

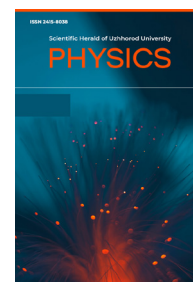
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Ionic memristive effects on the nanometre scale in metal oxides: Understanding the process of valence change

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Abstract

Relevance. The relevance of the study is due to the great potential of memristive effects, which are manifested in the change of material resistance under the influence of an external electric field and ionic fluxes.

Purpose. The aim is to analyse and study the mechanisms of ionic memristive effects, with a detailed consideration of the process of changing the valence of metal cations.

Methodology. The work was based on the study of nanometre-sized metal oxides TiO_2 and ZrO_2 . The materials were obtained by synthesis by chemical deposition using high-purity precursors.

Results. The obtained results open up wide opportunities for the practical use of ionic membrane effects. The study of ionic memristive effects in TiO_2 and ZrO_2 -based films has shown that the change in resistance occurs due to various mechanisms, including ionic migration, electrochemical reactions, and defect reorganization. Under the influence of an external electric field, a change in the resistance of both materials is observed. In TiO_2 , the resistance decreases with increasing voltage, while in ZrO_2 , an increase in resistance is observed. During additional experiments in the temperature range of 25–200°, it was found that temperature significantly affects the ionic membrane effects. With its increase, a noticeable increase in the intensity of these effects in both materials is observed.

Conclusions. The use of X-ray diffractometry and infrared spectroscopy revealed that changes in the valence of metal cations in both films occur under the influence of an electric field. The analysis of changes in the X-ray and infrared spectra showed the presence of modifications in the crystal and molecular structure in response to the electric field. In particular, the change in the positions and intensity of the peaks indicates a restructuring of the bonds in the crystal lattice. The paper proposes new studies to expand the understanding of these effects and to consider possible ways to improve membrane devices. The study of ionic memristive effects in TiO_2 and ZrO_2 is of great practical importance for the development of electronics and the creation of new generations of memristors and neuromorphic systems.

Keywords: radiation safety; ionising radiation; collective dose; exposure dose rate; gamma photons; drills; neutron energy

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Introduction

With the rapid development of nanotechnology and nanomaterials, the study of the electrical properties of materials on the n of the mechanism of valence change in these materials. An important aspect is the understanding of the process of changing the valence of metal cations, which can form the basis for the development of new memristors and electronic devices with the ability to learn and adapt.

The nanometre-scale ionic memristive effects in metal oxides are related to the resistive switching behaviour of materials based on these oxides used in memristors. The valence change mechanism is a bipolar resistive switching mechanism that plays a key role in such devices. In this mechanism, the movement of oxygen ions within the oxide semiconductor can change the resistance of the memristor with a change in valence. In the work of D.Y. Shovkoplyas & S.B. Tugay [1] describe in detail the mechanism of the membrane functioning, which is explained as the electromigration of oxygen ions under the influence of alternating electric fields. This mechanism is the main reason for the occurrence of an ambiguous current-voltage dependence in the contacts of a metal electrode with complex transition metal oxides. The most effective materials are films based on platinum and tantalum oxide.

According to the research of V.V. Shamaev *et al.* [2], the concentration of oxygen vacancies in such materials becomes very heterogeneous as they approach the surface. For example, yttrium-barium cuprate forms a thin, undersupplied layer in this region that has the properties of an antiferromagnetic dielectric. Since the change in metal valence is directly related to the change in resistance, it is interesting to note that the electrical resistance of the film decreases with the formation of oxygen vacancies. Thus, in the work of D.V. Zalevskii [3] studied ZnO films. As a result, the energy distance between the last filled and the first unoccupied levels decreases by two orders of magnitude. At this time, an internal electric field is formed in the direction of vacancy stacking. The potential distribution becomes linear with a pronounced difference along the direction of the vacancy filament, i.e. an internal bias voltage is formed. This conductive effect increases with the increase in the density of oxygen vacancies up to a certain concentration.

The method of producing films from metal oxides also plays a significant role in research, and I.M. Khodakovskii [4] introduced a technique for generating nanostructures through localized probe oxidation of conductive materials, such as semiconductor substrates and extremely thin metal films, which is equally essential in this context. During the experiment, the valence of the surface changes, and it is able to undergo oxidation when a positive voltage shift is applied to it relative to the probe. Y.O. Kravchenko [5] also found

an uneven distribution of elements in the cross-section of the coatings, which is due to radiation-stimulated processes and oxidation of the surface layer. Understanding the process of valence change in nanometre-scale ionic memristor effects in metal oxides is important for the development of high-performance applications in computing, digital and analogue circuits, including neuromorphic networks. For example, a titanium oxide-based memristor uses the drift of oxygen vacancies for switching, as pointed out by A.V. Lemeshko *et al.* [6] in their article. One of the important tasks in the development of neuromorphic systems is the effective implementation of these components.

Therefore, the main goal is to study and analyse ionic memristive effects, with a special emphasis on the process of changing the valence of metal cations. The study of ionic memristive effects in metal oxides allows better understanding the process of valence change and its impact on the electrical properties of memristive devices. A deep understanding of this process is important for the development of new materials, device architectures and systems that are characterized by high efficiency and long service life. The research and development of ionic memristive effects represent a significant challenge in science and technology that can significantly impact the future of modern electronics and nanotechnology. Understanding these phenomena opens up new opportunities for creating highly efficient and intelligent electronic systems that can adapt to the needs of modern society.

Materials and Methods

A comprehensive analysis of modern scientific works and literature sources on ionic membrane effects and their manifestation in nanometre metal oxides was carried out. In order to clarify the current state of research in this area, the basic information was identified and the key areas that have already been studied in previous studies were established. An experimental approach was used. In the course of the experiment conducted in 2023, nanometre-sized metal oxides, in particular titanium (TiO_2) and zirconium (ZrO_2), were used as objects for studying ionic membrane effects. The samples of materials were synthesized by the chemical deposition method using high-purity precursors. For the synthesis of TiO_2 and ZrO_2 films, the precursors $\text{Ti}(\text{OC}_3\text{H}_7)_4$ and $\text{Zr}(\text{OC}_4\text{H}_9)_4$ were used, respectively. Acetylacetone was added as a complexing agent to stabilize the zirconium butoxide solution in a 1:1 ratio. The addition of the stabilizer helped to avoid aggregation of the nanoparticles and ensured a homogeneous particle size distribution. Acetylacetone was also added to the $\text{Ti}(\text{OC}_3\text{H}_7)_4$ solution in a 1:1 ratio. Under vigorous stirring, a 1 n solution of HNO_3 in isopropanol was added to the already stabilized solutions dropwise to hydrolyse the substances before

the formation of films. The prepared clear solutions were separately applied to the previously cleaned glass substrates to obtain TiO_2 and ZrO_2 films. The films were left for one hour at room temperature to complete hydrolysis and then subjected to successive heat treatments at 100, 300, and 600°C. This method made it possible to obtain nanometre films with high purity and determine their structural and electrical properties. After the synthesis, the samples were washed from excess reagents and dried in a controlled humidity atmosphere. The synthesized materials were obtained in the form of thin films with a thickness of approximately 100 nm. Additionally, the films were subjected to vacuum treatment for final drying and achieving the desired properties and structure.

The structure and physical properties of the materials were characterized by X-ray diffraction (XRD) using a Bruker D8 Advance diffractometer (Germany). To determine the surface morphology and structure of the samples, a scanning electron microscope (SEM) Hitachi S-4800 (Japan) was used. For electrical measurements, an Autolab PGSTAT302N Potentiostat (Metrohm Autolab, the Netherlands) with the ability to change the applied voltage and record the current was used. To study the influence of temperature on ionic membrane effects, a series of experiments were conducted in which the changes in current and voltage were monitored at temperature changes from 25 to 200°C. The measurements were carried out in an atmosphere of controlled humidity and temperature. In parallel with the experiments, computer modelling was carried out using COMSOL Multiphysics. The specialized software was used to perform numerical simulations of ion fluxes and their effect on the valence of cations in metal oxides. To further understand the

behaviour of ions in the structure of materials, the data obtained from the experiments was subjected to statistical and mathematical analysis. The combination of methods helped in the qualitative study of ionic membrane effects in nanometre-sized metal oxides.

Results

The memristive effect is a phenomenon where the resistance of a material changes from its pre-fixed values when subjected to an external voltage or current shift [7]. One of the most important aspects is the interaction between cations and anions in the crystal structure of the metal oxide. When an external voltage is applied to a material, it can affect the arrangement of the Jordan bonds and the placement of cations. The mechanisms behind membrane effects can vary, but the main ones include ionic migration, electrochemical reactions, oxide decomposition, and defect reorganization. One of them is a change in the configuration of defects in the crystal structure of the material. When the voltage in the material is shifted, ions (metal cations) can move in the crystal structure. This leads to a change in the configuration of defects and the valence of metal ions, i.e., it is accompanied by the movement of ions in the crystal lattice of the material [8]. As a result of these processes, the electrical conductivity of the material changes, which is manifested as a membrane effect.

TiO_2 and ZrO_2 films with a thickness of approximately 100 nm were subjected to detailed characterization. Experiments have shown that under the influence of an external electric field, the resistance of both materials changes. For TiO_2 , a decrease in resistance is observed with increasing voltage, while for ZrO_2 , an increase in resistance is observed (Table 1).

Table 1. Measured resistance and voltage values for TiO_2 and ZrO_2 films

Resistance	TiO_2			ZrO_2		
	500 Ω	200 Ω	100 Ω	500 Ω	1000 Ω	2000 Ω
Voltage	2.0 V	2.2 V	2.5 V	2.5 V	3.2 V	3.8 V
	2.5 V	2.7 V	3.0 V	3.0 V	3.7 V	4.3 V
	3.0 V	3.2 V	3.5 V	3.5 V	4.2 V	4.8 V

Source: compiled by the author

From the data for TiO_2 , it was found that with an increase in voltage, there is a noticeable decrease in resistance, which indicates a change in the structure and conductivity of the material under the influence of an electric field. Conversely, in the case of ZrO_2 , there was observed a rise in resistance when subjected to an electric field. This characteristic suggests a distinct response to an external stimulus, which could be attributed to specific aspects of its electronic structure or its interaction with ions within the studied context. Under the influence of an external electric field, materials exhibit ionic membrane effects, which are

accompanied by changes in the valence of metal cations. This means that under the influence of an electric field, ions move in the material, changing their valence, which affects the electrical properties of the material and causes the memristive effect.

Additional experiments in the temperature range of 25-200°C showed that temperature significantly affects the ionic membrane effect, as shown in Figure 1. In particular, an increase in temperature led to a noticeable increase in the intensity of the ionic memristive effects in both films. This can be explained by the fact that a higher temperature promotes more active

ion movement processes in the material, which facilitates ionic migration and leads to more pronounced effects of metal cation valence changes [9]. It is worth

noting that high temperatures promote greater migration of defects in the crystal structure of the material, which can affect the efficiency of membrane switching.

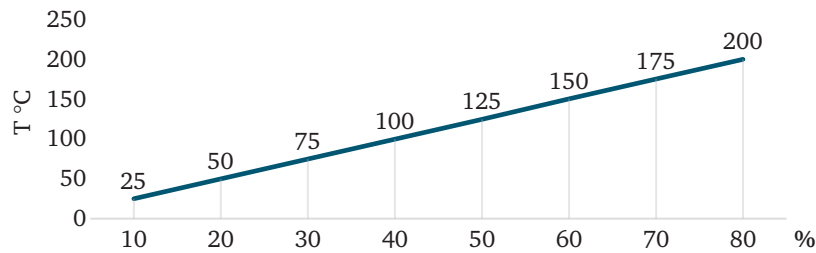


Figure 1. Graph of dependence of the intensity of ionic memristive effects on temperature

Source: compiled by the author

The change in the valence of metal ions is an important mechanism behind the memristive time-dependent characteristic of materials. In this case, the change in valence occurs due to the transfer of metal ions (cations) through the thin oxide film. When exposed to an electric field or current, metal ions can move in the crystal structure of the material [10]. This effect is based on the interaction between the metal oxide and the electrodes, which changes as a result of the applied electric field or current. When the electric field or current is reversed, metal ions are transferred from one metal electrode to another through the oxide film. This leads to a change in metal valence, as metal ions can have different degrees of oxidation. For example, the valence of one metal can change from zero (as a metal) to positive (as an oxide) or negative (as a reduced form). The process of changing the metal's valence is accompanied by a change in the electrical conductivity of the membrane. When metal ions are transferred through the oxide film, they change the location and structure of the film, which affects the electronic structure and conductivity of the system.

Each metal has different degrees of oxidation that affect its chemical properties. In materials that contain titanium (Ti) or zirconium (Zr), these metals can exist in different oxidation states or valencies. For example, in the case of titanium (TiO_2), titanium can have several oxidation states, including Ti(II), Ti(III), Ti(IV), etc. This means that each atom of titanium or zirconium can interact with the oxide matrix by ionic migration, changing its number of charges. When an electric field or current is applied, the titanium or zirconium ions can move in the crystal structure of the material. As a result, a single atom can lose or gain electrons, which changes its number of charges and, accordingly, its degree of oxidation. When an electric field or current is applied, the ions can switch between these different states, which affects the electronic structure and conductivity of the material. In metal oxides, metal ions can have different valences, such as $\text{Ti}^{3+}/\text{Ti}^{4+}$ or $\text{Cr}^{3+}/\text{Cr}^{6+}$. These changes in

valence can occur due to the interaction of ions with defects, as well as changes in the environment of the oxide ions. For example, vacancies in the oxide ion network can change the valence of a metal ion or create an ionic residue. Such changes in valence promote ion migration, which provides conductivity in metal oxides. In the absence of an electrical stimulus, there is an equilibrium between the different valence states, but when an external stimulus such as a voltage is applied, a difference in ion valences can occur, resulting in a change in the conductivity of the material.

The change in the resistance of materials under the influence of an electric field occurs due to ionic membrane effects, which affect the interaction of charged particles in the material. In the case of titanium oxide TiO_2 , with an increase in voltage, there is an active reorganization of the probabilities of ion passage in the crystal structure, which leads to a decrease in resistance. For zirconium oxide ZrO_2 , changes in the electronic structure and interactions of ions under the influence of the field are likely to cause an increase in resistance. These phenomena are associated with the movement of ions in the crystal matrix and their influence on the configuration and conductivity of the material. Metal oxides, such as titanium, chromium, zirconium, and others, are popular materials for membrane devices. They are known for their high stability, low resistance, and efficient switching, making them attractive for electronics applications.

Using X-ray diffractometry and infrared spectroscopy, changes in the valence of metal cations in both materials under the influence of an electric field were revealed. X-ray diffractometry allows determining the location of atoms in the crystal lattice and defining their distances. Infrared spectroscopy provides information on the interactions of atoms and groups of atoms in the sample. The analysis also revealed changes in the location of the peaks, which indicate changes in the distances between the atoms in the crystal lattice. This indicates that under the influence of an electric field, the valence of metal cations in both materials

changes. This indicates that the processes associated with ionic migration and changes in the configuration of defects in the crystal structure are active under the influence of an external electrical stimulus.

A comparative analysis of the ionic membrane effects for TiO_2 and ZrO_2 has been carried out. It was found that the nature and intensity of the effect depends on the chemical composition and on the intra-atomic structure of the crystal lattice, as well as on the location and mobility of ions in the material. In the case of TiO_2 , the regions of decreasing resistance were more active than the regions of increasing resistance. This indicates the important role of oxygen vacancies and cationic interstices in the mechanisms of the membrane effect for this material [11]. In ZrO_2 , on the contrary, the dominant influence of the regions of increased resistance is observed. This may be due to the peculiarities of the movement of oxygen ions in the structure of this material. Such a detailed analysis showed that the properties of ionic membrane effects strongly depend on the characteristics of a particular material and can be controlled by influencing its chemical composition and crystal structure. In addition to the comparative analysis of the ionic memristive effects in TiO_2 and ZrO_2 , a detailed study of the influence of other parameters, such as temperature and ion concentration in the electrolyte, on the nature and intensity of these effects was carried out. It was found that the ionic membrane effects in TiO_2 and ZrO_2 films manifest themselves differently depending on the experimental parameters, such as temperature and time of exposure to the electric field. Changes in the valence of metal cations occur not only under the influence of external stimuli, but also depending on the crystal structure of the material and its chemical composition. In addition, additional analyses of the structural and electronic properties of both materials under the influence of an electric field were carried out, which allowed gaining a deeper understanding of the mechanisms that determine the ionic membrane effects in these metal oxides.

The obtained results indicate that the process of changing the valence of metal cations in TiO_2 and ZrO_2 materials involves ionic migration. Under the influence of an external electric field, metal cations are transferred through the oxide film, which leads to a change in their redox state. As a result, the electronic structure of the material and its electrical conductivity change. In particular, the TiO_2 material shows a decrease in resistance with increasing voltage, indicating a change in the valence of titanium cations. In the case of ZrO_2 , an increase in resistance is observed, indicating a change in the valence of zirconium cations. This process is based on the transfer of metal ions through the oxide film, which occurs under the influence of an external electric field.

These studies indicate the great potential of using ionic memristive effects in the creation of high-performance and low-energy electronic devices and artificial intelligence systems [12-14]. It has also been found that ionic memristive effects can be used to create low-power, high-speed memory elements and logic gates, which opens up new opportunities for the development of modern electronic devices. Understanding these mechanisms is key to the development of new electronic devices and systems that use ionic memristive effects. The effect of conductivity change can be used to create memristors that are unstable charge storage devices. For example, when a voltage is applied to a memristor, ions can migrate from one electrode to another and thereby change the degree of conductivity of the material. When the current is switched off, the voltage stops affecting the memristor, but the changed state of conductivity can be saved. This makes it possible to store information in memristive materials. Additional research in this area could expand the understanding and use of these effects in modern technologies.

Discussion

One of the key findings of the study is the different nature of the membrane effects in TiO_2 and ZrO_2 . In particular, a decrease in resistance in TiO_2 and an increase in ZrO_2 were observed with increasing voltage. This indicates the importance of the chemical composition and crystal structure of the material for these effects, which are the basis of membrane devices. The essence of these devices is their ability to display multiple resistance values and switch between them, which is known as resistive switching. In another study conducted by C. Singh & N. Ray [15] looked at metal oxides such as HfO_x , TaO_x , and TiO_x , which have shown promise in memristive devices. During this experiment, various resistive switching mechanisms were evaluated, including filament formation and breakage, as well as barrier-type memristors. The results were very encouraging for NiO and TaO-based memristors. Given the use of metal oxides as the main components, such memristors have the potential to be the first in line for future alternatives to current technology, offering unique advantages. Comparing the results of the authors of this study with those of C. Singh & N. Ray [15], some similarities can be noted, especially in the context of titanium oxide (TiO_x). The experimental data in both studies demonstrate that TiO_x shows promise in membrane devices. At the same time, the importance of the chemical composition and crystal structure of the material for resistive switching is also indicated.

The results indicate different mechanisms underlying the membrane effects. An important aspect is ionic migration, which can cause changes in the valence of metal cations and, consequently, changes

in electrical conductivity. The mechanism of switching of resistive storage devices with a change in valence has long been recognized, and it is caused by the ionic movement of oxygen vacancies, which leads to a change in the valence of metal cations, as can be seen from the results of the study. In the work of A. Kindsmüller *et al.* [16] used hard X-ray, photoelectron emission microscopy (PEEM) to analyse local valence changes in Pt/ZrO_x/Ta membrane devices. The use of hard X-rays allowed obtaining information from deep layers, providing chemical data on buried components. By extracting X-ray photoelectron spectra from different parts of the PEEM images, it was demonstrated that zirconium dioxide in the working area of the device decreases compared to the neighbouring area, which confirms the change in valence in the ZrO_x film during electroforming. The change in valence in zirconium oxide-based films in this study can also be noted. In addition, the authors observed a decrease in the degree of oxidation of tantalum (Ta) in the low resistance state. This observation challenges the existing model because the conventional understanding is that the internal oxygen redistribution between ZrO_x and the Ta electrode during switching should result in the oxidation of the Ta layer in the low-resistance state. However, it is noteworthy that Ta actively participates in the switching process within devices, involving the release and re-incorporation of oxygen into the ZrO_x/TaO_x double layer during switching. This is supported by the degradation of the high-resistance state observed during endurance measurements conducted in a vacuum. Additional experiments at different temperatures confirmed the importance of ionic migration for the membrane effects. Increasing temperature promotes more active ionic movement, which increases the intensity of these effects. However, not only temperature changes have a significant impact. For example, in the work of K. Nagashima *et al.* [17] demonstrate how the environment affects memristive switching at the nanoscale using an open-top planar device. Planar-type devices such as NiO_x and CoO_x exhibited memristive behaviour under atmospheric pressure, while planar-type TiO_{2-x} devices did not exhibit memristive switching, even in the same environment. The change in ambient pressure and the use of a SiO₂ passivation layer in the case of planar TiO_{2-x} devices led to the manifestation of memristive behaviour. Thus, the results indicate that the thermodynamic interaction with the environment crucially affects the occurrence of memristive switching due to changes in the stability of the non-stoichiometry. Since this effect becomes more important for smaller devices with a higher specific surface area, adaptation of the environmental influence by means of appropriate passivation is important for high-density devices.

Based on the results obtained, several promising areas for further research are possible. This could

include expanding the range of materials used, analysing the influence of various parameters (e.g. pressure, temperature), and investigating the impact of memristive effects on specific additional applications. The results open up prospects for the use of memristive effects in various technologies, such as neural networks, mnemonics, and energy-efficient memories. S. Tappertzhofen *et al.* [18] focuses on the dynamics of filaments, nanoparticles, and clusters in a switching material. Furthermore, this highlights the progress made in employing voltage and current-based techniques like cyclic voltammetry to discern electrochemical reactions involved in resistive switching. It's emphasized that cations play a pivotal role in the switching process across various device types, a fact substantiated by the results. It is worth noting that these fundamental physical processes can potentially pave the way for a novel spectrum of energy-efficient electro-optical applications centered around ultrafast programmable memristive devices. The reference to S. Saylan *et al.* [19] offers insights into the development of HfO₂-based memristive systems featuring a p-silicon bottom electrode, which are designed to be compatible with complementary metal-oxide-semiconductor (CMOS) technology. These findings underscore the significance of selecting the appropriate top electrode to achieve distinct device characteristics. Both device structures, when evaluated, demonstrated repeatable, low-power, and shapeless bipolar resistive transitions. However, it's worth noting that Au/HfO₂/Si devices exhibited lower device-to-device reproducibility. Additionally, the Au/HfO₂/Si devices exhibited N-type negative differential resistance (NDR), suggesting that the activation of oxygen vacancy migration transitions through Joule heating is responsible for the SET (Set-Reset) process in the unstable unipolar mode.

In addition, the process of synthesis and development of oxide films is also an important aspect. In this work, a general material development methodology was applied. Study by I. Zrinski *et al.* [20] is based on the investigation of composite memristors based on the anodic oxidation of Hf and then deposition on Ta thin films. The structure consisted of the sequential deposition of thin layers of Ta and Hf. During the anodization process carried out in a citrate buffer electrolyte, nanoscale columnar structuring of Ta₂O₅ within HfO₂ occurred. This phenomenon was driven by the higher electrical resistance exhibited by HfO₂. With a narrower resistive path in HfO₂, the ionic current induced localized growth of tantalum oxide (Ta oxide) toward the interface with the electrolyte. This growth process follows the principles of the Rayleigh-Taylor instability. The authors also investigated the membrane properties of the resulting composite oxide depending on the Hf/Ta thickness ratio. One distinct zone with potential for membrane applications was identified. Here, both unipolar and bipolar

memristors with high stability and retention capacity were found. This is due to the formation of conductive filaments mainly along the interfaces between the oxides. In the course of research, there is a need to understand the mechanisms of resistive switching in various dielectric materials. In the studies of A. Younis & S. Li [21] highlight the available research methods. High-resolution microscopes, including transmission electron microscopy, scanning electron microscopy, and conductive atomic force microscopy, have been instrumental in gaining insights into these mechanisms. These advanced microscopy techniques have proven to be highly effective methods for studying and understanding the underlying processes [22; 23].

Summarizing the results, it is worth emphasizing that the valence change mechanism is an important factor in ionic memristive effects in metal oxides at the nanoscale, and understanding this mechanism is important for the development of high-performance computing systems and digital and analogue circuits. Studies indicate that various methods, including modelling, simulation, in-situ characterization and device simulation, have been used to study the mechanism of valence change in memristive devices.

Conclusions

In this paper, the ionic membrane effects in nanometre-sized metal oxides and their influence on the change of metal cation valence were discussed in detail. A comprehensive analysis of the literature and experimental results has provided a deeper understanding of the nature of these effects. In particular, it was found that bipolar valence change is a major trend in modern electronic materials and devices. The movement of mobile donor ions, which are mainly represented by oxygen vacancies and cationic interstitials, has been found to be a key mechanism for these

effects. Experiments have confirmed that under the influence of an external electric field, the resistance of both materials changes. TiO_2 exhibits a decrease in resistance with increasing voltage, while ZrO_2 shows an increase in resistance.

The results confirm that various mechanisms are behind the membrane effects, including ionic migration, electrochemical reactions, oxide decomposition, and defect reorganization. Additional experiments at different temperatures showed that temperature significantly affects the ionic membrane effects. Increasing the temperature led to a noticeable increase in the intensity of these effects in both materials. Using X-ray diffractometry and infrared spectroscopy, it was found that the electric field causes changes in the valence of metal cations in both materials. These results confirm that various mechanisms are behind the membrane effects, including ionic migration, electrochemical reactions, oxide decomposition, and defect reorganization.

Understanding memristive phenomena opens up new opportunities for creating highly efficient and intelligent electronic systems that can adapt to the needs of modern society. Further research into these effects is essential for the development of new types of nanoelectronic devices, such as memristors, that can store information and be used in artificial intelligence, neural networks, and other applications. Development in this area could lead to the creation of even more advanced technologies in the field of electronics and computer science.

Acknowledgements

None.

Conflict of Interest

None.

References

- [1] Shovkoplyas DY, Tugay SB. [Method for measuring the number of memristor overwrites](#). In: Proceedings of the XIII Scientific and Practical Conference “Perspective directions of modern electronics”. Kyiv: National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”; 2019. P. 182-6.
- [2] Shamaev VV, Zhitlukhina ES, Zalutskaya NM, Ochkan KO. Heterogeneous ordering of oxygen vacancies in yttrium-barium cuprate. *Met Adv Tech*. 2021;43(6):819–30. DOI: [10.15407/mfint.43.06.0819](#).
- [3] Zalevskii DV. Properties of materials for resistive random access memory [dissertation]. Kryvyi Rih: Kryvyi Rih State Pedagogical University; 2023. 169 p. DOI: [10.31812/123456789/7070](#).
- [4] Khodakovskii IM. [Methods and models of building memory devices using nano- and molecular technologies](#) [dissertation]. Kyiv: National Technical University of Ukraine “Igor Sikorsky Kyiv Polytechnic Institute”; 2019. 145 p.
- [5] Kravchenko YO. [Structure and properties of multi-layer and multi-element nanometer-scale coatings on the basis \(TiAlSiY\)N/MeN \(Me=Mo, Cr, Zr\)](#) [dissertation]. Sumy: Sumy State University; 2020.
- [6] Lemeshko AV, Antonenko AV, Petryk AV, Myronov SO. Neuromorphy systems as a tool for implementation of artificial intelligence. *Sci Notes Vernadsky KPI Ser Tech Sci*. 2023;34(74(3)):175–83. DOI: [10.32782/2663-5941/2023.3.1/28](#).
- [7] Chua L. Memristor – The missing circuit element. *IEEE Trans Circ Theory*. 1971;18(5):507–19. DOI: [10.1109/TCT.1971.1083337](#).

- [8] Yang Y, Zhang X, Qin L, Zeng Q, Qiu X, Huang R. Probing nanoscale oxygen ion motion in memristive systems. *Nat Commun.* 2017;8:15173. DOI: [10.1038/ncomms15173](https://doi.org/10.1038/ncomms15173).
- [9] Lu D, Jiang Q, Kiang Y, Li J, Zhang Q, Huang Y, Hou B. Influencing factors for the migration of zinc ions in metal oxide powders. *J Mater Res Technol.* 2023;24:1638–52. DOI: [10.1016/j.jmrt.2023.03.106](https://doi.org/10.1016/j.jmrt.2023.03.106).
- [10] Milano G, Miranda E, Fretto M, Valov I, Ricciardi C. Experimental and modeling study of metal-insulator interfaces to control the electronic transport in single nanowire memristive devices. *ACS Appl Mater Interf.* 2022;14(47):53027–37. DOI: [10.1021/acsami.2c11022](https://doi.org/10.1021/acsami.2c11022).
- [11] Dittmann R, Menzel S, Waser R. Nanoionic memristive phenomena in metal oxides: The valence change mechanism. *Adv Phys.* 2021;70(2):155–349. DOI: [10.1080/00018732.2022.2084006](https://doi.org/10.1080/00018732.2022.2084006).
- [12] Jeon YJ, An H, Kim Y, Jeon YP, Kim TW. Highly reliable memristive devices with synaptic behaviour via facilitating ion transport of the zeolitic imidazolate framework-8 embedded into a polyvinylpyrrolidone polymer matrix. *Appl Surf Sci.* 2021;567:150748. DOI: [10.1016/j.apsusc.2021.150748](https://doi.org/10.1016/j.apsusc.2021.150748).
- [13] Kwon KC, Baek JH, Hong K, Kim SY, Jang HW. Memristive devices based on two-dimensional transition metal chalcogenides for neuromorphic computing. *Nano-Micro Lett.* 2022;14:58. DOI: [10.1007/s40820-021-00784-3](https://doi.org/10.1007/s40820-021-00784-3).
- [14] Li Z, Tang W, Zhang B, Yang R, Miao X. Emerging memristive neurons for neuromorphic computing and sensing. *Sci Technol Adv Mater.* 2023;24(1):2188878. DOI: [10.1080/14686996.2023.2188878](https://doi.org/10.1080/14686996.2023.2188878).
- [15] Singh C, Ray N. Memristors and resistive switching in metal oxides. In: *Optical Properties of Metal Oxide Nanostructures*. Singapore: Springer; 2023. P. 431–55. DOI: [10.1007/978-981-99-5640-1_14](https://doi.org/10.1007/978-981-99-5640-1_14).
- [16] Kindsmüller A, Schmitz C, Wiemann C, Skaja K, Wouters DJ, Waser R, *et al.* Valence change detection in memristive oxide based heterostructure cells by hard X-ray photoelectron emission spectroscopy. *APL Mater.* 2018;6:046106. DOI: [10.1063/1.5026063](https://doi.org/10.1063/1.5026063).
- [17] Nagashima K, Yanagida T, Oka K, Kanai M, Klamchuen A, Rahong S, *et al.* Prominent thermodynamical interaction with surroundings on nanoscale memristive switching of metal oxides. *Nano Lett.* 2012;12(11):5684–90. DOI: [10.1021/nl302880a](https://doi.org/10.1021/nl302880a).
- [18] Tappertzhofen S, Di Martino G, Hodmann S. Nanoparticle dynamics in oxide-based memristive devices. *Phys Status Solidi A.* 2019;217(6):1900587. DOI: [10.1002/pssa.201900587](https://doi.org/10.1002/pssa.201900587).
- [19] Saylan S, Aldosari HM, Humood K, Abi Jaoude M, Ravaux F, Mohammad B. Effects of top electrode material in hafnium-oxide-based memristive systems on highly-doped Si. *Sci Rep.* 2020;10:19541. DOI: [10.1038/s41598-020-76333-6](https://doi.org/10.1038/s41598-020-76333-6).
- [20] Zrinski I, Minenkov A, Mardare CC, Hassel AW, Mardare AI. Composite memristors by nanoscale modification of Hf/Ta anodic oxides. *J Phys Chem Lett.* 2021;12(37):8917–23. DOI: [10.1021/acs.jpcllett.1c02346](https://doi.org/10.1021/acs.jpcllett.1c02346).
- [21] Younis A, Li S. Microscopic investigations of switching phenomenon in memristive systems: A mini review. *RSC Adv.* 2018;50(8):28763–4. DOI: [10.1039/C8RA05340E](https://doi.org/10.1039/C8RA05340E).
- [22] Bataiev YM, Bataiev MM, Kornienko OA, Lavrynenko OM, Pavlenko OYu. [EPR-spectral, magnetic, and ionic features of CeO₂, Yb₂O₃, Yb₂O₃-CeO₂ powders and ceramics based on REO oxides](#). *Sci Herald Uzhhorod Univ Ser Phys.* 2021;49:9–18.
- [23] Sargsyan G, Gukasyan P, Sargsyan H, Poveda R. Diffusion flames and a semi-empirical method for estimating the distribution of hydrogen molecules in propane flames. *Sci Herald Uzhhorod Univ Ser Phys.* 2023;53:42–52. DOI: [10.54919/physics/53.2023.42](https://doi.org/10.54919/physics/53.2023.42).

Іонні мемристивні ефекти нанометрового масштабу в оксидах металів: розуміння процесу зміни валентності

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Анотація

Актуальність. Актуальність дослідження обумовлена великим потенціалом мемристивних ефектів, які виявляються у зміні опору матеріалу під впливом зовнішнього електричного поля та іонних потоків.

Мета. Метою є проведення аналізу та вивчення механізмів іонних мемристивних ефектів з детальним розглядом процесу зміни валентності металевих катіонів.

Методологія. В основі роботи було дослідження нанометрових оксидів металів TiO_2 та ZrO_2 . Матеріали були отримані шляхом синтезу за методом хімічного відкладання, використовуючи високочисті прекурсори.

Результати. Отримані результати відкривають широкі можливості для практичного використання іонних мемристивних ефектів. У ході досліджень іонних мемристивних ефектів у плівках на основі TiO_2 та ZrO_2 встановлено, що зміна опору відбувається за рахунок різних механізмів, включаючи іонну міграцію, електрохімічні реакції та реорганізацію дефектів. Під впливом зовнішнього електричного поля спостерігається зміна опору обох матеріалів. У TiO_2 відбувається зменшення опору зі збільшенням напруги, в той час як в ZrO_2 спостерігається збільшення опору. Під час додаткових експериментів в температурному діапазоні 25-200 °C, виявлено, що температура суттєво впливає на іонні мемристивні ефекти. При її підвищенні спостерігається помітне збільшення інтенсивності цих ефектів в обох матеріалах.

Висновки. Використання рентгенівської дифрактометрії та інфрачервоної спектроскопії дозволило виявити, що під впливом електричного поля відбуваються зміни у валентності металевих катіонів у обох плівках. Аналіз змін у рентгенівських та інфрачервоних спектрах, засвідчив наявність модифікації кристалічної та молекулярної структури в реакції на електричне поле. Зокрема, зміна позицій та інтенсивності піків свідчить про перебудову зв'язків у кристалічній ґратці. У статті пропонуються нові дослідження, щоб розширити розуміння цих ефектів та розглянути можливі шляхи покращення мемристивних пристроїв. Дослідження іонних мемристивних ефектів у TiO_2 та ZrO_2 має важливе практичне значення для розвитку електроніки та створення нових поколінь мемристивних і нейроморфних систем.

Ключові слова: електронні пристрої; тонкі плівки; електропровідність; резистивне перемикавання; окисно-відновний механізм