

Radiation Hard Resistive Switching Performance of SrTiO₃ Thin Film-Based Resistive Switching Devices

This chapter describes the detailed report on the RRAM performance of SrTiO₃ thin film-based resistive switching devices. Firstly, we synthesized the phase pure SrTiO₃ powder to prepare the sputtering target via the conventional solid-state reaction method. The RF-sputtered amorphous SrTiO₃ thin films on FTO-coated glass substrates were studied for RRAM performance. The fabricated devices offer conduction bridge filament-based stable and low-voltage switching performance with good data retention capabilities. Further, the SrTiO₃ thin films were subjected to an irradiation chamber for swift heavy-ion irradiation and the effect of irradiation on switching performance was analyzed. The results show a reduced memory window as the irradiation fluence increased. However, the RRAM performance of the devices was stable even after the irradiation.

5.1 Introduction

Resistive random-access memory (RRAM) is an emerging non-volatile memory (NVM) technology have huge potential to replace conventional flash memories for storage applications [Meena et al., 2014]. Moreover, these devices offer a high tolerance towards the harsh radiation environment and hence can be game changers as a dense and compact memory option for memory applications in such conditions as nuclear plants and space. The current flash technology offers radiation resistance only upto a dose of a few krad thus these devices show abrupt behaviour in radiation-prone areas and need radiation-hard packaging of the device which further increases the cost and size. Besides that, the other charge base memories are also radiation sensitive with further downscaling. The limitations of these memory technologies to working in radiation harsh conditions result in the unavailability of high-density and fast memories. Hence there is a great demand for radiation-hard NVM technologies to be deployed in such environments to perform stable memory operations. For radiation stability analysis the RRAM devices have been explored and tested for different ionic radiation environments. Metal oxides including Ta₂O_x, ZnO, HfO₂, BiFeO₃ and BaTiO₃ have been widely studied for radiation stability in various electronic device applications and the results show the potential of these materials to be used in such conditions [Jacobs-Gedrim et al., 2018; Kumar et al., 2014; Li et al., 2022; Sharif et al., 2021; Solanki et al., 2013]. HfO₂ is the most explored binary oxide for radiation stability analysis and shows great potential. Among all metal oxides, the perovskite oxides show inherent radiation hard properties and are tested for various radiation environments. Alongside the radiation-hard nature, these perovskite oxides also show excellent resistive switching properties and have been studied for various memory applications. These materials offer great stability, long data retention and fast switching at low switching voltages. The matured deposition technique and a wide range of deposition temperatures are added advantages for RRAM devices with these materials. Both oxygen vacancy filament RAM (OxRAM) and conduction bridge filament RAM (CBRAM) have been observed for perovskite oxides-based RRAM. In OxRAM, the filament formation is modulated by the number of oxygen ions in a localized and directed manner that controls the radiation damage. The radiation exposure alters the structural properties and stoichiometry due to irradiation upto a certain level and the higher exposure may lead to data loss in RRAM devices. Hence heavy ion irradiation with lower fluence can affect the device's performance and their retention

capabilities. Furthermore, the CBRAM where the metal ion migration through the switching layer governs the filament formation and dissolution also offer the radiation hard RRAM performance. The perovskite oxide layers including LaFeO_3 , BaTiO_3 and AlFeO_3 have been used as switching layers for resistive switching applications [Chu et al., 2014; Rao et al., 2020; Schmitt et al., 2019]. There are very few studies on the irradiation effect on perovskite oxide-based RRAM and it needs to be explored more for their use in a radiation harsh atmosphere. As resistive switching is a trap-assisted and vacancy-governed phenomenon, radiation exposure can significantly improve the device's performance. In this chapter, we explore the radiation stability of SrTiO_3 thin film-based RRAMs against the varying fluence of swift heavy ions. Therefore, SrTiO_3 thin films were exposed to the Au^{9+} ions of 120 MeV energy for a different fluence of ions by varying the exposure time. Further, the surface morphological and RRAM properties were investigated concerning the ion exposure. The performances of the fabricated devices before and after irradiation were compared and analysed for the various performance parameters of RRAM.

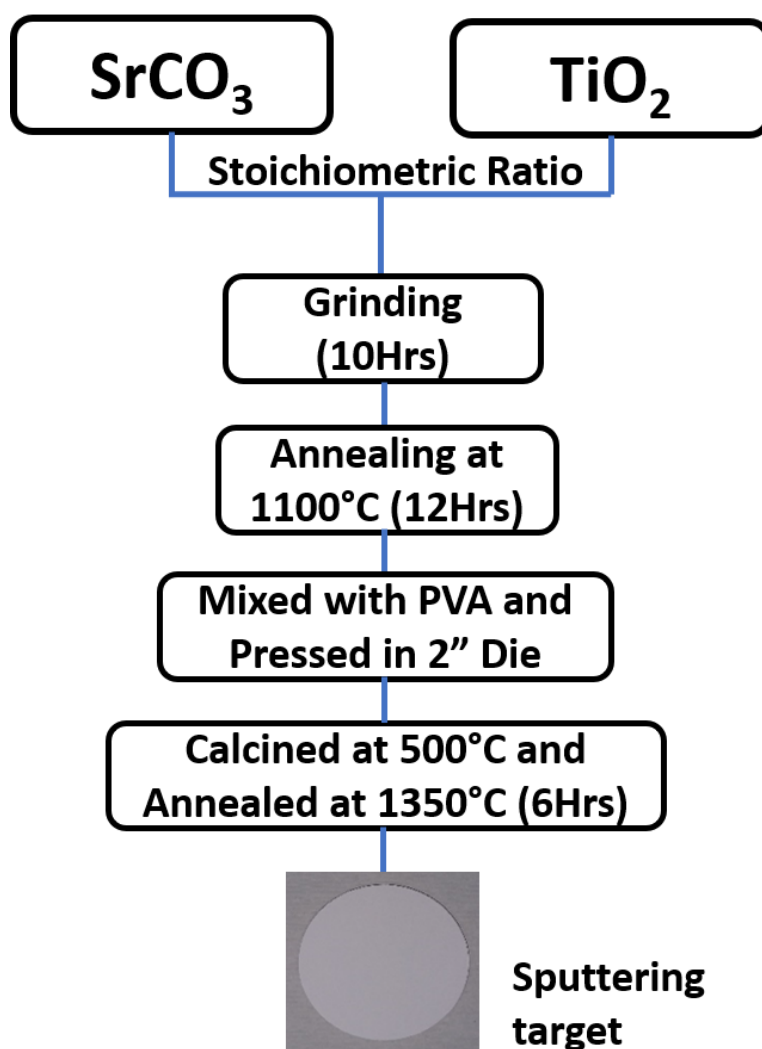


Figure 5.1: Process flow for the solid-state synthesis of SrTiO_3 powder and target preparation.

5.2 Synthesis and Characterization of SrTiO_3 Powder and Target Preparation

The SrTiO_3 powder was synthesized using the conventional solid-state reaction method. The stoichiometric ratio of SrCO_3 and TiO_2 were taken as starting material and thoroughly ground in an alcohol medium for 10 hours with intermediate heating for 4 hours at 600°C after 6 hours of grinding. Afterwards, the powder was annealed at 1100°C for 12 hours in a furnace for interatomic reaction to form SrTiO_3 . A few drops of 2 wt% PVA solution were mixed in

prepared powder as a binding agent and mixed in a mortar pestle. PVA-mixed SrTiO_3 powder was subjected under a hydraulic press in a 2-inch circular die and pressed to form a compact circular-shaped LaFeO_3 pellet to be used as a sputtering target to deposit the SrTiO_3 thin films. The prepared pellet was calcined at 500°C for 3 hours and further sintered at 1350°C for 6 hours. The process flow for the synthesis and target preparation is represented in figure 5.1.

The synthesized SrTiO_3 powder was characterized using the XRD system to determine the crystalline structure as shown in figure 5.2. 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 and the strong and narrow peaks as indexed in the figure confirms the orthorhombic phase. (JCPDS card no. 35-0374). In XRD spectra characteristic peaks of the SrTiO_3 powder appear at 32.10 , 40.03 , 46.45 , 57.6 , 68.0 , and 77.0° and are ascribed to the (110), (111), (200), (211), (220), and (310) planes of cubic symmetry of SrTiO_3 powder.

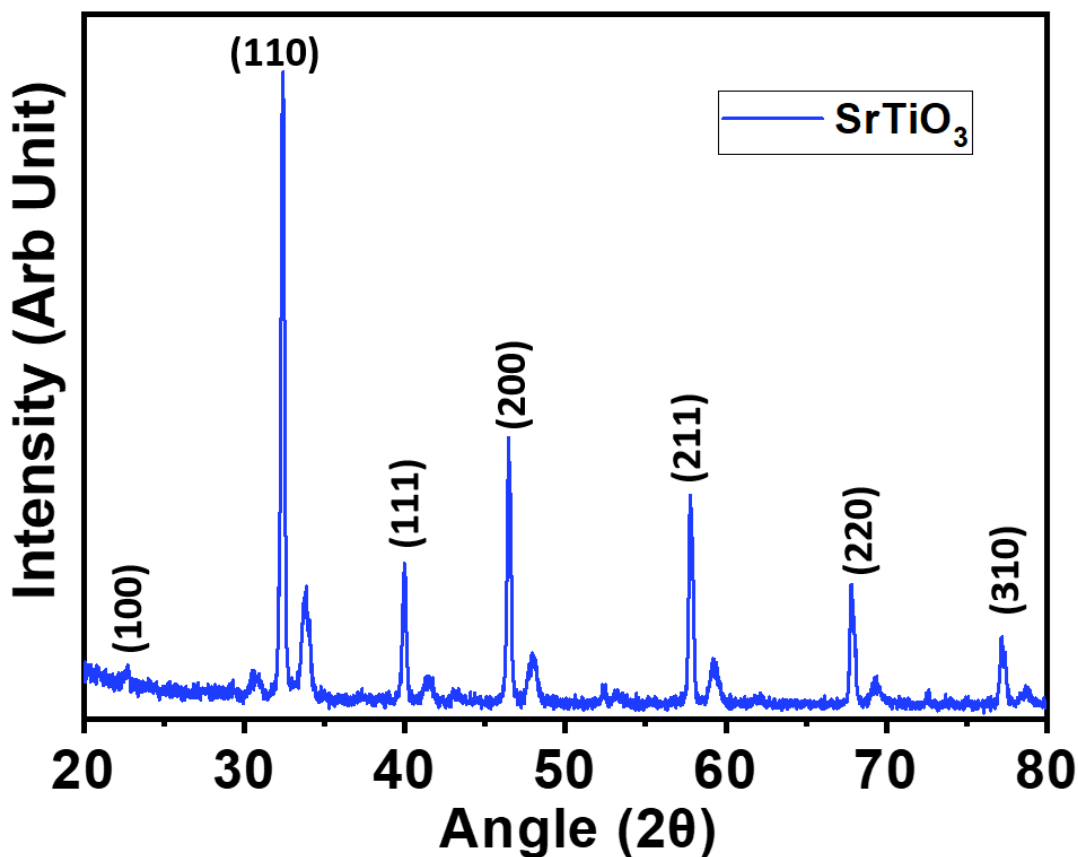


Figure 5.2: XRD spectra of synthesized SrTiO_3 powder.

5.3 Deposition of SrTiO_3 thin films and Au^{9+} Ions Irradiation

The SrTiO_3 thin films were deposited on the FTO-coated glass substrate by RF-magnetron sputtering using SrTiO_3 thin film. Firstly, we synthesized the SrTiO_3 compound using the conventional solid-state reaction method. FTO substrates were cleaned using a standard cleaning process before deposition and dried using nitrogen blowing. The thin-film depositions were carried out at room temperature with 80 watts of applied RF power and 35 SCCM argon flow after achieving a vacuum of 2×10^{-6} mBar. The working pressure of the process chamber was kept at 2×10^{-2} mBar during the deposition and the substrate-to-target distance was fixed at 5 cm. The deposition time was optimized to 90 minutes to get a thickness of 80 nm of SrTiO_3 thin film. The deposited samples were irradiated with 120 MeV Au ions at an incremental rate of ion fluence using the 15 UD pelletron accelerator at the Inter-University Accelerator Centre (IUAC), New Delhi. The 9th charge state was used for Au ions and the beam

current was maintained at 0.5 pA. Three different fluences of Ar ions were irradiated on am-BTO thin films as 3.3×10^{11} ions/cm², 6.6×10^{12} ions/cm² and 1×10^{13} ions/cm² by varying the exposure time. For uniform irradiation, the angle of the incident beam to the surface over the sample 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 LFO thin film was 20.44 μ m as calculated using SRIM. The irradiated thin films were characterized to analyse the change in surface morphologies using AFM.

5.4 Thin Film Characterization

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 5.3 (a-d). 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 126 nm, 117 nm, 99 nm and 107 nm for pristine, 3.3×10^{11} ions/cm², 6.6×10^{12} ions/cm² and 1×10^{13} ions/cm² respectively. The average surface roughness was 12.32 nm, 10.69 nm, 9.49 nm and 7.65 nm for devices pristine, 3.3×10^{11} ions/cm², 6.6×10^{12} ions/cm² and 1×10^{13} ions/cm² respectively. A significant surface roughness confirms the reduced grain size due to irradiation.

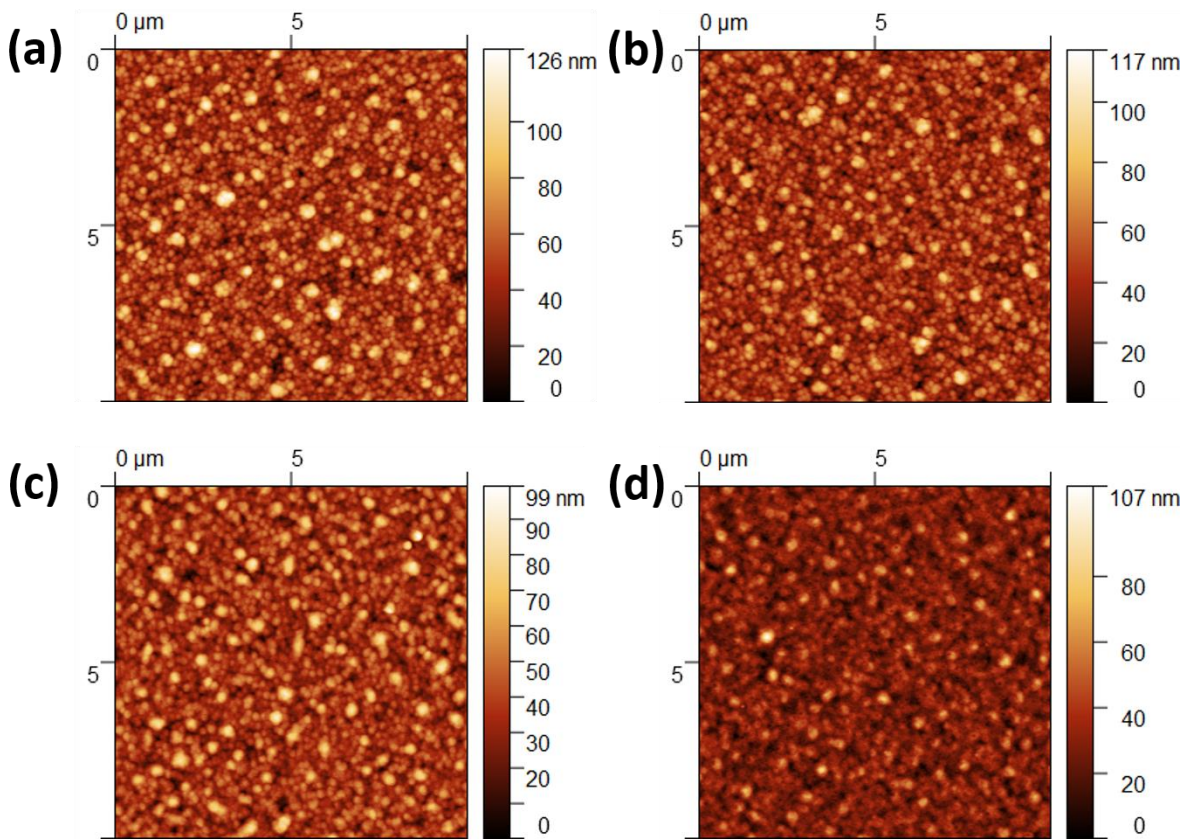


Figure 5.3: AFM images for SrTiO₃ thin films (a) Pristine (b) 3.3×10^{11} ions/cm² (c) 6.6×10^{12} ions/cm² (d) 1×10^{13} ions/cm².

5.5 RRAM Characteristic

The resistive switching performance of the fabricated devices on pristine and irradiated thin films was analyzed with conventional MIM configuration (Ag/SrTiO₃/FTO). To extract the

performance parameter of SrTiO₃-based resistive switching devices, we used the Keithley 4200-SCS system integrated with a probe station.

Complete current-voltage characteristics for an RRAM device give information about the set and reset voltage for the device. A complete voltage iteration from -4 V to 1.5V in dual sweep mode was applied in dual sweep mode to obtain the I-V characteristics for pristine, 3.3×10^{11} ions/cm², 6.6×10^{12} ions/cm² and 1×10^{13} ions/cm² irradiated SrTiO₃ thin film devices as shown in figure 5.4 (a-d) respectively. Initially, the pristine sample was characterized for a sweep from -4 V → 0 V → 1.5 V → 0 V → -4 V for more than 200 consecutive cycles as shown in Fig. 5.4 (a). The current path with voltage is represented in each figure (figure 5.4) with blue-coloured arrows to show the switching direction. The device shows the figure-of-eight (F8) resistive switching where the device moves to LRS for the positive polarity of applied voltage and HRS for negative polarity. Initially, with a negative voltage of -4 V the device starts with a low resistance state (LRS) and at ≈1.5 V the device switches to a high resistance state (HRS) forming free behaviour and with reversed polarity in the return cycle device gains its LRS back (set). The pristine device shows switching at 0.89 V (V_{set}) and -1.75 V (V_{reset}). Similarly, for a 3.3×10^{11} ions/cm² irradiated device, the resistive switching was observed for the same voltage iteration. The device shows switching at 1.15 V (V_{set}) and -2.79 V (V_{reset}). The voltage iteration was applied for a 6.6×10^{12} ions/cm² irradiated device. For the device, we observed a transition from abrupt to soft filament formation as shown in figure 5.4 (c). Further, the 1×10^{13} ions/cm² device was characterized and the obtained I-V curve reveals the soft forming and dissolution of filament. We observed a reduced memory window as the irradiation fluence was increased. On the other hand, the abrupt switching behaviour tends to soft filament formation with increased fluence. All four samples were characterized for more than 200 cycles out of which the 1st, 50th, 100th, 150th and 200th cycles have been presented in their I-V curve.

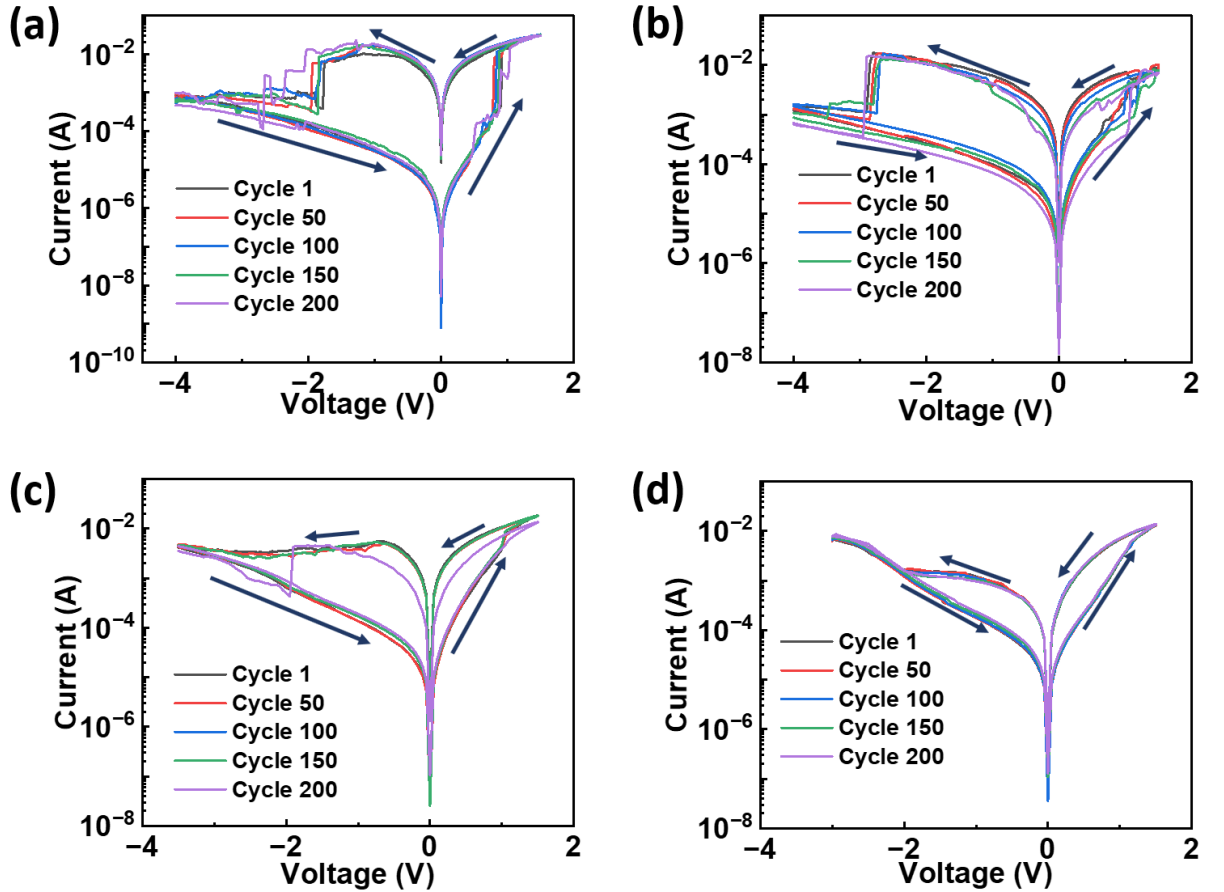


Figure 5.4: Current-voltage characteristics of SrTiO₃ RRAM devices (a) Pristine (b) 3.3×10^{11} ions/cm² (c) 6.6×10^{12} ions/cm² (d) 1×10^{13} ions/cm².

Retention time is an important parameter to be explored to justify the data retention capabilities of an NVM at a very low read voltage. Hence, we characterized all four devices to observe their retention stability over a period. The retention of all devices was recorded for more than 8000 seconds and at a read bias of 0.3 V for both states to observe the effect of irradiation on the data retention properties as shown in figure 5.5 (a-d). The retention characteristics show that all devices irrespective of the irradiation fluence are able to maintain the executed state (set or reset) over the tested period of 8000 seconds. However, with the increased fluence the read current decreased in comparison to the pristine device. There is no significant variation in the read current during the retention period was observed confirming the stable nonvolatile nature of the device even after the irradiation.

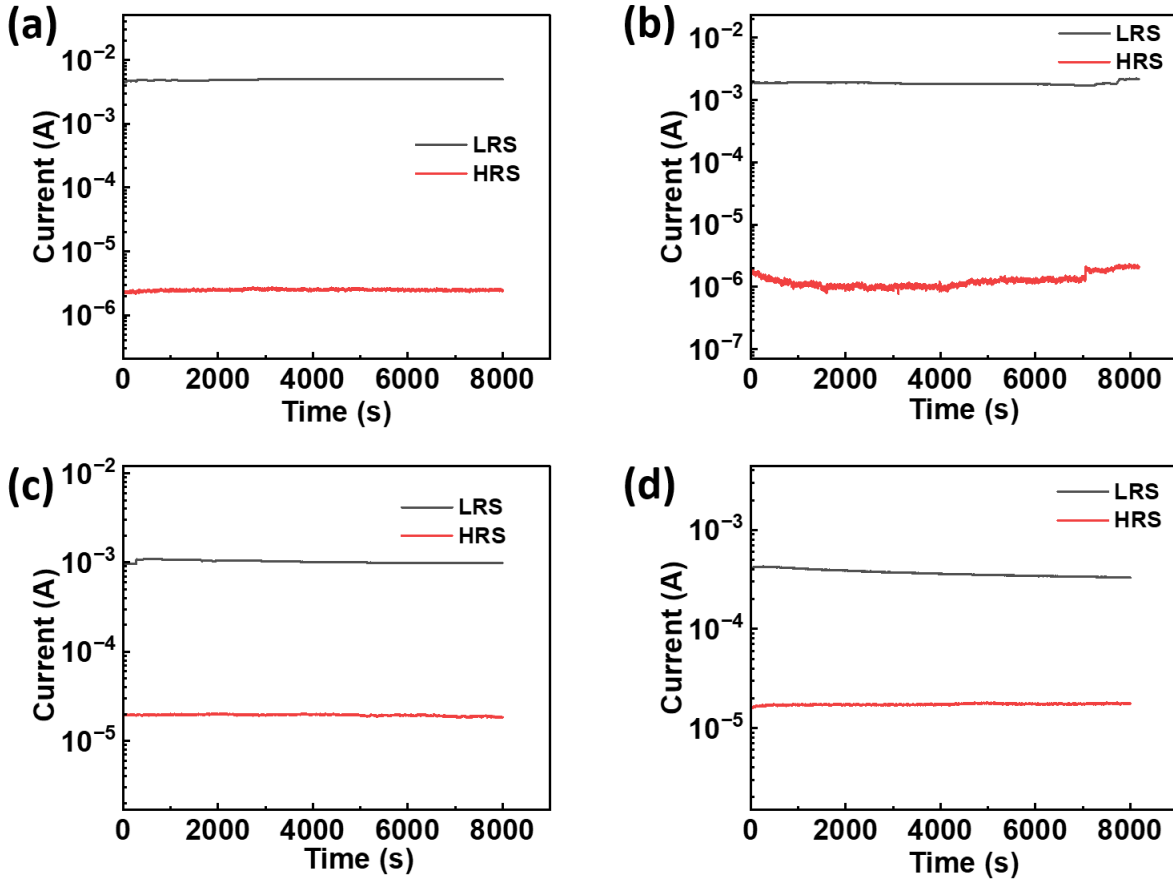


Figure 5.5: Retention characteristics of SrTiO₃ RRAM devices (a) Pristine (b) 3.3×10^{11} ions/cm² (c) 6.6×10^{12} ions/cm² (d) 1×10^{13} ions/cm².

The conduction through a thin film can be explained as a cumulative effect of various conduction mechanisms. These conduction mechanisms are generally expressed in terms of the slope of current with voltage and different values of slope attributed to different conduction mechanisms. Hence, the obtained I-V curves were plotted on a logarithmic scale to get an idea about the transport mechanism playing role in the switching of the devices as shown in figure 5.6 (a-d). The plotted log(I)-log(V) curves were linearly fitted to get the slopes for different regions for a COD(r^2) ≈ 0.99 . The current conduction mechanism in a memory cell for the HRS state is driven by the space charge limited conduction (SCLC). The conduction in trap-controlled SCLC region comprises three regions ($I \propto V^m$) based on the value of slope (m) are as ohmic region ($m=1$), Child's law region ($m=2$) and the steep current region ($m>2$). Hence, we can say that for the lower value of voltage (ohmic region), the generated carriers depend on the applied field and material properties. The charge carriers in the ohmic region do not travel across the entire film due to large relaxation time and hence it follows the ohm's law in this region. Further, as we increase the applied electric field the generated charge carriers overcome the thermally generated charge carriers and filled the trap sites in the film. The filling up of the all-trap sites brings the ohmic region to SCLC, where the injected charge carriers are allowed to

move freely across the film thickness and lead to a steep change in current to bring the current to the LRS state. Further, the analogue switching at higher fluence confirms the less and uniformly distributed trap sites for the devices and hence the soft formation of filament takes place.

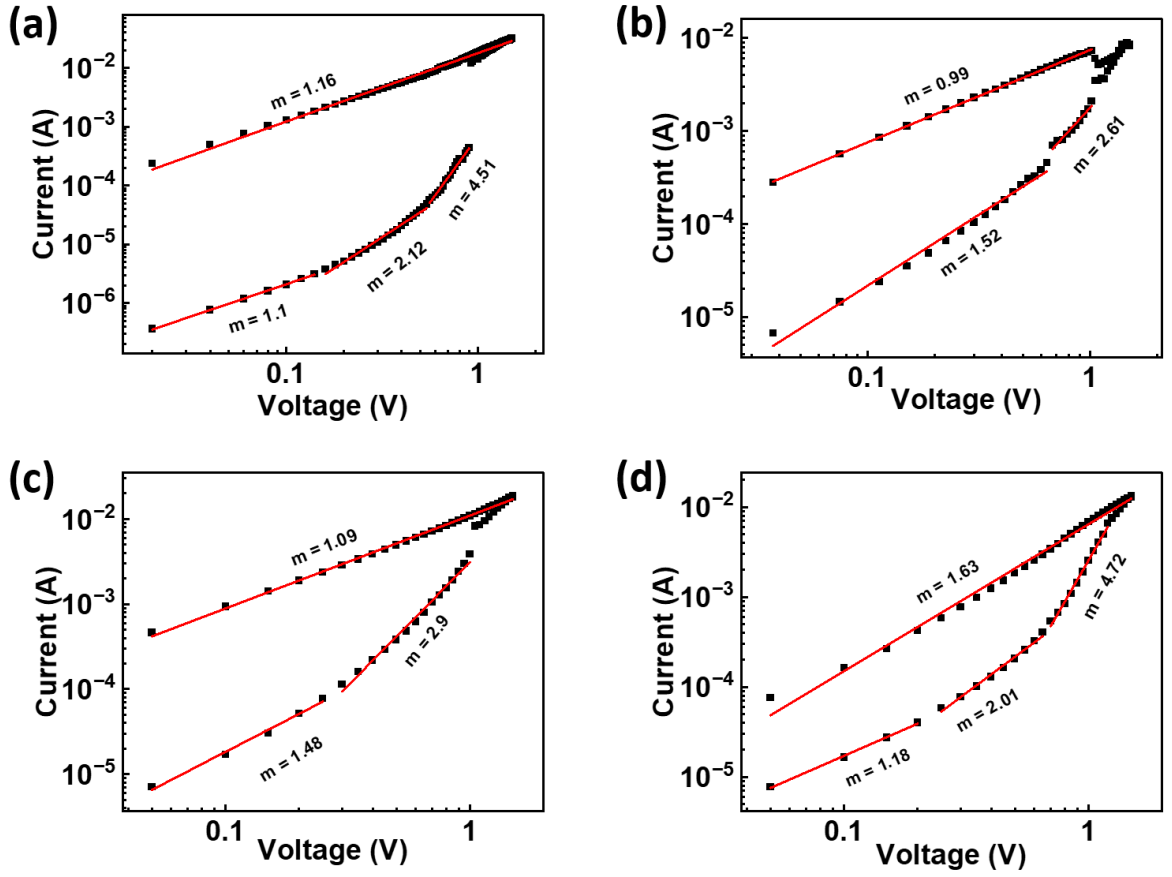


Figure 5.6: $\log(I)$ - $\log(V)$ plots of SrTiO_3 RRAM devices (a) Pristine (b) 3.3×10^{11} ions/cm² (c) 6.6×10^{12} ions/cm² (d) 1×10^{13} ions/cm².

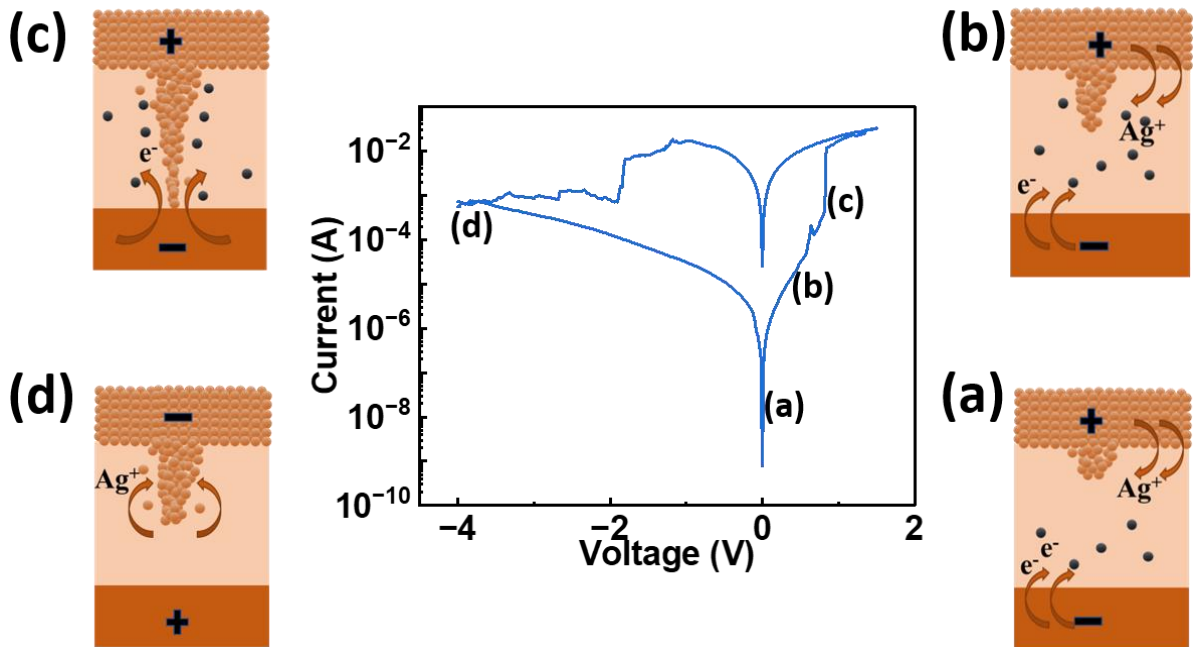


Figure 5.7: Schematic representation of metal bridge filament formation mechanism to explain the switching characteristics of SrTiO_3 RRAM devices. (a) Fresh Cell (b) Migration of Ag ions towards bottom contact (c) Filament formation (d) Filament rupturing.

The migration of Ag ions while applying the voltage sweep play the role in the switching of the device. The switching mechanism proposed for the devices is schematically represented in figure 5.7 (a-d). Initially, without voltage sweep, the devices show very high resistance and as the voltage sweeps to higher values the current starts increasing due to the migration of Ag ions figure 5.7 (a) and (b). As the metal bridge forms, there is a sudden rise in current observed and the device switches to LRS (figure 5.7 (c)). After switching to LRS the device current follows a linear path and with the decreased voltage value the current remains linear. At a sufficient negative bias, the migration of Ag ions toward the top electrode starts and the filament gets dissolved and the device again attains the HRS. The LRS represents the write or '1' and the HRS represents the erase process or '0'. The RRAM switching mechanisms are explained with different hypotheses but here we are using Ag as an electrochemically active contact and the Ag ion migration through the trap sites through the layer is the reason behind the resistive switching.

5.6 Conclusion

In conclusion, we synthesized the SrTiO_3 for the realization of resistive switching devices deposited using an RF-sputtering system. The fabricated devices have a stable RRAM behaviour at low operating voltages. Further, we analyzed the stability of the RRAM behaviour of the SrTiO_3 layers after irradiation of Au^{9+} ion with varying fluence upto 1×10^{13} ions/cm². The devices show stable RRAM performance even after the irradiation for the voltage sweep from -4 V to 1.5 V for more than 200 cycles. However, there is a significant reduction in the switching ratio from 655 (pristine) to 10 (6×10^{15} ions/cm²) but the retention curves reveal the stable data retention capability irrespective of irradiation for a period of about 8000 seconds. The abrupt switching behaviour changes to soft filament formation as the ion fluence increases showing the potential for neuromorphic application. A significant reduction after irradiation also confirms the reduced power consumption. The stable performance after irradiation and the same operating voltage proves the potential of these devices to be used in a radiation harsh environment.

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