Abstract: Egg albumen as the dielectric, and dissolvable Mg and W as the top and bottom electrodes are used to fabricate water soluble memristors. 4x4 cross-bar configuration memristor devices show a bipolar resistive switching behavior with a high to low resistance ratio in the range of $10^2$–$10^4$, higher than most other biomaterial-based memristors, and a retention time over $10^4$ sec without any sign of deterioration, demonstrating its high stability and reliability. Metal filaments accompanied with hopping conduction are believed to be responsible for the switching behavior of the memory devices. The Mg and W electrodes, and albumen film all can be dissolved in water within 72 hr, showing their transient characteristics. This work demonstrates a new way to fabricate biocompatible and dissolvable electronic devices by using cheap, abundant and 100% natural materials for the forthcoming bioelectronics era as well as for environmental sensors when the internet of things takes off.

Keywords: egg albumen, proteins, memristors, bipolar switch, dissolvability
1. Introduction

The advancement of microelectronics has completely changed the world from technology, space exploration to daily life, and the same trend will most likely continue. With the improvement of life standards and concerns for the environment, there is a trend to develop advanced electronics which is biocompatible, biodegradable and environmentally friendly. It would be extremely desirable to realize electronic devices and systems that can be implanted in body to implement dedicated and temporary tasks such as localized drug delivery, diagnosis/inspection etc, and then disappear within the body harmlessly. Similarly, electronics that can degrade naturally with no impact on the environment could help solve the problem of growing electronic-waste, a serious issue faced by the world nowadays. There is a growing desire to place dissolvable environmental sensors for agricultural use and pollution monitoring in the growing market of the internet of things where sensors communicate with base station for information exchange and action to be taken. It is important that these devices are not made from polluting and harmful materials. Great effort have been made to develop new types of biodegradable, biocompatible electronics using natural materials such as protein, DNA, nucleobases, gelatin, paper, etc, and various types of electronics devices and systems have also been explored, showing promising properties and characteristics for a number of applications.

Protein is a natural material with promising characteristics and properties for electronic applications. It has been used to fabricate field effect transistors (FETs), memoristors (sometimes called resistive switching devices), a new type of non-volatile memory devices with great potential for applications, and lab-on-chip structures etc. Egg albumen (or egg white) is a natural and abundant material, consisting of about 10% proteins (including albumins, mucoproteins, and globulins) and 90% water. It is biodegradable, bioresorbable, and environmentally friendly, thus it would be tremendously useful and interesting to explore the use of this material in electronics. Indeed, egg albumen has been used as an active or dielectric layer to fabricate resistive switching devices and thin film transistors with high performances, and used to enhance ultraviolet (UV) fluorescence with the incorporation of Au nanoparticles. Despite the progress, more work is needed to clarify the working mechanisms and improve their performance, reliability, stability etc of the devices. Also for future applications, more types of devices and operations are needed to provide complete electronic functions.

So far, the main focus and interests of bioelectronics have been on their compatibility and the
corresponding performances. However traditional electronics consist of semiconductor materials and conducting electrodes that are insoluble or dissolve at very slow rates though they may be biocompatible, thus restricting their applications as bioresorbable and biodegradable electronics. Efforts have been made to develop so-called transient electronics which can physically disappear or dissolve in or be reabsorbed by the human body or environment.\textsuperscript{17,18,19} Electronic devices made on ultrathin silicon films of a few tens of nanometers (nm) were found to dissolve in water over several days.\textsuperscript{17,20} Various metals such as magnesium (Mg), zinc (Zn), molybdenum (Mo), tungsten (W) and iron (Fe) were found to dissolve in water within several days when the thickness is less than a few hundreds of nanometers.\textsuperscript{21} These pioneering projects have opened the door for the development of unconventional transient electronics. Here we demonstrate transient memristor devices using natural egg albumen as the active layer, and water dissolvable Mg and W as the top electrode and bottom electrode respectively. Mg also has a low work function, the Mg electrode may improve the injection efficiency of electrons into dielectric film, while W, similar to the Au/Pt,\textsuperscript{2,3} is a relatively stable element, thus it is more suitable as bottom electrodes for the devices. We will show that the proposed bio-memristor devices not only have excellent performance compatible to oxide semiconductor based memristors,\textsuperscript{22} but also can dissolve in water within a short time period.

2. Experimental section

**Egg albumen films preparation.** The albumen films were prepared in a class-100 cleanroom. A stainless steel mesh spoon was used to separate the egg white and egg yolk. Untreated egg albumen has high viscosity, and direct spin coating would result in albumen films over 300 nm thickness even at speeds over 4000 rpm/min and non-uniform thickness, unsuitable for the devices fabrication with uniform performance. The egg white liquid was diluted in deionized (DI) water at a ratio of 1:15 to make thinner dielectric films for the device fabrication. The diluted liquid was sonicated for 5 min in order to thoroughly mix the albumen with DI water. The suspended solids in the liquid were filtered using dust-free cloth. The diluted albumen liquid was spun at 500 rpm for 5 sec and 4000 rpm for 40 sec on the Si substrate to obtain a film thickness of \~30 nm. The egg albumen film was then baked at 105 °C for 10 min. Devices showed unstable properties due to the high water content if they were dried at low temperatures. Raw egg white is soluble as it contains protein (including albumins, mucoproteins and globulins \textit{etc}), trace minerals, fats, vitamins and salts (ions like
Na⁺, K⁺ and Fe⁺ are floating within the albumen).¹³

**Crystal structure characterization.** The crystal structures of the albumen films and devices were analyzed using X-ray diffraction (XRD, Panalytical Empyrean) with Cu-κα radiation (λ=0.154 nm) at 40 keV and 40 mA. The diffraction patterns were obtained in the 2θ method with a scan range of 10–80°. For cross-sectional structural analysis, a scanning electron microscope (SEM, Hitachi S-4800) was used with an acceleration voltage of 3 keV. The roughness of the film surfaces was investigated by atomic force microscopy (AFM, SPI-3800N, Seiko Co.) under a tapping mode at 300 kHz.

**Device Fabrication and characterization.** Thermal oxidized silicon wafers with a ~300 nm silicon dioxide layer was used as the substrate for the demonstration purpose. The tungsten bottom electrodes were obtained through a photolithography and lift-off processing using positive photoresist (ARP 5350) in a cleanroom. Tungsten was sputtered using a direct-current (DC) magnetron sputtering system. W and Mg targets of purity 99.99% were used. The base pressure of the chamber was 3×10⁻³ Pa for W and 1×10⁻⁴ Pa for Mg deposition. The deposition pressure and sputtering power were 0.5 Pa (argon) and 200 W for both metals. After patterning the bottom W electrodes, blue film was used to cover the pads of the bottom electrodes, and the albumen dilution was spun on the wafer as shown in Fig. 1(a). The top Mg electrodes were formed by sputtering through a shadow mask as the albumen film may be damaged by solvent if a photolithograph process is used. 4×4 cross-bar memristors were fabricated for demonstration. The pads of top and bottom electrodes are 400×400 µm², the length of the electrodes is 4000 µm and the width of the electrodes is 100 µm. The electrical properties of the memristors were characterized using a semiconductor parameter analyzer (Agilent 4155 C) in ambient condition at room temperature, ~25 °C. To set and reset the device, a positive or a negative voltage was applied to the top electrode with the bottom grounded. For the sample dissolving experiments, DI water was used. The samples were directly immersed into the DI water at room temperature (~25 °C) and were optically inspected periodically.

### 3. Results and discussion

Demonstration devices consisting of 4×4 cross-bar memristors were fabricated on a silicon substrate with the 3-dimensional (3D) schematic structure shown in Fig. 1(a). Albumen was used as the dielectric layer, tungsten (~100 nm) as the bottom electrode and magnesium (~80
nm) as the top electrode. Initial investigation showed that the devices with thin dielectric layers are conductive with low resistance of a few tens of Ohms, and those with a thicker albumen film do not have the switching characteristics even a bias up to 20 V is applied, at this bias the devices are normally broken down. The thickness of the albumen was then fixed at around 30 nm for the devices shown in this paper.

Figure 1(c) shows the cross sectional view of the egg albumen film deposited on a silicon wafer with a thermally-grown SiO₂ layer. The surface of the albumen film after thermal baking is very smooth with an average surface roughness less than ~2 nm, which can be seen from the inset of the AFM image as shown in Fig. 1(d). Figure 1(e) shows the surface profile of the albumen film measured by KLA-TENCOR Alpha-Step surface profilometer. The high edge was caused by the blue film used to cover the electrode pads. The thickness of the albumen film is about ~30 nm, and is very uniform.

Figure 1(f) is the XRD spectrum of the albumen/W/SiO₂/Si structure. Since the thickness of albumen layer is only ~30 nm, the X-rays will simply penetrate through the layer into the layers underneath with no clear diffraction spectrum from the albumen. Four diffraction peaks can be seen, originated from the bottom tungsten electrode, corresponding to the (002), (210), (321) and (400) diffraction directions, respectively. The inset shows an XRD spectrum from an albumen film of ~2 μm thickness (multiple depositions with untreated albumen for
No obvious diffraction peak can be seen from the XRD pattern at the 2θ angle from 20 to 80 degrees, but only a peak at ~69° which is the (321) diffraction from the tungsten. These results imply that, after thermal baking, the albumen film is non-crystalline. Proteins are large molecules, consisting of one or more long chains of amino acid. In natural albumen, protein molecules are twisted and curled up together normally; different proteins are connected by a variety of weak bonds, e.g. hydrogen bonds. As albumen is mainly composed of a number of proteins with random orientations, it is not surprising that it appears non-crystalline.

Figure 2(a) shows a typical set-reset cycle of an albumen memristor with the bias applied to the top electrode and the bottom electrode grounded. Initially the device is in the high resistance state (HRS), i.e. the “OFF” state. The devices show a bipolar resistive switching behavior after processing. As the bias increases, the current increases steadily, and then increases abruptly when the bias reaches a threshold voltage of V~1.0 V (defined as the set voltage, V_set), limited by the preset compliance of 400 µA. The device is now in its low resistance state (LRS), i.e. the “ON” state. Once it is set, the current varies with voltage, but remains at the LRS. To reset the device, a reverse bias sweep is needed as shown in Fig. 2(a). At V~0.8V, the current of the device suddenly decreases, changing from the LRS to HRS. This remains unchanged even the reverse bias continuously increases to an absolute value larger than the set voltage. The voltage making the device change from the LRS to HRS is called V_reset.

The I-V curves are replotted in a double natural logarithm plot to clarify the mechanism of the switching behavior. For the LRS as shown in Fig. 2(c)&(d), the slope of the log(I)-log(V) curves is close to unity, indicating that the transportation is dominated by an Ohmic law for both positive and negative sweeps. For the HRS, the slope of the log(I)-log(V) curves are approximately 1 at the low voltage region, and is similarly dominated by an Ohmic law. In the medium voltage region (0.2V<V<0.5V), the slope is ~2, which is related to the ballistic transport of charges injected in the dielectric film, corresponding to the Mott-Gurney law, which is often regarded as the Child’s law. The slope continues to increase to about ~3 in the high voltage region above 0.5 V, which corresponds to a steep current increase region, and the behavior can be explained by the trap-controlled space charge limited current (SCLC) and trap-filling process. These behaviors are similar to those of the albumen and oxide-based memristors.
Figure 2. A full set-reset cycle for a Mg/Albumen/W memristor (a), superposition of I-V curves for 3 different memristor cells from the same cross-bar array measured 15 times each (b). Typical I–V curves of the albumen memristor devices plotted in a double logarithmic scale in positive (c) and negative (d) voltage sweeping, the colored lines are the fittings. Summary of the HRS and LRS resistance for 120 consecutive set-reset cycling tests (e) and retention tests of the HRS and LRS at a bias of 0.1 V (f). The HRS and LRS resistances of a memristor cell under different temperature with positive bias (g) and negative bias (h).

Figure 2(b) is the superposition I-V results of three memristors from one 4x4 array with each of the device tested for 15 times. A compliance current of 400 µA was applied to set the memristors from the HRS to LRS, while no current compliance was used when the reverse voltage was swept from 0 to 1.5 V for all the devices. It is clear from the figure, the values of $V_{set}$ and $V_{reset}$ change randomly with cyclic switching with a broad distribution. The average of the set voltage for the memristor is $\sim 1.0 \pm 0.4$ V, while that of the reset voltage is slightly narrower, $\sim 0.8 \pm 0.25$ V. Set and reset voltages with a broad distribution are commonly
observed from polymer and biomaterial based resistive switching devices, but the ranges of
the set and reset voltages of our devices are much narrower than those reported by Chen et al
using the egg albumen\textsuperscript{14} and even those of synthetic sericin protein.\textsuperscript{2} This is partially due to
the good uniformity of the albumen films deposited using the diluted albumen solution. The
scattering of the set and reset voltages of the memristors is attributed to inhomogeneity and
random rapture of conductive filaments as schematically shown by Fig. 3(c). The conductive
ions forming the conductive filaments are non-uniform and movable in the albumen film,
resulting in different values of the set and reset voltages. Although the set and reset voltages,
and the current levels scatter in a wider range, the overall hysteresis I-V characteristics
remain unchanged for all the devices and tests, indicating stable and uniform characteristics
of the devices and properties.

Figure 2(e) is the summary of the testing results of a device between the LRS and HRS for
up to 120 cycles. The memristor shows a relatively stable low resistance (~800±300 Ω),
while the resistance at the HRS varies largely as well as randomly in the range of 10^5~10^7 Ω,
a common characteristic behavior observed from resistive switching devices with polymers
and nature organic materials as the dielectric layers.\textsuperscript{2,14} The scattering of the resistances at the
HRS is larger than those at the LRS, and is also attributed to inhomogeneity and random
rapture of conductive filaments. These will lead to rapture of conductive filaments at different
locations and degrees, resulting in different values of the HRS. On the other hand, the
resistances of the LRS would not change much once the filaments are formed continuously,
thus resulting in less scattering in the resistance values. The average resistance ratio between
the HRS and LRS is quite large, about 1000 (10^2~10^4), which is much higher than the values
for the bio-substances based memristors,\textsuperscript{1,30,31} but lower than that reported by Wang et al,\textsuperscript{2}
who used synthetic sericin protein as the dielectric layer. The resistance ratio is also
compatible to most of the oxide-based memristors.\textsuperscript{22,32,33} Figure 2(f) shows the retention time
of the memristors recorded at room temperature at a voltage of 0.1 V. The resistances of
switching cells remain unchanged for a duration over 10^4 s tested without showing any sign
of deterioration (the device still worked well as the test stopped), demonstrating the very
stable nature of the devices and long information storage capability. Figure 2(g) and 2(h)
show the dependence of resistance at the LRS and HRS on temperature for the set and reset
condition respectively. The devices show no or extremely-weak temperature dependence if
any.
Figure 3. General scheme of peptide bonds (a) and disulfide bonds (b) synthesis between amino acids with different protein chains. Schematic drawings of the four switching processes for an albumen-based memristor (c): Initial state of a memristor with Mg and W as the top and bottom electrode, respectively. The colorful spheres represent different ions (i); When a positive voltage is applied to the top electrode, ions move along the electric field, and accumulate locally in strong field regions in the albumen layer (ii); meanwhile injected electrons from the bottom electrode reduce metallic ions such as Fe$^{3+}$ and Mg$^{2+}$ to metal elements. At a specific voltage, the filaments are formed to connect the top and bottom electrodes electrically, and the device is turned on, i.e. the LRS (iii); When applying a reset voltage, the conductive filaments are broken due to the oxidation of the metal elements by the injected electrons from the top electrode, the filaments are ruptured near the top electrode and the device gradually returns to the HRS (iv).

Most of the proteins in albumen are globular proteins, and are composed of amino acids with long protein chains. Natural albumen is linked together by many weak chemical bonds. During the thermal baking process, the weak bonds are broken and protein molecules are cross-linked with two dominant chemical bonds, namely the peptide bond and disulfide bond. Disulfide bond formation is an irreversible process (called coagulation), and is responsible for the thermally cross-linked solid albumen film.$^{34,35,36,37}$ Figure 3(a) and 3(b) illustrate the formation process of these two major bonds. During this, water molecules, electrons and hydrogen ions are generated. When the new bonds connect one amino acid to another, a network of interconnected proteins is formed.

The filamentary model is the most common model used to explain the resistive switching behaviors of oxide-based memristors though the mechanisms of filament formation are still a topic of debate.$^{1,14,38}$ Hopping conduction is another mechanism responsible for the resistive
Our devices showed a perfect Ohmic behavior at the LRS, indicating they are dominated by conductive filaments at the LRS, in agreement with the observation by Chen et al using conductive AFM. It was suggested that iron ions in albumen are the main elements for the formation of conductive filaments, and the oxidation \((\text{Fe} \rightarrow \text{Fe}^{3+} + 3e^-)\) and reduction \((\text{Fe}^{3+} + 3e^- \rightarrow \text{Fe})\) of iron elements are responsible for the switching behavior. For our devices, both Mg and W electrodes can dissolve in water easily as shown later and diffuse into the albumen film. They will also contribute to the formation of conductive filaments through the oxidation and reduction reactions, e.g. \(\text{Mg} \Leftrightarrow \text{Mg}^{2+} + 2e^-\). Since the filaments consist of various metal ions and elements, and the conduction of the filaments is a mixture of Ohmic conduction which may not be continuous paths, and hopping conduction. Conductivity of metals has a negative temperature coefficient, while hopping conduction has a positive temperature coefficient. The combined effects lead to weaker-temperature-dependent or temperature-independent characteristics as observed for both our devices and those in Ref.14.

Figure 3(c) is a schematic of the filamentary model. When a positive bias is applied to the top electrode, positive mobile ions move along the electric field towards the bottom electrode. Meanwhile electrons injected from the bottom electrode reduce the iron and magnesium ions, forming metal filaments between the two electrodes mixed with other ions, and the device is in the LRS. When a reverse bias is applied to the top electrode, a high density of electrons is injected from the top electrode owing to its low work function. Oxygen at the Mg and albumen interface may also move inside the albumen film. Both electrons and oxygen will oxidize iron and magnesium elements near the top electrode, rupturing the conductive filaments, and the device is turned to the HRS. Rupture of filaments is partial and near the top electrode, therefore a reset voltage smaller than the set voltage could restore the conductive path, leading to the LRS. For the HRS, injected electrons are captured by trapping defects in the albumen film and these behave as space charges. Amino acids are the decomposed products of proteins, and most amino acids are capable of absorbing metal ions or charges. Electrode material plays an important role in memristors. Albumen-based resistive switching devices with different electrode materials such as Mg, W, Al and Ag (not shown) have also been made, all showed excellent resistive switching behaviors though Mg has a much smaller work function (~3.66 eV) compared with 4.26, 4.28 and 4.55 eV of Ag, Al and W. These results indicate that the resistive switching behavior of albumen memristors and the resistances at both HRS and LRS are determined by the albumen film, not by the work
function of electrode material and the efficiency of the electron injection, thus it can be concluded that albumen is an excellent material for the fabrication of high performance memristors.

To demonstrate its application as transient electronic devices, we used Mg and W as the electrodes for the memristors. To test the biodegradability and dissolvability, the fabricated devices were immersed in DI water at room temperature. It is well known that Mg dissolves in water through the reaction of $\text{Mg} + \text{H}_2\text{O} \rightarrow \text{Mg(OH)}_2+\text{H}_2$, while that of W is $2\text{W} + 2\text{H}_2\text{O} + 3\text{O}_2 \rightarrow 2\text{H}_2\text{WO}_4$ with the end production soluble in water.

![Figure 4](image.png)

**Figure 4.** Microscopy images recording the dissolving of the cross-bar structure Mg/Albumen/W memristors in DI water (a-f). The electrodes pointing in the y-axis direction are the Mg top electrodes, and the W bottom electrodes are pointing in the x-axis direction. The thickness of both top and bottom electrodes are ~80 nm and ~100 nm, respectively.

Figure 4 shows the dissolution process for a cross-bar memristor chip. The top Mg electrodes dissolve rapidly after immersing in water for 40 min, and completely disappear after 2 hr in water (Fig. 4(c)). The cross-linked albumen layer was also found to dissolve in water gradually, but takes a longer time. Figure 4(c) and (d) show the bottom W electrodes intact after 10 hr in water due to the blockage by the thinning albumen layer which has a low dissolve rate due to the cross-linking nature of the albumen film. Once the albumen is dissolved in water, the W electrodes quickly dissolve in water. Isolated intact W patches can be seen from Fig. 4(e), indicating albumen dissolution in water is not uniform, possibly due to the non-uniform albumen layer thickness or inhomogeneous properties. Nevertheless, the whole chip almost disappears in the water after 72 hr (Fig. 4(f)) with only traces of residuals remaining. Thus we can conclude that memristors using these dissolvable materials are transient, which can be used as short period information storing units implanted in the human body or used in environmental sensors. On the other hand, the devices showed good reliability and stability at dry conditions. The resistances of the devices at the LRS remained
almost unchanged after storage at dry environment (RH≤30%) for over 3 months. For this work, Si was used as the substrate for demonstration. The results show if a suitable substrate such as polylactic acid (PLA) is used, then the whole electronic device package can be dissolved by water. PLA is a bio-safe material and water-soluble, and has been used in medical operation in human body, therefore PLA would be a good choice of the substrate for the transient electronics development.

4. Conclusions

In summary, cross-bar configuration transient memristors with egg albumen dielectric and dissolvable Mg and W electrodes were fabricated and their electrical properties were investigated. When a thin albumen film with a thickness of 30 nm was used, the devices showed bipolar switching behavior with HRS/LRS ratios in the range of $10^2$~$10^4$, which is higher than most of the biomaterials dielectrics based memristors and comparable to oxide-based memristors. The devices can store information over $10^4$ sec without any deterioration, showing their high stability and reliability. A filament model consisting of iron metallic elements accompanied with defect trapping-assisted hopping transportation has been proposed to explain the memory behavior and characteristics of the switching cell at the LRS, while SCLC is responsible for the conduction at the HRS. The cross-bar memory devices can be dissolved completely in DI water within 3 days owing to the use of dissolvable Mg and W electrodes, and the albumen. The results have demonstrated the possibility for information to be stored in transient electronic devices, opening the door for the fabrication of biocompatible, biodegradable electronic devices using cheap, abundant and natural materials for bioelectronic applications.

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