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Noise properties of Pb/Cd-free thick film resistors

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Abstract

Low-frequency noise spectroscopy has been used to examine noise properties of Pb/Cd-free RuO_2- and $CaRuO_3$-based thick films screen printed on alumina substrates. Experiments were performed in the temperature range 77–300 K and the frequency range 0.5–5000 Hz with multiterminal devices. The measured noise has been recognized as resistance noise that consists of background $1/f$ noise and components generated by several thermally activated noise sources (TANSs) of different activation energies. The total noise has been composed of the contributions generated in the resistive layer and in the resistive/conductive layers interface. These noise sources are non-uniformly distributed in the resistor volume. Noise intensity of new-resistive layers has been described by the noise parameter C_{bulk}. Pb/Cd-free layers turned out to be noisier than their Pb-containing counterparts; however, the removal of Pb and Cd from resistive composition is hardly responsible for the increase in the noise. In the case of RuO_2 layers noise increases most likely due to larger grain size of RuO_2 powder used to prepare resistive pastes. Information on the quality of the resistive-to-conductive layers interface occurred to be stored in the values of noise parameter C_{int}. Pb/Cd-free RuO_2-based resistive pastes form well-behaved interfaces with various Ag-based conductive pastes. In contrast, $CaRuO_3$-based paste forms bad contacts with AgPd terminations because the density of TANSs increases in the interface area.

(Some figures in this article are in colour only in the electronic version)

1. Introduction

Thick film resistors (TFRs) have a wide variety of applications. Developed over many years, they have achieved high quality and are commonly used in both commercial and specialized electronics. Their main features are a wide range of sheet resistances, high stability and low temperature coefficient of resistance (TCR). Even the noise figure, long considered as unsatisfactory, is now suppressed to acceptable levels. Materials used in cermet TFRs fabrication are RuO_2 and/or various ruthenates which are the ingredients of resistive pastes and Ag, Au, Pd and Pt which are contained in conductive pastes used for resistors' terminations. Both resistive and conductive pastes are also made of various kinds of glasses that usually contain Pb. Manufacturers optimized their products in order to offer systems of compatible pastes that form well matching resistive-to-conductive film interfaces as well as low ohmic, highly reliable joints with conventional Sn/Pb solders. The situation has changed only after the RoHS directive was introduced. First, the restrictions for the use of Pb-containing solders forced the manufacturers to work out new conductive pastes able to form good joints with Pb/Cd-free solders. Second, lead has started being eliminated from both conductive and resistive inks [1–5]. Consequently, new pastes

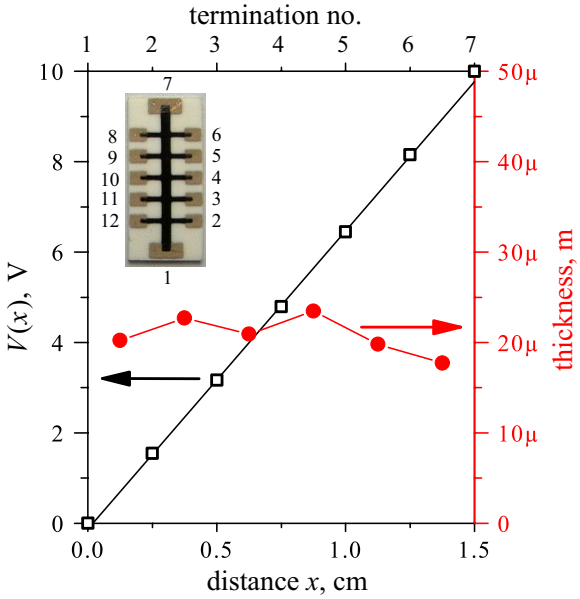

Figure 1. Layer thickness and voltage distribution $V(x)$ measured along the resistive layer of the sample P-202 Sz R-16-65 RuO_2. A solid line drawn through $V(x)$ data demonstrates that size effect is very small. The inset shows the sample's shape and contacts numbering scheme.

have recently appeared on the market, which are not as well described and optimized as their Pb-containing antecedents.

This paper explores the field of cermet TFRs manufactured with the use of novel materials prepared to fulfil the RoHS directive [2]. Several combinations of (i) resistive pastes made of RuO_2 or $CaRuO_3$ powder and glass of complex composition and (ii) conducting pastes based on Ag, Ag–Pd or Ag–AgPt–Pd have been used to manufacture TFRs on alumina substrates in the high-temperature process. We aim to provide a description and make an evaluation of the quality of the interface between resistive and conductive layers that form in these resistors. Our main experimental tool is the low-frequency noise spectroscopy (LFNS) which has recently been proved to be a very efficient method for such research [6–9]. This method enables the estimation of the noise parameters which qualitatively describe the strength of interaction between resistive and conductive layers as well as estimation of the noise index of the resistive layer itself which is also important, as in general there are a lack of studies on noise of Pb/Cd-free TFRs especially in a wide range of temperatures.

2. Samples

2.1. Geometry

Samples are designed as multiterminal devices. A resistive layer of $L = 15$ mm length and $w = 1$ mm width is terminated by two opposite current contacts and has several lateral voltage probes evenly spaced along both its sides. The advantage of such a geometry has been proved in many noise-oriented experiments [8, 10–13]. The shape of the sample TFR and contacts enumeration scheme are shown in the inset of figure 1.

2.2. Materials

The conducting constituent in resistive pastes is either RuO_2 or $CaRuO_3$. The mean grain size of RuO_2 powder has been estimated as $d \approx 1\,\mu$m [14]. The method of digital image processing and analysis was employed to obtain this value. For $CaRuO_3$ powder, the use of SEM allows the estimation of mean grain size of $d \approx 0.5\,\mu$m. $RuO_2/CaRuO_3$ powders are mixed together with Pb/Cd-free glass and ethylocellulose based organic vehicle to give resistive pastes containing 35%/27% of conductive phase by volume. Two types of glass were used. Both of them contain SiO_2, B_2O_3, Al_2O_3, V_2O_5, and metal oxides: either MgO, CaO, ZnO, Na_2O, K_2O (glass-R16) or BaO (glass-R10). Contacts to resistive films are made from Ag-based pastes. In particular, Ag, Ag–AgPt–Pd, and AgPd pastes were used as listed in table 1. All conductive and resistive pastes were developed as Pb/Cd-free materials according to the RoHS directive [15–17], and were produced at the Institute of Electronic Materials Technology (ITME), Warsaw, Poland. In table 1 samples used in this study, their description, details of fabrication and some features are collected.

2.3. Printing and firing

Resistive pastes were printed onto alumina substrates through a 200 mesh screen. After drying in 120 °C for 15 min, films were fired in a tunnel furnace gaining a final thickness of ~20 μm (figure 1). The process of firing followed a suitable temperature profile with the peak temperature at 850 °C lasting 10 min. Contacts to the films were made of conductive pastes in a very similar process. They were deposited onto substrates prior to resistive films printing.

2.4. Selection and entry tests

Several tens of resistors in six series have been manufactured. They were then aged at a temperature of 125 °C for 100 h. The drift of the resistance of RuO_2-based resistors was less than 0.1%, whereas for $CaRuO_3$-based resistors it usually exceeded 1%. In fact, out of three series of $CaRuO_3$-based resistors, only those with AgPd contacts survived the ageing, maintaining reasonable long-term stability. Therefore, only samples from this $CaRuO_3$-based series as well as samples from all three RuO_2-based series were used in noise measurements. For each series, one pair of samples that best match their resistance at room temperature was selected for further studies. The total resistance between terminations 1 and 7 ($R \equiv R_{1\text{–}7} = V_{1\text{–}7}/I$, where I is the biasing current and $V_{1\text{–}7}$ is the voltage between terminations 1–7) was used as a matching criterion. For all selected samples, voltage distribution along the resistive layer was measured (figure 1) to evaluate the size effect [8], and estimate sheet resistance R_{sq}. The size effect was calculated as the ratio of average resistance per square, $R_{1\text{–}7}w/L$, and 'bulk' sheet resistance $R_{sq} = V_{2\text{–}6}w/(L_{2\text{–}6}I)$, $L_{2\text{–}6}$ is the length of the sector 2–6 (i.e. the part of the main film that extends between contacts 2 and 6) and $V_{2\text{–}6}$ is the voltage across this sector. It stems from the data gathered in table 1 that for our Pb/Cd-free TFRs the size effect is negligible. The thickness of the

Table 1. Samples labelling and details.

Sample	Resistive paste: Conducting constituent	Resistive paste: Glass	Contacts: Conductive constituent	Contacts: Paste	Thickness (μm)	R_{sq} ($k\Omega$)	ρ (Ω cm)	Size effect
P-121 Sz R-16-65 RuO_2	RuO_2-35%	R-16	Ag	P-121	21.2	4.29	9.09	1.028
P-511 Sz R-16-65 RuO_2	RuO_2-35%	R-16	Ag–AgPt–Pd	P-511	20.4	4.28	8.77	1.028
P-202 Sz R-16-65 RuO_2	RuO_2-35%	R-16	AgPd	P-202	20.8	4.24	8.83	1.024
P-202 Sz R-10-73,5 $CaRuO_3$	$CaRuO_3$-26.5%	R-10	AgPd	P-202	20.7	17.53	36	1.035

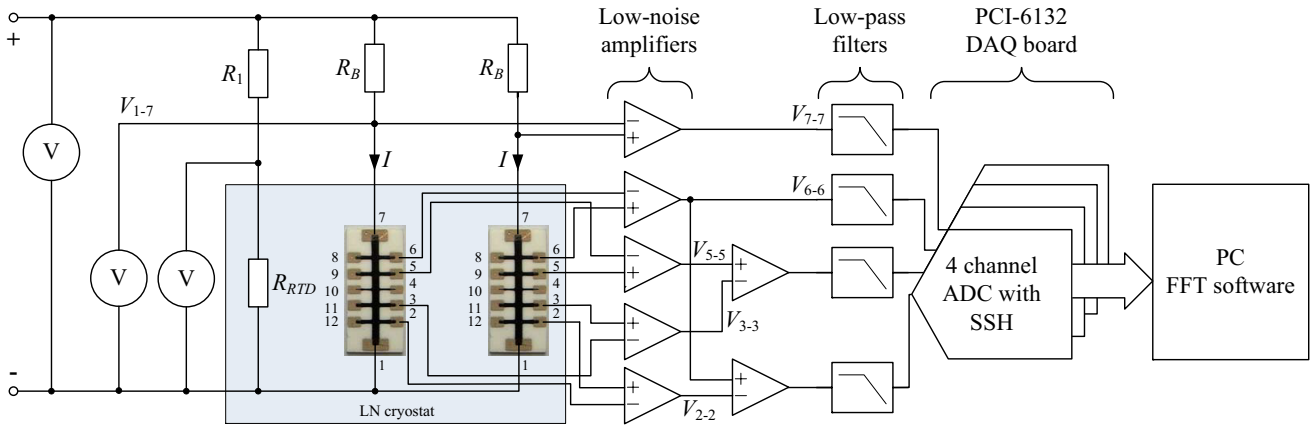

Figure 2. Measurement setup for low-frequency noise spectroscopy.

resistive film in between side probes was measured directly using a Vistronik C1 meter. The average film thickness was then used to calculate film resistivity ρ.

3. Noise measurements

3.1. Experimental setup

Low-frequency noise was measured in dc bridge configuration (see figure 2). A selected pair of samples was placed in the bottom arms of the bridge and biased through load resistors of much larger resistance. Only the samples and the calibrated temperature sensor (Pt-100 RTD) were inserted into an LN cryostat and subjected to cooling. The voltages from the bridge diagonal and sub-diagonals were conditioned in ac-coupled low-noise differential preamplifiers and low-pass filtered. A noise signal analyzer [18] was used to manage the experiment and calculate power spectral densities (PSDs) of measured voltages. Additional equipment shown in figure 2 was employed to monitor the actual temperature and record bias voltage and current. Everything was controlled via the GPIB interface.

The noise signal analyzer calculates the cross-power spectra of the voltages V_{X-Y} acquired from between a certain pair of voltage probes and the voltage V_{7-7} from between the terminations no 7. As the V_{2-2} contains a part of V_{7-7}, their cross-PSD refers to the fluctuations originated from these sectors of the resistors, which give a contribution to both voltages. This is illustrated in figure 3(a): PSD S_{2-2} measured (for different biases, $V \equiv V_{1-7} = 7.8$ V and $V = 0$) between the terminations no 2 refers to the noise signal generated in (i) contact no 1/main film interfaces, (ii) sectors 1–2 of the main resistive film, (iii) side legs no 2 that include resistive film lead and contact no 2. In contrast, cross-PSD of voltages V_{2-2} and V_{7-7} refers only to the signal generated in sectors 1–2 of the main film, so that $S_{2-2} > S_{2-2,7-7}$. As shown in figure 3(a), the difference is not much for biased samples as in this case the signal of component (ii) is much greater than the other two. However, the difference becomes quite large for $V = 0$, when all three components give signals of the same order.

In the experiment, noise generated in successive sectors of the resistor was of interest. Measurements have been made for sectors 1–7 (whole resistor), 1–6, 2–6, 3–5. Its PSD, S_V was measured with the cross-correlation method as described above. Among them, only sectors 2–6 and 3–5 have spectra that are free from noises generated in current and voltage contacts. Unlike these two, spectra acquired for sectors 1–7 include noise generated in both upper and lower current contacts, whereas spectra for sectors 1–6 contain noise generated only in lower current taps.

As shown in figure 3(a) noise spectra were measured for non-zero bias voltages (S_V) as well as with no bias (background noise $S_{V=0}$). Excess noise was then calculated as $S_{Vex}(f) = S_V(f) - S_{V=0}(f)$. Examples of the measured spectra are shown in figure 3(b): $1/f$ noise contributes most to non-equilibrium $S_V(f)$ dependence. Background noise in the case of cross-correlation measurements is dominated mainly by thermal noise of the resistors. Only for the spectra measured for the whole resistor is it described both by the source resistance and by the amplifier equivalent noise resistance, which is $\approx$1.1 kΩ. The spectrum $S_{V=0}$ shown in figure 3(b) refers to this case. As shown, $1/f$ background noise dominates

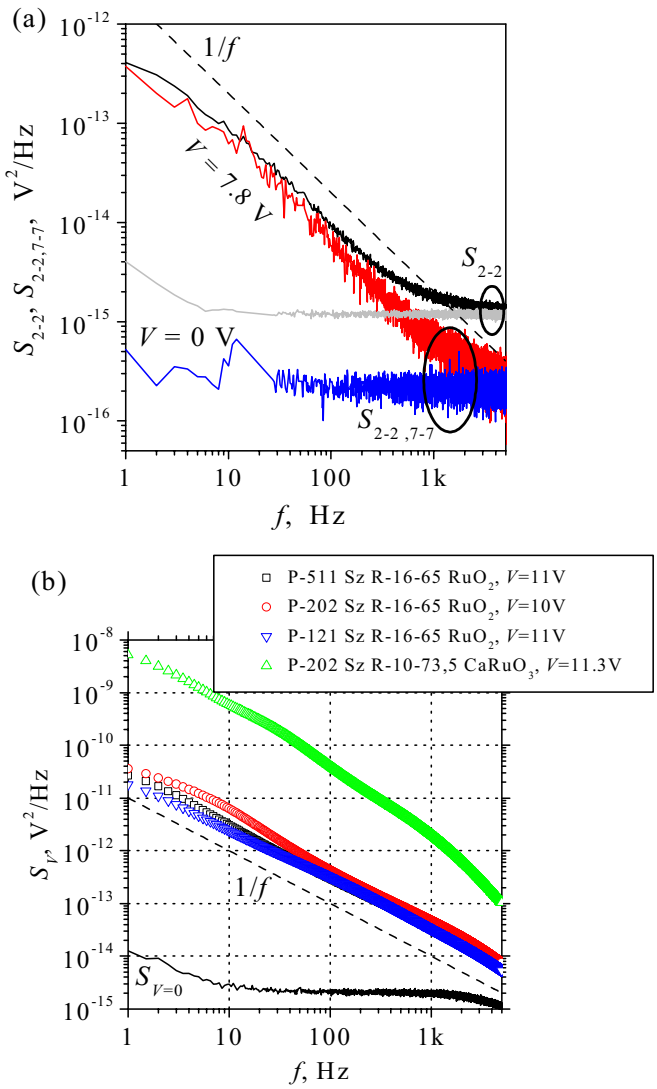

Figure 3. (*a*) PSD of voltage fluctuations measured directly at contacts 2–2 and cross-PSD measured for voltages V_{2-2} and V_{7-7}. Both were measured with bias ($V = 7.8$ V) and with no bias ($V = 0$) (*b*) Noise spectra measured at room temperature (symbols). Solid line shows background noise for the sample P-121 Sz R-16-65 RuO_2. In (*a*) and (*b*) dashed line shows the spectrum of pure $1/f$ noise.

only below 10 Hz and is much lower than the noise of the biased samples.

All signals are sampled simultaneously and spectra are calculated in real time in a frequency range from 0.5 Hz to 5 kHz with 0.5 Hz resolution employing 2^{19} point FFT. Only low-frequency part 0.5–5000 Hz is recorded for further processing.

3.2. Low-frequency noise spectroscopy

LFNS was used in the investigations of e.g. semiconductor materials and devices [19], UV detectors [20], gas sensors [21] and TFRs [6–8, 10, 11]. This method examines the evolution of low-frequency noise spectrum as a function of temperature. In our experiment, noise spectra were measured as a function of slowly ramping temperature in the range 77–300 K. Noise

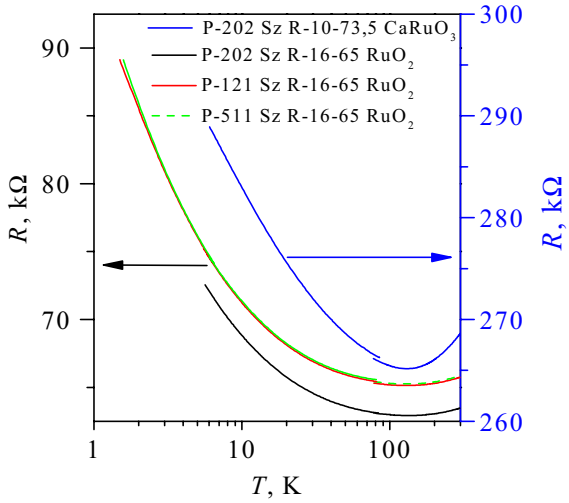

Figure 4. Resistance R versus temperature. In the range 77–300 K, resistances and noise spectra were measured simultaneously.

data are presented in the form of noise maps, i.e. 2D contour graphs of the product $f S_R(f)$ versus frequency and reciprocal temperature [7, 10, 11]. Sample noise maps are shown in figure 5. During these measurements, the resistance R of the samples was also recorded. R versus T curves obtained in these experiments are shown in figure 4. Below 77 K, $R(T)$ was measured in a helium cryostat.

4. Results and discussion

4.1. Resistance fluctuations

The dependence of noise intensity on the excitation voltage (or current) is one of the major tests for noise identification. Since noise spectra may include components like $1/f$ and/or Lorentzians, it is desirable to perform this test with respect to noise power in different frequency bands. Sample results are illustrated in figure 6 where the product $f S_{Vex}(f)$ averaged in frequency bands (decades) is plotted versus the bias voltage. Lines, if drawn through the points, would have a slope of 2. Thus, all parts of the spectrum depend linearly on excitation voltage square, which is a sign that all components of the noise originate from resistance fluctuations (resistance noise) [22]. PSD of these fluctuations can be calculated as $S_R(f) = S_{Vex}(f)/I^2$. This quantity is bias independent, and hence the spectra $S_R(f)$ are used in LFNS. Physical mechanisms that can lead to resistance fluctuations in TFRs were discussed in [7]. It stems from that discussion that fluctuating mobility is responsible for these fluctuations.

4.2. Thermally activated noise sources (TANSs)

The use of LFNS makes possible identification of TANSs in the measured noise signal and estimation of their activation energy E_a. On the maps like these in figure 5, TANSs appear as streaks [7, 23], whereas a smooth surface between the streaks refers to pure $1/f$ noise. The value of E_a can be calculated from the slope of the streak [6, 23]. Each value of the activation energy is associated with a two-state system localized in grain

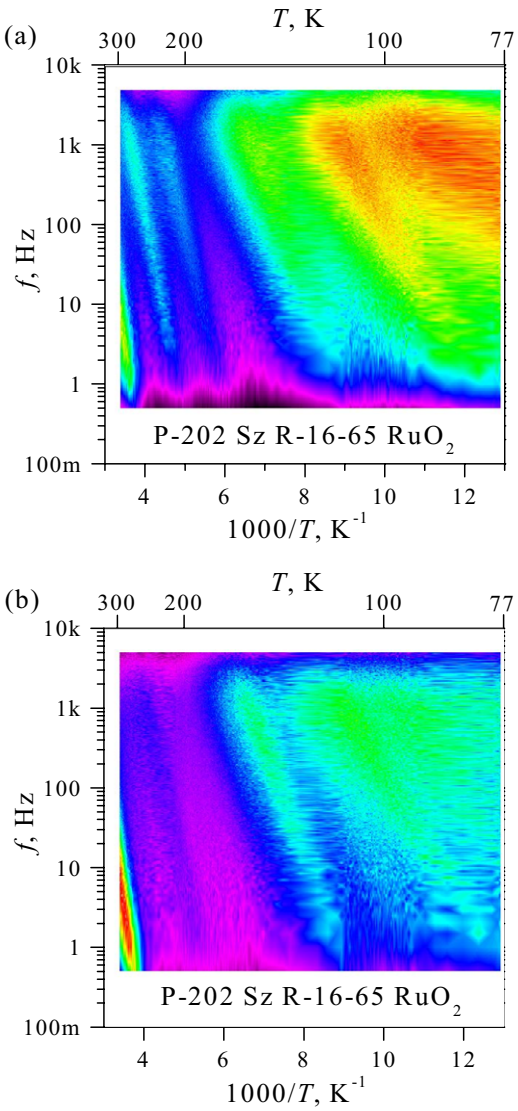

Figure 5. 2D filled contour graphs of the product $fS_R(f)$ versus frequency and reciprocal temperature (noise maps) measured for the sample P-202 Sz R-16-65 RuO_2. Maps were made of the spectra measured for sectors 1–7 (*a*) and 3–5 (*b*).

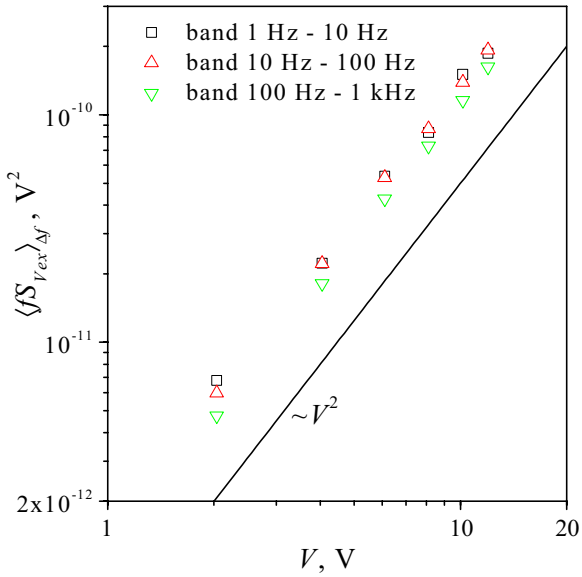

Figure 6. The product $fS_{V_{ex}}(f)$ averaged $\langle\rangle$ over frequency decades versus the bias voltage. Solid line indicates proportionality to V^2. The measurements were performed at room temperature for the sample P-121 Sz R-16-65 RuO_2.

boundaries and/or in the glass [7]. Transitions in these systems are thermally activated. They couple to (modulate) the local resistances. Only those that modulate critical resistances in the percolation path [24] contribute significantly to the overall resistance and can be detected in noise measurements. Therefore, merely few activation energies are observed for individual samples. The discrete set of their values differs from sample to sample but all values of E_a found in this work fall into the range 0.083–0.74 eV. These values are a bit lower than the value $E_a \approx 1.15$ eV found in [25], but fit well within the range of activation energies found in [7, 10, 26] for Pb-containing TFRs. For definiteness, one should note, however, that in [25] measurements cover a temperature range up to 800 K, where different TANSs are active.

Apart from detection of TANSs and their activation energies, noise maps give a more informative view on fluctuating phenomena that take place in TFRs. Noise maps shown in figure 5 refer to different sectors of the same resistor. The map of figure 5(*a*) refers to resistance fluctuations measured for sectors 1–7 whereas the map of figure 5(*b*) refers to internal sectors 3–5. Data on both maps were gathered simultaneously. As different streaks appear in figures 5(*a*) and (*b*) it is obvious that the intensity and number of TANSs vary from sector to sector. In other words, TANSs (and the corresponding two-state systems) are randomly distributed inside the resistor.

Another interesting phenomenon observed on the noise maps is spectra switching. It vertically 'cuts' the maps and divides the streaks into separate pieces (see figure 7). Physically, this means that at a certain temperature the TANS is accidentally turned on/off in a sharp manner. Possible reasons for this process were discussed in [8, 10] and involve dynamic current redistribution due to stress relaxation, and/or interacting fluctuators. Briefly, when current is redistributed (topology of percolation cluster changes) certain TANSs become more distant from the percolation network, hence they can no longer modulate critical resistances in this network and can no longer be observed as the fluctuations at the overall resistance. In our experiments spectra switching has not been observed for RuO_2-based TFRs. For $CaRuO_3$-based TFRs series, switching of the spectra was observed in the temperature range 150–160 K. It is interesting that in different cooling–heating cycles the switching of the spectra always took place in the same temperature range. As shown in figure 7, in different experiments the TANS of different activation energies and intensities appears. This means that the process of switching can turn on/off the TANS also in a time scale that exceeds a single experiment; that is, it is non-stationary in this time scale.

4.3. Noise scaling and decomposition

The intensity of all noise sources localized in a resistor's sector is given by the power of its resistance fluctuations $\langle \delta R^2 \rangle$.

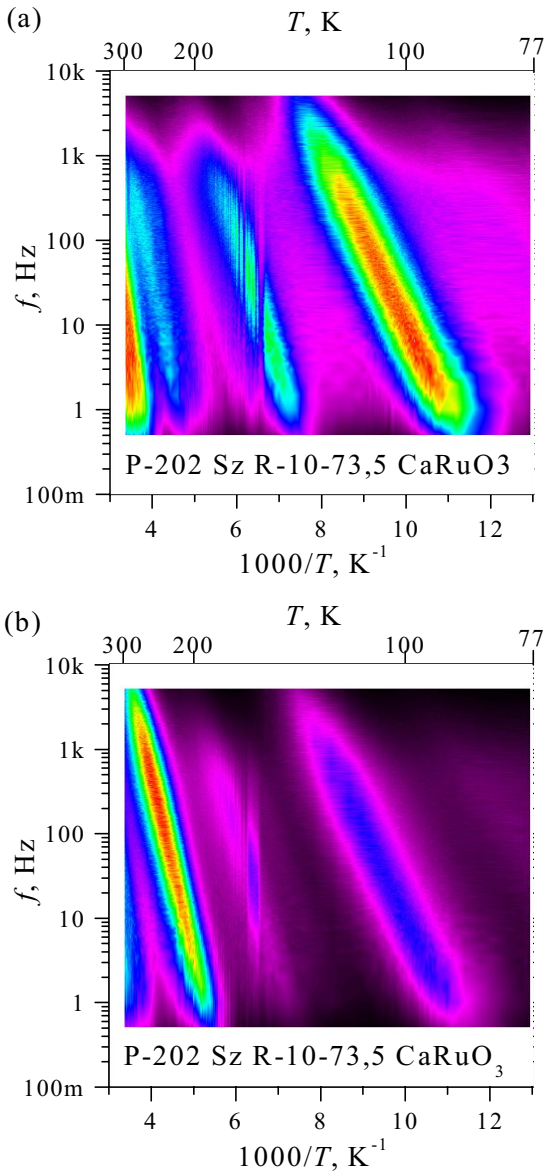

Figure 7. Noise maps for the sample P-202 Sz R-10-73,5 $CaRuO_3$, measured for sector 1–7 in two different experiments.

Exemplary plots of $\langle \delta R^2 \rangle$ versus temperature are shown in figure 8. As noise maps are sample dependent, so are the plots $\langle \delta R^2 \rangle(T)$. That is why the plots for RuO_2-based TFRs in figure 8 are different: different contacts are hardly responsible for these differences. For a $CaRuO_3$-based sample the number of TANSs, and the intensity of the noise they generate, increase in the sector close to the upper (no 7) resistor termination. For the remaining samples the density of the TANS in a resistor volume is more or less homogeneous. To prove it, the integral measure of noise [8],

$$s \equiv \frac{1}{T_2 - T_1} \int_{T_1}^{T_2} \int_{f_l}^{f_u} S_R(f, T) \mathrm{d}f \, \mathrm{d}T, \qquad (1)$$

was scaled versus the sector size. The integration in equation (1) should be over the surface as broad as possible. However, the measurement conditions describe the frequency and temperature limits of the integral: the frequency band 10–100 Hz has been chosen in order to omit (i) distortion of the spectra in the low-frequency limit caused by temperature drift, (ii) overlapping $1/f$ resistance noise by thermal noise in the high-frequency limit [8]. The temperature range 77–300 K was used due to the cryostat capabilities. Plotting the integral s versus the sector size enables decomposition of the measured noise into bulk and contact components. The approach is illustrated in figure 9 where the plots for the samples P-202 Sz R-16-65 RuO_2 and P-202 Sz R-10-73,5 $CaRuO_3$ are shown. The points referred to the internal sectors of the resistor very tightly follow straight lines that start at the plot origin. Such a linear increase in noise intensity is expected for spatially uncorrelated noise sources. The slope of the line gives bulk noise per square s_{sq} that can be used to calculate dimension-independent bulk noise intensity $C_{bulk} \equiv s_{sq}/R_{sq}^2 \times \Omega_{sq}$, where Ω_{sq} is the square volume. Parameter C_{bulk} is very helpful when comparing noise properties of different materials [8, 27, 28].

The noise generated in the interfaces of both current contacts can be evaluated as a difference between noise intensity measured for the whole resistor, s_{1-7}, and extrapolated bulk noise $s_{bulk} = L/w \times s_{sq}$. Namely $2s_{int} = s_{1-7} - s_{bulk}$. The 'quality' of the interface is described by contact-geometry-independent parameter, $C_{int} \equiv w s_{int}/s_{sq}$ [8]. Numerically, its value is the length of the hypothetical resistive film, which would have the noise intensity equal to the intensity of the interface noise. Parameters C_{bulk} and C_{int} have been calculated and are collected in table 2.

Due to the non-stationary behaviour observed for $CaRuO_3$-based samples, numerical values of integral s obtained for this resistor in different experiments are different. This explains scattering in the values of s observed for this sample in figure 9. The scattering is the largest for the value of s_{1-7}, which means that most non-stationary switchings occur in the interfaces. For other samples, the values of s_K are not scattered. As they were obtained for different bias voltages this is in line with the conclusion that stationary resistance fluctuations are the origin of the noise.

4.4. Noise of resistive films

It has been shown by means of theoretical considerations [29, 30] and verified experimentally [29, 31] that bulk noise of TFRs is proportional to resistivity ρ, $C_{bulk} = K'\rho$, when resistivity is changed by the content of conductive constituent of the resistive paste. As in this study samples with different $RuO_2/CaRuO_3$ contents are not available, we refer to our previous work of [8] in order to compare bulk noise of Pb/Cd-free compositions with its Pb-containing antecedents. In figure 10, data for TFRs studied in [8] have been plotted together with the current data, all as C_{bulk} versus resistivity. One can see that noise of $CaRuO_3$ films is the largest also when compared with non-Pb/Cd-free TFRs. Note, however, that resistivity of these films is relatively high.

Regarding Pb/Cd-free RuO_2-based resistive films, experimental points in figure 10 lie on the line with $K' = 2 \times 10^{-9}\,\mu\mathrm{m}^2\,\Omega^{-1}$, which is almost an order of magnitude larger than the value $K' = 4 \times 10^{-10}\,\mu\mathrm{m}^2\,\Omega^{-1}$ found in [8] for Pb-containing RuO_2 films. One may ask why such a large

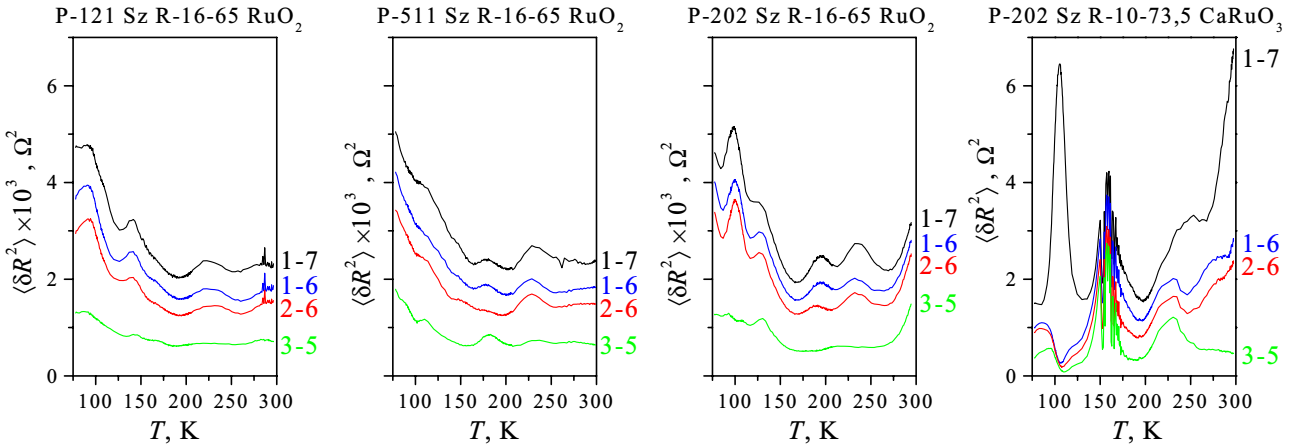

Figure 8. The power of resistance fluctuations $\langle \delta R^2 \rangle$ in band 10–100 Hz versus temperature for different sectors of the samples. All three graphs for RuO_2-based TFRs have identical vertical scale. $CaRuO_3$-based TFR has the values of $\langle \delta R^2 \rangle$ larger by three orders of magnitude.

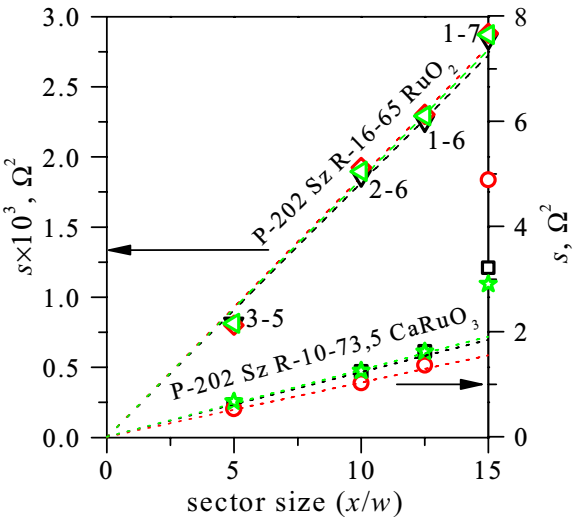

Figure 9. The integral s versus sector size (expressed in the number of squares in the sector). Different symbols refer to different measurements (cool–warm cycles) with different bias voltages. Sectors are labelled near RuO_2 series.

discrepancy appears. In our opinion the reason for this is the difference in RuO_2 grain size in resistive films studied in [8] where $d \approx 10$ nm and in this work, where $d \approx 1\,\mu$m. Although there are only a few studies concerning the influence of grain size on noise of TFR [29–33], it has been argued that increase in the grain size results in both larger resistivity [31–33] and bulk noise. From a theoretical point of view the relations $\rho \sim d$, $C_{\text{bulk}} \sim d^3$, and thus $C_{\text{bulk}} \sim \rho^3$ are expected when ρ is driven solely by the grain size of the conductive powder [30, 31]. Experimentally, the increase in sheet resistance with conductive constituent grain size was observed, e.g. in [29–33]. Much less frequent are noise versus grain size measurements. For $Bi_2Ru_2O_7$-based films the relation $C_{\text{bulk}} \sim R_{\text{sq}}^{2.4}$ was found in [31]. In [33, 34] an increase in noise intensity with an increase in grain size was observed for RuO_2-based TFRs. Obviously, our data are not rich enough to definitely and quantitatively verify the hypothesis, but it seems that increase in the value of C_{bulk} observed for our Pb/Cd-free RuO_2 films is caused by the increase in conductive constituent grain size rather than by Pb removal.

4.5. Interface noise

The parameter C_{int} can be used to evaluate the usefulness of various combinations of resistive and conductive pastes in forming well-behaved resistive/conductive films interfaces. A relatively large value of C_{int} indicates that the contact significantly contributes to the noise of the resistor, degrading performance characteristics of the device. Analysing the values of C_{int} gathered in table 2, one can conclude that Pb/Cd-free RuO_2 films form well-behaved contacts made of various Ag-based conductive pastes. On the other hand, the interface of the $CaRuO_3$-based sample is poor: $CaRuO_3$ films should not be terminated with AgPd contacts.

5. Summary

The LFNS technique was applied to study noise properties and evaluate systems of materials to be used in RoHS compliant TFRs technology. Four samples made of different combinations of Pb/Cd-free resistive and conductive pastes were examined in the temperature range 77–300 K. Two basic components of low-frequency noise were detected, namely $1/f$ noise and TANSs, each of which is resistance noise. In every sample, several TANSs were observed. Their activation energies seem to be resistor rather than material specific. TANSs were found to be non-uniformly distributed in the resistor volume.

Pb/Cd-free RuO_2-based resistive pastes form well-behaved interfaces with various Ag-based conductive pastes. In contrast, $CaRuO_3$-based paste forms bad contacts with AgPd terminations because the density of TANSs increases in the interface area. This knowledge will certainly be helpful in further optimization of materials systems used in the fabrication of Pb/Cd-free low-noise, stable and reliable TFRs. It could have been gained despite the fact that in all our samples the size effect, estimated from ordinary resistance measurements (table 1), was negligible. We came to these

Table 2. Noise parameters of Pb/Cd-free TFRs.

	Sample			
	P-121 Sz R-16-65 RuO_2	P-511 Sz R-16-65 RuO_2	P-202 Sz R-16-65 RuO_2	P-202 Sz R-10-73,5 $CaRuO_3$
$C_{bulk} \times 10^{24}$ (m^3)	198	190	215	8571
C_{int} (mm)	0.56	0.77	0.25	3.92

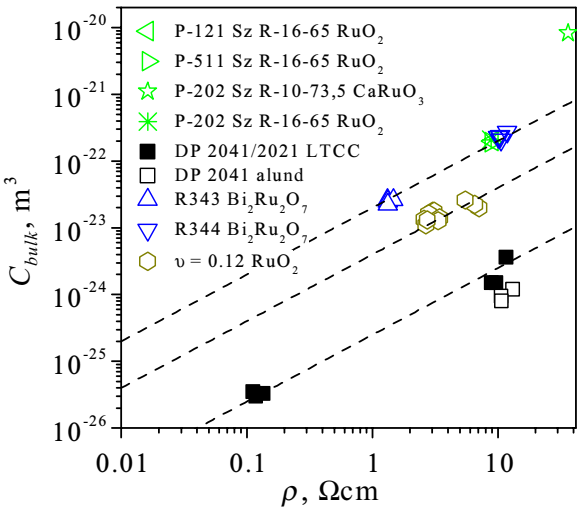

Figure 10. Comparison of the bulk noise of various TFRs. Lines are the plots of relation $C_{bulk} = K'\rho$ with different values of the coefficient K'.

conclusions due to the advantages of the research method we used. The information about the quality of resistive-to-conductive layers interface was stored in the values of noise parameter C_{int}.

The noise intensity of new-resistive layers has been described by another noise parameter, C_{bulk}. Its values have been calculated and compared with those available in the literature [8]. Pb/Cd-free layers were noisier than their Pb-containing counterparts; however, the removal of Pb and Cd from resistive composition is hardly responsible for the increase in the noise. Although for $CaRuO_3$ layers noise data are not available at all, in the case of RuO_2 layers noise increases most likely due to larger grain size of RuO_2 powder used to prepare resistive pastes.

The values of parameters C_{int} and/or C_{bulk} contribute to the noise index of a resistor—an important parameter for its applications and a valuable indicator of its reliability, long-term drift and lifetime [35] and an efficient tool in failure prediction of electron devices and circuits [36–38].

The region of low temperatures explored in the paper is of special interest as, since the 1970's, TFRs have entered the field of cryogenics, where they are used as temperature sensors [39–43]. They exhibit large sensitivity to temperature changes due to the resistance sharply increasing below several kelvin. Physical reasons for this increase are unknown. Thermally activated tunnelling [44], fluctuation-induced tunnelling [45, 46], conduction in a narrow band [47], variable range hopping (VRH) [48, 49], space charge limited transport [50], emissions over graded barriers [46] and weak localization [51] are considered as transport mechanisms—none is able to fully explain the feature. Our present results add a contribution to the practical aspect of the field: Pb/Cd-free compositions can be used as thermo-sensing layers in cryogenic RTD's. From figure 4 one can deduce that below 10 K these compositions maintain high sensitivity to temperature changes.

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