Chapter 8

Conclusion and Future Scope

The primary aim of this thesis work was to explore various approaches to enhance the performance of RRAM devices, more specifically for flexible electronics. In this chapter, various activities done for this thesis are summarised. In addition, the work is given along with the future scope.

8.1 SUMMARY

The primary aim of this thesis work is to fabricate RRAM with low switching voltages, high endurance, high reliability, and enhanced memory window. The journey towards this aim is comprehensively summarised, and also the inferences draw has been briefly explained as following:

I. Initially, the search for a switching layer and its deposition mechanism was extensively studied. Moreover, the combination of top and bottom electrodes was studied and optimized to obtain an ohmic switching layer-top electrode interface and a Schottky switching layer-bottom electrode interface. After a thorough literature survey and theoretical studies, the high-k metal oxides like AlO_x and HfO_x were chosen for the initial study of resistive switching behavior. Furthermore, the atomic layer deposition process with pre-defined deposition libraries was used for metal oxide deposition.

II. A novel multi-temperature deposition scheme was proposed where the oxygen vacancy concentration was manipulated using the water precursor pulse. The AlO_x switching layer was bifurcated into three segments with different thicknesses, where the top and bottom AlO_x layer's oxygen content was kept lower (means higher defects concentration), and the middle layer was a fully oxidized alumina. This structure provides two weak regions within the switching layer (at the two junctions of fully and partially oxidized AlO_x) as the conductive filament in the partially oxidized film will be stronger in comparison to the fully oxidized AlO_x. A decent improvement in the device performance was observed with reliable resistive switching characteristics exhibited at low voltages.

III. A hybrid switching layer architecture was explored for improvement in the endurance and memory window at comparatively lower switching voltages. The bilayer structure of poly(4-vinylphenol) (PVP)/HfO_x was examined where the PVP was employed to improved the reliability by controlling the conductive filament growth kinetics, and HfO_x was used to improve the memory window. The PVP concentration was optimized to be 2.5 wt.% as either no resistive switching or switching at higher voltages was observed at higher PVP concentrations. The pinholes present at the PVP surface guided the migration of Ag ions from the top electrodes, and towards the bottom electrode. This resulted in the switching voltages as low as 1.03 V set voltage and -0.68 V reset voltage with DC endurance of up to 3 × 10^2 cycles, AC endurance of decent 2 × 10^3 cycles, and memory window of 80. This enhanced performance is attributed to the pinholes at the PVP surface as with the increasing concentration, the pinholes density and dimensions were shrinking, and a poor or no resistive switching was observed in these devices. Finally, the reliability study was performed using the Weibull's distribution that confirms the reliable switching performance with almost similar switching voltages and sustained memory window. Also, the PVP pinholes didn't affect the sample yield, and almost >75% of devices were found working on the same sample.

IV. An ideal RRAM device must have sufficient memory window so that the two resistance levels are distinguishable for more than 10 years and in the endurance test as well. This objective was achieved by incorporating various concentrations of graphene oxide (GO) in the PVP solution to deposit the secondary switching layer while the 5 nm HfO_x was kept as the primary layer. The higher concentration of GO causes the rise in leakage current in the devices owing to the semiconducting behavior of GO as it turned into Reduced GO at a higher temperature, whereas, in the lower concentration of GO, the dielectric behavior of PVP was dominating resulting in similar switching performance as reported in the previous results. This resulted in the elimination of pinholes from the PVP surface, which decreases the leakage current, and the layered structure of GO provided better control over the growth and dissolution of conductive filament and enhanced the mechanical strength of the device. An excellent low voltage resistive switching behavior with switching voltages as low as 0.6 V set voltage and -1.46 V reset voltage was observed with a remarkable memory window of $>10^6$. Moreover, a decent DC endurance of 8 × 10^2 cycles and AC endurance of 1.4 × 10^3 cycles was achieved owing to the controlled growth and dissolution of conductive filament. The flexible RRAM device fabricated over a polyethylene terephthalate (PET) substrate demonstrated a decent switching performance with marginal degradation in OFF current up to 5 mm bending radius and reset failure at 2.5 mm radius. A significantly large memory window of $>10^3$ was maintained, and only a marginal variation in the switching voltage was observed. Furthermore, the devices were exposed to 150 continuous cycles of compressive and tensile strain corresponding to the ±5 mm bending radius. These devices exhibited almost negligible degradation in the memory window and no significant variation in the switching voltages. Also, a decent memory window of 4 × 10^3 was maintained during the retention time analysis for 10^4 s.

V. Finally, another 2-dimensional material Molybdenum Disulfide (MoS_2) was explored for further enhancement of device performance in terms of switching current reduction and device flexibility. The devices fabricated with a thin film of optimized concentration of MoS_2 in the PVP solution and an ultra-thin HfO_x layer resulted in an ultra-low switching current of 110 nA and hence extremely low set and reset power consumption of 270 and 0.1 nW. This ultra-low ON current is attributed to the formation of multiple weak Ag conducting filaments inside the switching layer. A decent memory window of 3 × 10^2 was observed with a decent retention time of over 10^4 s at 0.5 V read voltage and DC endurance of 5 × 10^2. The Weibull's distribution study of switching voltages confirms the reliable switching performance by the devices confirmed by high β values of 17 and 9.5 for reset and set voltages. Furthermore, the double log current-voltage curves suggested the space charge limited conduction and the ohmic conduction. The devices were tested under various extreme conditions such as higher temperatures and the bending strains. The device performed decently well under higher annealing temperature up to 473 K without any degradation in the switching performance. The current-temperature curve confirmed the metallic behavior of the conductive filament in the SET state as the LRS current tends to fall sharply with rising temperature indicating the negative temperature coefficient. The flexibility testing of the device confirmed the device's ability to withstand compressive and tensile strain under extreme bending conditions. Owing to the high mechanical strength of MoS_2, these devices exhibited nondestructive switching characteristics under the extreme bending radius of 2.5 mm while maintaining a decent memory window of ~75. Also, when the devices were exposed to continuous compressive and tensile strain, no degradation neither in the memory window nor in the switching voltage uniformity was observed for 100 cycles.

8.2 CONCLUSIONS

The After the extensive analysis of the results obtained from the various experiments carried out during this thesis research, the inference that can be drawn is that the PVP:2-D material composite along with the ultra-thin HfO_x layer can be an attractive option for implementing various RRAM based futuristic applications. The performance of an RRAM device primarily depends upon many factors, including electrode-switching layer interface quality, defects states in the switching layer, and the device dimensions. All these factors contribute and regulate the conductive filament formation and dissolution process. The devices fabricated with the PVP:GO composite has the potential to be used in memory applications where noise immunity is the primary concern as it demonstrated an I_{on}/I_{off} of $>10^6$. Also, they demonstrated significantly low switching voltages 0.6 V and -1.46 V with DC endurance of 800 cycles. The Ag/PVP:GO/HfO_x/ITO flexible RRAM devices exhibited decent electro-mechanical stability, and the device performance remained unaffected of the extreme bending strain for multiple cycles and longer duration. Another 2-D material MoS_2 was explored for memory applications has demonstrated a multifold reduction in the switching current. When GO was replaced with the MoS_2, an extremely low ON current of 500 nA was observed at a decently low set and reset voltages of 1.18 V and 0.34 V and retention of up to 10^4 s. This ultra-low ON current devices can be explored for high power efficiency applications as the SET and RESET power consumption in these devices has been observed to be 270 nW and 0.1 nW. This ultra-low ON current is attributed to the formation of nanosized multiple weak conductive filaments of Ag atoms, migrated through the switching layer under an extremely high electric field. The flexible Ag/PVP:MoS_2/HfO_x/ITO devices fabricated over the PET substrate demonstrated excellent flexibility, tested under extreme bending conditions of 2.5 mm bending radius. Although there was a development of cracks over the switching layer and the top electrode surface, the device still maintained a decent memory window. Hence, after looking at the performance parameters of polymer:2-D material composite switching layer based devices, we can conclude that these devices carry the potential to be used for the applications where high flexibility, low power consumption, and greater noise immunity is required.

8.3 FUTURE SCOPE

Although extensive research in the field of RRAM technology and related applications has been performed during the last decade. However, the understanding of resistive switching phenomena in these devices is a complex process. It demands a more in-depth study using sophisticated material and film analysis tools such as HRTEM, XPS, elemental mapping, CAFM, computational simulations, and other spectroscopic and imaging techniques. The exploration of more complex composite, alloys, doped, bilayer, and trilayer films makes this process even more challenging due to their unknown crystallographic structures and electronic states. The present work of this thesis has largely covered and met the set objectives; however, there is the future scope for improvement that can further enhance the performance of the reported devices. The following directions can lead towards further enhancement in the device performance and eventually implemented in computing and storage applications:

I. An in-depth study of film characterization before, during, and after the switching event can provide a clear picture of the resistive switching mechanism. In this regard, in place of using a sandwich structure, a lateral structure can help in doing the in-situ measurements.

II. Apart from GO and MoS_2, more 2-D materials such as hexagonal boron nitride, $MoSe_2$, $MoTe_2$, WS_2, and WSe_2 can be explored for preparing composite films with organic polymers such as polyvinyl alcohol and polyvinyl carbazole.

III. Scaling of device dimensions can be implemented for better device density and to examine the effect of scaling on device performance and the switching behavior. This can be achieved by using sophisticated lithography processing using electron-beam lithography and DUV lithography. Also, the switching layer thickness can be scale down by controlling the deposition parameters.

IV. The fabrication of these devices over non-conventional flexible or bio-degradable substrates such as paper, cloth, polyimide tapes, polydimethylsiloxane (PDMS), and metal foils can be an excellent study for future wearable and biodegradable electronics applications.

V. Currently, the latest and most exciting application of RRAM devices in the electronics industry is neuromorphic computing and in-memory computing. This computing system bypasses the conventional Von-Neumann architecture of processors. Hence, these devices can be explored for this application after extracting all the necessary electrical characterization data required for modeling and implementation of neuromorphic systems. IMP and MAGIC logic approaches can be explored for further extension of this work for in-memory computing and logic implementation based applications.

VI. As the proposed devices include the organic component in the device structure, the aging effect on the devices can be an excellent study. Also, the device can be exposed to various environmental conditions such as humidity, heat, and the device performance needs to be checked.