Materials Research Express

PAPER

Coexistence of memory and threshold switching behaviors in natural milk-based organic memristor

Peng Zhang, Jiahui Zhang, Kunjie Wang, Li Wang, Xianrong Liu, Yan Jing and Benhua Xu

1 Qinghai Provincial Key Laboratory of New Light Alloys, Qinghai Provincial Engineering Research Center of High-Performance Light Metal Alloys and Forming, Qinghai University, Xining 810016, People’s Republic of China
2 College of Chemistry and Chemical Engineering, Xi’an Shiyou University, Xi’an 710065, People’s Republic of China
3 Chemical Engineering College, Qinghai University, Xining 810016, People’s Republic of China

E-mail: xubenhua@qhu.edu.cn

Keywords: organic memristor, memory resistive switching, threshold resistive switching, natural biomaterials, spin-coating

Abstract
Natural biomaterials have attracted great interest for the fabrication of biocompatible memristors. Here, dense and smooth milk films were deposited on the Pt/SiO₂/Si substrate by spin-coating method and resistive switching (RS) devices based milk films with the configuration of Ag/milk/Pt/SiO₂/Si are fabricated for the first time. Furthermore, memory RS (MRS) and threshold RS (TRS) effects coexist in the devices, which can be controlled by appropriately setting the compliance current (Icc). The current conduction mechanisms of the devices with MRS and TRS effects are controlled by typical trap-controlled space charge limited current (SCLC) conduction and filamentary conduction mechanism. The good RS performances of the milk-based devices make them promising for sustainable bioelectronics and novel logic device applications.

1. Introduction

Resistance random access memory (ReRAM), which is based on resistive switching (RS) behavior, as a potential candidate for next-generation nonvolatile memories, has attracted a great deal of attention due to its several advantages, such as fast writing times, high densities, good endurance, long retention, and low operating voltages [1–4]. A ReRAM cell is generally composed of an switching layer sandwiched between two electron conductors. By applying an electrical field across the electrodes, the resistance can be switched between a high resistance state (HRS) and a low resistance state (LRS). Generally, RS behavior can be classified as two modes: nonvolatile memory RS and volatile threshold RS [5, 6]. In memory RS (MRS), both the HRS and LRS can be stably maintained without an external sustaining voltage, which is used for non-volatile RRAM applications. While in threshold RS (TRS), only the HRS is stable when no external bias is applied, which can be used as a selector in series with memory cell to subdue the sneak current paths between memory cells [7, 8]. Over the past few years, kinds of nonvolatile MRS and volatile TRS behaviors have been observed in diverse switching layer materials [9–12]. What’s more, it is found that the two types of RS behavior can coexist or transform to each other in the switching layer material of a single device, which is in favor of the development of integrated circuits.

Until now, it is demonstrated that diverse switching layer materials, such as binary oxides, semiconductor, halide perovskite, 2D materials and biomaterials, exhibit these RS modes, which can be controlled by appropriately setting the compliance current (Icc). Among them, natural biomaterials mainly involving protein and carbohydrate, which possess the advantages of widely available, cost-competitive, light-weight and capable of large area fabrication on flexible substrates [13–15], have attracted great interest for the fabrication of biocompatible and bio-integrated due to their important potential applications in RS memory devices [16, 17]. In 2015, Chen et al reported for the first time the fabrication of naturally silk protein based RS memory device with tunable RS properties [18]. Then, Li et al fabricated the biocompatible memory devices based on natural ferritin, which exhibited reliably inter-convertible RS behaviours [19]. The above reports suggest that the tunable RS properties of protein-based memory devices are derived from formation of conductive filaments and...
redox reaction in the protein-based switching layer through regulating the magnitude of \( I_{cc} \) presets. Thus, amount of protein-rich natural biomaterials have the potential to be employed in RS memory device with tunable RS properties.

Milk is one of the most common biodegradable, bioresorbable, environmentally friendly, natural and abundant liquid biomaterials. It mainly contains, on average, 3.4% protein, 3.6% fat, 4.6% lactose, 0.7% minerals and 87.7% water [20]. Milk is a mixture, which is analogous to egg albumen. Up to date, egg albumen has been used to fabricate various electronic devices and RS memory devices [21]. However, milk has not yet been explored for manufacturing bioelectronics devices. Hence, bovine milk would be tremendously useful in kinds of electronics, especially in RS memory devices. In this work, dense and smooth milk films were fabricated on the Pt/\( \text{SiO}_2/\)Si substrate by spin-coating method and we demonstrated for the first time that MRS and TRS behaviors coexist in the Ag/milk/Pt/\( \text{SiO}_2/\)Si device through regulating the magnitude of \( I_{cc} \) in set process.

2. Materials and methods

2.1. Device fabrication

Fresh milk was purchased from a supermarket. Then the milk was centrifuged at 4000 rpm for 10 min and middle part of supernatant was carefully collected by using pipet. After Pt/\( \text{SiO}_2/\)Si substrate was cleaned by deionized water and alcohol for several times, the obtained supernatant milk was spin-coated onto the Pt electrode at 500 rpm for 10 s and then 2000 rpm for 30 s. Then the obtained milk films on the Pt/\( \text{SiO}_2/\)Si substrates were annealed in the oven at 110 \( ^\circ \) C for 30 min. Finally, circular Ag electrodes with diameter of 200 \( \mu \) m were thermally evaporated through a shadow mask onto the milk films surface as top electrodes.

2.2. Characterizations

The morphology analyses were evaluated with TEM (FEI TecnaiTM F30). The SEM image was taken using scanning electron microscopy (SEM, Hitachi S-4800). The AFM images were scanned in tapping mode by atomic force microscope (AFM, MFP-3D, Asylum Research). Current—voltage characteristics were investigated by a Keithley 2400 source measurement unit.

3. Result and discussion

Fresh milk was purchased from a supermarket (figure 1(a)). Milk films were deposited on the Pt/\( \text{SiO}_2/\)Si substrate by spin-coating method and as a proof of concept, milk-based RS devices with the configuration of Ag/milk/Pt/\( \text{SiO}_2/\)Si were fabricated (figure 1(b)). The fabrication processes are described in the Supporting Information. The surface smoothness and flatness of the switching layer films have an important influence on the RS behaviors of the devices. Hence these two properties of milk films were characterized via scanning electron microscopy (SEM) and atomic force microscope (AFM). As shown in figure 1(c), milk films surface are smooth and flat. The cross-sectional SEM profile of the milk films is shown in the right inset of figure 1(c), which reveals that the milk films deposited on the substrate with a thickness around 310 nm are highly uniformity and compactness. Figure 1(d) depicts the AFM topography image of the milk films, and the root-mean-square roughness is 5.1 nm.

The RS characteristics of the Ag/milk/Pt/\( \text{SiO}_2/\)Si device clarified by current-voltage (\( I-V \)) curve in the atmosphere were then investigated. During \( I-V \) measurements, the DC voltage was applied from the top Ag electrodes while keeping Pt bottom electrodes grounded and then swept with sweeping direction and sequence in the figures. Figure 2(a) shows the typical \( I-V \) characteristics of the milk-based RS device, which was examined under \( I_{cc} \) of 1 \( \mu \) A. Initially, when the applied voltage sweeps from 0 V to threshold voltage (\( V_{th} \)) along the stage 1, the RS device exhibits low current conductive state (OFF state). With the voltage exceeding the \( V_{th} \) (0.92 V), the current suddenly increases to \( I_{cc} \) indicating the device transition from OFF state to high current conductive state (ON state). Before the subsequent voltage sweeping back to hold voltage (\( V_{hold} \)) (0.44 V), the device remains the ON state (stage 2). As the voltage reduces to less than \( V_{hold} \), the device switches back to OFF state. Then the applied voltage sweeps from 0 V to \( -1 \) V, the device transition from OFF state to ON state (stage 3 to stage 4). Figure 2(b) shows the retention characteristics of the devices under a 0.4 V readout voltage. These results indicate that all these milk-based devices display TRS effect at the set \( I_{cc} \) of 1 \( \mu \) A.

Figure 2(c) shows that the \( I-V \) characteristics of the milk-based devices are examined under \( I_{cc} \) of 100 \( \mu \) A. When the applied voltage sweeps from 0 V to 1 V, the device switches from OFF state to ON state at the set voltage of 0.68 V (stage 1 to stage 2). Then, applied voltage sweeps from 1 V to reset voltage (\( -0.4 \) V), the device still maintains ON state (stage 2 and stage 3). After the applied voltage excesses reset voltage, the device transitions from OFF state to ON state. Finally, the device returns to its original state along stage 4. The \( I-V \) features indicate that the milk-based device exhibits a typical nonvolatile bipolar RS effect. Figure 2(d) shows the
retention performance of the device. The read voltages of both the ON and OFF states are 0.05 V. The ON and OFF states of the RS memory device can be maintained 5000 s with the ON/OFF ratio of $10^3$. Then the RS characteristics of the devices were conducted when the $I_{cc}$ was increased to 10 mA. The $I$-$V$ curve showing in figure 2(e) indicates that the milk-based device exhibits a typical write-once-read-many-times (WORM) type MRS effect. Figure 2(f) shows that the ON and OFF states of the device can maintain up to 5000 s with an ON/OFF current ratio of $10^5$ at the reading voltage of 0.4 V.

From the aforementioned results, by controlling the magnitude the $I_{cc}$ in the SET process, the RS behaviors of the Ag/milk/Pt/SiO$_2$/Si device can transform from the volatile TRS effect to the non-volatile MRS effect. When the $I_{cc}$ of the device in set process is 1 $\mu$A, the TRS effect is observed. When the $I_{cc}$ is increased to 100 $\mu$A and 10 mA, the device exhibits a non-volatile MRS effect, which corresponds to non-volatile bipolar RS and WORM effect.

For purpose of further exploring the interesting RS behaviors of the milk-based device, the mechanisms of the RS effects at different $I_{cc}$ should be comprehended. It has been demonstrated that when a positive voltage is applied to the active metal top electrode, anodic dissolution of the active metal top electrode occurs according to this reaction equation

$$M \rightarrow M^{n+} + ne^-$$

where M is the active metal. Then active metal ions migrate into switching layer under the applied electric field between top and bottom electrode. During active metal ions migration process, metal ions are reduced to metal atoms and further form metal clusters [22, 23]. When the top electrode is Ag, Ag clusters are formed in the switching layer during the resistance transition, which contribute to form conductive filaments. Chen et al proved that Ag clusters are formed in the silk protein-based RS device during the RS processes and no metallic conductive filaments are formed during the Set and Reset processes [20]. Instead, conductive filaments are formed resulting of hopping of electrons between Ag atoms during charge trapping and detrapping processes.
Thus current conduction mechanism of the protein-based RS device with Ag as electrode may be controlled by typical trap-controlled SCLC conduction and filamentary conduction mechanism.

To understand the conduction mechanisms of the milk-based device, the positive parts of I-V curves in TRS effect tested at the low set \( I_{cc} \) of 1 \( \mu A \) are replotted in double-Ln scale as shown in figures 3(a) and (b). In OFF state, when the applied voltage is very low, the current in the switching layer is nearly a constant. As the voltage increases, the slope of \( \ln(I) - \ln(V) \) curve varies from 1.1 to 1.9, which indicates that the conduction mechanism conforms to the Ohmic conduction and SCLC conduction behaviors \([24]\). Then the slope increases to 9.9 with the voltage increase. When the applied voltage is beyond \( V_{th} \), the device completes the SET process, indicating filaments are formed in the switching layer \([25]\). Subsequently, in the process of applying negative bias, the device switches from ON state to OFF state at \( V_{hold} \) (0.44 V), and the slope changes from about 2.1 to 1.1.

According to the above analysis, a schematic illustration is represented to explain the conduction mechanism as shown in figures 3(c)–(f). Local Joule heating induced by the current in the RS process could be influenced the mobility of the Ag ions. In low voltage regime of the TRS effect, a few of dissolving Ag ions migrate into milk switching layer and form Ag clusters, which could act as trapping centers. Meanwhile, these traps are unoccupied and the injected excess carriers are dominated by the thermally generated carriers (figure 3(c)). With

Figure 2. (a) The I-V curves of the Ag/milk/Pt/SiO\(_2\)/Si devices under the set \( I_{cc} \) of 1 \( \mu A \). (b) Device to device distributions of the resistance of OFF and ON state. (c) The I-V curves of the Ag/milk/Pt/SiO\(_2\)/Si devices under the set \( I_{cc} \) of 100 \( \mu A \). (d) The retention characteristics of the device in (c). (e) The I-V curves of the Ag/milk/Pt/SiO\(_2\)/Si devices under the set \( I_{cc} \) of 10 mA. (f) The retention characteristics of the device in (e).
the voltage increase, these traps are gradually filled by the inject electrons, which resulting in the SCLC model (figure 3(d)). Then electrons hopping between Ag atoms lead to current increase suddenly to $I_{cc}$, which indicates the formation of filaments in the milk switching layer. Because of low $I_{cc}$, filaments formed in the switching layer are tiny and slight and rupture of conductive filaments occurs under the reverse voltage sweeping, as shown in figure 3(f). Thus, milk-based RS device exhibits TRS effect.

Figures 4(a) and (b) show the double-$\ln$ plots of $I$-$V$ curves in nonvolatile bipolar RS effect examined at the set $I_{cc}$ of 100 $\mu$A. In OFF state, the slope of $\ln(I)$-$\ln(V)$ curve is 0.96 at the beginning of applied voltage sweeping from 0 V to higher value, which indicates the Ohmic conduction. Then, the slope of $\ln(I)$-$\ln(V)$ curve increases from 1.53 to 2.09 before voltage exceeds Set voltage, which indicates that the conduction mechanism is dominated by typical trap-controlled SCLC conduction. When the applied voltage exceeds the Set voltage, the current suddenly increase to $I_{cc}$, which indicates the device switches from OFF state to ON state. In ON state, the slope of $\ln(I)$-$\ln(V)$ maintains around 1, which indicates the Ohmic conduction. For the negative bias region (figure 4(b)), when the applied voltage is beyond reset voltage, the slope switches to 1.83. Then the slope decreases to 1.12 with voltage sweeping. These conduction behaviors indicate that the conduction mechanisms conform to the Ohmic conduction and trap-controlled SCLC conduction. Then, a schematic illustration is represented to explain the conduction mechanism of set and reset processes. Because the $I_{cc}$ is increases to
100 μA in nonvolatile bipolar RS, more Ag ions migrate into milk switching layer and form more Ag clusters. During the voltage sweeps below the set voltage, the conduction mechanisms are similar to that of TRS behaviors. Due to more Ag atoms exist in the switching layer, more and thicker filaments generate in milk switching layer when the applied voltage is beyond SET voltage. In the negative bias region, when the voltage is beyond reset voltage filaments rupture because of the Coulomb repulsion effect\cite{26, 27}. The formation and rupture of filaments during applied voltage sweeping contribute to transformation between ON state and OFF state, which bring about MRS effect in milk-based RS device with a higher $I_{cc}$ at 100 μA.

Double-Ln plots of $I$-$V$ curves in WORM effect examined at the set $I_{cc}$ of 1 mA are shown in figures 5(a) and (b). In the OFF state, as shown in figure 5(a), the slope of ln($I$)-ln($V$) curve is 0.96, indicating the Ohmic conduction. With the applied voltage increasing, the slope varies from 0.96 to 2.23, which suggests that conduction mechanism is dominated by trap-controlled SCLC conduction. Interestingly, current occurs violently fluctuation in the rectangle marked with red-dotted lines with voltage increasing. When the applied voltage exceeds the switching voltage, the device switches from OFF state to ON state. In ON state, as shown in figure 5(b), the slope of ln($I$)-ln($V$) curve is around 1, indicating the Ohmic conduction. According to the front elaboration, a schematic illustration is displayed to explain the conduction mechanism of the RS processes. When the slope varies from 0.96 to 2.23, Ag ions migrate into switching layer and are reduced to form Ag atoms acting as trapping centers. In this region, the conduction mechanisms are still similar to that of TRS behaviors. Because the $I_{cc}$ is up to 1 mA, amount of Ag atoms form in the switching layer, which results in the formation of robust Ag filaments with localized high density. Hence, with the voltage increasing, current begin to appear fluctuation due to formation and rupture of the filaments and then these filaments maintain conducting, which switches the device from OFF state to ON state. Furthermore, these conducting filaments could not rupture in the subsequent voltage sweeping, which attributes to the device is constantly in ON state.

![Figure 4](image-url). Double-Ln plots of $I$-$V$ curves in nonvolatile bipolar RS effect tested at the low set $I_{cc}$ of 100 μA in the device in (a) OFF state and (b) the ON state. Schematic diagrams of TRS processes. (c) The formation of conductive path. (d) Rupture of conductive filaments.
4. Conclusions

In summary, dense and smooth milk films were deposited on the Pt/SiO₂/Si substrate by spin-coating method. We have demonstrated for the first time that the Ag/milk/Pt/SiO₂/Si device exhibits MRS and TRS effects by regulating the magnitude of \(I_{cc}\) in set process. Through analyzing the RS behaviors of the milk-based device, magnitude of \(I_{cc}\) in set process controls the formation, concentration and distribution of Ag atoms in the switching layer. The current conduction mechanisms of the devices with MRS and TRS effects are controlled by typical trap-controlled SCLC conduction and filamentary conduction mechanism, which are depict in the physical model we proposed. The good RS performances of the milk-based devices make them promising for sustainable bioelectronics and novel logic device applications.

Acknowledgments

This work was financially supported by the Natural Science Foundation of Qinghai Province (2019-ZJ-942Q), National Natural Science Foundation of China (51902171) and Thousand Talents Program of Qinghai Province.

Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

Conflicts of interest

There are no conflicts to declare.
ORCID iDs

Peng Zhang @ https://orcid.org/0000-0002-9418-0684

References

[1] Szt K, Speier W, Bihlmayer G and Waser R 2006 Switching the electrical resistance of individual dislocations in single-crystalline SrTiO$_3$, Nat. Mater. 5 312–20
[2] Lin W P, Liu S J, Gong T, Zhao Q and Huang W 2014 Polymer-based resistive memory materials and devices Adv. Mater. 26 570–6
[3] Liu Q, Sun J, Lv H, Long S, Yin K, Wan N, Li Y, Sun L and Liu M 2012 Real-time observation on dynamic growth, dissolution of conductive filaments in oxide-electrolyte-based ReRAM Adv. Mater. 24 1844–9
[4] Lai Y C, Wang Y X, Huang Y C, Lin T Y, Hsieh Y P, Yang Y J and Chen Y F 2014 Rewritable, moldable, and flexible sticker-type organic memory on arbitrary substrates Adv. Funct. Mater. 24 1430–8
[5] Rozenberg M J, Ionue I H and Sanchez M J 2004 Nonvolatile memory with multilevel switching: a basic model Phys. Rev. Lett. 92 178302
[6] He L, Liao Z M, Wu H C, Tian X X, Xu D S, Gross G L, Duebserg G, Shvets I and Yu D P 2011 Memory and threshold resistance switching in Ni/NiO core–shell nanowires Nano Lett. 11 4601–4606
[7] Chang S H et al 2011 Oxide double-layer nanocrossbar for ultrahigh-density bipolar resistive memory Adv. Mater. 23 4063–7
[8] Lee M J, Park Y, Suh D S, Lee E H, Seo S, Kimz D C, Kim J and Park B H 2007 Two series oxide resistors applicable to high speed and high density nonvolatile memory Adv. Mater. 19 5919–23
[9] Pan C, Ji Y, Xiao N, Hui F, Tang K, Guo Y and Lanza M 2017 Coexistence of grain-boundaries-assisted bipolar and threshold resistive switching in multilayer hexagonal boron nitride Advanced functional materials Adv. Funct. Mater. 27 1604811
[10] Alagoz H S, Chow K H and Jung J 2019 Low-temperature coexistence of memory and threshold switchings in Pt/TiOx/Pt crossbar arrays Appl. Phys. Lett. 114 165302
[11] Bae J, Hwang I, Jeong Y, Kang S O, Hong S, Son J and Ho Park B 2012 Coexistence of bi-stable memory and mono-stable threshold resistance switching phenomena in amorphous NbOx films Appl. Phys. Lett. 100 062902.
[12] Abbas H, Abbas Y, Hassan G, Sokolov A S, Jeon Y R, Ku B and Choi C 2020 The coexistence of threshold and memory switching characteristics of ALD HfO2 memristor synaptic arrays for energy-efficient neuromorphic computing Nanoscale. 12 14120–34
[13] Zalar P, Kamkar D, Naik R, Ouchen F, Grote J G, Bazan G C and Nguyen T Q 2011 DNA electron injection interlayers for polymer light-emitting diodes J. Am. Chem. Soc. 133 11010–3
[14] Zhang Y, Zalar P, Kim C, Collins S, Bazan G C and Nguyen T Q 2012 DNA interlayers enhance charge injection in organic field-effect transistors Adv. Mater. 24 4258–60
[15] Kim D H, Viventi J, Amsden J J, Xiao J, Vigeland L, Kim Y S and Rogers J A 2010 Dissolvable films of silk fibroin for ultrathin conformal bio-integrated electronics Nat. Mater. 9 511–7
[16] Sun B, Zhou G, Guo T, Zhou Y N and Wu Y A 2020 Biomemristors as the next generation bioelectronics Nano Energy. 75 104938
[17] Sun B, Guo T, Zhou G, Wu J, Chen Y, Zhou Y N and Wu Y A 2021 Battery-like self-selecting biomemristor from earth-abundant natural biomaterials ACS Appl. Bio Mater. 4 1976–85
[18] Wang H, Du Y, Li Y, Zhu B, Leow W R, Li Y and Chen X 2015 Configurable resistive switching between memory and threshold characteristics for protein-based devices Adv. Funct. Mater. 25 3825–31
[19] Zhang C, Shang J, Xue W, Tan H, Pan L, Yang X, Guo S, Hao J, Liu G and Li R W 2016 Convertible resistive switching characteristics between memory switching and threshold switching in a single ferritin-based memristor Chem. Commun. 52 4828–31
[20] Jensen R G 2002 The composition of bovine milk lipids: January 1995 to December 2000 J. Dairy Sci. 85 295–350
[21] He X, Zhang J, Wang W, Xuan W, Wang X, Zhang Q and Luo J 2016 Transient resistive switching devices made from egg albumen dielectrics and dissolvable electrodes ACS Appl. Mater. Interfaces 8 10954–60
[22] Zhu S, Sun B, Ranjan S, Zhu X, Zhou G, Zhao H, Mao S, Wang H, Zhao Y and Fu G 2019 Mechanism analysis of a flexible organic memristive memory with capacitance effect and negative differential resistance state APL Mater. 7 081117
[23] Zheng L, Sun B, Mao S, Zhu S, Zheng P, Zhang Y, Lei M and Zhao Y 2018 Metal ions reoxid induced repeatable nonvolatile resistive switching memory behavior in biomaterials ACS Appl. Bio Mater. 1 496–501
[24] Zhang P, Xu B, Gao C, Chen G and Gao M 2016 Facile synthesis of C095g8 quantum dots as charge traps for flexible organic resistive switching memory device ACS Appl. Mater. Interfaces 8 30336
[25] Jeon Y R, Abbas Y, Sokolov A S, Kim S, Ku B and Choi C 2019 Study of in situ silver migration in amorphous boron nitride CBRAM device ACS Appl. Mater. Interfaces 11 23329–36
[26] Du Y, Kumar A, Pan H, Zeng K, Wang S, Yang P and Wee A T S 2013 The resistive switching in TiO$_2$ films studied by conductive atomic force microscopy and Kelvin probe force microscopy AIP Adv. 3 082107
[27] Wu S et al 2013 Nonvolatile resistive switching in Pt/LaAlO$_3$/SrTiO$_3$ heterostructures Phys. Rev. X 3 041027