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Conduction in RuO_2-based thick films†

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The dependence of RuO_2-glass thick-film electrical conductivity on the concentration of metallic component reveals a metal–insulator transition. Resistance versus temperature characteristics measured in the range 4·2–400 K are presented for a set of seven composites of varying composition. The results obtained can be divided into two groups: composites incorporating $\geq 0{\cdot}12$ (per unit volume) of metallic component yield minima of $R(T)$ curves and possess parabola-like shapes, and composites with a small content of metallic component ($<0{\cdot}12$) show a negative temperature coefficient of resistance over the whole range of measured temperatures. In the insulating region, data are analysed in terms of various conduction mechanisms, giving rise to an understanding of electrical conduction in RuO_2-glass thick resistive films.

1. Introduction

This paper presents a series of temperature characteristics of resistance for RuO_2-glass thick resistive films and analyses them from the point of view of possible electrical conduction mechanisms responsible for their shape. Fresh arguments are provided for the existence of a critical concentration of metallic component in the investigated material, in which a metal–insulator transition occurs. The analysis is supported by suggestions concerning the microstructure of RuO_2-glass composites.

2. Experimental

Conventionally, RuO_2-glass films are produced by consecutive screen printing and the firing of pastes deposited on alumina substrates. This investigation concerns pastes that are binary mixtures of RuO_2 and glass powders with particle sizes of 34 nm and 550 nm, respectively, suspended in an inert organic vehicle. The latter was evaporated during the initial stage of the firing process. The firing process was carried out for 10 min in an air atmosphere belt-type furnace, reaching a peak temperature of 850°C. The glass used was 65% PbO, 25% SiO_2, 10% B_2O_3 (by weight). Seven composites were prepared with the volume fraction of metallic component varying from 0·05 to 0·32. The term 'metallic component' will be used hereafter for RuO_2 as it reveals metal-like electrical conduction with room temperature resistivity $\rho_m = 3{\cdot}4 \times 10^{-7}\,\Omega$m and a respective temperature coefficient of resistivity (TCR) of $5{\cdot}8 \times 10^{-3}\,K^{-1}$ (Ryden *et al.* 1970). Details of how the pastes and films were prepared are presented elsewhere (Bobran 1989, Bobran and Kusy 1991).

Resistance–temperature (R versus T) characteristics of the films were measured in a (Kriopan) variable-temperature-flow helium cryogenic system, allowing control

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of temperature in the range 4·2–300 K, and in a laboratory oven in the range 300–400 K. Measurements were carried out using the four probe method, i.e. constant DC current was supplied to the films and the DC voltage was measured at the voltage probes. Samples were commuted by an electronic scanner with the aid of PC/AT computer and measurements were realized by a (Keithley) DMM196 multimeter. Power dissipation in the sample during the measurement caused negligible contribution to the local temperature increase, which was of the order 10^{-4} K compared with the lowest temperature $T=4{\cdot}2$ K in the experiments.

3. Results

Temperature characteristics of resistance for RuO_2-glass films often indicate a minimum (see e.g. Vest 1975, Pike and Seager 1977, Kusy 1987, Abe and Taketa 1991, Bobran and Kusy 1991). The location of the minimum on the temperature scale depends strongly on the volume fraction v of conducting component and, as a rule, the smaller v the greater the temperature of the minimum T_m. The shape of the R versus T curves, which are usually measured in the range 77 to 400 K, is usually interpreted as a trade-off between metallic properties of RuO_2 and negative TCR processes like tunnelling or hopping.

Such a picture can roughly be applied to the set of characteristics presented in Figs 1 and 2. Seven R versus T curves are shown for composites with v ranging from 0·05 up to 0·32 and for a temperature variation from 4·2 K to 300 or 400 K. Figures 1 and 2 have separate coordinate systems. R is the resistance of one square film of average thickness 14 μm. Plots of activation energy W as a function of temperature

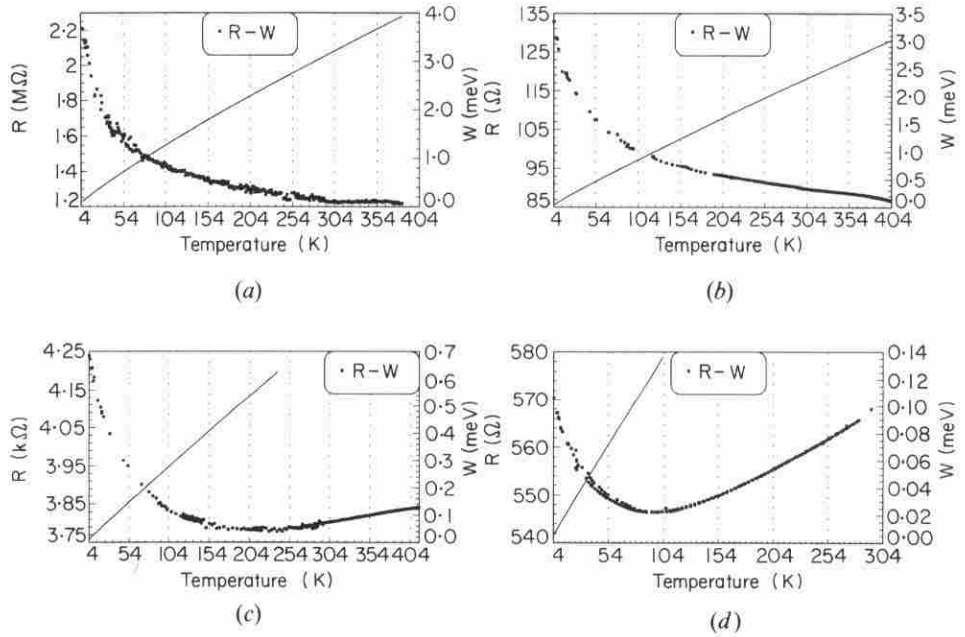

Figure 1. Resistance–temperature characteristics for RuO_2-glass composites: (*a*) $v=0{\cdot}05$; (*b*) $v=0{\cdot}08$; (*c*) $v=0{\cdot}12$; (*d*) $v=0{\cdot}17$. Plots of activation energies for negative TCR parts of R versus T are also included.

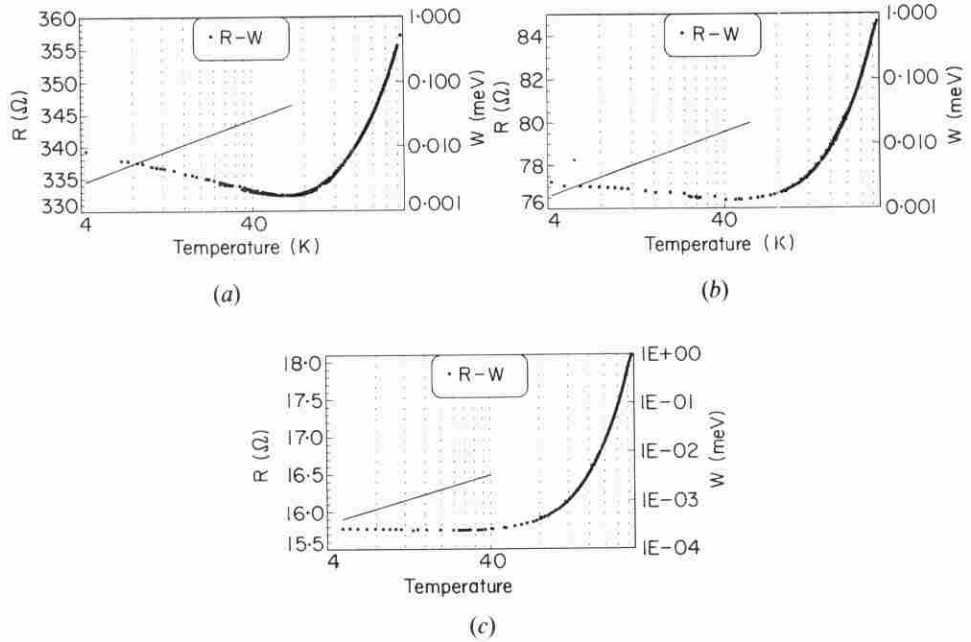

Figure 2. As in Fig. 1: (*a*) $v=0{\cdot}22$; (*b*) $v=0{\cdot}27$; (*c*) $v=0{\cdot}32$. Logarithmic scales of temperature were chosen to show some evidence of the linear dependence of R versus T for the negative TCR parts.

for the parts of the R versus T curves that reveal negative TCRs are also included. As can readily be seen, two curves relating to the lowest RuO_2 concentrations, $v=0{\cdot}05$ and $v=0{\cdot}08$, have no minimum and have negative slopes in the whole range of measured temperatures. The remaining characteristics indicate minima obeying the rule mentioned above, i.e. the minima shift towards the higher temperatures with v decreasing. The results for high concentrations of RuO_2 (Fig. 2) are plotted in log-linear coordinates to show some evidence for the linear dependence of the negative TCR parts of the curves in such a coordinate system.

Interpretation of the results obtained begins by applying two theoretical formulae and optimizing their parameters for the negative TCR parts of the characteristics:

$$R=R_0 \exp\left[\left(\frac{T_0}{T}\right)^x\right] \tag{1}$$

$$R=A\times R_0\times \ln T+R_0 \tag{2}$$

Equation (1) is characteristic for conduction with an activation energy; (2) has a form usually employed to interpret weak localization and electron–electron interaction effects in disordered two-dimensional systems. The results of optimization are summarized in the Table. Activation energies were calculated by differentiation of (1), thus obtaining (see e.g. Pollak and Adkins 1992)

$$W=\mathrm{d}(\ln R)/\mathrm{d}[(kT)^{-1}]=xkT_0^xT^{(1-x)} \tag{3}$$

v	$R_0(\Omega)$	T_0(K)	x	Error	$A[1/\ln K]$	$R_0(\Omega)$	Error
0·05	$5{\cdot}01\times10^{5}$	$1{\cdot}46\times10^{2}$	0·1355	$4{\cdot}33\times10^{2}$	$-8{\cdot}62\times10^{-2}$	$2{\cdot}42\times10^{6}$	$1{\cdot}62\times10^{-1}$
0·08	$2{\cdot}71\times10^{4}$	$3{\cdot}53\times10^{3}$	0·0740	$9{\cdot}64\times10^{3}$	$-6{\cdot}90\times10^{-2}$	$1{\cdot}48\times10^{5}$	$6{\cdot}67\times10^{-3}$
0·12	$1{\cdot}29\times10^{3}$	$2{\cdot}26\times10^{3}$	0·0285	$1{\cdot}86\times10^{-3}$	$-2{\cdot}84\times10^{-2}$	$4{\cdot}44\times10^{3}$	$2{\cdot}20\times10^{-3}$
0·17	$1{\cdot}93\times10^{2}$	$1{\cdot}05\times10^{3}$	0·0148	$1{\cdot}03\times10^{-4}$	$-1{\cdot}50\times10^{-2}$	$5{\cdot}85\times10^{2}$	$9{\cdot}73\times10^{-5}$
0·22	$1{\cdot}22\times10^{2}$	$9{\cdot}68\times10$	0·0076	$2{\cdot}82\times10^{-5}$	$-7{\cdot}51\times10^{-3}$	$3{\cdot}43\times10^{2}$	$2{\cdot}95\times10^{-5}$
0·27	$2{\cdot}81\times10$	$4{\cdot}92\times10$	0·0044	$8{\cdot}40\times10^{-6}$	$-4{\cdot}31\times10^{-3}$	$7{\cdot}77\times10$	$8{\cdot}40\times10^{-6}$
0·32	5·79	$5{\cdot}22\times10$	0·00098	$1{\cdot}68\times10^{-7}$	$-1{\cdot}05\times10^{-3}$	$1{\cdot}58\times10$	$2{\cdot}08\times10^{-7}$

Results of optimizing parameters R_0, T_0, x in (1) and R_0, A in (2) to fit experimental data. The measurement errors are calculated as

$$\sum_i \left(\frac{R_{\text{meas}}-R_{\text{optim}}}{R_{\text{meas}}}\right)^2$$

where R_{meas}, R_{optim} are resistances measured and obtained from optimization, shall be compared only in rows.

where k is the Boltzmann constant. This procedure yielded $W(T)$ plots shown in Figs 1 and 2. According to the very low values of exponents x compared with those predicted by various theories of electrical conduction with activation energies (for reviews see Shklovskii and Efros 1984, Sheng 1992), a nearly linear but weak increase of energy W versus temperature was obtained. The values of W were very small for all the composites investigated and never exceeded 4 meV. The greater the concentration of metallic component, the lower was the value of adequate activation energy. This result is consistent with other published results (Pike and Seager 1977, Hill 1980, Kubovy and Havlas 1988). One possible explanation for such phenomena is the trade-off between the metallic properties of RuO_2 and the negative TCR transport via MIMs which both contribute to the process of electrical conduction in RuO_2-glass composites. This interpretation has given reliable results in models presented elsewhere (Kusy 1987, Kusy and Listkiewicz 1988). Other authors suggest that electrical conduction is driven by the processes in a very small energy gap of width $\sim kT$ around the Fermi level of the glass. The impurity states may originate due to the creation of reactive layers on the interfaces between glass and RuO_2 grains. They reveal semiconducting characteristics (Abe *et al.* 1988). However, more likely is that they are formed by the diffusion of Ru atoms from the surface of RuO_2 grains. The latter process seems to be confirmed experimentally by Adachi *et al.* (1991) and has also been proposed by Kubový and Havlas (1988).

Our results do not reveal the Arrhenius behaviour, nor the behaviour typical of intergrain hopping (Abeles *et al.* 1975) and other models accounting for the exponent 1/2 (Pollak and Adkins 1992), nor variable range hopping (Mott 1968). We have tried to subdivide the negative TCR parts of the $R(T)$ curves to tend towards characteristics typical of the above phenomena, but with no effect. In fact, the change in resistance is relatively small over the whole range of temperatures used in our experiment. The biggest ratio of maximum to minimum resistances of slightly less than 2 was found for a composite of $v=0{\cdot}05$. This contradicts theories which anticipate change over decades of resistance.

Results of the optimization of experimental data by (1) yield another interesting conclusion which can be drawn from Fig. 3. According to Shklovskii and Efros

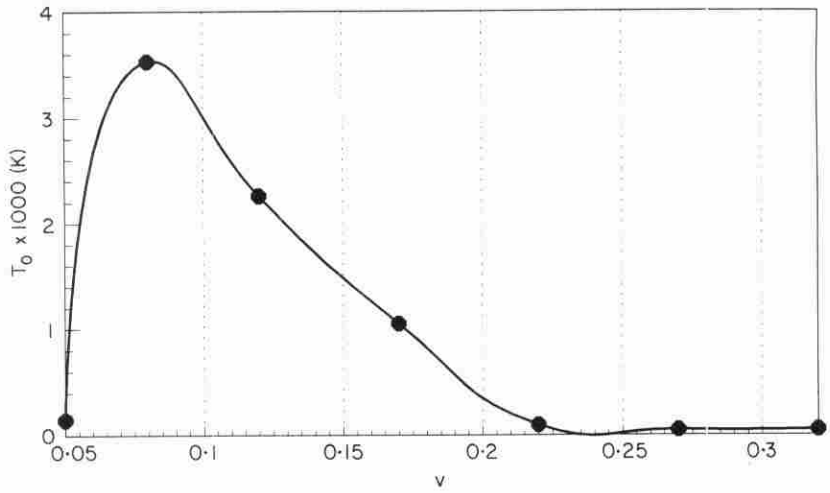

Figure 3. T_0 as a function of concentration of metallic component in a film. This parameter comes from optimizing experimental data from (1).

(1984), T_0 should decrease rapidly near the metal–insulator transition. Thus, the characteristic in Fig. 3 alludes to the statement that the investigated RuO_2-glass system reveals a metal–insulator transition region for $0{\cdot}08 < v < 0{\cdot}2$. It is a rather wide regime but this is in accordance with our earlier conclusions (Bobran and Kusy 1991, Bobran 1993). We identified the metal–insulator transition by observing qualitative changes in temperature characteristics measured in the range $77\,\mathrm{K} < T < 300\,\mathrm{K}$ for the series of composites. The other argument cited here in Fig. 4 is the S versus R curve, where S is the relative spectral power density of $1/f$

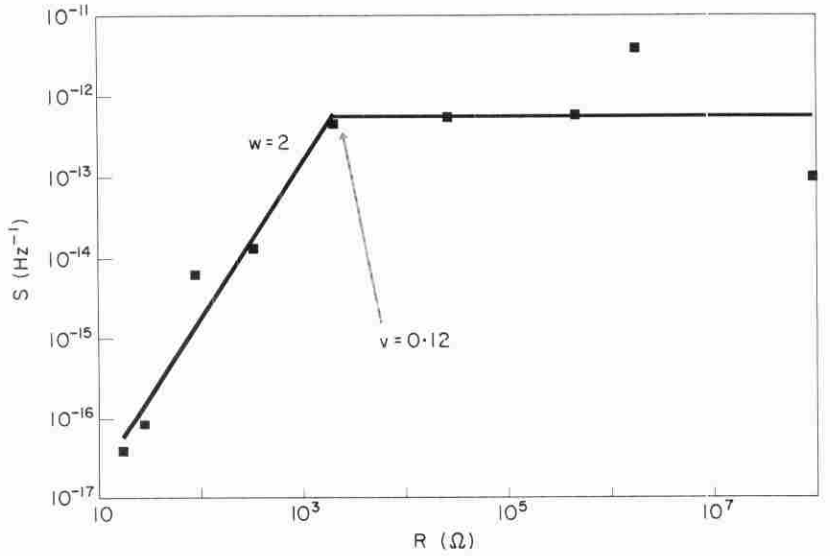

Figure 4. Relative spectral power density, S, of $1/f$ noise versus R. Both magnitudes are controlled solely by changing v.

resistance fluctuations, and both S and R are changed solely by changing v. It is seen that $v=0{\cdot}12$ is a critical concentration of RuO_2 responsible for a qualitative change of S versus R from the line of slope $w=2$ for small resistances towards the saturated region for larger resistances.

From the errors columns in the table it can be judged that only data for $v=0{\cdot}05$ are far better described by (1) than by (2). All other optimization results yielded similar errors both for (1) and (2). This is somewhat consistent with the result of Fig. 3 from which it was deduced that for $0{\cdot}08<v<0{\cdot}2$ both dielectric and metallic types of electrical conduction coexist, while $v=0{\cdot}05$ falls into dielectric regime. For $v=0{\cdot}32$ only a few data have been obtained for the negative TCR part of the R versus T curve ($T<30$ K) and more are needed for a more reliable interpretation.

Equation (2) has widely been used to describe weak localization and electron–electron interaction effects in two-dimensional films (e.g. Bergmann 1984, Lee and Ramakrishnan 1985). RuO_2-glass composites are three-dimensional. However they form a percolating mixture with high degree of segregation of conducting components (Pike 1978, Kusy and Kolek 1989). Thus some of their effective sizes for electrical transport may be of the same order as the film thickness. In general, temperature characteristics of resistance supported by appropriate magnetoresistance measurements allow us to distinguish some electrical conduction effects, e.g. positive magnetoresistance is expected for electron–electron interactions. Although it is known from the literature (Pike and Seager 1977) that magnetoresistance in thick resistive films is small and positive, more experiments need to be performed concerning the characteristics in magnetic fields at low temperatures to provide a more reliable interpretation of our results optimized by (2).

4. Conclusion

RuO_2-glass composites prepared by thick-film technology reveal a region of metal–insulator transition with concentrations of metallic component in the range $0{\cdot}8<v<0{\cdot}2$. Small activation energies obtained from R versus T measurements argue that electrical conduction is governed by a trade-off between the metallic properties of RuO_2 grains and the negative TCR properties of MIM structures or by impurity conduction of the glass.

For RuO_2 concentrations in the metal–insulator transition region, R versus T characteristics can be described equally by (1) and (2). Equation (2) is characteristic of electrical conduction of two-dimensional structures with weakly localized electrons and thick-film composites are three-dimensional, but RuO_2 composites are highly segregated structures and some of their effective sizes for electrical conduction may be of the same order as the film thickness.

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