Resistive switching in ZnO/ZnO:In nanocomposite

D A Khakhulin¹, Z E Vakulov¹, V A Smirnov¹, R V Tominov¹, Jong-Gul Yoon² and O A Ageev¹

¹ Research and Education and Centre "Nanotechnology", Southern Federal University, Taganrog, 347922, Russian Federation
²Department of Physics, Natural Sciences College, University of Suwon, Wau-ri, 445-743, Republic of Korea

Abstract: A lot of effort nowadays is put into development of new approaches to processing and storage of information in integrated circuits due to limitations in miniaturisation. Our research is dedicated to one of actively developed concepts – oxide based resistive memory devices. A material that draws interest due to its promising technological properties is ZnO but pure ZnO lacks in performance in comparison with some other transition metal oxides. Thus our work is focused on improvement of resistive switching parameters in ZnO films by creation of complex nanocomposites. In this work we report characterisation of a nanocomposite based on PLD grown ZnO films with inclusions of In. Such solution allows us to achieve improvements of main parameters that are critical for ReRAM device: \( R_{HRS}/R_{LRS} \) ratio, endurance and retention.

1. Introduction
Current crisis in microelectronics, caused by fundamental limitations that occur during further miniaturisation could be solved in a number of different ways [1], including implementation of \( A^{III}B^{VI} \) materials [2], carbon nanotubes [3], local oxidation technology [4] and some other concepts [5]. In that regard, one of the most widely discussed topics is non-volatile memory devices based on materials with resistive switching behaviour. Among a vast range of such substances certain attention is drawn by transition metal oxides [6], and a material of particular interest is ZnO, due its technological accessibility [7]. However, resistive memory devices (ReRAM), that implement pure ZnO, considered to be less effective, in comparison with devices implementing \( HfO_2 \), \( SiO_2 \) and \( TiO_2 \) [8]. Thus we experiment with ZnO/ZnO:In nanocomposite to improve both \( R_{HRS}/R_{LRS} \) and endurance, as well as retention characteristics for an implementation in a memory device.

2. Experiment
To obtain ZnO/ZnO:In nanocomposite we used pulsed laser deposition (PLD) equipment Pioneer 180 (Neocera, USA). ZnO and ZnO:In targets were consequently ablated by excimer KrF laser (\( \lambda=248\text{nm} \)). Energy density on target surface was maintained at \( 2\text{J/cm}^2 \). The quantity and frequency of laser pulses were 50,000 and 10Hz respectively. Target-substrate distance was 80mm. Nanocomposite films were deposited on silicon substrates. To characterise structural and electrical properties of these films we used following equipment. Structural studies were conducted using atomic-force microscopy (AFM) system Solver P47-Pro (NT-MDT, Russia), dual-beam scanning electron microscopy (SEM) system with focused ion beam module Nova Nanolab 600 (FEI, Netherlands) and Rigaku Miniflex 600 (Rigaku, Japan). For electrical studies electrometer Keithley 617 and semiconductor characterisation system Keithley 4200-SCS (Keithley Instruments, USA) were used. We implemented top-bottom
measurements layout: one of the electrodes was placed on an electrical contact to the bottom of the film and the second one to the film itself.

3. Results

3.1. Structural properties of ZnO/ZnO:In nanocomposite
To characterise morphology and thickness of the ZnO/ZnO:In films we conducted SEM and AFM studies. They showed, that we obtained nanocrystalline film with thickness around 80 nm and uniform roughness with average meaning of about 19 nm. Both SEM and AFM images of the film are given in figure 1 in part (a) and (b), respectively. Optimal thickness and roughness that allow to achieve optimal film properties for implementation as a ReRAM structure were determined during our previous research, which was dedicated to the influence of PLD process parameters on resistive switching in ZnO films.

![Figure 1(a,b,c).](image)

(a) SEM image of the films with a cross-section cut, demonstrating thickness and nanocrystalline structure of the film, and (b) AFM scan, showing surface morphology. (c) XRD pattern of ZnO/ZnO:In film on silicon substrate
We analysed composition of the film by XRD to exclude possibility of major influence of indium based compounds on resistive switching properties of ZnO/ZnO:In films. Structure-wise, films of ZnO/ZnO:In nanocomposite that were grown at target-substrate of 80mm show minor inclusions of Zn\textsubscript{1}In\textsubscript{2}O\textsubscript{6}, lack of In\textsubscript{2}O\textsubscript{3} and Zn\textsubscript{3}In\textsubscript{2}O\textsubscript{6}, unlike samples, that were grown with another target-substrate distances. Main peaks on XRD patterns correspond to ZnO, In and substrate. XRD pattern of ZnO/ZnO:In film on silicon substrate is shown in figure 1(c).

3.2. Electrical properties of ZnO/ZnO:In nanocomposite

ZnO/ZnO:In nanocomposite shows high resistance state to low resistance state switch ratio (R\textsubscript{HRS}/R\textsubscript{LRS}) of about 2 at U\textsubscript{read}=0.25V and up to about 500 at U\textsubscript{read}=2.25V. Resistive switching occurs at U\textsubscript{write}=2.5V and rewrite process at U\textsubscript{rewrite}=-3.5V. Current-voltage characteristics (CVC) of the film, that allow to estimate U\textsubscript{write} and U\textsubscript{rewrite} and R\textsubscript{HRS}/R\textsubscript{LRS} at different voltages is provided in figure 2(a). In terms of endurance characteristics film keeps switching stably from LRS to HRS for 25 cycles at U\textsubscript{read}=0.25V then switching properties degrade: R\textsubscript{HRS}/R\textsubscript{LRS} falls down due to decrease of R\textsubscript{HRS}, yet, resisting switching continues to occur for up to 100 cycles even with a lower resistances ratio. Endurance characteristic of the ZnO/ZnO:In nanocomposite is depicted in figure 2(b). Despite better R\textsubscript{HRS}/R\textsubscript{LRS} higher U\textsubscript{read} is not applied, since it leads to a faster degradation of endurance characteristics. Retention tests showed, that film could remain in LRS for about 10\textsuperscript{3}sec.

Figure 2(a,b). (a) CVC characteristics of the ZnO/ZnO:In, and (b) endurance test, obtained at U\textsubscript{read}=0.1V.

4. Conclusion

We studied resistive switching in PLD grown films of ZnO/ZnO:In nanocomposite. Our structural studies showed that switching properties that were obtained are linked to the processes in ZnO and ZnO:In rather than other compounds, that are inevitably formed in presence of oxygen. Electrical properties measurements showed that nanocomposite films show both good R\textsubscript{HRS}/R\textsubscript{LRS} and retention characteristics, while endurance characteristics are a matter of further improvement.

Thus, there are two main conclusions to be made. First of all, PLD allows us to form films of nanocomposites with controlled structural and electrical properties to be used as a part of a ReRAM device. Secondly, we may conclude, that inclusion of additional components to the film has a positive impact on its resistive switching properties. Further experiments with a ZnO:In as a nanocomposite component and introduction of other materials into ZnO could possibly lead to a major improvement of endurance characteristics, as well as R\textsubscript{HRS}/R\textsubscript{LRS}.  

3
Acknowledgements
This work was financially supported by Southern Federal University by grant VnGr-07/2017-02 and within the program of stimulation of international mobility. The work was executed on the equipment of Research and Education Centre "Nanotechnology" and Collective Use Centre "Nanotechnology", Southern Federal University and Laboratory of Physics of Natural Sciences College, University of Suwon.

References
[1] Carballo J A, Chan W T J, Gargini P A, Kahng A B and Nath S 2014 ITRS 2.0: Toward a re-framing of the Semiconductor Technology Roadmap 32nd IEEE Int. Conf. Comput. Des. ICCD 2014 139–46
[2] Ageev O A, Solodovnik M S, Balakirev S V and Eremenko M M 2016 Effect of GaAs native oxide on the Ga droplets formation during GaAs MBE growth J. Phys. Conf. Ser. 741 1–2
[3] Ageev O A, Blinov Y F, Il’in O I, Kolomiitsev A S, Konoplev B G, Rubashkina M V., Smirnov V A and Fedotov A A 2013 Memristor effect on bundles of vertically aligned carbon nanotubes tested by scanning tunnel microscopy Tech. Phys. 58 1831–6
[4] Avilov V I, Ageev O A, Kolomiitsev A S, Konoplev B G, Smirnov V A and Tsukanova O G 2014 Formation of a memristor matrix based on titanium oxide and investigation by probe-nanotechnology methods Semiconductors 48 1757–62
[5] Cavin R K, Lugli P and Zhirnov V V. 2012 Science and Engineering Beyond Moore’s Law Proc. IEEE 100 1720–49
[6] Pan F, Gao S, Chen C, Song C and Zeng F 2014 Recent progress in resistive random access memories: Materials, switching mechanisms, and performance Mater. Sci. Eng. R Reports 83 1–59
[7] Ageev O A, Dostanko A P, Zamburg E G, Konoplev B G, Polyakov V V. and Cherednichenko D I 2015 Effect of the processes in the laser ablation plume on the resistivity and morphology of nanocrystalline ZnO films Phys. Solid State 57 2093–8
[8] Ha S D and Ramanathan S 2011 Adaptive oxide electronics: A review J. Appl. Phys. 110