

Amorphous BaTiO₃ Thin Film Based Write Once Read Many Memories

In this chapter, Write once read many times (WORM) memory device based on resistive switching mechanism of sputtered amorphous BaTiO₃ (am-BTO) thin film in a metal-insulator-metal structure is fabricated on FTO coated glass substrate with silver top contact. Fabricated devices show the switching from a low-conductance state to a high-conductance state with the formation of conductive filament(s) in the am-BTO layer. The memory characteristics are investigated as a function of the thickness of the am-BTO layer, which is determined by varying the deposition time. Devices with all deposited thicknesses show data retention for more than 4000 seconds and 300 reading cycles. The device with 180 nm thickness shows a high on-off ratio of the order of 10⁶. The fabricated WORM devices exhibit good reading endurance and data-retention characteristics.

Further in this chapter, the effect of deposition temperature on surface morphology and write once read many times (WORM) resistive switching properties of RF sputtered BaTiO₃ (BTO) thin films has been demonstrated. A conventional sandwiched structure was used to fabricate the memory cell with FTO as the bottom electrode and silver as the top electrode. The devices exhibit switching from a high resistance state (HRS) to a low resistance state (LRS) with the conductive filament(s) formation through BTO active layer. The switching performances are investigated for different devices with different deposition temperatures, varying from room temperature (RT) to 450°C. All the devices are characterized for a voltage sweep of -1.5 V to 1.5 V with 12000 pulses for retention and 300 write-read erase read cycles. Shifting in the switching voltage to a lower value from 1.31 V (RT) to 0.49 V (450°C) is recorded with the increased deposition temperature. We observe the highest on-off ratio of 5.9×10⁶ for the sample deposited at room temperature and 0.9×10⁴ for the sample deposited at 450°C. The write-read erase read characterizations for over 1000 cycles were carried out for all four devices to test the device reliability and observe the stable read current over the period irrespective of erase cycles. The fabricated devices show stable and reliable reading endurance and data retention characteristics for more than 12000 s.

3.1 Introduction

With the rapid digitalization and widespread use of the internet of things, non-volatile memory also received a lot of attention for its use in electronic devices and logic storage units, as current Si-based electric memories are hitting their downscaling limits [Borghetti et al., 2010; Cho et al., 2011; Yang et al., 2013]. In such a scenario, resistive switching random access memory (RRAM) seems to be a good candidate for the next-generation memory technology due to its low power consumption, high-density integration and fast switching operation [Chen et al., 2017; Ielmini, 2016; Sawa, 2008]. Resistive switching random access memory has been studied for different types of memory characteristics such as write once read many (WORM) [de Brito et al., 2008], Dynamic random-access memory (DRAM) [Ling et al., 2006] and flash memory [Zhuang et al., 2010]. Among all types of resistive switching characteristics, WORM shows the permanent transition in its resistance state while applying a certain electric field (i.e. writing) across the device terminal. Hence the stable memory state after writing makes it a prime choice for applications where we need a stable and long-term archival of information, images and videos such as RF identification tags and other non-editable data devices [Möller et al., 2003;

Smith et al., 2004]. With the ability of stable and permanent storage WORM has many added advantages like low power consumption, high performance, ease of fabrication and integration to be used as the replacement of slow, expensive and bulky mechanical drives used in the conventional system for rapid and large data archival. In recent years a variety of materials have been studied for the realization of WORM characteristics which includes organic (polymer, semiconductor, hybrid and supermolecules) [Mukherjee et al., 2007; Nguyen et al., 2016; Shi et al., 2009; Yun et al., 2009] and inorganic (ZnO, NiO, Al-rich Al_2O_3 , HfO_2 and graphene oxide) [Li et al., 2015; Ooi et al., 2017; Qi et al., 2011b; Yu et al., 2012b; Zhu et al., 2009] materials. BaTiO_3 thin film-based resistive switching devices have been extensively studied with different substrates, deposition techniques and temperatures [Razi et al., 2021]. Metal oxide thin films are widely accepted for WORM application due to their environmental and long-term stability. There are many critical challenges (e.g. high uniformity, stable operation, high On-Off ratio and low voltage operations) associated with memory devices that need to be addressed for their practical application. Above mentioned issues can be suppressed by various methods of optimization like doping and deposition parameter alteration. Among the all methods the change in deposition parameter is the most suited method to get an optimum device performance. To alter the memory performance there are many factors, which can play a significant role like deposition time, argon to oxygen ratio and deposition temperature. Further, the high voltage writing operations and high switching time in the reported WORM devices have been demonstrated is need to be addressed to get optimum performance of the devices [Liu et al., 2014; Qi et al., 2011b; Yu et al., 2012a].

In the present study, we report the first ever WORM characteristics of RF sputtering deposited amorphous Barium titanate (BTO) deposited on FTO-coated glass. The thickness of the BTO layer is varied by varying the deposition time by keeping other parameters the same. Prepared samples were characterized using AFM. Simple device configuration Ag/am-BTO/FTO structures on glass are investigated as the function of thickness for WORM. For these devices, we perform the memory characterization and we observe the low switching voltage ($\leq 1.5\text{V}$), high on-off ratio ($\approx 10^6$), long-term data retention and good reading capability.

Further, the next section demonstrated the BTO thin film-based WORM devices fabricated on FTO with low voltage switching. The switching characteristics of the fabricated devices were analyzed as a function of deposition temperature, which was varied from room temperature to 450°C while keeping other parameters constant. The surface morphology of prepared thin films was analyzed using atomic force microscopy. Conventional metal insulator metal (MIM) configuration, Ag/BTO/FTO structured devices on glass were fabricated and investigated for WORM. We observed the shifting in switching voltage towards a lower side from 1.31 V to 0.49 V as the deposition temperature increased. All the devices characterized were stable during the long-term data retention and through hundreds of reading cycles. These results confirm the potential of BTO thin film as a WORM memory application with low voltage and reliable operations where the room temperature growth of BTO thin film makes it suitable for flexible electronics.

3.2 Synthesis and Characterization of BaTiO_3 Powder Prepared for Target

Here, The stoichiometric ratio of BaCO_3 (99.98%, Sigma Aldrich) and TiO_2 (99.8%, Sigma Aldrich) were used as starting material and mixed thoroughly with the help of a mortar pestle in an ethanol medium. The mixed compound was annealed at 1000°C for 5hrs and pressed into 2 inches die to form a sputtering target using a hydraulic press. The prepared pellet was sintered at 1300°C for 5 hours at atmospheric conditions. The material synthesis and target preparation process flow graph is given in figure 3.1.

The synthesized BaTiO_3 powder was characterized using the XRD system to determine the crystalline structure as shown in figure 3.2. The sample was scanned for a range of 2θ from 20° to 80° at a scan rate of 1° per minute. The obtained XRD spectra confirmed the perovskite structure of the material as it shows matches with JCPDS no. #892475 revealing the formation of

the cubic phase. The most intense peak (110) is found at $2\theta = 32.17^\circ$. The peaks at $2\theta = 22.20^\circ$ (100), 32.17° (110), 38.88° (111), 45.59° (200), 50.82° (210), 56.12° (211), 65.77° (220), 70.33° (300), 74.78° (310) and 79.01° (311) confirm the formation of perovskite barium titanate.

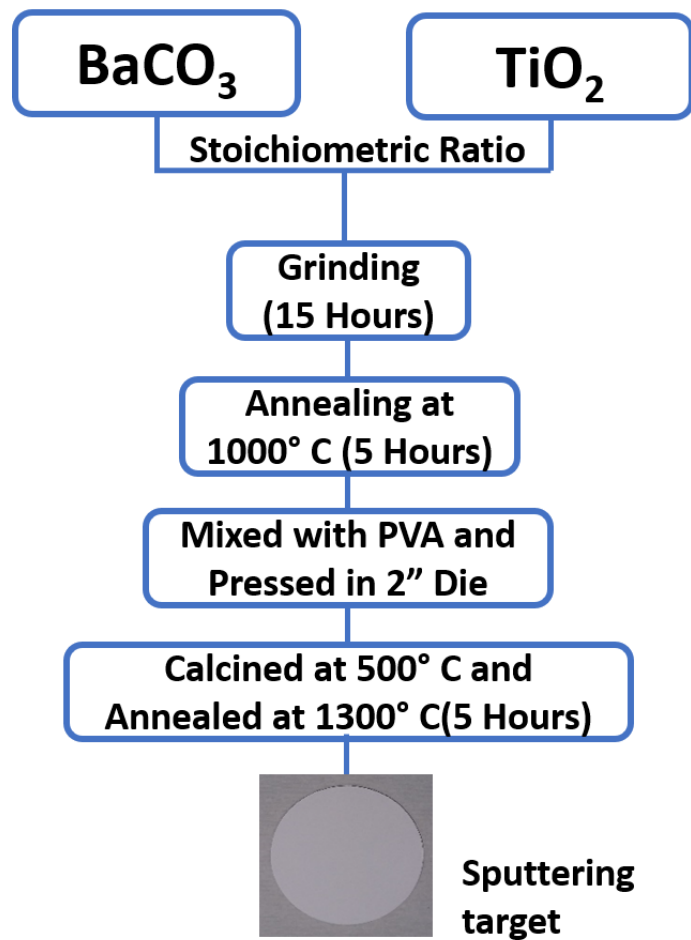


Figure3.1: Schematic representation of process flow for the synthesis of BaTiO₃.

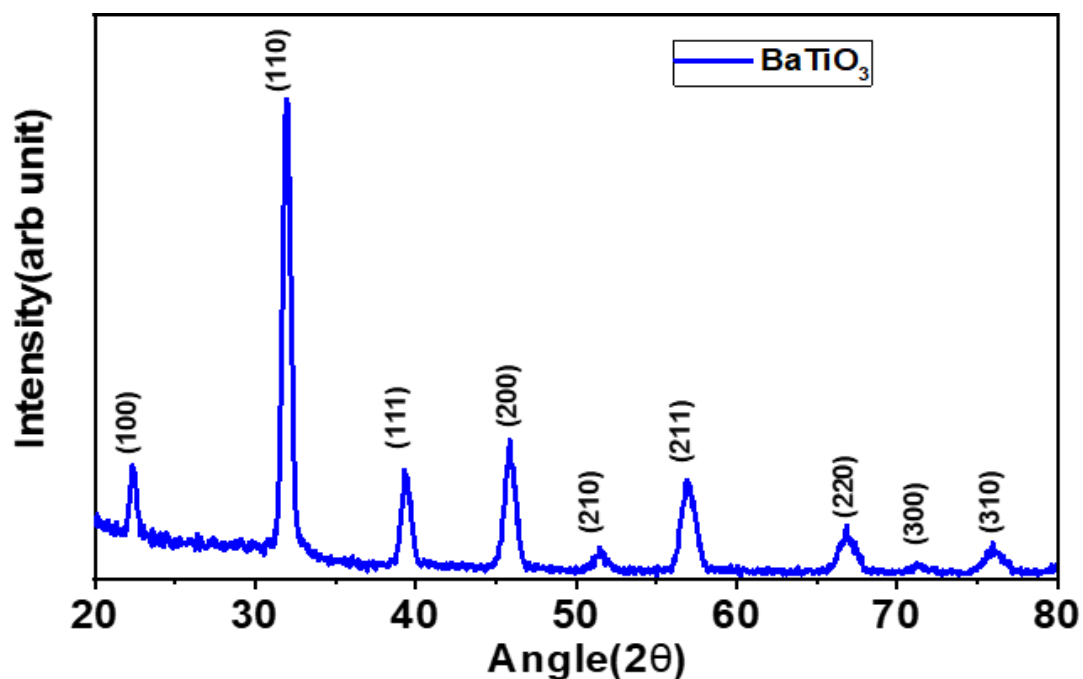


Figure3.2: XRD pattern of synthesized BaTiO₃ Powder.

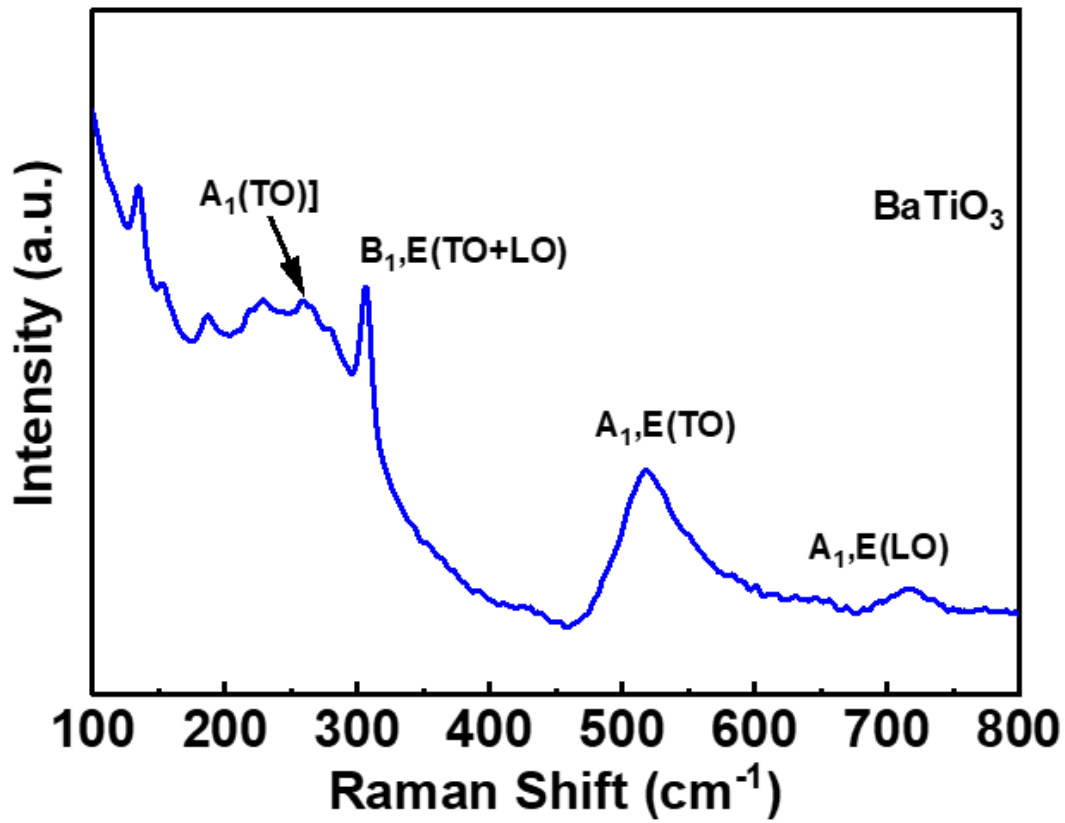


Figure 3.3: Raman spectra of BaTiO₃.

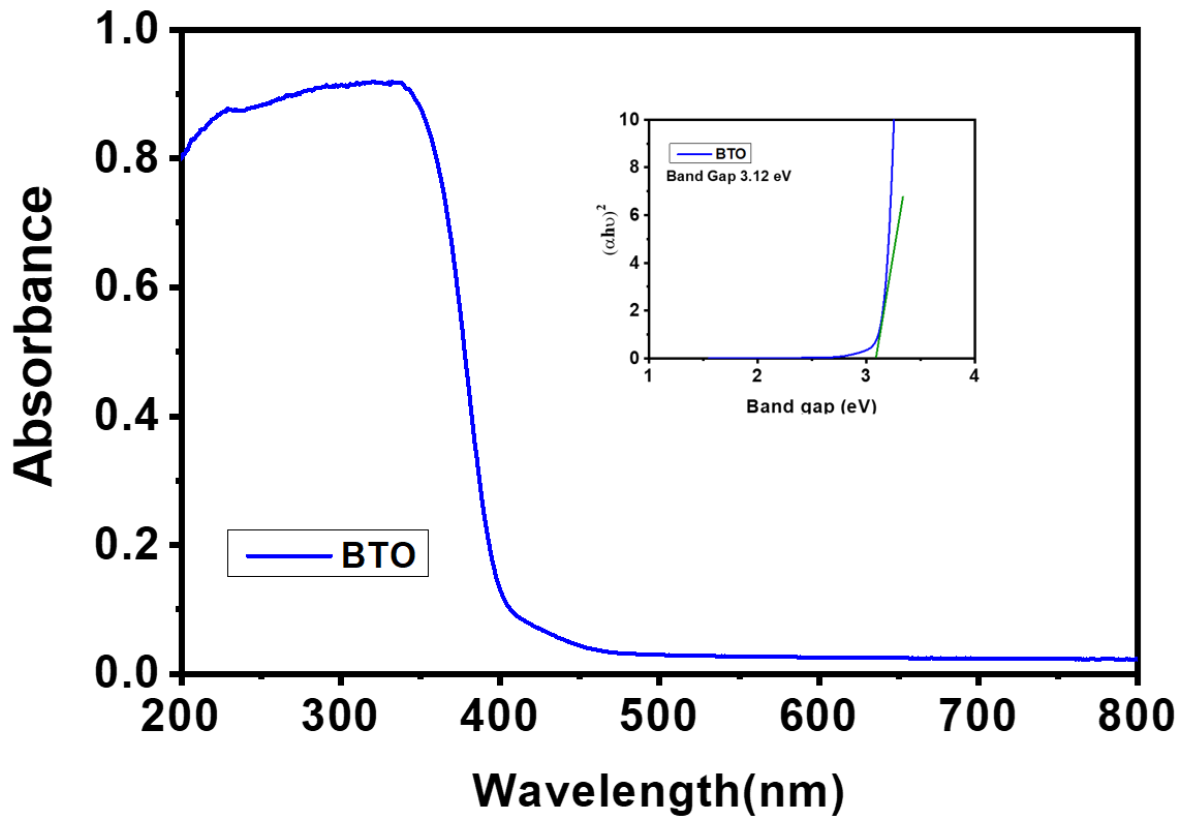


Figure 3.4: UV-Vis spectra of BaTiO₃ Powder and Tauc's plot for band gap (inset).

Further, the BaTiO₃ powder was characterized using Raman spectroscopy which provides information about local symmetry or short-range structure. Figure 3.3 shows the

Raman spectra of synthesized BaTiO₃ powder. The sharp peak at 307.7 cm⁻¹ confirms the B1 and E symmetries of transverse optical (TO) and longitudinal optical (LO) phonon modes [B1, E(TO+LO)]. The high-frequency band at 518 cm⁻¹ confirms the [A₁, E(TO)] mode and other dominant bands at 258 cm⁻¹ and 715 cm⁻¹ represents the [A₁(TO)] and [A₁, E(TO)] modes respectively. The observed other bands correspond to several phonon modes.

The optical absorption spectrum of BaTiO₃ powder was recorded for a wavelength range from 200- 800 nm as shown in figure 3.7. The optical absorbance spectra help to obtain the energy band gap of material and the transition in material. The BaTiO₃ have a direct band gap and the calculated value of the band gap was 3.12 eV.

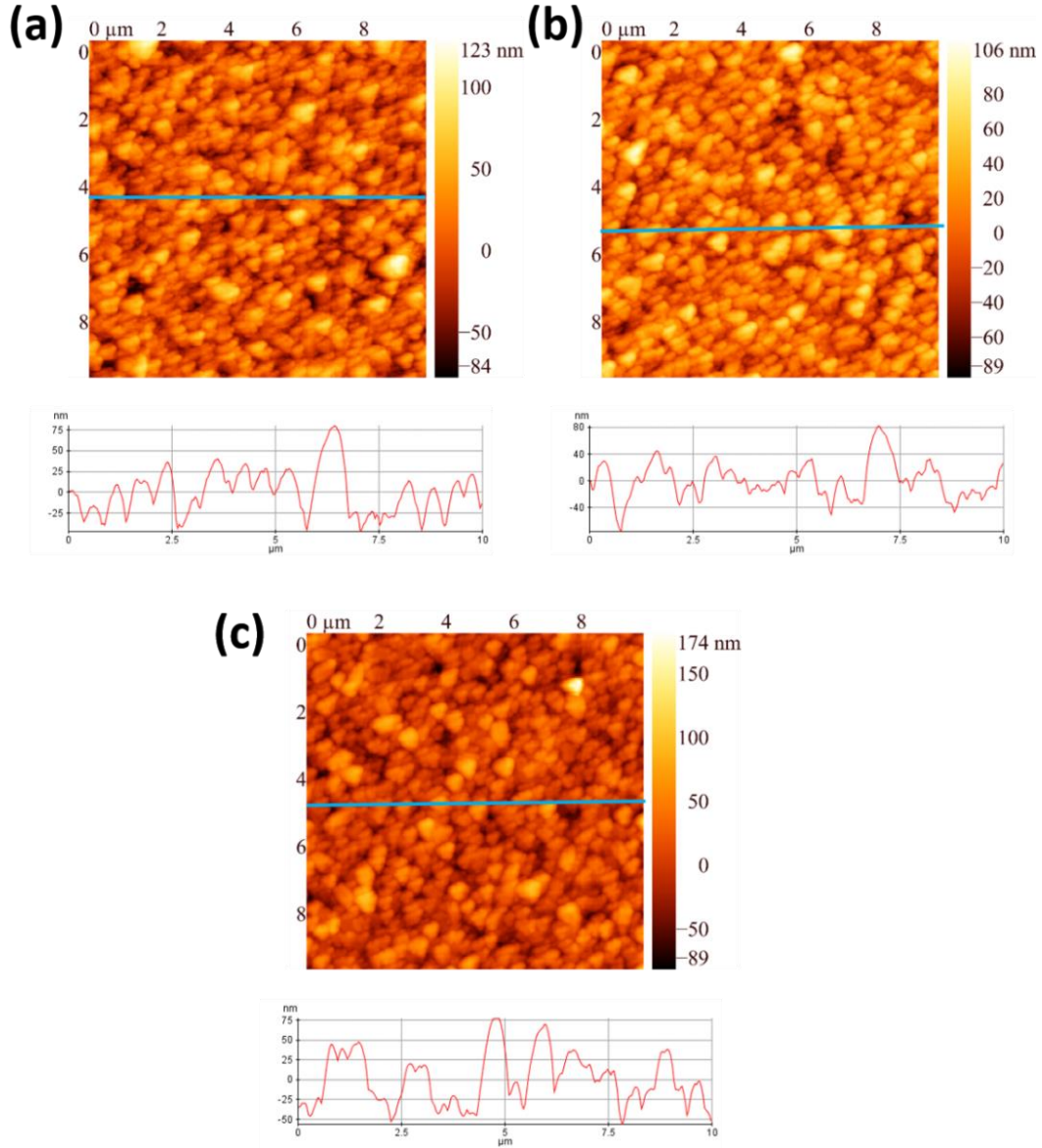


Figure 3.5: Atomic force microscopy (AFM) image of area 10 μm×10 μm was taken in non-contacting mode (NC-AFM) of the device (a) A, (b) B, and (c) C. The line profile of the surface is shown below the topography image.

3.3 Thickness-dependent WORM performance of am-BTO thin films

The prepared BTO sputtering target was used to deposit the amorphous BTO thin films for resistive switching device applications. Before deposition, the FTO substrates were cleaned using a standard cleaning process to remove the dirt and contamination from the surface to obtain good-quality thin films. We deposited the am-BTO thin film on FTO-coated glass by achieving the base pressure of 7×10^{-7} mbar at room temperature. A large number of depositions

were carried out to optimize the deposition. Finally, we optimized the deposition parameters as working pressure of 2×10^{-2} mbar, Ar flow (50SCCM) and applied RF power 50 Watt during deposition. The deposition time was varied to obtain the BTO thin films with different thicknesses of 120, 180 and 240 nm. Thicknesses of deposited thin films were confirmed using a surface profilometer (Dektak XT).

The Atomic force microscopy (AFM) study has been done for all three devices to check the surface morphology using Park System XE-70. All the images were taken in non-contact mode using NCST-Au tip with a scan speed of 0.75 lines per second and keeping the tip at a constant distance of 15 nm. The surface topography of area $10 \mu\text{m} \times 10 \mu\text{m}$ and its line profile of devices A, B, and C are shown in figure 3.5 (a)-(c), respectively. From the figures, we can see that the surface topography of the devices is almost the same. The surface of A has an average roughness of 20.71 nm and a root mean square (rms) roughness of 26.13 nm. In contrast, B and C have average roughness of 19.91 nm and 20.41 nm and rms roughness of 24.97 nm and 25.99 nm, respectively. Among all three devices, B has less rms roughness and also less number of small holes (black spots on the surface) on the surface. Less number of holes may decrease the leakage current for this particular device, and we will discuss it later. Line profiles on the images were drawn to take an idea of the height and sizes of the clusters. All three devices show collections of a particle having a diameter of 200 nm to 750 nm with a maximum height of 80 nm.

3.3.1 Device fabrication and memory characteristics of amorphous BaTiO₃ thin film

Conventional metal insulator metal(MIM) configuration was used to fabricate devices. Silver top contacts were deposited by thermal evaporation on am-BTO thin film using a circular shadow mask of 500 μm diameter. Ag/am-BTO/FTO devices were electrically characterized using 4200-SCS(Keithley) to analyze the WORM characteristics for -1.5 V to 1.5 V. The low conduction state(LCS) and high conduction state(HCS) were recorded for 4000seconds at 0.3 V before and after writing.

The devices were characterized electrically using two probes integrated with the Keithley 4200-SCS semiconductor analyzer to check the write-once-read-many (WORM) behaviour, stability, and reliability. Three devices have been made with different thicknesses of 120 nm, 180 nm, and 240 nm. To remember these, we named devices A, B, and C, respectively. Complete voltage iteration was applied to check the characteristics. At first, a voltage cycle of 1.5 V was applied, which means the applied voltage starts at -1.5 V and decreases to 0 V, then again increases to 1.5 V and comes back to 0 V and went to -1.5 V to complete the iteration. The path of applied voltage and corresponding current is shown in figure 3.6 with red arrows. With the application of -1.5 V, the devices remain at LCS, and with the decrease of negative voltage corresponding current decreases. Figure 3.6 (a), (b), (c) are showing the current-voltage characteristics of devices A, B, and C, respectively and (d) is showing the effect of stress on the performance of device B, where the absolute value of the currents in log scale is taken along the y-axis. For device A, with an increasing positive voltage, the current increases slowly in LCS. At a particular switching voltage of 1.09 V, conducting state switches to HCS and remain at a high current upto 1.5 V. while back iteration, the current remains at the same state (HCS). Although negative voltage was applied, the conducting state does not change. Hundreds of iterations were taken, but the state was being same. The current of LCS for A was in the range of microampere. The current increases to milliampere after switching of the device, which indicates the maximum on-off ratio is 3.8×10^3 at 0.3 V. device B and C show similar types of behaviour. For B, the LCS current is in the range of nano ampere. While increasing positive bias, the current went to the milliampere region at 1.25 V, which gives a very high on-off ratio of 4.6×10^6 at 0.3 V. The C device again shows LCS current at the microampere region and switches to HCS at 1.32 V applied positive bias. The maximum on-off ratio for this device is 1.2×10^3 . It has been noticed that the switching voltage is in increasing with increasing insulating oxide layer thickness of the devices, although the iteration voltage for all devices remains the same at 1.5 V. In the comparison of the three devices, the maximum on-off ratio is highest for B, and its

decreases for other two devices. The 1st, 10th, 20th, and 50th iterative cycle of the devices is shown in the figure below. For B as shown in figure 3.6 (d) we characterized the device for higher stress upto -4 V and observed 21% degradation in reading characteristics beyond -4 V as shown in the figure. The devices performed very well upto -4 V but beyond -4 V we observed the degradation or filament rupturing at higher stress. Hence, we can say that the device showed stable performance upto 4 V and beyond that, it starts degrading in its programmed state. After the first cycle, all other cycle remains at HCS, which means we can use these devices as highly stable and reliable resistive WORM.

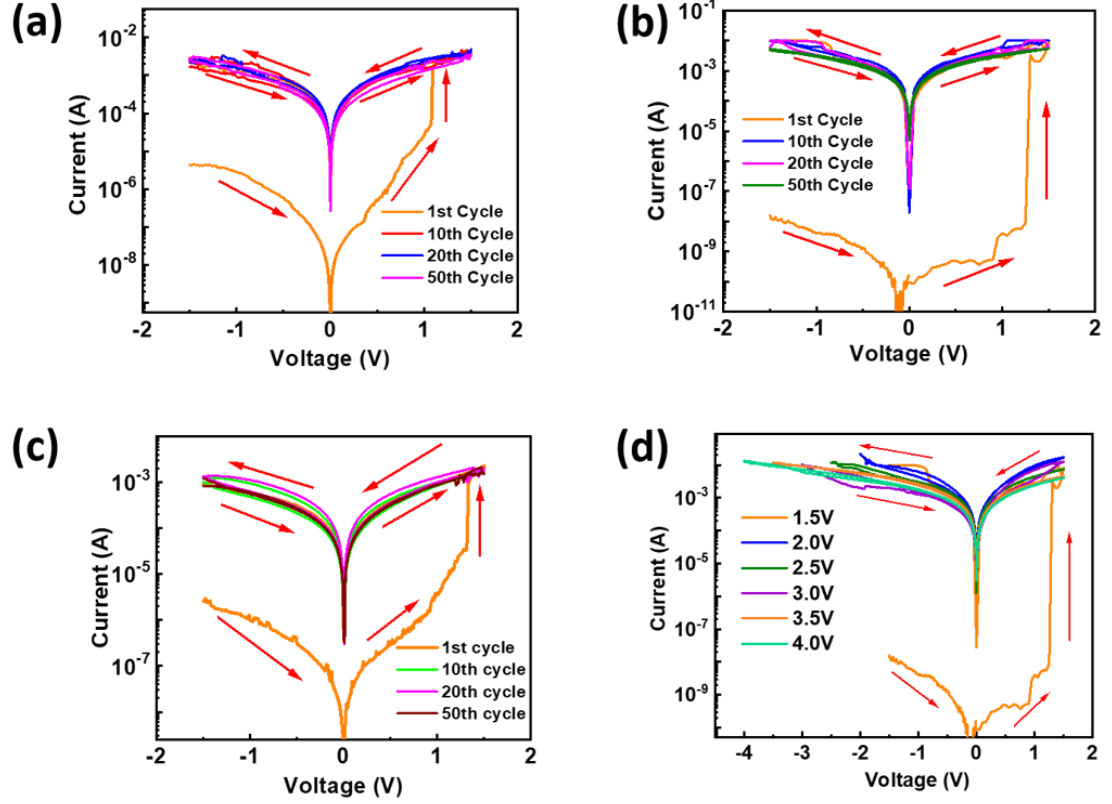


Figure 3.6: Current-voltage characteristics of the devices taken at a voltage loop of -1.5 V to 1.5 V. (a) for device A, the maximum on-off ratio is $\sim 10^3$. (b) B has a maximum ratio of $\sim 10^6$, and (c) C is showing $\sim 10^3$ (d) Effect of applied stress on B. The direction of applied bias and corresponding current is shown by red arrows.

The stability, reliability, and consistency of the devices have been checked by studying the data retention of the devices. The retention of A, B, and C is shown in figure 3.7 (a)-(c) respectively and the effect of reading voltage, annealing, and contact size on B is shown in figure 3.7(d)-(f) respectively. For the WORM device, it is impossible to erase data after writing because it changes its resistive state permanently after writing the data. To check the stability, conducting state before writing and after writing has been studied by giving a voltage pulse, and the corresponding conducting state has been noted. Four voltage pulses known as reading pulses were given to the device per second, and more than 4000 pulses were given. Before giving a write pulse, we read the current with a read voltage of 0.3 V, which was in LCS. After a voltage pulse of 1.5 V, named as writing voltage, the device switches to HCS. Again, that particular state was checked with a read pulse of 0.3 V. For both states, it remains extremely stable as shown in the figure below.

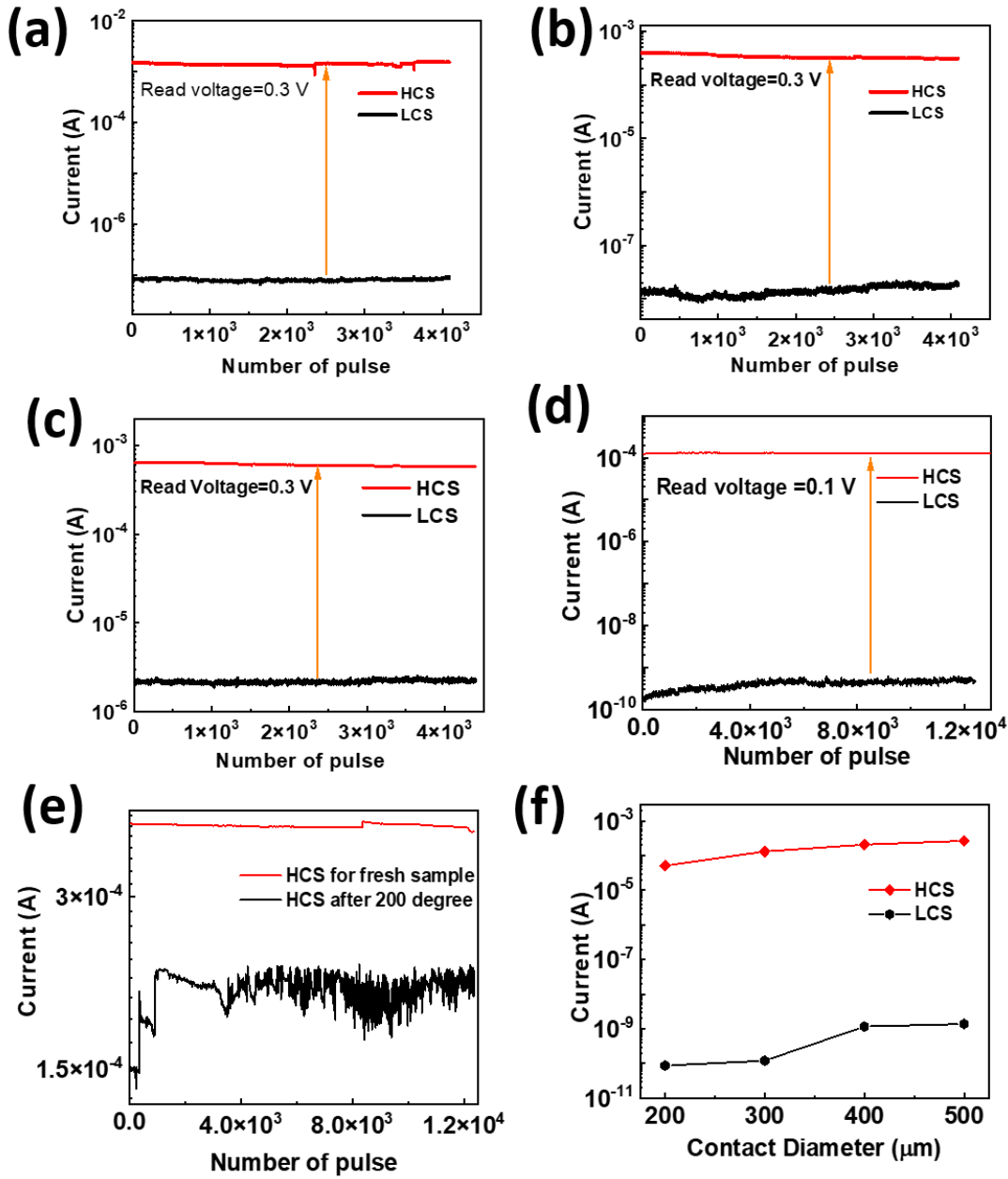


Figure 3.7: (a)-(c) Data retention of the devices A, B, and C respectively. All the devices read its data retention at a particular read voltage of 0.3 V. (d) reading current of 0.1V. (e) Effect of annealing on post-forming voltage for device B. (f) effect of contact diameter on device performance.

We found that the high reading current is a common issue in almost all WORM devices including the metal fuse and poly fuse devices. Hence, we characterized the devices for low voltage reading cycle and as we know that the reading current is a function of read voltage, we observed that there is a reduction in read current at low reading voltages. Since we have a high on-off ratio of the order of 10^6 so we can easily read the devices even at lower reading voltages to reduce the overall power consumption. We have tried to reduce the reading current by applying a low reading voltage (0.1 V) as shown in the figure below. The reading current decreased to 1×10^{-4} for 0.1 V reading voltage as shown in figure 3.7 (d).

Further, device B was characterized to observe the effect of annealing on the post-forming state (HCS) and hence we annealed device B at 200°C for 1hr in ambient conditions after recording its HCS current. After annealing for 1 hour, we characterized the device for HCS current for the same reading voltage as shown in figure 3.7 (e) and we observe a small reduction in HCS current. The reduction in the HCS current may be due to the migration of surface

vacancies during annealing. Figure 3.7 (f) shows the effect of contact area on the device performance. Device B was characterized for a variable contact size from 200 μm to 500 μm diameter deposited using a shadow mask. The device was characterized for reading current at 0.3 V for all contact sizes. We observed that with the increased contact area, the injected carriers also increased and hence results in an increased reading current. The area vs. current represents electrode-limited conduction rather than bulk-limited conduction. Since SCLC is bulk-limited conduction, it can't be applied when we use the area as a parameter to explain its effect on conduction. Moreover, it is known that as the contact area increases, the contact resistance decreases. This provides a smaller scattering probability at the electrode dielectric interface, which helps the carriers crossover the barrier at relatively lower thermal energy and gets injected into the dielectric medium. Thus, the conduction mechanism which may help explain the effect is the electrode limited. Hence, as the Switching mechanism is the result of the formation of conductive filaments, the area contact will influence the device resistance due to the formation of conductive filament locally.

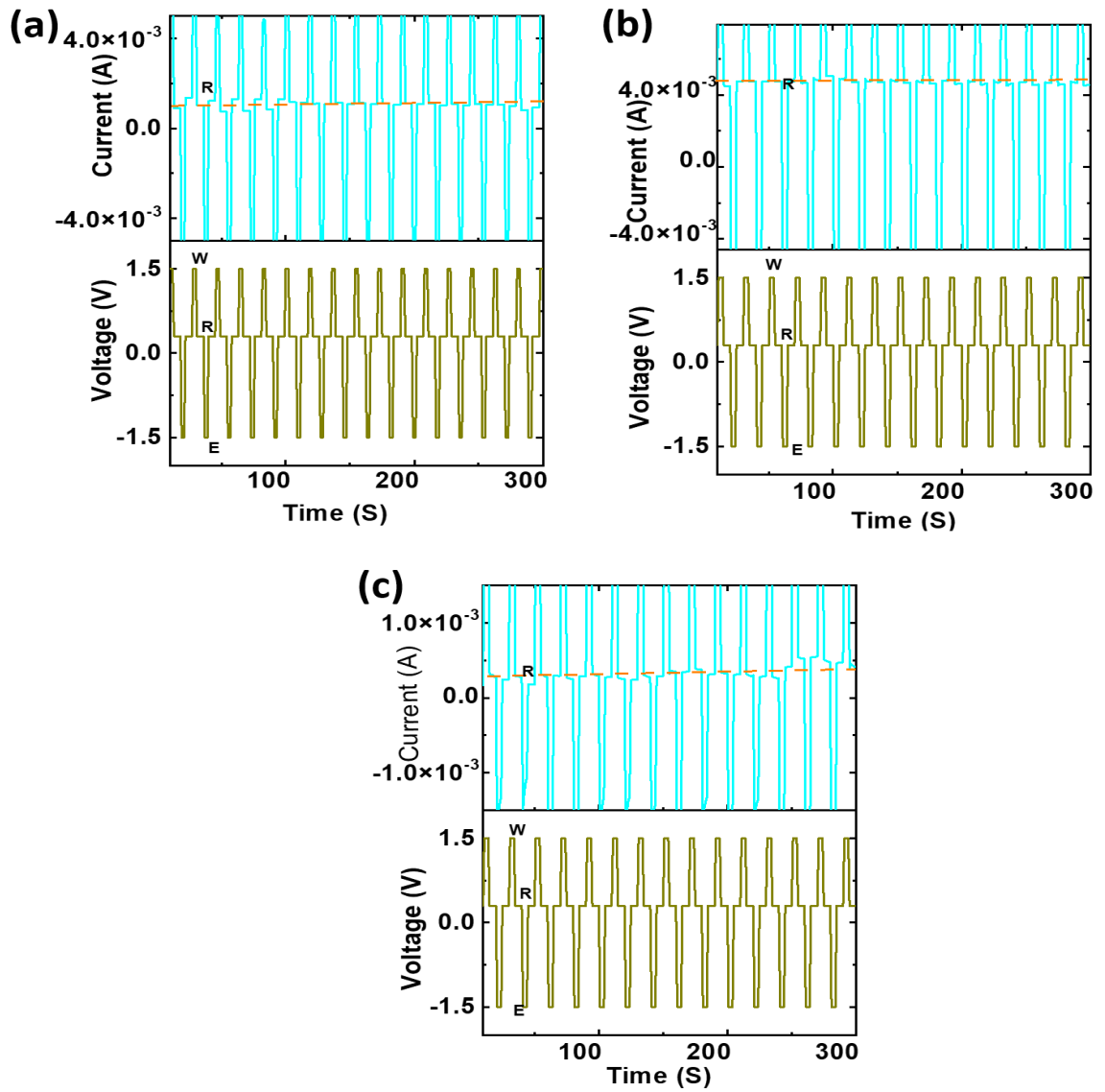


Figure 3.8: Write-read-erase-read cycle of three devices A, B, and C, respectively. The lower dark yellow colour plots are the applied write, read, and erase voltage while cyan colour lines show the corresponding current varying with time.

Write read erase read cycles of the devices were run to check if the written data can have accessed randomly or not and the consistency of the data even after a reverse bias was applied. The applied voltage pulse and corresponding current are shown in figure 3.8 (a)-(c) for three

devices. A write, erase and read voltage of 1.5 V, -1.5 V, and 0.3 V were taken for 4 seconds, 4 seconds, and 6 seconds. At first, a write voltage is applied for 4 seconds to reach the device to HCS then, read the current by applying a bias of 0.3 V. Again, an erase voltage of -1.5 V was applied for 4 seconds to check whether the written data is erasable or not, and then read the current at same read bias of 0.3 V. when 1.5 V is applied, the devices give high current in the range of milliampere (mA), then found at high current state during a reading at a bias of 0.3 V. Even after applying a reverse bias of -1.5 V, the device is found to be in the same state (HCS) and the read current gives the same current as the previous. The read current is shown with dashed lines which show the current is fixed before and after erase voltage. Hundreds of such cycles were taken to check its reliability, but all the devices remain extremely stable. From this, we can conclude these can be used as WORM devices.

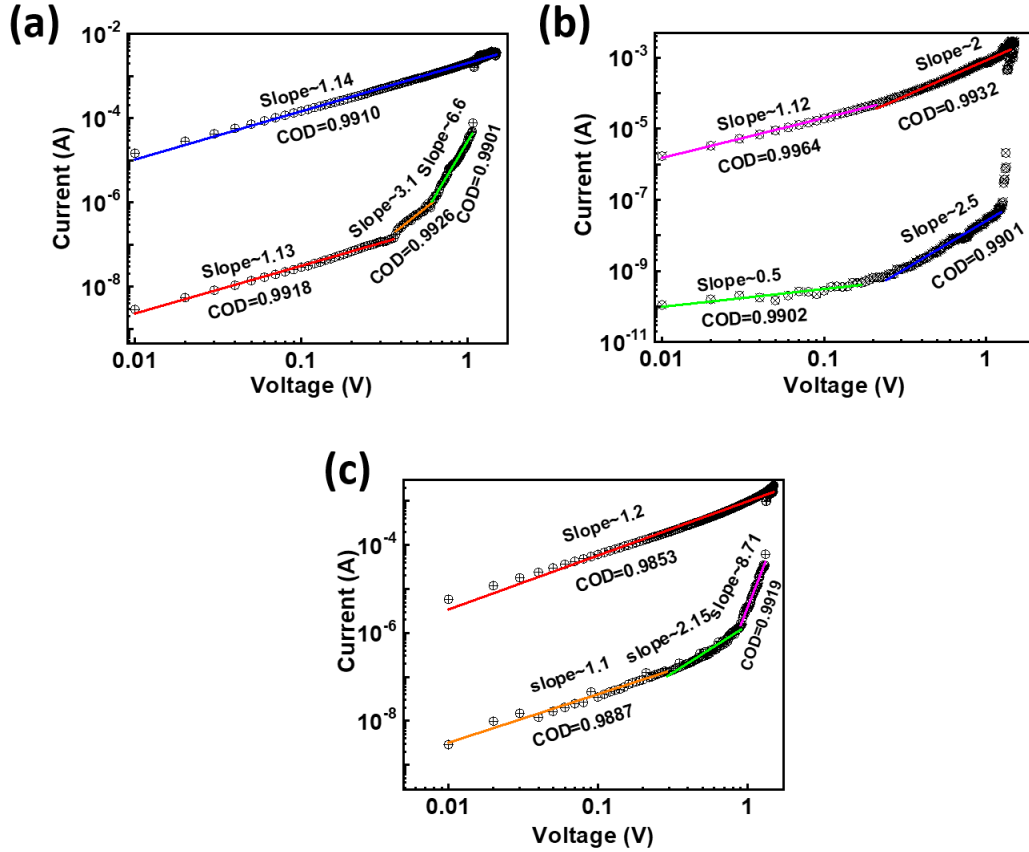


Figure 3.9: (a)-(c) current-voltage characteristics for the devices A, B, and C plotted in logarithmic scale. The plotted data were linearly fitted to get an idea of the current conduction mechanism through the active layer.

To take an idea about the current conduction mechanism, the positive side of current-voltage curves of all three devices have been plotted in a logarithmic scale and fitted the data as shown in figure 3.9 (a)-(c). All the log (I)-log (V) plots are showing multiple slopes with COD ($r^2 \approx 0.99$). Device A and C shows the linear current variation with applied voltage ($I \propto V$) then change its slope to more than 2 ($I \propto V^n, n \geq 2$) in LCS, and again show linear variation at HCS. At the same time, B has slopes of 0.5, 2.2 in LCS and 2, 1.2 in HCS. The linear variation of current in LCS implies the direct quantum mechanical tunnelling-induced conduction, in which oxygen ions (vacancies) and electrons can tunnel through a potential barrier. The higher slope of log (I)-log (V) plots ($I \propto V^n$) space charge limited conduction (SCLC). When the current varies quadratically with applied voltage ($I \propto V^2$), it represents the trap-free SCLC for the solid. The current density for SCLC is given by Mott-Gurney law

$$J = \frac{9\mu\epsilon_0\epsilon V^2}{8d^3} \quad (3.1)$$

Where μ is the mobility of the charge carrier, ϵ is the dielectric constant of the material, ϵ_0 is the permittivity of free space, V is the applied voltage, and d is sample thickness. The current variation ($I \propto V^n, n \geq 2$) at a moderate voltage (for both HCS and LCS) is due to SCLC with a trap state, which is given by

$$J_t = N_0 \mu \epsilon_0^{1-l} \left(\frac{\epsilon l}{N_t (l+1)} \right)^l \left(\frac{2l+1}{l+1} \right)^{l+1} \left(\frac{V^{l+1}}{d^{2l+1}} \right) \quad (3.2)$$

Where N_0 is the effective density of states in the valance band, N_t is the trap density, l is the exponent has a value greater than one. In HCS, the linear variation of current represents the ohmic conduction where the device behaves like a metal.

The switching behaviour WORM mechanism of the fabricated device can describe by filament formation by oxygen vacancies present in the active layer. The device schematic and formation of the filament are represented in figure 3.10 (a)-(c). Before applying the switching voltage, the oxygen vacancies are randomly oriented inside the active layer. When an electric field has been applied between two electrodes, some ions can move from one electrode to another, and the vacancies arranged themselves to start forming filaments. After applying sufficient bias, they form conducting filaments, and the device immediately went to HCS. The filament forms permanently because even after giving sufficient negative pulse, it does not switch to LCS. So, it can be used as a WORM device. Furthermore, in comparison to the three devices, B shows the lowest current among them. This can be described from the AFM topography image, as said earlier. From the three images, we can see that B has fewer pinholes, which are responsible for some metallic ion penetration through the active layer. In A and C devices, some metallic ions (Ag^+) penetrate through the device and increase the current to the microampere region. While B with fewer pinholes reduces the leakage current in remains in the nano ampere region.

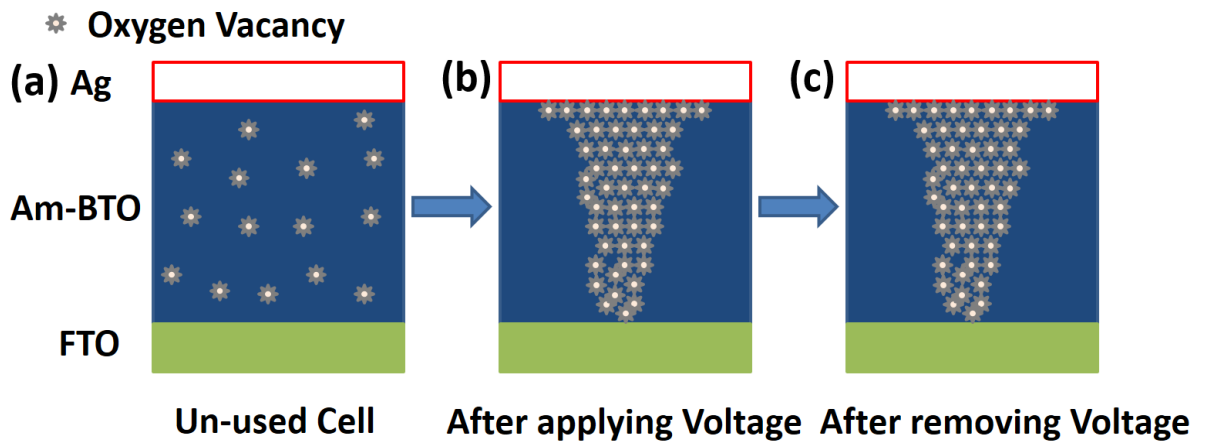


Figure 3.10: (a) schematic of the devices before applying bias where oxygen vacancies are not arranged. (b) Schematic represents the formation of the filament by oxygen vacancies inside the active layer after applying switching voltage (c) picture showing the WORM behaviour of the device in which it forms a permanent filament.

3.4 Temperature-dependent WORM performance of am-BTO thin films

The deposition temperature also affects the resistive switching performance as it alters the thin film properties. Further, the compatibility with CMOS technology must require a processing temperature of upto 450°C and hence we studied the performance of BTO thin film-based WORM devices as a function of deposition temperature. The deposition process was started after achieving a base vacuum of 8×10^{-7} mbar at room temperature. The deposition

parameters were kept fixed during the deposition of all the samples except the deposition temperature ranging from room temperature to 450° C. The working pressure, Argon flow, and RF power were 2×10^{-2} mbar, 50 SCCM and 50 watts respectively for different deposition temperatures such as RT, 150° C, 300° C, and 450° C. The deposition time was kept at 90 min for all the samples, and the substrate-to-target distance was held at 5 cm. The thickness of the prepared samples was verified using a surface profiler (Dektak XT), which was ~180 nm for all the samples. Further, we characterized the deposited thin films using AFM (XE-70, Park System) to study their surface morphology.

The surface morphology of deposited BTO thin films at different temperatures was analysed by AFM. The characterization was carried out using the NCST-Au tip in non-contact mode. The distance between the tip and surface was kept constant at 15 nm with a scan rate of 0.75 lines per second. The surface profile of area $10 \mu\text{m} \times 10 \mu\text{m}$ and their line profile for each device BTO-RT, BTO-150, BTO-300, and BTO-450 is shown in figure 3.11 (a)-(d), respectively. From the AFM images, we observed that the average surface roughness increased as we increase the deposition temperature. The highest roughness of the films is shown on the scale bar in figure 3.11. The highest roughness is 104 nm, 98 nm, 100 nm, and 96 nm, respectively for the devices. The average roughness was 9.28 nm, 9.56 nm, 9.67 nm, and 9.84 nm for devices BTO-RT, BTO-150, BTO-300, and BTO-450, respectively. We have observed the increment in average grain size as we increase the deposition temperature. The average particle size was .097, .103, 0.105 and 0.108 μm^2 for the sample BTO-RT, BTO-150, BTO-300 and BTO-450 respectively.

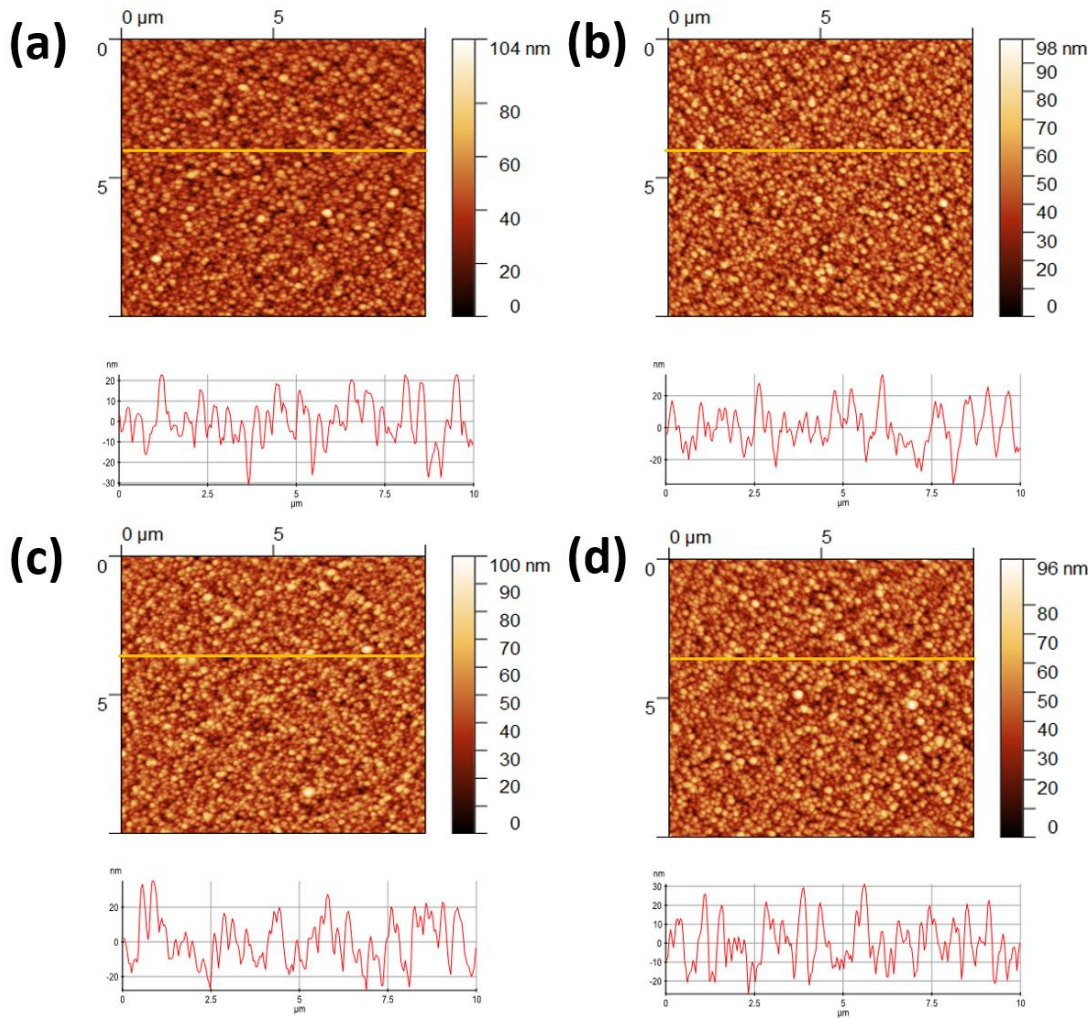


Figure 3.11: AFM image of area $10 \mu\text{m} \times 10 \mu\text{m}$ in the non-contacting mode of the device (a) BTO-RT, (b) BTO-150, (c) BTO-300 and (d) BTO-450. The line profile for each surface is shown below the topographic image.

The deposited BTO thin films at different temperatures were characterized for morphological analysis. The captured FESEM images for all four samples are shown in figure 3.12 (a-d). We observed an increased average granule size as the deposition was increased. The average grain diameter for BTO-RT was 200 nm while 240 nm for BTO-450.

3.4.1 WORM performance for different deposition temperatures

Similar to the previous study, the MIM configuration was used to fabricate the devices with Ag top contact deposited using a thermal evaporation system. A circular pattern of silver contacts with a diameter of 500 μm was deposited on the active layer (BTO) using a shadow mask by a thermal evaporation system. The fabricated devices were characterized using a semiconductor parameter analyzer (Keithley 4200-SCS) for a voltage range of -1.5 V to 1.5 V. The retention characteristics were recorded at 0.3 V for both HRS as well as LRS state.

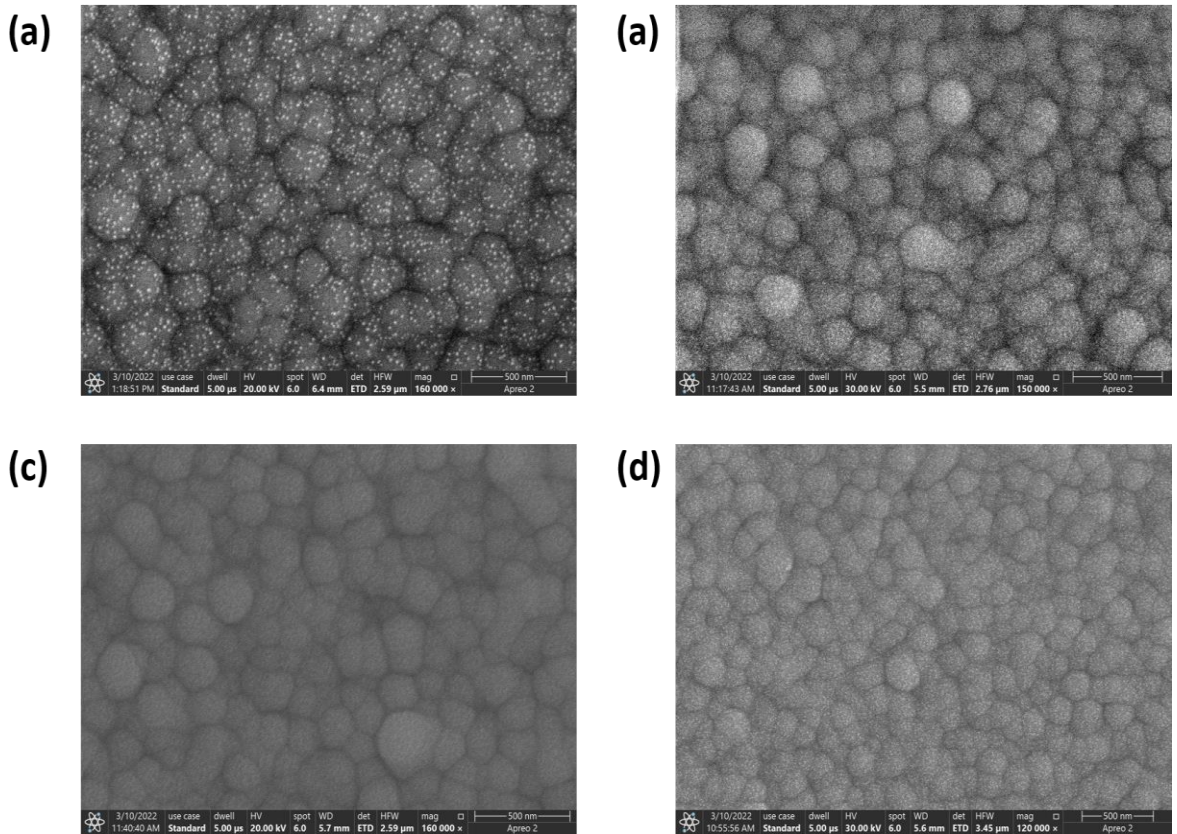


Figure 3.12: FESEM images (a) BTO-RT, (b) BTO-150, (c) BTO-300 and (d) BTO-450.

Further, we electrically characterized the fabricated Ag/BTO/FTO devices to study their write-once-read-many (WORM) characteristics, reliability, and stability using Keithley 4200-SCS integrated with a probe station. To test the WORM characteristics, a complete voltage cycle of -1.5 V to 1.5 V was applied, which means we started the cycle from -1.5 V and decrease to 0 V, then again increased upto 1.5 V and again come back to 0 V and then -1.5 V in the end. The current path with respect to the applied voltage is represented in figure 3.13 with the red-coloured arrow. Initially, with the applied voltage sweep, which starts from -1.5 V, the devices remain in HRS and the current decreases as the voltage decrease. Moreover, when a positive voltage is applied from 0 to 1.5 V the current starts increasing and at a certain voltage, it switched to LRS and remains in LRS. The current-voltage characteristics of devices BTO-RT, BTO-150, BTO-300, and BTO-450 are shown in figure 3.13 (a), (b), (c), and (d), respectively, where the y-axis is taken to represent the absolute value of current in the logarithmic scale. For device BTO-RT, it follows the same trend of the I-V curve as mentioned above, and at a particular switching voltage of 1.31 V, the device switches to LRS and remains in the same state

upto 1.5 V. With the return cycle 1.5 V to -1.5 V the device continues in the same state (LRS), even the application of negative voltage is not able to change the conduction state. Hundreds of cycles were taken to check the reset of the conduction state, but the conduction state remains the same for all the cycles. The current was switched to milliampere for LRS from microampere (HRS) due to switching with an on-off ratio of 5.9×10^6 at 0.3 V.

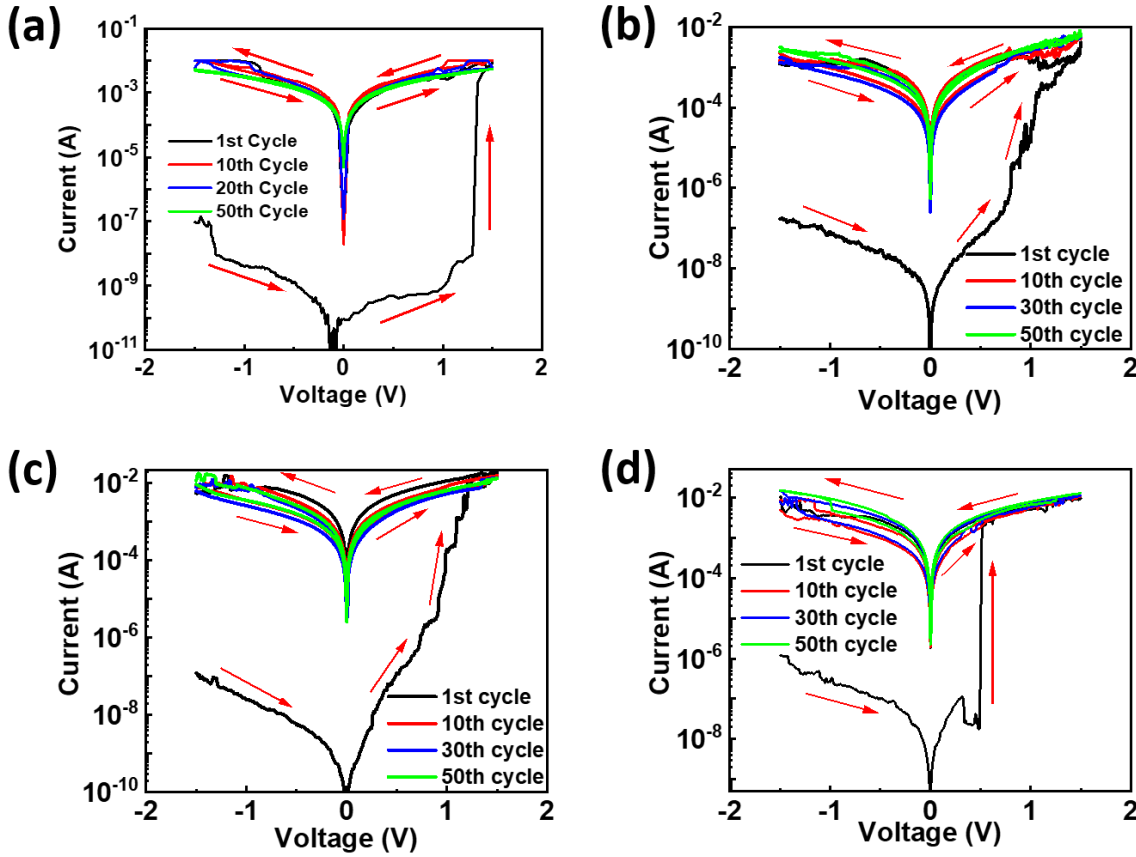


Figure 3.13: I-V characteristics of the devices for a voltage loop of -1.5 V to 1.5 V. (a) BTO-RT, (b) BTO-150, (c) BTO-300 and (d) BTO-450. The direction of the current path is shown by red arrows.

Similarly, for device BTO-150, the HRS current was in the microampere region, and with the increased voltage in the positive direction, the current switched to milliampere order at a switching voltage of 1.06 V. The observed value of the on-off ratio for the device is 5.4×10^4 at 0.3 V. The device BTO-300 has a similar HRS current of the order of microampere, and the switching voltage was 0.96 V. The value of the on-off ratio for the device is 2.3×10^5 at 0.3 V. Similarly, for BTO-450, the current was switched to milliampere from the microampere range at a switching voltage of 0.49 V with a maximum on-off ratio of 0.9×10^4 at 0.3 V. The above characterizations confirm that the switching voltage decreases with the increased deposition temperature for active layer (BTO) deposition, irrespective of iteration voltage. In comparison, the highest value of the on-off ratio was observed for BTO-RT and the lowest for BTO-450. All four devices were characterized for more than 50 iterative cycles, out of which the 1st, 10th, 20th, and 50th cycles are represented in figure 3.13 (a)-(d) for each device.

The data retention characterization has been carried out to check the fabricated WORM device's consistency, stability, and reliability. The retention characteristics of the devices BTO-RT, BTO-150, BTO-300, and BTO-450 are shown in figure 3.14 (a)-(d), respectively. In the WORM device, the change in the resistive state is permanent, so it is impossible to erase the data or regain the previous HRS state. Hence the retention was carried out by applying a voltage bias for a certain time before and after writing. One pulse per second was applied across the device to take the read and write state retention upto 12000 pulses. First, we record the

current at 0.3 V before applying the writing pulse (1.5 V), which is HRS. In the next step, a write pulse of 1.5 V was applied to switch the device to LRS, and after switching to LRS, we repeated the retention study for the state with a read pulse of 0.3 V. We found that all the devices show stable characteristics for both the states, as shown in the figure 3.14.

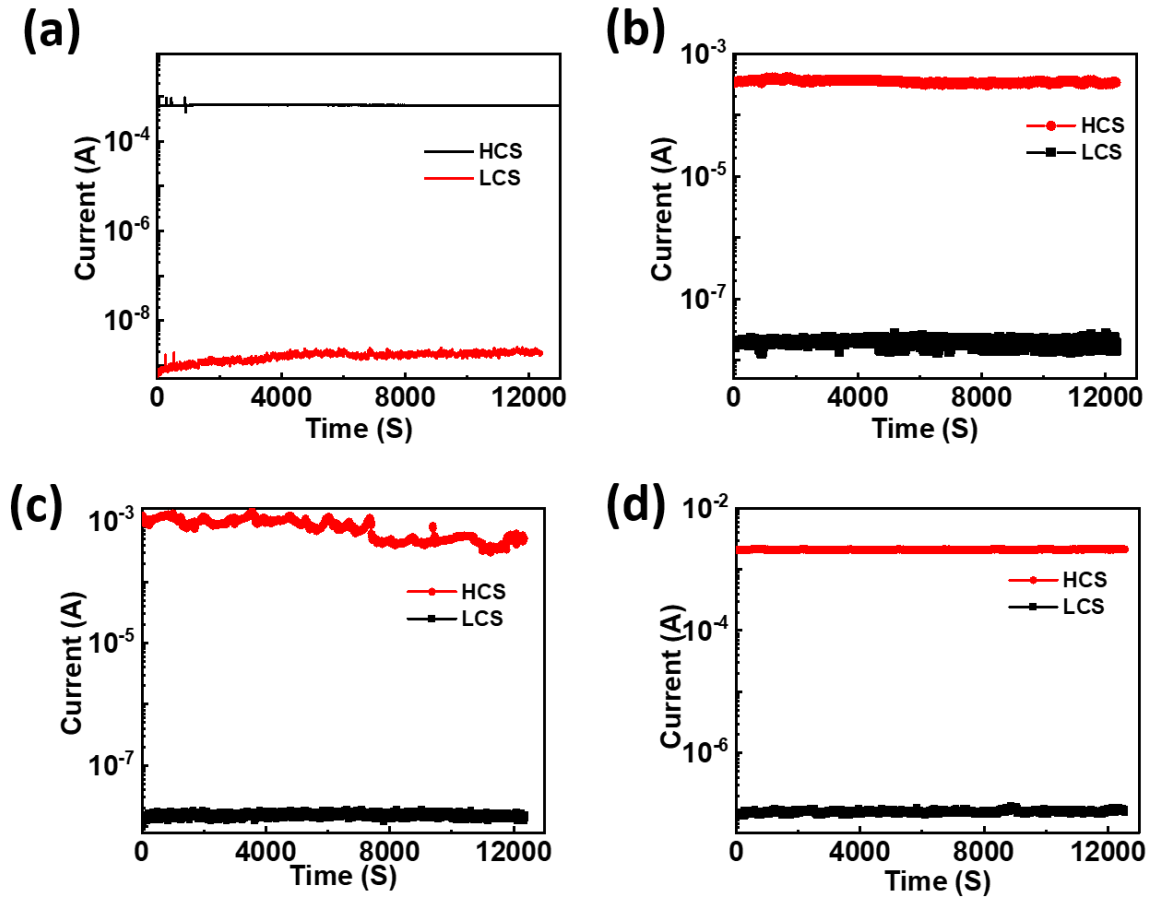


Figure 3.14: (a)-(d) Data retention of the device BTO-RT, BTO-150, BTO-300 and BTO-450 respectively. For all the devices the data retention was done for a read voltage of 0.3 V.

To verify the data readability and its consistency for a long time, we have characterized the devices for multiple write-read-erase-read cycles. The write-read-erase-read characteristics for all the devices with applied voltage pulses and their respective current are shown in figure 3.15 (a)-(d). For this, we applied write (1.5 V), read (0.3 V), and erase (-1.5 V) pulses for 4 s, 6 s, and 4 s respectively. At first, a write pulse of 1.5 V for 4 s across the device was applied to switch the devices to LRS. Afterwards, a read pulse of 0.3 V for 6 s followed by the erase pulse of -1.5 V across the devices was applied to check the probability of device reset. Again, a read pulse of 0.3 V was applied to see the effect of erase pulse on the reading current, and no effect on the read current was found even after applying negative voltage. So, it can be said that after applying a reverse bias across the devices, they can retain the same state. The read current (dashed line) is found to same as before by applying erase pulse. Hundreds of cycles were repeated for each device to check the stability and reliability of the devices, and we found that the devices were stable over an extended period. Based on the above-discussed performances of the devices, these can be implemented as WORM devices.

To analyze the current conduction mechanism for the fabricated devices, the I-V curve in logarithmic scale for the positive voltage side is shown in figure 3.16 (a)-(d). The plots of $\log(I)$ - $\log(V)$ were fitted to understand the type of conduction mechanism by finding the value of slope for the particular region with $\text{COD}(r^2) \geq 0.99$. All the fitted plots show the multiple values

of slope in different voltage regions. The linear variation in device current for HRS represents the conduction due to the direct quantum mechanical tunnelling of the oxygen vacancies (ions) and electrons via the potential barrier. In log (I)-log (V) plots the higher value of slope ($I \propto V^n$) represents the space charge limited conduction (SCLC). The quadratic variation in current with applied electric field represents a trap-free SCLC for that region. In LRS, the current follows a linear path for all the devices, which represents the ohmic conduction.

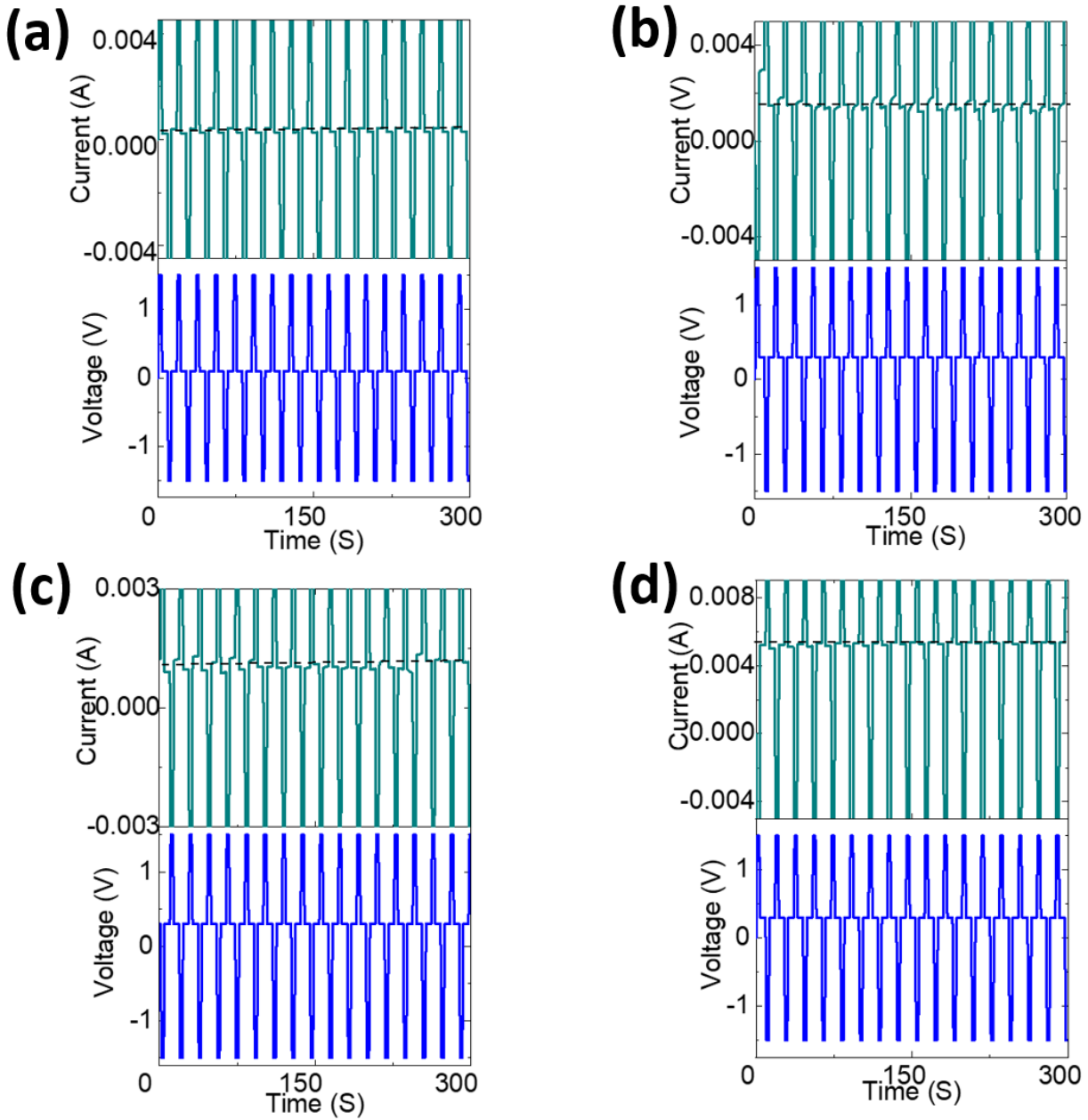


Figure 3.15: (a)-(d) Write-read-erase-read plot of all four devices BTO-RT, BTO-150, BTO-300, and BTO-450 respectively. The lower blue colour plots represent the write, read, and erase pulse and dark cyan colour plots are the corresponding current with time.

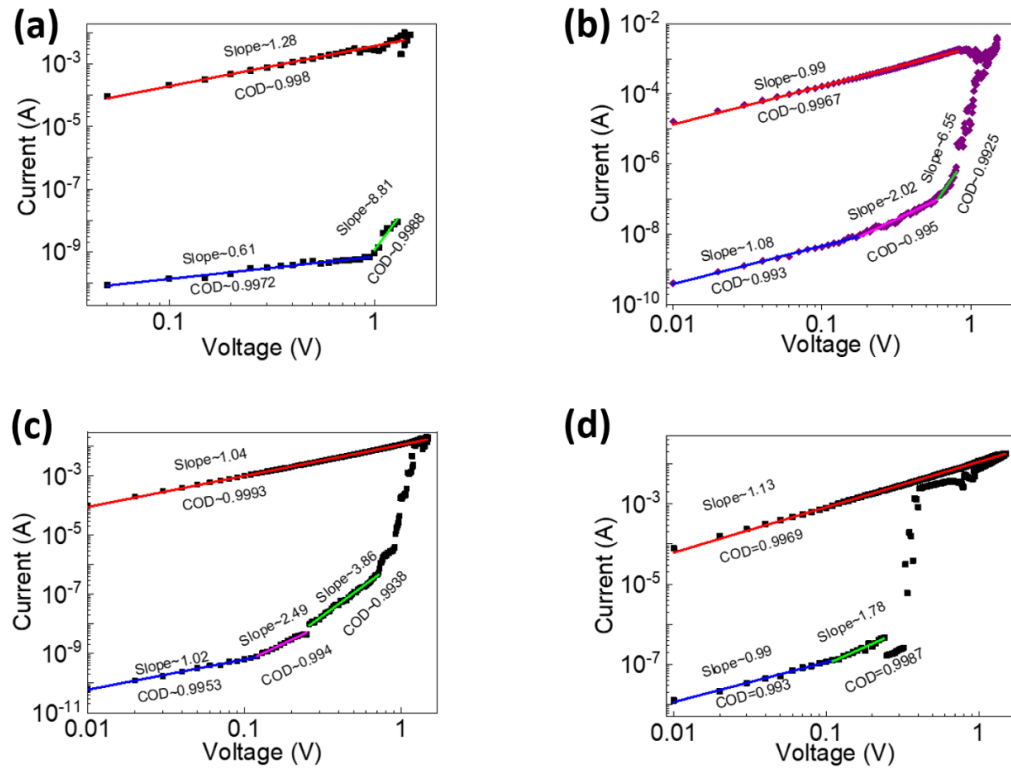


Figure 3.16: (a)-(d) I-V characteristics plotted in logarithmic scale for the devices BTO-RT, BTO-150, BTO-300, and BTO-450 respectively.

Furthermore, we have presented a comparison of our device performance with the work available in the literature as table-1 and it can be seen that for our devices the on-off ratio is very high at a relatively low switching voltage.

Table 3.1: Comparison of recent work in the WORM area with different active materials

Active Layer	Deposition Technique	Deposition Temperature	Programing Voltage	Switching Ratio	Read Current	Speed	Reference
IGZO	RF Sputtering	RT	7 V	10^4	3 mA	1 μ s	[Liu et al., 2014]
ZnO	MBE	400° C	12-20 V	10^5	50 mA	--	[Qi et al., 2011a]
rGO+P VP	Spin Coating	200° C	>4 V	10^5	2 mA	700ns	[Mamo et al., 2013]
NiO	Pulse Laser Deposition	RT	3 V	10^4	100 mA	1 μ s	[Yu et al., 2012a]
NiO	Spin Coating	550° C	3 V	10^4	0.2 mA	--	[Wang et al., 2018]
Silver np	Inkjet printing	50° C	2.6-5.5 V	$<10^8$	>1 mA	--	[Wang et al., 2016a]
Silver np	Inkjet printing	100° C	3 V	10^3	>20 mA	--	[Leppäniemi et al., 2014b]
PEDOT : PSS	Spin Coating	120° C	4 V	10^4	>10 mA	10 ms	[de Brito et al., 2008]
BaTiO ₃	RF Sputtering	RT-450° C	1.5V-0.49 V	10^6 - 10^4	$\leq$ 10 mA	105 ns	This Work

3.5 Conclusions

In conclusion, Ag/am-BTO/FTO devices with different thicknesses were realized for WORM memory characteristics based on the resistive switching phenomenon in MIM configuration. The devices show the switching from a low-conductance state (LCS) to a high-conductance state (HCS) by applying a low-voltage signal (1.5 V). The device with 180 nm thickness shows the best on-off ratio of the order of 10^6 compared to 120 nm and 240 nm thick samples. The low on-off ratio and high current are caused by the pinholes in the surface of the thin film in 120 nm and 240 nm samples. Further, the WORM behaviour was recorded by applying a voltage sweep from -1.5 V to 1.5 V, which switched the devices from HRS to LRS at a particular switching voltage, depending on its deposition temperature. The device BTO-450 shows the switching at 0.49 V with an on-off ratio of 0.9×10^{-4} . We found a reduction in switching voltage as a function of increased deposition temperature from RT to 450° C. On the other hand, the reduction in the on-off ratio was also observed for higher temperatures due to increased leakage current. The fabricated devices exhibit long-time data retention and good reading endurance.

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