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Flexible Eco-friendly RRAM with Albumen Switching Layer

5.1 Introduction

Natural materials like gelatin, nucleic acid, silk fibroin, and egg albumen have been explored as a switching layer [Scott and Bozano, 2007] in the fabrication of resistive memory devices. Among these organic biomaterials, egg albumen has an added advantage of easy and low cost availability and non-toxicity, though lacks on exploration for flexible memory devices. Egg albumen is a combination of 0.5% carbohydrates, 10.5% protein, and 89% water and is considered the best low cost protein for electronic devices [Rehman *et al.*, 2021].

5.2 Devices with Pristine Layer

A flexible resistive memory device with natural albumen from eggs as a dielectric layer is demonstrated. The Ag/Albumen/ITO RRAM devices have shown excellent resistive switching with high current on/off ratio and long memory retention time without showing relevant degradation for pristine state. Moreover, devices have maintained the memory characteristics even after being bent at 7.5 mm radius, indicating that egg-albumen can be a promising candidate for bio-sustainable flexible memory devices.

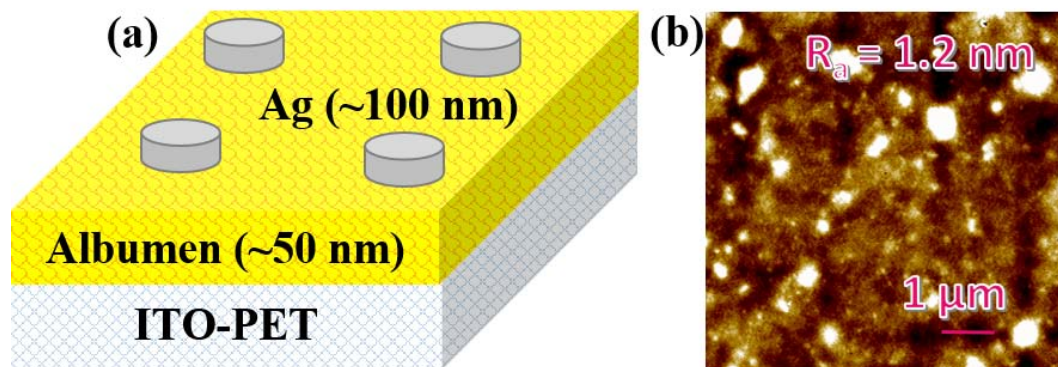


Figure 5.2.1: (a) Schematic of the fabricated device and (b) Atomic force microscope image of the albumen film.

5.2.1 Experimental Details

Indium tin oxide (ITO) coated polyethylene terephthalate (PET) substrate were used for the fabrication of flexible devices where ITO is used as the common bottom electrode. Albumen, a clear liquid, was extracted from white eggs procured from local market, and then mixed with de-ionized water in 1:1 ratio to prepare a solution. This solution was then ultra-sonicated for 1 hr for proper mixing followed by spin coating on the substrate to obtain a ~ 50 nm thick albumen film. Top circular silver (Ag) electrodes of diameter $100\ \mu\text{m}$ were deposited through shadow mask using thermal evaporation to obtain a thickness of ~ 150 nm. Thickness of the switching layer was measured by Burker's DektakXT surface profilometer. Atomic force microscope (AFM) images were taken using Park system's SPM XE-70 AFM system to study the surface morphology of the film.

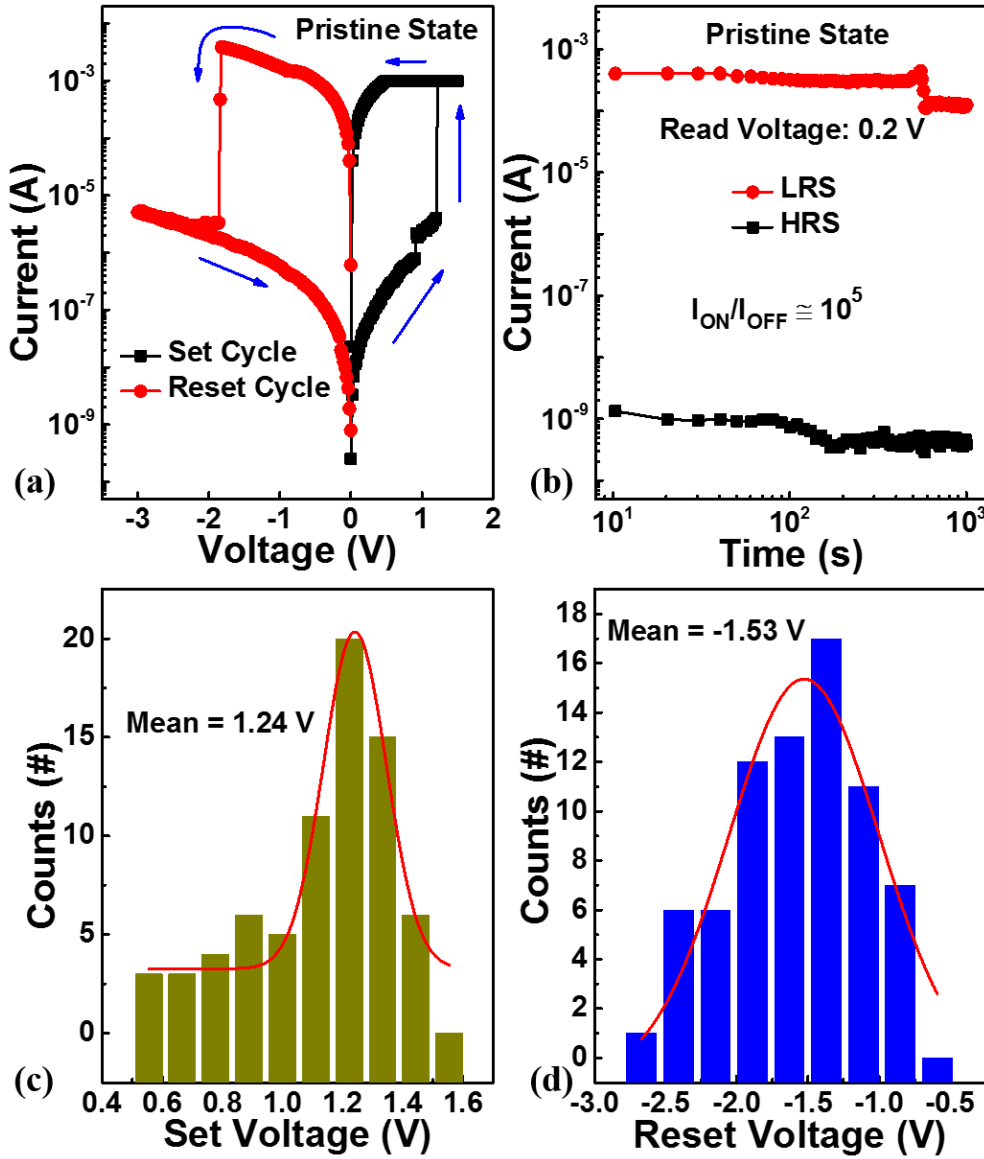


Figure 5.2.2: (a) I-V characteristic and (b) Retention of the device in pristine state. Distribution and Gaussian fitting of SET voltages (c) and RESET voltages (d) for multiple cycle operation.

5.2.2 Result and Discussion

Schematic of the Ag/ Albumen/ITO device and the surface morphology of the albumen switching layer is shown in Fig. 5.2.1(a) and (b) respectively. The obtained surface roughness of the film is around 1.2 nm, indicating a very smooth film and thus suitable for fabrication of electronic devices. Fig. 5.2.2(a) shows the I-V characteristics of the device in pristine state i.e., before any mechanical stress was applied on the device. The switching characteristics was obtained by applying a voltage sweep from $0 \rightarrow 2 \rightarrow 0 \rightarrow -3 \rightarrow 0$ V. A compliance current of 1 mA is applied during all the electrical measurements to protect the device from getting permanently damaged. The default state of a newly fabricated device was high resistance state (HRS) and after applying the positive voltage sweep the device changed its state from HRS to low resistance state (LRS). A negative voltage sweep is applied to change the state back to HRS. The device has shown an excellent switching characteristic with set voltage V_{set} around 1.2 V, reset voltage V_{reset} around -1.8 V and memory window of greater than 10^4 . The retention time plot of the device is obtained by applying a constant bias voltage of 0.2 V for 10^3 seconds at both the states. Fig. 5.2.2(b) shows the retention characteristics of the device indicating that the device is capable of holding its present state without any obvious degradation for 10^3 seconds with a memory window of around 10^5 . The distribution of set and reset voltages for 100 switching cycles are illustrated in Fig. 5.2.2(c) and 2(d) respectively. The obtained mean set voltage is around 1.2 V and reset voltage is around 1.5 V. This plot also indicates that the device with bare egg-albumen switching layer is capable of multiple cycle operation with some variation of set and reset voltages.

After completing electrical characterizations of device in pristine state the device was bent at a radius of 7.5 mm for 10 minutes and all the electrical characterizations were performed again to study the electro-mechanical stability i.e., change due to mechanical stress, of the device. Fig. 5.2.3(a) shows the switching characteristic of the device after bending when a voltage sweep is applied across the device. The plot indicates a reduced set ($V_{set} = 0.7$ V) and reset ($V_{reset} = -0.6$ V) voltage compared to that of the pristine device, which may be explained due deformations introduced in the film during bending [Dwivedi *et al.*, 2022a]. Fig. 5.2.3(b) shows the retention characteristics of the device after bending, indicating a clear window of around 10^4 for 10^3 seconds with a read voltage of 0.2 V. The voltage distribution plot of set and reset voltages after bending for 100 cycles is shown in Fig. 5.2.3(c) and (d) respectively, with mean set voltage of 1.14 V and mean reset voltage of -1.3 V.

The conduction mechanism of RRAM is still a matter of active discussion and double log I-V plot is among the accepted methods for estimating the underlying conduction mechanism. Fig. 5.2.4(a) shows the log (I)-vs-log (V) characteristics of the device for set cycle. The slopes of this plot under different regions gives the underlying conduction mechanism. The initial slope of ~ 1 during lower set voltage indicates the conduction due to thermally generated carriers. With increase in the applied set voltage the trap-assisted space charge limited conduction mechanism becomes significant which can be observed from the slope of > 2 . Once the metallic filament forms after V_{set} , the ohmic ($V \propto I^1$) conduction mechanism with a slope of 1 is obtained. Moreover, Fig. 5.2.4(b) shows the double log (I) - log (V) plot for reset cycle. Before the dissolution of metallic filament a slope of 1 is obtained because of the ohmic conduction. The arrow indicates the direction of voltage sweep applied to switch device from LRS to HRS and vice-versa. Fig. 5.2.4(c) shows the schematic of the conduction mechanism of the device. The formation of filament starts when a positive voltage is applied at the silver electrode. The silver gets oxidized to Ag^+ ($Ag \rightarrow Ag^+ + e^-$) upon application of positive voltage, this positive ion then moves towards the bottom electrode due to the present electric field. Upon reaching the bottom electrode Ag^+ gets reduced to elemental Ag ($Ag^+ + e^- \rightarrow Ag$) and starts acting as virtual bottom electrode. This process

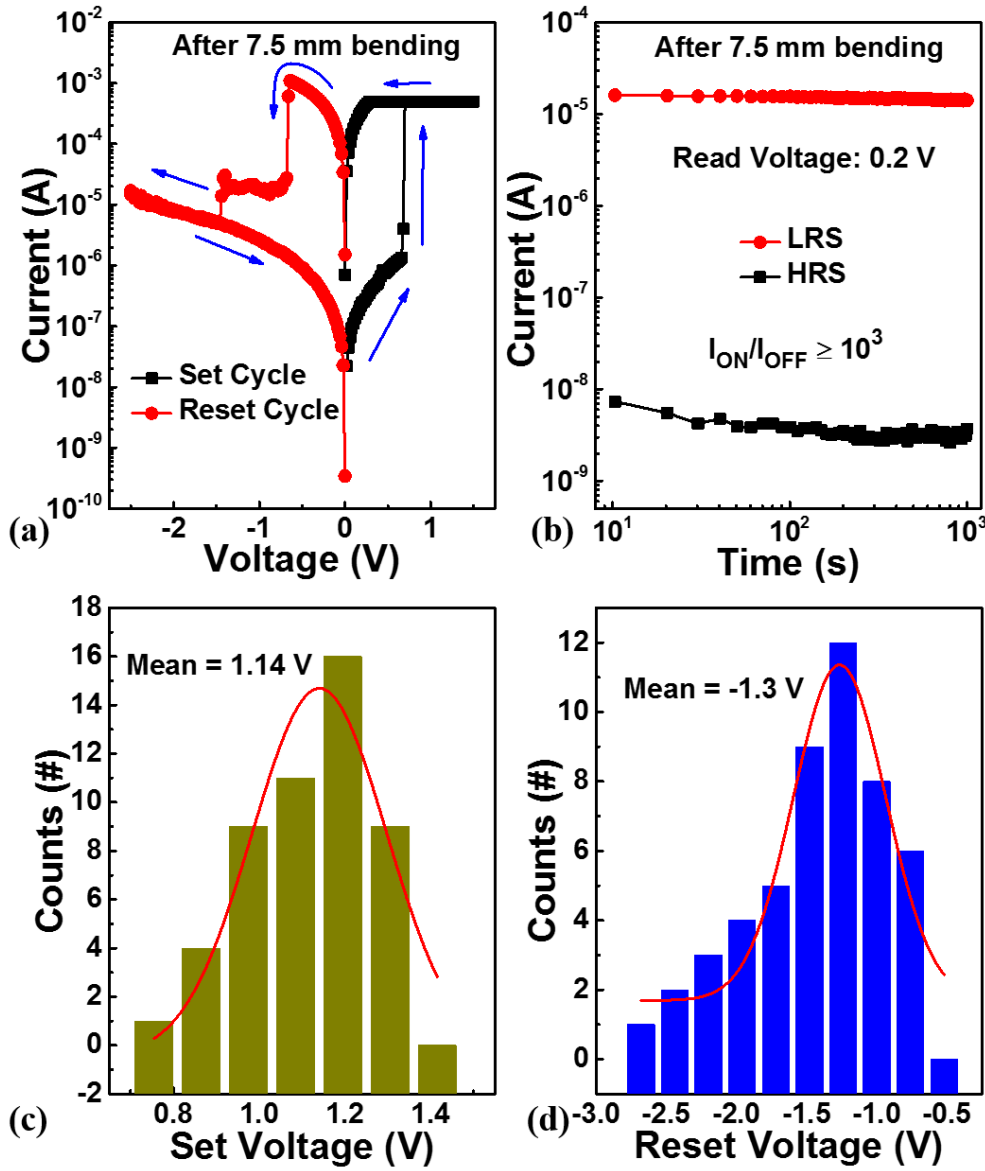


Figure 5.2.3: (a) Switching characteristics and (b) Retention characteristics of the device after 7.5 mm bending. Distribution and Gaussian fitting of SET voltages (c) and RESET voltages (d) for multiple cycle operation after bending.

continues till a conductive filament is obtained connecting both the electrodes. For reset process a negative voltage is applied at the top silver electrode thus dissolving the metallic filament which results in HRS of the device.

5.3 Flexible Hybrid Bilayer Devices

Although, albumen has been explored as a potential switching layer primarily in rigid RRAM devices [He *et al.*, 2016; Chen *et al.*, 2015], the reports on flexible RRAMs with albumen in pristine configuration are scarce [Dwivedi *et al.*, 2023a; Zhou *et al.*, 2017]. However, a low endurance remained a challenge in pristine albumen based flexible RRAM devices [Zhou *et al.*, 2017; Zhu

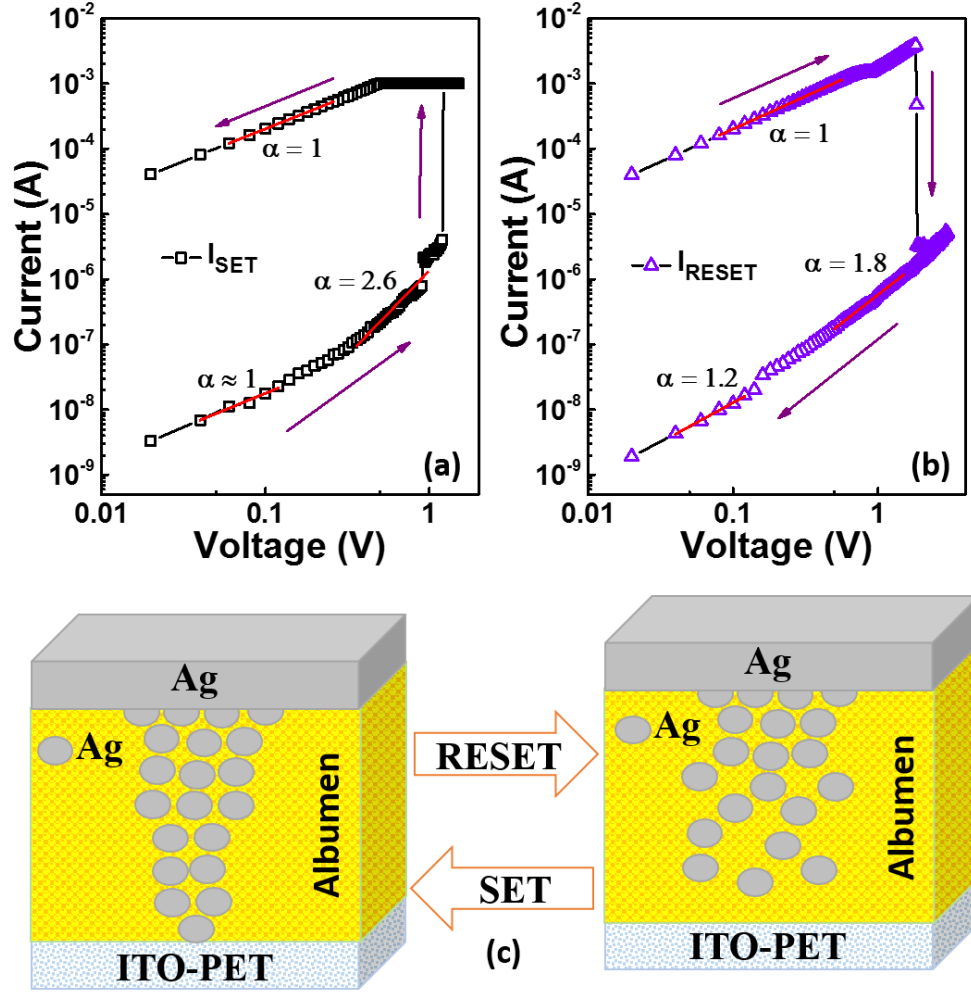


Figure 5.2.4: (a) Switching characteristics and (b) Retention characteristics of the device after 7.5 mm bending. Distribution and Gaussian fitting of SET voltages (c) and RESET voltages (d) for multiple cycle operation after bending.

et al., 2017]. Hybrid bilayer configuration of switching layer with ultra-thin HfO_x , offers a possible solution of this limitation [Dwivedi *et al.*, 2022a; Saini *et al.*, 2022a; Varun *et al.*, 2020]. The introduction of HfO_x layer induces two types of filaments, one composed of metal ion and other of oxygen vacancies, in the device. This gives rise to enhanced endurance characteristics of the device [Dwivedi *et al.*, 2022a; Sassine *et al.*, 2019]. Thus, the ultra-thin layer of inorganic dielectric (metal oxides) improves the memory characteristics, and the second layer of polymer enhances device's flexibility and electro-mechanical stability [Saini *et al.*, 2022a; Rehman *et al.*, 2016]. In this work, Egg-albumen, a natural polymer, in pristine and in bilayer combination with ultrathin HfO_x is explored as an active switching layer component in flexible resistive random access memory devices. The fabricated hybrid devices have shown excellent switching characteristic with current on/off ratio of greater than 10^4 , stable retention of both the low resistance and high resistance states, reliable multiple cycle switching, and very low switching power (with set power as $0.5 \mu\text{W}$ and reset power as 3.1 mW). To investigate the electro-mechanical stability, devices were bent with different bending radii and it was found that negligible degradation in device performance was observed till 5 mm bending radius.

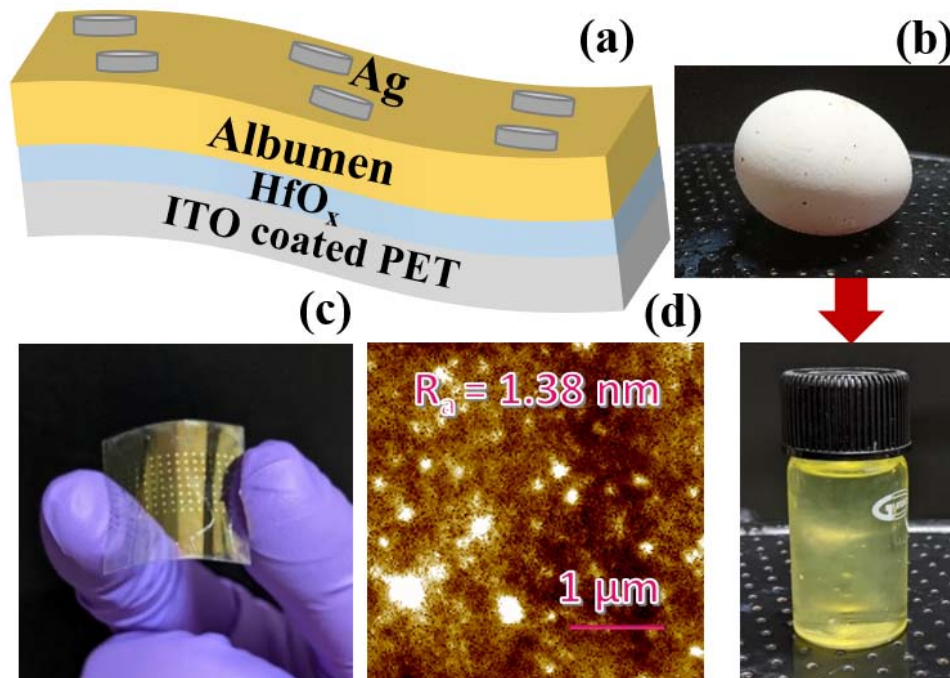


Figure 5.3.1: (a) Device Schematic. Digital image of (b) an egg and the prepared solution of egg-albumen with DI water, (c) Fabricated device. (d) Atomic force microscope (AFM) image of the obtained film for hybrid bilayer device.

5.3.1 Experimental Details

The devices were fabricated on flexible Indium-doped tin oxide (ITO) coated Polyethylene Terephthalate (PET) substrate with ITO acting as common bottom electrode (BE). A standard cleaning process was used to clean the substrate in isopropyl alcohol (IPA) ultrasonic bath for 10 minutes, followed by nitrogen blow to dry the substrate. Albumen solution was prepared by taking egg white from fresh chicken egg obtained from local market and mixing it with de-ionized (DI) water in 1:1 ratio. This mixture was then processed in an ultrasonicator for 30 minutes to obtain a uniform solution. For the hybrid bilayer device, a 5 nm ultra-thin layer of HfO_x was deposited on the cleaned ITO-PET substrate using Savannah S200 atomic layer deposition (ALD) system with Tetrakis(dimethylamido)hafnium(IV) and water as precursors. The prepared albumen solution was then spin coated at 500 rpm for 20 seconds followed by 4000 rpm for 40 seconds on HfO_x /ITO to obtain a uniform film. The coated film was annealed at 60 °C for 30 minutes to remove excess solvent, and a uniform film with thickness of around 50 nm was obtained. Finally, 150 nm thick, circular top electrodes (TE) of silver (Ag) with 100 μm diameter was deposited through a shadow mask, using a thermal evaporation system at high vacuum ($\sim 10^{-6}$ torr). Similar fabrication steps were followed for preparation of pristine egg-albumen device. Burker's DektakXT surface profilometer was used to measure the thicknesses of switching layers. Morphology of the albumen film surface was studied using atomic force microscopy (AFM) images taken by SPM XE-70 from Park systems. All the electrical characterizations were done on Keithley 4200 semiconductor characterization system. For investigating the effect of bending on devices, the devices were kept in bent condition at a particular bending radius constantly for 10 minutes, followed by measurement of switching characteristics in flat condition. Three different bending radii of 7.5 mm, 5 mm, and 2.5 mm were utilized for this study.

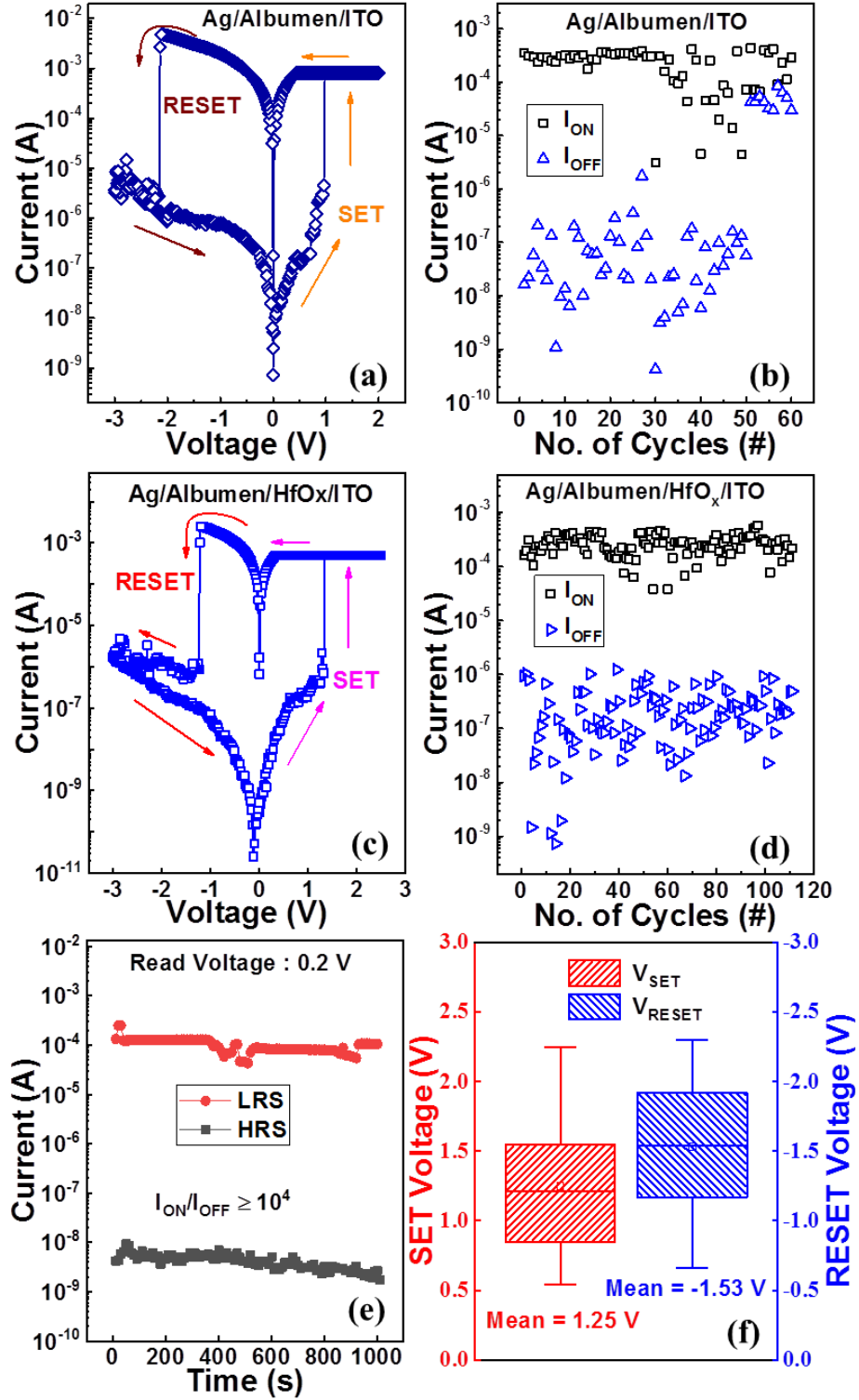


Figure 5.3.2: (a) I - V , and (b) Endurance Characteristic of Ag/ Albumen/ITO device. (c) I - V , and (d) Endurance Characteristic of Ag/ Albumen/HfO_x/ITO device. (e) Retention plot, and (f) V_{SET} and V_{RESET} distribution for Ag/ Albumen/HfO_x/ITO device.

5.3.2 Result and Discussion

The device schematic is shown in Fig. 5.3.1 (a), and Fig. 5.3.1 (b) shows the digital image of an egg and the prepared solution of egg-albumen with DI water. Fig. 5.3.1 (c) shows the digital image of the fabricated device, and the AFM image of the obtained thin film from the prepared solution on HfO_x is shown in Fig. 5.3.1 (d). The average roughness of around 1.4 nm indicates that the coated film of albumen is very smooth and suitable for further device fabrication. The I - V and endurance characteristics of Ag/Albumen/ITO device is shown in Fig. 5.3.2 (a) and (b) respectively. A linear dual voltage sweep of 0 to V_{max} for SET state and 0 to $-V_{max}$ for RESET state was applied on Ag top electrode while keeping ITO grounded, to obtain the switching characteristics. A compliance current (I_C) of 500 μA was maintained to protect the device from permanent breakdown during all the set cycles. The endurance characteristic plot was obtained by reading current at 0.2 V at both the states for multiple cycles. Fig. 5.3.2 (a) shows the complete switching cycle with $V_{SET} = 0.82$ V and $V_{RESET} = -2.2$ V, and a clear memory window with distinguishable states. This shows that albumen can be further investigated for the fabrication of flexible, low cost, and eco-sustainable memory devices. Fig. 5.3.2 (b) shows the endurance characteristic of the device, and it can be observed from this plot that the device has started losing its distinguishable states after 45 cycles, and completely lost its memory characteristics after 51 cycles. An ultrathin layer of HfO_x was introduced in the device for improvement of its memory characteristic. Fig. 5.3.2 (c) shows the switching characteristic of Ag/Albumen/ HfO_x /ITO hybrid bilayer device, with $V_{SET} = 1.3$ V and $V_{RESET} = -1.2$ V. The endurance characteristic of the hybrid bilayer device is shown in Fig. 5.3.2 (d). It can be observed that the hybrid bilayer device is able to maintain its distinguishable states for more than 110 cycles. It can be concluded from Fig. 5.3.2 (b) and (d) that the hybrid bilayer improves memory device performance, and thus hereon all the studies are focused on hybrid bilayer device. Fig. 5.3.2 (e) shows the retention plot of the device for 10^3 seconds with a clear current on/off ratio of $\geq 10^4$ and it is maintained without any major performance degradation. The retention characteristic is obtained by applying a read voltage of 0.2 V at both the low resistance state (LRS) and the high resistance state (HRS) of the device consecutively. This plot implies that the device is capable to hold its present state without any degradation for longer period of time, even with a continuous small electrical stress of 0.2 V. In HRS a reduction of current after some time may be attributed to the dielectric relaxation over longer period of time. The distribution of set voltages (V_{SET}) and reset voltages (V_{RESET}) for 100 cycles switching operation is shown in Fig. 5.3.2 (f). An average set voltage of 1.25 V and reset voltage of -1.53 V is obtained for the device. These results indicate that the fabricated device with biomaterial egg-albumen and ultra-thin HfO_x shows improved memory characteristics in pristine state and further studies can be performed to observe its memory characteristics after mechanical bending.

Results of investigation of effect of bending on devices are summarized in Fig. 5.3.3. As already stated earlier, three different bending radii of 7.5 mm, 5 mm, and 2.5 mm were utilized for this investigation. The I - V characteristics of the device at different bending radii is shown in Fig. 5.3.3 (a), indicating that the device can perform switching operations even after extreme mechanical bending. The current ratios obtained from retention plot of device at different bending radii is shown in Fig. 5.3.3 (b). The plot shows that after 7.5 and 5 mm bending, the device was able to retain its data without any significant degradation, however a significant decrement in the ratio can be observed after 2.5 mm bending. It can also be observed that after 2.5 mm bending the device retention capability has degraded and the device has started losing its data after 800 seconds of electrical stress. This degradation may be attributed to the permanent deformations or cracks developed in the device upon extreme bending. From Fig. 5.3.3 (a) it can be observed that after 2.5 mm bending the set voltage has reduced and reset voltage has increased, this may be

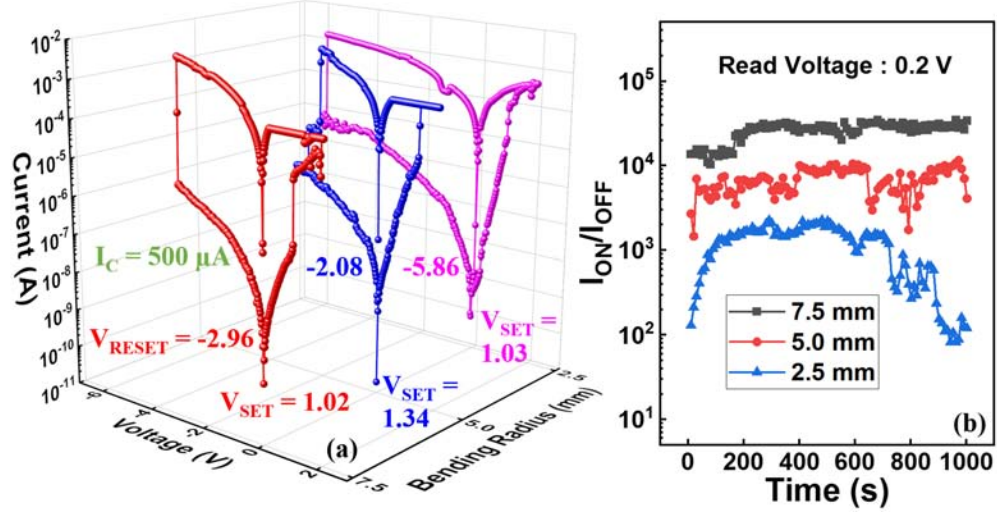


Figure 5.3.3: (a) I - V characteristics and (b) current on/off ratio vs time plot for 10^3 seconds at different bending radii of 7.5 mm, 5 mm, and 2.5 mm.

due to easiness in formation of filament in the the device because of the induced defects or cracks. This is an undesirable device behaviour and 2.5 mm bending can be treated as limit point, thus all the further studies are limited upto 5 mm bending radius. Fig. 5.3.4 shows the distribution of set and reset voltage at 7.5 mm and 5 mm bending radii. In Fig. 5.3.4 (a) the statistical distribution with Gaussian fit of set (V_{SET}) and reset (V_{RESET}) voltages of the device for 100 cycles after 7.5 mm bending is shown, with mean $V_{SET} = 1$ V and mean $V_{RESET} = -1.05$ V. Similarly, Fig. 5.3.4 (b) shows the distribution of the voltages after 5 mm bending with mean $V_{SET} = 0.89$ V and mean $V_{RESET} = -1.37$ V. It should be noted here that at this point the device has shown a switching of more than 300 cycles (100 pristine + 100 @ 7.5 mm + 100 @ 5 mm + few at 2.5 mm). A gradual decrement in the mean set voltages, from 1.25 V in pristine state (Fig. 5.3.2 (d)) to 0.89 V after 5 mm bending (Fig. 5.3.4 (b)), can be observed with decrease in the bending radius or with increment of mechanical strain. This slight degradation in performance can be attributed to assisted conducting filament formation process due to the deformations induced in the switching layer upon bending [Dwivedi *et al.*, 2022a]. The insulating layer develops some deformations upon application of mechanical stress and these deformations or crack density is proportional to the applied stress [Shang *et al.*, 2017]. These cracks act as predefined path to the metal ions and thus assists in formation and dissolution of filaments, and also governs the SET and RESET voltages [Dwivedi *et al.*, 2022a].

Table 5.3.1 shows the performance comparison of some recently reported devices based on egg-albumen as active switching layer. Current on/off ratio, set and reset power, and whether the device is fabricated on flexible substrate or not are the main parameters of the comparison. The I_{ON}/I_{OFF} ratio after bending is also included for flexible devices to compare the change in device performance after bending. The set (P_{SET}) and reset (P_{RESET}) power is calculated by taking current and voltage just before the sudden jump in the respective region. The table shows that the hybrid bilayer device of this study performs better than other reported devices even after extreme bending till 5 mm radius. Moreover, these hybrid bilayer flexible RRAM devices exhibit significantly higher I_{ON}/I_{OFF} ratio compared to many other rigid RRAM devices with inorganic bilayer combinations such as TiO_2/a -IGZO, ZnO/HfO_2 , AlO_x/AlO_y , and combinations of organic materials such as PMMA/MEH:PPV [Tarsoly *et al.*, 2022; Jain *et al.*, 2022; Huang *et al.*, 2020; Rehman

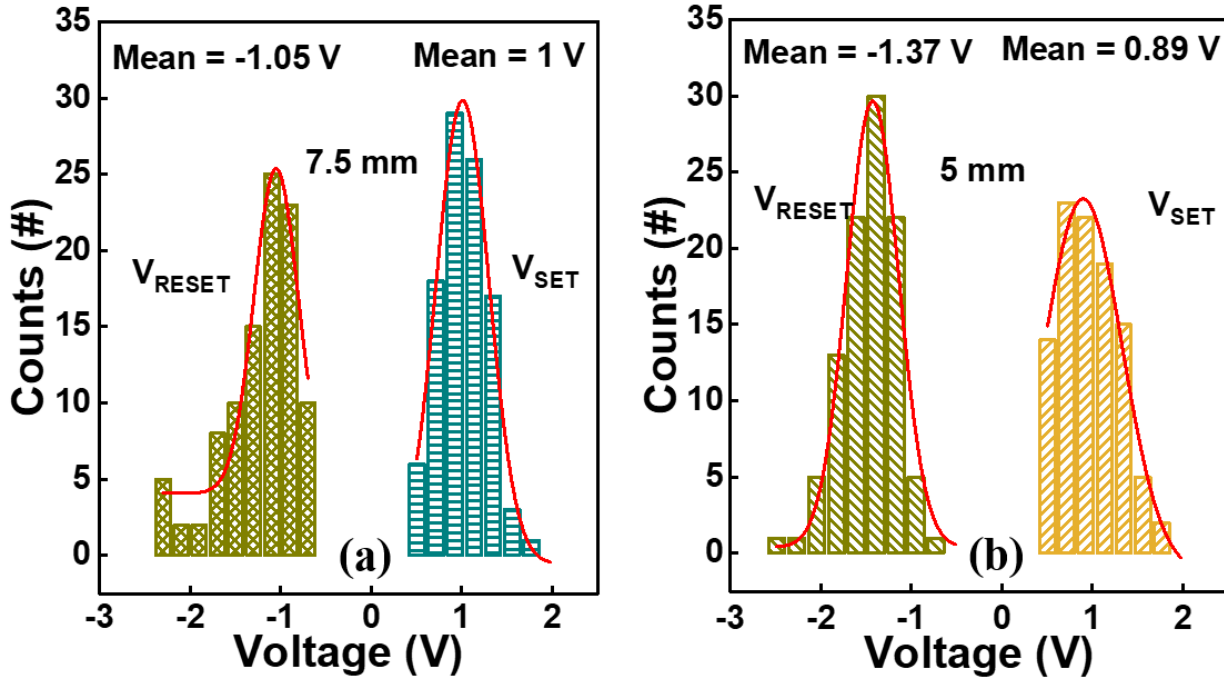


Figure 5.3.4: V_{SET} and V_{RESET} distributions of (a) 7.5 mm and (b) 5 mm bent device for 100 cycles each.

Table 5.3.1: Performance Comparison Table: Albumen/ HfO_x with pristine Albumen devices

S. No.	Structure & Type (Rigid/Flexible)	I_{ON}/I_{OFF} (Pristine, Bent)	P_{SET} and P_{RESET}	Ref.
1.	Mg/ Albumen/W, Rigid	$\geq 10^3$, NA	$10 \mu\text{W}$ & 0.8 mW	[He <i>et al.</i> , 2016]
2.	Al/ Albumen/ITO, Rigid	10^3 , NA	$0.6 \mu\text{W}$ & 360 mW	[Chen <i>et al.</i> , 2015]
3.	Ag/ Albumen/ITO, Flexible	$\sim 10^4$, $\geq 10^3$ @ 7.5 mm	$4.3 \mu\text{W}$ & 6.9 mW	[Dwivedi <i>et al.</i> , 2023a]
4.	Ag/ Albumen/ITO, Flexible	10^2 , $\geq 10^2$ @ 5 mm	$60 \mu\text{W}$ & 3.5 mW	[Zhu <i>et al.</i> , 2017]
5.	Au/ Albumen/Au, Flexible	10^4 , NA	$6 \mu\text{W}$ & 14 mW	[Zhou <i>et al.</i> , 2019]
6.	Ag/ Albumen/ HfO_x /ITO, Flexible	10^5 , $\sim 10^4$ @ 5 mm	$0.5 \mu\text{W}$ & 3.1 mW	This Work

et al., 2017].

Fig. 5.3.5 (a) and (b) show the double log I - V characteristics of the device with pristine (Ag/ Albumen/ITO) and hybrid bilayer (Ag/ Albumen/ HfO_x /ITO) respectively, for both the SET and RESET cycles. The slope of these curves in various region is the key parameter that helps in pre-

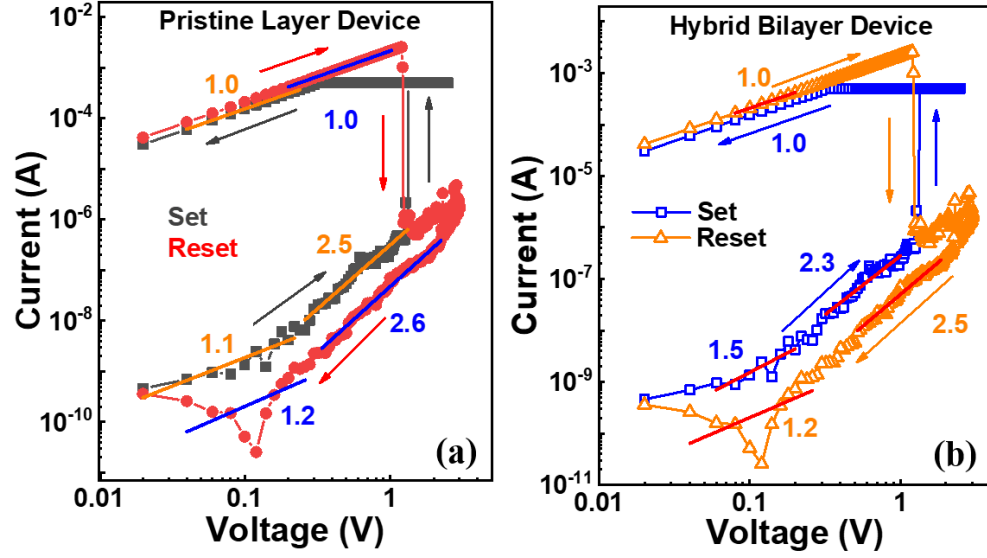


Figure 5.3.5: Log(I)-vs-log(V) plot for set and reset region and slopes in respective regions for (a) Ag/ Albumen/HfO_x/ITO, and (b) Ag/ Albumen/HfO_x/ITO device.

dicting the conduction mechanism in those region. It can be observed that in both pristine and hybrid bilayer devices the slope is 1 after SET, indicating that a metallic conductive filament is present in LRS of both the devices. Similarly, at higher applied voltage (around 1 V) the slope of greater than 2 also indicates space charge limited conduction (SCLC) mechanism in both the devices. Though conduction mechanisms in both the devices are similar for a respective region, the earlier discussions have shown that the hybrid bilayer devices perform better than the pristine devices. The conduction mechanism can be related with the filament formation and dissolution process as shown in Fig. 5.3.6, that shows SET and RESET process in Ag/ Albumen/HfO_x/ITO device.

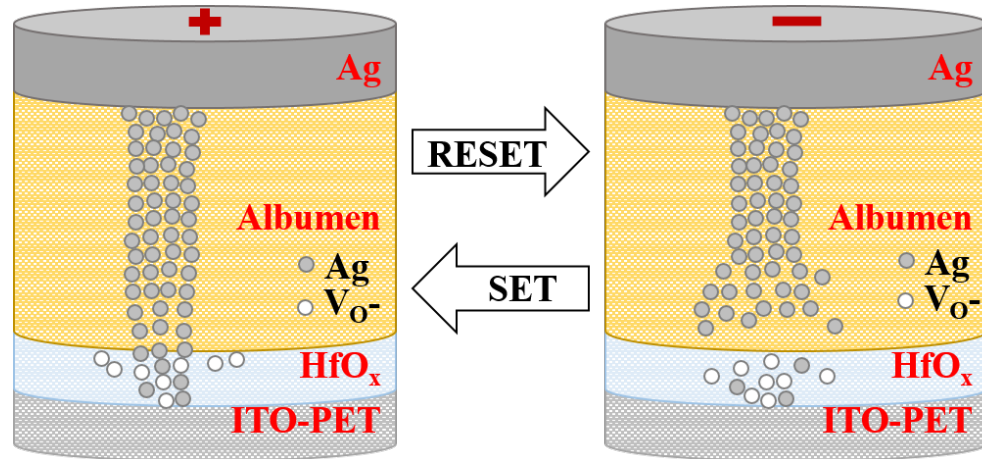


Figure 5.3.6: Schematic representation of the device in (a) SET state where filament is formed by applying positive voltage at the top active electrode, (b) RESET state where the filament has been dissolved by reversing the applied voltage.

When the device is in HRS and a low voltage is applied (set cycle), the current that flows is

due to leakage and thus a slope of < 2 is obtained in this region. In terms of filament formation process at this stage active metal ions have formed ($\text{Ag} \rightarrow \text{Ag}^+ + \text{e}^-$) and are about to start moving towards BE under the influence of the applied electric field. With increasing input voltage the Ag^+ ions start moving towards the BE electrode and formation of metallic filaments starts taking place. The conduction mechanism in this region is estimated by the slope of around 2, which indicates the SCLC mechanism. The region with slope greater than 2 is governed by trap assisted conduction mechanism. The moment a complete filament forms, a sudden jump in current is observed and is only limited by the compliance current. The sudden jump in current marks the transition of the device from HRS to LRS and is known as set cycle. After formation of filament it can be observed that a slope of 1 is obtained, which indicates Ohmic conduction mechanism. Moreover, to switch the device from LRS to HRS a negative voltage is applied and the process is known as reset cycle. Since a metallic filament is already present, a slope of 1 is observed for initial lower negative voltages indicating Ohmic conduction mechanism. With the increase of negative voltage the filament dissolution starts and after some time filament breaks. This can be observed as sudden decrease of current and marks the transition of device from LRS to HRS. Again in this region slope of greater than 2 indicates the trap assisted conduction and slope of 2 implies SCLC mechanism. At lower voltage slope around 1 shows Ohmic conduction mechanism through the insulating medium. The similar conduction mechanism is also applicable to hybrid devices. The silver ions from top electrode and oxygen vacancies from the metal oxide layer, both play their role in hybrid filament formation and dissolution process.

It can also be deduced from double log I - V plot that multiple conduction mechanisms co-exist during switching of the device. One thing that connects these conduction mechanisms is their exponential relation with the gap between conducting filament and opposite electrode, and electric field or applied voltage in the device at that time [Cheong *et al.*, 2021].

5.4 Conclusion

Initially, a low cost, eco-sustainable flexible RRAM device with pristine egg-albumen switching layer is demonstrated. The device has shown excellent switching characteristic with a high current on/off ratio of more than 10^4 and retention time of 10^3 seconds for both flat, and after 7.5 mm bending state. These results clearly indicate that albumen should further be explored for low cost, bio-sustainable, flexible resistive switching devices. Furthermore, devices in bilayer combination with ultrathin HfO_x layer have been fabricated and have shown excellent switching characteristics with high on/off ratio of greater than 10^4 , decent data retention time of 10^3 seconds, reliable multiple cycle switching of more than 300 cycles, with very low switching power of $0.5 \mu\text{W}$ and 3.1 mW for set and reset respectively.