Electro-physical and mechanical properties of films based on zirconium oxide in sensitive elements of MEMS

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Abstract. Studies have been carried out to obtain functional films based on zirconium oxide (ZrO$_2$, PZT) and to ensure the stability of their metrological characteristics under harsh operating conditions – over a wide range of temperatures, thermal shock and vibration for use in microsystem technology. The structural features of film structures for establishing the relationship "structure-property", as well as assessing the role of defects have been investigated.

Indispensable materials for electrical engineering, radio engineering, instrumentation and other fields use are oxide materials [1]. The search and development of new methods for synthesizing oxide materials capable to high-efficiency, non-energy-consuming and environmentally friendly technological processes are always relevant [2]. This paper presents the study results of thin zirconium oxide films for functional purposes. Yttria-stabilized zirconia films deposited by sol-gel technology on platinum substrates and heat treated in air at temperatures from 600 to 1500 °C from 0.5 to 3.0 h were the study objects. Samples heating and cooling was carried out together with the furnace. Specific volume resistivity ($\rho_V$), angle tangent of the dielectric loss ($\tan \delta$), dielectric constant ($\varepsilon$), compressive and bending strengths ($\sigma_{\text{com}}, \sigma_{\text{ben}}$) were measured for initial and heat-treated samples. Measurements of electro-physical and mechanical properties were carried out in accordance with GOST 5458-75. The phase composition and samples microstructure were studied by X-ray diffraction (diffractometer DRF-2, CuK$_\alpha$-radiation). The initial samples had a light gray color. Heat treatment at temperatures below 1000 °C did not lead to a noticeable change in the properties and samples color. Lighter sections appeared on the surface of the films after heat treatment at (1100 ± 100) °C, and at temperatures above 1300 °C the films were painted white. There was a significant decrease in strength properties and an increase in $\tan \delta$ films with increasing temperature and time of heat treatment. Also small changes were in $\rho_V$ and $\varepsilon$.

Carbon materials with protective films of stabilized zirconium dioxide have been tested under high-temperature irradiation. Irradiation was carried out in a helium atmosphere in a high-temperature reactor channel at 2000 °C. We provided fluency set from $5 \times 10^{19}$ to $2 \times 10^{20}$ neutrons/cm$^2$ controlling distribution of the flux density over the cell height and the irradiation time.

Irradiated samples have been used for determination by non-destructive methods change in dimensions, mass, density, electrical resistivity, modulus of elasticity. Then, flexural strength, thermal conductivity, and compressive strength were measured breaking the sample, so the adopted methods allowed obtaining maximum information from each irradiated sample.
Stabilized zirconium dioxide coating on graphite allowed the crystal lattice parameter \( c \) either not change, or slightly decrease (\( \Delta c/c \%, = 0.1–0.3 \)), parameter \( a \) did not change. Physical characteristics (specific electrical resistance \( \rho \) from 10–18 \( \mu \Omega \cdot \text{m} \), thermal conductivity \( \lambda = (100 \pm 5) \text{ W/mK} \), coefficient of linear thermal expansion (5.2 ± 0.3)\( \times 10^{-6} \text{ K}^{-1} \), tensile strength under compression \( \sigma\text{com} = 30–50 \text{ MPa} \), dynamic modulus of elasticity \( E = (6.2 \pm 0.3) \text{ GPa} \).

The crystal lattice parameter \( c_{\text{tot}} = 0.6712–0.7728 \text{ nm} \) increased upon irradiation, but the relative change of these properties decreased exponentially with the irradiation temperature. Mass loss due to oxidation and corrosion, cracking due to different forming speeds, films peeling from the substrate due to insufficient adhesion have been observed when using as a precursor metal alkoxide with an aging period more than 48 h (figure 1).

![Figure 1. Film peeling from the substrate when using precursor metal alkoxide with an aging period more than 48 h.](image1)

The initial crystallization in the precursor alkoxides reduced the strength characteristics and also reduced thermal and electrical resistivity. The phase composition and mechanical properties of films based on zirconium dioxide have been studied after firing in vacuum. It was found that \( \text{ZrO}_2 – 3 \% \) (mol.) \( \text{Y}_2\text{O}_3 \) films obtained by heat treatment at 1200 °C were dense samples of black color with an average grain size 50 nm containing \( T \) and \( T' \) phases. Oxygen vacancies in such film created as a result of annealing were caused a reduced volume of the unit cell of the tetragonal phase and also caused its stability under various mechanical influences until destruction, and at cooling up to –180 °C.

Piezo-ceramics is a promising material for the production of sensitive sensors and high-precision actuators. At present, lead zirconate titanate (PZT – Pb\((\text{Zr}_{1-x}\text{Ti}_x)\text{O}_3\)) is widely used in the electronics industry. The advantages of devices based on PZT materials include high sensitivity and accuracy, wide operating temperature range [3–4]. Precursor – ceramic PZT powder – was applied to silicon plates covered with platinum electrode, by electrophoresis in isopropyl alcohol. Under the applied electric field \( E = 100–300 \text{ V/cm} \), charged PZT particles in suspension with \((0.01–10 \text{ mass %})\) concentration were deposited to one of the electrodes within 0.5–10 min. After electrophoretic deposition PZT film was subjected to drying and annealing. The phase and structural film non-equilibrium have been studied with the help of XRD and (SEM) taking into account the multi-component ferroelectrics nature and complex structure of formation processes. Optimum regimes of electrophoretic deposition and high-temperature annealing were found. It was found that films with a thickness from 6 to 16 μm, which had been annealed at 880 °C during 20 min, had porous structure, and tuberous surface with micro-cracks (figure 2).

Amorphous phase presence was noted in the films. Film samples with a thickness from 7 to 10 μm obtained under the same conditions, but having annealing at 950 °C for 1 h, were solid, nonporous, and had a homogeneous polycrystalline structure. Using samples with Si-SiO\(_2\)-Ti/TiO\(_2\)-Pt-PZT heterostructures, it was shown that the perovskite texture was determined by two factors. \{111\} determines platinum layer orientation, \{100\} appears in the presence of PbO and/or TiO\(_2\) oxide phases at the interface between PZT and Pt in the activation case of diffusion processes by high-temperature annealing. Structural imperfections that arise during the films formation lead to micro stresses.

The elastic substrate interaction with the film can be considered as one of the reasons for the appearance of micro-stresses. The "film-substrate" system is a complex heterogeneous system with different mechanical characteristics (as it is observed in MEMS). The thinner film, the more
substrate influence has on the state of film lattice. Due to the vacancies diffusion to the surface and the "healing" of micro-cavities, the film volume decreases during annealing, and tensile stresses arise in it, which relax by the formation of cracks. Compressive macro-stresses, which relaxation leads to the surface folds were found in the films obtained from aged sols. Films made from fresh sols were not so susceptible to "folding." Significant differences in the parameters of massive and film ferroelectrics include a wide scatter of characteristics. Two factors are responsible for this phenomenon- structural imperfections and dimensional effects. Since the true dimensional effects essentially manifest themselves only at thicknesses less than 0.05 μm or at the sizes of their constituent particles less than 0.05 μm, the main influence on the properties of the resulting films was exerted by various structural defects.

![Figure 2. XRD and SEM of PZT films after annealing at: (a) – 880 °C during 20 min; (b) – 950 °C during 1 h.](image)

Thus, from the above results it follows that new approaches to thin film formation technology have provided coatings on complex profile large-sized substrates with an effective "price-property" ratio. A high efficiency of thin films structure optimizing for a particular application was shown by using metal alkoxides with different aging times.

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