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Dependence of the nanocomposite "glass-ruthenium compound" electrophysical parameters on the initial component properties

Ya.I.Lepikh, N.M.Sadova, V.A.Borshchak, N.P.Zatovska, A.A.Karpenko

The Interdepartmental Scientific and Educational Physics and Technical Center at MES and NAS of Ukraine, Odesa I.I.Mechnikov National University, 2 Dvoryanskaya Str., 65082 Odesa, Ukraine

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The structural-phase transformations in nanocomposite systems "glass — RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$ clusters" and their influence on the electrophysical parameters of the nanocomposite system have been studied. It is established that when creating a nanocomposite material, the wettability of particles of a functional material by glass and the glass chemical activity have a great influence on its conductivity. It is established that the main reason for the chemical decomposition of lead ruthenate and the formation of ruthenium dioxide during annealing the heterophase system is the presence of glass components with high acidity. The film resistivity decreases because the electrical conductivity of ruthenium dioxide is two orders of magnitude higher than the electrical conductivity of lead ruthenate. Thus, it is possible to control the parameters of nanocomposite GIS elements. It was revealed that heat treatment of "glass — RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$ clusters" systems causes the formation of new phase, as well as the rearrangement of energy zones of the system, which affects the film electrical conductivity.

Keywords: microelectronic sensors, composite materials, ruthenium oxide, lead ruthenate, ruthenium dioxide, thick-film elements, nanocomposites.

Залежність електрофізичних параметрів нанокомпозитних систем "скло-сполуки рутенію" від властивостей вихідних компонентів. *Я.І.Лепіх, Н.М.Садова, В.А.Борщак, Н.П.Затовська, А.О.Карпенко*

Досліджено структурно-фазові перетворення у нанокомпозитних системах "скло-кластери RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$" і їх зв'язок з електрофізичними параметрами нанокомпозитів системи. Встановлено, що при створенні нанокомпозитного матеріалу великий вплив на його провідність має змочуваність склом частинок функціонального матеріалу і хімічна активність скла. Встановлено, що основною причиною хімічного розкладання рутенату свинцю і утворення діоксиду рутенію при відпалюванні гетерофазних систем є присутність компонент скла з високою кислотністю. При цьому питомий опір плівки зменшується, тому що електропровідність діоксиду рутенію на два порядки вище електропровідності рутенату свинцю. Таким чином досягається можливість управління параметрами нанокомпозитних елементів гібридних інтегральних схем. Виявлено, що термообробка систем "скло-кластери RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$" викликає утворення нової фази, а також перебудову енергетичних зон системи, що позначається на електропровідності плівки.

Исследованы структурно-фазовые превращения в нанокомпозитных системах "стекло-кластеры RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$", и их связь с электрофизическими параметрами нанокомпозитов системы. Установлено, что при создании нанокомпозитного материала большое влияние на его проводимость имеет смачиваемость стеклом частиц функционального материала и химическая активность стекла. Установлено, что основной причиной химического разложения рутената свинца и образования диоксида рутения при отжиге гетерофазных систем является присутствие компонент стекла с высокой кислотностью. При этом удельное сопротивление пленки уменьшается, потому что электропроводность диоксида рутения на два порядка выше электропроводности рутената свинца. Таким образом достигается возможность управления параметрами нанокомозитных элементов гибридных интегральных схем. Выявлено, что термообработка систем "стекло-кластеры RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$", вызывает образование новой фазы, а также перестройку энергетических зон системы, что сказывается на электропроводности пленки.

1. Introduction

The development of nanotechnology in electronics covers not only active elements (lasers, photodetectors, etc.), but also those elements that are commonly called passive. These include, among others, modern multilevel hybrid integrated circuits (HIS) and microelectronic sensors based on "glass-RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$" systems. Annealing of such systems can be carried out at sufficiently high temperatures, because ruthenium dioxide does not dissolve in the glass matrix, which allows increasing the resistive paste annealing temperature to 1000°C. Ceramic-based products are in demand due to the possibility of creating resistive elements in a wide range of resistivity (fractions of ohms to 100 MOhm) with satisfactory temperature and time stability of resistance. This is also facilitated by the possibility of creating miniature constant and variable chip-resistors suitable for automated surface mounting and fabrication of multilayer resistive structures for GIS.

However, problems associated with structural-phase processes in such structures that significantly affect the electrophysical parameters of thick films based on "glass-RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$" structures remain open [1–3]. Until now, the data on the mechanisms of current transfer in resistive layers, as well as on the effect of micro- and nanosized inclusions on the mechanisms of conductivity in thick resistive films, are contradictory. Since composite materials are a multiphase heterogeneous system, which includes components with different physical and chemical properties, the study of the raw material properties, compositions of organic and inorganic binders, conductive and dielectric phases, morphology and geometric dimensions of their particles becomes relevant for creating thick-film elements taking into account new opportunities of nanotechnology [4–6].

2. Experimental

The influence of quantitative and qualitative (phase and granulometric) compositions of the initial components on the structural-phase processes and electrophysical parameters of thick films based on systems "glass — clusters RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$" has been studied.

The main components of composite systems of thick-film elements were fine powders of functional material (metals, metal oxides), which provide the formation of electrically conductive properties, and a special glass frit as a permanent binder.

Ruthenium compounds are injected into glass powder, which is heat-treated to produce a resistive or dielectric paste. Functional materials (conductive phase) were introduced into the paste in the form of small particles, the maximum size of which did not exceed 5 μm. Low-melting glasses were used as a permanent binder [4–6].

Analysis of the works in the field of using a permanent binder for nanocomposites showed that it is advisable to use borosilicate glasses containing barium, zinc and bismuth oxides as a glass component. Bismuth oxide helps to stabilize the paste dielectric constant, but does not affect the conductive part of the GIS elements and is introduced into the glass composition as a neutral material in this respect. It also improves the wetting and adhesion of glass to the substrate, takes part in the creation of the structure as a glass former, and replaces toxic lead oxide. Glasses containing boron oxide in concentrations from 5 to 15 mol.% partially crystallize, forming a crystal crust. An increase in the concentration of B_2O_3 in the glass composition enhances the crystallization ability.

Glass frit, on the one hand, ensures the adhesion of the functional material to the substrate; on the other hand, it creates a "rigid frame", fixing the position of the conductive particles in it.

RuO_2 was selected as a conductive phase. The shape and dispersion of the particles of the conductive phase significantly depend on the method of obtaining its powder. We obtained it by the decomposition of ruthenium hydroxychloride. At a temperature of 300–400°C, ruthenium dioxide is formed as round particles. For the formation of a homogeneous nanocomposite, the optimal size of annealed ruthenium dioxide particles is 0.05÷0.1 μm [7]. The maximum particle size of the powder should not exceed 0.2÷0.3 parts of the thickness of the annealed film layer. In such systems, the conduction mechanism of resistive layers is determined by the height of the potential dielectric barrier between the conductive particles and the distance between them. If the thickness of the dielectric layer between the conductive particles is less than 100 Å, then the main conduction mechanism is tunneling. When the distance between conducting particles is more than 100 Å, tunneling is unlikely, and only charge carriers whose energy exceeds the barrier height can overcome the potential barrier, i.e. thermionic emission becomes the main conduction mechanism [8].

3. Results and discussion

Our research has shown that the effect of a permanent binder (glass) affects not so much in the chemical interaction with the conductive phase, but rather the wetting and dissolution of its particles. The wetting of the functional material by the glass and the reactivity of the glass are important. If the glass forms a continuous layer around each conductive particle, the contact between the particles is broken. Therefore, it is necessary that the glass does not wet the particles completely, but to such an extent that the particles are fixed in the glass matrix. In addition, spatial inhomogeneities in the distribution of conductive microparticles in the glass matrix lead to an increased local voltage under the action of an electric field and micro-breakdowns in the insulating layer, which worsens the temporal stability of the electrophysical parameters of the nanocomposite and, consequently, devices based on it.

It is established that during the film annealing there is an interaction between the conductive phase of the resistor and the glass components [4–6]. Especially the glass properties (wettability and acidity) affect the processes of structural-phase interaction of the glass matrix with the conductive phase in the system "glass — $Pb_2Ru_2O_6$". Lead ruthenate reacts with some metal oxides (B_2O_3; Al_2O_3). This interaction is associated with acid-base properties and is realized when the acidic properties of metal oxides are more pronounced than in ruthenium.

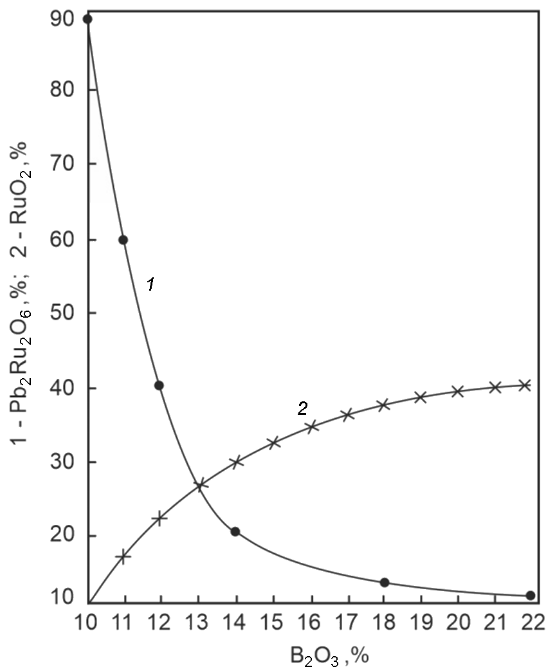

Fig. Dependences of the amount of the conductive phase (wt.%) in TLP resistors on the content of B_2O_3 in the permanent binder .

The study of the nanocomposite electrophysical parameters was performed by measuring its conductivity at different B_2O_3 compound contents. In our case, the permanent binder contains silicon and boron oxides, which acidic properties are more pronounced than in ruthenium. During paste annealing, they interact with lead ruthenate, displacing RuO_2 from it. Studies have shown that the main reason for the chemical decomposition of lead ruthenate and the formation of ruthenium dioxide during the annealing of heterophase systems is the presence of glass components with high acidity. Thus, the decomposition of lead ruthenate begins at the concentrations of B_2O_3 oxide ~ 10 %. Figure shows that as the content of B_2O_3 oxide in the constant binder resistive pastes increases, the concentration of $Pb_2Ru_2O_6$ decreases and the concentration of RuO_2 increases. In this case, the film specific surface resistance decreases, since the RuO_2 electrical conductivity is two orders of magnitude higher than the $Pb_2Ru_2O_6$ electrical conductivity.

X-ray structural analysis made it possible to conclude that glass is able to crystallize, as evidenced by the line revealed on the X-ray diffraction pattern at an angle $\theta = 15.5°$ ($d = 3.35$ Å). After heat treatment, additional very weak lines appeared at an angle $\theta = 12.1°$ ($d = 4.27$ Å) and $\theta = 29.5°$ ($d = 1.82$ Å), which indicates an increase in the concentration of the crystalline phase. The identification by the ASTM file showed that the lines belong to the α-SiO_2 (quartz) modification. Comparison of X-ray diffraction patterns of the glass before and after heat treatment showed intensification of the reflections from the crystalline phase, which can be interpreted as an increase in its content of the found lines of the found lines.

The presence of α-SiO_2 crystalline inclusions in the glass matrix leads to local changes in the conditions for glass melting and enveloping particles of the functional material with it, which cannot affect the formed film parameters. In addition, the formation of a new phase also causes the restructuring of the system energy zones. Since the crystalline phase α-SiO_2 found in the glass has a melting point above 1500°C, and the sintering of resistive layers usually occurs at temperatures up to 870°C, the glass crystalline phase does not melt and local structural disturbances appear in the matrix body, which affects the conditions for the formation of conducting chains.

In addition, random breaks in the conducting chains led to a violation of the general structure of the conducting chains in the body of the film. It was found that the presence of the α-SiO_2 crystalline phase in the glass increases the film resistance by about 10 %.

Comparison of X-ray diffraction patterns of the glasses before and after heat treatment showed that reflections from the crystalline phase are enhanced, which can be interpreted as an increase in the volume of the crystalline phase in these glasses after heat treatment.

4. Conclusions

Thus, heat treatment of nanocomposites "glass–clusters RuO_2, $Pb_2Ru_2O_6$, $Bi_2Ru_2O_7$" leads to the formation of new phases, as well as to the rearrangement of energy zones of the system, which affects the electrophysical parameters of the formed film. It has been established that the presence of a crystalline phase in glass fiber increases the resistance of the film. It was shown that the main reason for the chemical decomposition of lead ruthenate and the formation of ruthenium dioxide during annealing of the heterophase systems is the presence of glass components with high acidity. In this case, the resistivity of the composite film decreases because the electrical conductivity of ruthenium dioxide is two orders of magnitude higher than the electrical conductivity of lead ruthenate. Thus, the control of the parameters of the nanocomposite components of the GIS is achieved.

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