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Production, Structure and Properties of Coatings Based on Al_2O_3 Obtained by Magnetron Method

D.A. Kolesnikov[1], I.V. Sudzhanskaya[1], I.Yu. Goncharov[1,2], S.V. Lytovchenko[3], V.Yu. Novikov[1], E.A. Kudryavtsev[1], B.O. Mazilin[3], E.V. Krytsyna[1], V.M. Beresnev[3], O.V. Glukhov[4]

[1] *Belgorod State National Research University, 85, Pobiedy St., 308015 Belgorod, Russia*
[2] *Belgorod State Technological University named after V.G. Shukhov, Belgorod, Russia*
[3] *V.N. Karazin Kharkiv National University, 4, Svoboby Sq., 61000 Kharkiv, Ukraine*
[4] *National University of Radio Electronics, 14, Science Boulevard, 61166 Kharkiv, Ukraine*

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Al_2O_3 and Al_2O_3/ZrO_2 multilayer coatings were deposited by the magnetron method by sputtering the corresponding metal targets in a mixture of oxygen and argon gases. The microstructure of the cross sections to determine the thickness and elemental composition of the obtained coatings was studied by transmission and scanning electron microscopy. The surface morphology of Al_2O_3 coating samples was studied by scanning probe microscopy. It is shown that the formed Al_2O_3 coating and the Al_2O_3/ZrO_2 multilayer coating have a columnar structure with the columns oriented perpendicular to the surface. The columnar structure of multilayer coatings is not violated during the transition from layer to layer. The coating surface consists of globules with a diameter of about 20 nm. It was found that the Al_2O_3 coating has dielectric properties using the method of impedance spectrometry. Thus, it was shown that the magnetron method can be used to apply high-quality multilayer dielectric coatings, which can be used as thermal barrier coatings to protect the blades of high-temperature stages of aircraft engine turbines.

Keywords: Magnetron by sputtering, Multilayer oxide coatings, Structure.

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1. INTRODUCTION

Currently, Al_2O_3 coatings are widely used in the semiconductor industry in metal oxide semiconductor field effect transistors (MOSFETs) [1], buffer oxide layers in a metal-ferroelectric-insulator-semiconductor field-effect transistor [2], in solar cells [3], as protective layers in microelectromechanical systems [4]. High dielectric constant, good adhesive properties to many materials, high melting point and chemical compatibility with semiconductor processes have made Al_2O_3 a technologically used material [5, 6].

It is known that the properties of coatings are determined by the method and parameters of the process of their formation. The production of coatings by the magnetron method is a well-established method for creating dense and uniform coatings with high adhesive strength and repeatability. Metal oxide layers are widely used as thermal barrier coatings to protect turbine blades in the aviation industry. The need to obtain coatings of large thickness (about 100-150 microns) forces the use of multilayer coatings to relieve stresses in them also. In addition, the need to obtain coatings that are resistant to tensile stresses occurring during bending of a turbine blade dictates the requirements for a needle or column structure oriented perpendicular to the surface of the turbine blade.

The main advantage of magnetron systems is the high coating rate and low pressure of the working gas [7], which makes it possible to obtain complex multilayer coatings. The formed structures have low internal stresses, which is a significant factor when coating thin substrates. The objective of this work is to develop a coating technology that, with sufficient thickness, can be used as thermal barrier coatings on the blades of a high-temperature stage of an airplane turbine.

2. METHODS OF PREPARATION AND EXAMINATION OF THE SAMPLES

Al_2O_3 and Al_2O_3/ZrO_2 coatings were obtained by the magnetron method using the "NIKA 2012" multifunctional vacuum unit on silicon substrates with a titanium sublayer for microscopic studies and on aluminum substrate for dielectric studies to exclude the influence of the substrate.

The fine structure of the coatings was studied by transmission electron microscopy (JEOL JEM 2100). To study the structure of transverse cleavages of coatings and their composition, a QUANTA 200 3D scanning electron microscope was used. Surface topography images were examined using an NTEGRA Aura scanning probe microscope (SPM). The dielectric properties of the coatings were determined by impedance spectrometry using the "Novocontrol concept 43" installation.

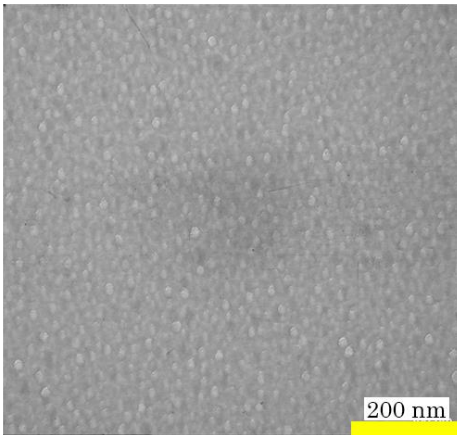
3. OBTAINING Al_2O_3 COATINGS

The Al_2O_3 dielectric coating was applied only to one (outer) surface of the plate. The plate was mounted with the working surface to the surface of the cathode in the chamber. The rotation of the sample around its axis during the coating deposition process was disabled.

After loading the sample and evacuating the vacuum to a pressure of 10^{-4} Pa, the samples were cleaned with a beam of medium-energy ions using a high-frequency ion source in an argon atmosphere. The argon pressure reached $(5\text{-}6)\cdot10^{-2}$ Pa. After that, the ion source was turned off, the argon supply was shut off, and a residual pressure of about 10^{-4} Pa was established. Then oxygen was introduced into the chamber. The oxygen pressure was about $(7\text{-}8)\cdot10^{-2}$ Pa. The radio frequency plasma generator (RPG) was turned on, a potential of – 100 V was applied to the sample. The surface of the sample was cleaned with oxygen, and then it was coated with an oxide film. RPG power was 500 W. The cleaning time by the ion source was 3 min, and by RPG – 2 min. The flow of oxygen into the chamber was 3-4 l/h. After cleaning the surface of the sample, the oxygen flow into the chamber increased to 6-7 l/h. Argon was passed through the jacket installed in the chamber surrounding the magnetron at a flow rate of 2-3 l/h, until the gas pressure in the chamber was about 0.4 Pa without turning off the RPG and without changing its power. The coating deposition time was 1 h.

4. RESULTS AND DISCUSSION

Bright field images of the coating microstructure obtained by transmission electron microscopy (TEM), as well as electron diffraction patterns of Al_2O_3 coatings, are shown in Fig. 1. As can be seen from Fig. 1, the coatings are glued globules of about 20 nm of size for Al_2O_3 films. Globules, in turn, are composed of smaller structural elements.



a

b

Fig. 1 – Images of microstructure (a) and electron diffraction (b) of Al_2O_3 coatings obtained using TEM

Studies of the structure of transverse cleaved coatings presented in Fig. 2 clearly demonstrate the columnar structure. SPM images of the topography of the coating based on aluminum oxide Al_2O_3 surface are shown in Fig. 3. The surface of the coating is the peaks of rounded pyramids projecting to a height of approximately 7-8 nm, the diameter of which is about 100 nm.

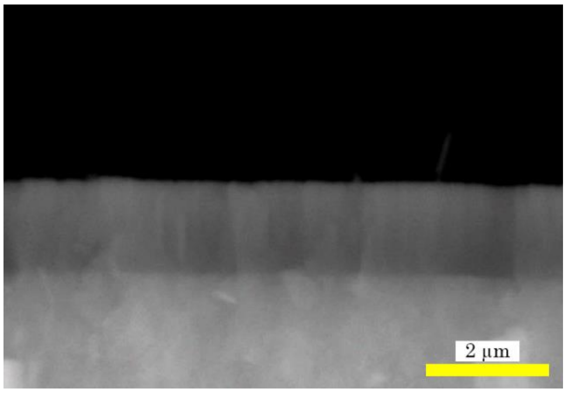
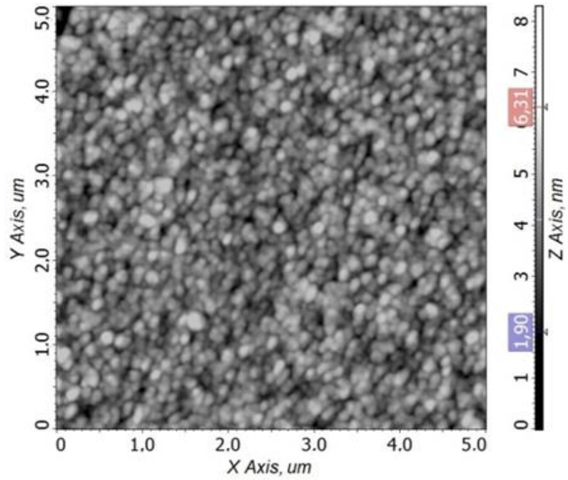
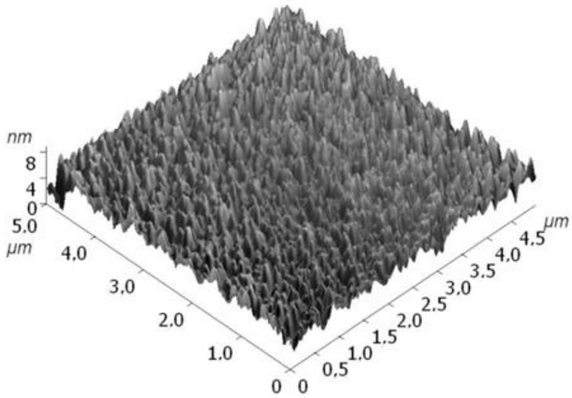


Fig. 2 – SEM cross section image of Al_2O_3 coating



a



b

Fig. 3 – Images of the surface topography of the Al_2O_3 coating obtained by scanning probe microscopy (a, b)

The elemental composition of the coatings was determined by analyzing the spectra of characteristic X-ray radiation (Fig. 4) arising from the interaction of electrons with the coating material.

Two large peaks corresponding to oxygen and aluminum are present in the spectrum. The ratio of oxygen and aluminum atoms in the coating is 40.94 to 59.06, which is very close to the stoichiometry of aluminum oxide Al_2O_3. The measured deviation of the material from stoichiometry may be due to the error of the device, which for aluminum is about 0.2÷0.3 %, but for oxygen it is about 3÷5 %.

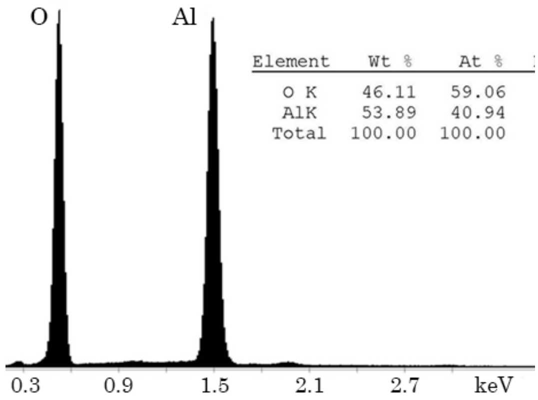


Fig. 4 – The spectrum of characteristic X-ray radiation and a table of the content of elements in the coating in terms of weight (Wt) and atomic (At) percentages

The dielectric properties of Al_2O_3 coatings were studied. The results of measurements of the dielectric constant (ε) and the dielectric loss tangent ($\tan\delta$) of Al_2O_3 coating as a function of frequency are shown in Fig. 5.

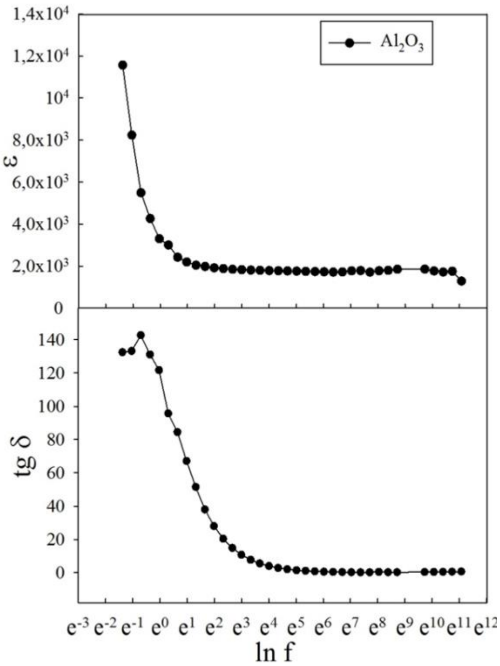


Fig. 5 – The frequency dependence of the real part of the complex dielectric constant (ε) and the dielectric loss tangent ($\tan\delta$) at room temperature for coatings based on aluminum oxides

An analysis of the dielectric constant ε and the dielectric loss tangent $\tan\delta$ as a function of frequency for coatings deposited by magnetron sputtering shows that ε and $\tan\delta$ monotonously decrease with increasing frequency. The nature of the curves indicates the absence of phase transitions and dielectric relaxation processes. The relatively high values of ε at all frequencies, as well as the high value of $\tan\delta$ at low frequencies, indicate the dielectric properties of the Al_2O_3 coating obtained.

5. OBTAINING MULTILAYER AL_2O_3/ZRO_2 COATINGS

The Al_2O_3/ZrO_2 multilayer coating was applied from two cathodes. The deposition mode with stops at each magnetron was 2 min for each magnetron. Total amount of layers is 40 (20 of each type). The total coating thickness is about 2 microns. Coating deposition time was 80 min. The first cathode was aluminum, the second one was zirconium with iron inserts, in order to obtain zirconia stabilized by iron oxide. The inserts are cylindrical with a diameter of 5 mm, so that in the erosion zone the percentage of the area occupied by the inserts relative to the area occupied by zirconium is about 6÷7 % (Fig. 6).

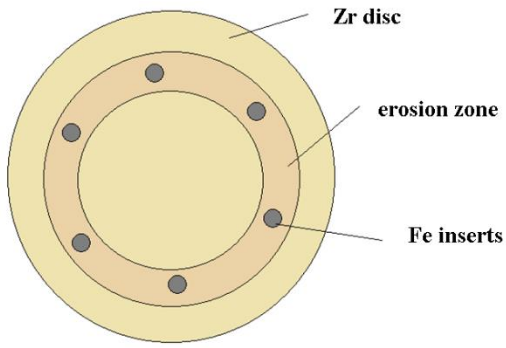


Fig. 6 – Schematic representation of a composite cathode for deposition of layers containing ZrO_2

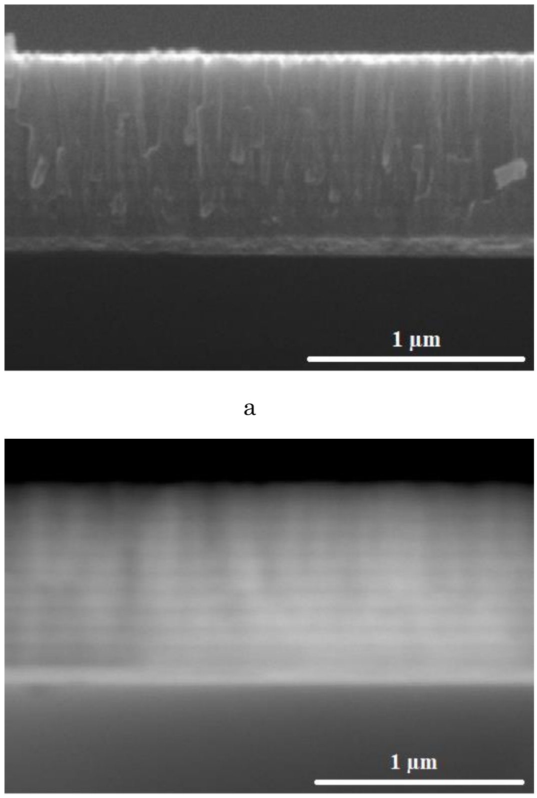


Fig. 7 – Cross section image of the Al_2O_3/ZrO_2 multilayer coating in topographic (SE-a) and phase (BSE-b) contrast obtained by scanning electron microscopy (SEM)

The substrate was cleaned at the same parameters as for the deposition of an alumina coating. In addition, a titanium buffer layer of about 150 nm thickness was deposited on the coating surface.

Initially, cathodes of Al and Ti were installed in the chamber. After applying the titanium sublayer, a zirconium cathode with iron inserts was replaced. A sublayer was applied in order to check the adhesion of the coating to titanium. A single-crystal Si substrate was selected in order to easily cross-chip. After air was let into the chamber, a part of the titanium sublayer was etched off by an ion source with argon supply for 10 s. Next, the ion source was turned off, oxygen was introduced into the chamber, argon was passed into the magnetron region, and a multilayer coating was deposited at the parameters presented below: gas pressure 0.5 Pa; Ar supply of 1.1 l/h for each magnetron; O_2 supply: flow directly into the chamber (3.2 l/h); magnetrons/aluminum target: voltage 770 V, current 5 A; zirconium composite target: voltage 930 V, current 5 A.

The current stabilization was used in both cases.

A columnar structure is clearly observed through the entire multilayer coating, which is associated with the dynamics of coating growth.

It should be noted that, despite the change in the phase composition in the layers, columnar structure disturbances are not observed over the entire coating thickness (Fig. 7). Most likely, such a structure is determined by the growth dynamics of the coating and does not depend on the type of substrate. Column coatings grow on both polycrystalline and single crystal substrates.

The direction of the axis of the texture and the degree of texturing of the coating material does not depend on the type of substrate, but on the growth rate and parameters of the coating process, which, in turn, affect the magnitude of micro and macrostresses in the films, and through them the structure and texture.

6. CONCLUSIONS

Dielectric coatings based on Al_2O_3 and a multilayer coating Al_2O_3/ZrO_2 were obtained by the magnetron method using the "NIKA 2012" multifunctional vacuum unit. The thickness of Al_2O_3 coatings was about 1.6 μm and of Al_2O_3/ZrO_2 multilayer coating was about 1.2 μm. Studies of the structure showed that the obtained Al_2O_3 coating and the Al_2O_3/ZrO_2 multilayer coating have a columnar structure with a size of structural elements less than 100 nm, which is caused by the growth dynamics of the coatings and depends on the parameters of the formation process. It was found that the resulting Al_2O_3 coating has dielectric properties used on the analysis of the dielectric constant and dielectric loss tangent.

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Отримання, структура і властивості покриттів на основі Al_2O_3, отримані магнетронним методом

Д.А. Колесніков[1], І.В. Суджанская[1], В.Ю. Новіков[1], С.В. Литовченко[3], Е.А. Кудрявцев[1], І.Ю. Гончаров[1,2], Б.О. Мазілін[3], Е.В. Крицина[1]. В.М. Береснєв[3], О.В. Глухов[4]

[1] *Бєлгородський Державний Національний Дослідницький університет, вул. Перемоги, 85, 308015 Бєлгород, Російська Федерація*

[2] *Бєлгородський Державний Технологічний Університет імені В.Г. Шухова, вул. Костюкова, 46, 308012 Бєлгород, Російська Федерація*

[3] *Харківський національний університет імені В.Н. Каразіна, пл. Свободи, 4, 61000 Харків, Україна*

[4] *Національний університет радіоелектроніки, бульвар Науки, 14, 61166 Харків, Україна*

Нанесення покриттів Al_2O_3 та багатошарових покриттів Al_2O_3/ZrO_2 здійснювали магнетронним методом шляхом розпилення відповідних металевих мішеней в середовищі суміші газів кисню та аргону. Мікроструктура поперечних зрізів, визначення товщини і елементний склад отриманих покриттів досліджували методом трансмісійної та растрової електронної мікроскопії. Морфологія поверхні зразків покриттів Al_2O_3 вивчалася методом скануючої зондової мікроскопії. Показано, що сформовані покриття як Al_2O_3, так і багатошарове покриття Al_2O_3/ZrO_2 мають стовпчасту структуру з орієнтацією стовпців перпендикулярно поверхні. Стовпчаста структура багатошарових покриттів не порушується при переході від шару до шару. Поверхня покриттів складається з глобул діаметром близько 20 нм. Методом імпедансної спектрометрії встановлено, що покриття Al_2O_3 має діелектричні властивості. Таким чином, було показано, що магнетронним методом можна наносити якісні багатошарові діелектричні покриття, які можуть бути використані в якості термобар'єрних покриттів для захисту лопаток високотемпературних щабель турбін авіаційних двигунів.

Ключові слова: Магнетроне осадження, Багатошарові оксидні покриття, Структура.