Filamentary Conduction in Aloe Vera Film for Memory Application

Zhe Xi Lim\textsuperscript{a}, Sasidharan Sreenivasan\textsuperscript{b}, Yew Hoong Wong\textsuperscript{c}, Feng Zhao\textsuperscript{d}, Kuan Yew Cheong\textsuperscript{a,}\textsuperscript{*}

\textsuperscript{a}Electronic Materials Research Group, School of Materials & Mineral Resources Engineering, Engineering Campus, Universiti Sains Malaysia, 14300 Nibong Tebal, Penang, Malaysia.
\textsuperscript{b}Institute for Research in Molecular Medicine, Universiti Sains Malaysia, 11800 Minden, Penang, Malaysia.
\textsuperscript{c}Department of Mechanical Engineering, Faculty of Engineering, University of Malaya, 50603 Kuala Lumpur, Malaysia.
\textsuperscript{d}Micro/Nanoelectronics and Energy Laboratory, School of Engineering and Computer Science, Washington State University, Vancouver, WA 98686, U.S.A.

Abstract

Aloe vera gel was extracted, formulated and deposited as thin films by a facile solution process for memory application. The memory cell features a simple structure, in which a dried Aloe vera film was sandwiched in between an Ag top and ITO bottom electrode that was deposited on a glass substrate. Digital information can be encoded and stored as different resistance states of the Aloe vera film. Experimental results reveal that bipolar resistive switching behavior of the Aloe vera film is due to electrochemical growth and dissolution of metallic filaments connecting the top and bottom electrodes. The resistive switching behavior is highly reproducible with an ON/OFF ratio of over 10\textsuperscript{4}, a retention time of over 12 h, and can endure more than 100 switching cycles. Therefore, the Aloe vera film can serve as a promising platform for sustainable development of green electronics.

\textsuperscript{*} Corresponding author. Tel.: +604-599 5259; fax: +604-594 1011.
\textit{E-mail address: srcheong@usm.my}
1. Introduction

Memory is a basic electronic device for many computer systems to store digital information before or after being processed by the central processing units (CPUs). Conventional memories are predominated by dynamic random-access memories (DRAMs) and flash memories, which respectively accounted about 58% and 39% of the total semiconductor memory sales in 2015 [1]. As the industry players draw economic sense by continuously down-scaling the memory devices, DRAMs and flash memories are approaching their physical miniaturization limits in near future. Consequently, several emerging memories including ferroelectric random-access memories (FRAMs), magnetic random-access memories (MRAMs), phase-change random-access memories (PRAMs), and resistive random-access memories (RRAMs) are being proposed as the next-generation memories for low-cost, high-density, and low-power information storage [2]. Of these emerging memories, RRAM appears to be a promising candidate due to their excellent down-scalability, fast switching speed, and 3-dimensional (3D) stacking capability. Generally, a RRAM cell is a two-terminal device composes of a resistance switching material interposing in between two electrodes. Digital information is encoded as either a high-resistance state (HRS) or a low-resistance state (LRS) of the resistance switching materials, which can be reversibly programmed by applying an appropriate electrical bias.

Resistance switching phenomena in a variety of inorganic and organic materials have been reported for RRAM application [3-5]. Recently, the increasing environmental awareness among electronics consumers have driven the search for green, biodegradable, and biocompatible materials as a sustainable solution to overcome the growing electronic waste (e-waste) epidemics [6]. Resistance switching phenomena have been demonstrated in several bio-organic materials, such as tobacco mosaic virus [7], silk proteins [8-11], DNA [12], enzymes [13], chitosan [14,15], starch [16], gelatin [17,18], cellulose nanofiber paper [19], chicken albumen [20], and Aloe vera (Aloe barbadensis Miller) gel [21-23]. Of these bio-organic materials, Aloe vera gel is of particular promising because it can be easily extracted from Aloe vera leaves and processed into thin films for various electronic applications. In particular, Aloe vera thin films demonstrate exceptional dielectric properties [24] that can be used in passive regions of organic field-effect transistors (OFETs) [25]. Meanwhile, resistance switching phenomena in thin films based on Aloe vera gel can be employed in active regions of memory devices. Write-once-read-many (WORM) memories can be realized with the permanent dielectric breakdown causing irreversible resistance change in thin films based on commercial Aloe vera gel [21]. Moreover, resistance switching due to charge trapping [22] and filamentary conduction [23] in thin films based on natural Aloe vera gel has also been demonstrated. These resistance switching phenomena make Aloe vera gel an appealing material for memory applications.

A comprehensive understanding of the resistance switching mechanisms is of paramount importance for device optimization and commercialization of the memory concepts. The resistance switching phenomena in most of the RRAMs based on bio-organic materials can be attributed to filamentary conduction [10-20, 23]. In these devices, the growth and rupture of a conductive filament bridging the two electrodes can be described within the framework of electrochemical metallization cells (ECMs) [26], programmable metallization cells (PMCs) [27], or conductive-bridging random-access memories (CBRAMs) [28]. Scanning electron microscopy (SEM) and transmission electron microscopy (TEM) have provided direct observation of the formation and dissolution of localized filaments in RRAMs based on inorganic and organic materials [29]. However, successful observation of the conductive filament using SEM and TEM requires either modifications from vertical to planar device structure [30,31], or complex preparation steps, such as ion milling and sample thinning [32], that are not applicable to bio-organic materials. Moreover, the characteristics of planar devices may not resemble vertical devices because the resistance switching materials are having larger surface area that is exposed to air, not to mention their interfaces with the substrates as well as limiting the down-scaling and formation of 3D stacking structure of the device.

In a previous study [23], resistance switching in thin films based on natural extracted Aloe vera gel was demonstrated for RRAM application. The RRAM features a minimalistic device structure, with the natural Aloe vera layer being sandwiched in between a top (Ag) electrode and a bottom (indium tin oxide, ITO) electrode. The resistance switching mechanism of the device is attributed to electrochemical growth and dissolution of a localized filament, as indirectly supported by the mechanism analysis based on DC current density–voltage (J–V) characteristics of the device. Since conduction in the LRS occurs at a randomized, localized filament region, the repeatability and reliability of the J–V characteristics are often questionable, as evidenced in the variations of ON/OFF ratio and read voltage window. In this paper, a statistical approach is applied to the measured J–V characteristics to provide a representative insight regarding the reversibility and reliability of the device. The filamentary conduction model in natural Aloe vera layer is further supplemented by performing depth profiling on
Zhe Xi Lim et al. / Procedia Engineering 184 (2017) 655 – 662

the device using time-of-flight secondary ion mass spectroscopy (ToF-SIMS). These experimental strategies should
able to provide a representative overview of resistance switching in the Aloe vera layer for reliable RRAM

2. Experimental

Natural Aloe vera gel was extracted from freshly harvested Aloe vera leaves according to the procedure
described elsewhere [22]. To isolate the content of polysaccharides, the natural Aloe vera gel was subjected to
alcohol precipitation. In this process, 20 mL crude gel was added with 40 mL ethanol (95 v/v%, Merck Millipore) in
a beaker and magnetically stirred at room temperature for 4 h. The mixture was left overnight in a refrigerator with
the temperature maintained at 4°C. The resulting precipitate (Aloe powder) was collected by centrifugation (Hettich
Rotina 38) at 20,000 rpm for 15 min and was then air-dried in a desiccator for 48 h prior used for device fabrication.

The Aloe vera-based RRAM features a minimalistic device structure as illustrated in Fig. 1. Here, the fabrication
procedure is briefly explained. ITO glass slides (7Ω/□, 220 ± 30 nm) were purchased from Zhuhai Kaivo
Optoelectronic Technology Co. (Guangdong, China) and were used as the device substrates. The ITO glass slides
were cut into a dimension of 1.5 × 1.5 cm² and were cleaned in an ultrasonic bath containing acetone (CMOS grade,
J.T. Baker), ethanol (95 v/v%, Merck Millipore), and deionized (DI) water for 30 min each step. Next, 50 mg Aloe
powder was dissolved in 10 mL DI water and the solution was spin-coated onto the ITO glass substrates at 3,000
rpm for 30 s. The spin-coated Aloe vera layer was thermally dried on a hotplate at 50°C, 80°C, 120°C, and 150°C
for 1 h. The device was completed after an array of 100-nm thick Ag (99.9985%, Alfa Aesar) was thermally
evaporated (Quorum Emitech K950X) at a base pressure of ~2.25 × 10⁻³ Torr through a metal mask, which defines
the device area to be 7.85 × 10⁻³ cm².

DC current–voltage (I–V) characteristics of the device were measured at room temperature and atmospheric
pressure using a source meter (Keithley 2450). In a typical setup, the device was placed on a probe station
(Everbeing PE-2) equipped with 2 probe arms, with the bias voltage applied on the top (Ag) electrode while the
bottom (ITO) electrode grounded. The measurement settings were configured through Keithley KickStart software
(v1.8.4.1) in a connected PC. The voltage sweeping rate was fixed at 2 V/s and a compliance current of 1 mA was
imposed to prevent permanent device breakdown. The measured current (I) was converted to current density (J)
using the relationship \( J = I/A \), where \( A \) is the device area. Depth profiling on the device was performed using ToF-
SIMS 5 spectrometer (ION-TOF GmbH, Germany) operated at a base pressure of ~10⁻¹⁰ Torr. The depth profile was
recorded using a 0.5 keV Cs⁺ sputter with an incident beam at an angle of 45° to the sample surface over an area of
7.85 × 10⁻³ cm².

3. Results and Discussion

A model for filamentary conduction in Aloe vera-based RRAM has been proposed in a previous study [23]. In
general, the key processes involved are (i) oxidation at the top electrode interface, (ii) ion transport within the Aloe
vera layer, and (iii) reduction and nucleation at the bottom electrode interface. Because of the limited amount of
mobile ions inside the pristine Aloe vera layer, a forming cycle with higher magnitude of voltage sweep (0 → 10 V)
is required to induce oxidation (Ag → Ag⁺ + e⁻) at the top electrode interface. Forming cycle was performed on 10
pristine devices and only the statistical mean is taken into subsequent considerations. Fig. 2a shows the
representative current density–voltage characteristics in the forming cycle for Aloe vera layer dried at
50°C. The current density measured in the pristine device increases gradually from $10^{-8}$ to $10^{-4}$ A/cm² as the applied bias is increased from 0 to 5.3 V. During this process, oxidation process occurs at the top electrode interface and consequently Ag⁺ ions are diffused into the Aloe vera layer. The diffused mobile ions are then transported within the Aloe vera layer drifted toward the bottom electrode under an applied electric field. The presence of voltage-gated ionic conduction channels in a leave of Aloe vera plant has been demonstrated [33], implying that Aloe vera gel can be a good ionic conductor. Reduction process ($\text{Ag}^+ + e^- \rightarrow \text{Ag}$) occurring at the bottom electrode causes nucleation
of Ag atoms that constitute a localized filament growing from bottom to the top electrode. The abrupt increase in current density from $10^{-4}$ to $10^{-1}$ A/cm² at the forming voltage (5.3 V) indicates the existence of an initial complete filament bridging the top and bottom electrodes, and the device undergoes a resistance state transition from HRS to LRS. In LRS, a large current density of $10^{-1}$ A/cm² is recorded as the device current is confined to a localized filament path, rather than homogeneously distributed current density in the HRS. This localized current conduction can be evidenced from the plot of resistance versus device area in the previous study [23].

After the initial forming cycle, the device proceeds into routine resistance switching cycles in which voltages of lower magnitude are needed to induce resistance switching. In this resistance switching cycle, the sequence of voltage sweeps is (i) $0 \rightarrow -1.5$ V, (ii) $-1.5 \rightarrow 0$ V, (iii) $0 \rightarrow 1.5$ V, and (iv) $1.5 \rightarrow 0$ V. A total of 100 resistance switching cycles were measured over 10 devices having gone through a forming cycle previously. Fig. 2b shows the representative $J$–$V$ characteristics of the Aloe vera layer dried at 50°C. The device can be reset and set at $-0.75$ V and 0.87 V, respectively, and the voltages are of smaller in magnitude if compared to the forming voltage of 5.3 V. The relatively smaller set and reset voltages can be attributed to the presence of mobile ions in the Aloe vera layer after the forming cycle, as proposed in the previous study [23]. In the reset process, the reverse bias voltage causes localized Joule heating in the filament [23, 26-28], leading to its dissolution (Ag → Ag⁺ + e⁻) and hence the device undergoes resistance state transition from LRS to HRS. The residual ions (Ag⁺) within the Aloe vera layer contribute toward the reformation of filament at a smaller set voltage when a positive voltage bias is being applied.

The drying temperature of the Aloe vera layer is critical in determining the device $J$–$V$ characteristics. Fig. 2c shows the variations of forming voltage when the Aloe vera layer is dried at different temperatures. The average forming voltage decreases from 5.3 V to 3.4 V as the drying temperature increases from 50°C to 150°C. The forming voltage is a strong function of film thickness [26-28]. Device with a thicker switching layer tends to electroform at higher voltage, as the travelling distance of mobile ions from top to bottom electrode is increased. This also implies that the Aloe vera thickness is reduced as the drying temperature increases. The reduction in Aloe vera thickness has been demonstrated using MProbe film thickness measurements in a former study [22]. Fig. 2d presents the $J$–$V$ characteristics in resistance switching cycle of the Aloe vera dried at different temperatures. The set voltage reduces considerably from 0.85 V to 0.42 V when the drying temperature is increased from 50°C to 150°C. Meanwhile, variations of the reset voltage in the range of $-1.12$ V to $-0.85$ V over the drying temperatures of 50°C to 150°C is less significant when compared to the set voltages. Similar findings have also been reported in devices based on gelatin [17,18] and chitosan [14]. The large variation of set voltages can be due to the random and localized nature of the filaments, which the growth conditions are dependent of several processes, namely (i) electron transfer rates at the interfaces, (ii) ionic transport in the bulk, and (iii) nucleation at a foreign substrate [26].

To determine the cumulative probability distribution, individual set and reset voltages were extracted from 100 continuous switching cycle measurements. Fig. 3a shows the cumulative probability distribution of set and reset voltages of the Aloe vera-based RRAMs. The average set voltages and the corresponding standard deviations for Aloe vera layer dried at 50°C and 150°C are $0.80 \pm 0.25$ V and $0.42 \pm 0.14$ V, respectively. The average reset voltages and the corresponding standard deviations for Aloe vera layer dried at 50°C and 150°C are $-1.09 \pm 0.06$ V and $-0.99 \pm 0.06$ V, respectively. Fig. 3b shows the variations of current density at HRS and LRS over the 100 continuous switching cycles. In HRS, current density fluctuation ranging between $10^{-8}$ and $10^{-6}$ A/cm² can be detected, while the LRS current density remains relatively constant at $10^{-3}$ A/cm² over the 100 continuous switching cycles. In LRS, the current density is confined to a conductive filament, which forms a stable conducting channel connecting the two electrodes. Meanwhile, in HRS, ionic current coupled with interfacial processes induce a fluctuating current flowing homogeneously throughout the Aloe vera layer. The current fluctuations have also been reported in other bio-organic RRAMs [17-19]. Nevertheless, ON/OFF ratios of $>10^5$ can be achieved in all tested devices over the 100 switching cycles. To evaluate the device retention performance, current densities in both LRS and HRS were measured under a continuous voltage stress and a readout voltage pulse of 0.1 V with an interval of 5 s was applied to monitor the current density over a period of 12 h. Fig. 3c shows the retention tests performed on the devices. No noticeable degradation in the current densities in both resistance states, except HRS current density of device with Aloe vera layer dried at 50°C. The increase in current density may be due to moisture absorption in the Aloe vera layer.

To elucidate the switching mechanism, the $J$–$V$ characteristics are replotted in a log–log scale and the experimental data is linearly fitted. Fig. 4a and b present the representative linear fitting plots during set and reset process of the device with the Aloe vera layer dried at 50°C, respectively. The HRS $J$–$V$ characteristics can be fitted
with two linear functions, one for the low voltage region (0–0.1 V) and another one for the high voltage region (0.1–1 V), while the LRS $J$–$V$ characteristics are fitted to a sole linear function. Fig 4c and d show the slope values of the linear fittings for all tested devices during set and reset process, respectively. The unity slope of the LRS fitted lines for both set and reset process indicates the presence of a conductive filament connecting the terminal electrodes. Current density confined in this metallic filament is governed by Ohm’s law. The slopes of linear fittings in HRS (low voltage region) are also close to 1, although some drying temperature effects can be noticed. In contrast, the slopes in HRS (at a high voltage region) deviate from unity, and this deviation becomes more significant (~2) as the drying temperature is increased. These findings are conforming to the theories of space-charge-limited conduction (SCLC), in which the current conduction is bulk limited due to the existence of charge traps in the Aloe vera layer.
More charge traps can be found in the Aloe vera layer as the drying temperature is increased. Fig. 5a and b shows the depth profiles of Ag, In, Sn, C, and H species as measured by ToF-SIMS for devices operated at HRS and LRS, respectively. Here, the intensity of each species was normalized with respect to their maximum values. The depth profiles of three distinctive regions, namely top electrode, Aloe vera layer, and bottom electrode are clearly revealed by Ag, C and H, and In species, respectively. The highest intensity of C and H species is recorded in the Aloe vera layer because Aloe vera gel is a bio-organic material with polysaccharides as its major composition. Notice that the depth profiles of C, H, In, and Sn species remain unchanged for devices operating in HRS and LRS. The depth profile change of Ag species is presented in Fig. 5c. Within the Aloe vera layer, Ag species in the LRS device has a higher normalized intensity as compared to the Ag species in the HRS device. This result implies the existence of a localized filament composed of Ag atoms bridging the terminal electrodes.

4. Conclusions

In conclusion, electrochemical formation and dissolution of filamentary paths in Aloe vera films are being explored for RRAM application. The RRAM features a basic device structure, in which an Aloe vera film is sandwiched in between an Ag top electrode and an ITO bottom electrode. The drying temperature can affect the physicochemical properties of the Aloe vera films, which in turns, can cause variation in the device parameters including forming, set and reset voltages. Filamentary conduction in the Aloe vera films is supported by the Ohmic current flowing in a metallic filament. The existence of localized, conductive filaments in the Aloe vera films is further supported by comparing the changes in normalized intensity of Ag depth profiles for devices operating in HRS and LRS. These findings provide a better understanding of filamentary conduction in Aloe vera films and will stimulate further device optimization and improvement.

Acknowledgements

This work was supported by FRGS no. 6071301, USM RUI no. 814216, and USM PRGS no. 8036018. Z. X. Lim gratefully acknowledges the MyBrain15-MyPhD scholarship given by Ministry of Higher Education (MOHE) Malaysia to finance his study in Universiti Sains Malaysia.

References


