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ZnO Memristive Nanostructures for ReRAM Application †

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Abstract: This paper is devoted to the fabrication of ReRAM elements based on TiN/ZnO/TiN/Al_2O_3 structures using scratching probe nanolithography of the atomic force microscope, as well as to the investigation of the resistive switching of the ReRAM elements. The regimes of scratching probe nanolithography on the photoresist film were investigated. The ReRAM elements were shown to exhibit a bipolar resistive switching with the ratio of HRS/LRS ratio up to 78.8 at reading voltage 0.5 V and maintaining a resistive state up to 10^5 s. The results can be useful for micro- and nanoelectronics elements manufacturing, as well as neuromorphic applications using probe nanotechnologies and nanocrystalline ZnO-based ReRAM elements prototyping.

Keywords: nanotechnology; neuromorphic systems; memristor; ReRAM; resistive switching; forming-free; nanocrystalline zinc oxide; pulsed laser deposition; scratching probe nanolithography

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1. Introduction

The von Neumann architecture was the main architecture of computing systems for half a century. In connection with the achievement of the resolution limit in the production of integrated circuits, a technological barrier has arisen to increase the scaling of the elements [1–3]. As a result, this led to a decrease in the speed of data exchange between the processor and the computer memory, which is especially important in applications related to processing large amounts of data [4]. One of the possible solutions to this problem is the transition of computer systems to an architecture similar to the architecture of the biological brain, which is an array of low-power computing elements (neurons) connected by parallel channels (synapses) interconnected by special channels (synapses) [5,6]. The actual method of technological implementation of this architecture is non-volatile resistive memory ReRAM based on metal oxide memristor structures connected by cross-data buses (cross-bar) [7,8]. One of the promising materials for memristor structures manufacturing is forming-free nanocrystalline zinc oxide (ZnO) by pulsed laser deposition (PLD) [9]. To produce neuromorphic systems based on forming-free nanocrystalline ZnO films on an industrial scale, it is necessary to carry out numerous studies on the effect of manufacturing modes and various control parameters on the resistive switching of ReRAM elements. In this regard, there is a need to develop a new nanolithography technique that allows local express prototyping of individual ReRAM elements, as well as diagnostics of their electrical and morphological parameters in situ. One of the promising methods for the formation of nanoscale structures is scratching probe nanolithography (SPN) of the atomic force microscope (AFM) [10–12]. The SPN method involves the modification of thin polymer films by the formation of profiled nanosized structures using the tip of the AFM probe.

In this work, we investigated the scratching probe nanolithography modes, based on the obtained modes, we fabricated ReRAM elements and investigated the resistive switching in them.

2. Materials and Methods

Forming-free nanocrystalline ZnO thin films were grown using a pulsed laser deposition technique. Sapphire wafer Al_2O_3 was used as a substrate. The TiN electrode bottom was deposited under the following conditions: wafer temperature: 600 °C, target–wafer distance: 55 mm, Ar pressure: 1 Torr, pulse energy: 400 mJ, number of pulses 10,000, frequency 10 Hz. ZnO films were deposited under the following conditions: substrate temperature 800 °C, number of pulses 20,000, wafer temperature: 500 °C, target–wafer distance: 55 mm, O_2 pressure: 1 mTorr, pulse energy: 400 mJ.

The photoresist/thinner film (FP-383/RPF383F) at volume ratios of 1:9 was transferred to ZnO using the centrifugal method at rotation speed at 4500 rpm. The thickness of the photoresist/thinner film was equaled 42.1 ± 3.2 nm.

Scratching probe nanolithography was performed using a Ntegra Probe Nanolaboratory (NT-MDT, Zelenograd, Russia) and a commercial cantilever NSG11 with 12.1 N/m spring constant. As a result, the dependences of depth and width on applied force and scan speed were obtained. Then, the 4 windows on photoresist film were formed. The TiN film as a top electrode on the photoresist was deposited using a magnetron sputtering method. The lift-off process was applied using dimethylformamide. As a result, 4 TiN/ZnO/TiN/Al_2O_3 devices were produced.

Electric measurements in spectroscopy mode were performed using Ntegra. The TiN bottom electrode was grounded. As a result, the current-voltage characteristics (CVC) were obtained for each device, as well as the dependence of the ratio of resistances in the high-resistance state (HRS) to the low-resistance state (LRS) HRS/LRS on the amplitude of the voltage pulse, cumulative probability, and retention test.

3. Results and Discussion

Figure 1 shows the results of experimental studies of scratching probe nanolithography modes on the photoresist. It was shown that an increase in applied force from 1 to 8 μN increased the depth of the nanostructure from 2.3 ± 0.5 to 54.4 ± 5.3 nm and the width of the nanostructure from 42.8 ± 4.3 to 89.2 ± 5.2 nm (Figure 1b). The nonlinearity of the obtained dependences can be explained by the inhomogeneity of the viscoelastic properties of the photoresist. It was also shown that increasing the scan speed from 1 to 5 μm/s decreased the depth of the nanostructure from 38.2 ± 4.3 to 24.4 ± 2.2 nm and the width of the nanostructure from 80.6 ± 7.3 to 63.2 ± 6.7 nm (Figure 1c). The result obtained can be explained by a decrease in the force and time of the probe on the FR when the scan speed increases. Based on the experimental results, complex nanostructures on the surface of the FR in the form of windows were obtained (Figure 1d).

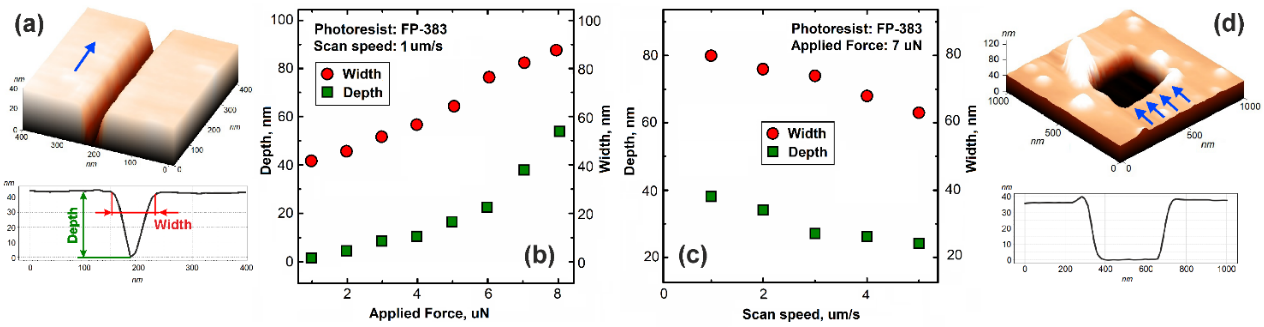

Figure 1. Study of scratching probe nanolithography modes on FP-383 photoresist: 3D-AFM image and AFM cross section of a single nanostructure (**a**); Dependencies of the photoresist puncture depth and structure width on the applied force (**b**) and scan speed (**c**); 3D-AFM image and AFM cross section of a complex nanostructure (**d**).

Figure 2 shows the results of experimental studies of the resistive switching in $TiN/ZnO/TiN/Al_2O_3$. The structures were shown to exhibit a bipolar resistive switching (Figure 2c) with HRS/LRS ratio of 56.6 for device 1, 35.5 for device 2, 78.8 for device 3, 38.4 for device 4 at reading voltage (U_{rd}) 0.5 V (Figure 2d). The variation in values can be explained by the different concentrations of oxygen vacancies for each device. Studies of the device with the highest resistance ratio (device 3) showed that increasing the voltage pulse amplitude from 0 to 3 V leads to an increase in the HRS/LRS ratio from 34.3 V to 78.7 V, and a decrease from 78.7 to 53.5 within voltages from 3 to 6 V (Figure 2f). The result can be explained by the degradation of the device due to breakdown at voltages higher than 3V. The cumulative probability analysis showed that the LRS varies from 6.4×10^8 Ω to 13.3×10^8 Ω, and the HRS varies from 2.2×10^{10} Ω to 5.1×10^{10} Ω (Figure 2g). The retention test showed that within 10^5 s the HRS decreased from 7.14×10^8 Ω to 6.72×10^8 Ω, and the HRS from 5.56×10^{10} Ω to 4.65×10^{10} Ω (Figure 2e).

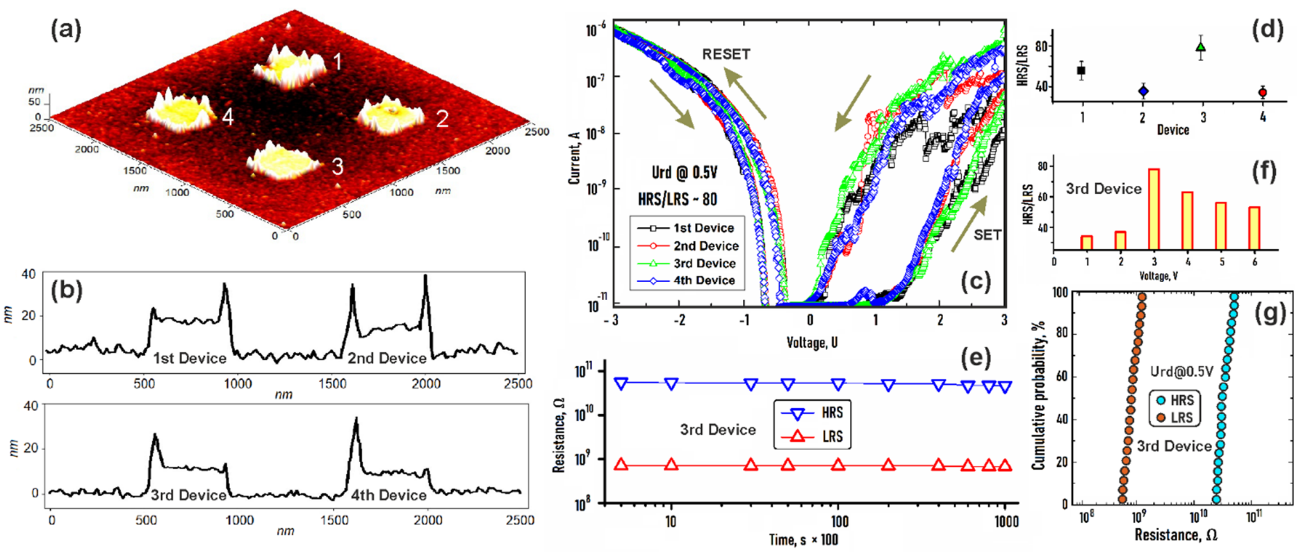

Figure 2. Resistive switching of the $TiN/ZnO/TiN/Al_2O_3$ structure (4 devices): (**a**)—3D AFM image of the ZnO film and TiN electrodes; (**b**)—AFM cross-section; (**c**)—current-voltage characteristics; (**d**)—HRS/LRS ratio; (**e**)—retention test; (**f**)—HRS/LRS ratio dependence on the amplitude of the CVC pulse (U_{rd} = 0.5 V); (**g**)—cumulative probability.

4. Conclusions

In summary, we investigated the scratching probe nanolithography modes, then fabricated and investigated $TiN/ZnO/TiN/Al_2O_3$ ReRAM structures. The devices were shown to exhibit a bipolar resistive switching effect with the HRS/LRS ratio up to 78.8 at reading voltage 0.5 V and maintaining a resistive state up to 10^5 s and more. The results can be useful for micro- and nanoelectronics elements manufacturing, as well as neuromorphic applications using probe nanotechnologies and nanocrystalline ZnO-based ReRAM elements prototyping.

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Conflicts of Interest: The authors declare no conflict of interest.

References

1. Jeong, D.S.; Hwang, C.S. Nonvolatile memory materials for neuromorphic intelligent machines. *Adv. Mater.* **2018**, *30*, 1704729.
2. Zhang, S.R.; Zhou, L.; Mao, J.Y.; Ren, Y.; Yang, J.Q.; Yang, G.H.; Zhou, Y. Artificial Synapse Emulated by Charge Trapping-Based Resistive Switching Device. *Adv. Mater. Technol.* **2019**, *4*, 1800342.
3. Brunner, D.; Soriano, M.C.; Van der Sande, G. Photonic reservoir computing. *Gruyter* **2019**, *8*, 19.
4. Leiserson, C.E.; Thompson, N.C.; Emer, J.S.; Kuszmaul, B.C.; Lampson, B.W.; Sanchez, D.; Schardl, T.B. There's plenty of room at the Top: What will drive computer performance after Moore's law? *Science* **2020**, *368*, 6495, eaam9744.
5. Tominov, R.V.; Vakulov, Z.E.; Avilov, V.I.; Khakhulin, D.A.; Fedotov, A.A.; Zamburg, E.G.; Ageev, O.A. Synthesis and Memristor Effect of a Forming-Free ZnO Nanocrystalline Films. *Nanomaterials* **2020**, *10*, 1007.
6. Kimura, M.; Sumida, R.; Kurasaki, A.; Imai, T.; Takishita, Y.; Nakashima, Y. Amorphous metal oxide semiconductor thin film, analog memristor, and autonomous local learning for neuromorphic systems. *Sci. Rep.* **2021**, *11*, 1–7.
7. Avilov, V.; Polupanov, N.; Tominov, R.; Solodovnik, M.; Konoplev, B.; Smirnov, V.; Ageev, O. Resistive Switching of GaAs Oxide Nanostructures. *Materials* **2020**, *13*, 3451.
8. von Witzleben, M.; Walfort, S.; Waser, R.; Menzel, S.; Böttger, U. Determining the electrical charging speed limit of ReRAM devices. *IEEE J. Electron Devices Soc.* **2021**, *9*, 667–678.
9. Smirnov, V.A.; Tominov, R.V.; Avilov, V.I.; Alyabieva, N.I.; Vakulov, Z.E.; Zamburg, E.G.; Ageev, O.A. Investigation into the Memristor Effect in Nanocrystalline ZnO Films. *Semiconductors* **2019**, *53*, 72–77.
10. Chang, S.; Yan, Y.; Li, B.; Geng, Y. Nanoscale manipulation of materials patterning through thermomechanical nanolithography using atomic force microscopy. *Mater. Des.* **2021**, *202*, 109547.
11. Miyashita, K.; Nishimura, S.; Toyofuku, T.; Shirakashi, J.I. Nanoscale patterning of NiFe surface by scanning probe microscopy scratch nanolithography. *J. Vac. Sci. Technol. B Microelectron. Nanometer Struct. Processing Meas. Phenom.* **2009**, *27*, 953–957.
12. Tominov, R.V.; Smirnov, V.A.; Chernenko, N.E.; Ageev, O.A. Study of the regimes of scratching probe nanolithography. *Nanotechnol. Russ.* **2017**, *12*, 650–657.