Effect of Addition of Graphite on Humidity-Sensing Property of Heat-Treated Silicone Film

Fusaoki UCHIKAWA* and Kozo SHIMAMOTO*

1 Introduction

Currently, a number of humidity-sensitive elements¹⁻³⁾ based on the protonic and other ionic conduction have been developed. It is important to consider the sensitivity and the level of electrical resistance for the development of those elements. However, it is most important to produce the elements with long term stability.

The authors^{4,5)} have investigated a heat-treated mixture of silicone polymer and inorganic materials as a humidity-sensitive element. We have found that the change in surface conduction could be reduced by means of an addition of graphite with the above-mentioned mixture⁶⁾.

In this experiment, the humidity-sensitive film was prepared using a silicone polymer, SiO₂ and graphite. The change of the humidity-sensing characteristic with time was examined with different addition ratios of graphite. The cause of stability in humidity-sensing property is discussed.

2 Experimental

The humidity-sensitive films were prepared by use of the method already reported^{4,5)}. Graphite powder (Wako Chemical) was mixed with the mixture of methylphenyl silicone polymer (varnish produced by Shin-etsu Chemical) and silica gel powder with various addition ratios (samples G₅: 5 w_i, %, G₁₀: 10 w_i, %, G₂₀: 20 w_i, %, G₃₀: 30 w_i, %, G₄₀: 40 w_i, %). A small quantity of talc particles was added to the mixture to improve the bonding performance to the substrate⁴⁾. Comb-shaped electrodes (0.2 mm in distance, 12 pairs) were formed on an α -alumina substrate using RuO₂ paste. A coating layer was formed by dipping this substrate into the above-mentioned mixture. After drying at

120°C for 20 minutes, the humidity-sensitive films ($\sim 15 \mu\text{m}$) were produced by heat treatment at 600°C for 1 h. In the heat treatment, 90% of the weight of organic groups in silicone polymer was decomposed and gasified⁶⁾. Approximately 70% of the weight of added graphite in each sample was oxidized and disappeared⁶⁾.

The humidity-sensing characteristic (relative humidity vs. impedance) was measured using a humidity generator (Ace Kenkyusho, AHC-1). Under the condition of applying an ac voltage of 1 V, an impedance of the sample was measured by means of an LCR meter (YHP, 4262 A) at 25°C. A dc voltage of 10 V was applied to the sample and the electrical conductivity was estimated in vacuum (10^{-3} Torr) using a conventional electrometer. Dropping a distilled water ($d=1.0 \text{ mm}$) on the surface of the films, the water contact angles were measured by a goniometer (Erma, G-1) at 25°C.

3 Results and Discussion

3.1 Humidity-sensing property

Figure 1 shows the effect of the addition

Fig. 1 Effect of the addition ratio of graphite on humidity-sensing characteristics of the films (G₅: 5 w_i, %, G₁₀: 10 w_i, %, G₂₀: 20 w_i, %, G₃₀: 30 w_i, %, G₄₀: 40 w_i, %)

* Materials & Electronic Devices Laboratory, Mitsubishi Electric Corp. (8-1-1 Tsukaguchi-Honmachi, Amagasaki, Hyogo, 661)

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ratio of graphite on the humidity-sensing characteristics of the films. The impedance (Z) and humidity sensitivity (slope of the curve) became low with increasing in graphite content. Sample G_{40} was not humidity-sensitive. The sensitivity of sample G_{30} was not sufficient for the practical humidity sensor. From the result already reported⁶⁾, the amount of adsorbed water of the film became lower by means of the addition of graphite. The decrease of impedance with the addition of graphite in Fig. 1 will have been caused by the electronic conduction in graphite.

Figure 2 shows the effect of the addition ratio of graphite on the impedance change ratio (Z'/Z) of the films at various humidities with exposure to laboratory air for 6 months. In all films except for sample G_{30} , the impedance change at the low humidity side was larger than that at the high humidity side. However, the impedance change decreased with increasing addition ratio of graphite. While sample G_{30} showed lowest sensitivity as shown in Fig. 1, the impedance change scarcely took place by exposure to air. Sample G_{20} is able to be used actually as the element for humidity sensor, because of the comparatively small impedance change and the high sensitivity. The increase of impedance after 6 months in Fig. 2 is believed to be caused by the increase of the surface OH concentration⁴⁾ as in the case of ceramic humidity-sensitive elements of the protonic con-

Fig. 2 Effect of the addition ratio of graphite on the impedance change ratio of the films at various humidities with exposure to air for 6 months

(Z : initial, Z' : after 6 months)

Fig. 3 Response times of adsorption and desorption for the humidity-sensitive film as a function of addition ratio of graphite (adsorption: 50→90%RH, desorption: 90→50%RH)

duction type.

Figure 3 shows the response times of adsorption (T_a : 50→90%RH) and desorption (T_d : 90→50%RH) for the humidity-sensitive films as a function of addition ratio of graphite (Gr). T_a was shorter than T_d . However, T_a and T_d became shorter and almost equal with increasing Gr . It is supposed that this tendency is due to the following reasons: The surface area of graphite powder is very small in comparison with those of silica gel and the thermal decomposition residue of silicone polymer. Accordingly, the surface area of the film would decrease with increasing Gr . The low surface free energy of graphite particles is well known. The mixed graphite would be the hydrophobic site of the absorbed water. The water repellency would be improved with increasing Gr .

3.2 Electronic conductivity and water contact angle

Figure 4 shows the electrical conductivity (σ_v) of the film in vacuum (10^{-3} Torr) as a function of Gr . σ_v apparently increased in Gr above 10 $w_i\%$. This phenomenon would be caused by the increase of the contact chance between graphite particles into the film. Accordingly, by the addition of graphite, the electronic conductivity of the film clearly increases in the condition without adsorption of water vapor. It is thought that the total conductivity of the film in the presence of adsorbed water is given by

$$\sigma = \sigma_e + \sigma_i \quad (1)$$

Fig. 4 Conductivity of the film in vacuum (10^{-3} Torr) as a function of addition ratio of graphite

where σ_e is the electronic conductivity and σ_i is the ionic one. For the conventional humidity-sensitive elements with protonic conduction, σ_e is negligibly smaller than σ_i . However, in the case of the graphite-added films, σ_e can not be negligible. As shown in Fig. 2, the impedance change in the low humidity side became small with increasing σ_e , i.e. increasing Gr. On the contrary, in the high humidity side, the ionic charge carriers would transfer into the adsorbed water films and the surface conductivity would be dominated by the content of water adsorbed. Accordingly, the impedance change of each film in the high humidity side is believed to be comparatively small.

Figure 5 shows the water contact angle (θ) on the surface of the films as a function of Gr. The film without addition of graphite, consisting of silica gel and the decomposition residue of silicone polymer, was porous and had the hydrophilic surface⁴⁾. However, θ increased with increasing Gr. This is caused by the ad-

Fig. 5 Water contact angle on the surface of the film as a function of addition ratio of graphite

ded graphite. It is well known that graphite has the low surface free energy. Generally speaking, in the element having large θ , the interaction⁷⁾ between H₂O and the surface would be small. Accordingly, it will be possible that the film is stabilized by the presence of graphite, decreasing the interaction with water vapor.

References:

- 1) Y. Sadaoka and Y. Sakai, *Denki Kagaku*, **51**, 873 (1983).
- 2) Y. Sadaoka and Y. Sakai, *Denki Kagaku*, **51**, 879 (1983).
- 3) Y. Shimizu, H. Arai and T. Seiyama, *Denki Kagaku*, **50**, 831 (1982).
- 4) F. Uchikawa, K. Miyao, K. Shimamoto and K. Nakanishi, *Am. Ceram. Soc. Bull.*, **63**, 1043 (1984).
- 5) F. Uchikawa, K. Miyao, H. Horii and K. Shimamoto, *Denki Kagaku*, **51**, 890 (1983).
- 6) F. Uchikawa and K. Shimamoto, to be published in *Am. Ceram. Soc. Bull.*
- 7) S. S. Barton and J. E. Koresch, *J. Chem. Soc., Faraday Trans.*, **79**, 1147 (1983).

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