Investigation of resistive switching of Zn$_x$Ti$_y$Hf$_z$O$_i$ nanocomposite for RRAM elements manufacturing

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Abstract. The resistive switching effect in Zn$_x$Ti$_y$Hf$_z$O$_i$ nanocomposite film, grown by pulsed laser deposition technique, was investigated. It was shown that Zn$_x$Ti$_y$Hf$_z$O$_i$ film surface had a granular structure with $0.8\pm0.4$ μm$^2$ grain size and $7.3\pm5.1$ nm grain height. Resistive switching from high resistance state (HRS) to low resistance state (LRS) was occurred at $0.9\pm0.4$ V, and from LRS to HRS at $1.5\pm0.2$ V. HRS/LRS ratio was 2.6. The results can be used for nanocomposite-metal-oxide-film RRAM fabrication.

1. Introduction

Development of the electronic devices technology in respect to a size reduction of integrated circuit elements and chip density is increasing using nanotechnology that allows fabrication of nanoscale structures with dimensions less than 50 nm. There are many types of electronic devices, including, in particular, high-speed memory devices with high-density integration and low power consumption [1, 2].

Pulsed laser deposition (PLD) is a promising technique as it allows growing films with control of crystalline quality and surface adhesion to obtain materials with complex stoichiometry [3-5]. There are a lot of structures that can be obtained in wide range of controlled properties by PLD: nanostructured films, single crystalline films, nanowhiskers, nanotetrapods, etc.

Resistive switching effect in oxide films is attractive for resistive random access memory (RRAM) development [6-10]. The main advantages of RRAM are non-volatility, high performance, small cell size, and low power consumption [6-10]. Resistive switching effect was observed in many oxide film (ZnO, TiO$_2$, HfO$_2$, NiO, Al$_2$O$_3$, SnO$_2$, WO$_3$, SiO$_2$, etc.) and it is expressed in the switching of resistance of oxide film between high and low resistance states after threshold electric field applying [6-10].
One of the main problems of RRAM is a large variation of switching parameters, both in write/reset of the same cell and in write/reset of the different cells. Using of nanocomposite metal oxides allows to solve this problem [11-14].

The aim of this work is the investigation of resistive switching effect in \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) nanocomposite film, grown by pulsed laser deposition.

2. Experiment details

Nanocomposite \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) thin film was grown by pulsed laser deposition. \( \text{Al}_2\text{O}_3 \) was used as a substrate. To deposite TiN bottom electrode the following conditions were used: substrate temperature 600°C, target–substrate distance 50 mm, laser pulse energy 300 mJ, number of pulses 7,500. After deposition, sample was taken out from a chamber in order to put a mask for forming clear boundary for measurements of nanocomposite film thickness. To form nanocomposite film, \( \text{ZnO, HfO}_2, \text{TiO}_2 \) targets were used for 51 cycles (2/3 of layers = 17 pulses (2 Hz), 1/6 of layers = 10 pulses (2 Hz), 1/6 of layers = 4 pulses (2 Hz), respectively). The deposition was performed under the following conditions: substrate temperature 400°C, target–substrate distance 50 mm, \( \text{O}_2 \) pressure 1 mTorr, laser pulse energy 300 mJ.

An AFM-image of the \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) film surface was obtained using atomic-force microscope Solver P47 Pro (NT-MDT, Russia) in semi-contact mode. The AFM-image processing was performed using Image Analysis software. The \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) film thickness was also measured using Solver P47 Pro by TiN/\( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) boundary scanning, and was equaled 12.3±0.7 nm. Investigation of structural parameters of the nanocomposite film was carried out using X-ray Powder Diffraction (XRD) and Energy-dispersive X-ray spectroscopy (EDX). Electrical measurements were carried out using semiconductor characterization system Keithley 4200-SCS (Keithley, USA) with W probes. During experiment TiN layer was grounded. Current-voltage curves were obtained from \(-2\) to \(+2\) V sweep for 50 cycles at the same point. To prevent thermal breakdown of the nanocomposite film, 1 mA compliance current was set during electric measurements. Read voltage was at 0.4 V.

3. Results and discussion

Figure 1 shows experimental investigation of \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) film morphology. It is shown that \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) film surface has a granular structure (figure 1 a) with 0.8±0.4 \( \mu \text{m}^2 \) grain size (figure 1 c) and 7.3±5.1 nm grain height (figure 1 b). The nanocomposite film thickness was investigated using AFM by scanning bottom electrode/nanocomposite film boundary and was equaled 12.3±3.7 nm.

Figure 1. \( \text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i \) film surface: a) – AFM-image; b) – profilogram along white line (a); c) – phase contrast.
Figure 2 shows investigation of structural parameters of $\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$ film. It follows from diffractogram (figure 2 a), (100) and (111) crystallites prevails for ZnO and HfO$_2$ phases, respectively. Figure 2 b and table 1 show results of energy-dispersive X-ray spectroscopy. It’s shown that there is 7.93% of Ti in the nanocomposite film, 3.93% of Zn, 4.42% of Hf.

![Figure 2](image1)

**Figure 2.** Investigation of structural parameters of the $\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$ film: a) – X-ray Powder Diffraction (XRD); b) – Energy-dispersive X-ray spectroscopy (EDX).

**Table 1.** Energy-dispersive X-ray spectroscopy of the $\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$ nanocomposite film.

| Element | C    | O    | Al   | Ti   | Zn   | Hf   | Totals |
|---------|------|------|------|------|------|------|--------|
| Weight(%) | 2.46 | 31.68| 49.58| 7.93 | 3.93 | 4.42 | 100.00 |
| Atomic(%) | 4.79 | 46.34| 43.01| 3.88 | 1.41 | 0.58 |        |

Average current-voltage curve of structure TiN/$\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$/W was performed from 50 current-voltage curves (figure 3 a) measured at the same point on the nanocomposite surface. It was shown, resistive switching from high resistance state (HRS) to low resistance state (LRS) was occurred at 0.9±0.4 V, and from LRS to HRS at -1.5±0.2 V. Resistance-cycle dependence was built based on obtained curves. It was shown that HRS was 6.5±1.8 kOhm, LRS was 2.5±1.1 kOhm. HRS/LRS ratio was 2.6 (figure 3 c).

![Figure 3](image2)

**Figure 3.** Experimental studies of resistive switching effect in $\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$ film: a) – averaged current-voltage characteristic of 50 sweep cycles at the same point on in $\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$ film surface; b) – endurance test of $\text{Zn}_x\text{Ti}_y\text{Hf}_z\text{O}_i$ film for 50 sweep cycles.
4. Conclusion
In summary, we have investigated resistive switching effect in nanocomposite Zn$_x$Ti$_y$Hf$_z$O$_i$ thin film, grown by pulsed laser deposition. We have shown that HRS was 6.5±1.8 kOhm, LRS was 2.5±1.1 kOhm. HRS/LRS ratio was 2.6. The results can be used for nanocomposite-metal-oxide-film RRAM fabrication.

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