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A capacitive humidity sensor using a γ-Al_2O_3 thin film formed by reactive ion plating has been fabricated and humidity characteristics of the sensor can be controlled by varying the conditions of deposition such as deposition rates, ambient gas pressures and the ratio of O_2 and Ar gas pressures.

As-deposited films of γ-Al_2O_3 are treated in boiling water, and it is found that γ-Al_2O_3 changes to γ-$Al_2O_3 \cdot H_2O$ (Boehmite).

The sensor treated in boiling water has been working in a quite stable state even in a high humidity region.

§1. Introduction

The crystal structure of alumina films (layers) formed by anodic oxidation[1] or vapor deposition[2] at the substrate temperature to about 900°C is cubic called as γ-Al_2O_3 and, in the case of deposition assisted by ions, crystalinity is improved at the relatively lower substrate temperature.[3] Raising the substrate temperature to above 1000°C the vapor deposits of alumina shows an α-Al_2O_3 structure[4] and this is consistent to the results that the vapor deposits of γ-Al_2O_3 on sapphire changes to α-Al_2O_3 by heating to about 1200°C.[5]

It is also known that γ-Al_2O_3 crystallites left at humid circumstances change to $Al_2O_3 \cdot H_2O$ called as Boehmite and the surface of Boehmite adsorbs the 4 or more layers of water molecules. These behaviors of γ-Al_2O_3 surfaces bring less promising results to the application as the humidity sensor. However, the sensor fabricated with alumina films formed by reactive ion plating have been working relatively stable in humid circumstances.[2] The difference of these two results mainly depends on the structure of the films grown on a substrate. For the practical use in a variety of fields, the passivation and aging process on alumina surfaces will be required.

In this paper, humidity characteristics of a capacitive humidity sensor formed under the controlled condition are described. The growth conditions of alumina films formed by reactive ion plating and their infuluence on film structures and humidity characteristics are discussed. The aging effect on stability of the sensor is also discussed briefly.

§2. Fabrication Process of a Capacitive Humidity Sensor and Its Structure

2.1 Structure of the capacitive humidity sensor

A structure of the humidity sensor fabricated in this experiment is shown in Fig. 1 schematically and its photograph is also shown in Fig. 2. After cleaning of the substrate surface such as boro-silicate glass or sapphire by O_2 plasma, lower electrodes are deposited by ion plating or sputtering. A thin upper electrode is formed by a

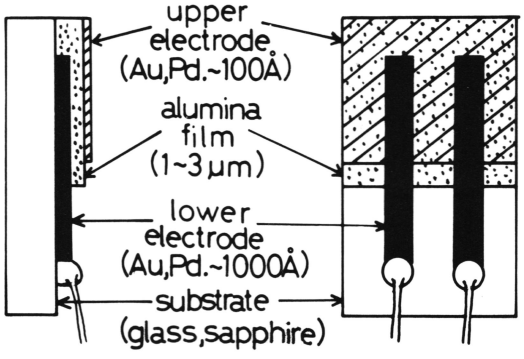


Fig. 1. Structure of the humidity sensor.

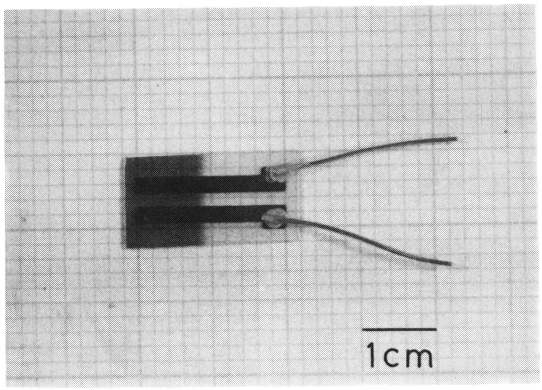


Fig. 2. Photograph of the humidity sensor.

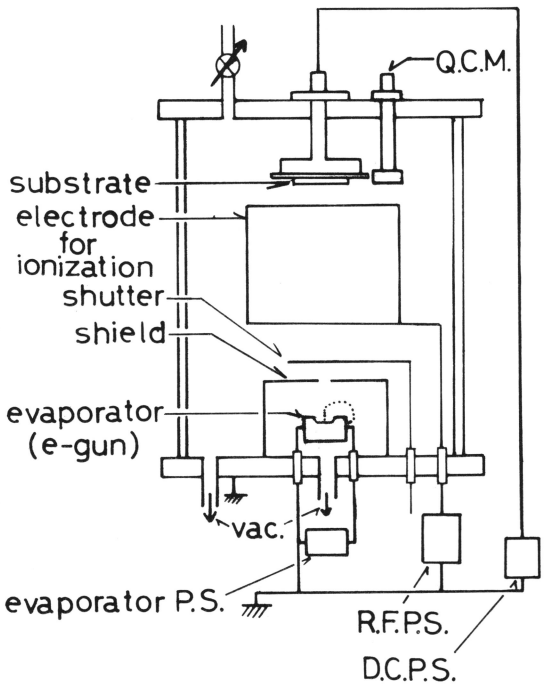


Fig. 3. System of reactive ion plating.

conventional vacuum deposition. The thickness of the upper electrode is determined by trial and error to satisfy the both conditions of an electrical conduction and a permeability to water molecules. The most suitable thickness for upper electrode is about 120 Å in mean thickness.

The two lower electrodes and the upper electrode form two capacitors and these two capacitors are connected serially.

A dielectric film (alumina film) is formed between these two electrodes.

2.2 Preparation of alumina films

Alumina films are deposited by reactive ion plating on a cleaned substrate where the lower electrodes are previously formed. The experimental apparatus is shown in Fig. 3 schematically, and the specially equipped parts are the ionization electrode, the variable leak valve and the differentially pumping chamber.

As an evaporator of Al, an electron gun is used to reduce impurity contamination and to get the constant rate of Al evaporation. The electron gun is mounted in the differentially pumped chamber ($\sim 10^{-6}$ Torr) to prevent the oxidation of the electron gun and evaporants (Al). Using the differential pumping chamber, the control of the O_2 gas pressure becomes easy during deposition.

The formation process of alumina films is as follows; after evacuation of the vacuum chamber to about 2×10^{-7} Torr, O_2 or mixture of O_2 and Ar is introduced to the pressure of about 10^{-3} Torr through the variable leak valve, and the R. F. power (13.56 MHz, 400W) is supplied to start glow discharge. Then Al is evaporated with a constant evaporation rate monitoring the quartz crystal microbalance (Q.C.M.) (the reading of Q.C.M. is the mass change of the alumina film).

Varying the deposition rate, the ambient gas pressure and the ratio of O_2 and Ar, the change of humidity characteristics is measured by a commercial constant humidity chamber.

The structure of the deposited films are examined by RHEED and SEM. The capacitance of the sensor is measured by an LCR meter operated at 1 MHz.

§3. Result and Discussion

3.1 Characterization of alumina films

A typical SEM photograph of the alumina film deposited at room temperature on a glass substrate is shown in Fig. 4. The surface of the film is fairly smooth compared with the alumina surface formed by anodic oxidation,[1] and at the cross section, the fine columnar structure can be observed. The crystal structure of this film is amorphous one with the trace existence of γ-Al_2O_3 in a polycrystalline state as shown in Fig. 5.

On the other hand, the electron diffraction pattens of alumina films formed on sapphire

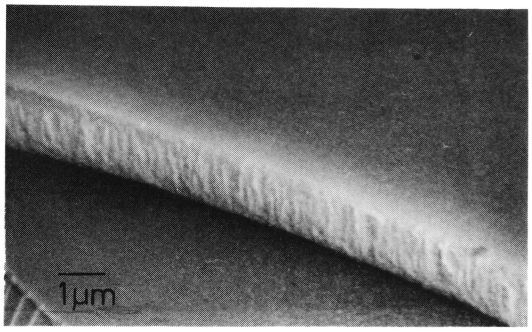


Fig. 4. SEM image of an alumina film/glass.

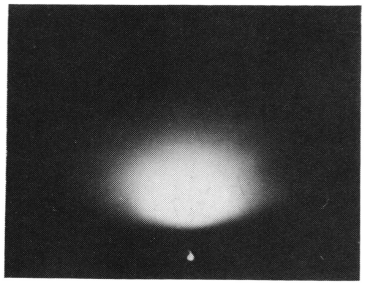


Fig. 5. RHEED pattern of Fig. 4.

substrates at room temperature, 300°C, and 500°C are shown in Fig. 6, (a), (b), (c) respectively. Raising the substrate temperature to 500°C, the epitaxial growth of γ-Al_2O_3 film is observed.

If the substrate temperature changes slightly during deposition, the structure of the films, especially in the thickness direction, changes drastically. Considering the reproducibility and uniformity of the alumina films, the film is deposited on the substrate kept at room temperature (the substrate is heated to about 110°C by thermal radiation from the electron gun and plasma).

3.2 Characteristics of relative humidity vs. capacitance

The capacitance change (ΔC) is normalized by the capacitance at relative humidity (R.H.) of 15% (C_{15}) and $\Delta C/C_{15}$ is plotted against R.H. as shown in Figs. 7, 8, and 9.

Varying the deposition rate, R.H.-$\Delta C/C_{15}$ characteristics and porosities* of deposited films are shown in Fig. 7. Increasing the deposition rate, both $\Delta C/C_{15}$, and the porosity decrease. It is considered that the decrease of the

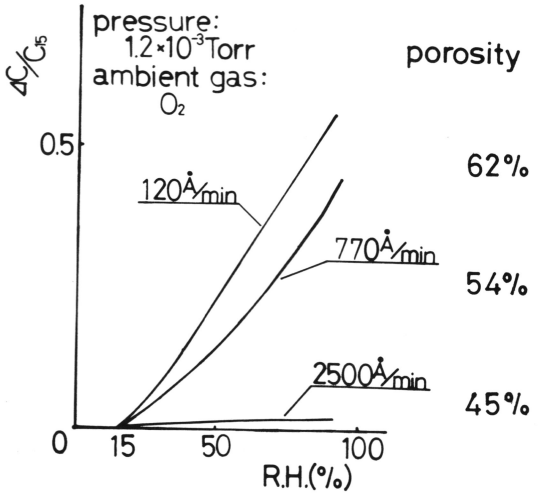
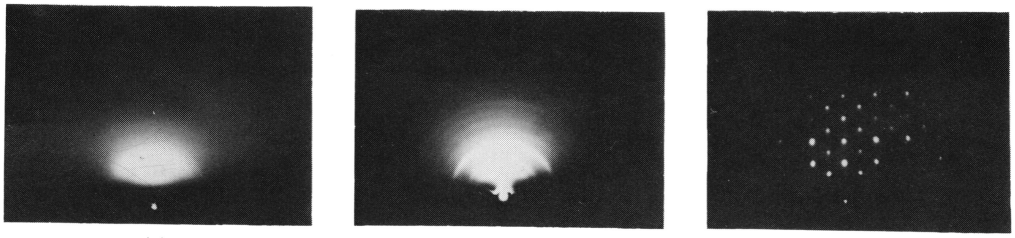


Fig. 7. Dependence of the deposition rate on R.H.-C.

*The porosity is obtained by comparing the density of γ-Al_2O_3 in a literature (bulk) and of the γ-Al_2O_3 film which is calculated from the mass of deposits measured by Q.C.M. and the thickness measured by optical interferometry and SEM.



(a) (b) (c)

Fig. 6. RHEED patterns of alumina films/sapphire,
Substrate temperature: a) 110°C
b) 300°C
c) 500°C.

porosity means the reduction of adsorption sites of water molecules such as micro-capillaries.[2] At the lower deposition rate, the columnar structure can be clearly observed in the cross section of the films by SEM. However, increasing the deposition rate, the cross sectional structure changes to smooth and this change is closely related to the decrease of $\Delta C/C_{15}$. At the higher deposition rate above 2500 Å/min, the deposited films give an electrical conduction and become brown in color.

Characteristics of R.H.-$\Delta C/C_{15}$, varying the ambient pressure, are shown in Fig. 8. The sensitivity increases, especially at a high humidity region, if the films are deposited in a lower vacuum and this behavior is probably due to the structure of films which is formed by stacking of the fine particles.

The amount of $\Delta C/C_{15}$ is also controlled by varying the ratio of O_2 and Ar pressure (Fig. 9). Increasing the partial pressure of Ar, $\Delta C/C_{15}$ becomes very small. The change of capacitance cannot be observed for the films having porosity of less than 50%.

3.3 *Stability and aging effect on the characteristics of the sensor*

A typical example of humidity characteristic is shown in Fig. 10. The capacitance of the sensor decreases gradually by applying the humidity cycles. After 7 or 8 humidity cycles, lowering of the capacitance disappears and the humidity characteristic becomes stable (lower

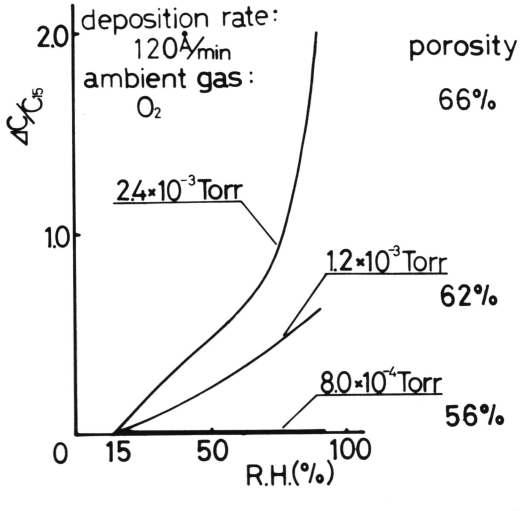


Fig. 8. Dependence of the ambient pressure on R.H.-C.

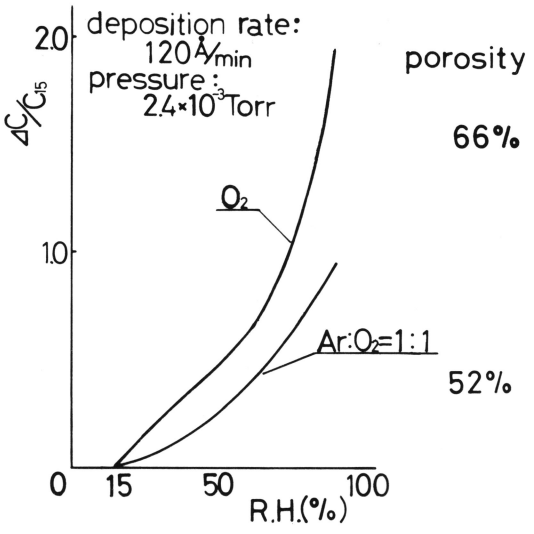


Fig. 9. Dependence of the ratio of Ar–O_2 gas on R.H.-C.

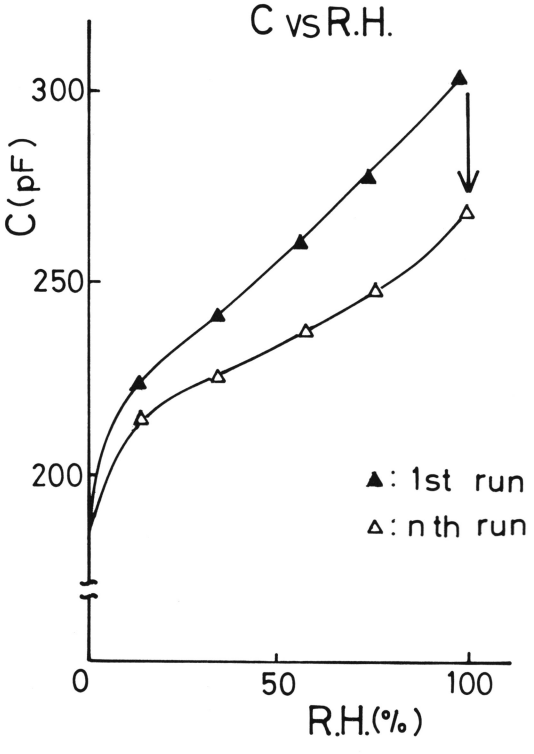


Fig. 10. Capacitance change due to humidity cycles. ($n \geq 7$).

curve). The mass of the absorbed water molecules in the alumina film is simultaneously measured by Q.C.M. and it increases gradually in the period of humidity cycles.

The result of humidity cycles is plotted agai-

nst time (days) in Fig. 11. At the beginning of the humidity cycles (~20 days), the decrease of capacitance (a) and the increase of the mass due to absorption of water molecules is clearly observed (b). Then, C and m_{H_2O} become stable. The accurate measurements of capacitance, however, show the finite decrease of capacitance of about 0.2 pF in 100 days. This decrease corresponds to R.H. of about 2%. The leakage resistance of the sensor also changes to a higher value of about 100 kΩ in 1 MHz. The sensor left at humid circumstances for 100 days or more has been working in a stable state.

It is considered that the gradual capacitance change for 100 days is due to the structure change of γ-Al_2O_3 to γ-$Al_2O_3 \cdot H_2O$, because if γ-Al_2O_3 is left at humid circumstances, it changes to γ-$Al_2O_3 \cdot H_2O$ (Boehmite) relatively in a short period. The alumina films deposited are boiled in distilled water at 120°C for 6 hours and the crystal structure of these films changes to γ-$Al_2O_3 \cdot H_2O$ as shown in Fig. 12. The sensor treated in boiling water shows the drastic changes as follows; the capacitance change due to R.H. decreases considerably, leakage resistance increases to about 100 kΩ in 1 MHz. After the treatment in boiling water, the sensor works in a quite stable state and the characteristic is similar to that of the sensor experienced the aging of 100 days.

§4. Conclusion

1. Humidity characteristics, porosity and crystalinity of γ-alumina films can be controlled by varying the condition of vapor deposition.
2. By applying the boiling treatment, a γ-alumina film on a glass substrate changes to a γ-$Al_2O_3 \cdot H_2O$ film, and the aging period of the sensor is considerably shortened.

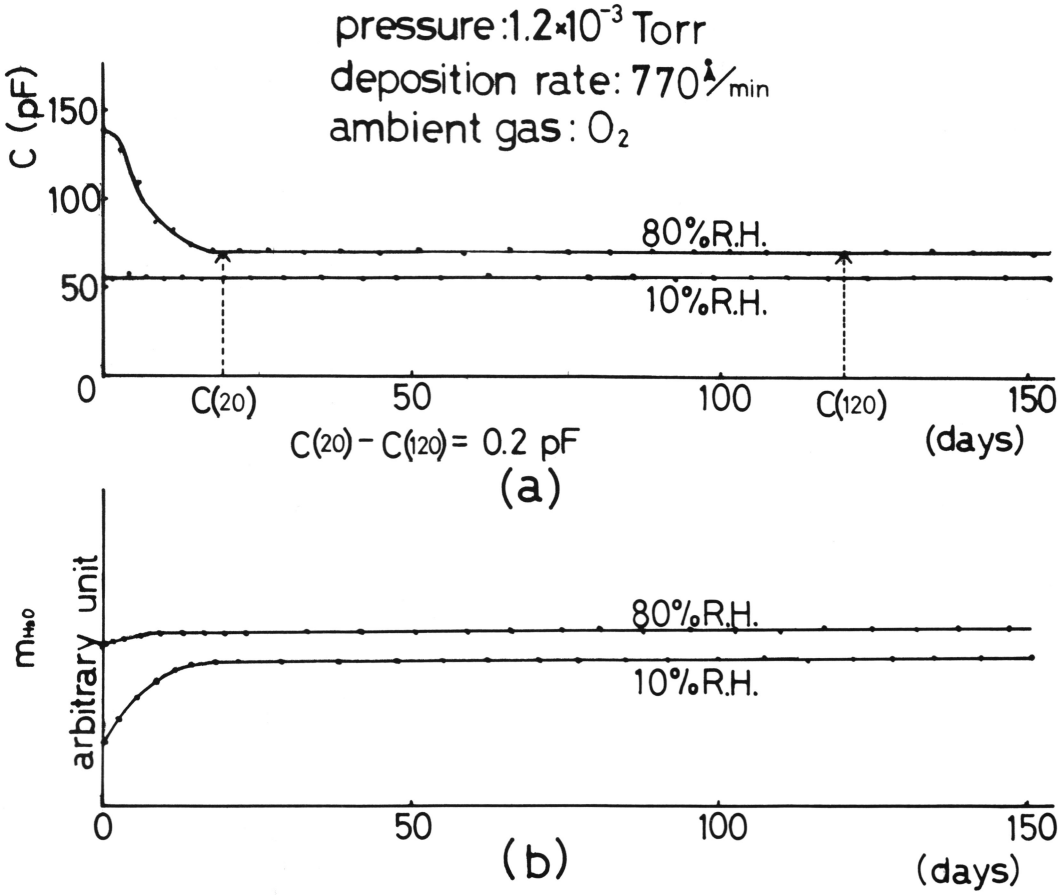


Fig. 11. Time dependence of
a) capacitance C(n)=The capacitance after n-days. (80%RH)
b) mass of H_2O.

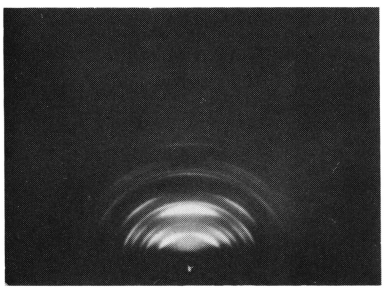


Fig. 12. RHEED pattern of γ-$Al_2O_3 \cdot H_2O$.

3. The sensor which works in a stable state in an accuracy of the constant humidity chamber can be fabricated.

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