DEPENDENCE OF NANOCOMPOSITE SYSTEM “GLASS - Pb₂Ru₂O₆, RuO₂” ELECTROPHYSICAL PARAMETERS ON PROPERTIES OF A GLASS AND STRUCTURALLY-PHASE TRANSFORMATIONS

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Background. Electrophysical parameters (EPhP) of hybrid integrated circuits (HIC) thick-film elements or sensor sensitive elements which are formed from “glass - Pb₂Ru₂O₆; RuO₂” heterophase systems on the given time are characterized by low reproducibility and significant instability. The degradation of thick-film elements characteristics is another problem.

Objective. The aim of the paper is to establish the influence on EPhP glass properties as nanocomposite binding agent, structural-phase transformations and mechanisms of electric conductivity.

Methods. Heat treatment of nanocomposites of different structure and their X-ray structure analysis were carried out. Changing of EPhP of films from nanocomposites of different structure, and also factor of linear thermal expansion depending on external factors were determined.

Results. Influence of glass properties and structural-phase transformations in nanocomposite systems “glass - Pb₂Ru₂O₆, RuO₂” was established at their annealing. A principal cause of lead ruthenate decomposition and dioxide ruthenium formation is not thermal dissociation of initial current-carrying phase, but chemical reaction at interaction between Pb₂Ru₂Oₓ and glass binding components. It is the consequence of stronger acid properties of binding metal oxides, in particular, boron oxide. Dependence of percentage content, in particular, a current-carrying phase on B₂O₃ concentration in constant binding are established.

Conclusions. The big content of boron oxide and glass high acidity is a principal cause of chemical decomposition of lead ruthenite and formation of dioxide ruthenium at “glass - Pb₂Ru₂O₆, RuO₂” nanocomposite systems annealing. The increase of investigated system nanocomposite layers conductivity, at contents of a current-carrying phase increase it is possible to explain by percolating transition owing to occurrence of conducting phase cluster in matrix structure.

Keywords: nanocomposite heterophase system “glass- b₂Ru₂O₆, RuO₂”; structural-phase transformations; electrophysical parameters

Introduction

The functional basis of thick-film semiconductor materials make, as a rule, oxide compounds of ruthenium, for example, Ru₂, Pb₂Ru₂O₆. As glass binding agent in structure of pastes enter lead-boron-silicate glasses [1]. Nevertheless, as researches have shown, nanocomposites based on “glass - Ru₂, Pb₂Ru₂O” have low reproducibility of electrophysical parameters (EPhP) [2-4].

Principal causes of such state are insufficiently investigated structural-phase transformations, mechanisms of nanocomposite electric conductivity and degradation processes [2-4].

It is established that at annealing of thick films there is an interaction between a current-carrying phase and glass components. The phase composition of thick-film elements is appreciably connected to a glass chemical compound. That’s why in the work the combined influence of glass properties and processes of structural-phase interaction of a glass matrix with a current-carrying phase on EPhP systems “glass - Ru₂, Pb₂Ru₂Oₓ” has been investigated.

Basic part

Influence of glass composition on EPh of “glass - Pb₂Ru₂O₇-x, RuO₂” heterophase systems has been investigated. Contents of lead ruthenate and the constant binding agent in paste inorganic components, made accordingly 20, 30, 35 weights %. The resistive films received by annealing the pastes applied on ceramics BK-94 at 850 °C, the time of stand at the maximal temperature made 15 minutes.

It is established that in pastes which contain in an initial state only Pb₂Ru₂O₇-x, after annealing on roentgenograms is observed not one crystal phase as it was necessary to wait, but two crystal phases, which correspond to compound Pb₂Ru₂O₇-x (with structure of pyrochlorine) and Ru₂ (with structure of rutile). Occurrence of dioxide ruthenium in layers cannot be connected with thermal dissociation of initial current-carrying phase (CCPh) as the temperature of annealing for this purpose is small. So, Ru₂ forms as a result of chemical reactions at interaction between Pb₂Ru₂O₇-x and binding agent components.

Lead ruthenate interact with some oxide metals. This interaction is connected to the acid-base properties
and realized because at these acids metals acid properties are expressed more strongly, than at ruthenium. In constant binding agent of resistive pastes in our case there are components which acid properties are expressed more strongly, than at ruthenium. Thus in paste annealing process components of a glass interact with lead ruthenate, displacing Ru₂ out of it. To oxides of acidic compound which enter into glass refer silicon, aluminium and boron oxides. It is established that the large contents of boron oxide and high glass acidity are principal causes of chemical decomposition of lead ruthenate and formation of ruthenium dioxide at annealing of heterophase systems. Destruction of lead ruthenate begins at acid B₂O₃ concentration ~ 10...20 % (Fig. 1).

The film surface resistivity decreases, as electric conductivity of Ru₂ is two orders higher than electric conductivity of Pb₂Ru₂O₆. With increase of B₂O₃ oxide concentration in glass the conductivity increasing begins at smaller concentration of Pb₂Ru₂O₆.

The content variation changes not only the acid-base (chemical), but also physical and chemical properties of glass binding agent. Changing of Pb/Si₂ ratio in structure of two-component glasses results in changing of basicity and reduction of temperature coefficient of linear expansion. Such property changing naturally influences also on formation of film elements circuit resistors physical properties. With increase of PbO concentration acidity grows, that is concentration of Ru₂ grows, resistance falls. The reduction of the surface resistivity $p_s$ at increasing of PbO concentration proceeds under the parabolic law with extreme value at 80 % PbO (Fig. 2).

The further increasing of $p_s$ is connected with the fact that concentration of PbO is increased due to decomposition Pb₂Ru₂O₆. Introduction of bivalent metal acids into glass structure raises $p_s$. The particularly large influence make PbO, BaO, CaO. It is reflected in increase of $p_s$ of dielectric barriers between the particles of conducting phase.

Whether this process proceeded under the action only the acide-base interaction which results in RuO₂ accumulation in film bulk their resistance should be steadily to decrease.

Fig. 1. Dependence of percentage contents of a current-carrying phase on concentration B₂O₃ in constant binding agent (1 - Pb₂Ru₂O₆; 2 – RuO₂)

![Fig. 1](image1)

Fig. 2. Dependence of the surface resistivity on Pb contents in the structure of two-componential glasses. Content of Pb₂Ru₂O₆ in an initial composition, %: 1 - 20, 2 - 35, 3 - 50

Nevertheless, this value changes not monotonously, under constant binding agent compound, but under some law with extreme value (Fig. 2).

Changing of glass compounds can result in gradual change (reduction) of an internal deformation pressure in a film, in its removal and even development in an opposite direction [5]. Such changing of an internal pressure can be reflected in change of thickness of dielectric barriers between the particles of the current-carrying phase and be imposed on processes, which proceed at formation of the film properties.

At studying of concentration dependence of film electroconductivity it is established, that at increase of Pb₂Ru₂O₆$\gamma$ conducting phase concentration up to 30 % and above prompt growth of film conductivity takes place. It is possible to explain such increase by percolating transition electroconductivity owing to occurrence of cluster of conducting phase in a glass
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matrix. It was marked, that with increase of $B_2O_3$ oxide concentration in glass the conductivity increasing begins at smaller $Pb_2Ru_2O_{7-x}$ concentration owing to increase of concentration of more high conducting $Ru_2$ phase in matric-disperse system.

As the mechanism of current transport it was considered electron carry between separate conducting grains owing to thermionic emission which assumes presence of activating process. The mechanism of electron tunneling has been considered also. Temperature-activating component can appear because of redistribution of charges between the conductive islands. Probable is tunnel-resonant conductivity owing to presence of impurity in a glass matrix.

Electric conductivity of thick films on a basis of ruthenates has the mixed character of conductivity as a combination of processes which proceed in a current-carrying phase and glass phase. The current-carrying phase has metal conductivity. Charge carrier moving through thin glass phase layers, surrounding a current-carrying phase, occurs on the help of tunnel effect in energetically narrow zone which turns out at glass doping by ions which diffuse from a current-carrying phase.

It is established, that varying of glass binding agent compound in system $PbO-SiO_2-B_2O_3$ changes not only the acide-base (chemical), but also physical and chemical properties of glass binding agent. Change of ratio $PbO-SiO_2-B_2O_3$ in structure of three-componential glasses results in changing of basicity, and also for change of temperature coefficient of linear expansion (TCLE) (Fig. 3).

As the basic glass forming component of glassy bond of nanocomposit it is selected bismuth oxide which gives an opportunity to receive more fusible glasses. Doping impurity ($SiO_2$, $CdO$, $ZnO$, $MgO$, $B_2O_3$) picked up so that to provide necessary film element physicotechnical characteristics in structure of integrated circuits and composites materials.

Reduction of glass softening beginning temperature up to 400 – 430°C allows lowering resistive materials annealing temperature on 100 – 150°C, that considerably reduces expenses for their manufacturing.

**Conclusions**

The high contents of boron oxide and high acidity of glasses is a principal cause of chemical decomposition of lead ruthenate and formation of ruthenium dioxide at annealing of heterophase systems. Destruction of lead ruthenate begins at concentration of $B_2O_3$ acid about 10... 20 %. The ratio of components of the alkaline and acid character should be less then 1. In this case, this amount is about 0.5. With increasing of $B_2O_3$ oxide concentration in glass the conductivity increasing begins at smaller $Pb_2Ru_2O_{7-x}$ concentration.

Increasing of resistive layers conductivity at increasing the current-carrying phase content it is possible to explain by percolating transition owing to cluster conducting phase occurrence in a glass matrix.

As the physical mechanism of current passage is the possible of electron transferring between separate conducting grains with the help of thermionic emission, which assumes presence of activating process. The mechanism of electron tunneling also takes place.

The structure varying changes not only the acidic-alkalide (chemical), but also physical and chemical properties of SC. Changing of ratio $Pb/SiO_2$ in structure of the two- componential glasses results in changing of basicity, and also for reduction of temperature coefficient of linear expansion. Such changing of properties naturally influences on formation of resistor physical properties. With $PbO$ increasing the acidity grows, that is the concentration of $RuO_2$ grows, resistance falls.

Changing of $PbO-SiO_2-B_2O_3$ ratio in structure of three-componential glasses results in changing of basicity, and reduction of temperature coefficient of linear expansion.

**References**


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Залежність електрофізичних параметрів нанокомпозитів систем “стекло – Pb$_2$Ru$_2$O$_6$, RuO$_2$” від властивостей скла і структурно фазових перетворень

Проблематика. Електрофізичні параметри (ЕФП) товстоплівкових елементів гібридних інтегральних схем (ГІС) або чутливих елементів сенсорів, які формуються з гетерофазних систем “стекло – Pb$_2$Ru$_2$O$_6$, RuO$_2$”, на даний час характеризуються низькою відтворюваністю і значною нестабільністю. Проблемою є також деградація вихідних характеристик товстоплівкових елементів.

Мета досліджень. Встановити вплив на ЕФП властивостей скла як зв’язуючого нанокомпозитів, структурно-фазових перетворень і механізми електропровідності.

Методика досліджень. Проводилися термообробка різного складу нанокомпозитів і рентгеноструктурний аналіз. Визначалась зміна ЕФП плівок з нанокомпозитів різного складу, а також коефіцієнт лінійного термічного розширення в залежності від зовнішніх чинників.

Результати досліджень. Встановлено вплив властивостей скла і структурно-фазових перетворень в нанокомпозитних системах “стекло – Pb$_2$Ru$_2$O$_6$, RuO$_2$” при їх відпалюванні. Основною причиною розкладання рутеніту свинцю і утворення діоксиду рутеніту є не термічна дисоціація початкової структурної фази, а хімічна реакція при взаємодії між Pb$_2$Ru$_2$O$_7$ і компонентами скліноподібного зв’язуючого. Це є наслідком сильних кислотних властивостей оксидів металів зв’язуючого, зокрема оксиду рутенію. Встановлено, зокрема, залежності процентного вмісту структурної фази від концентрації B$_2$O$_3$ в постійному зв’язуючому.

Висновки. Великий вміст оксиду бору і висока кислотність скла – основна причина хімічного розкладу рутеніту свинцю і утворення діоксиду рутеніту при відпалюванні нанокомпозитних систем “стекло – Pb$_2$Ru$_2$O$_6$, RuO$_2$”.

Збільшення провідності нанокомпозитних шарів досліджуваної системи при зростанні вмісту структурної фази можна пояснити перколоційним переходом внаслідок виникнення кластера провідної фази у складі матриці.

Ключові слова: нанокомпозитна гетерофазна система “стекло-Pb$_2$Ru$_2$O$_6$, RuO$_2$”; структурно-фазові перетворення; електрофізичні параметри