UDC 544.187.2; 621.315.59

*SH. D. KURMASHEV, T. M. BUGAEVA, T. I. LAVRENOVA, N. N. SADOVA*

Odessa I.I.Mechnicov National University
Odessa, 65026, Ukraine, e-mail: kurm@mail.css.od.ua. Tel. (0482) — 746-66-58.

# INFLUENCE OF THE GLASS PHASE STRUCTURE ON THE RESISTANCE OF THE LAYERS IN SYSTEM "GLASS-$RuO_2$"

Influence of quantitative and qualitive (phase and granule-metric) composition of initial components on the electro physical properties of thick films on the base of the systems "glass — clusters $RuO_2$, $Bi_2Ru_2O_7$" was investigated. At the fixed values of functional material content $m_f$ ($RuO_2$) and glass phase $m_g$, the increase of mass of crystalline phase $m_{cr}$ leads to decrease of conductivity, therefore to the increase of resistance of resistive layer.

## 1. INTRODUCTION

Development of submicron and nanotechnology in electronics involves not only active elements (lasers, photodetectors and etc) but also those elements, which are recognized as passive. They also include the resistors of the integrated circuits. As it is generally known, the resistance compositions on the basis of dioxide of ruthenium ($RuO_2$) have good electro physical properties [1]. Thick-film structures on the basis of the systems "glass-$RuO_2$, $Bi_2Ru_2O_7$" used as the conductive resistive elements of the hybrid integrated circuits, are little affected by high temperatures, as dioxide of ruthenium does not dissolve in a glass matrix. It allows to increase annealing temperature of resistance pastes up to 1000°C. But the problems, related to structural-phases transitions resulted from external factors, which influence electro physical properties of thick films on the base of $RuO_2$, $Bi_2Ru_2O_7$, are still unsolved. There is no one statifactory model of conductivity mechanisms in the separate components of ceramic layers and also information about contribution of micro- and nano-geometry defects to the conductivity mechanisms of thick resistance films. Composition materials belong to multi phase heterosystems, which include components with different physical and chemical properties.

The study of properties of initial components, organic and inorganic compositions, conductive and dielectric phases, morphology and particle size distribution become the primary goals in production of thick-film elements.

In the present work , the influence of quantitative and qualitive composition (phase and granule-metric) of initial components on the electro physical parameters of thick films on the base of the systems "glass — clusters $RuO_2$, $Bi_2Ru_2O_7$" was investigated.

## 2. EXPERIMENTAL

The main components of the composition systems of thick film elements are:

– small-dispersion powders of functional material (metals, oxides of metals), which provide formation of conducting paths;

– special glass frit carrying out the role of permanent binder.

Functional materials (conducting phase) are brought into paste as ultrafine particles with the maximal size lower than 5 μm. The glasses are used as permanent binder. On one side, the glass frit provides the adherence of metal-enamel elements. On the other side it creates "hard framework", fixing position of conducting particles inside the structure.

The shape and dispersion of particles of conducting phase ($RuO_2$) strongly depends on the ruthenium dioxide powder fabrication method. Usually, it is obtained by hydrochloric ruthenium decomposition. At a temperature a 300-400°C ruthenium dioxide forms as ultrafine spherical particles. The optimal size of annealed particles is (0,05 ÷ 0,1) μm. Maximal size of the ruthenium dioxide particles shouldn't exceed (0,2 ÷ 0,3) parts of thickness of annealing layer. Character of conductivity of resistive layers concerns by potential barrier height of dielectric layer between conducting particles. If the dielectric layer between conducting particles is less than 100 Å, the tunnel current is the basic mechanism of conductivity. If the layer is more than 100 Å, tunnel effect is improbable and charge carriers with energy higher than the height of barrier can go over it. Thermal emission becomes the basic mechanism of conductivity.

The influence of permanent binder (glasses of different types) seems to be not so strong in chemical interaction with a conducting phase, but it increases through moistening and dissolution of its particles. Moistening of functional material by glass and chemical activity of glass have more important meaning. If glass forms a thick continuous layer round every conductive particle, the contact between particles is violated. Consequently, it is needed, that glass moistened particles not fully, but rather enough, that particles were fixed in a matrix.

Electro physical properties of capacitance-resistance elements largely depend on ratio of conductor phase and permanent binder concentrations. Dependence of electro physical properties of composition structures on the basis of "glass-$RuO_2$" from ratio of conducting phase $RuO_2$ and glass concentrations, sizes of particles of glass and temperature of annealing was investigated. The films were made from powders of lead-boron-silicate glass of marked № 279, 2005

(PbO, $SiO_2$, $B_2O_3$, $Al_2O_3$) with the fixed sizes of particles (0.5; 1; 3 and 5 μm) and functional material $RuO_2$ with the sizes of particles (0.05 ч 0.1) μm.

The system of analysis of images "QUANTIMET — 720" and raster electronic microscope were used for researches. Investigations of glasses phase composition were carried by x-ray technique on DRON-2 with silicon grating monochromator (voltage 16 kV, intensity of current 2 mA).

Dependence of resistance of the resistors from concentration ratio of conductor phase and glass at the fixed temperature of annealing (870°C) has been obtained (fig. 1).

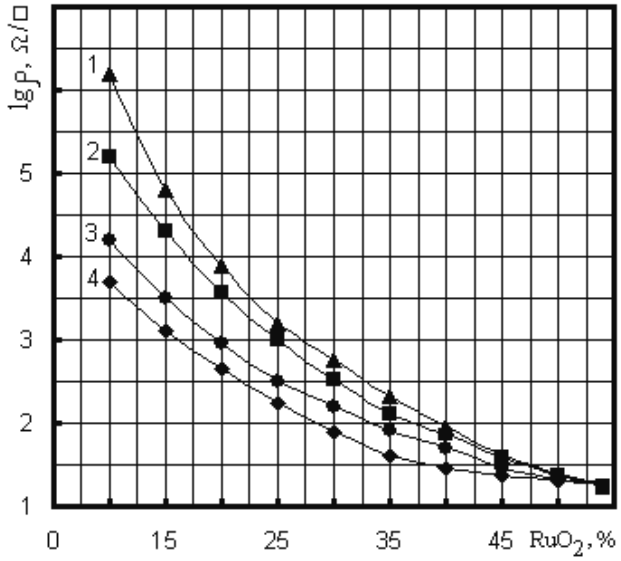


Fig. 1. Dependence of surface resistivity of thick layers from concentration ratio of conductor phase and glass. Size of glass particles, μm: 1 — 0.5; 2 — 1; 3 — 3; 4 — 5

The samples with low content of ruthenium dioxide had the most influence from glass-frit particle size on resistance of resistors. Resistance of films increased with the enhance of glass portion. The highest rate of resistance raise took place for glass-frit with the particles size of 0,5 μm. With increase of $RuO_2$ concentration, the resistance approaches to the saturated value and does not depend on the glass-frit particles size.

Dependence of resistance from the particle sizes for high resistivity films is affected by coalescence of the particles and the influence of the components dispersion on the geometrical sizes of. With glass particles size decreasing, the current chainlets length increases and their cross section area decreases. It is observed mixed type of conductivity in the systems "$RuO_2$ — glass". The charge transport processes take place in the conducting phase and glass-frit. In layers with high resistivity, the main contribution in conductivity is performed by glass-frit. Therefore, the state of this phase acts important role in the process of charge transport.

If the influence of high-quality composition of conducting (functional) material is usually investigated in details, usually, the glass is considered an amorphous homogeneous environment. However, in the process of investigations it is set, that glasses can be crystallized as result of heat treatment. The x-ray radiation can stimulate crystallization [2]. In addition, particles of functional material can become the nucleation centers of crystallization of glass matrix. The presence of the crystallites in a matrix can cause local changes of glass melt point and coating of functional material particles by glass at heat treatment of film. It leads to change of the parameters of the formed layer.

The phase composition of glasses has been determined by XRD method. At first, the initial content of the particles has been investigated. It was found XRD peak at $\theta=15,5^0$ (d = 3,35 Å) on the XRD diagram of glasses №2005 in the initial state. The XRD diagram of glass №279 did not have any peaks, related to crystalline phase.

For determination of influence of heat treatment on the phase state of glass, it was performed the annealing procedure at 870°C during 10 minutes. At the same time, the samples were separated on two groups to take in account influence of x-ray radiation. The first group was annealed with subsequent XRD analysis. The second one was processed by the consequence XRD-annealing-XRD.

After annealing, XRD peak at $\theta=15,5^0$ of №2005 samples (first group) increased in comparison to the initial state. Weak peaks appeared at $\theta=12,1^0$ (d = 4,27 Å) and $\theta=29,50^\circ$ (d = 1,82 Å) in XRD curve of the second group after x-ray irradiation and annealing, that testifies to the increase of concentration of crystalline phase. Identification of the observed peaks within card index of ASTM showed that the peaks belonged to α-$SiO_2$ (quartz) modification. Comparison of the XRD diagrams of glasses №2005 before and after heat treatment showed that X-ray reflections from crystalline phase increased as a result of increase of volume of crystalline phase in these glasses after heat treatment. Glasses №279 of first and second groups remained amorphous.

The obtained results allowed to make some conclusions about the influence of heat treatment on phase composition of glasses:

– glass №279 had strong amorphous structure, the crystalline phase nucleation disappeared by time and never appear after the heat treatment;

– glass №2005 already contained the crystalline phase in the initial state, the volume of crystalline phase increased with time in all stages of heat treatment.

Thus, it is found that heat treatment caused formation of new phases, and also rebuilding of energetic zones of the system. As the crystalline phase found in glass α-$SiO_2$ had the temperature of melting over 1500°C, and coalescence of resistance layers took place usually at 870 °C. The crystalline phase of glass didn't melt and there were local structural deviations in the volume of matrix, that influenced the formation of conducting chainlets. In addition, the random breaks of conducting chainlets made disorder of structure of chainlets of conductivity in the volume of the film. It is set that presence of crystalline phase α-$SiO_2$ in glass increases resistance of the sample (~ 10%).

Properties of glass phase play an important role in conductivity of films. In fiq.2, the dependence of surface resistivity of thick films from the percent concentration of crystalline phase $m_{cr}$ in glass-frit is presented. It is seen that with the increase of $m_{cr,}$ the resistance of films increased.

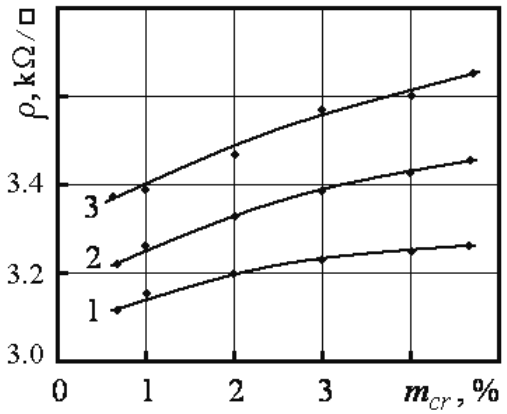


Fig. 2. Dependence of surface resistivity of films from percent concentration of crystalline phase $m_{cr}$ in glass-frit. Table of contents of glass-frit in the system "glass — clusters $RuO_2$ " $m_g$, %: 1 — 40; 2 — 50; 3 — 60

## 3. DISCUSSION

Electrical properties of the films on the base of the systems "glass — clusters $RuO_2$, $Bi_2Ru_2O_7$" are defined by the mechanisms of conductivity, which strongly depend on physical properties of initial components and microstructure of layers. The structure of films depends on the technological factors of their fabrication and properties of initial components. Phase composition of glass-frit is also an important factor.

In [2] it was obtained mixed character of conductivity as combination of processes which flow in conducting phase and glass-phase. The conducting phase had metallic conductivity. Charge transport through the thin layers of glass-phase, surrounding the conducting phase, takes place by means of tunneling effect in a low energetic zone, which appears after doping of glass with ions, diffunding from the conducting phase.

Through research of resistance layers on basis $RuO_2$, it was determined traces of presence of cristobalite in the layers– one of crystalline modifications $SiO_2$, which decreased conductivity of resistors. According to that, it is interesting to develop a model which explains influencing of crystalline phase $\alpha$-$SiO_2$ in amorphous glass matrix on conductivity of thick resistance films, based on the system "glass — clusters $RuO_2$".

A thick-film element can be presented as aggregate of conducting chainlets from one electrode to other, which consist of conducting particles of functional material. Conducting *i*-chain appears with probability $p_i$, which includes probability of that all elements of chainlet are conductors ($p_1$) and probability of continuity of chainlet in a glass matrix from one electrode to other ($p_2$). It means that $p_i = p_1 \cdot p_2$. In this model probability $p_1$ of conductivities of all elements of chainlet is proportional to mass part of functional material $m_f$ in bulk of dry powder in paste $m_p$: $p_1 = k_1 \cdot m_f / m_p$. Here $k_1$ is coefficient of proportion. Probability of formation of continuous chainlet from one electrode to other is proportional to mass of functional material $m_f$ and inversely proportional to mass *of* glass-frit $m_g$: $p_2 = k_2 \cdot m_f/m_g$. Here, $k_2$ is coefficient of proportion. Mass of powder $m_p = m_f + m_g$.

In the case of presence of crystalline phase in glass it is necessary to take into account another factor. The presence of crystalline phase $SiO_2$ in fusible glass is equivalently adding unfire-polished particles in the glass, beacause temperature of melting of any of modifications $SiO_2$ is considerably higher than the temperature of sintering of layer. Under sintering, the local regions of the "not-melts" are formed in the glass, which prevent the process of forming of structure in the limited areas. The "not-melts" restrict the distribution of liquid glass and formation of homogeneous sintered structure. The particles of functional material in these regions do not form good contacts because of lack of pressing forces which arise up at sintering of glass. Thus, the non sintered and non conductive contacts appear, what is equal to the breaks of leading chainlets.

For calculation of possibility of formation of non-conducting contacts, it is necessary to put $p_3$ (the probability of that all contacts are conducting between the elements of chainlet) in equation for $p_i$, that is equal to $p_i = p_1 \cdot p_2 p_3$. With the increase of mass of crystalline phase $m_{cr}$ in glass-frit and functional material powder mass $m_p$, the probability $p_3$ is decreased: $p_3 = 1 - k_3 \cdot m_{cr}/m_p$. Here $k_3$ is coefficient of proportion. From the resulted equations for $p_1$, $p_2$ and $p_3$, it is not difficult to get $p_i$.

As a thick-film resistor in this case is presented as system which consists of aggregate of conducting chainlets, its conductivity equals $\sigma = \sum_{i=1}^{N} \sigma_i p_i$ , where $\sigma_i$ is conductivity of $i$ –th chainlet, $N$ is the amount of chainlets.

If all chainlets are formed in identical terms, it is possible to assume that $p_i = p$. Then

$$\sigma = p\sum_{i=1}^{N}\sigma_i = k_1 k_2 \frac{m_f^2\left(m_f + m_g - k_3 m_{cr}\right)}{m_g m_p^2}\sum_{i=1}^{N}\sigma_i .$$

It is obviously seen from this expression, that increase of maintenance of crystalline constituent $m_{cr}$ in a glass phase $m_g$ results to increase of resistance of thick film, what was confirmed experimentally (fig.2).

## CONCLUSIONS

Most influence of sizes of particles of glass-frit on resistance of resistors at the fixed temperature of annealing takes place for samples with low content of ruthenium dioxide. Resistance of layers increases with the increase of content of glass.

At the fixed values of functional material content $m_f$ ($RuO_2$) and glass phase $m_g$, the increase of mass of crystalline phase $m_{cr}$ leads to decrease of conductivity, therefore to the increase of resistance of resistive layer.

**References**

1. Панов Л. И. Опыт совершенствования толстопленочной технологии / Л. И. Панов, Р. Г. Сидорец // Технология и конструирование в электронной аппаратуре. — 2002. — №1. — С. 43-46.
2. Курмашев Ш. Д. Влияние кристаллической фазы $SiO_2$ на электрофизические компоненты композиционных структур на базе стекло-$Bi_2Ru_2O_7$/ Ш. Д. Курмашев, Т. И. Лавренова, Т. Н. Бугаева // Тезисы докл. XXII научн. конф. стран СНГ "Дисперсные системы". — Одесса, 2006. — С. 215.

UDC 544.187.2; 621.315.59

*Sh. D. Kurmashev, T. M. Bugaeva, T. I. Lavrenova, N. N. Sadova*

**INFLUENCE OF THE GLASS PHASE STRUCTURE ON THE RESISTANCE OF THE LAYERS IN SYSTEM "GLASS-$RuO_2$"**

Influence of quantitative and qualitive (phase and granule-metric) composition of initial components on the electro physical properties of thick films on the base of the systems "glass — clusters $RuO_2$, $Bi_2Ru_2O_7$" was investigated. At the fixed values of functional material content $m_f$ ($RuO_2$) and glass phase $m_g$, the increase of mass of crystalline phase $m_{cr}$ leads to decrease of conductivity, therefore to the increase of resistance of resistive layer.

**Key words:** sructure, phase, resistance, layer.

УДК 544.187.2; 621.315.59

**ВЛИЯНИЕ СТРУКТУРЫ СТЕКЛЯННОЙ ФАЗЫ НА СОПРОТИВЛЕНИЕ РЕЗИСТИВНЫХ ПЛЕНОК В СИСТЕМЕ "СТЕКЛО-$RuO_2$"**

*Ш. Д. Курмашев, Т. Н. Бугаева, Т. И. Лавренова, Н. Н. Садова*

Исследовано влияние количественного и качественного (фазовый и гранулометрический) состава исходных компонентов на электрофизические параметры толстых пленок на базе систем "стекло — кластеры $RuO_2$, $Bi_2Ru_2O_7$". При заданных величинах содержания функционального материала ($RuO_2$) и стеклянной фазы увеличение массы кристаллической фазы приводит к увеличению сопротивления резистивной пленки.

**Ключевые слова:** структура, фаза, сопротивление, плёнка.

УДК 544..187.2; 621.315.59

**ВПЛИВ СТРУКТУРИ СКЛЯНОЇ ФАЗИ НА ОПІР РЕЗИСТИВНИХ ПЛІВОК В СИСТЕМІ "СКЛО-$RuO_2$"**

*Ш. Д. Курмашев, Т. Н. Бугаева, Т. И. Лавренова, Н. Н. Садова*

Досліджено вплив кількісного та якісного (фазовий і гранулометричний) складу вихідних компонентів на електрофізичні параметри товстих плівок на базі систем "скло — кластери $RuO_2$, $Bi_2Ru_2O_7$". При заданих величинах вмісту функціонального матеріалу ($RuO_2$) і скляної фази збільшення маси кристалічної фази призводить до зменшення величини провідності, тобто до збільшення опору резистивної плівки.

**Ключові слова:** структура, фаза, опір, плівка.