Materials Letters 166 (2016) 311–316

Contents lists available at ScienceDirect

Materials Letters

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

Fabrication of zinc stannate based all-printed resistive switching device

Ghayas-ud-din Siddiqui [a], Junaid Ali [a], Yang-Hoi Doh [b], Kyung Hyun Choi [a,*]

[a] *Department of Mechatronics Engineering, Jeju National University, 690-756, Republic of Korea*
[b] *Department of Electronic Engineering, Jeju National University, 690-756, Republic of Korea*

ARTICLE INFO

Article history:
Received 17 October 2015
Received in revised form
3 December 2015
Accepted 10 December 2015
Available online 11 December 2015

Keywords:
Electrohydrodynamic atomization
Memristor
Resistive Switching
Printed memory

ABSTRACT

This paper describes resistive switching in $ZnSnO_3$ thin film deposited by electrohydrodynamic atomization. The field emission scanning electron microscope analysis showed uniform surface morphology for thin films. The active layer, a thin film comprised of $ZnSnO_3$ nano-cubes was printed between screen printed silver (Ag) electrodes on glass substrate. Resistive switching behavior of the Ag/active layer/Ag sandwich structure was confirmed by current voltage analyses. The 3×3 array of memristors thus fabricated, showed characteristic OFF to ON (high resistance to low resistance) transition at low voltages, when operated between ± 2 V, at 100 nA compliance currents. The memristor array exhibited stable room temperature current–voltage hysteresis, low power operation, retentivity in excess of 24 h. An $R_{OFF}/R_{ON} \approx 10{:}1$ was observed at $V_{Read} = 100$ mV for more than 100 voltage stress cycles. All memory bits showed similar current voltage characteristics with respect to resistive switching parameters.

1. Introduction

Properties of nanomaterials differ from atoms, molecules, and bulk counterparts [1–4]. Although resistive switching has been a fringe of research frontiers for over half a century, active research in the field took off after the successful fabrication of memristor at Hewlett-Packard labs [5], thus proving mathematical model by Chua [6]. The proposed potential applications include, however are not limited to ultimate high density, competent and durable memory devices [7–9], neuromorphic application [10,11], and analog computing [12].

In last couple of decades, research in nanotechnology has delivered numerous new forms of nanomaterials and several different methods to fabricate them. Research on the zero, one and two dimensional nanomaterials has provided many new properties in order to improve device characteristics. The increasing overlap of research areas for daily life applications, has accelerated the growing demand for devices based on biocompatible materials. Among biocompatible materials, $ZnSnO_3$ has been in highlights for non-hazardous biodegradation of various dyes [13]. $ZnSnO_3$ has also been explored for nanogenerator [14,15], multilayer electrodes [16], photo catalysis [17], gas [18,19], chemical [20], and humidity sensing [21].

Electro-hydrodynamic atomization (EHDA) phenomenon, discussed in detail by Poon [22] has proved itself as preferred low-cost, non-contact, and efficient material printing technique. It has been used in a variety of thin film applications such as, OLED [23], and Schottky diodes [24], thin film resistive switches [25–27].

A memristor switches its resistance on passage of suitable magnitude of electric current. Usually a thin film, sandwiched between two electrodes works as an active material. The two resistance states, a high resistance state (HRS), 'OFF' state and a low resistance state (LRS), or 'ON' state [28] are attributed to thermal, electronic and/or ionic effects [29].

This study is primarily focused on exploring a $ZnSnO_3$ based 3×3 array of memristors. EHDA deposited $ZnSnO_3$ thin films were sandwiched between screen printed Ag electrodes on glass substrates. The $ZnSnO_3$ nanocubes were synthesized as previously reported [30]. UV–visible spectral analysis was used to analyze the transmission/absorption and evaluate the bandgap of the thin film. The thin films showed up to 88% optical transmittance for visible and a relatively higher absorption in UV region of electromagnetic spectrum. The calculated bandgap of the films was about 4.2 eV. Memristive behavior in Silver (Ag)/active layer/Ag sandwich array was studied using current–voltage hysteresis. The resistive switching devices thus fabricated, showed characteristic OFF to ON (high to low resistance) transition when operated between ± 2 V, characterized at 100 nA compliance currents. The fabricated devices exhibited a stable state retentivity of well over 24 h at room temperature, and a promising low power $R_{OFF}/R_{ON} \approx 10{:}1$ for more than 100 switching cycles

---

[*] Corresponding author.
E-mail address: amm@jejunu.ac.kr (K.H. Choi).

http://dx.doi.org/10.1016/j.matlet.2015.12.045
0167-577X/© 2015 Elsevier B.V. All rights reserved.

2. Experiment details

2.1. Materials and methods

For synthesis of $ZnSnO_3$ nanocubes, the precursor zinc sulfate heptahydrate ($ZnSO_4 \cdot 7H_2O$) (F. Wt 287.56) and sodium stannate trihydrate ($Na_2SnO_3 \cdot 3H_2O$) (F. Wt 266.71) were purchased from Duksan Pure Chemicals, South Korea. Triton, acetone, and ethanol solvents were purchased from Daejon Chemical and Metal, South Korea. Highly conductive Ag nanoparticle paste was purchased from MicroPE® PARU (Conc. 80 wt%). Viscosity of $ZnSnO_3$ colloidal ink was measured by VM-10A viscometer. The optical transmittance of thin films was collected by UV/VIS/NIR Spectrophotometer, (Shimadzu UV-3150 Japan). A non-contact (NV-2000 Universal) surface profiler in phase shifting interferometry (PSI) mode, with nanoscale accuracy for surface roughness measurement, was used to image the surface topography and (JEOL, JEM 1200EX II) field emission scanning electron microscope (SEM), were used to analyze the surface morphology of printed nanocomposite films on Ag coated glass substrates. Film thickness was measured by a non-destructive, thin film-thickness measurement instrument (K-MAC ST4000-DLX), based on interference spectrum of white light incident on the film surface. The electrical characterizations of resistive switching devices were carried out using a semiconductor device analyzer (B1500A, Agilent, USA). The crystal structure of nanocubes was determined by the X-ray diffraction (XRD), Rigaku D/MAX 2200H diffractometer with Cu Kα radiation ($\lambda = 1.5406$ Å, 40 kV, 250 mA, 8° min^{-1}) using a fixed glancing incidence angle (2°).

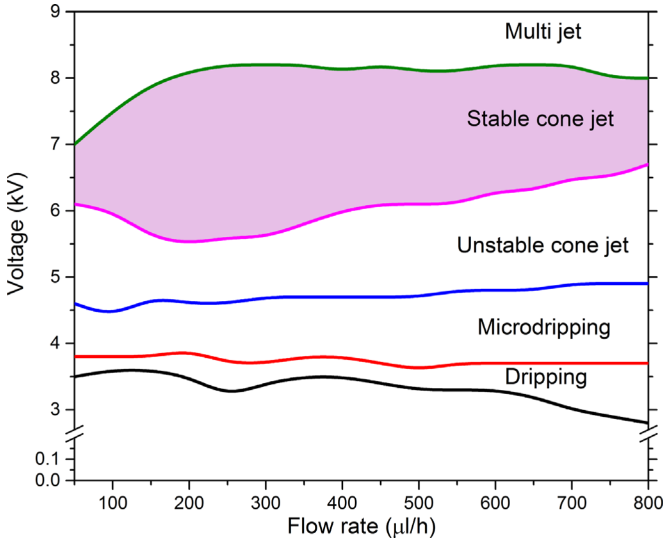

Fig. 2. Operating envelope illustration for the different EHDA modes at ink flow rate and applied voltage.

2.2. Device fabrication

Prior to deposition, glass substrates were cleaned by acetone, ethanol and deionized water in sequence by bath sonication, for 5 min each, at room temperature and dried in air. Afterwards, the substrates were cleaned by ultraviolet-ozone exposure for 5 min and oxygen plasma treated for 3 min to get rid of organic residues off the substrate surface. A semi-auto screen printer manufactured by SUNMECHANIX was used for electrode deposition. Fig. 1 shows complete device fabrication sequence employed here. Bottom Ag electrodes were screen printed on cleaned glass substrates and sintered at 120 °C for 30 min. $ZnSnO_3$ active layer was deposited by an in-house built EHDA system [25–27,30], using a metallic capillary nozzle (inner diameter = 210 μm) (Havard 33G) at 15 mm standoff distance. $ZnSnO_3$ ink was sonicated and magnetically stirred for 5 min each prior to EHDA. Ink ($ZnSnO_3$ in solvent) was fed to the liquid chamber via Teflon tube to nozzle by a syringe pump (Hamilton Model 1001 GASTIGHT syringe). The flow rate was controlled by using the pressure control system. Fig. 2 shows the overall operating envelop flow rate (50–800 μl/h) versus applied voltage (kV) using 210 μm diameter nozzle, at constant nozzle to substrate standoff distance of 15 mm. Initially at flow rate of 200 μl/h, a dripping mode appeared from voltage of 3.5–3.7 kV. Further increasing voltage, micro-dripping appeared until 4.6 kV. The cone jet remained unstable from 4.6 to 5.5 kV. The desired atomization of ink in the stable cone-jet mode was achieved from 5.5 to 8 kV. Beyond 8 kV, the jet disintegrated, into the multi-jet mode. The substrate was placed on a computer controlled translation stage, and substrate movement was varied from 1 to 3 mm/s to establish uniform coverage of about 1 × 2 cm^2, at fixed standoff distance. The optimum atomization mode called stable cone jet mode, was used for final deposition thin films at 5.8 kV applied voltage and 200 μl/h ink flow rate. The film was

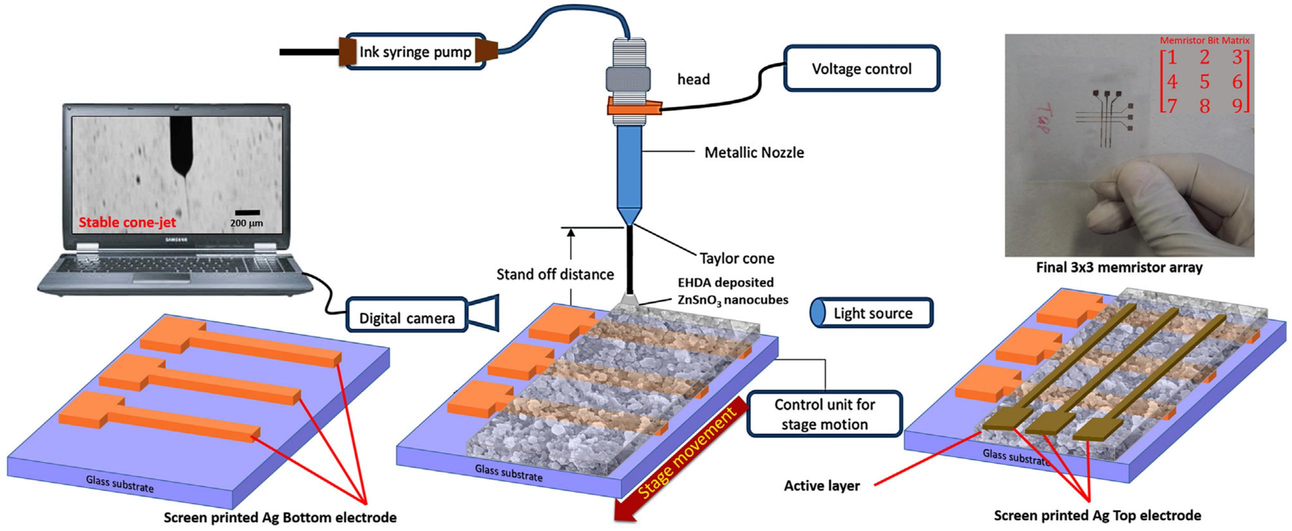

Fig. 1. Schematic illustration of zinc stannate 3 × 3 memristor array fabricated by electrohydrodynamic atomization and screen printed electrodes. The inset shows stable cone jet mode employing 210 μm metallic nozzle at 15 mm standoff distance. The digital camera photograph of final 3 × 3 memristor array is also shown with memristor bit matrix.