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FEATURES OF INTERACTION OF COMPONENTS IN "GLASS- $Pb_2Ru_2O_{7-x}$, RuO_2" HETERO-PHASE SYSTEMS

Resistance pastes on basis RuO_2 differ by a relative chemical inactivity. Large maintenance of boron oxide and high acidity of glasses are the main reasons of chemical $Pb_2Ru_2O_{7-x}$ decomposition and formation of ruthenium dioxide under annealing of the hetero-phase systems. The increase of resistive layers conductivity with the growth of conduction phase maintenance can be explained by percolation transition because of conducting phase cluster formation in the glass matrix. The increase of conductivity begins at lower concentrations $Pb_2Ru_2O_{7-x}$ with growth of B_2O_3 concentration in glass. The transfer of electrons between separate conducting grains by means of thermo electronic emission with the presence of activating process is the possible current mechanism. Mechanism of electrons tunneling also takes place.

INTRODUCTION

Thick-film technology is one of the basic methods of radio electronic apparatus complex miniaturization. Resistors and conductive elements in the general volume of hybrid integrated elements take large space. Resistance pastes on basis RuO_2 differ by a relative chemical inactivity. They can be made with the wide range of surface resistance, low values of temperature coefficient of resistance (TCR). Dioxide of ruthenium (rutile) does not dissolve in a glass matrix, what allows to promote the temperature of annealing to 1200^{0}C and to get resistance compositions properties which insignificantly depend on the annealing profiles. Large positive TCR is compensated due to glass-binding or special alloying additions in small concentrations. With the purpose of economy of expensive pure ruthenium in the paste, ruthenium compounds with appropriate crystalline structure similar to pyrclorine are widely used in resistance pastes $M_2Ru_2O_7$. In particular, the lead ruthenate obtained by sintering at 800–880^{0}C of dioxide of ruthenium and oxide or salt of lead mixture is used. Such material has low surface resistance and cubic crystalline structure.

It is known that forming of ruthenic resistors thick films is accompanied by difficult chemical processes [1]. During the paste annealing the interaction between the conductive phase of resistor and glass and binding compound appears. The phase composition of resistor base on $Pb_2Ru_2O_{7-x}$ strongly related to chemical composition of permanent and temporal binding compounds of the resistance paste.

The influence of the glass composition on conductivity of the hetero-phase system of "glass- $Pb_2Ru_2O_{7-x}$, RuO_2" was studied in the present work.

RESULTS AND THEIR DISCUSSION

The $Pb_2Ru_2O_{7-x}$ content and permanent binding compound in the inorganic components of the studied pastes were 30 and 70 w %, correspondently. Resistance films have been obtained by annealing of the pastes, deposited on ceramics at 850 ^{0}C. The exposition time at maximal temperature was 15 min.

It was figured out that in pastes containing only $Pb_2Ru_2O_{7-x}$ before annealing, two crystalline phases were observed in X-ray-diagram, corresponding to pyrclorine $Pb_2Ru_2O_{7-x}$ and rutile RuO_2 phases. The appearance of ruthenium dioxide in the layers is impossible to explain by thermal dissociation of initial conduction phase (CCP), because the annealing temperature is not enough for activation of this process. Consequently, RuO_2 appears as a result of chemical reactions via interaction between $Pb_2Ru_2O_{7-x}$ and binding components of resistive paste.

It is known that $Pb_2Ru_2O_{7-x}$ interacts with some metal oxides. This interaction is affected by acid-base transitions and can be realized because acidic properties of those metal oxides are stronger than in case of ruthenium. Therefore, it is possible to conclude that in our case in the permanent binding compound of resistive paste there are components with acid stronger properties than ruthenium. Thus, RuO_2 is formed within chemical reaction, affected by interaction of binding components of the paste with $Pb_2Ru_2O_{7-x}$.

In glass resistors composition there are silicon, aluminum and boron oxides belonging to acid type. In [1] from the method of X-ray-phase analysis results it was published that only B_2O_3 destroys $Pb_2Ru_2O_{7-x}$ completely. We studied pastes based on glasses containing silicon and boron oxides. In fig.1 the change of $Pb_2Ru_2O_{7-x}$ and RuO_2 content in resistors on the basis of the system of "$Pb_2Ru_2O_{7-x}$ — Pb-Si-B- glasses" is presented. It can be seen that with the increase of B_2O_3 content in binding components of resistive paste $Pb_2Ru_2O_{7-x}$ concentration diminishes and RuO_2 in thick films concentration increases. These results are similar to the data, published in [1]. Thus, appearance RuO_2 in resistors is affected by Ru substitution with boron in $Pb_2Ru_2O_{7-x}$.

Instability of $Pb_2Ru_2O_{7-x}$ in resistance pastes results not only from the B_2O_3 presence in glass composition. The process of formation of ruthenium dioxide begins with the certain concentration of boron oxide. Lead ruthenate collapses in resistors with glasses, which have concentration of acid-type oxides close or higher to lead oxide concentration. In fig.1 $Pb_2Ru_2O_{7-x}$ decomposition of begins at the acid B_2O_3 concentrations about 10...20 %. It was found, that only in glasses with $Pb_2Ru_2O_{7-x}$ content no more than 30% noticeable increase RuO_2 takes place. Consequently, interaction of $Pb_2Ru_2O_{7-x}$ with binding components of the paste starts if the glass contains boron oxide and has certain base properties. The relation of basic and acid components must be less than 1. In our case this value was 0.5.

The content of temporary binding components in the paste composition plays considerable role. The increase of ruthenium dioxide maintenance in the resistors obtained from pastes with organic binding agent based on fat passes through the stage of metallic ruthenium formation with subsequent oxidization to ruthenium dioxide. Therefore, it can be explained that considerable $Pb_2Ru_2O_{7-x}$ decomposition (fig. 1) takes place under the boron oxide concentration up to 20%, while $Pb_2Ru_2O_{7-x}$ maintenance in the initial component is more than 30%. It points to the fact that transition function of lead ruthenate transformation to ruthenium dioxide is partly provided by temporary organic binding agent.

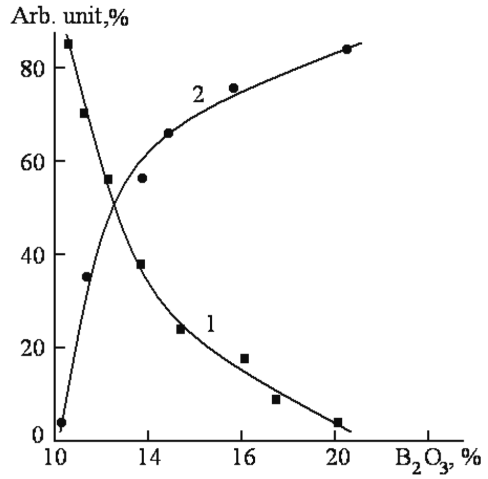

Fig.1. Dependence of CCP percentage content on the concentration B_2O_3 in permanent binding agent. 1 — $Pb_2Ru_2O_{7-x}$; 2 — RuO_2

Electrical properties of the obtained layers were studied. It was found that with the increase of conductive phase-permanent binding agent ration in pastes (CCP:CS) the surface resistance of the films goes down (fig.2) and the TCR values comes from the positive values to negative. Thus, the investigated layers show the features described by classic dependence of the layer properties on its composition for thick-film resistive materials. The dependence is conditioned by diminishing of dielectric layers thickness between the CCP particles and ramification of their cluster chains under decreasing of the bulk part of CS. The change of microstructure of $Pb_2Ru_2O_{7-x}$ and RuO_2 resistors under the increase of CCP maintenance in resistive layers was confirmed by microscopic studies performed before [2]. The resistive elements based on RuO_2 have lower resistance and TRC value is much higher in the positive values region in comparison with thick-film resistors (TFR) based on $Pb_2Ru_2O_{7-x}$ (with the identical bulk part of CCP). It is explained by higher conductivity of RuO_2 clusters.

Different electrical properties are shown by resistive elements with the identical CCP concentration but with the different dispersion parameter of initial phases. It is explained by influence of CCP and CS particle sizes on microstructure and electrical properties of the hetero-phase systems. It is known that thinner initial powders of ingredients are, i.e. the higher the active surface area, the higher resistivity and smaller and even negative TCR values show thick-film resistors. However, the opposite dependences can take place and [2].

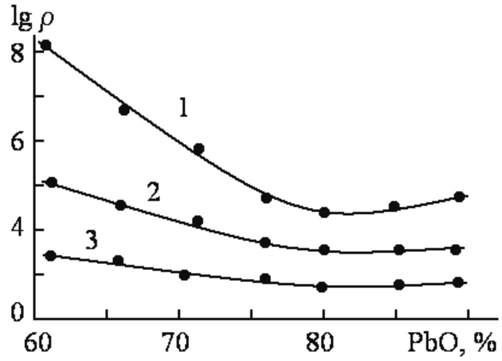

Fig.2 Dependence of surface resistance on PbO contents in two-component glasses composition. $Pb_2Ru_2O_{7-x}$ content in initial composition, %: 1 — 20, 2 — 35, 3 — 50.

Composition varying changes not only acid-basic (chemical) but also physical and chemical properties of CS [3]. Change of PbO/SiO_2 ration in two-component glasses composition causes the change of basicity, and also to decrease of linear expansion temperature coefficient (TCLE). Such change of properties appropriately influences on electrical properties of TFR. Acidity grows with PbO growth, i.e. concentration RuO_2 grows, resistance decreases (fig.2). If this process occurred only as acid-basic interaction, resulting in RuO_2 accumulation in bulk films, their resistance must constantly decline. However, this value doesn't change monotonically with CS composition, but according to dependence with the extreme value (fig. 2). The change of glasses composition can lead to gradual change (diminishing) of internal deformation tension in resistive films, to its removal and even development to opposite direction. Such change of internal tension can be reflected on the change of dielectric barriers thickness between the CCP particles and to be interfered with the processes occurring under TFR forming.

The investigation of concentration dependence of resistive films conductivity showed that the resistive films conductivity considerably grows with the increase of concentration of conducting phase $Pb_2Ru_2O_{7-x}$ up to 30% and higher. Such increase is explained by conductivity percolation transition because of conducting phase cluster formation in a glass matrix. It was emphasized that with growth of B_2O_3 concentration in glass the increase of conductivity begins at the lower $Pb_2Ru_2O_{7-x}$ concentrations because of high-conducting phase RuO_2 concentration increase in the matrix-dispersible system.

The transfer of electrons between separate conducting grains by means of thermo electronic emission with the presence of activating process was supposed as the conductivity mechanism. The mechanism of electrons tunneling was also considered. A temperature-activating component can appear from the redistribution of charges between the conductivity isles. Tunnel-resonance conductivity is possible because of admixtures presence in the glass matrix.

CONCLUSIONS

Large maintenance of boron oxide and high acidity of glasses are the main reasons of chemical $Pb_2Ru_2O_{7-x}$ decomposition and formation of ruthenium dioxide under annealing of the hetero-phase systems.

The increase of resistive layers conductivity with the growth of conduction phase maintenance can be explained by percolation transition because of conducting phase cluster formation in the glass matrix. The increase of conductivity begins at lower concentrations $Pb_2Ru_2O_{7-x}$ with growth of B_2O_3 concentration in glass.

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FEATURES OF CO-OPERATION OF COMPONENTS IN HETERO-PHASE SYSTEMS OF "GLASS- $Pb_2Ru_2O_{7-x}$, RuO_2"

Abstract

Resistance pastes on basis RuO_2 differ by a relative chemical inactivity Large maintenance of oxide of the coniferous forest and high acidity of glasses, is principal reason of chemical decomposition of $Pb_2Ru_2O_{7-x}$ and formation of dioxide of ruthenium at burning of the hetero-phase systems

As the physical mechanism of current-conduction the transfer of electrons is credible between separate conducting corns by means of thermic-emission emission supposing the presence of activating process.

Key words: RuO_2 resistive pastes, $Pb_2Ru_2O_{7-x}$ compounds, hetero-phase systems.

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ОСОБЕННОСТИ ВЗАИМОДЕЙСТВАИЯ КОМПОНЕНТОВ В ГЕТЕРОФАЗНЫХ СИСТЕМАХ "СТЕКЛО — - $Pb_2Ru_2O_{7-x}$, RuO_2 "

Резюме

Резистивные пасты на основе RuO_2 отличаются относительной химической инертностью. Большое содержание оксида бора и высокая кислотность стёкол — основная причина химического разложения рутенита свинца и образования диоксида рутенита при обжиге гетерофазных систем.

В качестве физического механизма токопротекания вероятен перенос электронов между отдельными проводящими зёрнами посредством термоэлектронной эмиссии, предполагающей наличие активационного процесса. Также наблюдался механизм. туннелирования электронов

Ключевые слова: рутенит свинца, туннелирование электронов, гетерофазные системы.

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ОСОБЛИВОСТІ ВЗАЄМОДІЇ КОМПОНЕНТІВ У ГЕТЕРОФАЗНИХ СИСТЕМАХ "СКЛО — - $Pb_2Ru_2O_{7-x}$, RuO_2 "

Резюме

Резистивні пасти на основі RuO_2 характеризуються відносною хімічною інертністю. Великий склад оксиду бора і висока кислотність скла — основна причина хімічного розкладу рутеніта свинця і утворення діоксида рутеніта при обжигу гетерофазних систем.

В якості фізичного механізму струмопротікання вирогіден перенос электронів проміж окремими провідними зернами за допомогою термоелектронної емісії, при наявності активаційного процесу. Також спостерігався механізм. тунелювання электронів

Ключові слова: рутеніт свинця, тунелювання электронів, гетерофазні системи.