Current Applied Physics 16 (2016) 757–762

Contents lists available at ScienceDirect

Current Applied Physics

journal homepage: www.elsevier.com/locate/cap

Printed non-volatile resistive switches based on zinc stannate ($ZnSnO_3$)

Shawkat Ali, Jinho Bae*, Chong Hyun Lee

Department of Ocean System Engineering, Jeju National University, 102 Jejudaehakro, Jeju 63243, South Korea

A R T I C L E I N F O

Article history:
Received 14 December 2015
Received in revised form
8 March 2016
Accepted 18 April 2016
Available online 20 April 2016

Keywords:
$ZnSnO_3$
Memristor
EHD
Resistive switches
Resistive memory

A B S T R A C T

We present all printed non-volatile resistive switches based on zinc stannate ($ZnSnO_3$) for the memory applications. The device is fabricated on a flexible poly(ethyleneterephthalate) (PET) substrate through electrohydrodynamic (EHD) technique, where active layer of $ZnSnO_3$ (~130 nm) is deposited on the indium tin oxide (ITO) coated PET and a 100 μm silver line is deposited with thickness of 350 nm and length of 2 mm as a top electrode. The device exhibits resistive switching behavior at dual polarity voltage ±8 V. The measured value of high resistance state (HRS) and low resistance state (LRS) are 250 MΩ and 7.6 MΩ respectively. Nine (9) memristors are fabricated on a single substrate and their variability from device to device is measured to be 1 MΩ and 48 MΩ for LRS and HRS respectively. Furthermore, the device showed bendability down to 8 mm diameter and ON/OFF endurance for more than 200 cycles. Mechanical and surface morphology characterizations are carried out by using mechanical stress machine and field emission scanning electron microscopy (FE-SEM).

1. Introduction

Modern semiconductor industry try to follow the Moore's law such as reducing device size and increasing density, but the existing silicon based materials and technologies are approaching to their physical limits where the feature size cannot be reduced accordingly [1,2]. Therefore, recent research trends are exploring new devices, technologies and functionalities to fulfill the increasing demands of small size, high density, and simple architecture. To overcome these problems, a memristor is becoming a key component [3,4]. The invention of the memristor got the potential to extend the Moore's law for Boolean computing due to its non-volatile nature and high scalability down to 4 F^2 [5]. Since the HP group gave the physical memristor realization in 2008 [6], resistive switches has got more and more attention because of its wide range of potential applications non-volatile memory, resistive switching, high density, and simple crossbar array [7,8]. A vey common structure of a memristor is metal insulator-metal (MIM). Hence, for the fabrication of an intermediate insulated layer of a memristor, organic insulators [9,10], amorphous silicon [4], ferroelectric material [11], Zirconium oxide [12], Zinc oxide [18], and titanium dioxide [6] are used. Many researchers are investigating new materials for the active layer of memristor to make the memristor as a switching device in the replacement of transistor [13–18].

In this paper, we propose zinc stannate ($ZnSnO_3$) material [19] for the active layer of memristor that is fabricated through electrohydrodynamic (EHD) technique. The $ZnSnO_3$ material is sandwiched between bottom ITO and top silver electrode to make metal insulator metal (MIM) structure of a single memristor. Multiple memristors are fabricated on a single substrate with common bottom electrode and active layer with same fabrication parameters (active layer thickness) to investigate variability. The fabrication facility EHD is operated at ambient conditions and 35% humidity level throughout the experiment. The device is characterized electrically, mechanically, and for surface morphology by using probe station, automatic bending machine, XRD and FE-SEM. The proposed device exhibited a stable resistive switching behavior for more than 200 cycles, good retention time, and flexibility down to 8 mm. As the memristor architecture is very simple, metal insulator metal (MIM), it can be fabricated with variety of fabrication techniques including sol-gel, spin casting, electrostatic spray deposition (ESD), electro hydrodynamic (EHD), roll to plate, and screen print [20–24]. All fabrication techniques have their advantages and disadvantages. Some of them need vacuum chambers, heat, and a special environment to process the fabrication of a device. Among them, the EHD is eco-friendly process that is

* Corresponding author.
E-mail address: baejh@jejunu.ac.kr (J. Bae).

http://dx.doi.org/10.1016/j.cap.2016.04.012
1567-1739/

suitable at ambient conditions for prototyping and mass production [25]. More details about EHD fabrication can be found in our previous work [26].

The proposed device is fabricated by using EHD technique as following: (1) An ITO coated PET substrate sample of 2 × 2 cm^2 was cut and treated with ethanol, DI water and UV respectively, (2) active layer was deposited on ITO coated PET and cured, (3) lastly silver electrodes were deposited and cured again. Fabrication of the proposed device is discussed in Section 2, characterizations are described in Section 3, and conclusion is given in Section 4.

2. Materials and fabrication of the proposed device

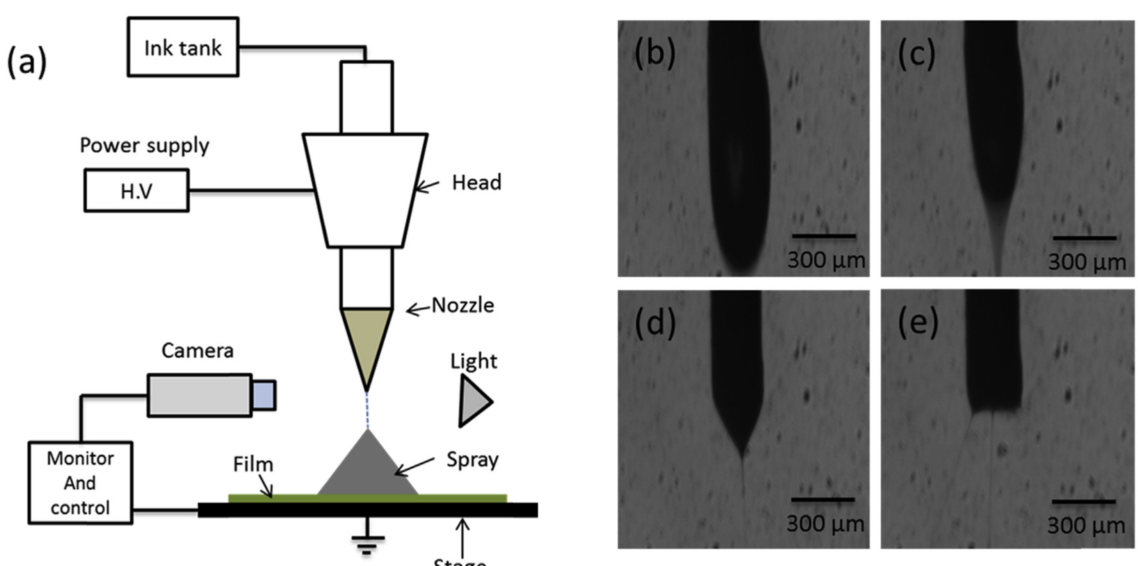
Ink for the active layer of the memristor was prepared as zinc stannate ($ZnSnO_3$) powder 0.78 gm was dispersed in 20 ml ethanol and 0.15 ml of ethanolamine was added. Solution was placed on a magnetic stirrer for 24 h at 70 °C, and then bath sonicated for 10 min and filtered with 5 μm filter. Prepared ink was mixed with *N*- *N* Dimethylformamide (DMF) with ratio 1:0.25 to increase the electrical conductivity of the solvent to enable the ESD phenomenon. For silver electrodes, ink was prepared as: Silver (Ag) nanoparticle paste 55%wt was diluted in 10 ml ethylene glycol solvent, ink was mixed for 1 h on magnetic stirrer and then 30 min bath sonication.

The schematic diagram of the EHD system is shown in Fig. 1a, where the main components are shown. Prior to begin with EHD printing, the substrate was treated with ethanol and deionized water for 10 min each followed by ultraviolet (UV) ozone for 5 min. Ink solution was pumped to a metallic nozzle to deposit on the ITO coated PET. While tuning the EHD for stable cone jet for Ag and zinc stannate inks by varying applied voltage and ink flow rate, different modes of spray were observed including dripping mode, unstable cone jet mode, stable cone jet mode and multi cone jet mode, as their images are shown in Fig. 1b–e. We got the EHD optimum parameters for zinc stannate experimentally by applying ink flow rate as starting from 50 μl/h and increasing to 800 μl/h with incremental step of 50 μl/h and applied voltage from 0 kV to 8 kV. The same procedure was applied for the Ag electrodes deposition. We found that 200 μl/h and 4.2 kV were the optimum parameters for the stable cone-jet of zinc stannate with 210 μm internal diameter of nozzle and for the Ag electrodes 6 kV, 60 μl/h and 110 μm inner diameter of nozzle. Parameters of the EHD system during deposition of the active layer and silver electrodes as shown in Fig. 1f. First, the active layer of $ZnSnO_3$ was deposited and cured at 130 °C for 4 h. Afterward, the Ag top electrodes were deposited (350 nm) on the active layer and cured at 80 °C for 30 min. Multiple memristor devices were fabricated on a single substrate as the layout diagram is shown in Fig. 2a. All the devices sharing the active layer and bottom electrodes, whereas the top electrodes are separately deposited for each device. The fabricated memory device is shown in Fig. 2b, the inset shows zoomed image of the devices where the PET substrate, active layer and top Ag electrodes can be seen.

3. Characterizations

3.1. Surface morphology

The EHD fabricated memory devices were analyzed for their morphology characteristics by using FE-SEM. Fig. 3a shows the cross sectional FE-SEM image of the single resistive device, it can be seen that the active layer is properly deposited over the ITO coated PET substrate. Although the active layer and top Ag electrodes are deposited through open air operated EHD system, even though the layers are properly deposited with a little variation in the thickness. To analyze the active layer for more surface morphology details, FE-SEM image was taken as the image is shown in Fig. 3b.



(f)

Layers	Applied Voltage (KV)	Applied flow Rate (μl/h)	Stand off Distance (mm)	Substrate Velocity (mm/s)
$ZnSnO_3$	4.2	110	11	1
Ag	6	20	1.2	3

Fig. 1. (a) Schematic diagram of the electro-hydrodynamic atomization (EHDA) fabrication system, (a) Dripping mode, (b) Unstable jet mode, (c) Stable cone jet mode, (d) Multi jet mode, (f) Operating parameters of the EHDA deposition process.