure of about 10^{-3} Torr through a variable leak valve, and the RF power (f=13.56 MHz, 400 W) is supplied for starting glow discharge. Then Al is evaporated with a constant evaporation rate of about 1.5 μm/h.

In plasma formed by RF discharge, neutral atoms, ions and radicals are reactive, because these species are to be equivalent high temperature state. Then, Al evaporated in oxygen plasma forms aluminum-oxide by controlling RF power, O_2 pressure and evaporation rate.

When the growth rate of alminum-oxide films is about 4 μm/h, the structure of the film is amorphous in the range of the substrate temperature from room temperature to 200°C, and raising the substrate temperature (200 ~ 500°C), the structure of the film changes to $\gamma-Al_2O_3$. By SEM and replica TEM observation, the appearance of the film surface is smooth and the characteristic structure (pores) observed for the anodized film surface cannot be found.[13)]

§3. Humidity Test Chamber

A humidity test chamber designed in this experiment is a simple one following the definition of relative humidity. A stainless-steel chamber (~7*l*) evacuated to 10^{-2} Torr is set in a constant temperature bath and the desired amount of water measured by a microsyringe is injected into chamber directly (Fig. 5). In this system, the amount of 1 μl corresponds to the RH=0.8% at 20°C. Changing the amount of the injected water, the desired relative humidity is obtained in a few seconds without detectable change of temperature measured by a thermistor. A quartz crystal micro-balance (QCM) and a calibrated humidity sensor are mounted to the chamber as shown in Fig. 6. The mass (Δm_{H_2O}) of the water molecules absorbed in an aluminum-oxide film is measured by QCM. The mean thickness Δd_{H_2O} of the absorbed water layer are caliculated from these values.

§4. Result

The change of C and Δd_{H_2O} varying RH are shown in Fig. 7 (a) and (b) respectively.

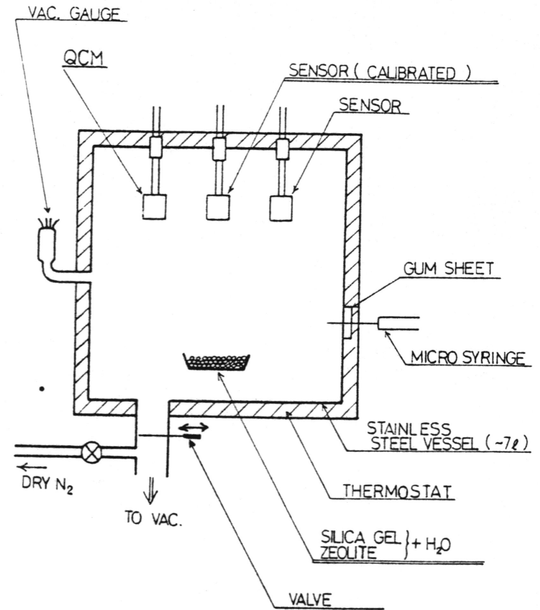

Fig. 5. Humidity test chamber.

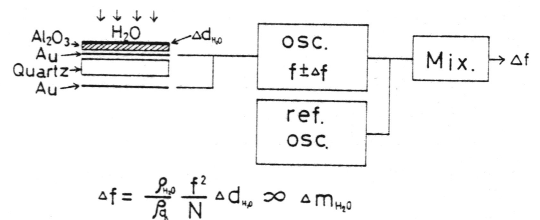

Fig. 6. Construction of quartz crystal microbalance.

After several runs (n≳5) of humidity cycles, C and Δd_{H_2O} change downward especially in the high RH region, and the RH characteristic of the sensor is to be a stable state as shown in lower curves of the figures. The sensors experienced the humidity cycles are quite stable against exposure in a high humidity circumstance (~90%) for 100 hours and immersion in boiling water for 30 minutes. It is also found that the behavior of capacitance due to RH change is relatively linear except the region of low humidity (0 ~ 10%).

The response of the sensor is measured as follows: the sensor in an evacuated chamber is quickly taken out to humid circumstances and, after measurements, the sensor is replaced to zero-humid circumstance. If the standard humidity cell (~1*l*) is used for this purpose, the change of humidity in the cell caused by the

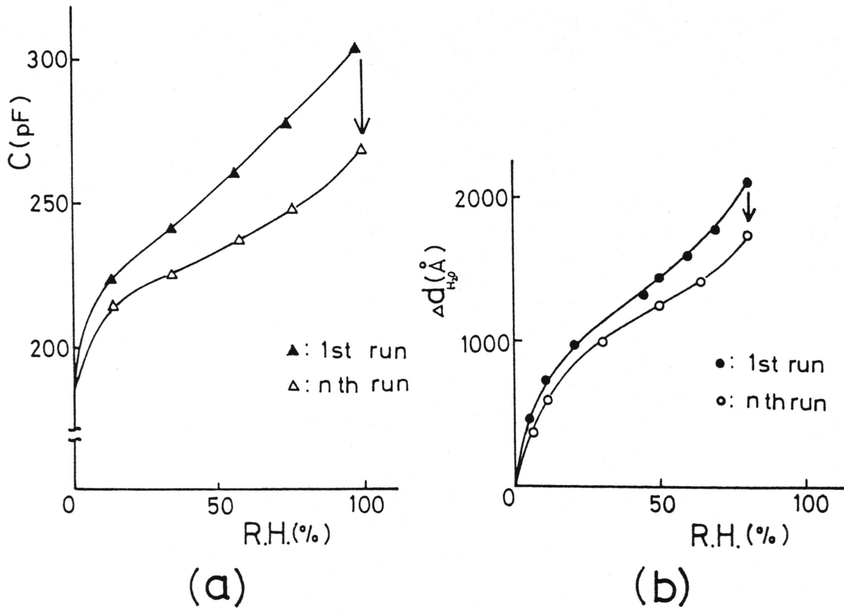

Fig. 7. Characteristics of C-RH and Δd_{H_2O}-RH.

artifact for inserting a sensor influences the response characteristics of the sensor. The results of response measurements are shown in Fig. 8(a) and (b) for C and Δd_{H_2O} respectively. The rapid raise of the curve is observed at the beginning of the measurement, and the succeeding gradual changes of C and Δd_{H_2O} found in the figures are due to the gas flow (temperature change) by the gas introduction or evacuation. If the humidity changes gradually, the complicated behacior of C and Δd_{H_2O} will be removed. In principle, it is considered that the response time of the sensor is about a few seconds.

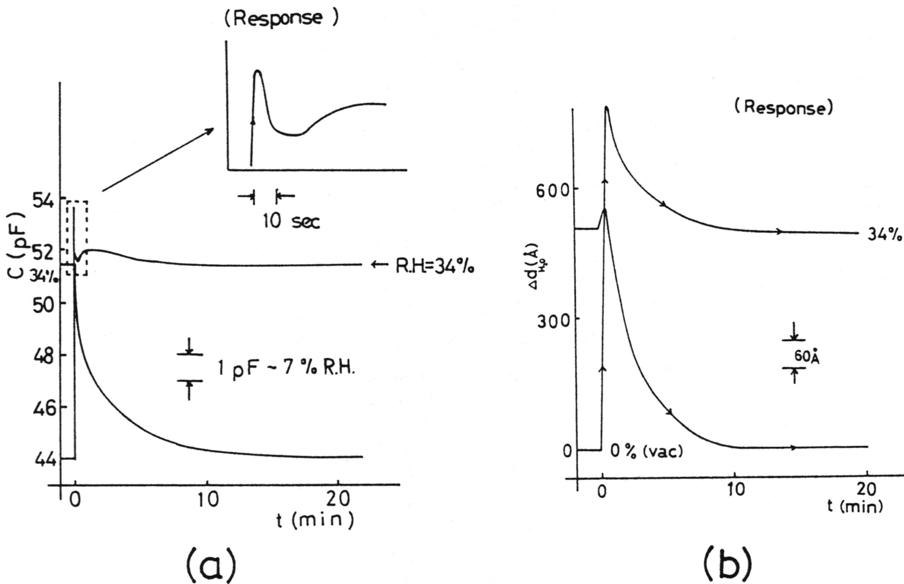

Fig. 8. Response characteristics.
a) C-t
b) Δd_{H_2O}-t.

§5. Discussion

From the results of Fig. 7 (a) and (b), the relationship between C and Δd_{H_2O} is plotted in Fig. 9. It is found that the change of C is proportional to Δd_{H_2O}, which is linearly related to Δm_{H_2O} except the low humidity region.

Now, a model for water absorption in an aluminum-oxide film is stated in Fig. 10 (a) and (b). If the water molecules are absorbed uniformly from the whole surface of the film, the relationship of C and Δm_{H_2O} is given as shown in (b). On the other hand, if the water molecules are absorbed perpendicularly along the capillaries as observed in anodized film, C of the film changes linearly (a). Considering the results of Fig. 9, the model of (a) is plausible. If C of the film is calculated from the amount of water molecules absorbed in the film by using the dielectric constant of liquid water ($\varepsilon_s = 60$ at 20°C),[14] it is confirmed that the change of C due to RH variation coincides to the measured value shown in Fig. 7.

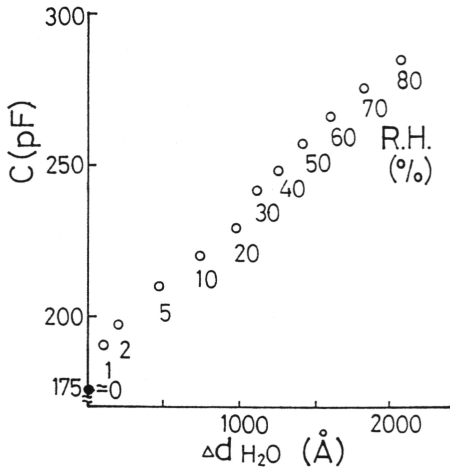

Fig. 9. Relationship of C-Δd_{H_2O}.

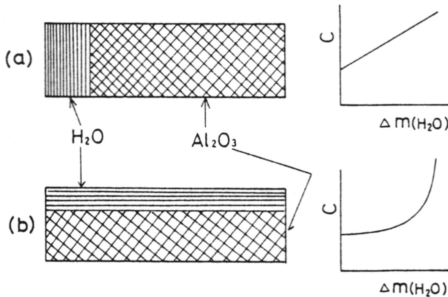

Fig. 10. Models of water absorption in an Al_2O_3 thin film and corresponding C-Δm_{H_2O}.

Consequently, the condensed phase (liquid water) of water molecules may be formed in aluminum-oxide films. Considering the mechanism of C change (model (a)) and also the smoothness of film surfaces, micro-capillaries must exist in the aluminum-oxide film. Probably, the condensation will take place at micro-capillaries (capillary condensation).

The formation process of micro-capillaries through the film perpendicular to the film surface is probably due to the growth mechanism of the film from vapor phase, i.e. the growth rate of the film perpendicular to the substrate surface is relatively high compared to the growth rate along the substrate surface.

In conclusion, the sensor utilizing an aluminum-oxide film gives a quite stable C change, especially even in the high humidity region. It is also found that the change of C is due to the "liquid water" condensed in micro-capillaries corresponding to RH.

References

1) F. W. Dummor: J. Research NBS **20** 723 (1938).
2) M. Pope: U.S. Patent 2,728,831 (1955).
3) K. Nakamura, *et al.*: Electroanalytical Chem. and Interfacial Electrochem. **47** 175 (1974).
4) W. J. Smith, *et al.*: Bull. Am. Meteol. Soc. **35** 60 (1954).
5) H. Isogai, *et al.*: Instr. Technol., July, 49 (1974).
6) C. M. Stover: Rev. Sci. Instr. **34** 632 (1963).
7) K. W. Misevich: IEEE Trans. Ind. Electron. and Control Instr. **IECI-16** 106 (1969).
M. Tokano, T. Inuzuka and Y. Nabeta: Tech. Rep. of Electron Devices, IECE Japan **ED-80-13** (in Japanese).
8) Miura and Yamamoto: Tech. Rep. IEE Japan **EDD-79-48, CH-79-34** (1979) (in Japanese).
9) Patent: Showa 51,23689.
10) S. D. Senturia *et al.*: Appl. Phys. Lett. **30** 106 (1977).
11) T. Nitta: Ceramics **15** 346 (1980).
12) A. C. Jason: "*Humidity and Moisture*" Ed. Wexler **1** 372 (1965) REINHOLD PUBL.
M. G. Kovac *et al.*: Solid State Tech. p. 35 Feb (1978).
13) C. J. L. Booker and J. L. Wood: Brit. J. Appl. Phys. **8** 347 (1957).
14) H. Fröhlich: *Theory of Dielectrics* (Clarendon Press Oxford 1958).