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DEPENDENCE OF NANOCOMPOSITE SYSTEM “GLASS - $PB_2RU_2O_6$, RUO_2” 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 - $Pb_2Ru_2O_6$; RuO_2” 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 - $Pb_2Ru_2O_6$, RuO_2” were 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 $Pb_2Ru_2O_{7-x}$ 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 B_2O_3 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 - $Pb_2Ru_2O_6$, RuO_2” nanocomposite systems annealing.
The increase of investigated system nanocomposite layers conduction, 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- $b_2Ru_2O_6$, RuO_2”; structural-phase transformations; electrophysical parameters

Introduction

The functional basis of thick-film semiconductor materials make, as a rule, oxide compounds of ruthenium, for example, Ru_2, $Pb_2Ru_2O_6$. As glass binding agent in structure of pastes enter lead-boron-silicate glasses [1]. Nevertheless, as researches have shown, nanocomposites based on “glass - Ru_2, Pb_2Ru_2O” 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 - Ru_2, $Pb_2Ru_2O_6$” has been investigated.

Basic part

Influence of glass composition on EPh of “glass - $Pb_2Ru_2O_{7-x}$, RuO_2” 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 temperature 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 $Pb_2Ru_2O_{7-x}$, after annealing on roentgenograms is observed not one crystal phase as it was necessary to wait, but two crystal phases, which correspond to compound $Pb_2Ru_2O_{7-x}$ (with structure of pyrochlorine) and Ru_2 (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, RuO_2 forms as a result of chemical reactions at interaction between $Pb_2Ru_2O_{7-x}$ 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 Ru_2 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 B_2O_3 concentration ~ 10...20 % (Fig. 1).

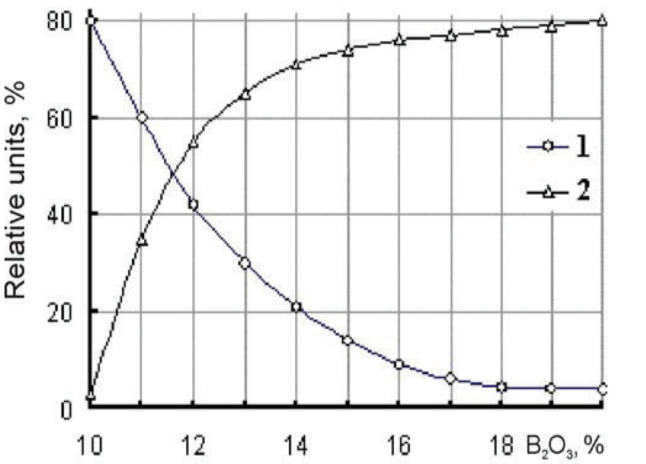

Fig. 1. Dependence of percentage contents of a current-carrying phase on concentration B_2O_3 in constant binding agent (1 - $Pb_2Ru_2O_6$; 2 – RuO_2)

The film surface resistivity decreases, as electric conductivity of Ru_2 is two orders higher than electric conductivity of $Pb_2Ru_2O_6$. With increase of B_2O_3 oxide concentration in glass the conductivity increasing begins at smaller concentration of $Pb_2Ru_2O_6$.

The content variation changes not only the acid-base (chemical), but also physical and chemical properties of glass binding agent. Changing of Pb/Si_2 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 Ru_2 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 $Pb_2Ru_2O_6$. Introduction of bivalent metal acides 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 RuO_2 accumulation in film bulk their resistance should be steadily to decrease.

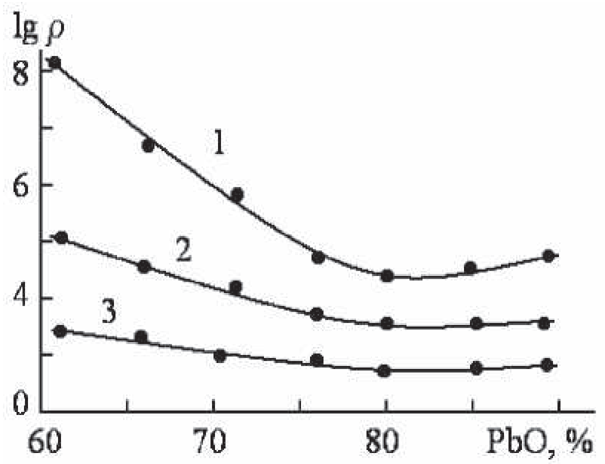

Fig. 2. Dependence of the surface resistivity on Pb contents in the structure of two-componential glasses. Content of $Pb_2Ru_2O_6$ in an initial composition, %: 1 - 20, 2 - 35, 3 - 50

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 elecrtoconductivity it is established, that at increase of $Pb_2Ru_2O_{7-x}$ 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 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 highconducting 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-SO_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).

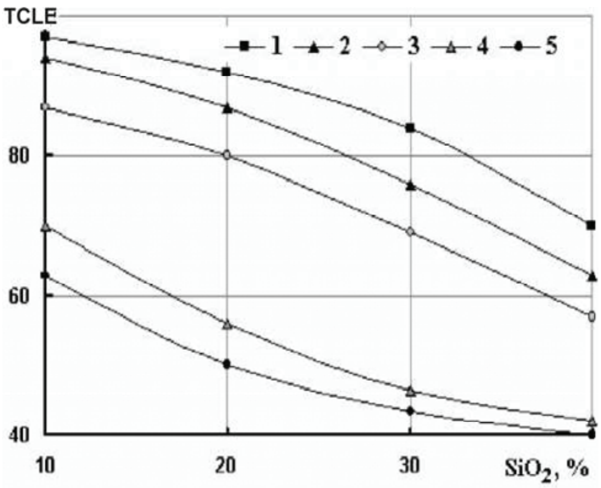

Fig. 3. Dependence of temperature coefficient of linear expansion (TCLE,α – 10^{-7}degree^{-1}) on changing of SiO_2 contents thanks to PbO. Content of B_2O_3, %: 1 - 10, 2 - 20, 3 - 30, 4 - 50, 5 - 60

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 – 430^0 C allows lowering resistive materials annealing temperature on 100 – 150^0C, 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 currentpassage 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.

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Залежність електрофізичних параметрів нанокомпозитів систем “скло – $Pb_2Ru_2O_6$, 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 “скло – $Pb_2Ru_2O_6$, 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. Визначалася 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 “скло – $Pb_2Ru_2O_6$, RuO_2” при їх відпалюванні. Основною причиною розкладання рутеніту свинцю і утворення діоксиду рутенію є не термічна дисоціація початкової струмопровідної фази, а хімічна реакція при взаємодії між $Pb_2Ru_2O_{7-x}$ і компонентами скляного зв’язуючого. Це є наслідком сильніших кислотних властивостей оксидів металів зв’язуючого, зокрема оксиду бору. Встановлено, зокрема, залежності процентного вмісту струмопровідної фази від концентрації B_2O_3 в постійному зв’язуючому.

Висновки. Великий вміст оксиду бору і висока кислотність скла – основна причина хімічного розкладу рутеніту свинцю і утворення діоксиду рутенію при відпалюванні нанокомпозитних систем “скло – $Pb_2Ru_2O_6$, RuO_2”.

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

Ключові слова: нанокомпозитна гетерофазна система “скло-$Pb_2Ru_2O_6$, RuO_2”; структурно-фазові перетворення; електрофізічні параметри

Лепих Я.И., Лавренова Т.И.

Зависимость электрофизических параметров нанокомпозитов систем “стекло – $Pb_2Ru_2O_6$, RuO_2” от свойств стекла и структурно фазових превращений

Проблематика. Электрофизические параметры (ЭФП) толстопленочных элементов гибридных интегральных схем (ГИС) или чувствительных элементов сенсоров, которые формируются из гетерофазных систем “стекло – $Pb_2Ru_2O_6$; RuO_2”, на данное время характеризуются низкой воспроизводимостью и значительной нестабильностью. Проблемой является также деградация выходных характеристик толстопленочных элементов.

Цель исследований. Установить влияние на ЭФП свойств стекла как связывающего нанокомпозитов, структурно-фазовых преобразований и механизмы электропроводности.

Методика исследований. Проводились термообработка нанокомпозитов разного состава и рентгеноструктурный анализ. Определялось изменение ЭФП пленок из нанокомпозитов разного состава, а также коэффициент линейного термического расширения в зависимости от внешних факторов.

Результаты исследований. Установлено влияние свойств стекла и структурно-фазовых превращений в нанокомпозитных системах “стекло – $Pb_2Ru_2O_6$; RuO_2” при их отжиге. Основной причиной разложения рутената свинца и образования диоксида рутения является не термическая диссоциация начальной токопроводящей фазы, а химическая реакция при взаимодействии между $Pb_2Ru_2O_{7-x}$ и компонентами стеклянного связующего. Это является следствием более сильных кислотных свойств оксидов металлов связующего, в частности, оксида бора. Установлены, в частности, зависимости процентного содержимого токопроводящей фазы от концентрации B_2O_3 в постоянном связующем.

Выводы. Большое содержание оксида бора и высокая кислотность стекла – основная причина химического разложения рутенита свинца и образования диоксида рутения при отжиге нанокомпозитных систем “стекло – $Pb_2Ru_2O_6$; RuO_2”.

Увеличение проводимости нанокомпозитных слоев исследуемой системы при возрастании содержимого токопроводящей фазы можно объяснить перколяционным переходом вследствие возникновения кластера проводящей фазы в составе матрицы.

Ключевые слова: нанокомпозитная гетерофазная система “стекло-$Pb_2Ru_2O_6$, RuO_2”; структурно-фазовые преобразования; электрофизические параметры