acta physica slovaca vol. 46 No. 2, 169 – 173 April 1996

ELECTRONIC TRANSPORT IN THICK FILM RESISTORS AT LOW TEMPERATURES AT LOW TEMPERATURES[1]

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Received 31 July 1995, accepted 8 February 1996

The electrical conductivity of various RuO_2 - based thick film paste resistors was investigated at low temperatures. It was shown that models based on tunnelling of charge carriers between conductive grains and on hopping of carriers between localized impurity states in the glass matrix via thermal activation can describe the electrical conductivity of thick film resistors in the low temperature region. At very low temperatures, however, the hopping mechanism in the impurity band of the glass matrix seems to play the dominant role in the electronic transport.

1. Introduction

Thick film materials have been used for many years to manufacture an increasing variety of resistor networks, hybrid integrated circuits, hybrid integrated networks and components for segments of the electronic industry. The structure of thick film paste resistors has been shown by several researchers [1, 2, 3] to be of a more complicated nature than a mixture in which a conductive phase is dispersed in an insulating glass matrix. During the firing in the manufacturing process, the glass apparently diffuses between the conductive particles and possibly also a litle into the particles, and on the other hand some conductive particle material is thought to diffuse into the glassy interfaces, doping the glass.

Concerning the electronic transport in thick film resistors, each conduction path may contain metallic (sintered) and insulating (nonsintered) contacts between conductive grains. The charge transport through the sintered contacts is metallic and through the nonsintered contacts may be due to tunnelling through the glassy interface between conductive particles [4, 5]. In this process charge carriers are transported from one metallic grain to another via thermal activation and the charging energy $e^2/2C$, which is required to place an electron on or from a grain of capacity C, plays an important

[1]Presented at 9th Czech and Slovak conference on magnetism, Košice, Slovakia, August 28-30 1995

role there (resembling the situation in dielectric granular metals). However, if a band of localized states is formed by impurities that diffused into the glass, hopping between localized impurity states (as in doped semiconductors) must be also taken into account [4, 6].

Up to now it was not clearly indicated whether the tunnelig mechanism or the narrow impurity band mechanism provide an appropriate description of the electrical conductivity in thick film resistors at low temperatures.

The temperature dependence of the electrical conductance for the both of these cases (for tunnelling in granular metals as well as for hopping in doped semiconductors) can be generally described in the form

$$G(T) = G_o \exp[-(T_o/T)^p] \quad (1)$$

where G is the conductance and G_o and T_o are parameters. The exponent $p = 1$ represents the high temperature Arrhenius behaviour and the value $p = 1/4$ the low temperature behaviour of Mott's variable range hopping. The value $p = 1/2$ comes in doped semiconductors from variable range hopping with a Coulomb gap at the Fermi level, which originates from the Coulomb interaction between localized carriers [7]. To granular metals in the dielectric regime, in which the electrical conduction is considered to be by electron hopping between conductive grains, this approach has been extended by [8]. Another approach for granular metals [9] based on the distribution of the grain charging energy (resulting from the distribution of grain sizes) interprets $p = 1/2$ in equation (1) as a crossover from the high temperature Arrhenius behaviour to the low temperature behaviour of Mott's variable range hopping law.

In this contribution the electrical conductivity of various RuO_2 based thick film paste resistors is investigated between 50 mK and 80 K. The obtained results are discussed within the framework of doped semiconductors and granular metals, with the aim to estimate the role of the impurity band mechanism and the mechanism involving tunnelling between conductive grains at low temperatures.

2. Samples

The used thick film resistors (TFRs) were printed using standard screen printing technique from commercial RuO_2 pastes of sheet resistivities 1 k$\Omega/sq.$, 10 k$\Omega/sq.$ and 100 k$\Omega/sq.$ of producer Tesla Lanškroun, Czech Republik. After deposition the films were dried for 15 minutes at 150°C and afterwords fired for 1 hour in a thermal profile recommended by the producer of the paste, with the highest temperature of 850°C and duration of 10 minutes. As substrates polycrystalline Al_2O_3 was used. Even if the detailed composition of the pastes belongs to the know-how of the producers, there are common features which characterize the structure of these pastes. The paste usually consists of a mixture of conductive RuO_2 particles, lead - borosilicate glass particles and of an organic carrier which gives the paste good rheological properties during the deposition. The fireing melts the glassy particles and links them and the oxide particles together with the substrate. The sheet resistance of various thick film resistors depends at the same producer on the concentration of conductive transition metal oxide particles in the paste.

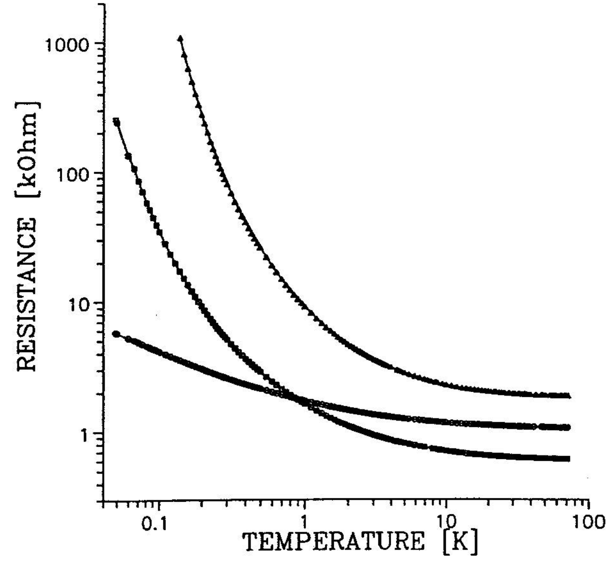

Fig. 1 Temperature dependence of RuO_2 based thick film paste resistors. Sheet resistivities: 1 k$\Omega/sq.$ (o), 10 k$\Omega/sq.$ (□) and 100 k$\Omega/sq.$ (Δ).

Scanning electron microscopy pictures have shown that the microstructure of the prepared TFRs consists of RuO_2 particles and RuO_2 clusters randomly distributed in the glass matrix. The diameter of particles / clusters was estimated to be in the range between 0.2 and 1 μm.

Further experimental details are published elsewhere [10].

3. Results and Discussion

The observed resistance data ($R = 1/G$) in the temperature range between 50 mK and 80 K of the measured pastes are shown in Fig. 1. As the temperature dependence in the whole temperature range has a negative derivative, we suppose that there are no metallic spans between the sides of the samples.

A useful analysis [11] of the electrical resistivity data in terms of equation (1) consists of computing the logarithmic sensitivity (LS) $S = -d(ln(R))/d(ln(T)) = -(T/R).(dR/dT)$, which for expression (1) yields p from the negative slope of a straight line when plotting $ln(S)$ vs. $ln(T)$. The LS of the recieved experimental data was computed by means of a standard numerical derivative analysis and the results are plotted in Fig. 2. As can be seen in this figure, for all samples the negative slope is the highest at high tempertures (close to 1) and decreases with decreasing temperature. (The slopes for $p = 1$ and for $p = 1/2$ are represented by dashed lines.) This showes that in measured thick films a change of electrical conductance from a $G \sim exp[-(T_o/T)]$ behaviour to a behaviour close to $G \sim exp[-(T_o/T)^p]$, with $p < 1$, towards lower tem-

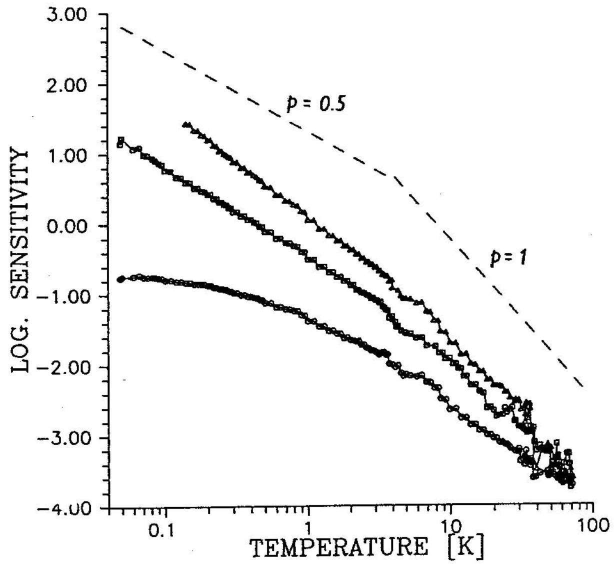

Fig. 2 Temperature dependence of the logarithmic sensitivity for various resistors: 1 k$\Omega/sq.$ (o), 10 k$\Omega/sq.$ (□) and 100 k$\Omega/sq.$ (△). The dashed lines represent the slopes for exponents $p = 1$ and $p = 1/2$.

peratures can be observed, indicating a gradual crossover from nearest neighbour to variable range hopping or tunnelling.

The temperature dependence of the activation energy $E_a = -d(lnG) / d(1/k_BT)$ is displayed in Fig. 3. At higher temperatures (above about 5 K) the recieved activation energy corresponds to charging energies of RuO_2 particles or clusters in thick films, at lower temperatures, however, E_a rapidly decreases reaching energies much smaller than the charging energies ($E_a \approx 1\ meV$ for 0.1 μm particles and $E_a \approx 0.1\ meV$ for 1 μm clusters).

The small values of activation energies below 1 K as well as the values of exponent p ($p < 1$) in the same temperature range suggest that at lowest temperatures the electrical conductivity in thick film resistors is realized through variable-range hopping between impurity states in the glass matrix, which arise during the firing in the manufacturing process. Because of large distances between distant conductive particles, which lead in typical insulators to a very low tunnelling probability [12], tunnelling beyond naerest neighbour particles would be negligible at these small activation energies.

We conclude that in RuO_2 - based thick film paste resistors the electrical conductivity cannot follow the temperature dependence described by equation (1) with a single exponent p in the whole measured temperature range. The exponent p decreases with decreasing temperature, from p close to 1 at higher temperatures to $p < 1$ at lowest temperatures, and its decrease depends on the concentration of conduction particles in the paste. The behaviour of p and the dependence of the obtained activation energy

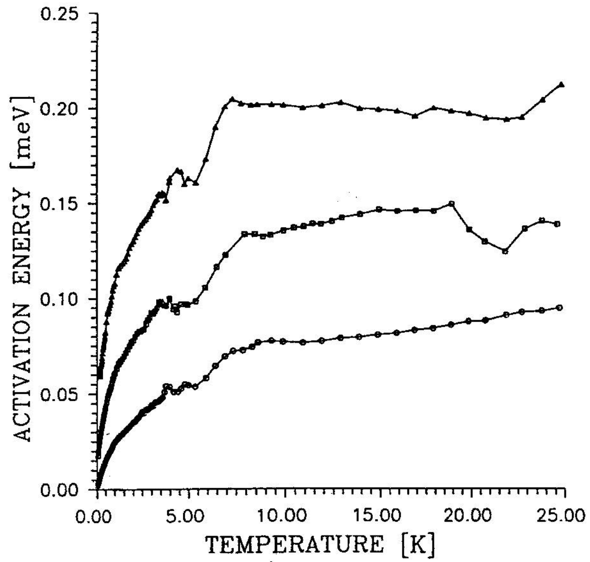

Fig. 3 Temperature dependence of the activation energy. Resistors: 1 k$\Omega/sq.$ (o), 10 k$\Omega/sq.$ (□) and 100 k$\Omega/sq.$ (△).

indicate that whereas at higher temperatures both tunnelling between conductive particles and hopping between localized impurity states in the glass matrix can contribute to the conductivity of thick films, at lowest temperatures variable range hopping within impurity band states seems to be dominant.

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