

## Structure and properties of Mg, Al, Ti oxide and nitride layers formed by ion-plasma sputtering

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Dielectric layers of Al<sub>2</sub>O<sub>3</sub>, MgO, AlN and TiO<sub>2</sub> were formed by using ion-plasma sputtering method. Their microstructure and electrophysical properties in the range of 20 – 400°C were investigated. The conductivity mechanism, depth of traps and losses mechanism were established. The ohmic contact formation was revealed in TiO<sub>2</sub>/40X13 system through which an injection of charge carries from the alloy into the dielectric layer occurs and its contribution to the electric equivalent circuit of substitution was assessed.

**Keywords:** structure, properties, oxide layers, nitride layers.

Методом іонно-плазменного напилення отримані діелектричні шари Al<sub>2</sub>O<sub>3</sub>, MgO, AlN і TiO<sub>2</sub>. Досліджено їх мікроструктуру та електрофізичні властивості в діапазоні 20 – 400°C. Встановлено механізми провідності, глибина залегання ловушок і механізми втрат. Встановлено утворення омического контакту в системі TiO<sub>2</sub>/40X13, через який відбувається інжекція носіїв заряду зі сплаву у діелектричний шар, та оцінено його внесок в електричну еквівалентну схему заміщення.

**Порівняльна оцінка структури та властивостей шарів з оксидів та нітрідів Mg, Al, Ti, сформованих іонно-плазмовим напилюванням.** В.Я.Підкова, І.В.Бродніковська, З.А.Дуриагіна, В.Я.Петровський.

Методом іонно-плазмового напилення одержано діелектричні шари Al<sub>2</sub>O<sub>3</sub>, MgO, AlN та TiO<sub>2</sub>. Досліджено їх мікроструктуру та електрофізичні властивості у діапазоні 20 – 400°C. Встановлено механізми провідності, глибину залягання пасток та механізми втрат. Встановлено утворення омичного контакту в системі TiO<sub>2</sub>/40X13, через який відбувається інжекція носіїв заряду зі сплаву у діелектричний шар, та оцінено його внесок в електричну еквівалентну схему заміщення.

### 1. Introduction

Development of the modern instruments determines the requirements to the constructive materials and functional coatings which operate reliably in conditions of high temperatures, corrosive environments, erosive wear etc. For such coatings it is important to increase their heat resistance and adhesion to various substrates. They must

be resistant to the high temperatures, thermal cycling and mechanical blows. Approaches to formation of dielectric coatings are being intensively developed by surface engineering methods. As starting materials usually oxides and nitrides of various elements — Al, Si, Mg, Ba, Ti, Zr or multicomponent compounds based on oxides are used [1].

Requirements to protective dielectric coatings depend on the conditions of their

exploitation. That is why the choice of the coating should be made depending on the type of the environment, the state of the surface and the nature of the substrate material. This is particularly true for the dielectric coatings of film resistive elements that work at the high temperatures (200 – 350°C) for a long time. Such coatings should not peel away from the substrate during thermal cycling from the working to the room temperature. During extended exploitation, their structure should not undergo phase transformations which can cause changes of the dielectric properties. Such coatings must have an increased resistance to the gaseous and liquid environments.

## 2. Experimental

Oxides and nitrides of Mg, Al, Ti layers were deposited by the modes (Table) differing by the process duration ( $\tau$ ), substrate bias potential ( $E$ ), pressure ( $P$ ) and current plasma arc ( $I$ ). To ensure a better adhesion of the coatings the substrate pre-heating was carried out by using a heater installed directly into the reaction chamber of the ion-plasma system. In addition, the final cleaning of the substrate in a stream of argon plasma by using helicon source in the "column" regime was performed for 30 min. The methodology of the layers deposition is described in more detail in [2].

Study of the structure of the formed surface layers was carried out by scanning electron microscope JSM-6490LV (JEOL, Japan), with an analytical console for the element analysis (INCA Energy+Oxford). In order to assess the current losses increase and growth of the breakdown voltage of the dielectric layers, the electrical properties were investigated on alternating current. To determine the electric characteristics of the layers, a foil contact was pressed to their surface and then — an electrode. A steel substrate was used as the bottom contact (Fig. 1). Measurements of the capacitance ( $C$ ) and dielectric loss tangent ( $\text{tg}\delta$ ) at frequencies 120 Hz, 1 kHz, 10 kHz and 100 kHz were taken by bridge method with an RLC-meter in the parallel equivalent circuit regime. Magnitude of the measurement error was 0.05 %.

Calculations of the static dielectric permeability or of the real part of the complex dielectric permeability ( $\epsilon' = \epsilon$ ) (1) were made by the flat capacitor model (2)

$$\epsilon^* = \epsilon' - i\epsilon'', \quad (1)$$

Table. Regimes of ion-plasma sputtering

Layer	Substrate	$\tau$ , min	$P$ , Pa	$IE$ , V	$I$ , A
Al <sub>2</sub> O <sub>3</sub>	AMg2	10	1.9	-60	35
TiO <sub>2</sub>	40X13	10	2.6	-60	30
MgO	AMg2	20	1.9÷2,6	-60	32
AlN	40X13	40	5.9	-60	40

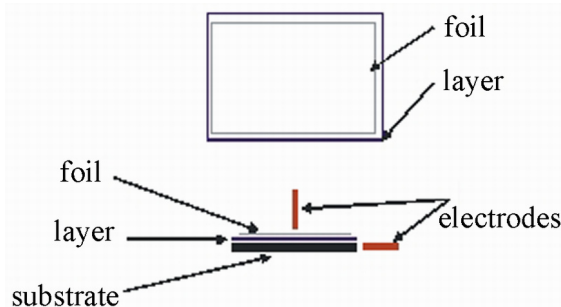


Fig. 1. Schematic representation of the electrophysical measurements.

where the dielectric losses coefficient is determined from the equation  $\epsilon'' = \epsilon' \text{tg}\delta$ .

Then

$$C = \frac{\epsilon' \epsilon_0 S}{d}, \quad (2)$$

where  $S$  — the contact area (foil),  $d$  — thickness of the dielectric layer.

The composite conductivity at the alternating current is described by:

$$\sigma(\omega) = \sigma_0 + 2\pi f \epsilon' \epsilon_0 \text{tg}\delta, \quad (3)$$

where  $\sigma_0$  — electric conductivity at the direct current. However, at high frequencies in the dielectric with few leading impurities, the first term can be neglected.

Thus, active conductivity or the real part of the complex admittance (4) was determined by the formula (5):

$$Y^* = Y' + iY'', \quad (4)$$

$$Y' = \sigma_a = 2\pi f \epsilon' \epsilon_0 \text{tg}\delta, \quad (5)$$

when its imaginary part is

$$Y'' = 2\pi f \epsilon' \epsilon_0. \quad (6)$$

For majority of dielectrics  $\sigma_a(\omega)$  is a growing power function of frequency and it is expressed by the formula:

$$\sigma(\omega) = \omega'', \quad (7)$$

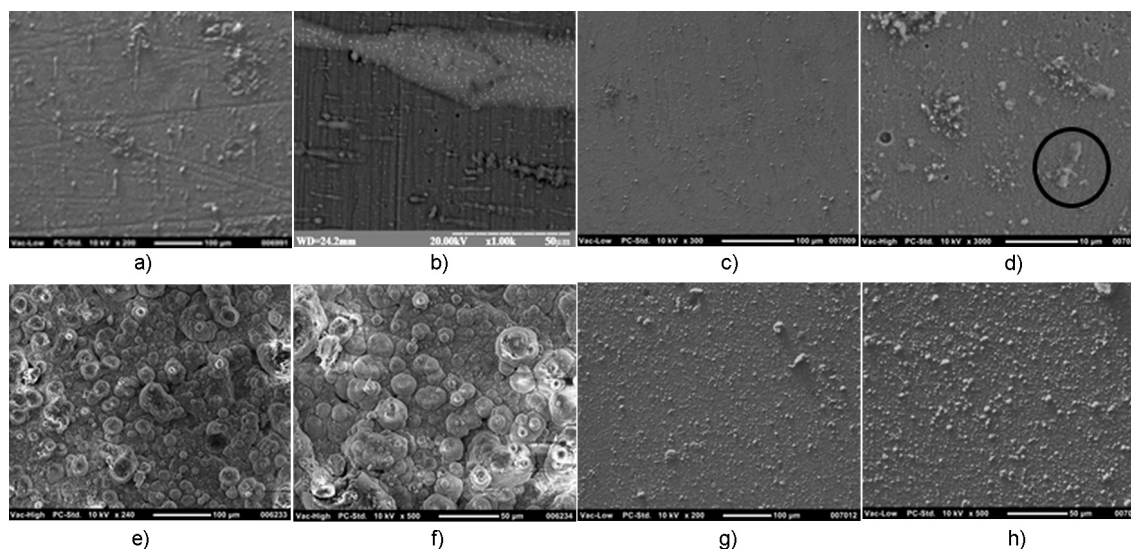


Fig. 2. SEM surface microstructure of the dielectric layers: a, b —  $\text{Al}_2\text{O}_3$ ; c, d —  $\text{TiO}_2$ ; e, f —  $\text{MgO}$ , g, h —  $\text{AlN}$ .

where  $n$  the power index is dielectric response of the system related to its structure and was determined by inclination angle of the electroconductivity frequency dependence built in logarithmic coordinates.

Measurements of the dielectric characteristics temperature dependences were conducted in the regime of indirect heating — cooling of the samples in a furnace with the temperature change rate  $4 \pm 1^\circ\text{C}/\text{min}$  within the temperature range of  $20 - 400^\circ\text{C}$ .

### 3. Results and discussion

Investigation of the formed layers surface topology by the electronic microscopy method shows a difference in their structure. In particular, the oxide aluminium layer has a homogeneous, smooth and non-porous structure of the surface (Fig. 2a). There prevails anorientation of certain surface structure elements in the form of elongated protrusions. Their volume constitutes about 50 %. With the higher magnification it is seen that these elongated conglomerates have the two-phase structure and consist of fine-grained densely packed grains (Fig. 2b). Taking into account that the oxide aluminum formation occurs through aluminum oxidation on the substrate surface we can assume that incomplete oxidation is possible in the process of the layer growth. In this case, unoxidized particles will increase the electric conductivity of the dielectric layer.

The  $\text{TiO}_2$  layer surface is homogeneous (Fig. 2c) without the expressed porosity or other discontinuity of the layer. In some

parts of the layer surface, ellipse inclusions are present and may belong to one of the modifications of the  $\text{TiO}_2$  layer — anatase or rutile (Fig. 2d).

The  $\text{MgO}$  layer consists of round-shape grains with different degrees of dispersion. The grain formation occurs on the substrate surface with ions, atoms and droplet fractions of magnesium. Therefore, the size of the formed grains is widely fluctuated. It is possible that the grain growing is carried out by the "island" mechanism where the formed grain is the basis for the formation of new centers of crystallization and their subsequent growth (Fig. 2e, f). Thus, the newly grown grains are formed in the clusters of different sizes. Due to their specific structure, grains are characterized by a large specific surface separation. Previously, it was found that  $\text{MgO}$  phase is formed after the ion-plasma sputtering of magnesium in oxygen atmosphere. Diffraction peaks of  $\text{MgO}$  phase show its polycrystalline nature. Furthermore, the presence of the  $\text{MgO}$  phase with a deviation from stoichiometry towards oxygen deficiency was found [3].

The high density of the structure and uniformity across the surface area of the  $\text{AlN}$  layer surface was found by analyzing its microtopology. High values of the substrate bias potential and pressure during the regime of ion-plasma sputtering contributed to increasing the aluminum ions rate, grinding the structural constituents and qualitative forming of the layer structure [4].

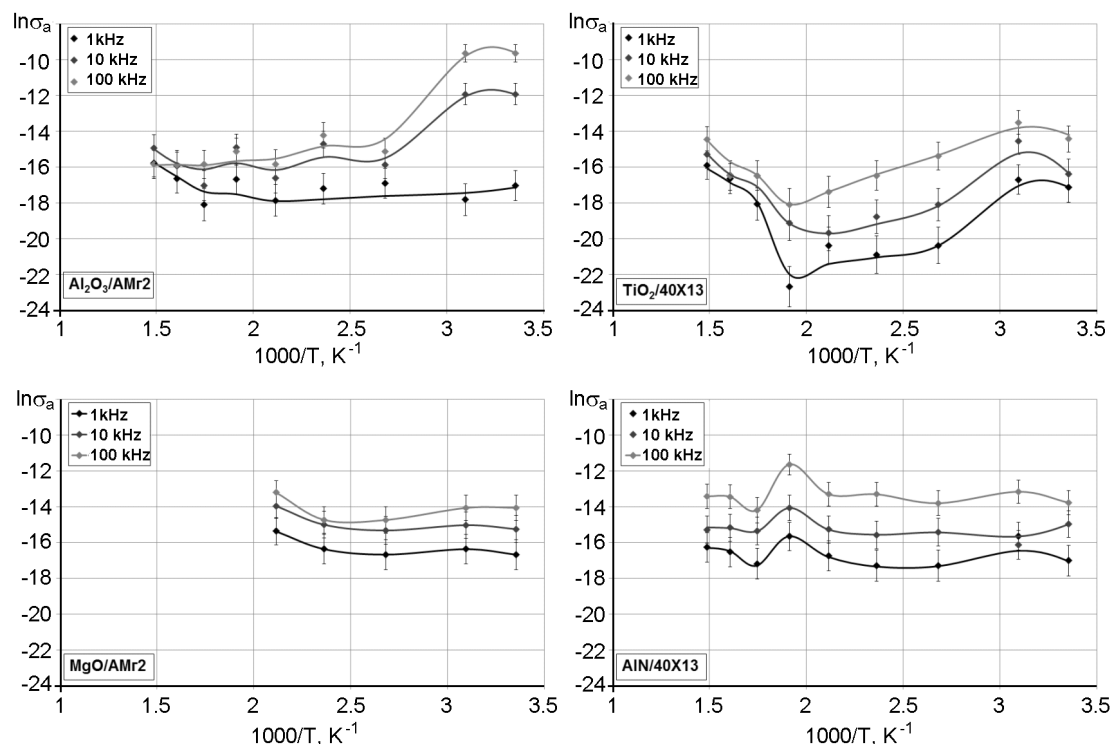


Fig. 3. Temperature dependences of the active complex conductivity component at frequencies of 1 kHz, 10 kHz, 100 kHz.

Electric conductivity of the  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{AlN}$  layers at low frequencies remain almost unchanged at the room temperature and are approximately  $3 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$ ,  $7 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$  and  $3 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$ , respectively. In the  $\text{Al}_2\text{O}_3$  dielectric layers (at the temperatures above  $300^\circ\text{C}$ ) and in  $\text{MgO}$  (at the temperatures above  $150^\circ\text{C}$ ) monotonic increase of the conductivity caused by thermal activation of the charge carriers from energy levels  $0.63 \text{ eV}$  and  $0.35 \text{ eV}$ , respectively, begins. In the  $\text{AlN}$  dielectric layers at temperature of  $250^\circ\text{C}$  the sharp increase of conductivity by almost an order of magnitude is observed. Then its value returns to the initial values. This indicates the formation of the localized trap level with the activation energy of  $0.47 \text{ eV}$  in these layers.

Electric conductivity of  $\text{TiO}_2$  decreases from  $4 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$  to  $1 \cdot 10^{-10} \Omega^{-1} \cdot \text{m}^{-1}$  with the temperature growth from the room one to  $250^\circ\text{C}$  and increases to  $1 \cdot 10^{-7} \Omega^{-1} \cdot \text{m}^{-1}$  with the temperature growth to  $400^\circ\text{C}$ .

The obtained results differ from the data obtained by the authors of [5] who investigated the electric properties of thin dioxide titanium films sputtered on glass substrates. They showed that in the tempera-

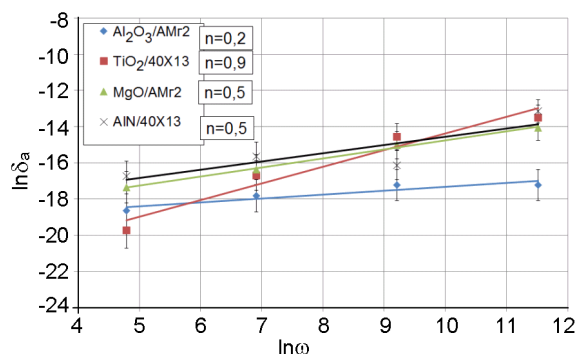


Fig. 4. Frequency dependences of the complex conductivity active component at  $50^\circ\text{C}$ .

ture range of  $40 - 200^\circ\text{C}$  the electric conductivity of  $\text{TiO}_2$  with the activation energies of  $0.13 - 0.39 \text{ eV}$  appears. At the same time, on the example of the  $\text{Si}/\text{TiO}_2/\text{Al}$  structure (the barrier of  $\text{TiO}_2/\text{Al}$  for electrons is  $1 \text{ eV}$ ), the authors of [6] established the two-zone model of conductivity in  $\text{TiO}_2$ . According to this model,  $\text{TiO}_2$  layers, similarly to  $\text{Si}_3\text{N}_4$  films, have electron and hole traps acting as recombinant centers. The later, in the case of positive or negative displacement, inject into the valence band or conductivity zone, respectively.

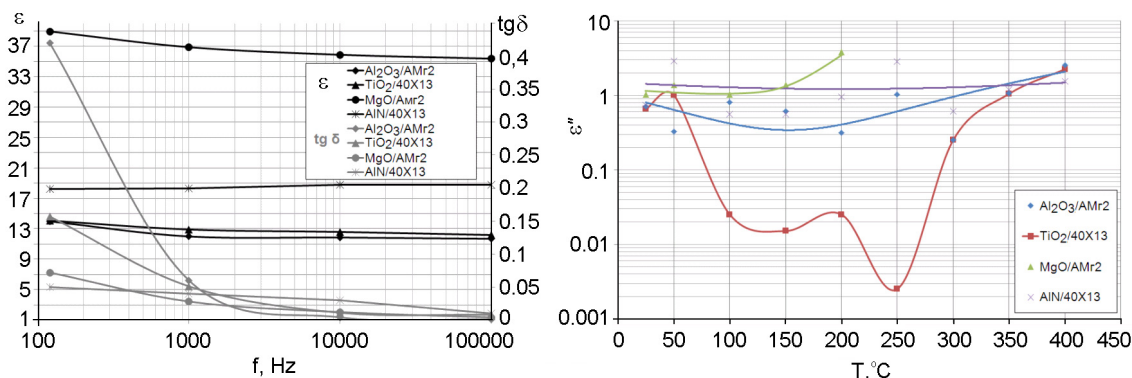


Fig. 5. Frequency dependences of relative dielectric permittivity, dielectric loss tangent of the coatings at 25°C (a) and temperature dependences of the dielectric loss coefficient at frequencies of 1 kHz (b).

Thus, the conductivity decrease in our investigated systems "substrate-dielectric layer" can be connected with mobility decrease of the carriers injected into the dielectric layer from steel substrate. Therefore, we can assert that on the border of the division of  $\text{TiO}_2/40\text{X13}$  system investigated there is accumulation of the near-surface area of semiconductors and realization of the ohmic contact. The conductivity increase at the temperatures above 250°C is caused by thermal activation of 0.73 eV deep traps (the band gap of  $\text{TiO}_2$  is 3.2 eV).

As it is seen from the temperature dependences of electric conductivity of the dielectric layers at alternating current (Fig. 3) and from their frequency dependence (Fig. 4), in all investigated systems the conductivity increases linearly with the frequency growing. The conductivity increase is caused by a delay of the slow polarization mechanisms. Moreover, the dependence differs for investigated materials: in the  $\text{Al}_2\text{O}_3$  layers  $n = 0.2$ , whereas for  $\text{MgO}$  and  $\text{AlN}$  —  $n = 0.5$ . In the dioxide titanium layers  $n$  grows to 0.9.

Dielectric losses cause dielectric heating, which can lead to accelerated aging or to the thermal breakdown, especially in the cases when the dielectric losses are connected with electric conductivity [7]. Therefore, while choosing the substrate material and dielectric layer in the process of designing electrotechnical products it is necessary to assess the type and the order of dielectric loss values which may occur at the given operating conditions.

In addition, such changes are sensitive indicators of the processes, which may occur in the dielectric structure. For all dielectric layers in the tested frequency range

( $10^2 - 10^5$  Hz) (Fig. 5a) the dielectric loss tangent is decreased by hyperbolic low: from 0.42 to 0.001 in the  $\text{Al}_2\text{O}_3$  layers; from 0.16 to 0.008 in  $\text{TiO}_2$ ; from 0.07 to 0.004 in  $\text{MgO}$  and from 0.05 to 0.01 in  $\text{AlN}$ . The slight decrease of the dielectric constant was observed: from 14 to 11.7 in the  $\text{Al}_2\text{O}_3$  layers, from 14 to 12.2 in  $\text{TiO}_2$ , from 39 to 35.4 in  $\text{MgO}$  and increasing from 18.2 to 18.8 in  $\text{AlN}$ . The decrease of the dielectric constant in this case is caused by electronic or ionic thermal polarization which dielectric contribution is usually quite small ( $10^{-3} - 10^3$ ) and the frequency dispersion falls on frequency range ( $10^5 - 10^{10}$  Hz for electronic and  $10^4 - 10^7$  Hz for ionic conductivity) [8]. Decrease of the dielectric loss tangent with frequency increasing characterizes the losses caused by the electric conductivity.

With the increase of the temperature in the  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{AlN}$  layers there is a general tendency to increase the dielectric loss tangent (Fig. 5b) in all temperature range of 20 – 400°C due to the electric conductivity losses. In the  $\text{TiO}_2$  layers to temperatures 250°C decrease of the dielectric losses is observed. This correlates with the decrease of the electric conductivity (Fig. 3). This type of losses means that dioxide titanium dielectric layers are described by a more complex parallel-successive replacement scheme which reflects the ohmic contact contribution, unlike the parallel RC-scheme fit as a model for dielectric response description in the above cases.

#### 4. Conclusions

It is shown that the dielectric layers structure on the substrate surface is formed

by ions, atoms and drop fraction of the corresponding cathodes.

It is established that conductivity of  $\text{Al}_2\text{O}_3$ ,  $\text{MgO}$  and  $\text{AlN}$  at low frequencies hardly changes at the room temperature and reaches nearly  $3 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$ ,  $7 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$  and  $3 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$ , respectively. Above  $300^\circ\text{C}$  in  $\text{Al}_2\text{O}_3$ ,  $150^\circ\text{C}$  in  $\text{MgO}$  and  $250^\circ\text{C}$  in  $\text{AlN}$  the materials electric conductivity grows with the activations energies of 0.63 eV, 0.35 eV and 0.47 eV, respectively. The  $\text{TiO}_2$  layers electric conductivity decreases from  $4 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$  to  $1 \cdot 10^{-8} \Omega^{-1} \cdot \text{m}^{-1}$  and increases with the activations energy of 0.73 eV at the temperature growth to  $400^\circ\text{C}$ . It allowed us to establish the ohmic contact formation in the system "40X13 substrate —  $\text{TiO}_2$  dielectric layer".

In choosing the substrate material and the dielectric layer for constructing a film resistive element it is necessary to assess the type and order of the dielectric losses

values occurring in the operation conditions.

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