

ENVIRONMENTAL FRIENDLY THICK FILM RESISTORS WITH WIDE RESISTANCE RANGE

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This paper presents the results on investigation of lead-free and cadmium-free resistive paste compositions based on calcium ruthenate (CaRuO_3) and ruthenium dioxide (RuO_2), that sheet resistance exceeds $10 \text{ k}\Omega/\text{q}$. Two regulations: *Waste Electrical and Electronic Equipment Directive* (WEEE), and *Restriction of Hazardous Substances* (RoHS) were established on July the 1st 2006. They forced the electronics equipment producers to discontinue using lead, cadmium and a few other substances. The *Surface Mounted Devices* (SMD) resistors, that exist in almost every modern electronic device contain thick film resistive layer, according to new regulations cannot contain hazardous substances. The series of new RoHS compliant resistor pastes with resistance range $10 \Omega/\text{q}$ - $10 \text{ k}\Omega/\text{q}$ were elaborated by the authors in 2007. The RuO_2 was used as a functional component. However the consumers expect the resistor pastes with the sheet resistance in the range $10 \Omega/\text{q}$ - $1 \text{ M}\Omega/\text{q}$. Such a resistance range was available using old lead-containing glass and a functional phase containing bismuth ruthenate. However it is considered that such wide resistance range can not be obtained with the use of RuO_2 and lead-free glasses. Therefore the authors decided to use calcium ruthenate that exhibits higher resistivity than RuO_2 . The authors used successfully some lead-free glasses that were compatible with ruthenium dioxide as well as investigated completely new glass compositions. The use of CaRuO_3 instead of RuO_2 in the same lead-free glass increased the obtained sheet resistance about 500 times with no negative impact on *Temperature Coefficient of Resistance* (TCR). No humidity sensitivity was observed. The resistors' SEM surface and fractures was taken. The length effect on TCR was measured.

Key words: RoHS, ruthenium, thick film resistor

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1. INTRODUCTION

Two regulations: Waste Electrical and Electronic Equipment Directive (WEEE), and Restriction of Hazardous Substances (RoHS) was established on July the 1st 2006. They forced the electronics equipment producers to discontinue using lead, cadmium and a few other substances. The SMD resistors, that exist in almost every modern electronic device contain thick film resistive layer, that according to new regulations cannot contain hazardous substances.

Two years after the RoHS and WEEE regulations were launched there are no lead-free thick film resistor pastes which would cover all customer's demands. The world's biggest pastes producers have started offering lead free resistor pastes for sale, however the sheet resistance range of that pastes is very narrow and covers only the low ohm values from $1 \Omega/\square$ to $10 \Omega/\square$ [1]. Moreover the producer recommends this product only for low stability and with limited precision demanding purposes like heaters, lightning and surge arrest protection applications. Customers expect the resistance values at least up to $100 \text{ k}\Omega/\square$ with TCRs (*Temperature Coefficient of Resistance*) within $-200 \div +200 \text{ ppm}/^\circ\text{C}$. The thick film resistors that were based on lead oxide glasses, for example R-340 resistor series by ITME, filled the range between 10Ω to $1 \text{ M}\Omega$. For long time, there was no alternative for RuO_2 powder regarding lead-free resistor. According to investigations described in [2-3] the resistors based on RuO_2 powder provide good electrical properties up to $1 \text{ k}\Omega/\square$, while the higher resistances were difficult to achieve and their stability was not good enough. The resistors showed in [4] proved that it is possible to achieve stable thick-film resistors in the range from $10 \Omega/\square$ up to $10 \text{ k}\Omega/\square$ using lead and cadmium free glass and RuO_2 powder. In [3] the authors obtained calcium ruthenate and used it in resistor pastes. However the achieved sheet resistance was at most $2 \text{ k}\Omega/\square$.

The authors of this paper present the results of investigations CaRuO_3 and RuO_2 based resistive compositions with various glasses in respect of obtaining pastes with over $10 \text{ k}\Omega/\square$ sheet resistances.

2. EXPERIMENTAL

The thick film resistor paste consists of conductive phase (Ru based), lead and cadmium free glass and organic vehicle.

2.1. Conductive phase

The authors used two different Ru-compounds for resistor paste preparation: one RuO_2 and second CaRuO_3 .

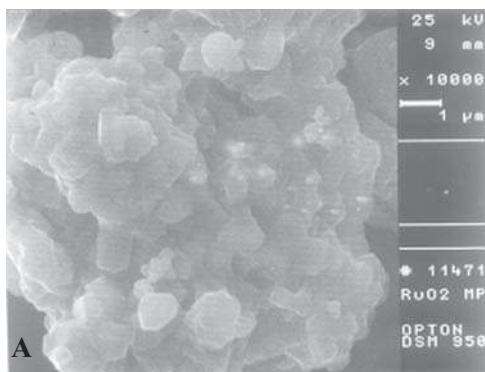


Fig. 1A. SEM picture of a pure RuO₂ powder.

Rys. 1A. Zdjęcie SEM surowego proszku RuO₂

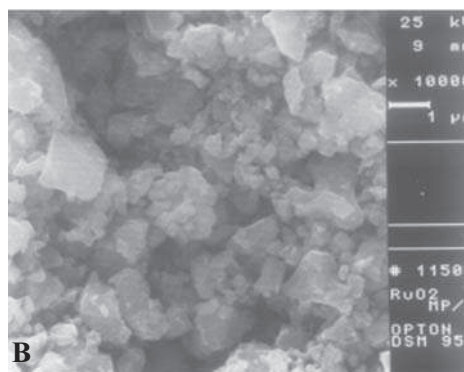
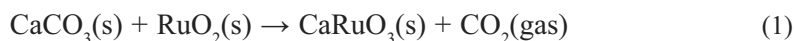


Fig. 1B. SEM picture of a milled and sieved RuO₂ powder.

Rys. 1B. Zdjęcie SEM proszku RuO₂ po mieleniu i przesiewaniu.

RuO₂ powder was delivered by Polish State Mint. The SEM photographs of unprocessed powder is presented in Fig. 1A. The average grain size was 2 μm. The upper acceptable limit of grain size for resistive paste is 1 μm, therefore the powder was processed in ball mill for 48 hours. After sieving through 0,028 mm mesh screen, the powder was ready for the thick film compositions. The SEM of a post processed RuO₂ powder is presented in Fig. 1B. After processing the average grain size decreased to 1 μm.

The CaRuO₃ powder was obtained by the authors from RuO₂ powder by a chemical reaction:



The reaction was performed in a solid state by grinding stoichiometric amounts of RuO₂ and CaCO₃ in acetone, drying at 100°C and then sintered. The process was carried under four different conditions, at temperatures: 925, 1000, 1100, 1150°C. Each sample was annealed for 6 hours. Reaction of CaCO₃ according to (1), accompanied by CO₂ evolution, causing decrease of the sample mass.

The mass loss is a good indicator of a reaction progress. The theoretical maximum weight loss is equal to 18,88%. The dependence between the annealing temperature and weight loss is presented in Fig. 2. The maximum weight loss is reached at temperatures between 1100 and 1150°C. Further temperature increase does not improve the reaction progress. The effect of annealing time on the weight loss was also investigated. The total 14 hours of annealing in 1100°C brings insignificant change below 0,1% in weight loss. Basing on these results the temperature 1100°C and annealing time 6 hours have been chosen for resistors preparation. This procedure leads to maximum empirical weight loss 19,2% which is 0,3% more than theoretical one. The difference could be a result of incomplete water removal .

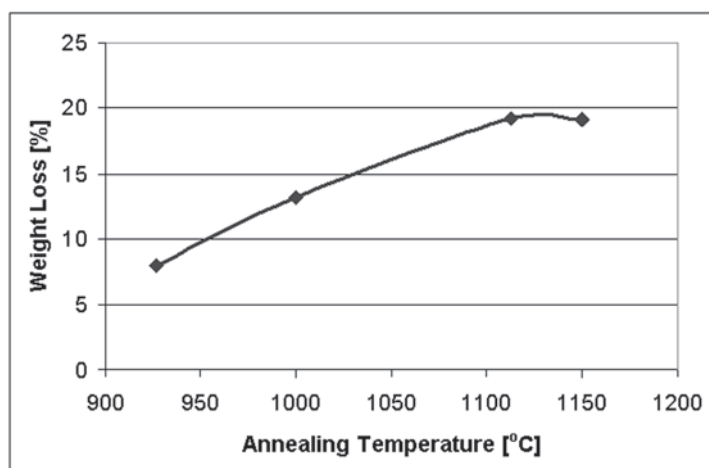


Fig. 2. Weight loss vs. annealing temperature dependence.

Rys. 2. Zależność utraty masy w funkcji temperatury wygrzewania.

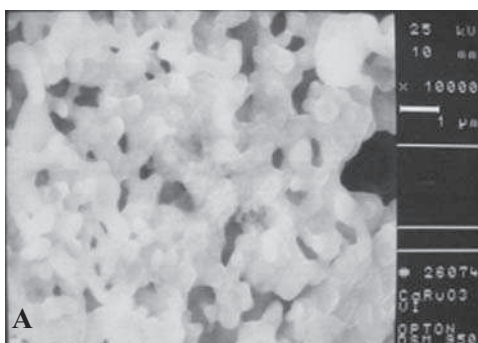


Fig. 3A. SEM picture of a pure CaRuO_3 .

Rys. 3A. Zdjęcie SEM surowego proszku CaRuO_3 .

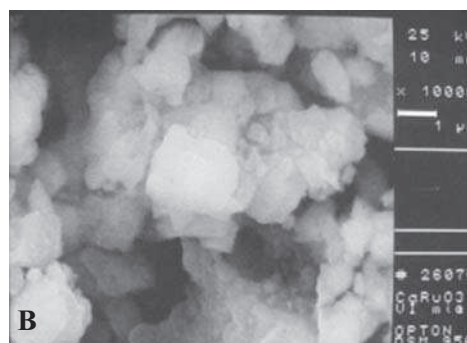


Fig. 3B. SEM picture of a milled and sieved CaRuO_3 powder.

Rys. 3B. Zdjęcie SEM proszku CaRuO_3 po mieleniu i przesiewaniu.

SEM picture of obtained CaRuO_3 powder is presented in Fig. 3A. The powder has smaller average grain size (below $1 \mu\text{m}$) than previously used RuO_2 . Nevertheless, this powder was milled for 8 hours to decrease grain size deviations. The SEM picture of processed CaRuO_3 powder is presented in Fig. 3B. The aggregates of particles, up to $3 \mu\text{m}$, were observed as a result of humidity interference.

2.2. Glass

Two Pb-free borosilicate glass compositions were used. Glass 1 contains BaO modifier while Glass 2 contains CaO modifier and other additives. These metal oxides are used to prevent the release of RuO₂ as the result of CaRuO₃ dissociation, in course of firing of the resistor.

Table 1. Characteristic temperatures of used glass.

Tabela 1. Temperatury charakterystyczne użytych szkliw.

Glass no.	Softening temperature	Melting temperature
Glass 1	740°C	810°C
Glass 2	700°C	840°C

The characteristic temperatures of both glasses are very similar (Tab. 1). The amount of modifiers in glass was optimized to govern the melting temperature slightly below firing temperature that was 850°C.

2.3. Organic vehicle

The organic vehicle was based on ethylcellulose in solvents with high boiling temperature. The composition and properties are similar to those used in lead containing resistive pastes (in R-340 by ITME).

2.4. Preparation

The lead-free silver-palladium-platinum conductive paste (P-511 of ITME) was used for resistor termination. This paste is compatible with lead-free solders [5] and exhibits similar resistance to migration as standard silver-palladium paste.

The resistive films were prepared using RuO₂ and CaRuO₃ powders. Each powder was mixed with Glass 1 and Glass 2, thus resulting in four resistor composition. The ratio of glass/conductive phase (expressed in percents) has been varied. The all compositions used in experiment are presented in Tab. 2.

Table 2. Investigated glasses and functional phases compositions.

Tabela 2. Badane mieszaniny szkliw i faz przewodzących.

Glass + functional phase composition	Investigated range of glass content
Glass 1 + RuO ₂	44% - 75%
Glass 1 + CaRuO ₃	60% - 75%
Glass 2 + RuO ₂	60% - 75%
Glass 2 + CaRuO ₃	60% - 75%

The conductive and resistive layers were prepared subsequently: screen printing (AMI Presco type 242) on alumina substrate (0,63 mm thick), drying at 125°C for 30 minutes and firing in BTU 41-654 belt furnace at standard 60 minutes profile at the peak temperature 850°C.

The pattern for thick films included resistors of various lengths (1,2,3,4 mm). The resistive layer overlapped the conductive layer for 0,25 mm at each side.

2.5. Measurements

The thickness of a dried resistive film was measured. The resistance and hot TCR of a fired layers were measured. The sheet resistance was calculated according to pre-fired layer thickness and X,Y geometry. The SEM photographs of a surface and fracture were taken. The influence of humidity on electrical properties was estimated as follows. Resistors were stored in room temperatures for 60 days and it's resistance was measured, then dried for the possible moisture removal and measured again.

3.RESULTS

The composition according to the Tab. 2 were prepared, and it's resistance and TCR were measured.

The electrical properties of resistors based on Glass 2 + CaRuO₃ were unsatisfactory. The resistance of this compositions with 60% of glass was ~143 kΩ/□ which fits the purpose of this investigation. However the TCRs varied from -1440 up to +53 ppm/°C, that were beyond the acceptable range. The higher glass contents 65% and 70% resulted in resistance to increase above the multimeter's range (>20 GΩ). Therefore the authors stopped further investigations of Glass 2 with CaRuO₃.

The sheet resistance of the other three compositions versus glass content is presented in Fig. 4. The authors focused on the sheet resistance values over 10 kΩ/□. The resistance between 10 kΩ/□ and 100 kΩ/□ has been achieved using these three compositions by varying the glass content between 65% up to 70% for Glass 1 + CaRuO₃ and Glass 2 + RuO₂, and between 65% and 75% for Glass 1 + RuO₂. The measurements of TCRs, presented in Fig. 5, shows considerable difference between the compositions. The TCRs of Glass 1 + RuO₂ varies from -500 ppm/°C to -760 ppm/°C which is outside the aimed range. In respect of TCR, the optimal glass content for this compositions is 45%. However, the resistance is ~100 Ω/□, far from the aimed value. The authors in their previous work [4] used Glass 1 + RuO₂ for preparing 100 Ω/□ paste and proved its good electrical properties and dense, free of cracks sintered layer. The TCR's of Glass 2 + RuO₂ and Glass 1 + CaRuO₃ are very similar. The first composition maintains the TCR +/-200 ppm/C for 62% ÷ 72% glass contents. That covers the resistance range from 3 kΩ/□ up to 250 kΩ/□. The

CaRuO₃ based composition provide the acceptable TCR for the glass contents 66% ÷ 70% providing the resistance range from 10 kΩ/□ to 60 kΩ/□. The further attempts of achieving higher resistances for this composition were unsuccessful. For the glass contents over 71% the TCR of this compositions became unpredictable.

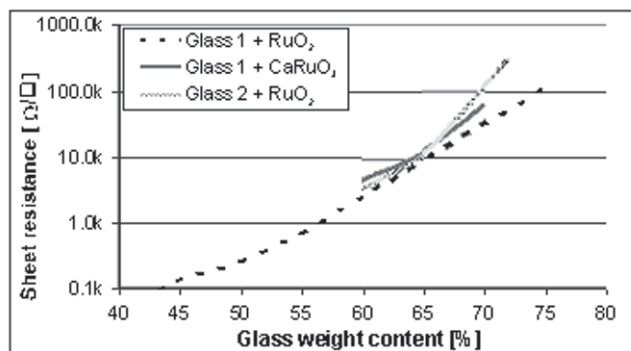


Fig. 4. Sheet resistance vs. glass content.

Rys. 4. Rezystancja powierzchniowa w funkcji zawartości szkliva.

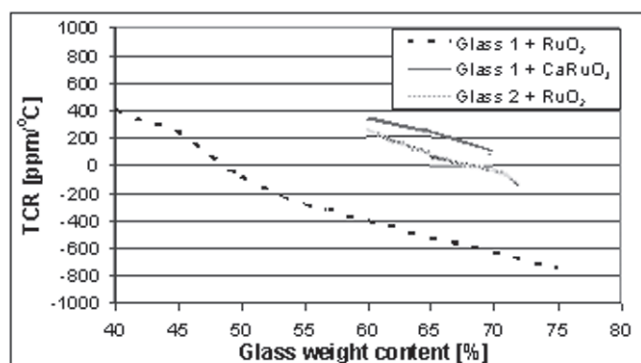


Fig. 5. TCR vs. glass content.

Rys. 5. TWR w funkcji zawartości szkliva.

The resistance of investigated resistors was stable during 60 days of storage in room temperature.

After drying no measurable resistance change was observed. Probably moisture do not penetrate the resistive layers.

The fractures and surfaces presented in Fig. 6-7 correlates with these facts. No cracks, voids, pores were observed. The surface roughness do not exceed 1 μm. White spots on photographs corresponds to Ru aggregates. In CaRuO₃ based com-

position the aggregates of Ru are larger and not so uniform distributed as in case RuO₂ based composition.

The grain dimensions of CaRuO₃ powder used in part of investigated thick films is smaller than RuO₂. It is harder to distribute small particles properly, that additionally tends to aggregate. Moreover the sheet resistance depend in grain size of conductive phase. Smaller grain sizes result in lower resistance providing the glass volume content is constant. That facts could explain failure in obtaining higher resistances than 60 kΩ/□ in case of this particular CaRuO₃ powder. Probably the longer annealing temperature during obtaining CaRuO₃ could increase the average grains dimensions.

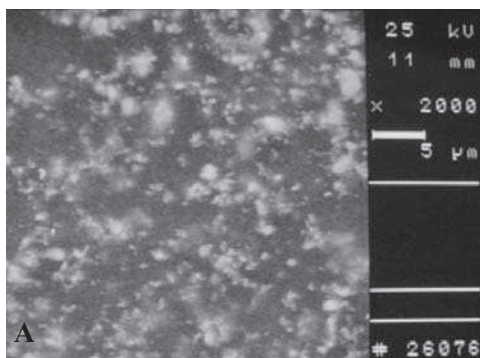


Fig. 6A. SEM Surface of Glass 2 + RuO₂ with 70% glass content.

Rys. 6A. Zdjęcie SEM powierzchni „Szkliwo 2 + RuO₂” z 70% zawartością szkliva.

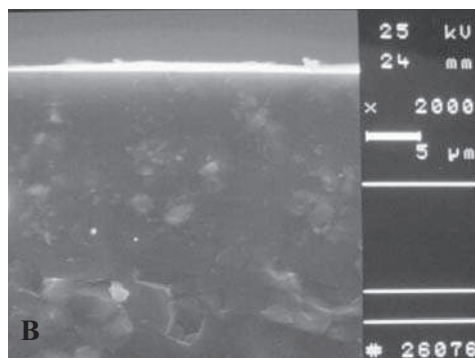


Fig. 6B. SEM fracture of Glass 2 + RuO₂ with 70% glass content.

Rys. 6B. Zdjęcie SEM przełomu „Szkliwo 2 + RuO₂” z 70% zawartością szkliva.

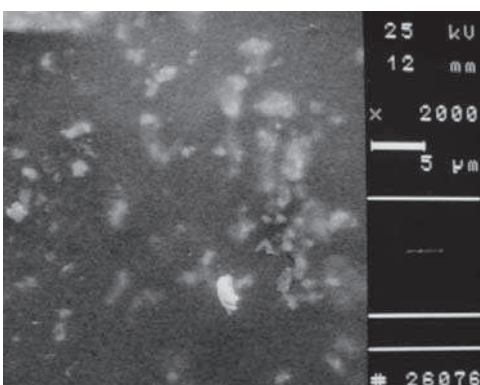


Fig. 7A. SEM Surface of Glass 1 + CaRuO₃ with 70% glass content.

Rys. 7A. Zdjęcie SEM powierzchni „Szkliwo 1+CaRuO₃” z 70% zawartością szkliva.

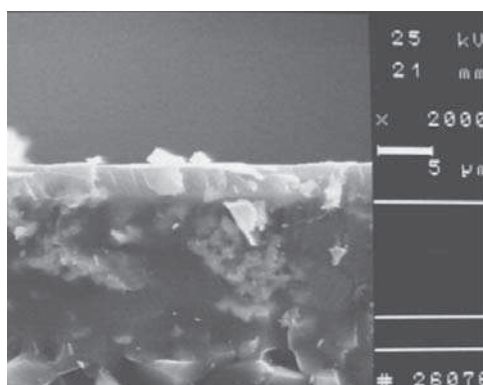


Fig. 7B. SEM fracture of Glass 1 + CaRuO₃ with 70% glass content.

Rys. 7B. Zdjęcie SEM przełomu „Szkliwo 1 + CaRuO₃” z 70% zawartością szkliva.

In Fig. 8 the influence of width on TCR is shown. Due to diffusion at the resistor termination the electrical parameters including TCR may be disturbed. Shorter resistors are more affected due to small intrinsic resistive layer unaffected by diffusion. The length effect of resistive layers was investigated (Fig. 6). Glass 1 + RuO₂ composition (100 Ω/□) is the most susceptible to diffusion, that expose in considerable TCR disturbance for short resistors. The high RuO₂ content (55%) could increase diffusion rate as mentioned in [6]. The TCR of other compositions nearly do not depend from resistor's length. Probably because lower Ru-compounds content (30%).

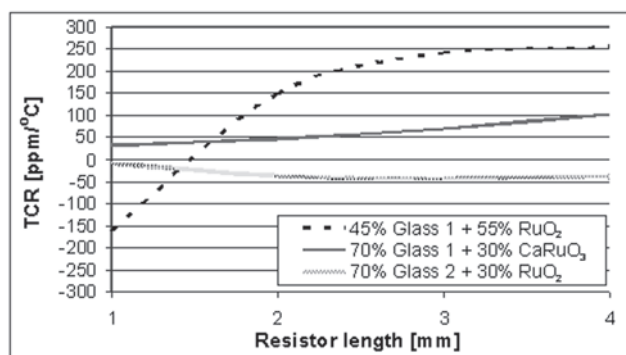


Fig. 8. The length effect on TCR.

Rys. 8. Wpływ długości rezystora na TCR.

4. CONCLUSION

The authors obtained CaRuO₃ powder that is suitable for resistive pastes. The optimal reaction parameters were discovered. The high-ohm resistors with the use of CaRuO₃ and RuO₂ were obtained. The resistors on CaRuO₃ exhibit the resistances up to 60 kΩ/□, whereas one composition with RuO₂ achieved 250 kΩ/□. The authors will continue the research of optimal glass for CaRuO₃ conductive phase.

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EKOLOGICZNE GRUBOWARSTWOWE REZYSTORY O SZEROKIM ZAKRESIE REZYSTANCJI

Autorzy zaprezentowali wyniki badań rezystorów wolnych od ołowiu i kadmu opartych na rutenianie bizmutu (CaRuO₃) i dwutlenku rutenu (RuO₂), o rezystancjach przekraczających 10 kΩ/□. Począwszy od 1 lipca 2006 roku zgodnie z unijnymi uregulowaniami prawnymi WEEE (*Waste Electrical and Electronic Equipment Directive*) i RoHS (*Restriction of Hazardous Substances*) stosowanie ołowiu i kadmu w układach elektronicznych zostało ograniczone. Zakaz ten obejmuje pasty rezystywne szeroko stosowane w elektronice m.in. w elementach do montażu powierzchniowego (SMD). Autorzy w 2007 r. zaproponowali serię past rezystywnych o zakresie rezystancji 10 Ω/□ - 10 kΩ/□. Pasty bazowały na dwutlenku rutenu i nie zawierały w swoim składzie ani ołowiu ani kadmu. Tym niemniej konsumenci oczekują pełnego zakresu rezystancji 10 Ω/□ - 1 MΩ/□. Uzyskanie takich wartości było możliwe poprzez zastosowanie w pastach rezystywnych szkliv ołowiowych oraz fazy przewodzącej rutenianu bizmutu. Jednakże uzyskanie tych rezultatów przy zastosowaniu szkliv bezołowiowych oraz dwutlenku rutenu nie jest możliwe. Z tego powodu autorzy postanowili zastosować rutenian wapnia w roli fazy przewodzącej, który ma wyższą rezystywność od dwutlenku rutenu. Autorzy uzyskali dobre rezultaty używając niektórych szkliv bezołowiowych, które dotychczas się sprawdziły w połączeniu z dwutlenkiem rutenu jak również zaproponowali zupełnie nowe kompozycje szkliv. Zastosowanie CaRuO₃ zamiast RuO₂ wraz z jednym ze szkliv zaowocowało uzyskaniem 500 razy wyższej rezystancji bez wpływu na TWR.. Nie zaobserwowano wpływu wilgoci na właściwości warstw rezystywnych. Obserwowano przełomy i powierzchnie warstw rezystywnych techniką SEM, jak również zbadano wpływ długości na właściwości rezystorów.

Słowa kluczowe: RoHS, rezystor grubowarstwowy, ruten