Temperature Dependence of the Electrical Conduction in RuO$_2$-based Thick Film Resistors

BI-SHIOU CHIOU and JER-YUAN SHEU
Department of Electronics Engineering and Institute of Electronics, National Chiao Tung University, Hsinchu, Taiwan 30043
Republic of China

In this paper, the temperature dependence of resistance of two generic RuO$_2$-based resistors is investigated. The resistor compositions studied are 80 wt.% glass (63 wt.% PbO - 25 wt.% B$_2$O$_3$ - 12 wt.% SiO$_2$, designated as G1) - 20 wt.% RuO$_2$ and 80 wt.% glass (55.5 wt.% PbO - 22 wt.% B$_2$O$_3$ - 10.5 wt.% SiO$_2$ - 12 wt.% Al$_2$O$_3$, designated as G2) - 20 wt.% RuO$_2$. The sheet resistance of resistor 80 wt.% G1 - 20 wt.% RuO$_2$ fired at 850°C decreases as the temperature is increased from 100 K to ~400 K, remains a minimum value at temperatures 400 K ~690 K, and then increases as the temperature is further raised. A negative temperature coefficient of resistance (TCR) of ~−480 ppm/°C is obtained from 100 K to 500 K. The TCR becomes less negative when temperature increases. Three models for conduction mechanism of thick film resistors are employed to explain the experimental results. A modified model, consisting of both tunneling and parallel conduction approaches, is proposed to elucidate the change in slope in the resistance-inverse temperature curve as well as the temperature dependence of the resistance. In addition, an equivalent circuit model is proposed to describe the electrical behavior of the thick film resistors.

Key words: Thick film resistors, electrical conduction, TCR

INTRODUCTION

Thick film resistors are fabricated by sintering together an intimate mixture of conductive and vitreous nonconductive materials. The sintered films show a distribution of conducting particles in the insulating glassy matrix. The electronic transport mechanism in this type of heterogeneous media has been a topic of interest to scientists and engineers. Some investigators attributed the conduction mechanism in thick film resistors to percolative tunneling of electrons through conductive grains embedded in the glassy matrix of the resistive layer and assumed that the resistance of percolation paths dominated the resistance of the resistor system. This model fits well with the blending curve of thick film (cermet) resistor systems. However, it gives very little insight on the temperature dependence of the electrical conduction in these resistors.

Pike and Seager, using a conductive model with tunneling barrier between metal oxide particles, proposed a temperature dependence of resistance $R(T)$ as:

$$R(T) = R_b(T) + R_m(T)$$

$$= \frac{1}{2} R_{bo} \left( \frac{\sin aT}{aT} \right) \left( 1 + \exp \frac{E}{kT} \right) + R_m(1 + bT)$$

where $R_m$ is the conductive phase resistance; $R_{bo}$ is the tunneling barrier resistance; $E$ is the barrier height; $k$ is Boltzmann's constant; $T$ is absolute temperature; $R_{bo}$, $R_m$, and $b$ are constants depending on the tunneling barrier and conductive phase; respectively. The parameter $a$ depends on the insulator barrier height.

Smith and Anderson, employing an effective medium treatment to describe the thick film resistor system, proposed a parallel conduction mechanism to take account of the transition of conduction between the metallic-like conductive predominant and the insulative glassy layer predominant.

$$\sigma = \sigma_0 \left[ \exp(-E_1/kT) + \exp(-E_2/kT) \right]$$

where $\sigma$ is the resistivity of the material system; $E_1$ and $E_2$ are the activation energies for the two conduction processes.

Cattaneo et al., using a percolation approach, showed that the temperature dependence of resistivity $\rho(T)$ of Ru-based thick film resistors on 96% Al$_2$O$_3$ fitted the equation:

$$\rho(T) = \frac{T}{\beta} \exp(T_0/T)^{1/4}$$

where $\beta$ is a constant; $T_0$ is the activation temperature which is a function of conductive density, grain size, and glass characteristics.

In this research, the temperature dependence of the resistance of two generic RuO$_2$-based thick film resistors is investigated. Various models are applied to explain the electrical conduction of the material system. A modified model is proposed to elucidate the electrical transport of thick film resistors.
The resistor systems selected was RuO$_2$ as conducting phase and glass as matrix. The glass compositions employed are 63 wt.% PbO - 25 wt.% B$_2$O$_3$ - 12 wt.% SiO$_2$ (G1) and 55.5 wt.% PbO - 22 wt.% B$_2$O$_3$ - 10.5 wt.% SiO$_2$ - 12 wt.% Al$_2$O$_3$ (G2). Densities of glasses are 4.599 g/cm$^3$ and 4.179 g/cm$^3$ for G1 and G2, respectively. Glass G1 has been extensively studied for the application in thick film microelectronic technology.$^3$ Glass G2 is obtained by adding 12 wt.% Al$_2$O$_3$ to G1 to increase the high temperature viscosity.$^{10,11}$ Resistor formulations were prepared with appropriate amounts of RuO$_2$ powders (<0.5 μm), Frit G1, and Frit G2. The mixed powders were blended with ~40 vol% screening agent consisting of 10% N-300 ethyl cellulose in butyl carbitol solvent for two hours in a roll mill.

A Pd/Ag conductive (Johnson Matthey TR4940) was printed, dried, and fired on 96% Al$_2$O$_3$ substrate (AISiMag 614). The resistor ink was printed through a 230 mesh stainless steel screen, dried at 120°C for 5 min to remove the solvent, at 350°C for 10 min to decompose the cellulose, and then sintered at a temperature range from 700 to 900°C for 10 min to obtain the resistor network. Resistors with various aspect ratios ranging from 0.12 to 3.7 were fabricated.

### EXPERIMENTAL PROCEDURES

The sheet resistance as a function of temperature for the resistor composition 80 wt.% G1 - 20 wt.% RuO$_2$ is given in Fig. 1. The sheet resistance decreases rapidly initially, reaches a minimum at temperature range from 400 to 690 K, and then increases as the temperature is further raised. The thick film resistor consists of conductive chains distributed in an insulating glass matrix. The electric transport is via the conducting RuO$_2$ particles and the interfacial barrier between the neighboring conductives.$^{12}$ The electrical resistance $R$ is a series combination of the metallic resistance attributed to the conductive RuO$_2$ particles and the resistance due to the interfacial barrier. The temperature coefficient of resistance (TCR) and room temperature resistivity of RuO$_2$ are $\sim +8000$ ppm/°C and $3.6 \times 10^{-5}$ Ω·cm$^{13}$ respectively. For glass G1, the values are $\sim 44000$ ppm/°C (TCR) and $>10^{13}$ Ω·cm(room temperature resistivity).$^{10,11}$ On the basis of the data shown in Fig. 1, one obtains a negative TCR of $-480$ ppm/°C from 100 to 500 K, a positive TCR at 500 K and above, and a room temperature resistivity of $5.6 \times 10^{-5}$ Ω·cm for a resistor composition of 20 wt.% RuO$_2$ - 80 wt.% glass G1, i.e. 7.6 vol% RuO$_2$ - 92.4 vol% glass G1. Around 400°C, the resistance decreases abruptly and then increases again. It is argued that this change in resistance is due to the relaxation of the glass employed, since glass G1 has a strain point of $\sim 350$°C. A linear combination of the properties of RuO$_2$ and G1 does not yield the TCR and resistivity of the resistor body. This suggests that the electronic characteristic of the interfacial barrier plays an important role on the electrical behavior of the thick film resistors.

Figures 2 and 3 give the temperature dependence of the relative resistance, $R_T/R_{25°C}$, for resistor compositions 80 wt.% G1 - 20 wt.% RuO$_2$ and 80 wt.% G2 - 20 wt.% RuO$_2$ (87 vol% G2 - 13 vol% RuO$_2$), respectively, fired at various temperatures. As exhibited in Figs. 2 and 3, one finds that the larger the low temperature $R_T/R_{25°C}$, the smaller the high...