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CONTROL OF ELECTRICAL PROPERTIES OF RuO_2 THICK FILM RESISTORS

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Oxides of various elements have been added to RuO_2 thick film resistors and the electrical properties of the resultant resistors have been examined.

It is found that almost all the oxides of transition metals, rare earths, and antimony used as additivies can closely control the resistivity and TCR of the resistors to obtain a required value. In addition, it is found that the principle of superposition applies to the additives.

Key words: Thick-film resistors, hybrids, ruthenium-dioxide

1. INTRODUCTION

RuO_2-based thick film resistors are widely used to fabricate hybrid integrated circuits. The electrical properties of these resistors vary, depending on blend ratio of RuO_2 to glass, particle sizes of RuO_2 and the glass powder, and the glass composition.[1,2] In general, the RuO_2 based thick film resistors with low glass content exhibit low surface resistivity and high positive temperature coefficient of resistance (TCR) while resistors with high glass content have high surface resistivity with large negative TCR.[3]

Therefore, to make resistors with TCR close to zero, various elements can be added to the RuO_2/glass composition. It is important to know what kinds of elements should be added and how the electrical properties of resistors are affected by such elements. However, little has been published about such effects.[4,5]

This paper deals with an experimental study of the adding effects of oxides of various elements to RuO_2 thick film resistors.

2. SPECIMENS AND MEASUREMENTS

The inorganic content of the specimens consisted of RuO_2 powder with an average particle size of 370 and lead borosilicate glass of $52PbO:35SiO_2:10B_2O_3:3Al_2O_3$ with an average particle size of 1.2 μm and a softening point of 600°C. These RuO_2 and glass powders were blended in various ratios; then various oxides were added from zero through four weight percents. The resultant mixtures were formulated to give screen-printable thick film pastes by dispersing in vehicles consisting of resin and solvents. These pastes were printed on 96% alumina substrate with pre-fired Au/Pt terminations, dried and fired at 700 through 900°C for 8 minutes. The geometry of the resistor was 2 mm × 4 mm × 12 μm.

Surface resistivity (hereafter just referred to as resistivity), ρ_S, was measured by standard techniques. The TCR was measured by measuring the change of resistance

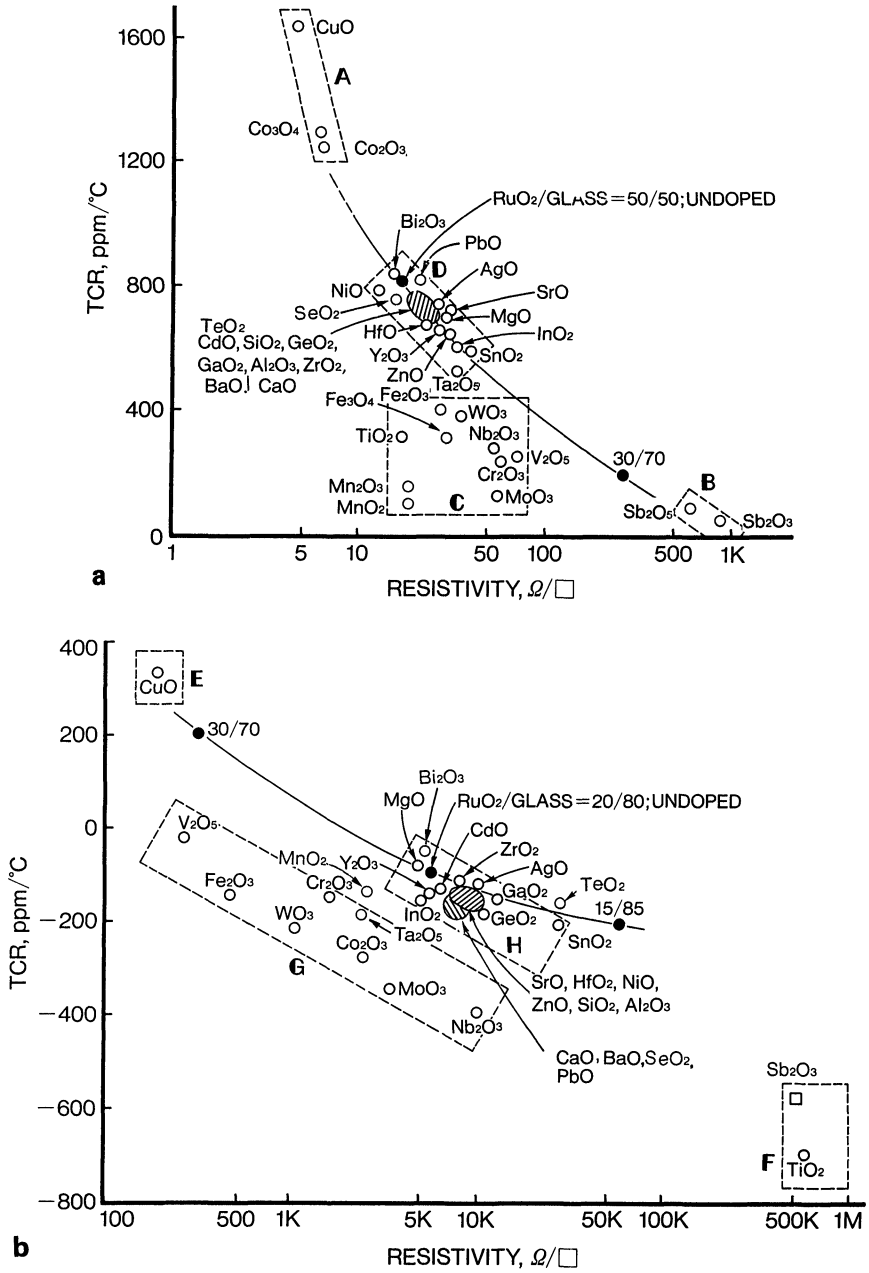


FIGURE 1 Resistivity versus TCR. Specimens were fired at 850°C. (a) 4wt% oxides were added to RuO_2/glass=50/50. (b) 2wt% oxides were added to the RuO_2/glass=20/80. (□; Sb_2O_3 at 0.5wt%.).

over two temperature intervals - 'hot TCR' between +25°C and + 125°C, and the 'cold TCR' between −55°C and +25°C.

TABLE I
Additives used relative to the periodic table of the elements.

Group	I_A	II_A	III_A	IV_A	V_A	VI_A	VII_A				I_B	II_B	III_B	IV_B	V_B	VI_B	VII_B	VIII_A
Period	H																	He
1	1																	2
2	Li	Be											B	C	N	O	F	Ne
	3	4											5	6	7	8	9	10
3	Na	Mg						VIII_B					Al	Si	P	S	Cl	Ar
	11	12							X		X		13	14	15	16	17	18
4	K	Ca	Sc	Ti	V	Cr	Mn	Fe	Co	Ni	Cu	Zn	Ga	Ge	As	Se	Br	Kr
	19	20	21	22	23	24	25	26	27	28	29	30	31	32	33	34	35	36
5	Rb	Sr	Y	Zr	Nb	Mo	Tc	Ru	Rh	Pd	Ag	Cd	In	Sn	Sb	Te	I	Xe
	37	38	39	40	41	42	43	44	45	46	47	48	49	50	51	52	53	54
6	Cs	Ba	*	Hf	Ta	W	Re	Os	Ir	Pt	Au	Hg	Tl	Pb	Bi	Po	At	Rn
	55	56	57–71	72	73	74	75	76	77	78	79	80	81	82	83	84	85	86
7	Fr	Ra	Actinides															
	87	88	89–103															
				La'	Ce	Pr'	Nd'	Pm	Sm'	Eu	Gd'	Tb	Dy	Ho	Er	Tm	Yb	Lu
	* Lanthanides			57	58	59	60	61	62	63	64	65	66	67	68	69	70	71

X: Groups A and E, □: Groups B and F, △: Groups C and G, ○: Groups D and H, □' and △': Groups J and K

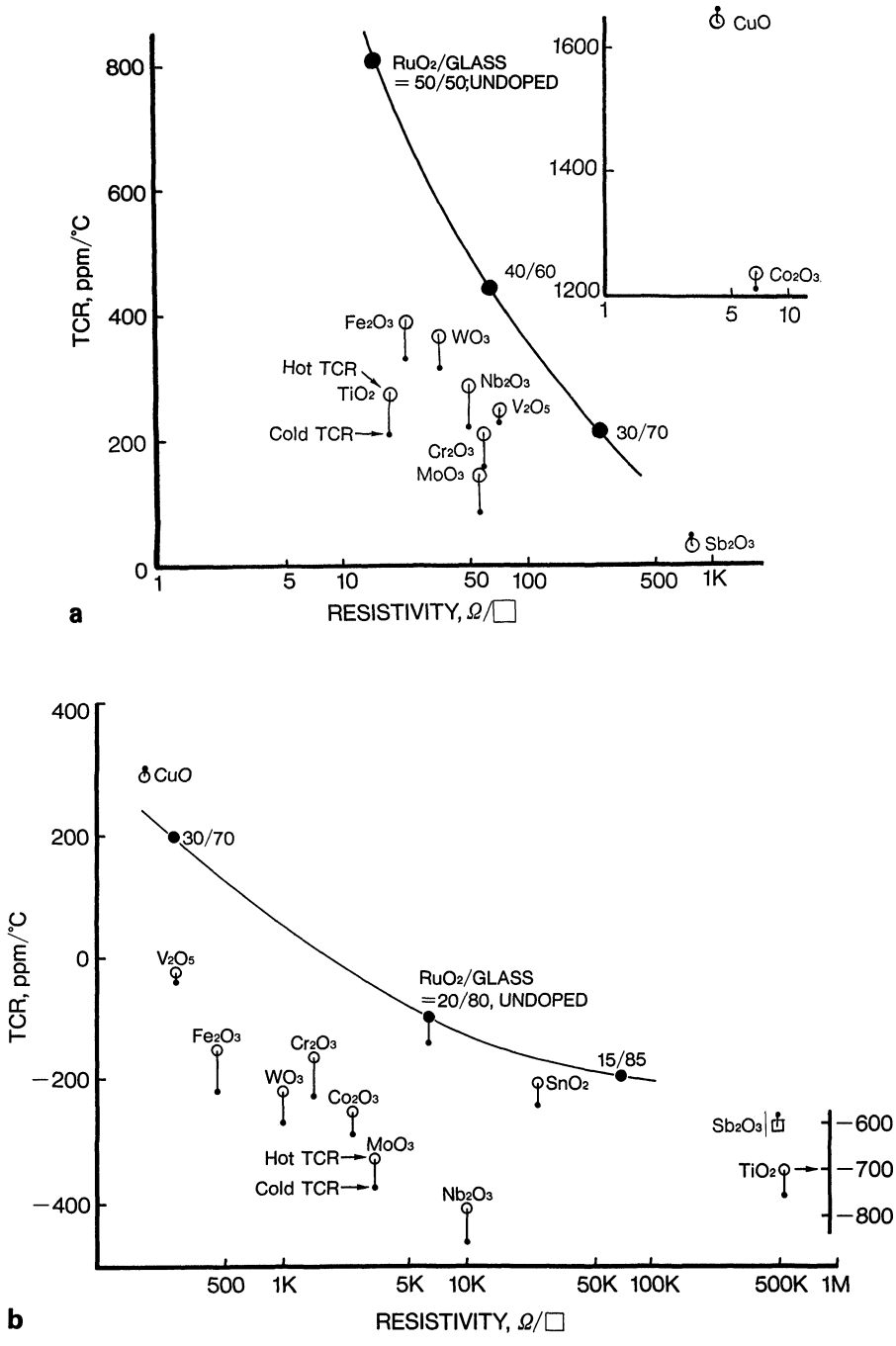


FIGURE 2 Resistivity versus hot and cold TCR. Specimens were fired at 850°C. (a) 4wt% oxides were added to RuO_2/glass=50/50. (b) 2wt% oxides were added to RuO_2/glass=20/80. (□; Sb_2O_3 added at 0.5wt%.).

3. RESULTS AND DISCUSSION

3.1 Effects of Additives

Two and four weight percent of various additives were added to resistors with RuO_2/glass ratio 50/50 and 20/80, and resistivity change and TCR were measured. The results are shown in Figure 1(a) (RuO_2/glass=50/50) and (b) (20/80). The solid lines in these figures are resistivity vs. TCR plots for undoped resistors with various RuO_2/glass ratio. The resistors with lanthanum oxide additivies were found to exhibit unique changes (see Figures 3 and 4).

It was found that the additivies could be divided according to their effects into four groups A, B, C, and D in Figure 1(a) and also four groups E, F, G, and H in Figure 1(b). The effects of the additives are more prominent in resistors with high glass content than in those having low glass content. The dopeing effects are as follows:

1) Additivies belonging to groups A and E reduce resistivity substantially and shift the TCR greatly in the positive direction.

2) Additives belonging to groups B and F increase resistivity substantially and shift the TCR in the negative direction.

3) Additives belonging to groups C and G have little effect on resistivity but shift the TCR in the negative direction.

4) Additives belonging to groups D and H have little effect on resistivity or the TCR.

As seen in the figures, in the case of resistors having low resistivity, Ti and Mn can decrease the TCR without causing any accompanying resistivity change. For resistors having a high resistivity, Mo can decrease the TCR substantially.

Table I shows the elements in the periodic table whose oxides have been used as additives; these will be discussed in relationship to the figures as a whole:-

1) Elements belonging to Groups II_A and $_B$, III_A and $_B$, IV_A and $_B$ (without Ti), and VI_B have oxides that have no effect on resistivity and the TCR of the resistors.

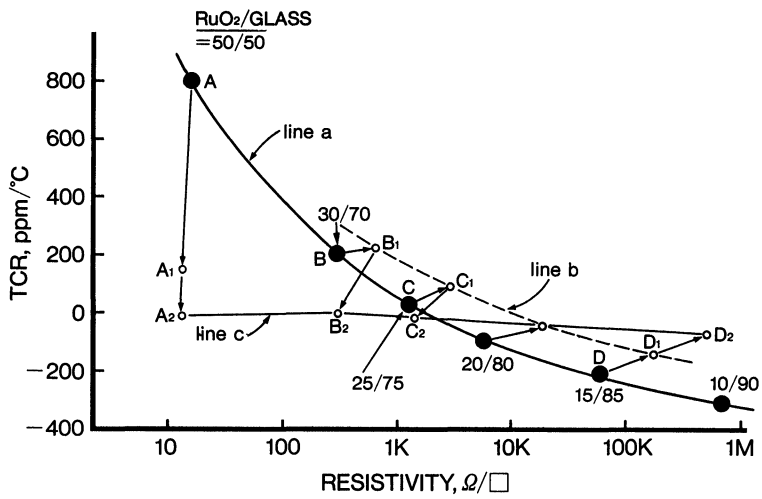


FIGURE 3 Relation between resistivity and TCR for specimens with added lanthanum oxides. 2wt% oxides were added to RuO/glass=15/85. Specimens were fired at 850°C.

2) Oxides of almost all the transition metals and rare earth elements can decrease the TCR with little resisitivity change.

3) Cu and Sb have the reverse effect to (2) on the electrical properties of the resistors.

As only 'hot TCR' are indicated in Figure 1, both hot and cold TCR values were measured for resistors with additives which had a large effect on resistivity. The results are shown in Figure 2.

Specimens doped with additives of group G (except vanadium) show resistivity changes that are relatively large and have larger differences between hot and cold TCR values. However, cold TCR values of the resistors with Sb oxide and Cu oxide additives tend to be a little higher than the hot TCR value and are more positive.

Figure 3 shows the relation between resistivity and TCR when lanthanide oxides are added. Resistivity changes and the difference between hot and cold TCR values are more prominent in some resistors with lanthanide oxides than the values seen in undoped and the other additive-doped resistors. The relation between the ionic radii of the lanthanide additives and the resistivity of resistors with added lanthanide oxides are illustrated in Figure 4. La, Pr, and Nd raise the resistivity almost ten times as much as that of undoped resistors even by adding these elements in only two weight percent. In the case of resistors with La_2O_3 additive, resistivity changes considerably while the difference between hot and cold TCR is relatively small compared with those of undoped resistors Ce and Dy oxide additives reduce the resistivity, although the effect is limited. As to the extent of resistivity changes caused by additives with atomic numbers from La to Gd, it would appear that the smaller the ionic radius, (i.e. the larger the atomic number), the smaller the resistivity changes become, though there are some exceptions. However, the effects of Ce, Pr and Tb having both trivalence and quadrivalence are different from those of the lanthanide group element which has only trivalence.

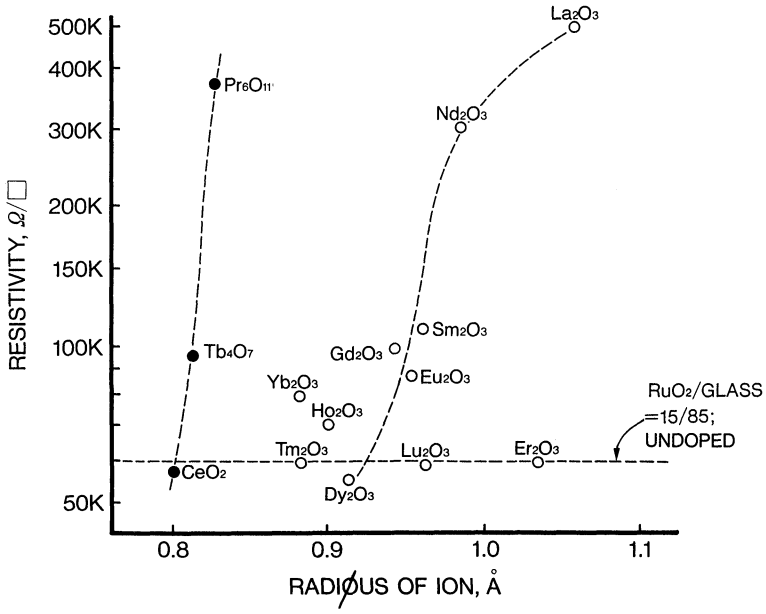


FIGURE 4 Radius of ion vs resistivity for lanthanide additives. 2wt% lanthanide oxides were added to RuO_2/glass=15/85. Specimens were fired at 850°C

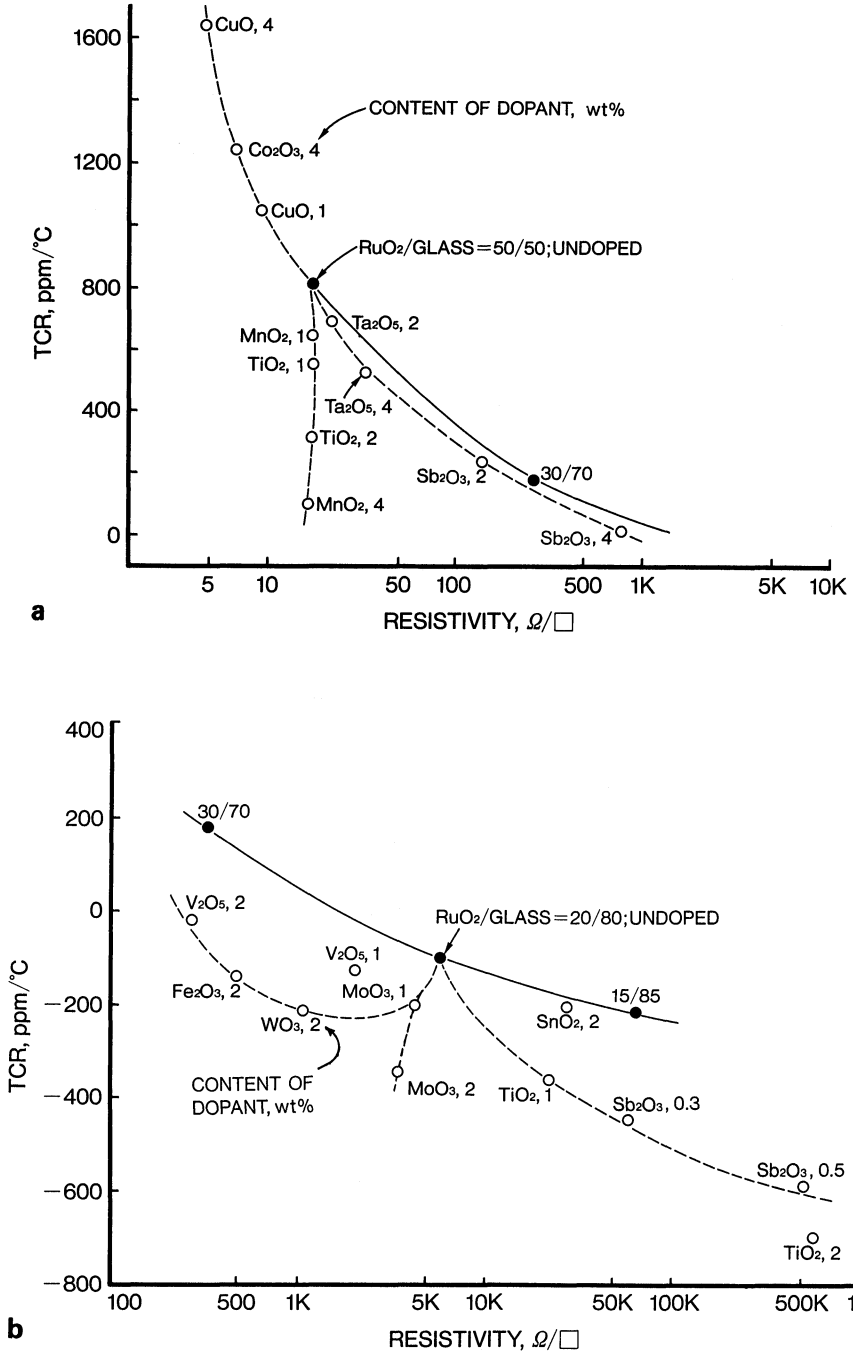


FIGURE 5 The effects of additives on specimens fired at 850°C. (The number indicates the % amounts of additives). (a) shows RuO_2/glass=50/50 value; (b = shows RuO_2/glass=20/80 value.).

3.2 *Dependence on Preparation Conditions*

The dependence of the amount of the addition and the firing condtions on RuO_2 thick film resistors were studied. Oxides of some transition metals and Sb oxide were found to substantially change the electrical properties compared with other additives, and to cause a peculiar change of the properties.

Figures 5 (a) and (b) indicate the dependence of the electrical properties (ρ_S, TCR) on the quantity of the additives. When the quantity of additives was changed, change of the electrical properties shared almost the same trend as the resistivity vs. TCR curves for undoped resistors. However oxides of Mn, Ti, and Mo behaved differently.

Oxides of Ti, Sb, Cu and La also have unique effects as seen in Figures 5 (a) and (b). Therefore, it was decided to examine in detail how resistivity and the TCR of the resistors changed due to changing the quantities of additives and the firing temperature. The results are shown in Figure 6. The effects of these oxides are summarized below:

1) Cu oxide can be used as a dopant that decreases the resistivity and shifts the TCR in the negative direction.

2) Sb and Ti oxides are dopants that increase the resistivity but cause a shift of the TCR in the negative direction.

3) La oxide is a dopant that increases the resistivity with little change of the TCR.

The effects of additives were pronounced for resistors with high glass content. It may be that the reaction of additives to RuO_2 resistors is easier with glass than with the conductive element of the thick film resistor, and this reaction of additives with glass causes the change of electrical properties.

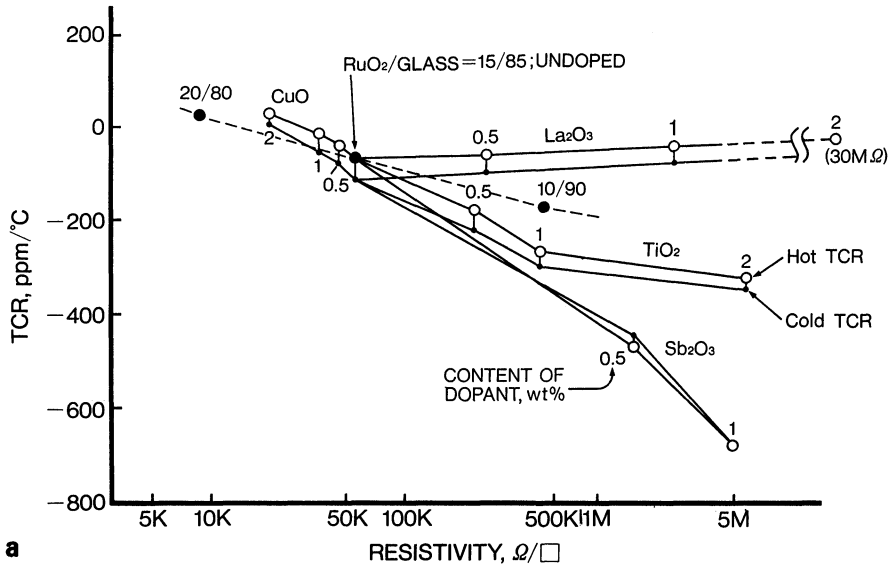
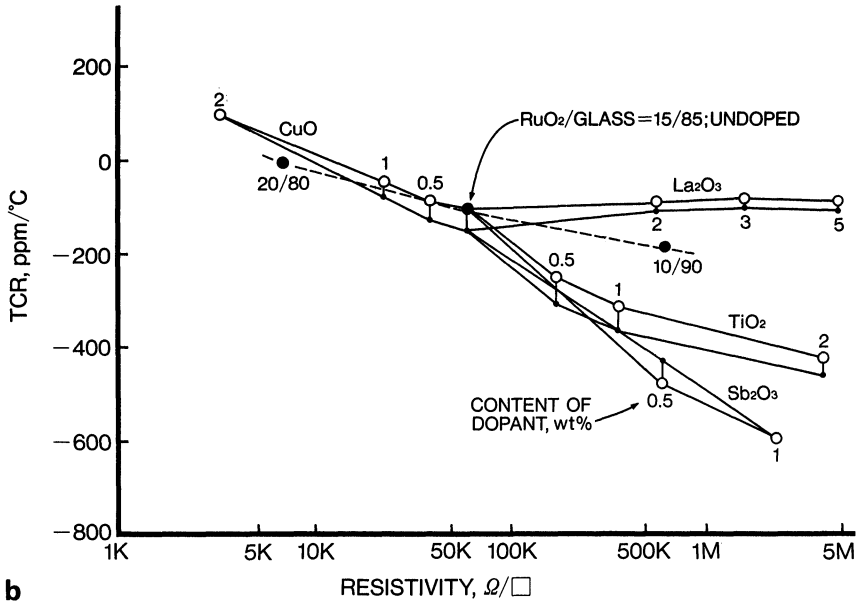


FIGURE 6A (Figure 6 b and c continued on the next page)



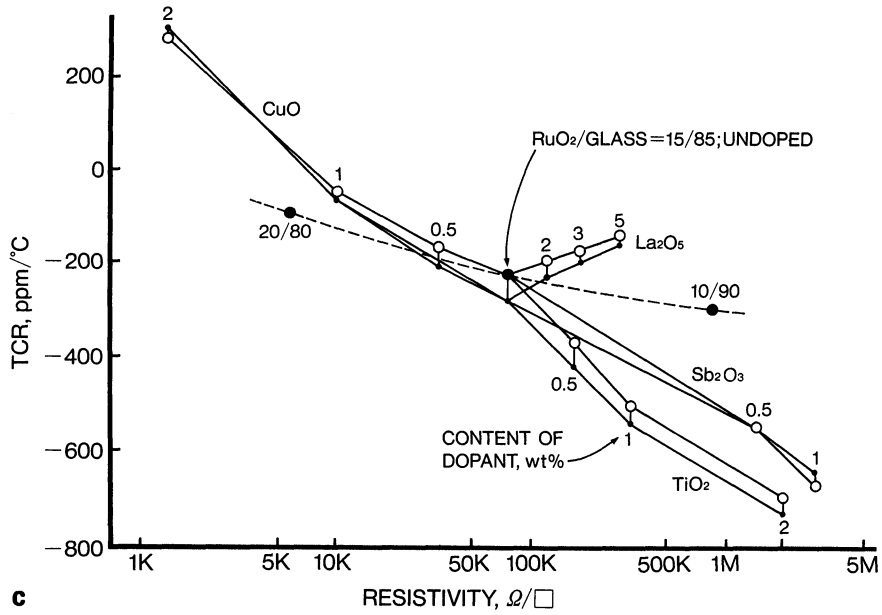


FIGURE 6 The effects of the % amounts of additives and firing temperatures on RuO_2/glass=15/85 specimens. (The number indicates the % amount of the additives.) (a) firing temperature of 700°C, (b) 800°C, (c) 900°C.

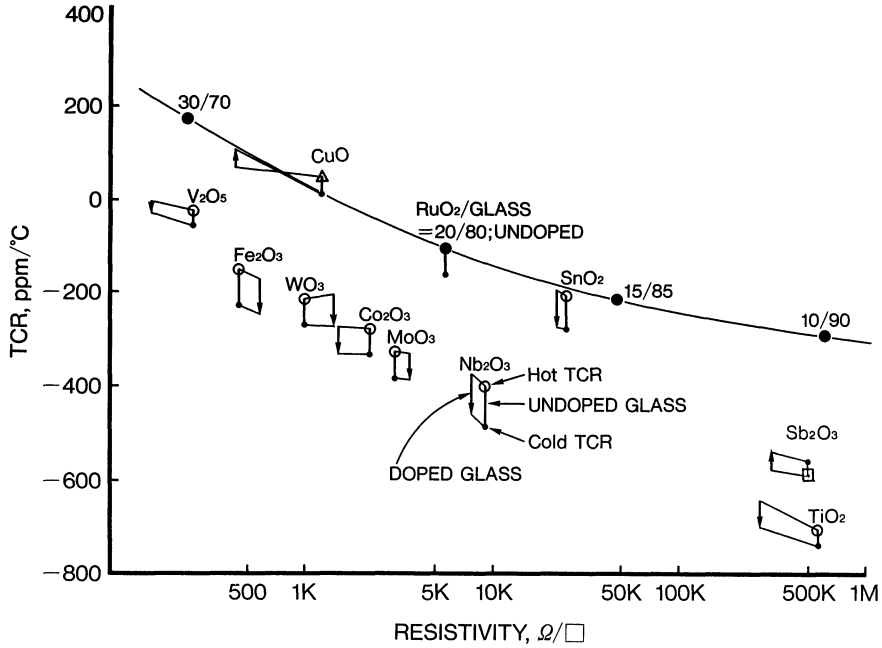


FIGURE 7 Resistivity versus TCR of resistors used doped glass and undoped glass frits. The RuO_2/glass=20/80 specimens were fird at 850°C. Arrows show resistivity and TCR of the resistors used doped glass frits. (□; 0.5%Sb_2O_3 added; △; 1 wt% CuO added.

Therefore, as one of the fundamental experiments to obtain the clue to know under what conditions additives are important in resistors, resistors were made with glass which contained additives which had been found to greatly affect the electrical properties. The electrical properties of the resistors were compared with the properties of resistors composed of RuO_2, glass frits, and additives, separately. The results are shown in Figure 7.

The effects of additives are not very different whether the additives are contained in glass before mixing with the RuO_2 or they are blended as a mixture with RuO_2 and the glass frits.

X-ray diffraction analysis was undertaken to ascertain the cause of the electrical properties of the resistors doped with oxides of certain transition metals (and Sb oxide) being so different. No new phases or ordered lattice structure were detected. However, it has been reported that by heat treatment of solid solutions, such as transition metal alloys and intermetallic compounds, after adding dopants in several weight percent, ordered lattices are formed in the solid solutions and this can explain the observed behaviour of the electrical and magnetic characteristics.[6,7] It is therefore necessary to study in detail the microstructure of the resistors under various firing temperatures and firing time. On the basis of such study, relationships between additives and the electrical properties can be analysed. Investigation in this area will be the subject of future papers.

3.3 Superposition

The effects of the interaction of additives when two or three kinds of additives are simultaneously added to RuO_2 thick film resistors have been investigated.

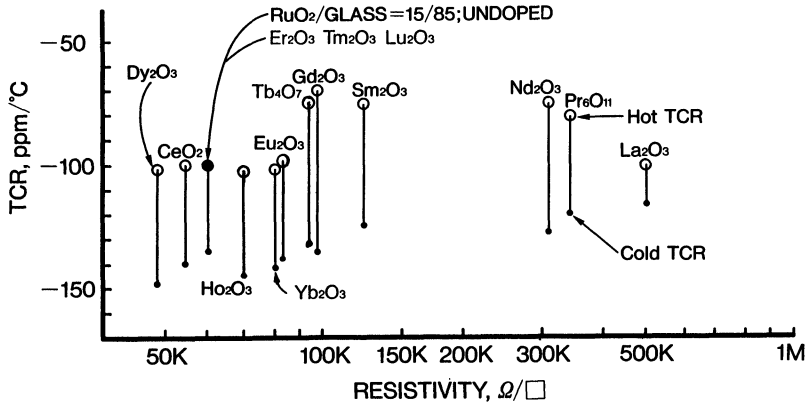


FIGURE 8 Superposition effect of additives. Specimens were first at 850°C.

Figure 8 shows the results of such experiments. Solid line (a) is that of undoped resistors. When 2wt% La_2O_3 is added to the resistors with RuO_2/glass of 30/70(B), 25/75(C), 20/80, and 15/85(D), resistor properties shift on to line (b). When 3 wt% MnO_2 is added to resistor B_1 (resistivity 850Ω, TCR 220ppm/°C), it shifts to point B_2 (400Ω, −10ppm/°C). C_1 (40kΩ, +100ppm/°C) changes to C_2 (1.5kΩ, −10ppm/°C) by adding 3wt% WO_3. D_1 (230kΩ, −80ppm/°C) changes to D_2 (805kΩ, −15ppm/°C) by adding 2wt% Pr_6O_{11}. When 4wt% MnO_2 is added to undoped resistor A (16Ω, +800ppm/°C), it shifts to A_1 (13Ω, +250ppm/°C) and with the addition of 0.5wt TiO_2 it changes to A_2 (12.5Ω, −10ppm/°C).

In summary, even if a few additives are added simultaneously to undoped resistors, the results are the same as the sum of the effect of each additive, which means the effect of superposition works between each additive .

4. CONCLUSION

Various oxides were added to RuO_2 thick film resistors and the electrical properties of the resultant resistors were examined. As a result, it has been found that each oxide caused one of four effects, grouped as below:

1) To reduce the resistivity, ρ_S, substantially and to shift the TCR considerably in the positive direction.

2) To increase the resisitivity substantially and to shift the TCR considerably in the negative direction.

3) To have little effect on resisitivity and to shift the TCR substances in the negative direction.

4) To have little effect on either resistivity or the TCR.

It has also been found that when a few kinds of additives are added simultaneously, the effects of the interaction of the additives are the sum of the effect of individual oxides and thus the principle of superposition works with additives.

By making use of these effects of additives, it is possible to manufacture RuO_2 thick film resistors having resistivity and the TCR controlled closely to the value required.

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