Formation of ZnO memristor structures by scratching probe nanolithography

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Abstract. This work presents the results of the formation and investigation of Al₂O₃/ZnO:In/ZnO/Ti memristor structures. It is shown that using Ti layer can improve memristive effect. Resistive switching from high resistance state (HRS) to low resistance state (LRS) occurred at 2.1±0.3 V, and from LRS to HRS at -1.5±0.3 V. Endurance test showed that HRS was 5.51±0.13 GΩ and LRS was 0.25±0.05 GΩ. HRS/LRS coefficient equalled to 22. The results can be useful for micro- and nanoelectronics elements manufacturing, as well as micro- and nanosystem engineering using probe nanotechnologies and for ZnO-based RRAM fabrication.

1. Introduction
Development of the next generation computer memory is the promising direction of electronics. One of the promising types of memory is non-volatile resistive random access memory (RRAM) based on metal oxide memristor structures; it has high-density integration, low-power consumption, and fast write/read operations. Zinc oxide (ZnO) is the promising material, which is widely used in electronic element developments, sensors, and microsystem technology. ZnO demonstrates memristor effect and is compatible with semiconductor technology [1-6]. To fabricate ZnO-based RRAM, it is necessary to carry out prototyping and investigations of ZnO memristor structures. Thus, it is necessary to develop new nanolithography techniques, which allow fabricating the structure of RRAM elements at lower expenses and within shorter periods than conventional methods of photo- and electron-beam lithography [7,8]. One of the promising methods for the formation of nanoscale structures is scratching probe nanolithography (SPN) of atomic force microscope (AFM) [9-11]. The SPN method involves the modification of thin polymer films by the formation of profiled nanosized structures using the tip of the AFM probe. Through the profiled nanosized structures, various technological operations (deposition and etching) could be performed. The advantages of SPN include high resolution and the absence of physical templates. Various structures of the elements of nanoelectronics and microsystem engineering were formed using SPM [12-15].

The aim of this work is fabrication of ZnO thin film-based memristor structures using scratching probe nanolithography, and investigation of memristor effect on them.

2. Experiment details
ZnO thin film was grown using pulsed laser deposition technique (Fig. 1a). Al₂O₃/ZnO:In was used as a wafer. Deposition was performed under the following conditions: wafer temperature 400°C, target-
wafer distance 50 mm, \(O_2\) pressure 1 mTorr, and pulse energy 300 mJ. The solution of photoresist/thinner (FP-383/RPF383F) at volume ratios of 1:10 was transferred onto ZnO using the centrifugal method at the rotation speed of a Laurell WS-400B-6NPP centrifuge 5000 rpm (Fig. 1b). After the deposition of the film, the photoresist/thinner film was dried at a temperature of 90°C for 25 min. Thickness of the photoresist/thinner film was equal to 75.1±3.3 nm.

Scratching probe nanolithography (SPN) on the photoresist/thinner film was performed using a Solver P47 Pro scanning probe microscope (NT-MDT, Russia) (Fig. 1c). Thus, array of the 9 squared nanostructure-grooves was formed (Fig. 1d). Then thin Ti film was deposited using BOC Edwards Auto 500 system (Fig. 1d). After that lift-off process was applied using dimethylformamide (Fig. 1e).

Electric measurements of the \(Al_2O_3/ZnO:In/ZnO/Ti\) structure was carried out using Probe Nanolaboratory Ntegra (NT-MDT, Russia). ZnO:In film was grounded during measurements. W\(_2\)C AFM probe was used as a top electrode (Fig. 1f). AFM images were obtained in semicontact mode.

3. Results and discussion

Figure 2 shows experimental investigation of ZnO films morphology. It is shown that ZnO film surface has a granular structure with 0.35±0.26 nm roughness (Fig. 1b). The ZnO film thickness was investigated using AFM by scanning bottom electrode/ZnO film boundary and was equal to 10.2±3.4 nm.

Figure 3 shows experimental investigation of Ti structures morphology. AFM profiles of all 9 Ti structures were obtained (Fig. 3b) and it was shown that thickness of Ti structures was 2.5±0.4 nm. Ripped edges of Ti structures are the result of lift-off process.

Figure 4 shows current-voltage characteristic (CVC) of \(Al_2O_3/ZnO:In/ZnO/Ti/W_2C\) structure. at -3 to +3 voltage sweep. It was shown, that \(Al_2O_3/ZnO:In/ZnO/Ti/W_2C\) structure had nonlinear bipolar behaviour when the electric potential gradient was the dominant parameter of memristive effect [16]. Resistive switching from high resistance state (HRS) to low resistance state (LRS) occurred at -3.0 V (SET), and from LRS to HRS – at 2.1 V (RESET) (Fig. 4a).

Investigation of memristive effect uniformity of \(Al_2O_3/ZnO:In/ZnO/Ti/W_2C\) structure in a single point (endurance test) showed that HRS was 5.51±0.13 GΩ and LRS was 0.25±0.05 GΩ (Fig. 4b). It was shown that HRS/LRS coefficient was equal to 22 at -3 to +3V voltage sweep. Read voltage was -2V. HRS/LRS = 22 is sufficient for RRAM fabrication [17].

Figure 1. Process diagram of formation and investigations of \(Al_2O_3/ZnO:In/ZnO/Ti\) memristor structures: (a) ZnO film growth; (b) deposition of photoresist to the ZnO film surface; (c) nanostructures formation on the photoresist surface using scratching probe nanolithography; (d) Ti film deposition; (e) lift-off process; (f) electric measurements.
To evaluate Ti film impact to memristor effect in Al₂O₃/ZnO:In/ZnO/Ti/W₂C structure, electric measurements in Al₂O₃/ZnO:In/ZnO/W₂C structure were carried out. Endurance test of Al₂O₃/ZnO:In/ZnO/W₂C structure showed that HRS was 2.16±0.17 GΩ and LRS was 0.31±0.06 GΩ. Resistive switching from HRS to LRS occurred at -3.0 V, and from LRS to HRS – at 2.5 V. HRS/LRS coefficient was equal to 7 at -3 to +3V voltage sweep. Read voltage was also -2 V. HRS/LRS = 7 is insufficient for RRAM fabrication [17].

Figure 2. Photoresist surface morphology: (a) AFM-image; (b) AFM profile along line on (a).

Figure 3. 3×3 array of Ti structures: (a) AFM-image; (b) AFM profile along line on (a).

Figure 4. Electric measurements of Al₂O₃/ZnO:In/ZnO/Ti/W₂C structure: (a) current-voltage characteristic at -3 to +3V voltage sweep; (b) endurance test.
Analysis of the results shows that the addition of Ti layer in the Al₂O₃/ZnO:In/ZnO/Ti/W₃C structure leads to the increase in the HRS/LRS coefficient and to the decrease in RESET voltage.

The increase in the HRS/LRS coefficient may be due to the increase in the additional concentration of oxygen ions at the Ti/ZnO interface, which leads to an increase in the quantity of recombining pairs "oxygen vacancy-oxygen ion" during the transition of the film from LRS to HRS, which in turn leads to an increase in the length of the destroyed section of the nanosized conduction channel.

4. Conclusion
In summary, we fabricated and investigated Al₂O₃/ZnO:In/ZnO/Ti memristor structures. It was shown that using the Ti layer could improve memristive effect. Resistive switching from high resistance state (HRS) to low resistance state (LRS) occurred at -3.0 V, and from LRS to HRS – at 2.1 V. Endurance test showed that HRS was 5.51±0.13 GΩ and LRS was 0.25±0.05 GΩ. HRS/LRS coefficient was equal to 22. The results can be useful for micro- and nanoelectronics elements manufacturing, as well as micro- and nano-system engineering using probe nanotechnologies, and for ZnO-based RRAM fabrication.

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