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# Nanoscale Potential Fluctuations in Zirconium Oxide and the Flash Memory Based on Such Fluctuations

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X-ray photoelectron spectroscopy, EXAFS, XANES, spectral ellipsometry and quantum-chemistry calculations were used to examine the atomic and electronic structure of non-stoichiometric amorphous  $ZrO_x$  slightly enriched with zirconium. The experimental data show that the  $ZrO_x$  material consists of stoichiometric  $ZrO_2$ , metallic Zr and zirconium suboxides  $ZrO_y$ . The structure of  $ZrO_x$  is analyzed using the Random Bonding and Random Mixture models. A model of nanoscale spatial potential fluctuations in  $ZrO_x$  is substantiated. In this model, the potential fluctuations for electrons and holes arise due to the local fluctuations of bandgap energy in the range from 0 to 5.4 eV. A  $ZrO_x$ -based flash memory element with giant retention time is proposed.

For five decades, silicon oxide  $SiO_2$  and silicon nitride  $Si_3N_4$  have been two key dielectrics in silicon-based devices. Presently, both are being replaced with high- $\kappa$  dielectrics, like  $HfO_2$ ,  $ZrO_2$ ,

Ta<sub>2</sub>O<sub>5</sub> and Al<sub>2</sub>O<sub>3</sub><sup>1, 2</sup>. Slightly non-stoichiometric, metal-enriched high-κ dielectrics are examined as a storage medium in charge-trap flash memory devices. Oxygen vacancies and oxygen polyvacancies in high-κ dielectrics are used as traps in those devices<sup>3</sup>. It is believed that oxygen vacancies play a key role in dielectric reversible switching between states with low and high resistance under current pulse (resistive effect). Intensive studies aimed at the development of resistive random-access memory (ReRAM) are carried out now<sup>4-6</sup>. ReRAM have attracted great attention due to their simple structure, low power consumption, high-speed operation, high-density integration, multibyte switching. A number of binary metal oxides have been investigated for ReRAM applications. Non-stoichiometric zirconium oxide (ZrO<sub>x</sub>) is one of the promising materials for ReRAM<sup>7-9</sup>.

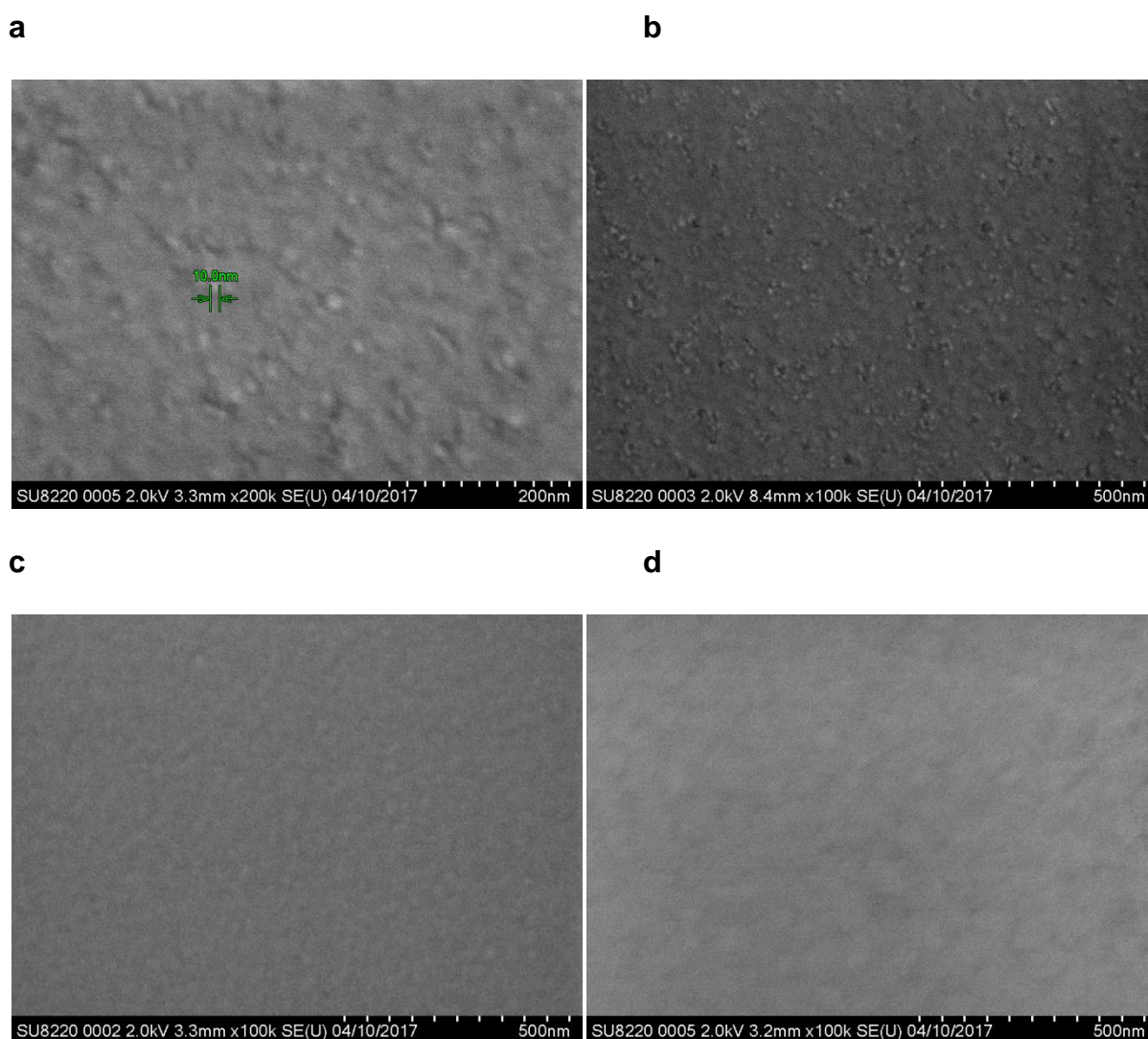
The atomic and electronic structure of ZrO<sub>2</sub> was studied experimentally<sup>10-15</sup> and theoretically<sup>14, 16-19</sup>. The study of nonstoichiometric zirconium oxide ZrO<sub>x</sub> is of much interest from the viewpoint of fundamental knowledge. A variation of the chemical composition (stoichiometry) of ZrO<sub>x</sub> leads to a dramatic change of the electronic structure of the material, thus offering a possibility to control its physical (optical and electric) properties.

The purpose of the present study was to investigate the atomic and electronic structure of nonstoichiometric zirconium oxide ZrO<sub>x</sub> to justify the nanoscale potential fluctuations caused by a fluctuation of spatial chemical composition.

## **The Structure of ZrO<sub>x</sub>**

According to reflection high-energy electron diffraction (RHEED) data, all the ZrO<sub>x</sub> films were amorphous. Surface field emission scanning electron microscopy (FESEM) images of the ZrO<sub>x</sub> films are shown in Fig. 1. Evidently, the variation of the nanoscale uniformity of ZrO<sub>x</sub> films with a change of stoichiometry «x» is observed. In ZrO<sub>x</sub> films (x=1.4) heavily enriched with the metal, metallic of round-shaped Zr clusters were identified. The diameters of the clusters ranged in the interval from 2 to 20 nm, the mean diameter being about 10 nm (Fig. 1a). In the images, the clusters look as bright round points. With increasing the oxygen concentration in the films, the

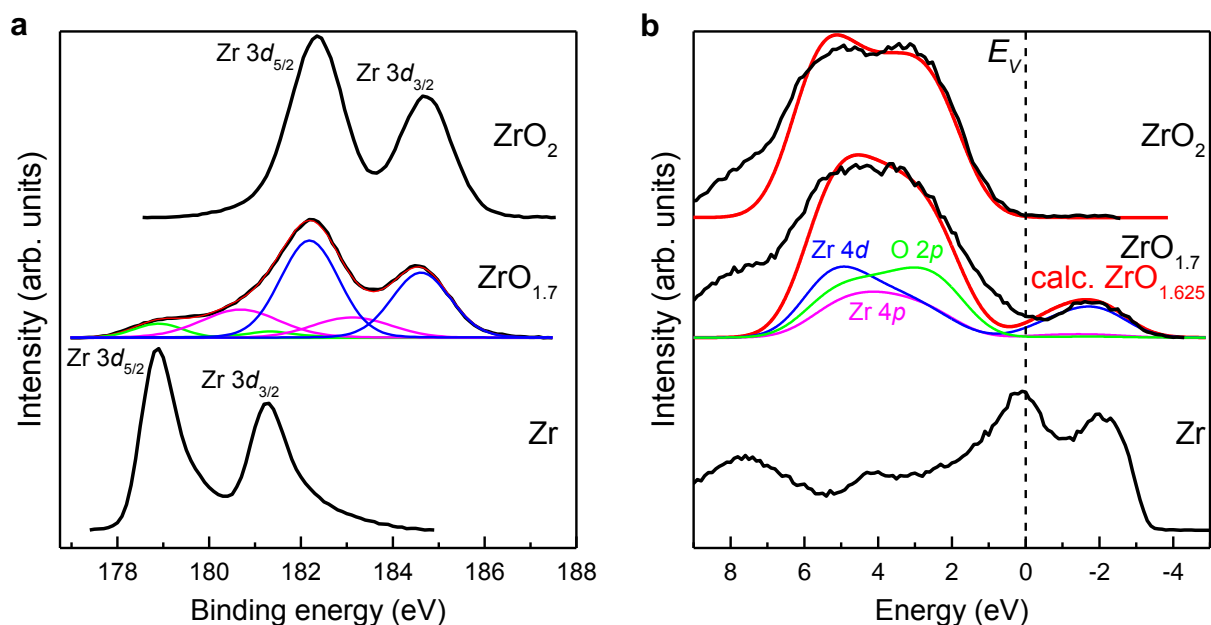
light spots grow in sizes, and their diameter increases to 20 nm (Fig. 1b,c). Nearly stoichiometric films look uniform (Fig. 1d).



**Figure 1 | FESEM-images of the  $ZrO_x$  film surface.** The metallic Zr clusters are seen as light round spots against the dark background. (a), (b) –  $ZrO_{1.4}$  at different scales, (c) –  $ZrO_{1.7}$ , (d) –  $ZrO_2$ .

The X-ray photoelectron spectra (XPS) of the Zr  $3d_{3/2,5/2}$  level in nearly stoichiometric zirconium oxide, in non-stoichiometric  $ZrO_{1.7}$  enriched with the metal and in metallic Zr are shown in Fig. 2a. The deconvolution of the experimental  $ZrO_{1.7}$  spectrum has shown that the dominating high-energy signal was due to stoichiometric  $ZrO_2$ , whereas the low-energy signal pointed to the presence of zirconium suboxides ( $ZrO_y$ ) (Fig.2).  $ZrO_{1.7}$  enriched with the metal exhibited three

signals, two signals being due to stoichiometric  $\text{ZrO}_2$  and due to  $\text{ZrO}_y$ , respectively, and the third low-energy signal due to metallic Zr. The peak deconvolution due to the  $\text{Zr } 3d_{3/2,5/2}$  level in  $\text{ZrO}_x$  shows that  $\text{ZrO}_{1.7}$  contains  $\approx 10\%$  of metallic Zr,  $\approx 15\%$  of  $\text{ZrO}_y$  and  $\approx 75\%$  of  $\text{ZrO}_2$ .



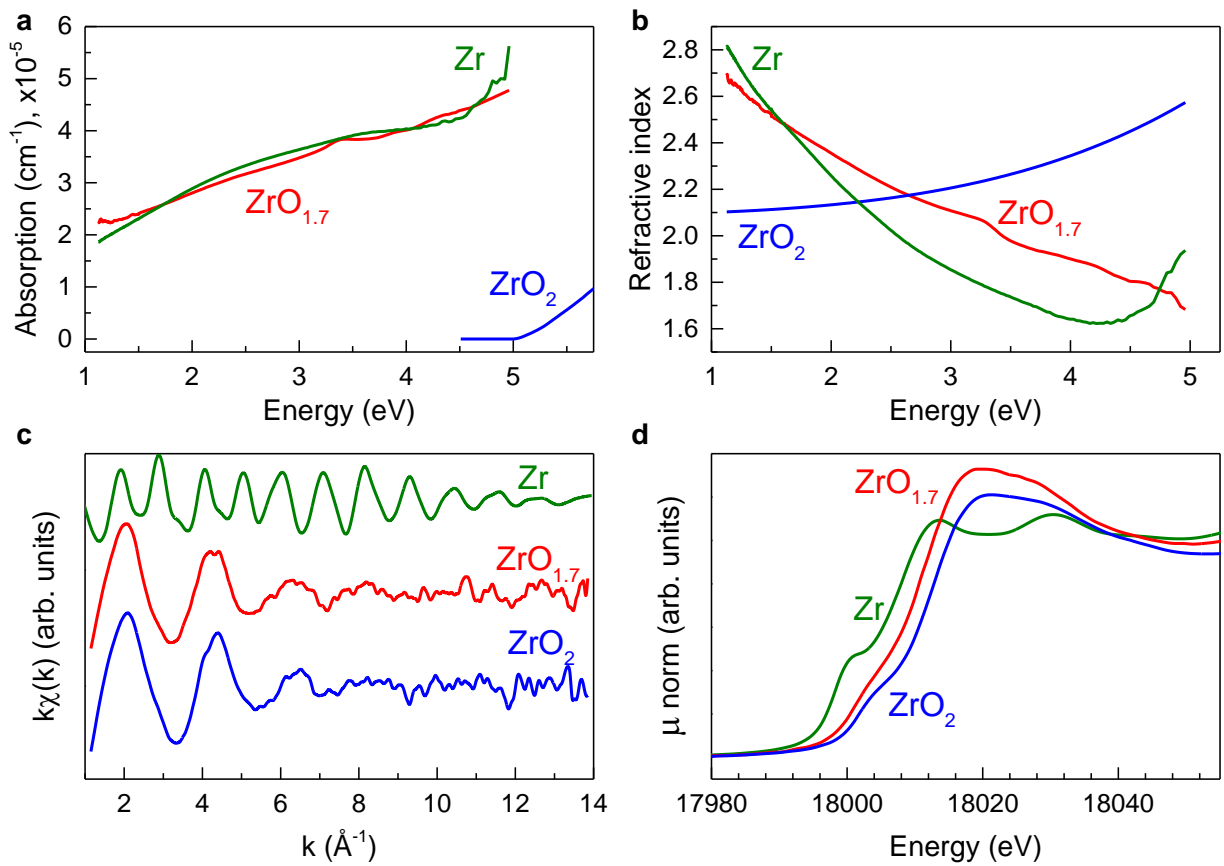
**Figure 2 | X-ray Photoelectron Spectra.** (a) The peak due to the Zr 3d level in  $\text{ZrO}_2$ ,  $\text{ZrO}_{1.7}$ , and in Zr (black curves). The color curves show the  $\text{ZrO}_{1.7}$  spectra decomposition into Gaussian functions: the blue curve refers to  $\text{ZrO}_2$ ; the purple curve refers to  $\text{ZrO}_y$ ; the green curve - to Zr; and the red curve - to the sum of all the four components. (b) The experimental, and calculated (black and red curves, respectively) valence-band XPS of  $\text{ZrO}_2$ ,  $\text{ZrO}_{1.7}$  and Zr. The top of the valence band  $E_V$  is set to zero energy. The thin color curves indicate the type of the atomic orbitals (Zr 4d, Zr 4p, and O 2p) of which the XPS of  $\text{ZrO}_{1.625}$  is formed.

The experimental and calculated valence-band XPS of  $\text{ZrO}_2$ ,  $\text{ZrO}_{1.7}$  and metallic Zr are shown in Fig. 2b. A proof for the presence of oxygen vacancies in  $\text{ZrO}_x$  is the formation in the valence-band XPS of a peak with a maximum at an energy approximately 2 eV higher than the valence-band top  $E_V$  (Fig. 2b). The position of the peak, as well as its width and intensity, well comply

with the calculated XPS for m-ZrO<sub>2</sub>, in which, per each 24 atoms there are three oxygen vacancies that form deep occupied defect states in the band gap. The deconvolution of the calculated spectrum of ZrO<sub>x</sub> into the contributions due to individual atomic orbitals shows that the main contributions to the ZrO<sub>x</sub> valence-band XPS are due to the 4*d* and 4*p* states of zirconium and due to the 2*p* states of oxygen (Fig. 2b). The peak above the valence-band top is almost completely formed by the 4*d* states of zirconium.

The spectral dependences of the absorption coefficient in ZrO<sub>2</sub>, ZrO<sub>1.7</sub> and in Zr are shown in Fig.3a. The fundamental absorption edge in stoichiometric ZrO<sub>2</sub> at the energy of 5.0 eV. The optical absorption in ZrO<sub>1.7</sub> monotonically increases in the energy range from 1.2 to 5.0 eV. Similar behavior is also observed in Zr. Thus, the optical absorption in ZrO<sub>1.7</sub> is due to the metallic phase.

The spectral dependence of the refraction index in ZrO<sub>2</sub>, ZrO<sub>1.7</sub> and in Zr is shown in Fig. 3b. In ZrO<sub>2</sub>, the “normal” refraction-index dispersion is observed. In the range of quantum energies from 1.2 to 5.0 eV, the refraction index monotonically increases in the value from 2.10 to 2.58 with the increasing quantum energy (Fig. 3b). Such behavior is characteristic for dielectrics at quantum energies lower than the bandgap  $E_g$ . In ZrO<sub>1.7</sub>, an “abnormal” refractive index dispersion typical of metals is observed. The refractive index magnitude monotonically decreases as the quantum energy increases in the range from 1.2 to 5.0 eV. Similar behavior is also observed in Zr (Fig. 3b).



**Figure 3 | Optical and Zr *K* edge X-ray absorption spectra of ZrO<sub>1.7</sub>, Zr and in ZrO<sub>2</sub>.** (a) Spectral dependence of the absorption coefficient  $\alpha$  (for ZrO<sub>2</sub> taken from ref. <sup>20</sup>). (b) Spectral dependence of the refractive index  $n$ . (c) EXAFS and (d) XANES spectra.

According to ref. 10-12, 15, ZrO<sub>2</sub> has several polymorphic modifications. Only monoclinic (m-) ZrO<sub>2</sub> is stable at room temperature. As a starting structural model for the examined material, we used the monoclinic structure<sup>21</sup>. In m-ZrO<sub>2</sub>, a zirconium atom is surrounded by seven oxygen atoms. The experimental Zr *K* edge X-ray absorption spectra is shown in Fig. 3c, d. A very significant disordering of the structure is observed for samples of oxides prepared without annealing (Fig. 3c). In the process of modeling extended X-ray absorption fine structure (EXAFS) ZrO<sub>2</sub> spectra, the coordination number for oxygen atoms was fixed,  $N_{\text{Zr-O}}=7$ , and seven shortest separations Zr-O (average value  $R_{\text{Zr-O}}=2.140$  Å) and one (average) separation  $R_{\text{Zr-Zr}}=3.31$  Å were calculated. As a result of studying the simulation, it was found that, in the ZrO<sub>x</sub> sample, the mean Zr-O separation was  $R_{\text{Zr-O}}=2.135$  Å and the oxygen coordination number proved to be  $N_{\text{Zr-O}}=5.7$ ,

which value was smaller than the coordination number in  $ZrO_2$  (probably, due to oxygen vacancies).

From Fig. 3d, it is seen that the absorption edge of  $ZrO_x$  X-ray Absorption Near Edge Structure (XANES) spectra is shifted to lower energies with respect to  $ZrO_2$ ; the difference between the energy positions of the absorption edges in  $ZrO_2$  and  $ZrO_x$  is about 1 eV. Such a shift corresponds to an average charge at Zr atoms in the examined  $ZrO_x$  films being reduced in comparison with the Zr charge in  $ZrO_2$ . The latter can be indicative of both the presence of excess Zr in the oxides, in which the first coordination sphere of zirconium has the composition  $Zr_\nu O_{6+\nu}$  with  $\nu \leq 1$  (since the average stoichiometric formula is  $ZrO_{1.7}$ ), and the presence of a small quantity of a metal phase (<10%).

For simplicity, consider the structure of  $ZrO_x$  with the example of the simplest cubic phase. The cubic phase of  $ZrO_2$  consists of  $ZrO_8$  structural units. The replacement of one oxygen atom with a zirconium atom results in the formation of a  $ZrZrO_7$  structural unit, whereas the replacement of two, three, or four oxygen atoms with two, three, or four zirconium atoms, respectively, yields  $ZrZr_2O_6$ ,  $ZrZr_3O_5$ , or  $ZrZr_4O_4$  structural units, respectively. Hypothetically, in a similar manner,  $ZrZr_5O_3$ ,  $ZrZr_6O_2$ ,  $ZrZr_7O$ , and  $ZrZr_8$  structural units can be formed. However, the replacement of more than four oxygen atoms with zirconium atoms turns out to be impossible because of geometric limitations. The radius of the oxygen atom is 0.48 Å, whereas the radius of the zirconium atom is 2.06 Å. According to the EXAFS data, the length of the Zr-O bond is 2.135 Å. As a result, the replacement of a larger amount of oxygen with zirconium atoms for an eight-coordinated central zirconium atom turns out to be impossible.

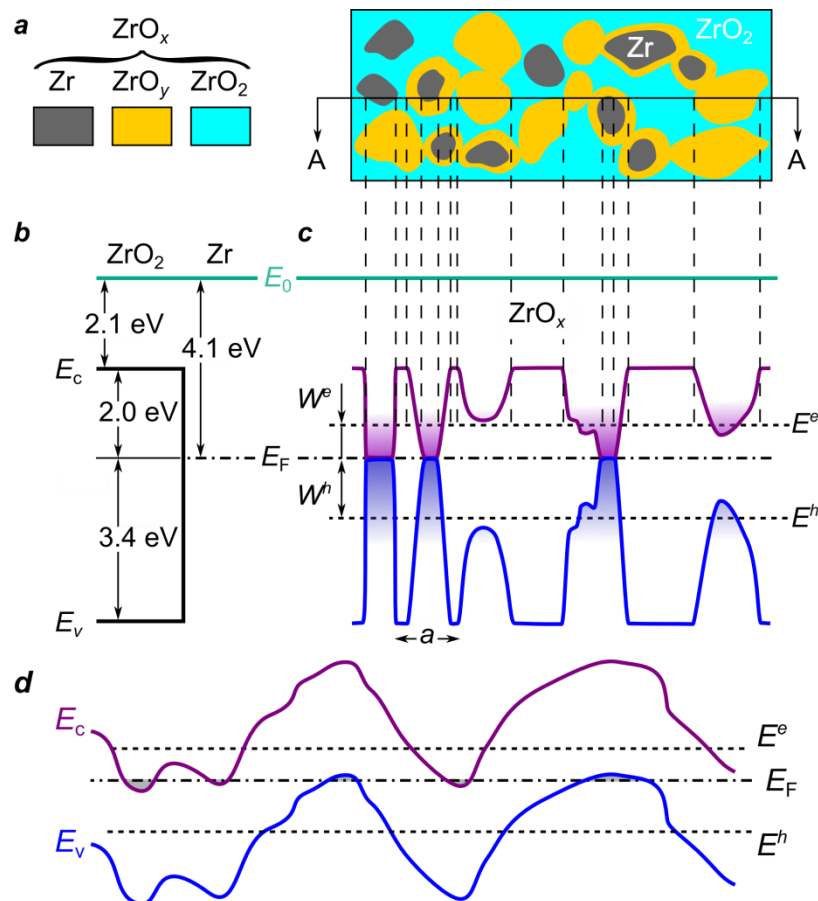
In the Random Bonding model,  $ZrO_x$  consist of a random mixture of  $ZrZr_\nu O_{8-\nu}$  structural units with  $\nu=0, 1, 2, 3, 4, 5, 6, 7$  and 8. Such a model fails to describe the  $ZrO_x$  structure. In the Random Mixture model,  $ZrO_x$  presents a mixture of  $ZrO_2$  and Zr. The experiment points to the presence of  $ZrO_2$  and Zr in  $ZrO_x$ ; however, XPS and data point to the occurrence of  $ZrO_y$  suboxides involving  $ZrZr_\nu O_{8-\nu}$  structural units as well. Thus, neither the Random Bonding model nor the Random



Mixture model adequately describes the structure of  $ZrO_x$ . According to the experimental data, the  $ZrO_x$  consists of  $ZrZr_vO_{8-v}$  structural units; however, the distribution of the structural units in the material is not a random one like the distribution that appears in the Random Bonding model.

### The model of nanoscale potential fluctuations in $ZrO_x$

Below, we substantiate an Intermediate Model for the  $ZrO_x$  structure. According to the XPS, EXAFS and spectral ellipsometry data,  $ZrO_x$  consists of  $ZrO_2$ , Zr and a small amount of  $ZrO_y$  suboxides.  $ZrO_y$  may appear at the  $ZrO_2/Zr$  interface, in the volume of  $ZrO_2$  and in the volume of the Zr. A two-dimensional representation of the  $ZrO_x$  structure in the Intermediate Model is shown in Fig. 4a.



**Figure 4 | The Intermediate Model of nanoscale potential fluctuations in non-stoichiometric  $ZrO_x$ .** (a) Two-dimensional model for the structure of  $ZrO_x$ . (b) The energy diagram of the  $Zr/ZrO_2$

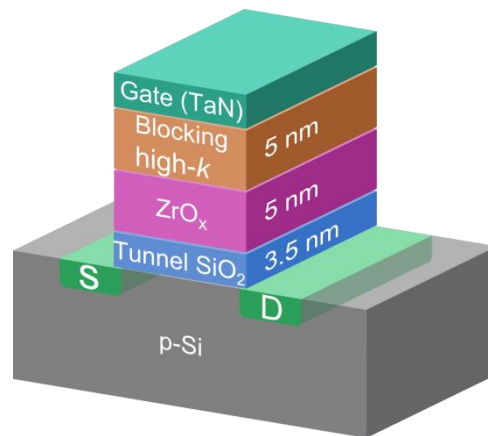
interface: the green solid horizontal line shows the electron energy with respect to one in vacuum  $E_0$ , and the dash-and-dot line shows the position of Fermi level  $E_F$  in Zr. (c) One-dimensional model for potential fluctuations in  $ZrO_x$ :  $E^e$  and  $E^h$  are the percolation levels for electrons and holes;  $W^e$  and  $W^h$  are the barriers for excitation of electrons and holes from the Fermi level to the electron and hole percolation levels, respectively;  $a$  is the characteristic spatial scale of potential fluctuations; (d) One-dimensional Shklovskii-Efros model for potential fluctuations in doping-compensated semiconductors;  $E_F$  is the Fermi level in the semiconductor;  $E^e$  and  $E^h$  are the percolation levels for electrons and holes<sup>22</sup>.

According to this model,  $ZrO_x$  consists of three phases:  $ZrO_2$ ,  $ZrO_y$  and Zr. The band diagram of  $ZrO_x$  is shown in Fig. 4b. The bandgap energy of  $ZrO_2$  is  $E_g=5.4$  eV<sup>23</sup>. The electron affinity of  $ZrO_2$  is  $\chi=2.1$  eV<sup>23</sup>. The work function of metallic Zr is 4.1 eV. According to the Intermediate Model, spatial fluctuations of the chemical composition give rise to the local spatial fluctuations of the bandgap energy in  $ZrO_x$  (Fig.4c).  $E_g$  in  $ZrO_x$  varies in the range from 0 to 5.4 eV. The conduction-band edge position, with respect to the electron energy in vacuum  $E_0$ , varies in the range from 2.1 eV to 4.1 eV. The latter quantities define the maximum fluctuation scale of conduction-band-edge energy position  $E_c$  in  $ZrO_x$ . The energy position of valence-band top, with respect to the electron energy in vacuum, varies in the range from 4.1 eV to 7.5 eV. The height of the potential barrier for holes at the Zr/ $ZrO_2$  interface defines the maximum fluctuation scale of the valence-band top position  $E_v$  in  $ZrO_x$ . According to the structural measurements, the typical spatial scale of potential fluctuations in  $ZrO_x$  falls into the range from 2 nm to 20 nm (see Fig. 1).

### **The possibility of using $ZrO_x$ as a storage medium in flash memory devices**

The operating principle of state-of-the-art flash memory devices is based on the accumulation (localization) of electrons or holes at deep traps in silicon nitride<sup>24, 25</sup>. The lifetime of electrons and holes in localized states amounts to 10 years at 85 °C. According to Fig. 4, metallic zirconium clusters in a  $ZrO_2$  matrix act as deep potential wells (traps) for contact-injected electrons and holes.

Thus, there arises a possibility to use, as the storage medium in flash memory elements, instead of silicon nitride, nonstoichiometric  $ZrO_x$  slightly enriched with the metal (see Fig. 5).



**Figure 5 |** A flash memory element using  $ZrO_x$  as the storage medium.

According to Fig. 4, the depth of the potential wells due to metallic Zr for electrons and holes in  $ZrO_x$  is 2.0 and 3.4 eV. For comparison, the energies of the electron and hole traps in silicon nitride are equal to 1.4 eV<sup>26</sup>. Thus, it can be expected that the potential wells due to metallic Zr in  $ZrO_x$  will be capable of ensuring a giant retention time, or giant lifetime of electrons/holes in localized states.

The flash memory element is similar to the traditional field-effect transistor (FET) in which, instead of the gate dielectric, a three-layer dielectric is used (Fig. 5). A thermally grown 3.5-nm thick silicon oxide layer functions as the tunnel dielectric. Over the tunnel oxide, a 5-nm thick storage layer of  $ZrO_x$  is provided. Over the storage dielectric, a low-conducting blocking high- $\kappa$  dielectric is used. As the latter dielectric,  $Al_2O_3$  is appropriate for use<sup>24</sup>. Tantalum nitride TaN is normally used in state-of-the-art flash memory elements as a conducting gate.

On the application of a negative voltage pulse to the gate, the injection of holes from the silicon through the tunnel oxide leads to the injected holes trapping at the metallic clusters in  $ZrO_x$ . As a result, a positive charge gets accumulated in  $ZrO_x$ . This positive charge attracts the electrons

at the silicon/tunnel oxide interface, and an inversion charge due to electrons forms in the silicon. The inversion layer forms a conducting channel that connects the source and the drain. Here, the FET resistance is low, and this state corresponds to logic “zero”. Since the metallic clusters in  $ZrO_x$  act as deep traps, the lifetime of electrons in a localized state is large, exceeding ten years.

On the application of a positive voltage pulse to the gate in the flash memory element, the electrons tunneling from the silicon through the tunnel oxide become trapped at the metallic clusters in  $ZrO_x$ . A negative charge accumulated in the storage medium ( $ZrO_x$ ) attracts holes in the silicon substrate, and the conducting channel vanishes. The FET resistance here is high, corresponding to logic “unity”. Such a state can be stored during more than ten years. Thus, the proposed flash memory element has two stable states: “zero” and a “unity”.

According to Fig.4, the depth of the potential well for electrons and holes due to metallic Zr in  $ZrO_x$  amounts, respectively, to 2.0 and 3.4 eV. For comparison, the energies of electron and hole traps in silicon nitrides amount to 1.4 eV. An estimation shows that the lifetime for an electron trapped at zirconium at temperature 150 °C is approximately one hundred years. Thus, the “metallic” potential wells in  $ZrO_x$  are capable of ensuring a giant retention time in such flash memory devices.

## **Discussion**

$ZrO_x$  consists of stoichiometric  $ZrO_2$ , metallic Zr and zirconium suboxides  $ZrO_y$ . XPS and EXAFS experiments are indicative of the presence of stoichiometric  $ZrO_2$ . The presence of metallic Zr is evidenced by XPS and spectral ellipsometry data. XPS and XANES data point to the presence of  $ZrO_y$  suboxides in  $ZrO_x$ .

The large radius of the zirconium atom, 2.06 Å, in comparison with the radius of the oxygen atom, 0.48 Å, makes the formation of  $ZrZr_vO_{8-v}$  structural units with  $v > 4$  impossible. Indeed, because of the large radius of the zirconium atom, the formation of Zr-O bonds with a bond length in the interval of 2.03 to 2.27 Å becomes improbable. That is why the clusters of  $ZrO_2$  and Zr with

a small fraction of  $ZrO_y$  suboxides, consisting of  $ZrZr_vO_{8-v}$  structural units with  $v < 4$ , form in the material.

In the Shklovskii-Efros model, the potential fluctuations have an electrostatic nature, and they are due to the spatial fluctuations of the concentrations of charged donors and acceptors in perfectly compensated semiconductors<sup>22</sup>. In the latter case, the bandgap energy remains unchanged, and the built-in electric field promotes a spatial separation of the electron and holes.

In the model of potential fluctuations in non-stoichiometric  $ZrO_x$  proposed in the present paper, the local spatial potential fluctuations for electrons and holes are due to the local fluctuations of bandgap energy. Unlike in the Shklovskii-Efros model, the neutrality at each point of the space is in  $ZrO_x$ . The second difference is that the local electric fields for electrons and holes are directed in one and the same direction, promoting the localization of the charge carriers of both types at one and the same spatial point. Previously, the model of potential fluctuations due to the local spatial fluctuations of the chemical composition was substantiated for nonstoichiometric  $SiO_x$ <sup>25-27</sup> and for nonstoichiometric  $SiN_x$ <sup>27-29</sup>. The difference between the models of potential fluctuations in tetrahedral nonstoichiometric silicon nitride and oxide consists in that the minimum local bandgap energies in  $SiN_x$  and  $SiO_x$  are equal to the bandgap energy of silicon (for crystalline and amorphous Si, we have respectively  $E_g=1.1$  and  $1.6$  eV<sup>30</sup>), whereas the minimum local bandgap energy of  $ZrO_x$  is equal to zero.

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## **Author contributions**

V.A. Gritsenko designed the study and developed the nanoscale potential fluctuations model and flash memory element based on  $ZrO_x$ . T.V. Perevalov performed quantum-chemical simulations. V.N. Kruchinin carried out the spectroellipsometric measurements. V.S. Aliev and A.K. Gerasimova synthesized the samples. S.B. Erenburg, S.V. Trubina, K.O. Kvashnina performed and analyzed EXAFS and XANES experiments. I.P. Prosvirin performed XPS measurements.

## Methods

**Sample preparation.** Thin (~50 nm)  $ZrO_x$  ( $x < 2$ ) films were prepared using Ion Beam Sputtering Deposition (IBSD<sup>31</sup>) on the «Spector» installation (Veeco, USA) on the pre-prepared silicon wafers (Si(100), n-type,  $\rho = 4.5 \Omega \times \text{cm}$ ). Before deposition, the substrates were pre-cleaned in a hydrofluoric acid (HF) solution. The metallic zirconium ( $Zr > 99.9\%$ ) target was sputtered by  $Ar^+$  ions with the energy of 1.2 keV and a current density on the target surface of about  $1 \text{ mA} \cdot \text{cm}^{-2}$  in the presence of high purity oxygen ( $O_2 > 99.999\%$ ). The growth chamber was pre-pumped up to a pressure of  $\sim 10^{-5}$  Pa before argon and oxygen flow feeding. The pressure in the growth chamber during the zirconium oxide deposition process was about  $1.5 \times 10^{-2}$  Pa. The zirconia films synthesis rate was controlled by using quartz sensor MAXTEC-400. The substrate was initially at room temperature and it did not exceed  $\sim 70$  °C during the film growth process. The oxygen content in the  $ZrO_x$  was varied by changing the  $O_2$  partial pressure using the gas flow controller.

**Film morphology.** The  $ZrO_x$  morphology was investigated by the reflection high-energy electron diffraction (RHEED) technique on an EF-Z4 device at the accelerating voltage of 50 kV. The nanoscale visualization of film surfaces was carried out using a scanning electron microscope (SEM) Hitachi-su-8220 with a field emission cathode (FESEM) by using a secondary electron detector SE(U) at magnifications  $\text{Mag} = 5\text{kx}, 10\text{kx}, 20\text{kx}, 60\text{kx}$ . The accelerating voltage was 2 kV. The distance from the tip of the objective lens to the sample surface (WD) was 3.5 mm. The instrumental microscope resolution was about 0.8 nm at 15 kV.

**X-ray photoelectron spectroscopy.** The X-ray photoelectron spectra (XPS) measurements were performed on a SPECS machine equipped with an X-ray source with a twin Al/Ag anode, an ellipsoidal crystal X-ray monochromator FOCUS-500, a PHOIBOS 150 hemispherical electron energy analyzer and an ion source. The spectra were obtained using the monochromatic  $Al K\alpha$

radiation ( $h\nu = 1486.74$  eV) and the fixed analyser pass energy of 20 eV under ultrahigh vacuum conditions. The binding energy was calibrated using the C 1s peak at 284.8 eV related to adventitious hydrocarbons for the as-inserted surface. To damp the surface charging effect, the low energy electron gun FG-20 ( $I = 0.8$  mA,  $E = 2$  eV) was used. The relative element content ([O]/[Zr] atomic ratio) was defined using the detailed spectra of Zr 3d and O 1s and the known element sensitivity factors<sup>32</sup>. To define the integrated peak intensity correctly, the background was subtracted by the Shirley method.

**X-ray absorption spectroscopy.** Extended X-ray Absorption Fine Structure (EXAFS) and X-ray Absorption Near Edge Structure (XANES) measurements were performed assisted with the European Synchrotron Radiation Facility (ESRF) at beamline BM20. The incident energy was selected using the Si(111) double crystal monochromator. Higher harmonics rejection was achieved by two mirrors with Rh surfaces. The size of the X-ray beam was 5 mm (horizontal) x 0.2 mm (vertical). The XAFS (X-ray Absorption Fine Structure) spectra were measured in the fluorescence mode using a 12-element Ge detector. The incident flux of X-ray quanta on the Zr *K* edge was  $\sim 1 \times 10^{10}$  ph/s. The incident angle on the sample was  $\sim 1^\circ$ . Three scans of EXAFS data (from 250 eV below to 800 eV above Zr *K* edge (17998 eV)) were collected at room temperature. It should be noted that the signal-to-noise ratio for the spectra of the studied samples is small; after  $10 \text{ \AA}^{-1}$ , reliable EXAFS modulations are practically absent, which objectively testifies the structural disorder of the samples (amorphous, multiphase, nonstoichiometric, vacancy in the structure).

The EXAFS spectra were analysed by the Artemis and Athena software<sup>33</sup>. The Fourier transformations of EXAFS oscillation were carried out within  $3.0 - 11.0 \text{ \AA}^{-1}$ . The fitting was performed in the *R*-range of  $1.0 - 3.1 \text{ \AA}$  with *k*- and *k*<sup>2</sup>-weights. The EXAFS amplitudes and phase-shifts were calculated by FEFF (an automated code for *ab initio* calculations of XAFS)<sup>34</sup> for the

crystallographic data<sup>35</sup>. The fitting quality was estimated by the difference between the model and experimental Fourier transformed EXAFS function (*R*-parameter).

**Spectroellipsometry.** The optical properties (refractive index  $n(\omega)$  and absorption coefficient  $\alpha(\omega)$  dispersion), as well as film thicknesses, were determined by spectroscopic ellipsometer «SPECTROSCAN» (produced by ISP SB RAS). The spectral dependences of the ellipsometrical angles  $\Psi$  and  $\Delta$  were measured in wavelength range  $\lambda = 250\text{--}900$  nm. The spectral resolution of the instrument was 2 nm, the recording time of one spectrum was in no excess of 20 s, the angle of incidence of the light beam was  $70^\circ$ . We used a four-zone measurement technique followed by averaging over all four zones. The solution of the inverse problem of ellipsometry and fitting the spectral dependences of the ellipsometrical angles  $\Psi(\lambda)$  and  $\Delta(\lambda)$  were performed in accordance with the basic equation of ellipsometry:

$$\operatorname{tg} \Psi \cdot e^{i\Delta} = \frac{R_p}{R_s}, \quad (1)$$

Here  $R_p$  and  $R_s$  are the complex light reflection coefficients for the waves polarized in the incidence plane and perpendicular to the plane, respectively. These coefficients depend on the optical constants and layer thicknesses. To calculate the dispersion dependences of refractive index  $n(\lambda)$  and absorption coefficient  $k(\lambda)$ , a model of semi-infinite reflecting medium (an isotropic substrate – air) was employed. Thus, in the whole spectral range, the spectral dependences of polarization angles were fitted for  $m$  points of the spectrum by minimizing the error function:

$$\sigma^2 = \frac{1}{m} \cdot \sum_{i=1}^m \left[ (\Delta_{\text{exp.}} - \Delta_{\text{calc.}})^2 + (\Psi_{\text{exp.}} - \Psi_{\text{calc.}})^2 \right] \quad (2)$$

$\Psi(\lambda)$  and  $\Delta(\lambda)$  were also fitted using the approximate dispersion model proposed by Lorentz and Drude. The dispersion dependences calculation are performed independently for each spectrum point.

**Quantum chemistry.** Quantum-chemistry calculations were performed for monoclinic (m-) ZrO<sub>2</sub>. Simulations were performed in terms of the hybrid density functional theory (DFT) in the periodic supercells model using a B3LYP functional in the Quantum-ESPRESSO code<sup>36</sup>. Hybrid exchange-correlation functional B3LYP was adopted to reproduce the correct zirconium oxide band gap value 5.5 eV. The calculations were made using the following electronic configuration of the constituent elements: Zr [Ar] 4s<sup>2</sup>4p<sup>6</sup>5s<sup>2</sup>5d<sup>2</sup> and O [He] 2s<sup>2</sup> 2p<sup>4</sup>, where the core configurations are shown in the parentheses. The potentials of nuclei and core electrons were described by atomic norm-conserving pseudopotentials. The plane-wave cutoff energy was selected to ensure the convergence of the total cell energy to 0.005 eV/atom and was taken equal to 80 Ry. The oxygen-depleted non-stoichiometric zirconium oxides were simulated by a oxygen atoms removing and a subsequent relaxation of all atoms in the 24-atom supercell. The valence band XPS were calculated by summing the partial densities of states of the valence orbitals taken with the weight factors equal to the corresponding photoionization cross-sections<sup>37</sup>, with Gauss function broadening with the FWHM of 0.7 eV.

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