THE EFFECT OF VARIOUS FACTORS ON THE RESISTANCE AND TCR OF RuO₂ THICK FILM RESISTORS — RELATION BETWEEN THE ELECTRICAL PROPERTIES AND PARTICLE SIZE OF CONSTITUENTS, THE PHYSICAL PROPERTIES OF GLASS AND FIRING TEMPERATURE

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Thick film resistors were prepared with different variables, they included various conductive particle sizes, glass particle sizes, glass softening temperatures, thermal expansion coefficients of the glass, mixing ratios of the conductive element and glass, firing temperatures, firing cycles, etc. The relation between these factors and electrical properties of the thick film resistors was studied. As a result, it was found that when a specific glass is chosen, its R-TCR curve, which indicates the relation between resistance and TCR of a thick film resistor, is unconditionally fixed regardless of various preparation factors, and the R-TCR curve can be moved only by changing the thermal expansion coefficient of the glass. In addition, the higher the resistance and the larger the thermal expansion coefficient of glass, the larger the resistance change against the external force.

INTRODUCTION

Thick film resistors have been widely used as circuit elements in hybrid IC's. Few basic studies have been carried when compared with studies concerning their practical use. Up to now, the important reports concerning the basic studies of thick film resistors include those that deal with the relation between microstructure and electrical properties of resistors and particle sizes of the glass and RuO₂¹, conduction mechanism^{2,3}, temperature characteristics of the resistor⁴,

effects of adding materials⁵, difference in thermal expansion coefficient between resistor and substrate⁶, etc. However, it seems that there is no study which has investigated the relation between electrical properties and factors such as particle size of the conductive material, glass particle size, and preparation condition. In this paper we present the experimental results of our investigation in order to clarify the relation between these factors and the electrical properties of thick film resistors.

SPECIMENS

RuO₂ powder, with an average particle size of 0.15 μm , or 0.35 μm and glass powder, having various thermal expansion coefficients, as shown in Table I, were used as resistor components. These RuO₂ and glass powders were blended with various mixing ratios, ranging from 5/95 to 33/67. The mixtures were uniformly dispersed into the organic vehicles to obtain screen printable pastes. These pastes were printed on a 96% alumina substrate with prefired Pd/Ag conductors. After printing, dried specimens were fired at between 600 and 900°C, as shown in Table I, for 10 minutes. In these cases, a differential thermal analysis was conducted for each glass, and the firing temperature at which the glass viscosity, η , became $\log \eta = 4.0$ was selected for the standard value. The geometry of the resistor was 2 mm $\times$ 2 mm $\times$ 12 μm .

RESULTS AND DISCUSSION

The change in resistance and TCR as a function of RuO₂ concentration was studied. The obtained results are shown in Figure 1. When the RuO₂ concentration was less than a few volume percent, the electrical conduction was controlled by the reactive layers created on the surface of the glass particles by the reaction between RuO₂ and glass rather than mutual contact of the RuO₂ particles⁷. Therefore, the RuO₂ concentration dependence of resistance is large while the change in TCR is small. On the other hand, when the RuO₂ concentration was approximately 20 vol. % or more, the electrical current was conducted by the path which was formed by mutual contact between RuO₂ particles⁸.

TABLE I
Physical and electrical properties of glass

Glass	Coefficient of thermal expansion ($\times 10^{-7}/^{\circ}\text{C}$)	Softening temperature ($^{\circ}\text{C}$)	Firing temperature ($^{\circ}\text{C}$)	Volume resistivity ($\Omega\text{ cm}$)	Main components
A	40	690	850	$\sim 10^{15}$	PbO, SiO ₂
B	45	475	730	$\sim 10^{16}$	PbO, SiO ₂ , B ₂ O ₃
C	50	600	850	$\sim 10^{16}$	PbO, SiO ₂ , B ₂ O ₃
D	59	695	850	$\sim 10^{15}$	PbO, SiO ₂ , CaO
E	69	470	700	$\sim 10^{16}$	PbO, B ₂ O ₃ , ZnO
F	73	500	630	$\sim 10^{14}$	PbO, SiO ₂ , B ₂ O ₃
G	86	445	600	$\sim 10^{13}$	PbO, B ₂ O ₃ , ZnO
H	95	400	650	$\sim 10^{13}$	PbO, SiO ₂ , B ₂ O ₃
I	99	400	750	$\sim 10^{15}$	PbO, B ₂ O ₃ , ZnO
J	108	480	730	$\sim 10^{14}$	PbO, SiO ₂ , ZnO
K	111	450	700	$\sim 10^{15}$	PbO, SiO ₂ , B ₂ O ₃
L	50	510	650	$\sim 10^{16}$	PbO, SiO ₂ , B ₂ O ₃
M	50	670	900	$\sim 10^{16}$	PbO, SiO ₂ , B ₂ O ₃
N	63	560	750	$\sim 10^{15}$	PbO, SiO ₂ , B ₂ O ₃ **
P	63	575	780	$\sim 10^{15}$	PbO, SiO ₂ , B ₂ O ₃
Q	63	590	800	$\sim 10^{15}$	PbO, SiO ₂ , B ₂ O ₃

* : Different thermal expansion coefficient

** : Different softening temperature

FIGURE 1 Sheet resistance versus TCR. Using glass C, RuO₂ concentration and diameter are changed.

Therefore, the resistance hardly changed even though the RuO₂ concentration changed, and the TCR of a resistor have a tendency to move to that of RuO₂. In Figure 1 the resistance and TCR dependence on the RuO₂ diameter is also shown. In the high resistance region, the resistor prepared using larger RuO₂ particles shows a tendency to have a higher resistance even in the case with the same RuO₂ concentration. However, in the low resistance region, the diameter of the RuO₂ hardly influenced the resistance. (Hereafter, we call the curve R-TCR curve, which indicates the relation between resistance and TCR of thick film resistor.)

Figure 2 shows the relation between glass particle size and firing temperature and electrical properties. In the case of resistors made by the same mask screen, the larger particle size of glass, the higher the RuO₂ concentration distributed along each glass particles, and the lower the resistance. There is almost no difference in resistance and TCR between the specimen whose RuO₂/glass composition is 25/75 and firing temperature is 900°C and the specimen, 15/85 and

FIGURE 2 Sheet resistance versus TCR. (a) Glass particle size is 1 μm , (b) 2 μm , (c) 3 μm .

(c)

FIGURE 2 continued

700°C; also 7/93, 850°C and 4/96, 750°C. These specimens seem to differ somewhat in microstructure, especially the RuO₂ concentration of the conductive path, and the difference must affect the electrical properties. The reason why such a difference is not observed is the focus of our investigation.

When the mixing ratio of RuO₂/glass is high, the resistance is small and TCR has a positive value. As the mixing ratio is reduced, the resistance increases and TCR moves to the negative direction. When the mixing ratio is high, the firing temperature affects the TCR change rather than the resistance change, and when the ratio is low, the inverse relation is observed.

According to the decrease in the RuO₂/glass ratio or increase in firing temperature, the point which indicates the relation between resistance and TCR shifts in the high resistance direction along the R-TCR curve shown in Figure 1.

The relations between firing temperature and the resistance and the TCR are shown in Figure 3. From the firing temperature of 400°C to the softening point of each glass, the resistance decreased and the TCR suddenly increased from a negative value to a positive value

(a)

(b)

FIGURE 3 (a) Firing temperature dependence of sheet resistance. (b) Firing temperature dependence of TCR. (c) Sheet resistance versus TCR.

(c)

FIGURE 3 continued

with increasing firing temperature. The resistor that contained lower viscosity glass had a minimum (or maximum) point at lower temperature in the firing temperature-resistance (or temperature-TCR) curve. The R-TCR curve obtained by this experiment is shown in Figure 3(c), which is almost the same form as seen in Figure 2. When the glass content is decreased, the heat capacity of the resistor decreased and the minimum of resistance with a maximum TCR appeared at the higher firing temperature. These tendencies became more conspicuous with increasing glass viscosity. However, the maximum or minimum in the curve are all at approximately the same temperature. At each temperature in which a maximum or minimum appeared, glass flow did not occur. Therefore, the glass particles are not joined mutually and the microstructure of the resistors are all of same state independent of the glass viscosity.

From the previously mentioned electrical properties, a glass seems to behave in the resistor as follows: the lower the viscosity of the glass, the tiny glass particles which are smaller than average size soften at a lower temperature. The large glass particles are then joined by the tiny particles. The surface area of the glass particles in

the resistor decreased and the RuO₂ content distributed on each glass particle increased with the RuO₂ particles mutually joining. As a result, the resistance decreased and the TCR shifted to the metallic value of RuO₂ (TCR of RuO₂ sintered film and single crystal of RuO₂ are about 3600 ppm/°C and 7000 ppm/°C, respectively²).

However, with increasing firing temperature, the resistance increase and the TCR moves the negative direction. This change seems to be attributed to the glass opening a gap in the RuO₂ particles of the chain path built up by the RuO₂ particles. The lower viscosity glass can easily flow into the gap of RuO₂ particles and form a glass layer between the RuO₂ particles. As a result, the resistor containing lower viscosity glass has a higher resistance at the same firing temperature.

If the glass layer is formed, the resistor should have high resistance. However, in our experiment, an extreme increase in resistance could not be detected. This phenomenon occurred due to the creation of a reactive layer⁷, which shows semiconductive characteristics and was formed by the reaction between the RuO₂ and the glass.

As the firing temperature is raised, the glass between the RuO₂ particles flowed out of the RuO₂ particle drain. The TCR thus showed metallic characteristics because of the mutual re-contact of the RuO₂ particles.

Figure 4 shows the relation between resistance and TCR and firing cycle. The resistance was measured at the AD region for the whole resistance, at the AB or CD region for interaction between conductor and resistor and at the BC region to avoid any influence of the conductors. Applying a constant current to the AD region, the resistance was calculated by measuring the voltage between the probes.

The relation between resistance or TCR of each region and firing cycle is shown in Figures 4(b) and (c). Since the thermal expansion coefficient of commercially available 96% alumina substrate, α_{sub} , is $70 \sim 74 \times 10^{-7}/^{\circ}\text{C}$, the α_{glass} of glass F is nearly equal to that of the alumina substrate. Since the α_{glass} of glass J is larger than that of substrate⁶, the resistor will be under a tensile force from the substrate⁶. By refiring, the state of force-force free is repeated, and generation of microcracks or destruction of the conductive path occurs, then the resistance and TCR changes. However, in the case of the glass C resistor, whose α_{film} ($\alpha_{\text{film}} \cong \alpha_{\text{glass}}$) is smaller than α_{sub} of substrate, a compression acts on the resistor from the substrate⁶,

FIGURE 4 (a) Measuring method and points. Applying a constant current to the AD region, the resistance was calculated by measuring voltage of each region. This figure is a case of BC region measurement. (b) Firing cycle versus resistance change. (c) Firing cycle versus TCR. (d) Sheet resistance versus TCR.

(c)

(d)

resulting in no cracks or destruction of the conductive path. Therefore, the resistance and TCR scarcely change.

The resistance change and TCR change of the AB or CD region, resistor-conductor interface, are smaller than those of the region, in which the conductor has no influence. This result is due to Ag diffusion from the conductor to the resistor⁹. Since the resistance change of the resistor-conductor interface is small, the resistance of the AD region has a smaller value than the BC region, (pure resistor part). The forms in R-TCR curves are not the same as each other due to the difference of the thermal expansion coefficient of each glass. However, as shown in Figure 4(d), the electrical properties change along the R-TCR curve similarly to that given by other preparation factors.

Figure 5 shows the relation between α_{glass} of glass and the electrical properties of the resistor. In the case of $\alpha_{\text{glass}} < \alpha_{\text{sub}} (\cong \alpha_{\text{glassF}})$, increasing the difference between α_{glass} and α_{sub} , the TCR moves in a positive direction, and the R-TCR curve saturate quickly. On the other hand, for the case of $\alpha_{\text{glass}} > \alpha_{\text{sub}}$, the reverse phenomena

FIGURE 5 R-TCR curve dependence on thermal expansion coefficient of glass.

occurred. As seen in Table I, saturation of the R-TCR curve does not depend on the glass resistivity but the difference in thermal expansion coefficients between substrate and glass.

The electrical resistance of thick film resistors changes by applying an external force. Accordingly, the influence upon the strain characteristics by the preparation condition or physical properties of the glass was examined. The sample was deflected by using the three point bending method shown in Figure 6. When a thick film resistor has an applied external force, the relation between the applied strain F , and resistance change, dR/R , is as follows¹⁰:

$$dR/R = \epsilon F$$

The proportionality constant, ϵ , is called the gauge factor and is a characterization factor for the strain characteristics of thick film resistors.

Figure 7(a) shows the firing temperature dependence of ϵ . As seen in this figure, ϵ has a large value when a high resistive resistor is fired at a high temperature. Figure 7(b) and (c) shows the variation between resistance or TCR and ϵ . The ϵ becomes larger if a glass with a large thermal expansion coefficient is used.

The resistance change by an external force is due to microstructure change in the conductive path formed by RuO_2 particles. In a low resistive resistor, in which many conductive particles are contained,

FIGURE 6 Three point bending method.

(a)

(b)

FIGURE 7 (a) Firing temperature versus gauge factor. (b) Sheet resistance versus gauge factor. (c) TCR versus gauge factor.

(c)

conductive RuO₂ particles exhibit a buffer effect against external forces, and weaken the tension or compression. As a result, the resistance change is small. However, in the case of a highly resistive resistor, whose conductive path has a low RuO₂ concentration, a change of contact state between conductive particles gives rise to an immediate resistance change.

CONCLUSION

Thick film resistors were prepared with different variables, they included various conductive particle sizes, glass particle sizes, glass softening temperatures, thermal expansion coefficients of the glass, mixing ratios of the conductive element and glass, firing temperatures, firing cycles, etc. The relation between these factors and electrical properties of the thick film resistors was studied. As a result, the following facts have been determined.

- (1) When a specific glass is chosen, its R-TCR curve, which

indicates the relation between resistance and TCR of a thick film resistor, is unconditionally fixed regardless of the various preparation factors.

(2) The points which indicate the relation between the resistance and TCR shifts to a higher resistance along the R-TCR curve when the firing temperature rises, the RuO_2 particle size increases, glass particle size decreases, the softening temperature of glass decreases or the RuO_2 /glass mixing ratio increases.

(3) As the firing temperature rises, the TCR shifts from a positive to negative value.

(4) When the firing temperature is near the softening temperature of the glass, the resistor has a minimum (maximum) value for resistance (TCR). The minimum (maximum) values are equal and independent of glass viscosity if the RuO_2 /glass ratio is fixed.

(5) The lower the viscosity of the glass, the higher the resistance at a particular firing temperature.

(6) The R-TCR curve can be moved by changing the thermal expansion coefficient of the glass. When the thermal expansion coefficient is increased, the TCR moves to negative direction.

(7) The higher the resistance and the larger the thermal expansion coefficient of glass, the larger the resistance change against the external force.

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