Capacitive Humidity Sensing Element with a Structure of Ta-Ta₂O₅-MnO₂-Counter Electrode and Its Humidity Response

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A capacitive humidity sensing element with a structure of Ta-Ta₂O₅-MnO₂-counter electrode has been developed. The electric capacitance of the element varies with a relative humidity change of the atmosphere, which resulted in a relative humidity sensing element. Capacitance of 120-230 nF for 0-100% RH was obtained in the element of tantalum substrates with 0.8 mm in diameter and 25 mm in length. From a frequency dependence of the capacitance and the dissipation factor of the element, a humidity sensing mechanism of the element was proposed: in a low humidity region water vapor plays a role of a counter electrode and in a high humidity region the dielectric constant of water vapor is related to the capacitance change of the element. Several kinds of reliability tests of the element were carried out under various temperatures and humidities. The element worked for more than 8000 h in usual living atmosphere, and even in a polluted atmosphere when a filter of an activated carbon fiber sheet was applied. The element can be used in a humidity ON-OFF switch and a thermo-hygrometer with a small electronic circuit.

1 INTRODUCTION

Anodically formed tantalum oxide films have been widely used as dielectric materials for tantalum solid electrolytic capacitors. The capacitors consist of tantalum sintered anode bodies, tantalum oxide dielectric films, manganese oxide layers, and counter electrodes¹⁻⁴). We have found that humidity response behavior of the interface between the Ta₂O₅ film and the MnO₂ layer can be varied with changing a covering ratio of the tantalum oxide films to the manganese oxide layers. A treatment of the Ta-Ta₂O₅-MnO₂ element in a high temperature and humidity atmosphere can make a desired configuration of the interface between Ta₂O₅ and MnO₂, which

resulted in a humidity sensing element^{5, 6}). The element has highly performed characteristics, i.e. quick response for humidity change and high reliable characteristics under various humidities and temperatures in comparison with other types of elements^{7, 8}).

In this paper are studied 1) a preparation process and a structure of the element with the humidity responsible tantalum oxide film, 2) electrical properties of the element for various humidity change, 3) reliability of the element in several kinds of atmosphere, and 4) several applications of the element. A humidity sensing mechanism is newly proposed for the element with a structure of Ta-Ta₂O₅-MnO₂-counter electrode.

2 EXPERIMENTAL

2.1 Preparation of Ta-Ta₂O₅-MnO₂ sensing element

Figure 1 shows a preparation process of a

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Ta-Ta₂O₅-MnO₂ sensing element. A tantalum wire (99.99% pure, 0.8 mm in diameter, and 30 mm in length) was anodized at 30 V in a concentrated phosphoric acid solution for 10 min at 85°C. A manganese oxide layer was provided on the surface of the tantalum wire with an anodic tantalum oxide film by pyrolyzing an aqueous Mn(NO₃)₂ solution. A specific gravity of the Mn(NO₃)₂ solution was 1.15 and the solution was pyrolyzed at 250°C. The conductive counter electrode of a colloidal carbon and a silver paste was formed on the surface of the manganese oxide layer; the silver paste was a mixture of silver particles and an organic resin. The tantalum wire was fixed in a metal case with vent holes by soldering. Finally the element was treated at 85°C and 90% RH for 165 h. Figure 2 shows a construction of the element obtained.

2.2 Measurement of humidity response of the element

A humidity response and temperature characteristics of the element were measured in a precise humidity generator of Nihon-Kogaku SRH-IR at temperature range of 10-40°C. The element was set in 0% RH atmosphere for longer

Fig. 1 Preparation process of a humidity sensing element with the Ta-Ta₂O₅-MnO₂ structure.

Fig. 2 Construction of the element.

than 30 min and a relative humidity of the generator was varied at a rate of 1% RH/min. The capacitance and the dissipation factor of the element and the frequency dependence were measured with a digital LCR (Inductance-Capacitance-Resistance) meter of YHP 4261A at each relative humidity. The capacitance was also measured with a digital dc capacitance meter, in which dc voltage was applied to the element in a CR circuit. The capacitance value was obtained by measuring a charging time reaching a pre-set voltage.

A water vapor adsorption behavior of the element was studied in the following manner. The element was set in a glass sample tube in a thermal analyzer of Shimadzu TGA-31. The sample numbers examined at one time were 16 with no housing case. Air from the precise humidity generator mentioned above was introduced into the glass sample tube and weight changes caused by water vapor adsorption and desorption to the elements were recorded.

Reliability of the element was estimated at

the temperature range of 25-105°C. In a polluted atmosphere, the element with a filter was examined for 8000 h. Activated carbon fiber sheets were used as the filter; the filter consisted of phenolic resin-based activated carbon fibers and pulps.

3 RESULTS AND DISCUSSION

3.1 Humidity response of Ta-Ta₂O₅-MnO₂ element

Figure 3 shows relationship between capacitance of the element and relative humidity at 25°C. In Fig. 3, a dotted line and a solid line show results of the element with no treatment at 85°C and 90% RH and with the treatment, respectively. As shown in the figure, a sensitivity of the element for humidity change increased considerably with the treatment. It was revealed that the treatment for 165 h in 85°C and 90% RH was enough to get a humidity sensing element with a high sensitivity.

Consequently, the element with the treat-

Fig. 3 Relationship between capacitance of the element and relative humidity at 25°C. Dotted line; before the treatment at 85°C and 90% RH, Solid line; after the treatment.

Fig. 4 Capacitance response of the element for humidity change.

ment showed a sensitivity for a humidity change of 1.7 nF/%RH in a humidity region of 40-80% RH: 0.3 nF/%RH for elements with no treatments. The element also showed a slight temperature response of 1.1 nF/deg. in the temperature region between 10°C and 40°C.

Figure 4 shows a capacitance response of the element for a humidity change. When a relative humidity of the atmosphere changed, the capacitance value of the element reached a steady state value in 5 min.

Figure 5 shows a relationship between an amount of water vapor absorbed to the element and relative humidity. With increasing relative humidity, the element gradually absorbs water vapor. Between 50 and 60% RH, the adsorption curve shows different slopes; below and above this point, the adsorption rates are about 3.5×10^{-6} g/%RH and 22×10^{-6} g/%RH, respectively. A considerable hysteresis of the element was observed in the water vapor adsorption behavior, although the relationship of capacitance vs. relative humidity of the actual element showed

Fig. 5 Water vapor adsorption behavior of the Ta-Ta₂O₅-MnO₂ structure of the elements.

slight hysteresis of about 2% RH at 50% RH. The hysteresis of the water vapor adsorption was predominantly attributed to an organic resin in the conductive counter electrodes with silver particles. Only a part of the absorbed water related to a humidity response of a capacitance of the Ta-Ta₂O₅-MnO₂ structure.

3.2 Equivalent circuit and humidity sensing mechanism of elements

Figure 6 shows a model of an interface between Ta₂O₅ and MnO₂ layer of the element. The MnO₂ layer contacts with the Ta₂O₅ layer in two different ways; at one part (part (a)), the layers directly contact each other and at the other part (part (b)), the layers contact via an air gap. Assuming electrical circuits are shown in the model in Fig. 6, where C₁ and C₂ are capacitances of the Ta₂O₅ at part (a) and (b), respectively. R_{s1} and R_{s2} are contact resistances between Ta₂O₅ and MnO₂ at part (a) and (b), respectively. C_a and R_a are a capacitance and a resistance of the air gap or water vapor intruded to the gap, respectively. R_a and R_{s2} are related to a leakage current caused by water vapor intruded to the

gap. The electrical circuits thus obtained can be simplified to an equivalent circuit as shown in Fig. 7, where R_s and C correspond to a resistance and a capacitance at part (a), respectively, and C_p a capacitance at part (b). Parallel resistive elements, i.e. R_{s2} and R_a can be neglected as a leakage current of the element is very small. It was assumed that R_s, C, and C_p were independent both of a voltage applied and a current flowing.

In the equivalent circuit suggested above, R_s, C, and C_p can be obtained from equations 1, 2, and 3 with capacitances (C₁' and C₂') and dissipation factors (tanδ₁ and tanδ₂) of the element measured

Fig. 6 Model of interface between Ta₂O₅ and MnO₂ layer of the element.

Fig. 7 Equivalent circuit of the element.

Table 1 Frequency dependence of the capacitance of the humidity sensing element.

	120 Hz		1 Hz		R_s (Ω)	C (nF)	C_p (nF)
	C(nF)	$\tan\delta$	C(nF)	$\tan\delta$			
31% RH	78.6	0.22	57.4	0.27	0.94×10^4	52.07	32.76
66% RH	111.0	0.19	81.6	0.28	0.61×10^4	70.59	47.16
98% RH	159.3	0.16	144.8	0.11	0.94×10^4	66.79	104.71

at two different frequencies (ω_1 and ω_2), e.g. 120 Hz and 1 kHz.

$$R_s = (\omega_2 C_1' \tan \delta_1 - \omega_1 C_2' \tan \delta_2) / (C_1' C_2' \tan \delta_1 \tan \delta_2 (\omega_2^2 - \omega_1^2)) \quad \text{Eq. 1}$$

$$C = (C_1' \tan \delta_1 / \omega_1 R_s (1 - \omega_1 R_s C_1' \tan \delta_1))^{1/2} \quad \text{Eq. 2}$$

$$C_p = C_1' - C (1 - \omega_1 R_s C_1' \tan \delta_1) \quad \text{Eq. 3}$$

Table 1 shows a frequency dependence of capacitances and dissipation factors of the elements at 31, 66, and 98% RH. The calculated values of R_s , C, and C_p at each humidity are also shown in Table 1. Figure 8 shows a relationship between capacitance (C and C_p) and relative hu-

Fig. 8 Humidity dependence of C and C_p .

midity. As seen from Fig. 8, C_p strongly depends on the relative humidity change: 32.76 nF of C_p at 31% RH increases to 104.71 nF at 98% RH. On the other hand, C is dependent on the relative humidity in the lower humidity region and independent in the higher humidity region: 52.07 nF of C at 31% RH increases to 70.59 nF at 66% RH and becomes almost constant above 66% RH.

In the equivalent circuit shown in Figs. 6 and 7, the behavior of C and C_p can be explained in two ways as follows. In the first case, with an intrusion of water vapor into the gap of part (b), water vapor in the gap caused the changes in C_a , resulting in a change in C_p . In the second case, with water vapor intrusion, water vapor in the gap plays a role of an equivalent counter electrode for the Ta_2O_5 layer, resulting in a change in C_1 , C_2 , and C_a : C increases in the equivalent circuit in Fig. 7.

Judging from the result of Fig. 8 and the consideration on C and C_p described above, in the lower region of a relative humidity, i.e. under 66% RH, the water vapor absorbed plays a role of an equivalent counter electrode of the present element. In the humidity region above 66% RH, water vapor predominantly affects a capacitance change of part (b): a series capacitance of water vapor and a dielectric Ta_2O_5 film are significantly associated with the change of the capacitance at part (b).

Consequently, in the atmosphere of absolutely dry, i.e. 0% RH, only the manganese oxide layer of part (a) plays a role of a counter electrode of the dielectric tantalum oxide layer. With increasing relative humidity, water vapor intruded and reached the surface of the tantalum oxide of part (b) and the water plays roles described above, resulting in a humidity response of the capacitance of the element.

3.3 Reliability and application of the Ta_2O_5 - MnO_2 element to capacitive humidity sensor

As described in the previous sections, the element with a Ta - Ta_2O_5 - MnO_2 structure shows several features in high humidity response. The

Fig. 9 Life test of the element at room temperature.

Fig. 10 Field test of the element in a polluted atmosphere.

characteristics of the element meet with demands for a capacitive humidity sensor.

In addition to the humidity response, the element has high reliability for a practical use. A capacitance change during the life test in

ordinary atmosphere at room temperature is shown in Fig. 9: the capacitance of the element shows stable behavior up to 8000 h.

Figure 10 shows a capacitance change of the element during the life test in polluted atmosphere: the capacitance of the element shows about 8% decrease against the initial value in the field life test with filters of activated carbon fiber sheets in 8000 h. Exhaust gas and particles of dust in the atmosphere were trapped in the filter and harmful substances did not reach to the humidity sensing surface of the element.

Figure 11 shows a temperature dependence of electric output change ($\Delta RH\%$) caused by the capacitance drift after 200 and 2000 h. The element shows a stable behavior in the temperature range up to 70°C; the capacitance change of the element in 2000 h at 70°C resulted in 7% RH of the electric output change.

Two examples of unique applications of the element are proposed to humidity sensing apparatus, i.e. a humidity ON-OFF switch and a digital thermo-hygrometer. Figure 12 shows the example of the application, i.e. an electric circuit for humidity switch with the element. In the circuit, a capacitance change of the element was

Fig. 11 Relationship between a capacitance drift of the element and temperatures of the atmosphere.

Fig. 12 Capacitance detection circuit for humidity sensing.

detected by measuring a charging time at dc step voltage application. ON-OFF signal can be obtained for an air-control unit, a plain paper copier, etc. Figure 13 shows the other example of the application, i.e. a digital thermo-hygrometer. The circuit consisted of sensing elements, RH-pulse width converter, temp.-pulse width converter, temp.-compensator, oscillator, divider, counter, latch, decoder, and display unit. The element was charged and the pulse width which depended proportionally on the relative humidity change was digitized with the oscillator. The digital output of the relative humidity of an atmosphere is readily obtained with the element and the electric circuit, which can be applied for a thermo-hygrometer in many fields.

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Fig. 13 Block diagram of the digital thermo-hygrometer with the capacitive humidity sensing element.

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