

Radiation stability Analysis of Amorphous BaTiO₃ Thin Film-Based Memory Device

This chapter observed the effect of Ar-ion irradiation on the WORM memory performance of am-BTO thin films. The BTO thin films were deposited at room temperature for a thickness of 180 nm all the deposition parameters and fabrication processes were kept the same as discussed in the previous chapter. Am-BTO thin films were subjected to an irradiation chamber to get exposed to Ar-ions with different fluence. The ion fluence for a sample was controlled by varying the deposition time. After irradiation, the samples were characterized to analyse the morphological changes due to irradiation as a function of fluence using AFM. Further, the electrical characterizations were to analyse the WORM memory performance of the pristine and irradiated samples. AFM images of the samples reveal that there is a significant reduction in the surface roughness as we increase the irradiation fluence. The memory characteristics of the pristine and irradiated samples show that there are no significant changes were observed due to irradiation and hence the results show the potential of am-BTO thin film WORM memory devices to be used in harsh radiation environments.

4.1 Introduction

Resistive switching devices are emerging as a potential solution to the current memory requirement of data storage in electronic and computation applications as they offer advantages like fast switching, high-density storage, longer retention and low power consumption over conventional memory technology [Chen, 2016]. The resistive switching-based devices have been realized in various forms like RRAM, NDR and WORM [Chen et al., 1999; Hsu et al., 2022; Milo et al., 2019]. Over the period the applications involving the permanent data archival with no further change made the resistive switching-based WORM memory devices over the metal fuses due to their low voltage and fast operations. WORM memory devices are widely used in RF id tags and large-volume permanent data storage applications. Different material systems including binary and ternary metal oxides, organic semiconductors, polymers and composites have been explored as active layers for the WORM memory devices. Among all materials, metal oxides have gained huge attention because they offer a stable, reliable and large memory window. The matured deposition techniques for the growth of high-quality thin films are an added advantage for metal oxide-based devices. Metal oxides including NiO, IGZO, ZnO, SrTiO₃ and BaTiO₃ have been reported for WORM memory devices.

The memory devices have to get deployed in normal as well as the hazardous environment. The hazardous environment includes radiation harsh and corrosive atmospheres such as in nuclear plants and space applications. As the modern world is growing and exploring advanced areas through various space missions, efficient memory devices are desirable. Although the current memory techniques and their packaging techniques are mature enough to be used for radiation harsh applications but the miniaturization limit is an issue and hence the resistive switching techniques seem to be a potential candidate to solve the purpose. It is observed that the radiation harsh and ionizing atmosphere affects the device performance of electronic devices and further lead the failure. Thus, it is very important for an electronic device to be get tested in such an environment before deployment in such places to observe the device's reliability under radiation conditions. The metal oxide-based gas sensors, photodetectors and varactors have been explored for a performance test in a radiation harsh

environment [Butcher et al., 2010; Kaur et al., 2020; Pavlovskaja et al., 2004; Ranwa et al., 2016; Sagade et al., 2009]. However, for resistive switching devices, there are very few such studies have been carried out so far. Low-energy ion beam irradiation is the most popular technique to explore radiation damage at the laboratory scale. The radiation doses over a long period in space can be simulated by selecting the energy and fluence of ions in a short period. The radiation exposure to the material alters the material properties like structural, optical and electrical performance and the alterations in performance and properties strongly depend on the nature of the material. Besides binary oxide, the ternary oxides including $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$, $\text{Pb}_{1-x}\text{Zr}_x\text{TiO}_3$, LiNbO_3 , SrTiO_3 and BaTiO_3 have been studied for irradiation-induced performance alteration for various electronic applications [Barala et al., 2017, 2020; Kumari et al., 2017; Li et al., 2013; Schrempel et al., 2006]. Perovskite oxides show a high tolerance towards radiation and there are no significant changes in the electrical properties. The binary oxide-based memristors also have been explored for radiation tolerance studies and show good potential to be used in radiation harsh environments. The irradiation effects particularly depend on the phase of the material and grain size. A recent report on the effect of Ar^+ ion irradiation on a single crystalline LiNbO_3 memristor shows a reduction in operating voltage while maintaining surface uniformity. The LiNbO_3 film thickness was reduced due to the sputtering effect and memristor properties were improved [Xie et al., 2021]. Although there are few reports available on irradiation studies for metal oxide-based RRAM but the irradiation studies for WORM resistive switching devices are quite unexplored. Therefore, in this study, RF-sputtered amorphous BaTiO_3 (am-BTO) thin films have been explored for the study of irradiation-induced performance modulations. The optimized am-BTO thin films show the WORM memory behaviour as discussed in the previous chapter. The effect of 1.8 MeV Ar ions was studied as a function of varying fluence of ions from 1×10^{15} to 6×10^{15} ions/ cm^2 on the surface morphology and WORM memory performance of am-BTO thin film-based WORM devices.

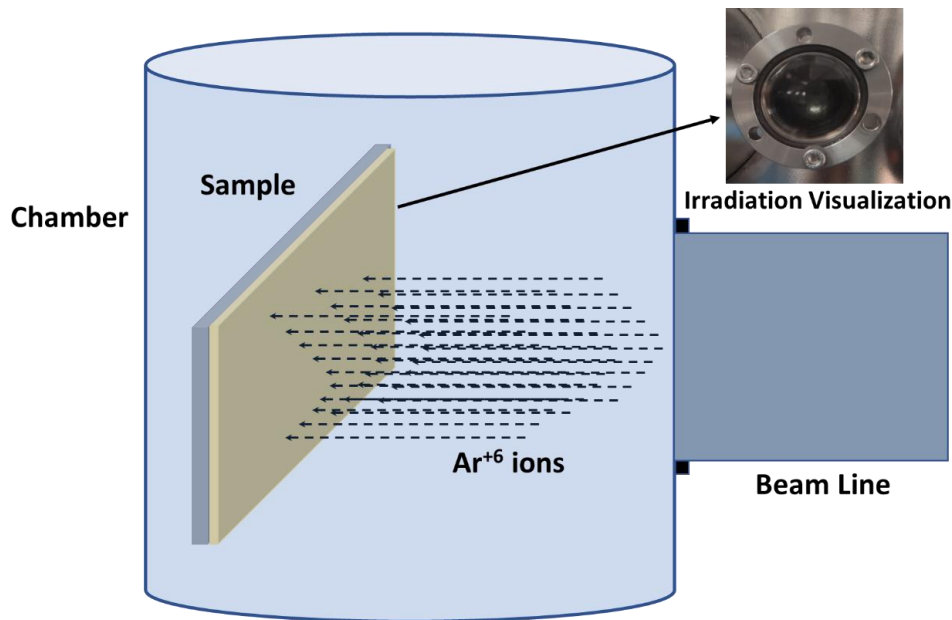


Figure 4.1: Schematic diagram representation of irradiation exposes to sample.

4.2 Thin film deposition and Irradiation Details

Amorphous BTO thin films were deposited on FTO-coated glass substrates using RF sputtering system at room temperature. After achieving a high vacuum, the depositions were carried out at a working pressure of 2×10^{-2} mbar with the Ar flow of 50 SCCM and RF power of 50 watts as discussed in the previous chapter. The film thickness was 180 nm for a deposition time of 90 minutes. The deposited samples were irradiated with 1.8 MeV Ar ions at an incremental rate of ion fluence using the low energy ion beam facility (LEIBF) at Inter-University Accelerator Centre (IUAC), New Delhi. The 6th charge state was used for Ar ions and the beam current was maintained at 1 μA . Three different fluences of as ions were irradiated on

am-BTO thin films as 1×10^{15} ions/cm², 3×10^{15} ions/cm² and 6×10^{15} ions/cm² by varying the exposure time. For ease of representation, the pristine, 1×10^{15} ions/cm², 3×10^{15} ions/cm² and 6×10^{15} ions/cm² irradiated samples were named as BTO-P, BTO-Ar1, BTO-Ar2 and BTO-Ar3 respectively. To achieve uniform irradiation, over the sample surface, the angle of the incident beam to the surface was kept at 90°. All samples were scanned for an area of 1×1 cm² during irradiation. The penetration depth of Ar ions for the am-BTO layer was 2.15 μ m as calculated using SRIM. A schematic representation of the irradiation process is shown in figure 4.1.

Further, the irradiated samples were used to prepare the resistive switching devices in a common bottom electrode configuration by depositing the Ag top electrode using a thermal evaporation system. A shadow mask with a circular dot pattern of 500 μ m diameter was used to shape the electrodes.

4.3 Thin Film Characterizations

The effect of ion irradiation on the morphology of the irradiated samples for different influences was characterized using AFM. The characterization was carried out in non-contact mode using the NCST-Au tip. The set point was kept at 15 nm during the deposition and the scan rate was 0.75 lines per second. The surface profile for all four samples including pristine and irradiated was recorded for the area of 10×10 μ m² as shown in figure 4.2. From the figures, we can observe that the average surface roughness is drastically reduced as the irradiation fluence was increased. The scale bar along with the AFM images shows the highest roughness of the sample. The highest roughness has an irregular pattern concerning influence and it was 93 nm, 25.2 nm, 55 nm and 31.1 nm for BTO-P, BTO-Ar1, BTO-Ar2 and BTO-Ar3 respectively. The average surface roughness was 9.73 nm, 1.42 nm, 1.91 nm and 0.65 nm for devices BTO-P, BTO-Ar1, BTO-Ar2 and BTO-Ar3 respectively. A significant surface roughness confirms the reduced grain size due to irradiation.

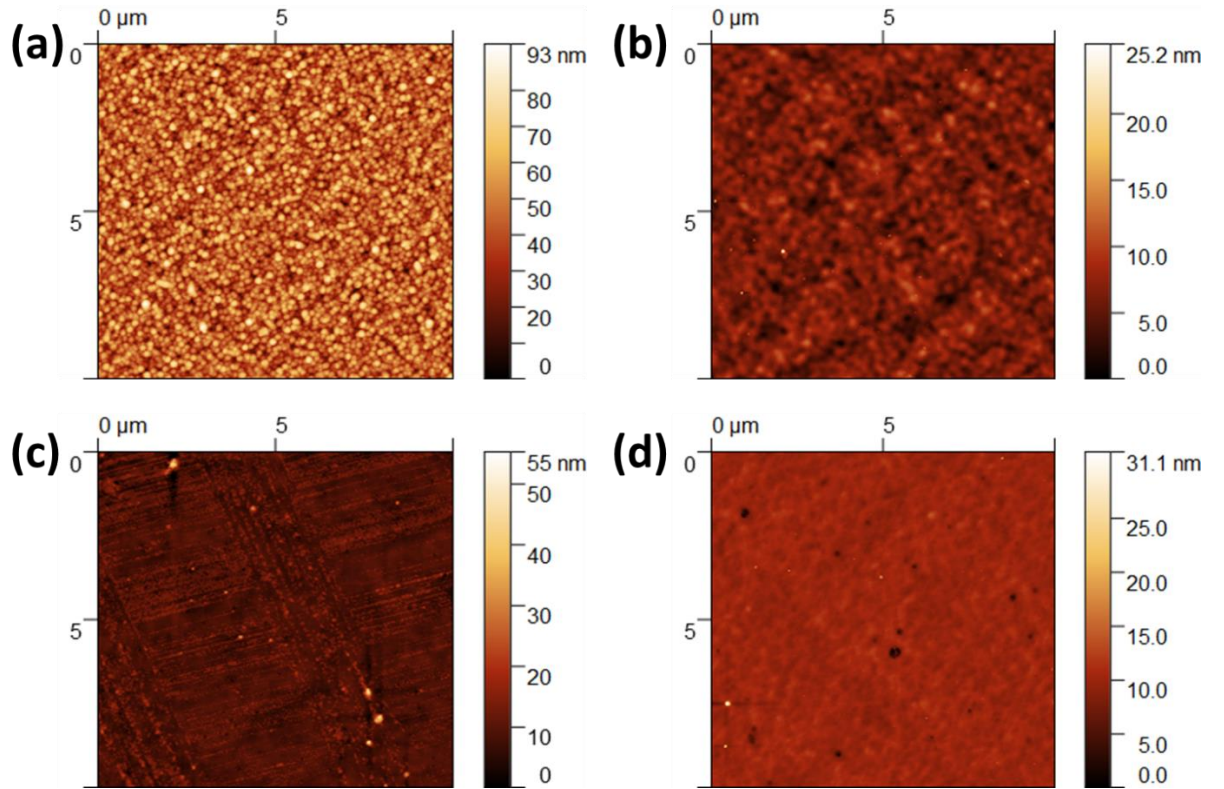


Figure 4.2: AFM image of area $10 \mu\text{m} \times 10 \mu\text{m}$ in the non-contacting mode of the device (a) BTO-P, (b) BTO-Ar1, (c) BTO-Ar2 and (d) BTO-Ar3. The line profile for each surface is shown below the topographic image.

4.4 Resistive Switching Characterizations

After the deposition of top contact, the devices were electrically characterized for the analysis of memory performance before and after irradiation using a semiconductor parameter analyzer (Keithley 4200-SCS). All four devices were characterized to get I-V, retention and write read erase read characteristics to define the effect of irradiation on the memory performance of am-BTO thin films.

To test the resistive switching characteristics, a voltage sweep from -1.5 V to 1.5 V in dual sweep mode was applied to the devices. The current versus voltage (I-V) characteristics for all four devices are given in figure 4.3. The current path for the devices is represented with the blue arrows in the I-V characteristics. Initially, for a fresh cell, the voltage sweep starts from -1.5 V the devices are in HRS and as we move towards the origin the current decreases till 0 V and further starts increasing as we move towards higher values. Moreover, as the applied voltage increases the device current abruptly switches to higher values and attains the LRS. The I-V curves for the devices confirm that the device remains in LRS irrespective of applied sweep either positive or negative and hence the WORM memory characteristics. In the I-V characteristics, the y-axis represents the absolute value of current on a logarithmic scale. For pristine devices, the I-V characteristics show the WORM memory behaviour as discussed earlier. As shown in figure (a) the resistive switching takes place at 1.24 V and after switching the device remains in LRS permanently even after applying a negative bias for a longer time. The device was characterized for hundreds of cycles to check whether the conduction state is getting changed or not and we observed that it remains in LRS.

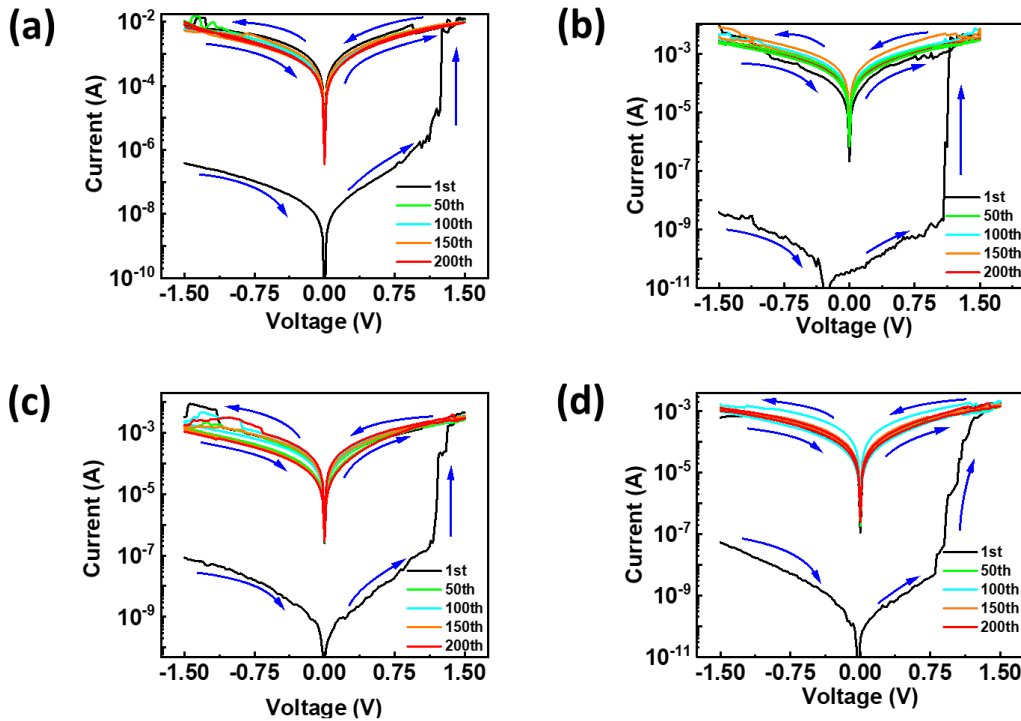


Figure 4.3: I-V characteristics of the device for a voltage loop of -1.5 V to 1.5 V. (a) BTO-P, (b) BTO-Ar1, (c) BTO-Ar2 and (d) BTO-Ar3. The direction of the current path is shown by red arrows.

Similarly, the I-V characterization for the Ar⁶⁺ ions irradiated device with a fluence of 1×10^{15} ions/cm² was carried out to observe the effect of ion irradiation on WORM properties. We observed that the device is showing the WORM properties as for a pristine device but there was a slight reduction in the switching voltage in comparison to the pristine device as shown in figure 4.3 (b). The device switches at a voltage of 1.15 V and the LRS current was also reduced. Further, the device irradiated with the fluence of 3×10^{15} ions/cm² shows the same I-V characteristics and maintains the WORM behaviour irrespective of the irradiation. A slight

reduction in the switching voltage was observed as that of pristine and 1×10^{15} ions/cm² irradiated sample. The switching voltage recorded was 1.12 V which shows a negligible change in comparison to the 1×10^{15} ions/cm² irradiated device. Similarly, for 6×10^{15} ions/cm² irradiated device the switching occurs at 0.9 V which is further less than the devices characterized earlier. From the above characterizations, we can confirm that there is a slight reduction in the switching voltage as we increased the radiation fluence. All the devices are showing stable performance as it was recorded for more than 200 cycles as shown in the figure. We found that there is a slight reduction in LRS current with the increased radiation fluence. The results suggest reduced leakage as the irradiation increase but the WORM behaviour is stable over the irradiation period.

The retention characteristics were recorded to check the retention capabilities over the period for all devices. The retention curves of the pristine and irradiated samples are shown in figure 4.4. As discussed previously the transition in the resistance state for WORM memory devices is permanent and hence it is impossible to erase or rewrite the data. To record the retention in HRS the fresh cell was subjected to a bias of 0.3 V for more than 12000 seconds and the respective current was recorded. Further after applying the write pulse of 1.5 V the device switches to LRS and after switching to LRS the read bias of 0.3 V was applied to the cell to record the retention for the write state for the same time duration. All four devices show excellent retention with negligible variation in read current. The read current was observed to decrease as we increased the fluence of irradiation for both the states (HRS and LRS). The retention curves support the I-V characteristics of the devices and the reduced leakage current was observed for the higher fluence. The improved read performance was observed as a function of irradiation without compromising the device stability. Further, we observed an increased on/off ratio as the fluence of irradiated ions increased.

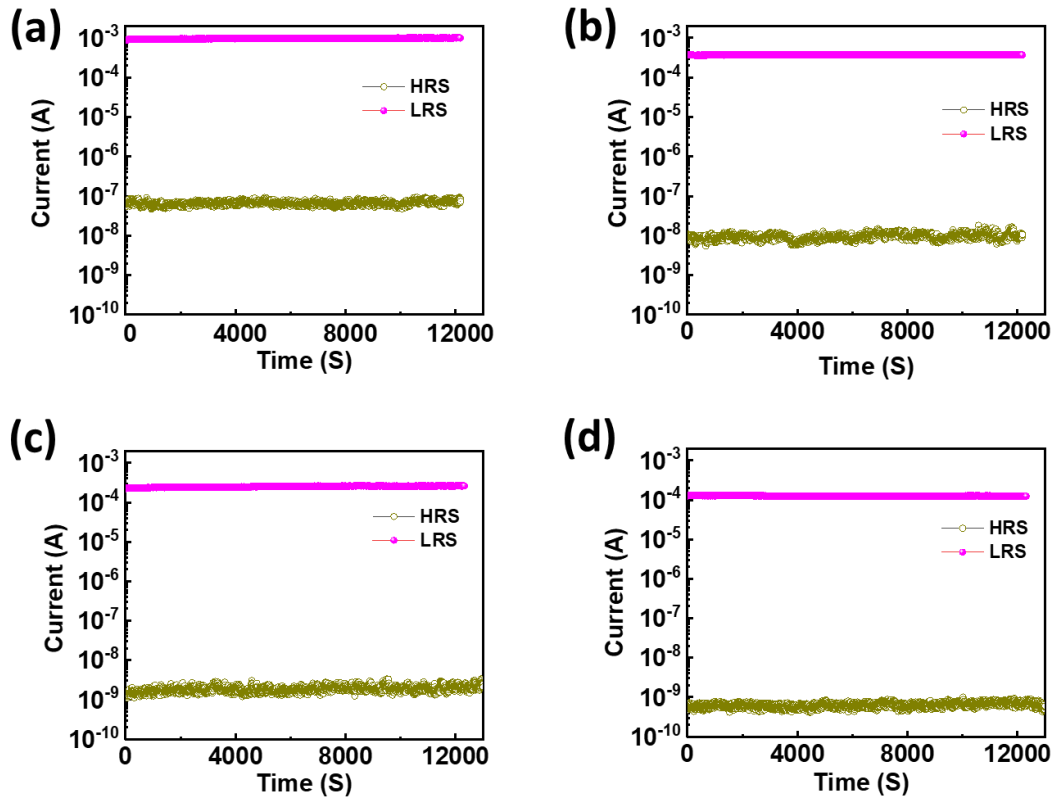


Figure 4.4: Data retention of the device (a) BTO-P, (b) BTO-Ar1, (c) BTO-Ar2 and (d) BTO-Ar3 respectively. For all the devices the data retention was done for a read voltage of 0.3 V.

Memory devices especially WORM are rapidly going through the read process over the period to fetch the data and hence stable data readability and consistency are a must. To verify

the stable data readability for pristine and irradiated devices the multiple write-read erase read cycles were performed. A pulse voltage comprises of 1.5 V write signal for 4 Seconds followed 0.3 V read signal for 6 seconds and an erase signal of -1.5 V for 4 seconds as shown in figure 4.5. Initially, the write signal of 1.5 V switches the devices to LRS and then a read bias of 0.3 V was applied for 6 seconds. After execution of the write and read cycles, the erase signal of -1.5 V was applied to observe the possibility of the device getting reset for 4 seconds. The respective current to each state is provided above the voltage pulse curve of each device. More than a hundred cycles were performed to check whether there is any change in the read current during the rapid execution of the memory process. The obtained curves reveal that there is a negligible variation in read current after both the read and erase process. Further, the data confirms the reduced read current as we increased the fluence of Ar ions irradiating the samples but with the increased irradiation the device stability remains unaffected. Hence, we can say that the WORM memory device's performance has resistance towards radiation.

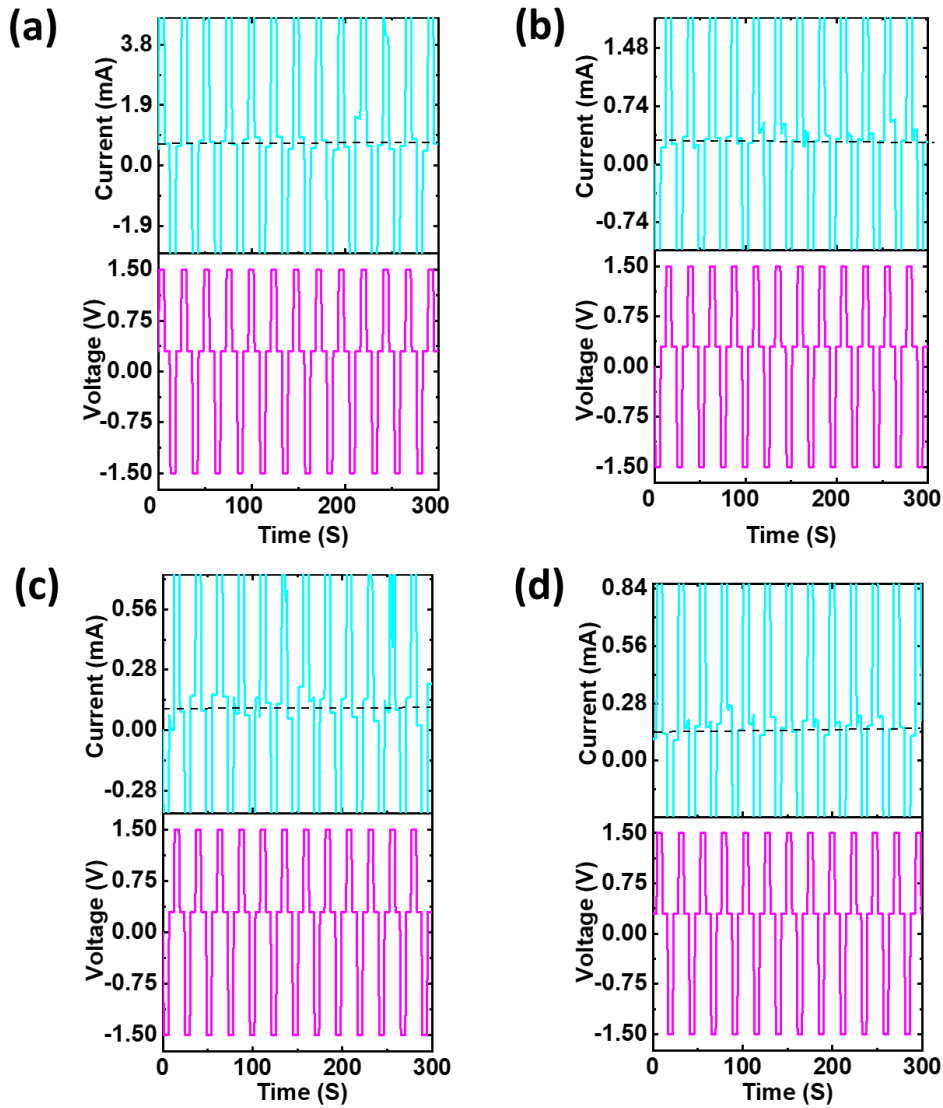


Figure 4.5: Write-read-erase-read plot of all four devices (a) BTO-P, (b) BTO-Ar1, (c) BTO-Ar2 and (d) BTO-Ar3. The lower blue colour plots represent the write, read and erase pulse and dark cyan colour plots are the corresponding current with time.

The I-V characteristics of all four devices were further plotted on a logarithmic scale to analyze the conduction mechanism behind the switching. The log (I)-log (V) plots for pristine and irradiated samples are shown in figure 4.6. Each plot was fitted in different parts as per slope change for the region with COD ($r^2 \geq 0.99$). Initially, the linear variation in current represents the conduction due to the quantum mechanical tunnelling of ions and electrons through a potential barrier. The higher values of slopes further represent the conduction due to

trap-assisted space charge-limited conduction (SCLC). For LRS, the current follows a linear path confirming the ohmic conduction. The schematic representation of filament formation is explained in the previous chapter. The reduction in the device current as the radiation fluence increases confirms the reduction in the leakage current of the am-BTO layer. The reduction in the read current will improve the power consumption for the devices with increased radiation. As far as the WORM memory performance is concerned the am-BTO layer shows excellent resistance towards the Ar-ion irradiation up to a fluence of 6×10^{15} ions/cm².

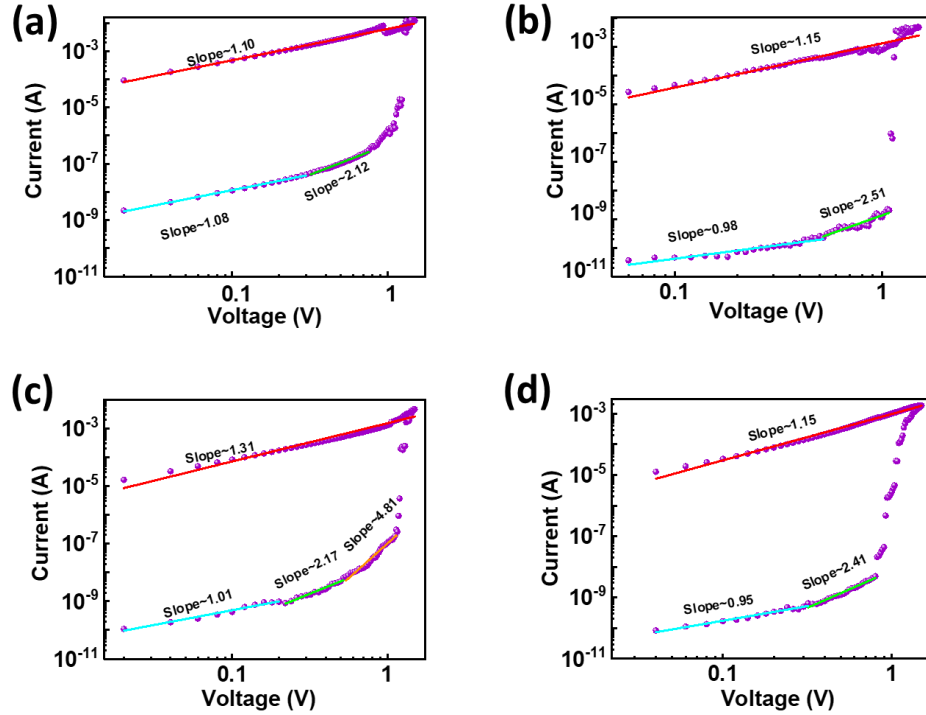


Figure 4.6: I-V characteristics plotted in logarithmic scale for the device (a) BTO-P, (b) BTO-Ar1, (c) BTO-Ar2 and (d) BTO-Ar3 respectively.

4.5 Conclusion

Ar ion irradiation significant role in the alteration of thin film morphologies and memory performance. For this, 1.8 MeV Ar⁺⁶ ions were used to irradiate the am-BTO thin film deposited using an RF-sputtering system with different fluence including 1×10^{15} , 3×10^{15} and 6×10^{15} ions/cm². Further, the surface morphology results show a drastic reduction in the surface roughness as the irradiation fluence increased. The WORM characteristics were recorded for a voltage range of -1.5 V to 1.5 V as a function of irradiation to analyze the effect of irradiation on the memory performance of the am-BTO resistive switching devices. A slight reduction from 1.24 V to 0.9 V in the switching voltage was observed as the irradiation fluence was increased. The switching ratio was almost the same for all the devices of the order of 10^4 with good data retention capabilities. The lower read current due to irradiation confirms the low leakage current. The reduced grain size shown by the AFM data supports the read current changes. All devices were able to manage the WORM memory characteristics confirming the radiation-hard nature of am-BTO thin film-based WORM memory devices.

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