Fabrication of printed memory device having zinc-oxide active nano-layer and investigation of resistive switching

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\textbf{A R T I C L E  I N F O}

Article history:
Received 5 December 2011
Received in revised form 7 June 2012
Accepted 20 June 2012
Available online 28 June 2012

Keywords:
Resistive switching
Bistable device
Inkjet printing
Electrohydrodynamics
Zinc oxide

\textbf{A B S T R A C T}

An all printed resistive memory device, a 9-bit memristor, has been presented in this study consisting of $3 \times 3$ memristor crossbars deposited via electrohydrodynamic inkjet printing process at room conditions. Transparent zinc oxide active nano-layers, directly deposited by electrospay process, are sandwiched between the crossbars to complete the metal–insulator metal structure consisting of copper–zinc oxide–silver, where Cu and Ag are used as bottom and top electrodes respectively. The 9-bit memristor device has been characterized using current–voltage measurements to investigate the resistive switching phenomenon thereby confirming the memristive pinched hysteresis behavior signifying the read–write and memory characteristics. The memristor device showed a current bistability due to the existence of metal–oxide layer which gives rise to oxygen vacancies upon receiving the positive voltage hence breaking down into doped and undoped regions and a charge transfer takes place. The maximum ON/OFF ratio of the current bi-stability for the fabricated memristor was as large as $3 \times 10^3$, and the endurance of ON/OFF switchings was verified for 500 read–write cycles. The metal–insulator–metal structure has been characterized using X-ray diffraction, X-ray photoelectron spectroscopy and scanning electron microscope techniques.

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1. Introduction

Since Leon Chua’s revolutionary work proposing a memory-resistor or “memristor” as the fourth basic circuit element, lots of research has been dedicated to the topic and many researchers have come up with many interesting memristor devices [1,2]. The important characteristic of a memristor is that it shows a resistance that depends on the history of the current passing through it [3]. This property is very much useful from the view point of memory related devices and makes memristor a candidate to be used, for example, in learning networks [4].

After the successful demonstration of a working memristor by Strukov et al., the memristor and the phenomenon of resistive switching in metal–insulator–metal (MIM) structures has found a new life [5,6]. Strukov et al. basically demonstrated the coupling of electronic and atomic transport under the influence of external voltage which resulted in the existence of memristance in the proposed nano-scale system. The primary characteristic of the memristor device is its “pinched hysteresis loop”, that is, when energized by a biasing voltage, the resulting current–voltage ($I–V$) characteristic present a Lissajous curve that cannot be reproduced with any network of the other fundamental passive devices [6].

The origin of resistive switching in memristors is still unclear. However a general understanding is that resistive switching is initiated by the partial dielectric breakdown on the application of some voltage (set phase) and Joule heating altering the material along a discharge path which is provided by the metal electrode adjacent to the insulator or because of the presence of newly formed sub-oxides. During the reset phase, the conductive path provided by the metal electrode gets thermally damaged by the high power density [7]. A detailed description on the resistive switching phenomenon has been given by Waser and Aono [8].

Different semiconducting materials have been found to demonstrate resistive switching that includes solid-state amorphous Si, chalcogenides, organic materials, carbon nanotubes, perovskite oxides and binary transition metal oxides [9–20]. Jeong et al. [21] and Son et al. [22] demonstrated resistive switching phenomenon in the graphene based flexible organic bistable
devices where graphene sandwiched between the aluminum electrodes was used as the MIM structure.

Among the metal oxides, zinc oxide is becoming a popular material for memristive devices apart from TiO2 and ZrO2. Bistable switching properties of ZnO films have also been observed and studies on ZnO being used as active layer with different MIM combinations have been presented with different fabrication processes [23–28]. Zinc oxide (ZnO) has received tremendous attention for its use in many other exciting applications as well such as thin film transistors and solar cells [29,30]. ZnO is a wide band gap material and because of its appealing properties like excellent transparency, low-cost, non-toxicity, easy availability and high inertness in reduction environments, it offers many advantages over other semi-conducting metal oxides.

In this paper, an innovative all-printed memristive device consisting of transparent ZnO nano-particle film as active layer is introduced which is sandwiched between memristor crossbar structure consisting of Cu as bottom and silver as top electrode on Si substrates. The metal electrodes and ZnO film have been prepared using a very simple and low cost process known as electrohydrodynamic inkjet method, which is usually known as electrospraying when used for film formation and electrophoresis printing when used for making metallic patterns [31–35]. One of the main advantages of the aforementioned process is that it takes place at room temperature and hence precludes the use of expensive equipment. Cu has been chosen as the bottom electrode material because of its high affinity toward oxygen to get oxidized therefore an oxygen deficient region is naturally formed between the Cu electrode and the ZnO film. A complete electrical characterization with the emphasis on resistive switching behavior in the printed Cu–ZnO–Ag memristor structure has been presented in the paper to confirm the memristor performance. The device exhibited strong electrical hysteresis and history-dependent conductance on the I–V curves. Furthermore the X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS) and scanning electron microscope (SEM) characterizations are given in the paper to validate the compositional integrity of the printed memristor.

2. Experimental details – device fabrication

2.1. Electrohydrodynamic printing and spraying system

The system used for the memristor crossbar and active layer fabrication, consisted of following components with their description:

Metallic Capillary (Harvard Apparatus): Different metallic nozzles were used for electrospray of ZnO layer and electrodes’ fabrication. For electrospraying of active layer a metallic nozzle, made of high-quality stainless-steel with inner diameter of 410 μm inner and 720 μm outer diameter was used (Harvard Apparatus 72-5435). For the electrodes’ fabrication the capillary with 100 μm inner and 210 μm outer diameter was used (Harvard Apparatus 72-5506).

Capillary holder (NanoNC): A stainless steel universal capillary holder was used to hold the metal capillary and to get it mounted on the y–z stage movement.

Syringe Pump (Harvard Apparatus, PHD 2000 Infusion): Connected to the capillary, the syringe pump maintained the minimum required flow rate of the ZnO ink solution for the electrospray purposes.

Pressure Controller System: For the fabrication of top and bottom electrode, a pressure controller system had been used. A lab made system consisting of pressure regulators (SMC VBNQA-02 GN and SMC IR1000-01 BG) was used.

2.2. Fabrication of bottom electrode

Highly doped Si wafer substrates, with an area of 4 cm², coated with a 300 nm layer of SiO2 were provided by Korea Research Institute for Chemical Technology (KRICT). Cu ink containing pure Cu nano-particles was bought from Hanwha Chemicals, Korea. The physical properties of the ink are listed in Table 1 and the operating parameters for the printing of electrodes are given in Table 2. The conductivity and surface tension of the ink were measured by conductivity meter (EUTECH Instruments – ECOSCAN CON 6) and surface tension meter (SEO-Phoenix). The measurement of viscosity was carried out with a stress-controlled viscometer (Sekonic Viscomate VM-10A). The dielectric constant of the ink was measured using a dielectric constant meter (BROOKHAVEN

Fig. 1. Schematic diagram of the electrophoresis printing system used for the fabrication of the memristor device.
Cone-jet mode of electrohydrodynamic printing was used during the printing process. A detailed description of the deposition of metallic patterns via electrohydrodynamic printing using cone-jet mode can be found elsewhere [37]. Fine Cu electrodes of approximately 100 μm width and 120 nm thick were fabricated successfully. Three electrodes, 1 mm apart, were fabricated to make a 3 × 3 memristor cross-bar having 9-bit memory device at the center of the substrate. The advantage of using highly-doped Si substrate is that it gives a conducting medium between the metal capillary and the ground plate thereby reducing the substrate effects on the generated electric field [38]. Therefore the required voltage for the cone-jet ejection during patterning over the substrates was the same as that without the substrate. The 300 nm SiO₂ layer provides the required insulation medium between the adjacent electrodes. Printed electrodes were sintered at 350 °C for 2 h in nitrogen environment to prevent them from oxidation.

2.3. Fabrication of ZnO layer

2.3.1. ZnO solution preparation

ZnO nano-particles were obtained from Sigma–Aldrich and were used as received. Non-ionic surfactant, Triton X-100 (Sigma–Aldrich) was used as a wetting agent for better dispersion of ZnO particles. The solid content was kept at 10 wt.%. ZnO nanoparticles dispersed in ethanol (99.9%, OCI Company Ltd.) were sonicated for 8 min with pulsed signals at a frequency of 0.6 kHz before mixing with Triton (0.015%). The solution was then stirred for 5 h at 70 °C using a magnetic stirrer. The physical properties of the prepared ink are listed in Table 1.

2.3.2. Active layer fabrication

The fabrication of active layer on the already deposited bottom electrode was carried out at room conditions using the equipments listed previously according to the same process as has been discussed in our previous research [39]. The operating process parameters for the layer fabrication are summarized in Table 2. A thin consistent layer of ZnO nano-particles have been achieved via the direct deposition electrospray process as discussed in the previous sections. The deposited layers were sintered at 500 °C for 5 h before the deposition of top electrode over them. It must be noted here that a mask with the dimensions 1 × 1 cm was used to cover 1 cm² of the substrate where the bottom electrodes were in the center of this area, see Fig. 2.

2.4. Fabrication of top electrode

Top electrodes were deposited using oil-based silver nanoparticle colloidal ink, NPK-040, obtained from NPK, Korea. The properties of the said ink are mentioned in Table 1. A detailed note on the fabrication of silver electrodes using this system has been given in our previous research [32]. The top electrodes were printed on the already fabricated bottom electrode and active layer in a fashion similar to a ladder structure giving the memristor device a crossbar shape sandwiching the active layer between the top and bottom electrodes thereby creating a memory bit at the junction of electrodes, as shown in Fig. 2. The operating parameters for the printing of electrodes are given in Table 2. The completed memristor device was sintered at 150 °C for 1 h for top electrode sintering as a final step in the printed memristor fabrication process.

3. Results and discussions

3.1. Memristor crossbar and active layer

Memristor bottom and top electrodes were produced from Cu and silver nano-particle colloidal inks respectively, via electrohydrodynamic inkjet printing process while the transparent active layer was fabricated via electrospray process as discussed in the previous section. All the layers were produced in a reproducible manner. Fig. 3 represents a microscopic view of the fabricated memristor device. A largely smooth crossbar is visible showing the
bottom and top electrodes. ZnO active layer is not visible because of its transparent nature. The width of the bottom electrode is approximately 100 ± 10 μm while that of top electrode is 70 ± 10 μm. The top electrodes are 600 ± 50 μm apart while the distance between consecutive bottom electrodes is 1 ± 0.1 mm. The SEM image of the deposited active layer, after sintering for 500 °C for 5 h has been presented in Fig. 4. As can be seen the layer was granular because of the presence of nano-particles, and the morphology was a little rough. However this roughness can be advantageous from the point of view that in this way the attach-ability of the top electrode would be better as compared to a very smooth surface. The deposited layer contained negligible pores and was nearly uniformly distributed. Some big agglomerates were present which can be attributed to the preferential landing phenomenon of the electrospray process [40–42]. Fig. 5 presents the highly magnified cross-sectional SEM micrograph of the Cu–ZnO–Ag junction. The average thickness of the top and bottom electrode was approximately 120 nm and 180 nm respectively, while that of active layer was approximately 140 nm. A distinct boundary was visible at the interface of the three layers and some cracking was visible at the interface of ZnO film and Ag electrode. The surface of the Ag electrode presented the hillock-effect which is characteristic of printed metal patterns and is discussed elsewhere [40]. Hillocks in the Cu electrode are not visible but we cannot rule out their presence as they might have been subdued by the ZnO layer over them and not visible in the figure. Overall, keeping in mind the process simplicity, the MIM morphology was very good and the printed memristor can be a fascinating alternative for memory fabrication. The crystal structure of the MIM structure was investigated by XRD analysis and the results are presented in Fig. 6. Si substrate’s peaks have been omitted for simplicity and Cu peaks were taken with Cu patterns deposited separately on glass. Since Cu has a very strong affinity toward getting oxidized, thereby reducing the conductivity of the patterns resulting in higher power losses in micro-electronic devices, therefore Cu patterns were sintered in a nitrogen environment at 350 °C after their printing process. Silver patterns were sintered at 150 °C for 1 h before the measurements. The XRD patterns of the individual layers conformed to JCPDS Card 4-783 for silver top electrode, JCPDS card 36-1451 for ZnO active layer and JCPDS Card 85-1326 for Cu bottom electrode. There is no indication of Cu being oxidized and hence remained in its purest state until subjected to the memristor application. ZnO films exhibited hexagonal wurtzite structure which confirmed the stability of the films in testing conditions and long constancy of the device i.e. higher number of read—write cycles. Since the Electrospray process occurs at room conditions, it is very important to monitor the purity of the deposited active layer, as any impurity will considerably reduce the performance of the final memristor device. Therefore to further confirm the purity of the ZnO active layer, the XPS spectrum of as deposited ZnO on glass, sintered at 500 °C for 5 h has been given in Fig. 7. All of the peaks on the curve are ascribed to Zn, O and C elements and no peaks of impurities were observed. The presence of C is attributed mainly to the residuals from the acetate solution [43]. Although C significantly affects the performance of ZnO, however, the trace amounts, as presented here, are not of much importance and can be neglected safely. The composition of the films as ascribed by XPS analysis was Zn:O:C = 28:64:8 approximately. Nevertheless, it remains a topic of research interest and future studies can be performed to achieve ultra pure ZnO films through electrospraying of nano-colloidal solutions having organic solvents.\[43\]
3.2. Investigation of resistive switching in the memristor device

The 9-bit memristor device, as schematized in Fig. 2, was characterized for resistive switching and other related phenomenon primarily using the Agilent B1500A Semiconductor Device Analyzer. Fig. 8 embodies the basic resistive switching curves of the first memristor bit for 1st, 100th and 500th I−V sweep; see Fig. 2 for bit markings. Before resistive switching operation, an appropriate positive or negative voltage is usually applied to establish the conducting paths in the MIM structure and to get a soft breakdown, known as the electroforming process which was done for all the bits before characterizing them for resistive switching phenomenon. The inset in Fig. 8 represents such a curve. Electroforming process was observed at approximately 2.5 V. This process transforms the stoichiometric ZnO layer into a non-stoichiometric layer by extracting the oxygen vacancies, therefore forming an Ohmic contact between the bottom electrode and doped region of the active layer while a Schottky contact develops between the top Ag electrode and un-doped region of the active layer. The conducting paths develop only at the area surrounding the sandwich structure and the remaining area remains passive. The noise in the curve is thought to be because of phonon structures occurring because of interband transitions in the active layer and is best explained by Pagina and Sotnik [44,45]. After the electroforming process, a regular I−V sweep in the sequence of 1.25 → 0 → −1.25 → 0 → 1.25 V was applied. The memristive double-loop I−V hysteresis was exhibited by the device and bistable resistance can be switched up to many read−write cycles. For the first sweep, with the increase in the positive biasing voltage, the resistive switching occurred at approximately 1.2 V depicting the resistive switching to a low resistance state (LRS) or write state. From 1.2 to 1.25 V, an un-defined fluctuation occurred. The LRS to high resistance state (HRS) occurred at approximately −1.25 V when the device was switched to off state or read state. Fig. 9 shows the semi-log plot of the I−V sweep for the first bit at 1st, 100th and 500th I−V sweep. Bipolar resistive switching is clearer here, i.e. when the positive biasing sweep has been applied to the device at HRS, the set process occurred and the bit was switched to LRS. An On/Off ratio of $1 \times 10^3$ has been achieved for the fabricated device. The sample remained in the LRS during the ensuing decreasing bias and the backward transition to the HRS occurred after the completion of 0 → −1.25 → 0 V cycle as signified by the anti-clock I−V hysteresis. Further sweeps in the same range (1.25−−1.25) yielded repeatable results, however the HRS to LRS switching occurred at a bit higher voltage (1.25 V) and LRS to HRS transition occurred at lower voltages (−1 V). It must be noted here that the observation of resistive switching until 500 sweeps is just for demonstration purpose that the suggested printing process can successfully be employed in the fabrication of memory devices with suggested MIM structure. However it does not relate to the reliability and endurance of the device which are quantified usually after more than $10^{10}$−$10^{12}$ sweeps which can only be expected upon the maturity of the printing process and used materials when extremely uniform layers and completely conformable layer interfaces can be achieved.

For further investigation of the resistive switching mechanism, the I−V curves have been re-drawn for the HRS and LRS states using log−log scales, as presented in Fig. 10. Two distinctive regions with different slopes in the HRS state were observed as shown by the dashed line and the thick black line. The slope of the dashed line,
fitting the currents at voltages between 0 and 1 is approximately 1, thereby satisfying the linear Ohmic current model, while that of thick black line, fitting the currents between voltages 1 and 1.25 is approximately 4.5. The number of carriers injected into the active layer was significantly higher in this voltage range, and the I–V data consequently followed a typical space charge limited current (SCLC) with a trap model, which is known as the trapped charge–limit current mechanism [22,44]. The large slope value of the fitting line indicates that the traps in the active layer were exponentially distributed over energy in the ZnO band gap. After the switching to the LRS, the I–V curve again can be fitted using the Ohmic current model. Fig. 11 produces the endurance test of the memristor device. Barring some magnitude fluctuations, steady resistive switching characteristics were observed over 500 read–write operations. The resistance values were calculated at 0.5 V for each read–write cycle. These results confirm the electrode and active layer compatibility in stable resistive switching for satisfactory number of read–write cycles for a non-volatile resistive-random access memory (R-RAM) application.

To complete the electrical characterization, the hysteresis curves of 5th (middle) and 9th (last) bit are given in Fig. 12. The consistency in the device performance is visible as the transition from the HRS to the LRS occurred at almost the same voltages (∼1.3 V) as occurred in the first bit. Similarly the reverse transition, from LRS to HRS, also occurred at comparative voltages (∼1.3 V) as compared to that for the first bit. Also the amount of current being drawn by the memristor device or the resistance of the device also came out to be consistent with that of the first bit. The slightly different switching behavior of two bits should be attributed to non-uniformity of ZnO layer and possible electrode defects.

It is also worth mentioning over here that the uniformity of the ZnO layer affects the power requirements of the device. The layers in this study are not very uniform and hence if compared to the performance with very uniform layers with almost same thickness fabricated via Molecular Beam Epitaxy technique [46,47], the power requirements get reduced as the device operates on much less current and also endurance of the device will be improved considerably.

4. Conclusions

A completely printed memristor device, exhibiting bistable resistive switching phenomenon has been presented in this paper for the first time. The 9 bit memristor has been fabricated by the electrohydrodynamic printing and electrospray techniques for the fabrication of top and bottom electrodes and active layers respectively. Cu is used as the material for bottom electrode while Silver is used as top electrode. Commercially available inks are used in the electrohydrodynamic printing process. ZnO ink has been synthesized dispersing ZnO nano-particles in Ethanol. The fabricated memristor device showed stable and reliable resistive switching behavior over 500 read–write cycles. The device operated at a maximum of 1.5 V and exhibited an On/Off ratio of ∼1 × 10³. Active layer uniformity is a cause of concern apart from some hillocks on the electrode which effect the device power requirements. The memory bits portrayed identical I–V characteristics w.r.t. resistive switching parameters hence confirming the Cu–ZnO–Ag MIM structure to be a potential candidate for its successful deployment in R-RAM applications with electrohydrodynamic fabrication technique potentially opening new horizons in the manufacturing of memory devices.
Acknowledgments

This research was supported by Basic Science Research Program through the National Research Foundation of Korea (NRF) funded by the Ministry of Education, Science and Technology (2010-0026163).

References