використовуються електричні або термоелектричні ефекти, треба використовувати напівпровідники з домішковою провідністю і слабовиродженими носіями струму. Для цієї мети найкраще підходять леговані напівпровідники в яких домінує розсіювання носіїв струму на іонізованих домішках. Непараболізм енергетичної зони, який має місце в зонах енергії Кейна, замітно понижує максимальні значення термоелектричної чутливості напівпровідникових кристалів.

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NEW SERIES OF RESISTIVE PASTES BASED ON ZnO · B₂O₃ · MoO₃ · Bi₂O₃ · Al₂O₃ GLASS

Наведено результати розробки і дослідження нових резистивних паст, які не містять благородних металів.

Paper presents results of design and research on new series of resistive pastes which do not contain noble metals.

1. INTRODUCTION

A new series of resistive pastes based on B_2O_3-MoO_3-ZnO-Bi_2O_3-Al_2O_3 is presented in this paper. It is a modification of the previous one described in [1, 2, 3]. The modified pastes enlarged the range of sheet resistivity of the pastes series, as well as they could be applied in the structure "resistor on dielectric" [7]. Resistor terminations were made of silver or nickel pastes [4]. The elaborated set of materials allows to produce thick film structures without use of noble metals.

The previous attempts to elaborate resistive pastes without the use of non noble metals were based on application of the mixture of oxides from group VB such as CrO_3, MoO_3, WO_3 [5]. The obtained layers were electrically unstable because of the reoxidation processes during firing in too high temperature (>750°C).

The basic assumption of our solution was to find a composition which fired in lower temperatures (600-690°C) exhibit suitable properties for thick film resistive layers. Instead of a composition consisting of an metal oxide (conductive phase precursor), glass and reducing agent we applied compositions consisted of a glass composed of different metal oxides such as PbO,

Bi_2O_3, CdO, ZnO, TiO_2, $SiO_2B_2O_3$, Al_2O_3, BaO, NeO and the most important – the precursor of conducting phase – MoO_3 and the reducing agent – boron. The sheet resistivity was changed by adding certain amount of an "inert" glass which was not reduced by boron during firing process. The elaborated paste series consisted of pastes of sheet resistivity in the range from 50 $\Omega/\square$ to 100 k$\Omega/\square$ and TCR (temperature coefficient of resistance) below 150 ppm/^{o}C.

The other advantage of the paste series is that they can be fired in air, in conventional thick film belt furnace and there id no need to apply an inert atmosphere as it was necessary for the resistive pastes based on SnO_2 and LaB_6. The elaborated pastes could be also applied not only on alumina substrates, but also on glass, metal etc. since their firing temperature is much lower than for conventional ones.
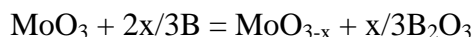
2. RESISTIVE PASTES COMPOSITION

Conventional resistive thick film pastes based on ruthenium compounds are composed of:
– conductive phase that is ruthenium dioxide or bismuth rutenate or their mixture,
– isolative phase that is glass most often lead-boro-silicate,
– organic vehicle.

Different electrical properties of the layers obtained from the pastes are obtained by adding the first two phases in suitable proportions.

Our first elaborated resistive paste series based on molybdenum glasses [6] did not contain the separate conductive phase. This was created during firing the screen printed layer in chemical reaction between the molybdenum oxide contained in the glass and the reducing agent – boron as is written below:

$$MoO_3 + 2x/3B = MoO_{3-x} + x/3B_2O_3$$

Thus, compositions based on molybdenum glasses, as most promising, have been chosen. Reduced MoO_2 is the main conductive phase for these compositions. It is worth mentioning that MoO_2 exhibits metallic conductivity with volume resistivity $\rho_r = 8.8*10^{-5}$ $\Omega*$cm at temperature 25°C. For comparison, RuO_2 has $\rho_r = 4.0*10^{-5}$ $\Omega*$cm.

Quantitative analysis of crystalline phases present in resistive layer, related to boron content in the pastes based on glasses containing MoO_3, Bi_2O_3 and ZnO has shown that apart from MoO_2 and Bi, a non-conductive crystalline phase α-$ZnMoO_4$ was detected. The presence of the latter phase confirms the role of ZnO in crystallising process. Boron presence causes almost immediate creation of MoO_2 that comes to a maximum value around 6% of boron. Bi appears at much higher level of boron (2-3%) and the curve of Bi concentration becomes steeper at boron content of 4-6%. The content of α-$ZnMoO_4$ drops down with growth of boron amount.

An employment of some other oxides to glasses was found beneficial for resistor properties. For example, TiO_2 was improving highly negative TCR's of high ohm resistors (to -300 ppm/°C, for 30 k$\Omega/\square$ paste and -500 ppm/°C, for 100 k$\Omega/\square$ paste). Nd_2O_3 could be used as a modifier of thermal coefficient of expansion (TCE). It helped to achieve compatibility of resistive layer with alumina substrate and to improve stability of resistors.

The different pastes from the series contained different glasses. The resistivity was created by changing the glass composition and the quantity of boron. Boron was reducing molybdenum trioxide at firing temperature and the conductive phase was created:

$$MoO_3 + 2x/3B \rightarrow MoO_{3-x} + x/3B_2O_3$$
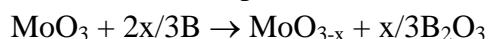
This system has shown several disadvantages. Boron was also damaging PbO and/or Bi_2O_3 contained in the glassy insulator:

$$PbO + 2y/3B \rightarrow PbO_{(1-y)} + y/3B_2O_3$$

$$3PbO + 2B \rightarrow 3Pb + B_2O_3$$
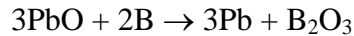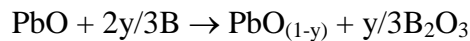
The pastes were also sensitive to firing temperature.

To avoid that kind of draw back a new resistive pastes system has been elaborated. It was based on:

– glass based on molybdenum oxide and other metal oxides,

– glass "inert" to reduction with boron,

– reducing agent (boron),

– organic vehicle.

All the pastes from the series contained the same glass based on molybdenum oxide and the same "inert" glass. The glass creating the conductive phase was composed of molybdenum trioxide and other oxides like: ZnO, B_2O_3, Bi_2O_3, Al_2O_3. The glass creating the conductive phase was composed of molybdenum trioxide and other oxides like: ZnO, B_2O_3, Bi_2O_3, Al_2O_3. The resistivity of the pastes was regulated by changing the content of the "inert" glass in the paste. The proportion of boron and the glass with molybdenum oxides was stable. The pastes were prepared in a standard way. They contained 25% of organic vehicle based on ethylcellulose N-7 and N-22. The pastes were printed and fired using standard equipment and techniques.

A set of glasses not reduced by boron has been examined. The authors tried to compose the glasses without heavy metals oxide for ecological reasons. The glass compositions are presented in Table 1.

Table 1

**The compositions and properties of glasses resistant to reduction
with boron during thick film process**

Glass type	The glass composition	Processing temp. ^{o}C	$\alpha_{20-300} \times 10^{-6}$	T_g ^{o}C	DTM ^{o}C
1	2	3	4	5	6
A	Bi_2O_3. B_2O_3. SiO_2	1300	9.05	420	580
B	BaO. B_2O_3. SiO_2. Al_2O_3. MnO	1400	5.5		
C	SiO_2. Al_2O_3. B_2O_3. Na_2O. K_2O	1600	4.05	560	760
D	SiO_2. ZrO_2. Al_2O_3. BaO. CaO. K_2O	1600	9.93	686	766
E	SiO_2. B_2O_3. BaO. Al_2O_3	1300	6.1		
F	B_2O_3. Na_2O	1400	10.5	385	465
G	B_2O_3. ZnO. Na_2O	1400	8.21	432	482
H	B_2O_3. Na_2O	1300	10.0	375	420
I	B_2O_3. CdO. ZnO. Na_2O. BaO. CaO	1400	9.36	435	472

As a result of the investigations we decided to apply in all pastes of the series :

– a glass ZnO.B_2O_3.MoO_3. Bi_2O_3.Al_2O_3 as a glass containing the precursor of conductive phase,

– boron as a reducing agent in constant ratio to the glass mentioned above,

– an inert glass B_2O_3 CdO. ZnO. Na_2O. BaO. CaO in different proportions to the glass containing the precursor of conductive phase to obtain certain resistivity,

– and organic vehicle.

It is also worth mentioning that the solution of applying one glass containing the precursor of conductive phase and the same "inert" glass allows to blend the pastes from the series to obtain the layers of certain sheet resistivity not present in the series.

3. PROPERTIES OF THE ELABORATED LAYERS

The resistive pastes compositions and the properties of the obtained layers are presented in table 2. The pastes were screen-printed on standard 96 % alumina substrate and fired at the peak temperature in the range of $580 - 700^{o}C$.

Dependence of sheet resistivity and temperature coefficient of resistance (TCR) versus the "inert" glass content in paste is presented in Fig. 1. The layers were fired at $680^{o}C$. Sheet resistivity is growing with the glass content, while TCR changes from positive to negative values.

Table 2

The paste composition and properties of elaborated resistive layers

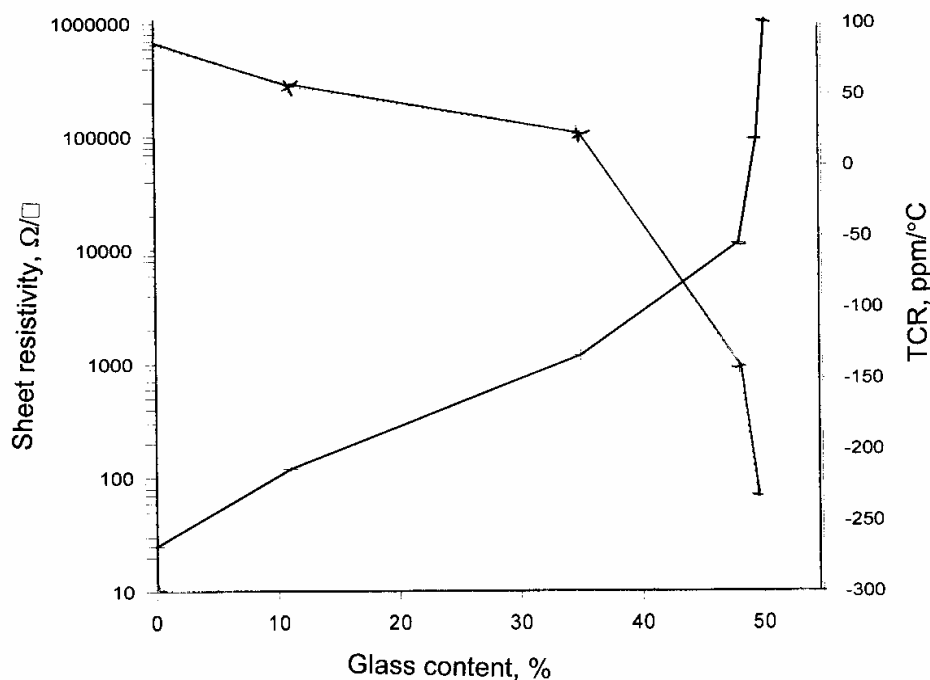| Symbol of paste	Inert glass content in the pastes	Firing temp. of layers	Layer thickness	Sheet resistivity $k\Omega/\square$	TCR ppm/^{o}C
R-811	0	680	21	0.025	85
R-812	11	680	25	0.12	56
R-813	35	680	30	1.2	22
R-814	48	680	27	15	-142
R-815	49.5	680	24	98	-232
R-816	50.2	680	23	1080	>-500

Fig. 1. The influence of J type inert glass content in resistive pastes
on sheet resistivity and TCR of resistive layers fired at $680^{o}C$

Fig. 2 presents the sheet resistivity and TCR of the layers versus firing temperature. The elaborated layers are not very sensitive to firing temperature changes compare to the layers without the inert glass content [1]. $680^{o}C$ were chosen as the optimal temperature for firing these layers. Layers fired at this temperature exhibit very good stability.
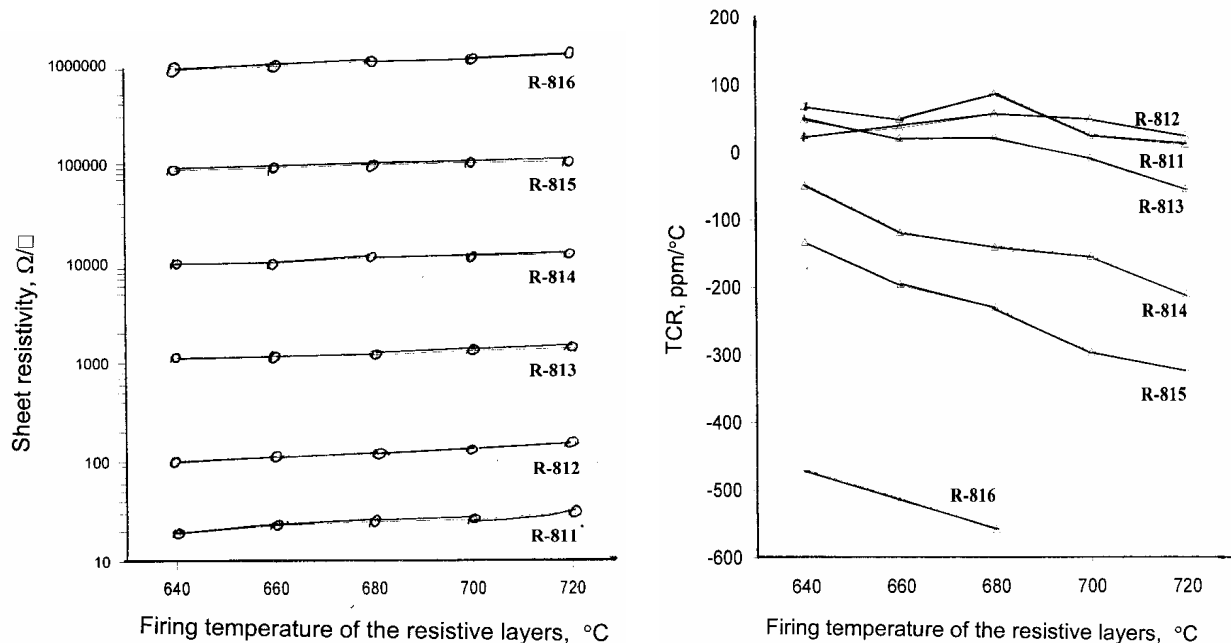

Fig. 2. Sheet resistivity and TCR of resistive layers dependence versus
firing temperature of the layers

4. CONCLUSIONS

The elaborated resistive pastes series based on $ZnO \cdot B_2O_3$ MoO_3 Bi_2O_3 Al_2O_3 glass and contains molybdenum trioxide MoO_3, which reduced by boron during the firing process produces molybdenum oxides enable to conduct electrical current. Sheet resistivity of the layers depends on the "inert" glass content in the pastes.

The elaborated pastes exhibit several advantages compare with the previous series [1]:

– application of the "inert" glass in the pastes composition enables to broaden sheet resistivity range in the paste series, as well as improves the electrical stability of the layers,

– all pastes in the series contain the same basic glass (the conductive phase precursor) and the inert one only in different ratio; this allows to blend the pastes and obtain the pastes of different sheet resistivity,

– obtained layers exhibit low temperature coefficient of resistance and are resistant to heat and current,

– resistive layers are compatible with nickel and silver layers, therefore the resistor termination could be made of this non noble pastes; this solution is very economically attractive.

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ПРИСТРОЇ ДЛЯ ДИНАМІЧНОЇ КОМПЕНСАЦІЇ РЕАКТИВНОЇ ПОТУЖНОСТІ В ЕНЕРГОСИСТЕМАХ

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Досліджено проблему динамічного компенсування реактивної потужності в енергетиці та її вплив на покращання якості електроенергії, на краще використання наявних енергетичних потужностей та ліній пересилання електроенергії. Проаналізовано роботу функціональних елементів керованої енергетичної електроніки на основі тиристорних та МОН-вентилів. Запропоновано пристрої для динамічної компенсації реактивної потужності зі зменшеним впливом на якість енергосередовища.

The problem of the dynamic var compensation in power systems and its impact on improving the quality of electric power as well as on a better employment of the available power capacities and electric energy transference lines have been discussed. The work of the functional elements of the guided power electronics based on the thyristor and metal-oxide-semiconductor valves has been analyzed. Setups for a dynamic compensation of the reactance var power with the decreased impact on the quality of the power environment have been suggested.

Впровадження в енергетиці силової електроніки дозволяє розв'язати фундаментальну проблему динамічного компенсування реактивної потужності. В українській енергетиці широко використовується статичне компенсування реактивної потужності. Компенсуючі ємності батарей конденсаторів і синхронні компенсатори розраховані на номінальну потужність енергооб'єкта. У цій одній точці досягають достатньо високої степені компенсації реактивного струму. Реальна практика експлуатації енергооб'єктів визначається значними відхиленнями від розрахункового режиму і при використанні статичних компенсаторів в лініях пересилання енергії наявні великі реактивні струми, що приводить до недовикористання генераторів електричної енергії і некорисного завантаження ліній пересилання енергії.