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Effect of Binder Glass Crystallization on Electrical Properties in RuO_2-Thick Film Resistor

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In thick film resistors, the characteristics of the frit and the reaction between glass frit and conductor material play an important role for their electrical properties In this study, various glass frits in the system of $60RO\cdot 20SiO_2\ 15B_2O_3\cdot 5Al_2O_3$(RO=PbO,ZnO,CdO; mole%)were mixed with RuO_2 and coated on 96% alumina substrate. Only the glass frit containing PbO was reacted with RuO_2 in RuO_2-thick film resistor and produced the new crystalline phase of $Pb_2Ru_2O_{6.5}$. Their electrical resistivities strongly depend on the amount of $Pb_2Ru_2O_{6.5}$ crystalline phase obtained, which varied with firing temperature. The sheet resistivities of these resistors were varied from 10^3 to 10^6 Ω/□ depending on heat treatment, and the absolute value of TCR was decreased as the heat treatment temperature increased. However, RuO_2 did not reacted with the glass frits containing ZnO nor CdO. and the resulting resistors showed very high sheet resistivities.

Key words : Thick film resistor, Glass frit, RuO_2, Temperature coefficient of resistance, Crystallization

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I. Introduction

Recently, the thick film resistor has been widely used in the field of hybrid microelectronics with the improvement of electronic products, and the studies on electrical properties have also been carried out extensively. The thick film technology is the technology of coating thick film pastes on a substrate, such as alumina, by screen printing method and firing to remove the organic vehicle and to form dense adherent films.[1] Most thick film pastes are chemically and physically designed for use on 96% alumina because of its excellent conbination of physical properties and low cost. Other substrate materials are also available, e.g., BeO, AlN, SiC and porcelain enameled steel.

By proper selection of powders and processing conditions, the thick films of resistors or dielectrics suitable for use in hybrid microelectronics can be formed. The thick film pastes are the mixture of a functional material (conductors or dielectrics) and binder glass frit in organic vehicle systems. Pd, PdO and Ag have been used as a conducting material in a thick film resistor, but oxide such as RuO_2 and $Bi_2Ru_2O_7$ becomes more popular for the conducting material because of their high electrical conductivity and chemical stability.[2]

The binder glass frit plays an important role in controlling electrical properties of a thick film resistor, and helps the sintering of conducting materials.[3] When the thick film pastes are coated and heat-treated, the liquid phase is partially formed on the surface of glass powder and surrounds the conductor particles, which promotes the sintering in the coat layer In this case, the most popular compositions of the glass frit are alumino silicate and lead borosilicate glass systems.[4] The amount of glass frit in the thick film resistor varies from several percentage to 90% depending on the electrical property required.

In addition to the characteristics of the conducting material and the glass frit, it must be considered the effect of the microstructure of the surface coat layer on the electrical property of the resistor. When the mixture of the binder glass frit with conducting material is coated and fired. conducting material may react with glass powder and produce a new crystalline phase, which can affect the electrical property of the resultant resistor.[5,6]

On the other hand, the electrical property of the thick film resistor is estimated by the measuring of temperature coefficient of resistance (TCR), which is calculated from the measured sheet resistivities at various temperatures. For most applications, it is desirable to have a small TCR and the value of the commercial products ranges from +500 ppm/°C to -500 ppm/°C. With good processing techniques and using the proper pastes, it is possible to maintain a TCR of less than ±50 ppm/°C over the temperature range of -55°C to 125°C.

In this work, several binder glasses with different compostions were prepared and their physical properties were measured. RuO_2 was chosen for the conductiong material and the sheet resistivity variation of the thick film resistor, which is related to the crystalline phase obtained after firing, was studied.

II. Experimental Procedure

1. *Glass preparation*

Table 1. Glass Compostions (mole%)

	PbO	CdO	ZnO	SiO_2	B_2O_3	Al_2O_3
P60	60			20	15	5
C60	-	60				
Z60	-		60			

Three different glass batches with the composition of $60RO-20SiO_2-15B_2O_3-5Al_2O_3$ (mol%: RO=PbO, ZnO, CdO) were obtained by mixing the reagent agent chemicals of SiO_2, H_3BO_3, Al_2O_3, PbO, $CdCO_3$ and ZnO as shown in Table 1. The well mixed glass batch was melted in a Pt-crucible at 850~1400°C depending on the glass composition for 2 hours. For the better homogeneity of the glass, the obtained glass melt was quenched and crushed on a stainless steel plate, and then remelted at the same melting condition of the first melt. The obtained glass melt was poured in a graphite mold and annealed for the physical property measurement of the bulk glass. Glass powder, to coat on alumina substrate, was prepared by quenching and grinding the glass melt to the size of less than 44 μm in an agate mortar grinder.

2. *Physical property measurement*

2.1 *Themal properties of bulk glass*

The thermal expansion coefficient and the softening point of the glass were measured by dilatometer (BAHR GERATEBAU; German) and softening point tester (Harrop SP-3A), respectively. To measure the thermal expansion, each glass sample was prepared with the size of 0.5 mm × 0.5 mm × 35 mm.

2.2 *Electrical resistivity of bulk glass*

For the electrical resistivity measurement, glass disc with 25 mm of diameter and 2 mm of thickness was prepared and each side of the disc was coated with gold by ion coater. The electrode dimension was set according to ASTM D 150-87.[9] The electrical resistivity of the bulk glass was measured by an electrometer (Keithley 617) in a small electrical furnace at the temperature range of 25~350°C.

2.3 *Temperature coefficient of resistance of thick film resistor*

The electrical property of the thick film resistor was examined by measuring of the temperature coefficient of resistance (TCR). The thick film resistor with the size of 2 cm × 2 cm was prepared by spraying the mixture of 5% RuO_2 and glass frit with various compositions on an alumina substrate, and the both edges of the resistor were coated with gold by ion coater. The sheet resistivity of the resistor was measured by an electrometer (Keithley 617) in a thermostatic oven (ANDO TO-19) at -55~145°C.

Then the sheet resistivity (ρ_s) was calculated by using the following equation,

$$\frac{\rho}{t} = \rho_s = R\frac{w}{l}$$

where R is a measured resistance; w: width, l: length and t: thickness

The hot and cold temperature coefficient of resistance (TCR) was calculated by the equations as follows;

$$\mathrm{H-TCR} = \frac{R_{145℃} - R_{25℃}}{R_{25℃}\ \Delta T} \times 10^6 \quad (\mathrm{ppm/℃})$$

$$\mathrm{C-TCR} = \frac{R_{25℃} - R_{-55℃}}{R_{25℃}\ \Delta T} \times 10^6 \quad (\mathrm{ppm/℃})$$

2.4 *X-Ray diffraction alnalysis*

The crystallization of the coated layer of the thick film resistor was examined by thin film X-ray diffractometer (Philips, PW3719) with Cu target of 40 kV acceleration voltage, 1.5° incident angle, 0.08/sec scan speed.

III. Results and Discussion

1. *Thermal properties of bulk glass*

The thermal expansion coefficients of the bulk glasses containing 60 mole% of ZnO, CdO and PbO were 44.6×10^{7}/°C, 85.5×10^{7}/°C and 109×10^{-7}/°C, respectively. Generally, the thermal expansion coefficient is affected by free space in a glass structure and an anharmonicity of the thermal vibration of atoms in the lattice. That is, the bigger the ionic radius is, the greater the anharmonic thermal vibration is, and hence the thermal expansion coefficient increases with the ionic radius.[7] The ionic radius of Zn^{2+}, Cd^{2+} and Pb^{2+} are 0.74Å, 0.97Å and 1.21Å, respectively. This is why the PbO containing glass has the highest thermal expansion coefficient.

The measured softening points(Littleton softening point) of the bulk glasses containing 60 mole% of ZnO, CdO and PbO were 698°C, 619°C and 400°C, respectively.

The softening point of a glass depends on the bond strength between a modifier cation and an oxygen in the structure and the bond strength relates to the ionization energy because the modifier cation ionically bonds to the oxygen. That is, the higher the ionization energy is , the stronger the bond strength is. The ionization energy of Zn^{2+}, Cd^{2+} and Pb^{2+} are 17.96 eV, 16.91 eV and 15.03 eV, respectively, and therefore, the ZnO containig glass showed the highest softening point.

2. *Resistivity of bulk glass*

To measure the electrical resistivity of the bulk glass, glass discs with 25 mm of diameter and 5 mm of thickness were prepared. The surface of the specimen was polished and coated with gold by ion coater. The measurement of the electrical resistivity was carried out in a furnace at the elevated temperature between 25°C and 350°C.

The electrical resistivity was about 10^{13} Ω·cm at room temperature for all composition of glasses but it decreased to 10^{9}~10^{11} Ω·cm at 350°C as shown in Fig. 1. As the temperature increases, the glass structure will be relaxed because of the increasing lattice vibration by thermal energy, and then the divalent cations (Zn^{2+}, Cd^{2+}, Pb^{2+})in the glass structure will have enough energy for ionic migration. It is believed that the movement of divalent cations in this glass structure is attributed to the electrical conduction.

3. *Crystallization of glass coat*

The glass frit was coated on a 96% alumina substrate, without RuO_2, by spray coating method, and then the sample was fired at various heat treatment temperatures. The thin film XRD patterns for these samples are shown in Fig. 2.

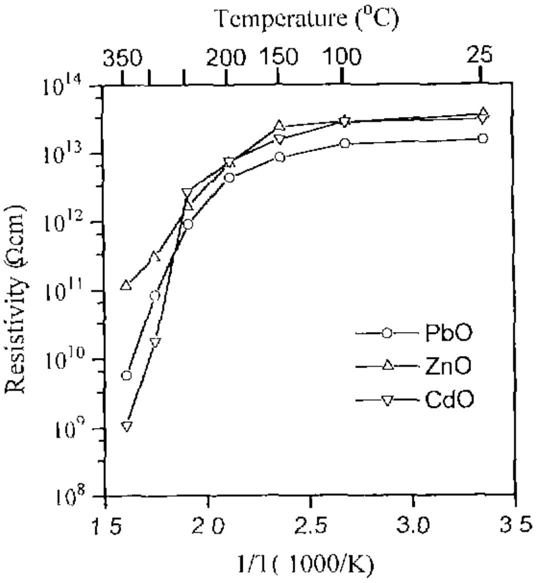


Fig. 1. Resistivity change of bulk glasses in $60RO \cdot 20SiO_2 \cdot 5Al_2O_3 \cdot 15B_2O_3$ system.

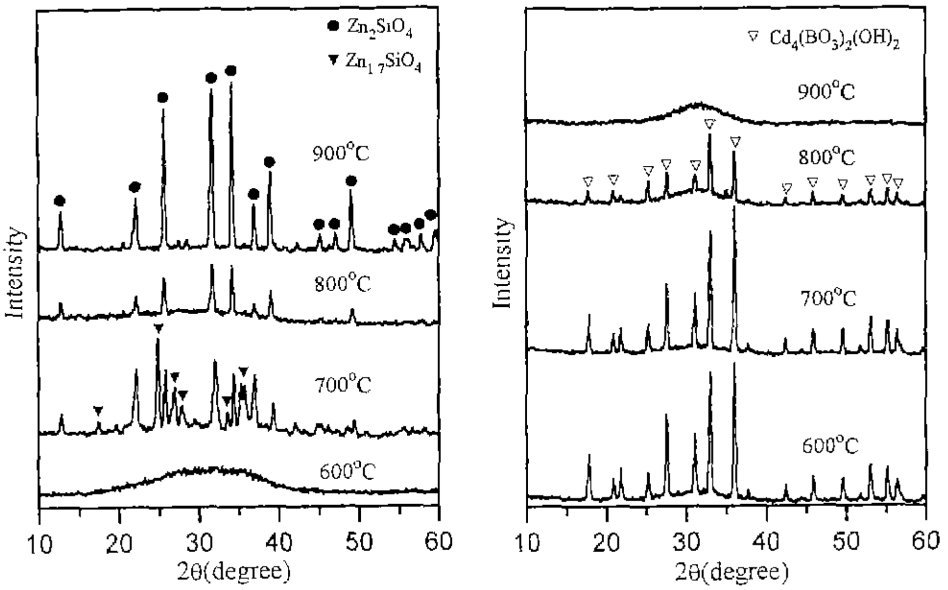
In the glass frit containing 60 mole% of ZnO, only glass phase was observed after firing at 600°C but the crystalline phase of Zn_2SiO_4 and $Zn_{1.7}SiO_4$ were shown at 700°C. The $Zn_{1.7}SiO_4$ crystal disappeared when the sample was heat-treated over 800°C but the Zn_2SiO_4 crystal remained. In the glass frit containing 60 mole% of CdO, $Cd_4(BO_3)_2(OH)_2$ crystalline phase was formed in the temperature range of 600°C and 800°C, and this crystal was melted at 900°C. On the other hand, no crystalline phase was observed in the glass frit containing 60 mole% of PbO, which was coated and fired in the temperature range of 600°C and 900°C.

4. *Surface reaction in thick film resistor*

The mixed powder with 5 vol% of RuO_2 and glass frit containing 60 mole% of ZnO, CdO and PbO was coated on the 96% alumina substrate, and then heat-treated at 400~900°C for 10 minutes. The surface of the thick film resistor was examined by thin film XRD.

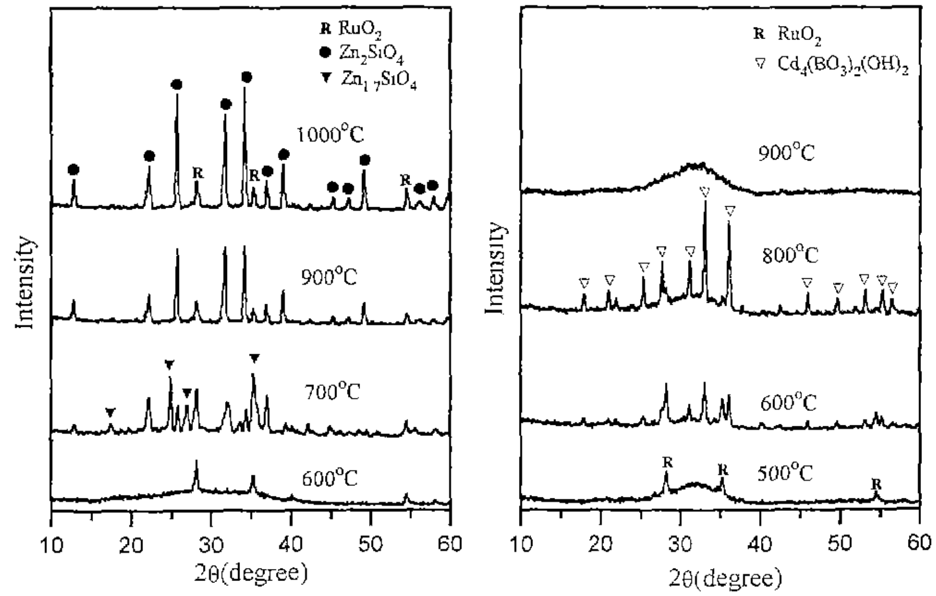
When the thick film resistors, which were prepared by mixing conductor, RuO_2, with ZnO or CdO containing binder glass frit, were heat-treated, no reaction was observed between RuO_2 and glass frit and the crystalline phase of Zn_2SiO_4 and $Cd_4(BO_3)_2(OH)_2$ was coexisted with RuO_2(Fig. 3). The obtained resistor surface finish was poor because of the poor wetting behavior of these frit mixture to alumina.

No crystalline phase as mentioned above, was observed when PbO containing glass was coated and fired. When the mixture of the glass frit and RuO_2 was coated and fired, however, the coated layer was crystallized as shown in Fig. 4. RuO_2 particles in the coat layer melted into the glass phase at 400°C and a new crystalline phase, $Pb_2Ru_2O_{6.5}$, was formed at 600~900°C. That is, the



(a) Z60 (b) C60

Fig. 2. XRD patterns of coated glasses, which were heat treated at various temperatures.



(a)Z60+$RuO_2$5 vol% (b)C60+$RuO_2$5 vol%

Fig. 3. XRD patterns of coated ZnO and CdO glasses with 5 vol% of RuO_2 after heat treated at various temperatures.

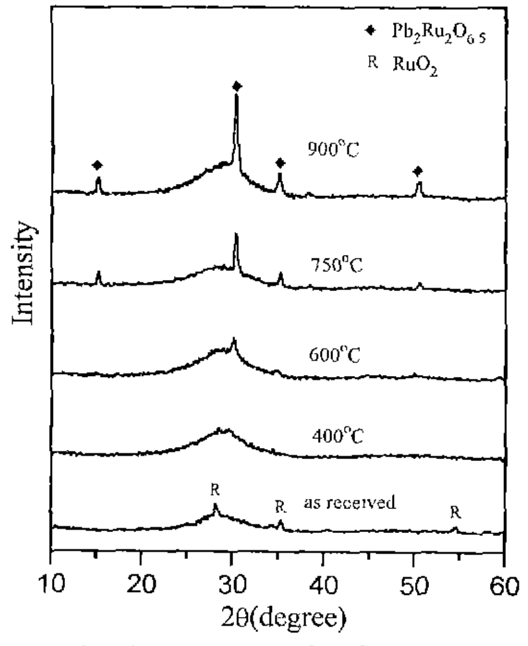


Fig. 4. Thin film XRD patterns of PbO glass coat with 5 vol% of RuO_2 after heat treated at various temperatures.

conducting material, RuO_2, dissolved into the glass at below 400°C and $Pb_2Ru_2O_{6.5}$ crystal was precipitated at over 600°C from Ru^{4+} and Pb^{2+} ions in the glass phase.

The schematic diagram of the surface reaction of the thick film resistor containing RuO_2 and binder glass frit was depicted in Fig. 5. RuO_2 powder with the size of about 2~3 μm is dispersed among the binder glass particle with under 40 μm in the coat layer. When heat-treated, RuO_2 does not react with the glass frit containing ZnO or CdO, and Zn_2SiO_4 or $Cd_4(BO_3)_2(OH)_2$ are formed from the glass phase only. However, the PbO containing glass frit is reacted with RuO_2 and then new crystalline phase, $Pb_2Ru_2O_{6.5}$, is formed with glass phase. It is expected that the amount of new crystalline phase increases with the firing temperature.

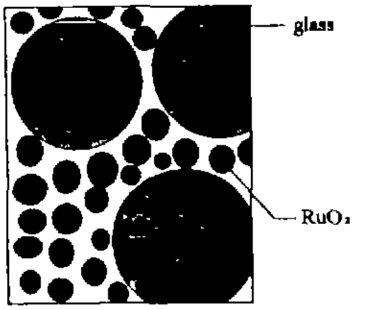
5. Electrical property of thick film resistor

The sheet electrical resistivity of the thick film resistor, made from RuO_2 and glass frit containing 60 mole% of PbO, is shown in Fig. 6. And the temperature coefficient of resistance (TCR) values, calculated from the resistance measurement at -55°C, 25°C and 145°C, are tabulated in Table 1.

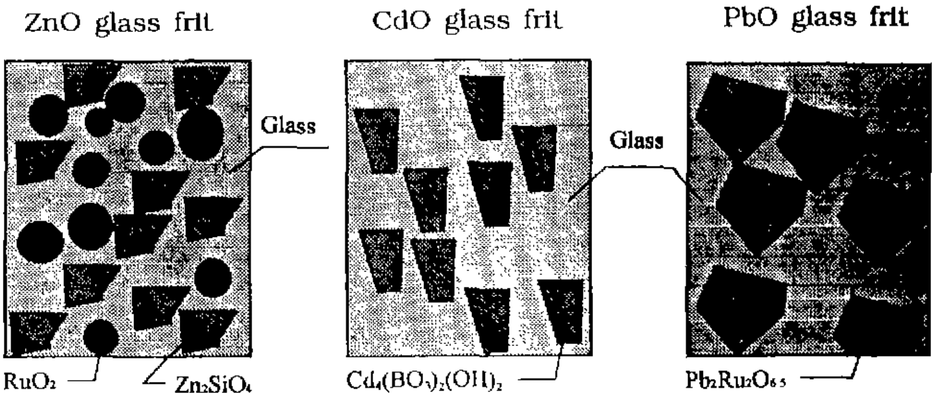
As the heat treatment temperature of the resistor changed from 600°C to 900°C, the resistances were varied from 1270 kΩ, 690 kΩ, 142 kΩ to 1.54 kΩ, 1.57 kΩ, 1.61 kΩ at the measuring temperatures of -55°C, 25°C, 145°C, respectively. This indicates that the amount of $Pb_2Ru_2O_{6.5}$ crystal present in the thick film resistor plays an important role in electrical conduction. That is, the resistivity sharply decreases with the content of the crystal.

When the thick film resistor is fired at lower temperature, the sheet electrical resistivity decreases with measuring temperature, which is a characteristic electrical phenomenon in ceramics.[8] When the coat is fired at 900°C, the resistivity increases with measuring temperature, the sheet electrical resistivity showed a typical electrical phenomenon in metal. Therefore, it can be said that the glass phase dominates the electrical property for the sample fired at a lower temperature, while the crystalline phase dominates the electrical property for the sample fired at a higher temperature.

The resistor fired at the temperature range of 800°C



(a) before firing



(b) after firing

Fig. 5. Schematic diagram of crystal formation in RuO_2-RO·SiO_2 B_2O_3 Al_2O_3 glass thick film resistors at 900°C.

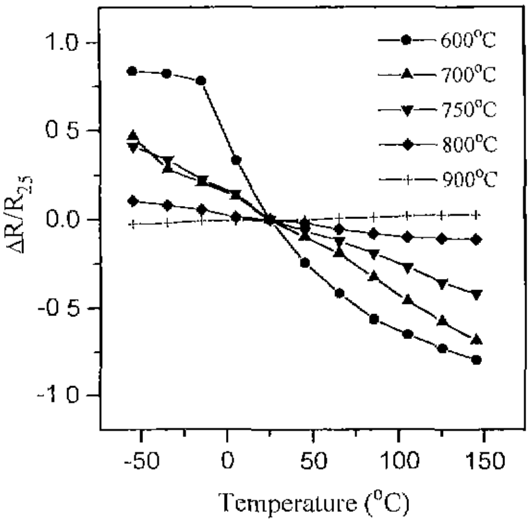


Fig. 6. Temperature-resistance characteristics of the resistor sintered at various temperatures.

Table 2. TCR of Thick Film Resistor with PbO Glass
(TCR: ppm/°C)

firing temp.	$R_{-55^\circ C}$ (kΩ)	$R_{-25^\circ C}$ (kΩ)	$R_{-115^\circ C}$ (kΩ)	H-TCR	C-TCR
600°C	1270	690	142	-6618	-10507
700°C	78.4	53.3	17.0	-5675	-5886
750°C	7.10	5.02	2.92	-3486	-5179
800°C	1.66	1.50	1.33	-944	-1333
900°C	1.54	1.57	1.61	212	239

and 900°C shows its lowest absolute value, and the TCR can be controlled to zero by choosing the appropriate heat-treatment temperature and soaking time.

IV. Conclusions

Three different glass frits of 60%RO-20%SiO_2-15%B_2O_3-5%Al_2O_3(RO=PbO, ZnO, CdO) are mixed with RuO_2 and coated on 96% alumina substrate. By examining the coat glass characters and the electrical properties of the obtained thick film resistor, the conclusions can be drawn as follows;

1. The thermal expansion coefficient sharply decreased in the order of ZnO, CdO, PbO in 60RO-20SiO_2-15B_2O_3-5Al_2O_3(RO=ZnO, CdO, PbO) glass system, and the softening point showed wide difference with the variation of glass composition. The electrical resistivity of the bulk glass was about 10^{13} Ω·cm at a room temperature for all glasses.

2. Glass frit containig ZnO or CdO crystallized into Zn_2SiO_4 and $Cd_4(BO_3)_2(OH)_2$ without reacting with RuO_2, when it is fired.

3. RuO_2 in the thick film resistor dissolved into PbO

containing frit and crystallized into $Pb_2Ru_2O_{6.5}$ crystals when the resistor was heat-treated at over 600°C.

4. The temperature coefficient of resistance increased with the firing temperature of the thick film resistor, and the absolute value of TCR becomes zero in the firing range of 800°C and 900°C.

From these results, it can be said that the electrical properties of the thick film resistor strongly depends on the crystallization phenomena of the glass frit-RuO_2 mixture which is coated on an alumina.

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