Vol. **113** (2008) *ACTA PHYSICA POLONICA A* No. 1

Proceedings of the CSMAG'07 Conference, Košice, July 9–12, 2007

Microstructural Analysis and Transport Properties of RuO_2-Based Thick Film Resistors

S. Gabáni, K. Flachbart, V. Pavlík

Institute of Experimental Physics, Slovak Academy of Sciences
Watsonova 47, 04001 Košice, Slovakia

A. Pietriková

Department of Technologies in Electronics
Faculty of Electrical Engineering and Informatics
TU Košice, 04200 Košice, Slovakia

and M. Gabániová

Research and Development, U.S. Steel Košice, s.r.o., 04454 Košice, Slovakia

RuO_2-based low temperature sensors appear as very good secondary thermometers, mainly in the temperature range below 4.2 K. This is due to their high temperature sensitivity and small magnetoresistance. Both properties are strongly influenced by the manufacturing process (mainly by firing temperature and firing time). In our contribution we show that the microstructure of sensors and the temperature dependence of their resistance $R(T)$ down to 50 mK, in case when all sensors are prepared from the same paste, can be strongly influenced by change of the firing temperature from 800°C to 900°C. The paper also presents results on the X-ray microanalysis and the analysis of electrical conductivity of these sensors.

PACS numbers: 85.40.Xx, 72.80.–r, 73.40.Rw

1. Introduction

RuO_2-based thick film resistors are often used as secondary thermometers, mainly in the temperature range below 4.2 K. This is due to their relatively high temperature sensitivity and low dependence on applied magnetic field [1, 2].

Microstructural analysis of many samples prepared under usual conditions has shown [3, 4] that RuO_2 clusters with a mean size of 250 nm and comparatively

short inter-cluster distances are formed within the glass matrix. Each of these clusters consists of a large number of ultrafine RuO_2 particles (with a mean size of about 20 nm) separated by a glass layer less than 2 nm thick, i.e., the conductive metal oxide particles remain suspended in the dielectric glass matrix.

Different transport mechanisms controlled by the microstructure of thick film resistors have been identified [3] for various RuO_2 volume fractions f_{RuO_2}. In limiting cases of high and low RuO_2 content the metallic or ionic, respectively, transport prevails. For intermediate concentrations, $0.05 \leq f_{RuO_2} \leq 0.2$, hopping and tunnelling transport of charge carriers are superposed [3, 5, 6].

The aim of this work has been the investigation of electrical and structural properties of RuO_2-based resistors in dependence on the most important technology (processing) parameter — the firing temperature [7].

2. Experimental details

The RuO_2-based thick film resistors were prepared by standard screen printing technique from a commercial paste of sheet resistivity 10 k$\Omega/\Box$ produced by DuPont Electronics, USA. Recently it has been shown that the most pronounced change in the temperature dependence of resistance $R(T)$ was due to various firing temperature (the highest temperature, T_{peak}, in firing profile) [7]. Therefore, for our investigation RuO_2-based resistors with different firing profiles 60/15/800°C, 60/15/850°C and 60/15/900°C (total firing time in minutes/peak time in minutes/T_{peak}) were chosen. The temperature dependences of electrical resistance down to 50 mK were carried out in a ^{3}He–^{4}He dilution refrigerator. The sample resistance was measured in the four probe arrangement using an ac-resistance bridge. As thermometers commercially calibrated Lake Shore sensors were used. Structural and X-ray microanalysis were carried out by energy distribution X-ray (EDX) assisted scanning electron microscopy SEM (FEI EDAX).

3. Results and discussion

The received resistance ($R(T) \sim \exp(T_0/T)^x$) dependences, and from them calculated local activation energies $W(T) = \mathrm{d}(\ln R)/\mathrm{d}(1/kT)$ and logarithmic sensitivities $S(T) = x(T_0/T)^x$ (k is the Boltzmann constant, x and T_0 are characteristic parameters) exhibit significant changes for resistors prepared under various firing temperatures T_{peak} (see Fig. 1). The typical strong increase in $R(T)$ towards low T becomes less expressive with increasing T_{peak}. Moreover, if a resistor with firing profile 60/15/800°C is re-fired, but with $T_{\mathrm{peak}} = 900$°C, then its $R(T)$ behaviour becomes nearly same as for a resistor with original firing profile 60/15/900°C. This can be useful for tuning the $R(T)$ dependence of already produced RuO_2-based sensors. The acquired values of W are very small for all investigated sensors and never exceed 0.4 meV. Moreover, the greater T_{peak} is, the lower the corresponding $W(T)$ value becomes.

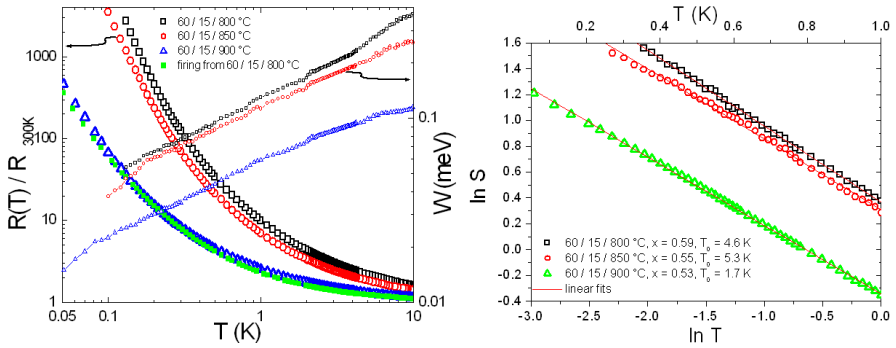

Fig. 1. Temperature dependences of relative resistance $R(T)/R_{300\ K}$, activation energy $W(T)$ and logarithmic sensitivity $S(T)$ for various firing profiles (60/15/800°C — squares, 60/15/850°C — circles and 60/15/900°C — triangles) of RuO_2 sensors preparation.

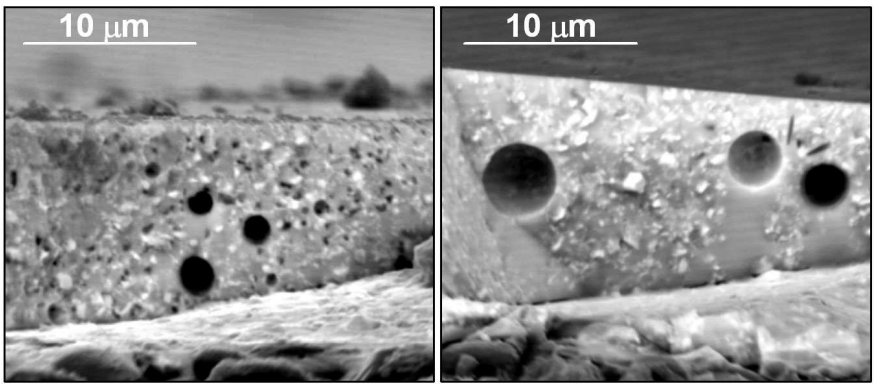

Fig. 2. Cross-section microstructure of RuO_2-based sensors with firing temperature of 800°C (left) and 900°C (right). RuO_2 grains (white particles) are distributed in glass matrix (shadow part). Black "particles" mean bubbles or cavities (vacuum).

The model, which has fitted best the $R(T)$ dependences at the lowest temperature, was the variable range hopping model ($R(T) \sim \exp(T_0/T)^x$). From the linear dependence of $\ln S(T) \sim (-x \ln T)$ (Fig. 1), parameters $x = 0.59$, 0.55, or 0.53 for resistor with $T_{\text{peak}} = 800$, 850, or 900°C, respectively, were received. It means that with increasing firing temperature the values of x become closer to 0.5, which corresponds to density of states variation at the Fermi level expected to result from repulsive Coulomb interaction between localised carriers (the Shklovskii–Efros hopping law) [7].

The reason for these behaviours of $R(T)$ and corresponding $W(T)$ and $S(T)$ is the most probably connected with the diffusion of Ru atoms or tiny RuO_2 particles from the surface of RuO_2 grains into the dielectric glass matrix and also additional diffusion of atoms from conductive Ag–Pd pads or Al_2O_3 substrate

[3, 5–7]. These diffused atoms can create impurity in-gap states in a very small energy gap of width $\sim kT$ around the Fermi level of the glass, and so lowers the activation energy for hopping (tunnelling).

In order to obtain additional information about the RuO_2-based sensors, microstructural analysis was performed. The surface and perpendicular cuts from the middle of two sensors with different firing temperature of 800°C and 900°C were observed (Fig. 2). SEM graphs show the differences in their granulate structure: a higher homogeneity (distribution of RuO_2 particles, less number of cavities and bubbles) and partially growth RuO_2 grains or catenation for sensors with the firing temperature of 900°C.

The most remarkable results of the X-ray analysis is the observation of presence of metallic atoms in the glass matrix and their concentration increase with increasing firing temperature, for example: Ru (5.9 → 6.2 wt%), Ag (1.0 → 1.7 wt%), Pd (1.0 → 1.6 wt%), Al (1.3 → 2.2 wt%), or C (2.6 → 6.4 wt%). Surface mapping by X-ray scanning confirmed the increase in Ru and Al atoms concentration in the glass matrix with increasing firing temperature.

Acknowledgments

This work was supported by the Slovak Scientific Grant Agency VEGA — contracts 2/7054, 1/3167/06 and APVV 51–016604, and by the contract I/2/2003 of the Slovak Academy of Sciences for the Centre of Excellence. Liquid nitrogen for experiments was sponsored by U.S. Steel Košice, s.r.o.

References

[1] L.G. Rubin, *Cryogenics* **37**, 341 (1997).

[2] I. Bat'ko, K. Flachbart, M. Somora, D. Vanický, *Cryogenics* **35**, 105 (1995).

[3] N. Nicoloso, A. LeCorre-Frisch, J. Maier, R. J. Brook, *Solid State Ionics* **75**, 211 (1995).

[4] T. Yamaguchi, Y. Nakamura, *J. Am. Ceram. Soc.* **78**, 1372 (1995).

[5] K. Flachbart, V. Pavlík, N. Tomašovičová, C.J. Adkins, M. Somora, J. Leib, G. Eska, *Physica Status Solidi B* **205**, 399 (1998).

[6] K. Bobran, A. Kusy, A.W. Stadler, G. Wilczynski, *Int. J. Electron.* **78**, 113 (1995).

[7] S. Gabáni, V. Pavlík, K. Flachbart, J. Varga, A. Pietriková, *Czech. J. Phys.* **54**, D663 (2004).