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Flexible Eco-friendly RRAM with Gelatin Switching Layer

4.1 Introduction

Nature-based bio-polymer has been explored as switching layer in RRAM devices for high performance with inherent advantages of biodegradability, biocompatibility and non-toxicity [Rehman *et al.*, 2021]. Due to wide availability, easy processing, low cost, flexibility, and printability, many categories of biomaterials, such as nucleic acids [Qin *et al.*, 2015], proteins [He *et al.*, 2016], plant and animal extracts [Chang and Wang, 2014], have been widely explored for the fabrication of biodegradable and organic resistive switching devices [Scott and Bozano, 2007]. Gelatin is a natural protein that is extracted from animals and insects. It is a suitable material for low cost, solution processed device fabrication, and it can be used as a dielectric material in resistive memory devices [Chang and Wang, 2014], but flexible RRAM devices using active metal as top electrode and based on this natural material were scarcely investigated.

4.2 Devices with Pristine Layer

In this study a high performance flexible electrochemical metallization (ECM) type RRAM devices with biomaterial gelatin as a resistive switching layer with silver (Ag) as top electrode have fabricated and investigated. In ECM RRAM, an active metal is used as a top electrode, thus conductive filament is formed due to migration of active metal ions and this type of RRAM is also known as conductive bridge RRAM [Zahoor *et al.*, 2020]. The device exhibits excellent bipolar switching behavior with longer retention property demonstrating its potential for promising applications.

4.2.1 Experimental Details

Indium tin oxide (ITO) coated polyethylene terephthalate (PET) is used as the flexible substrate for the fabrication of RRAM devices with ITO acting as bottom electrode. Firstly, substrate cleaning was done by using ultrasonic bath in isopropyl alcohol (IPA) for 10 minutes followed by drying in nitrogen blow. A 3 wt% gelatin solution in water was spin coated on top of ITO-PET to obtain a ~ 100 nm thick gelatin layer. Top Ag electrodes (~ 150 nm thick) of diameter of $100\ \mu\text{m}$ were deposited through shadow masks using thermal evaporation with high vacuum of $\sim 10^{-6}$ Torr. Keithley 4200-SCS semiconductor characterization system was used to perform all the electrical characterizations.

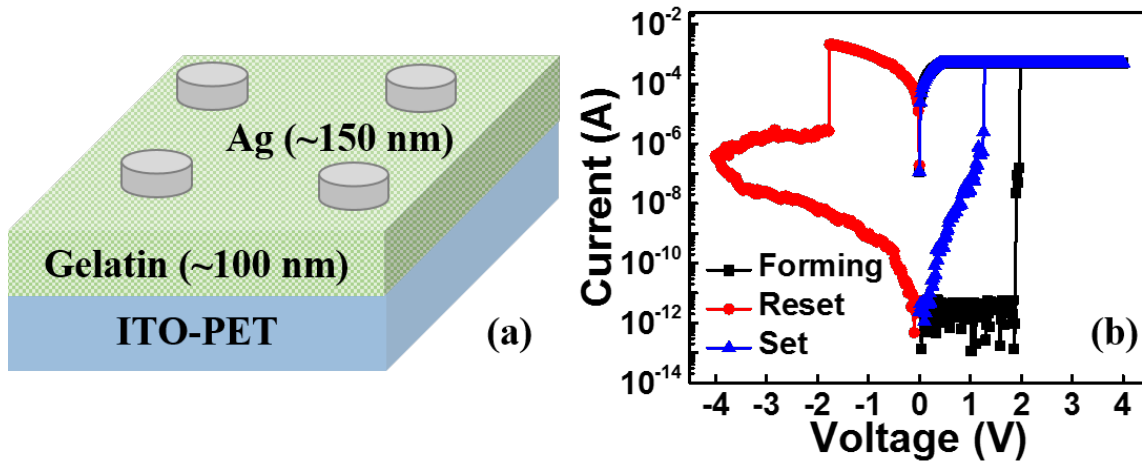


Figure 4.2.1: (a) Schematic of the fabricated device, and (b) Switching characteristics with forming, reset and set curves.

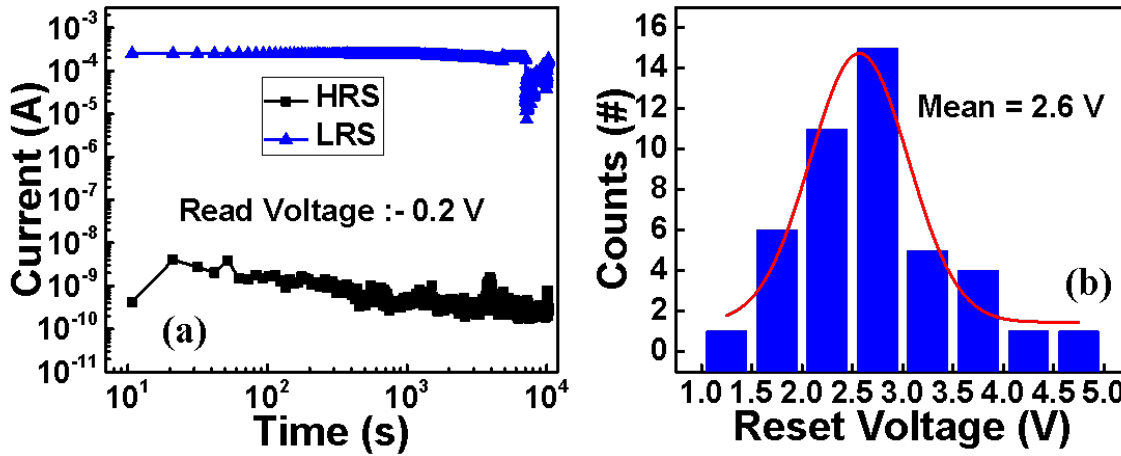


Figure 4.2.2: (a) Retention Characteristics for 10^4 seconds, and (b) Reset voltage distribution and its Gaussian fit.

4.2.2 Result and Discussion

Fig. 4.2.1(a) shows the device schematic of the fabricated device. I-V characteristics of a typical device is shown in Fig. 4.2.1(b) shows. When a positive voltage is applied at the Ag electrode for the first time, filament formation takes place and the forming curve of I-V graph is obtained which requires a higher voltage, i.e. ~ 2 V in this case. At this point, a sudden jump in current can be observed and the device obtains low resistance state (LRS). A compliance current of $500 \mu\text{A}$ was applied to save the device from any damage. The device switches from LRS to high resistance state (HRS) and vice-versa upon applying the corresponding voltages. From the graph one can observe that $V_{\text{FORMING}} = 2$ V, $V_{\text{SET}} = 1$ V and $V_{\text{RESET}} = -2$ V. Fig. 4.2.2(a) shows the retention characteristic of the device. As it can be seen from this characteristics, the device is capable of holding a given state for more than 10^4 seconds without any obvious deterioration in the memory window.

A read voltage of 0.2 V was applied to read the current state and an I_{on}/I_{off} ratio of greater than 10^5 was obtained. Fig. 4.2.2(b) shows the distribution of reset voltage for 45 cycles. The distribution follows the Gaussian curve with the mean value of 2.6 V. Double log I-V curve is widely

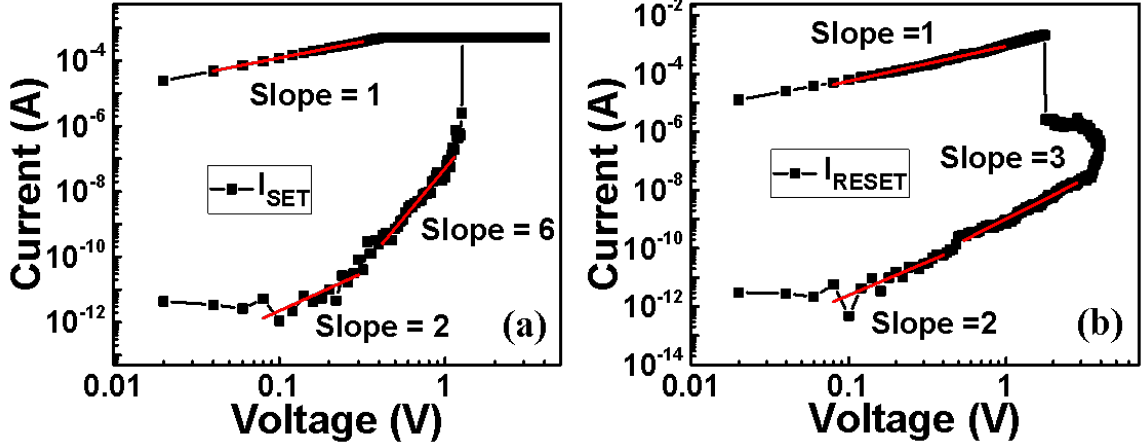


Figure 4.2.3: Double log I-V Characteristics for (a) SET and (b) RESET cycle.

used to understand the conduction mechanism of the device both in set and reset process [Varun *et al.*, 2020]. Fig. 4.2.3(a) shows the $\log(I)$ vs $\log(V)$ curve during set cycle with different slopes in different regions. The device is initially in the HRS and thus very small current is obtained initially. A slope of 2 can be observed at this initial stage indicating Mott-Gurney's conduction mechanism [Cheong *et al.*, 2021]. As the voltage is increased the trap-controlled space charge limited conduction (SCLC) mechanism comes into picture and a higher slope is obtained. At set voltage a complete filament formation occurs and thus a jump in current is observed. Now, since the filament is there, the device shows ohmic conduction ($I \propto V^1$), till it changes its state to HRS. Similar observations can be made from Fig. 4.2.3(b) for reset cycle. A schematic of conduction

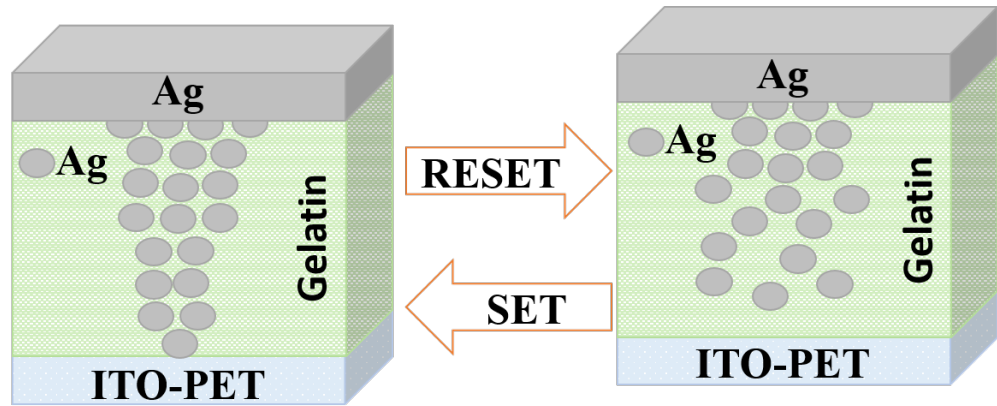


Figure 4.2.4: Schematic demonstrating the switching mechanisms.

mechanism is shown in Fig. 4.2.4 to illustrate the switching mechanism in the device. When a positive voltage is applied to the Ag electrode, silver gets oxidized and breaks into silver ion i.e., $Ag \rightarrow Ag^+ + e^-$. These Ag^+ ions move towards the bottom electrode under the influence of the

downwards pointing electric field and get reduced to Ag at the bottom electrode. This process is continued till a conducting filament forms connecting both the electrodes. At this stage, the device is in LRS. When a sufficiently high negative voltage is applied at the top electrode, the filament dissolves, and the device enters into HRS region.

4.3 Flexible Hybrid Bilayer Devices

Flexible resistive random access memory (RRAM) devices with biomaterial gelatin and ultra-thin HfO_x hybrid bilayer dielectric exhibiting excellent resistive switching behaviour are demonstrated. The secondary HfO_x layer has enhanced the device performance by regulating the formation and rupture of conducting filament [Sassine *et al.*, 2019]. The gelatin layer provides an advantage of better flexibility and mechanical strength. The devices exhibited excellent switching characteristics with a memory window of more than 10^5 and data retention time of 10^4 seconds. The flexible devices have also exhibited reliable switching performance without any obvious degradation at different bending radii.

4.3.1 Device Fabrication

Indium-doped tin oxide (ITO) coated Polyethylene Terephthalate (PET) was used as a substrate to fabricate the devices. The substrates were cleaned using standard cleaning process of ultrasonic bath in isopropyl alcohol (IPA) for 10 minutes and then dried with Nitrogen (N_2) blow. A 5 nm thin HfO_x layer, using Savannah S200 atomic layer deposition (ALD) system with Tetrakis(dimethylamido)hafnium(IV) and water as precursors, was deposited over the 130 nm ITO bottom electrode (BE) at 75°C . Gelatin solution was prepared by mixing 120 mg of gelatin powder with 4 ml of deionized (DI) water and stirred continuously for 2 hrs at 60°C to make it uniform. This solution was spun at 2000 rpm for 60 seconds over HfO_x and annealed at 50°C for 1 hr to remove the solvent, which resulted in a film thickness of 100 nm. Finally, Ag as top electrode (TE) with 150 nm thickness was deposited using high vacuum thermal evaporation system through a shadow mask with circular patterns of 100 μm diameter. The HfO_x precursor and gelatin powder are procured from Sigma Aldrich and used without any further purification. Burker's DektakXT profilometer was used to measure the thickness of the materials. Keithley 4200 semiconductor characterization system has been used for performing electrical characterizations.

4.3.2 Result and Discussion

Schematic of the fabricated device along with its atomic force microscopy (AFM) result and digital image is shown in Fig. 4.3.1(a)-(c) respectively. The surface morphology results from AFM shows that the gelatin film is very smooth with a RMS roughness around 3 nm, indicating that gelatin makes high quality thin films which is suitable for device fabrication. Fig. 4.3.2(a-c) shows the switching characteristic, endurance and retention of the pristine or unbent device. The switching characteristic of the devices is carried out by applying a continuous sweep voltage of $0 \rightarrow V_{max} \rightarrow 0 \rightarrow -V_{max} \rightarrow 0$. One can observe that there is a forming curve with $V_{forming} = 2.8\text{ V}$ in the Fig. 4.3.2(a), it is obtained when a voltage sweep is applied to a freshly prepared sample for the first time. During forming, the formation of filament occurs for the first time and thus a higher voltage is required. At the end of forming i.e., when the complete filament is formed, a sudden jump in current is observed and the device is said to have entered a low resistance state. After this the device remains either in low resistance state (LRS) or high resistance state (HRS) at any given time, but the state before forming can never be achieved as there will always be traces of

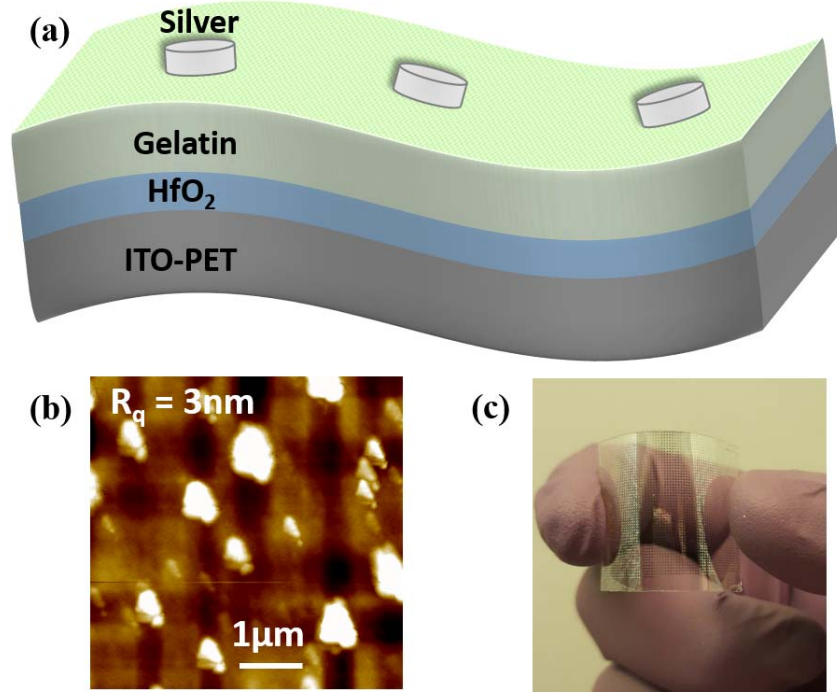


Figure 4.3.1: (a) Device Schematic, (b) AFM image, and (c) Digital image of the fabricated devices.

filament present in the insulating or dielectric layer. A compliance current is required to protect the device from damage when it switches from HRS to LRS. The switching behaviour of the device is obtained while keeping the total current limited to $500\mu\text{A}$ to prevent permanent dielectric breakdown of the device. Fig. 4.3.2(a) shows that the devices exhibited excellent switching behaviour with remarkably low on-current of $1\mu\text{A}$ and V_{set} and V_{reset} of 2.2 and -2 V, respectively. Fig. 4.3.2(b) shows the endurance characteristic of the device, where the device showed decent switching characteristic with a memory window around 10^5 . It shows that the device has a distinguishable LRS and HRS even after continuous switching or multiple cycle operation. Retention characteristic of the device is shown in Fig. 4.3.2(c), where a read voltage of 0.2 V has been applied to both the states one by one to observe any degradation in memory window. It can be observed that even after 10^4 seconds, no sign of degradation is present, which indicates that the device can hold its state for a longer period of time. The I-V characteristic of multiple devices are shown in Fig. 4.3.2(d), which indicates that a good switching characteristic is obtained from other devices as well, with some device to device variation. An increase in current can be observed in the endurance plot (Fig. 4.3.2(b)), this may be attributed to the injection of more Ag into the switching layer after each cycle. As there will be more Ag disbursed in the medium in HRS state, a higher off current is observed. In the retention plot (Fig. 4.3.2(c)) a reduction of current is observed which indicates that the read voltage is low enough to allow dielectric relaxation over longer period of time. The conduction mechanism in a RRAM device is yet to be fully understood and the double log I-V characteristics are used to estimate the conduction mechanism in a given region.

Fig. 4.3.3(a) shows the logI-logV characteristic of the device during set process. In lower voltage region a slope of ~ 1 is observed because of thermally generated minority carriers conduction. Before the formation of filament a slope of ~ 2 is obtained, indicating space charge limited conduction (SCLC) mechanism in this region. In this region one can observe that there are irregularities present and thus a large region is considered to calculate the slope. The region with a positive

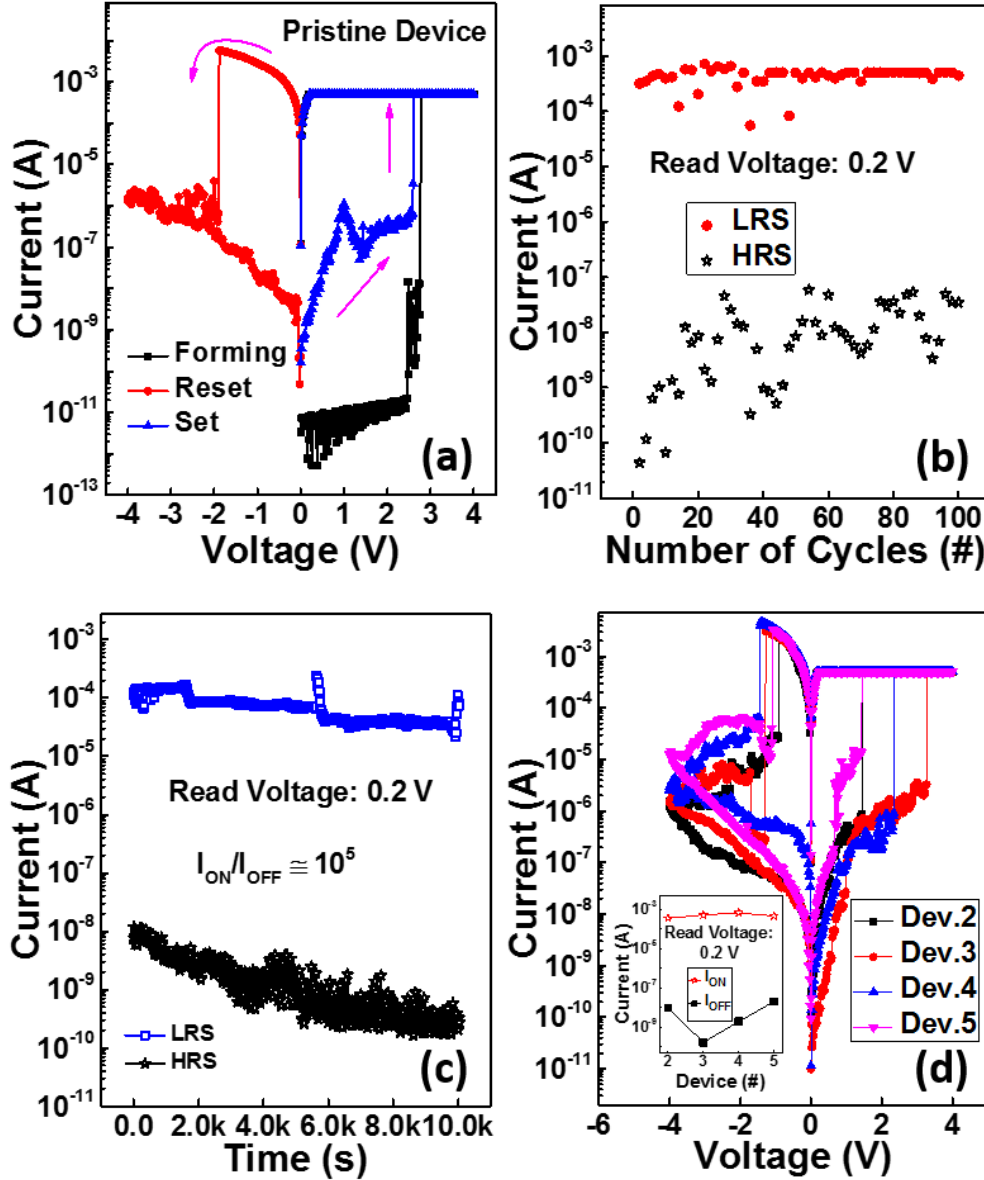


Figure 4.3.2: (a) I-V Characteristics, (b) Endurance, (c) Retention and (d) Multiple device switching characteristics, inset shows I_{on} and I_{off} of different devices in pristine state.

slope greater than 2 indicated trap filled assisted conduction and thus the formation of Ag filament. While the negative slope indicates the breakage of filament which can be attributed to the movement of oxygen ions during this process. After the formation of filament slope of 1 indicates the Ohmic conduction which supports the notion that a metallic filament has been formed. Similarly, Fig. 4.3.3(b) shows the double log I-V characteristics during reset process, as initially there is a conducting filament, during initial voltage range a slope of 1 is obtained indicating the ohmic conduction. After the device reaches reset state, the filament dissolves and slope of 3 indicates the conduction mechanism due to trap filled limited conduction mechanism. Further increase in voltage dissolves the filament more and thus no increase in current with the increase in voltage is observed. When the applied voltage is reduced at lower voltage, the supplied power becomes insufficient to induce any change in the material and thus the device shows a near linear I-V rela-

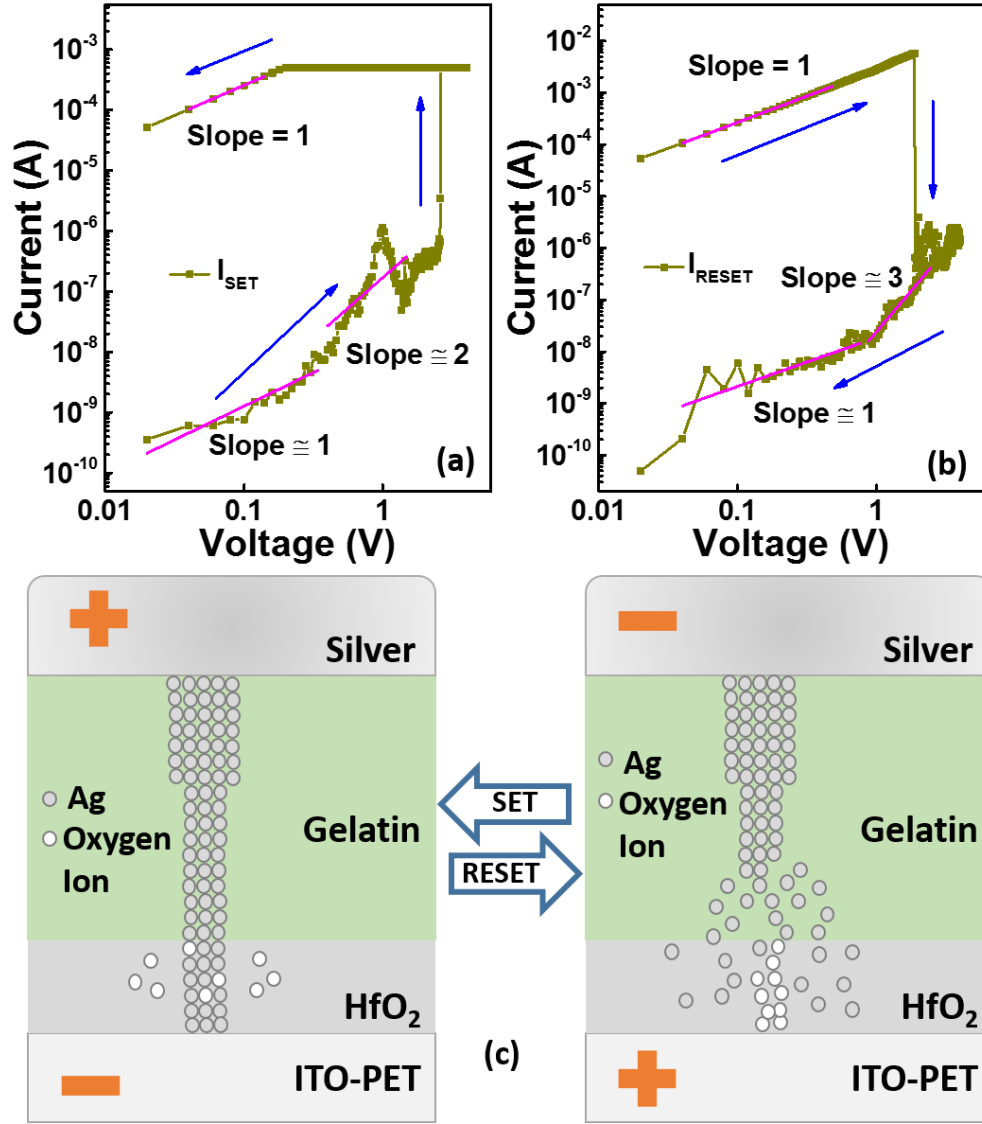


Figure 4.3.3: LogI-LogV of (a) set and (b) reset region. (c) Schematic of conduction mechanism. All are for pristine state device.

tionship with slope around 1 and remains in a high resistance state. The schematic of conduction mechanism is illustrated in Fig. 4.3.3(c) during both set and reset process. During set process a positive voltage sweep is applied to the top electrode which oxidizes the Ag electrode to Ag^+ ion ($Ag \rightarrow Ag^+ + e^-$). These ions start migrating towards the bottom electrode due to the electric field present in that region. The moment these ions come in contact of bottom electrode they get reduced to Ag atom ($Ag^+ + e^- \rightarrow Ag$) and the formation of conducting filament starts. This process continues to take place with the tip of filament acting as the virtual bottom electrode, till a filament connecting both the electrodes forms. The movement of oxygen ions plays a very important role during set and reset process. Upon application of electric field, the oxygen ions present in HfO_x layer move in opposite direction to that of Ag ions due to having opposite charge [Wong *et al.*, 2012]. This movement may disturb or hinder the Ag filament formation process and can cause a small decrement of current during set process. The exact mechanism of filament forma-

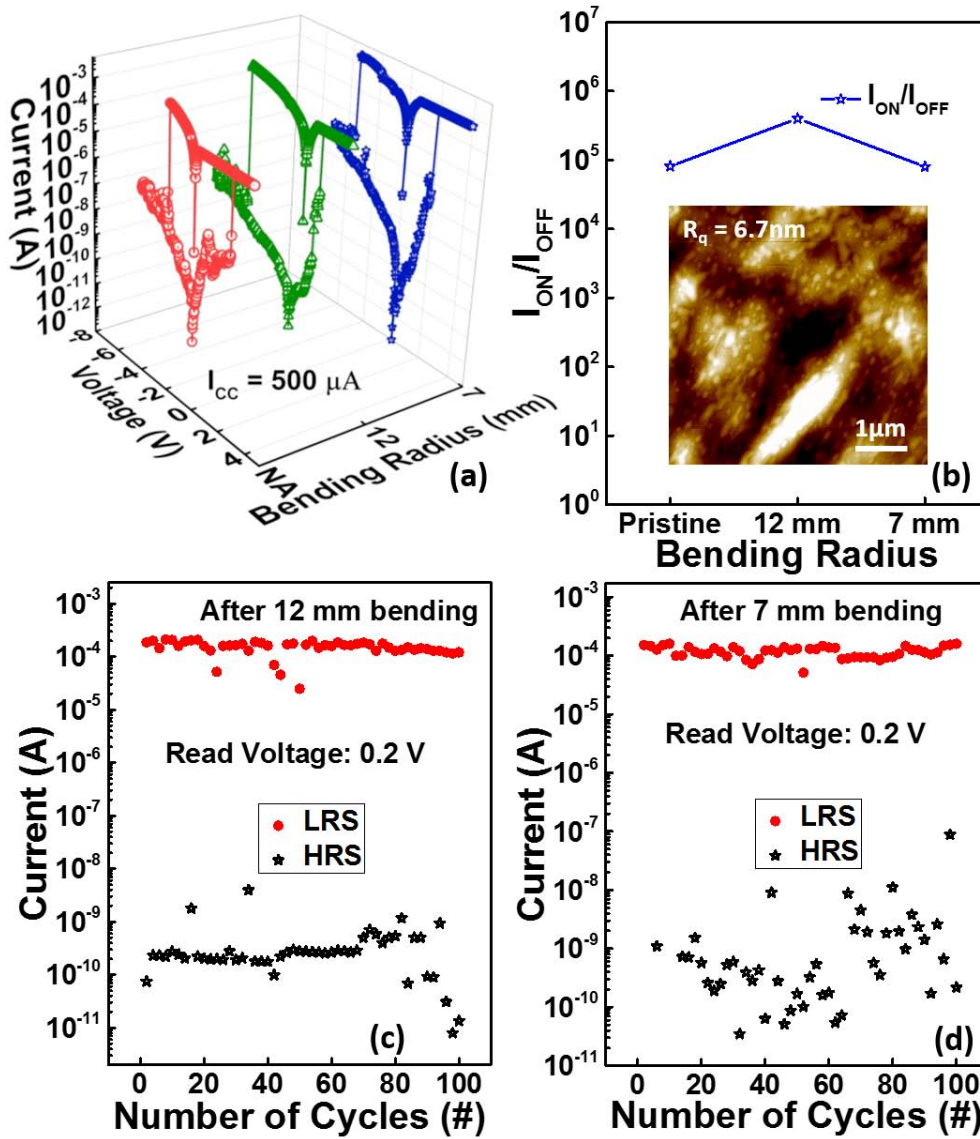


Figure 4.3.4: (a) I-V Characteristics at different bending radii, (b) I_{on}/I_{off} at different bending radii. Inset shows AFM image of bent device, (c) Endurance after 12 mm bending and (d) Endurance after 7 mm bending.

tion and dissolution in hybrid RRAMs is not very clear and still under investigation [Sassine *et al.*, 2019],[Tsai *et al.*, 2021]. The moment a complete filament forms, a sudden jump in current can be observed in I-V characteristics, indicating that the set voltage ($V_{set} = 2.2 \text{ V}$) has been reached and device is now in LRS. In this region a filament is there for conduction, this supports the results from double log I-V characteristics where a slope of 1 is obtained after reaching set voltage. To change the state of the device to HRS, a negative bias voltage sweep is applied to the Ag electrode. When a negative voltage sweep is applied, after some voltage, the Ag atom from the filament first oxidizes and then start moving towards the top electrode. This gives rise to dissolution of filament in the insulating layer which can be observed in I-V curve as the region where the current suddenly drops and HRS is obtained.

After characterizing the sample in pristine state, the sample was subjected to 0.53% and 0.91%

strain by first bending at 12 mm followed by 7 mm radius for 10 minutes and all the electrical characterizations were done. The percentage strain is calculated as

$$Strain(\%) = \frac{t_s + t_f}{2R_{bending}} \times 100 \quad (4.1)$$

where t_s and t_f are thickness of substrate and film, and $R_{bending}$ is the bending radius [Suo *et al.*, 1999]. Fig. 4.3.4 shows the resistive switching characteristics, I_{on}/I_{off} ratios and endurance characteristics of the device at different bending radii. From Fig. 4.3.4(a) it can be observed that a lower set voltage, $V_{set} = 1$ V for 12 mm bent device and $V_{set} = 1.5$ V for 7 mm bent device, compared to pristine device is obtained. The compliance current was kept as $500 \mu A$ for all I-V measurements. The off-current has also reduced to approx. 10 nA, thus increasing the memory window from the previous pristine state. Fig. 4.3.4(b) shows the I_{on}/I_{off} of the devices at different bending radii and a ratio of $\geq 10^5$ can be observed in all cases with 12 mm device showing a slightly higher ratio. The current on-off ratio is calculated from the retention characteristics of the devices carried out in similar manner as for pristine device in Fig. 4.3.2(c). The inset of Fig. 4.3.4(b) shows an AFM image of the bent device showing increased surface roughness of ~ 7 nm and stretched surface. The endurance characteristics of the 12 mm bent device is shown in Fig. 4.3.4(c) shows that even after 100 cycle of switching a memory window of greater than 10^5 is maintained at the reading voltage of 0.2 V. Fig. 4.3.4(d) shows the endurance characteristic of the 7 mm bent device, a more distributed HRS is present in this case. One can also observe that in endurance plots, the off-current has reduced to the range of nano ampere. These results indicate that the bending has not degraded the sample and the device is showing excellent switching characteristics even after 7 mm bending radius. As it can be seen from these results, almost unchanged switching behaviour of these flexible RRAM devices were obtained after these bending conditions. The primary reason for this may be attributed to the perpendicular direction of the filament to the strain direction, causing least effect on the current conduction. It is important to note that though there is a change in the length of the surface of the device upon bending, the thickness of the device is least impacted upon bending. In this situation, the length of the filament remains almost unchanged, leading to stable switching behaviour.

The double log I-V characteristics in Fig. 4.3.5(a) and (b) shows the conduction mechanism of the 7 mm bent device in set and reset region respectively. Same as pristine device an initial slope of around 1 can be attributed to the thermally generated minority carrier conduction. The slope of ~ 8 before set region (Fig. 4.3.5(a)) indicates the SCLC's trap filled limited conduction mechanism in that region. After the filament has been formed a slope of 1 indicates the ohmic conduction and supports the fact that a metallic filament has been formed. Similarly in reset region (Fig. 4.3.5(b)) as long as there is a filament slope of 1 can be observed. After the filament dissolves or ruptures a slope of approx. 2.5 indicates SCLC mechanism. Fig. 4.3.5(c) shows the schematic of the conduction mechanism during set and reset process. The conduction mechanism will be similar to that of pristine device, except that now the film has undergone mechanical stress. Same as pristine device during set process the conducting filament forms due to migration of Ag ions and oxygen ions. As the sample was bent, the insulating layer has experienced stress and thus some temporary or permanent deformations/ defects has been introduced in the film and the size of deformations/ defects can be related to the bending radius, marked in red oval in fig. 4.3.5(c). These stress induced deformations in the film act as a predefined path for the movement of ions during formation and dissolution of the filament. Since a path is already there for the filament formation, it takes lower power for the filament formation or set process and thus a lower set voltages can be observed for 7 mm and 12 mm bent devices in Fig. 4.3.4(a) compared to pristine device

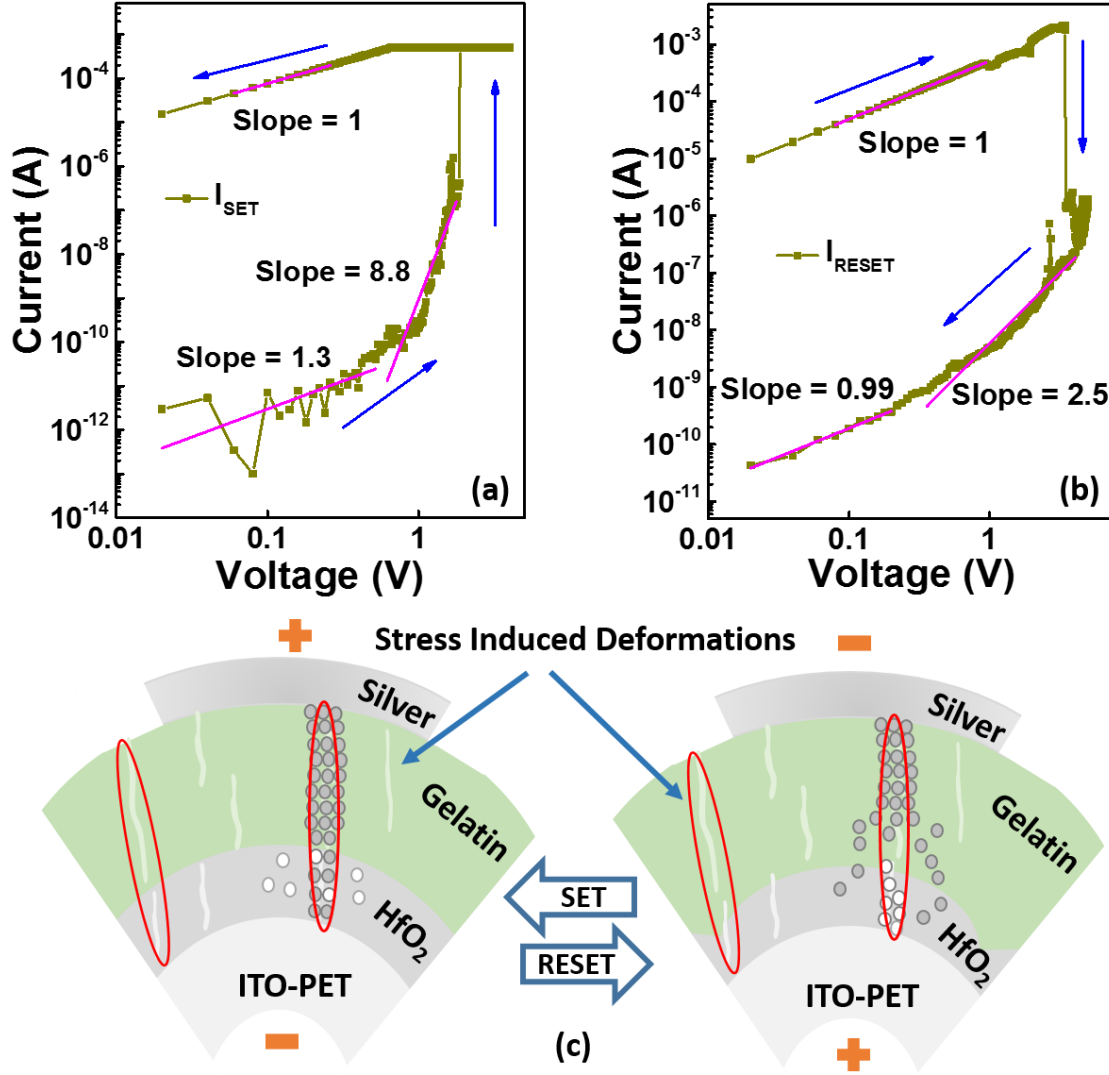


Figure 4.3.5: LogI-LogV of (a) set and (b) reset region. (c) Schematic of conduction mechanism. All graphs are for bent device.

(Fig. 4.3.2(a)). The induced defects also play an important role during the reset process. When a significantly high negative voltage is applied to the Ag electrode, the dissolution of filament starts and Ag ions start moving towards Ag electrode. When there was no predefined path this movement of ions was random to a large extent at individual level. Thus it may happen that even after filament dissolution, the ions or vacancies are present in nearby area or defect locations and results in higher off current. While during the reset process with stress induced defects, most of the ions tend to move in the predefined path and thus leaving lesser number of ions for conduction in reset state. This can be verified by the lower off current in endurance characteristics of the bent devices (Fig. 4.3.4(c-d)) as compared to that of pristine device (Fig. 4.3.2(b-c)), where a change of approx. 10 times can be observed. Moreover, though the electrical stability in environment and humidity were not performed in this study, gelatin based memory devices have shown almost zero variation in current on-off ratio when kept in atmospheric environment (relative humidity: 70% to 88%) even after 3 weeks of exposure, and similarly a negligible effect of temperature till 80 °C [Ge *et al.*, 2017].

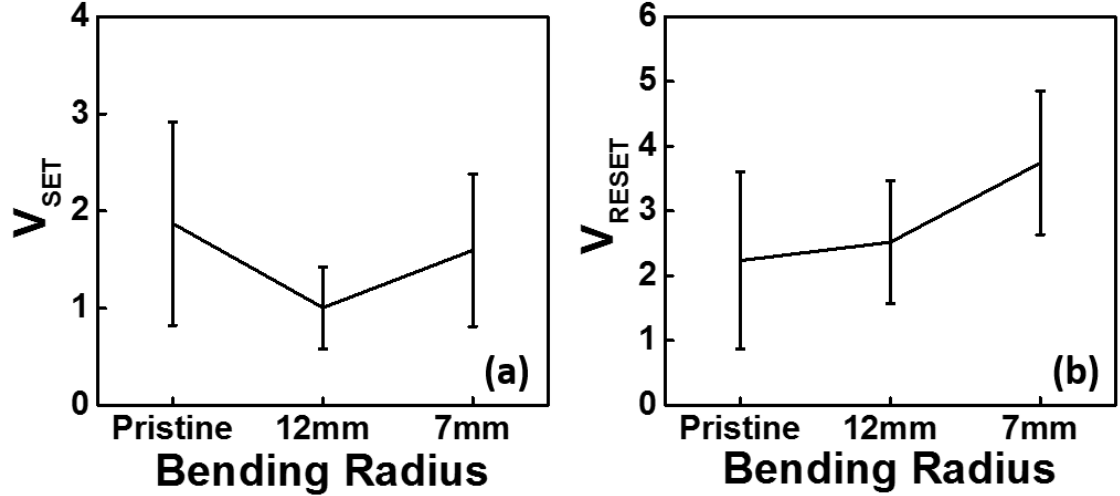


Figure 4.3.6: Distribution of (a) set voltage (V_{set}) and (b) reset voltage (V_{reset}) at different bending radii.

Fig. 4.3.6 shows the distribution of set voltages and reset voltages at different bending radii. The mean and standard deviation of the set voltage (Fig. 4.3.6(a)) has reduced after bending, indicating that the filament formation is assisted. This supports the above discussed conduction mechanism and presence of stress induced deformations or defects in the insulating layer after bending, which assists the migration of ions during filament formation. The distribution of V_{reset} in Fig. 4.3.6(b) shows that the mean reset voltage is increasing with the decrease in bending radius. This indicates that the filament breakage or dissolution takes more power implying that a thicker filament is present. This is again in-line with the suggested filament formation mechanism in the bent device. A small increase in the set voltage at 7 mm bending may be attributed to the high reset voltage at that bending radius, as a higher reset voltage requires a higher set voltage and vice-versa.

Table 4.3.1 shows the comparison of some organic (gelatin based) and hybrid bilayer memory devices. The comparison is based on the parameters like I_{on}/I_{off} ratio, number of reported cycles, set and reset power, and whether the reported device is flexible or not. In the reported flexible devices the change in current ratio after bending is also considered, as it shows the mechanical stability of the film. The required set and reset power has been calculated by considering current and voltage just before the sudden change during respective process. The table shows that even after bending, the memory devices in this study performs better than other reported memory devices using similar materials or combination of materials.

4.4 Conclusion

Initially, RRAM device fabricated with biodegradable gelatin as the insulating layer exhibiting high current on/off ratio and retention is demonstrated. The device showed excellent memory characteristics, and retention of data more than 10^4 seconds shows that it has good reliability over a longer period of time. The high I_{on}/I_{off} ratio of greater than 10^5 indicates very distinct on and off states suitable for reliable memory applications. These preliminary results show that biomaterial gelatin is a suitable material for exploration of high performance RRAM devices for future eco-sustainable electronics.

Table 4.3.1: Performance Comparison of Gelatin/HfO₂ device with reported pristine and hybrid devices

S. No.	Insulating Layer	I_{on}/I_{off}	No. of Cycles	P_{set} & P_{reset}	Flexibility Study	Year; Ref.
1.	Gelatin	$\geq 10^5$	120	5.6 μ W & 192 mW	No	2014; [Chang and Wang, 2014]
2.	Gelatin	$\geq 10^3$	80	8 μ W & 45 mW	No	2018; [Ge <i>et al.</i> , 2017]
3.	Al chelated Gelatin	$\geq 10^4$	60	3.6 μ W & 300 mW	No	2015; [Chang and Wang, 2015]
4.	Self Healing Gelatin	$\geq 10^5$ ($\sim 10^3$ @ 7 mm)	150 (40 after bending)	7 μ W & 24 mW	Yes	2020; [Chang <i>et al.</i> , 2020]
5.	HfO ₂ /MoS ₂ -Pd	$\geq 10^3$	200	16 μ W & 10 mW	No	2018; [Wang <i>et al.</i> , 2018]
6.	Gelatin/HfO ₂	$\geq 10^5$ ($\geq 10^5$ @ 7 mm)	100 (100 after bendings)	1.25 μ W & 10.53 mW	Yes	This Work

Thereafter, a high performance flexible RRAM device with gelatin and HfO_x hybrid bilayer has been presented. These devices have demonstrated excellent and reliable switching characteristics with an I_{on}/I_{off} ratio of greater than 10^5 and have not shown any sign of degradation during 10^4 seconds of data retention. The devices have retained this electrical characteristics and memory window even after undergoing extreme bending till radius of 7mm. A reduction in set voltage is observed after bending the device which can be attributed to the formation of stress induced deformations or defects. These results indicate that the organic/inorganic hybrid bilayer RRAMs can be a promising candidate for high performance flexible memory devices.