3
Investigation of Resistive Switching Behavior of Selected Materials and Combinations

This chapter focuses on the investigation of resistive switching behavior in the selected materials and their combinations, including poly(4-vinylphenol) (PVP), poly(N-vinylcarbazole) (PVK), molybdenum disulfide (MoS_2), molybdenum diselenide ($MoSe_2$), titanium dioxide (TiO_2), and their composites. These materials are explored for their potential as active switching layers in RRAM devices, emphasizing their distinct contributions to switching mechanisms, operating voltages, and reliability. By leveraging the unique properties of each material such as the flexibility of PVP and PVK, the high charge-trapping capability of MoS_2 and $MoSe_2$, and the robust conductivity of TiO_2, this study provides valuable insights into tailoring material combinations for enhanced device performance. The results open new possibilities for creating low power and highly reliable RRAM devices for flexible and wearable electronic applications.

3.1 Introduction

The rising demand for advanced memory technologies that are lightweight, wearable, flexible, and energy-efficient is driven by the increasing interest in emerging applications such as RFID tags, smartwatches, autonomous vehicles, healthcare systems, and flexible electronics. Among various candidates, RRAM has garnered significant attention as a promising data storage solution [Wang et al., 2020, Gao et al., 2019, Lee et al., 2020]. RRAM offers several key advantages, including cost-effectiveness, low power consumption, high storage density, ease of fabrication, and seamless compatibility with CMOS technology, making it an attractive alternative to traditional memory devices [Dwivedi et al., 2022, Saini et al., 2023]. In RRAM devices, both electrode and dielectric materials play a crucial role in determining the resistive switching mechanism. A wide variety of materials have been investigated as switching layers for flexible RRAM devices. These materials include transition metal oxides (TMOs), graphene oxide (GO), transition metal carbides and nitrides (MXenes), polymers, and transition metal dichalcogenides (TMDs) [Sun et al., 2023]. TMOs, such as hafnium oxide (HfO_x), titanium oxide (TiO_x), and aluminum oxide (AlO_x), are among the most extensively studied materials due to their well suitable resistive switching behavior. Flexible RRAM devices with pristine layers of TMOs show low I_{ON}/I_{OFF} and endurance, for example Al/TiO_2/Al had been shown to exhibit decent switching behavior with endurance of over 50 cycles and I_{ON}/I_{OFF} around 10 [Jeong et al., 2010]. Improvement in the switching characteristics of TMO based flexible RRAM devices had been demonstrated by introducing bilayer structures, for example, the endurance of Pt/HfO_2/TiO_2/ITO flexible RRAM device was improved to >500 cycles essentially due to shifting of the point of rupture and formation of filaments from electrode-insulator interface to insulator-insulator interface [Lanza et al., 2019]. Though TMOs show high potential due to excellent film qualities [Wong et al., 2012], there are disadvantages such as high processing temperature and lack of mechanical flexibility which limits their utilization in fabrication of flexible electronic devices [Lanza et al., 2019]. The other promising categories of materials for flexible RRAMs are polymers such as PVPy, PVP, and PVK, which can help in adding low temperature processing ability and mechanical flexibility [Dlamini et al., 2022, Ali et al., 2017, Saini et al., 2023]. These materials inherently have mechanical flexibility, and are eco-friendly and mostly solution processed leading to overall low cost.[Dlamini et al., 2022, Ali et al., 2017] The resistive switching in the polymers can be attributed to formation and rupture of metallic, or carbonaceous filament.[Lee et al., 2015]. A new class of materials i.e., 2-D materials have gained tremendous attention recently and their exploration for resistive switching has become a major research area.[Hui et al., 2017, Park et al., 2022, Chen et al., 2022, Feng et al., 2023] Among various 2-D materials, GO is one of the earliest reported material that had shown resistive switching behavior in Cu/GO/Pt device structure with I_{ON}/I_{OFF} around 20 and endurance up to 100 cycles.[He et al.,

2009] It exhibits high electronic and thermal conductivities, impermeability, and easier processing methodologies at room temperature like the Langmuir–Blodgett technique, drop casting, and spin coating [Hui et al., 2017, Liu et al., 2016]. The reported devices have shown decent switching behavior with pristine, reduced, and blended GO [Varun et al., 2020, Park et al., 2022, Wang et al., 2012]. It has also been explored in bilayer combination with polymers like PVA, which improved the device performance as presence. Hybrid RRAM devices integrate multiple materials, such as polymers, metal oxides, and 2D materials, to overcome the limitations of individual components, thereby enhancing performance and functionality. The combination of flexible, solution-processable polymers like PVP and PVK with inorganic materials such as MoS_2, $MoSe_2$, and TiO_2 creates systems with complementary properties. These hybrid materials demonstrate reduced switching variability, lower operating voltages, and improved I_{ON}/I_{OFF}, making them highly suitable for low voltage memory applications. For instance, the formation of oxygen vacancies in TiO_2 synergizes with the charge-trapping capabilities of MoS_2 and $MoSe_2$, leading to enhanced resistive switching behavior. Furthermore, the mechanical flexibility of polymers ensures consistent performance under bending or stretching, which is critical for wearable electronics. Hybrid systems also enable multilevel resistive switching, facilitating high-density data storage, and their scalability makes them ideal for developing low-power, flexible, and reliable memory devices. This chapter explores the resistive switching behaviors of materials like PVP, PVK, TiO_2, MoS_2, $MoSe_2$, and their combinations, emphasizing their switching mechanisms and performance metrics to advance their application in next-generation memory technologies.

3.2 Fabrication of RRAM Devices with Various Pristine, Composite, and Hybrid Layers

All active layer materials such as PVP, PVK, MoS_2, and $MoSe_2$ and flexible substrate were procured from Sigma-Aldrich Inc. ITO-coated PET substrate was used as the BE for fabricating the flexible RRAM device, with ITO serving as the BE. Before commencing the fabrication process, the substrates were completely cleaned through ultrasonication in methanol and isopropyl alcohol (IPA), followed by drying with nitrogen gas. Each active layer was made by solution processed method. Polymer solution was prepared with suitable solvent by ultrasonication. 2D materials was prepared by liquid phase exfoliation process. Liquid phase exfoliation is considered a very simple, low cost, and low temperature solution processed top-down approach for preparing 2D materials. In the top-down approach, bulk materials (typically layered solids such as $MoSe_2$, MoS_2, or WS_2) are broken down into smaller nanosheets or flakes, often by mechanical or chemical means. The step-by-step process of liquid phase exfoliation used in this work is shown in Figure 3.1.

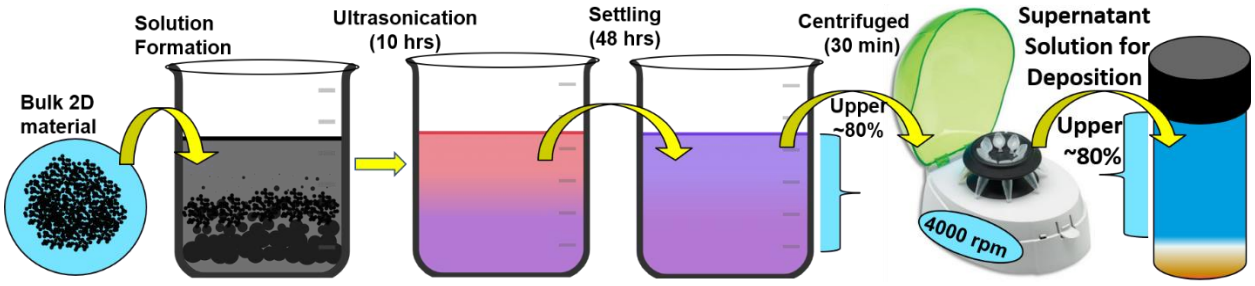


Figure 3.1 Liquid phase exfoliation process of 2D materials.

In this process, the bulk material is dispersed in a suitable solvent, and external force like ultrasonication were applied to separate the individual layers from the bulk. These external forces break the van der Waals interactions between the layers of the material, exfoliating them into few-layer or monolayer sheets. After ultrasonication, the solution was left to settle for 48 hours to separate the heavier particles. Approximately 80% of the solution was carefully extracted and centrifuged at 4000 rpm for 30 minutes. The upper portion of the resulting supernatant was then collected for deposition onto the BE. Thin film of TiO_2 of thickness 10 nm was deposited over ITO

at 150 °C using Savannah S200 thermal ALD system using tetrakis(dimethylamido)titanium (IV) and deionized water as precursors. Finally, using thermal evaporation under the high vacuum, ~200-nm-thick circular Ag TEs were deposited using shadow mask. Keithley 4200 SCS was used for the electrical characterization of the devices. The device structure and digital image of fabricated flexible RRAM device is shown in Figure 3.2(a & b). The chemical structure of PVP, PVK, MoS_2, and $MoSe_2$ are shown in Figure 3.2(c - f) respectively.

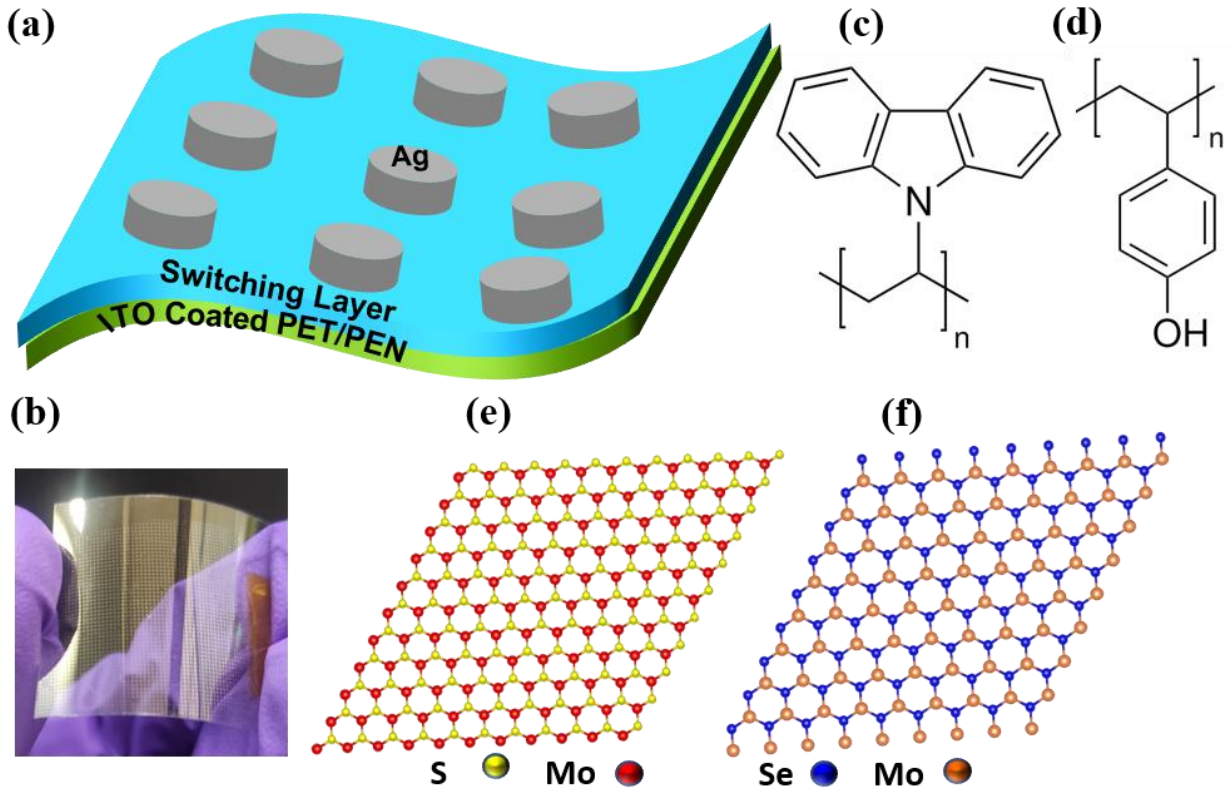


Figure 3.2 (a) Device Structure, **(b)** digital image of fabricated flexible RRAM. Chemical structure of PVP **(c),** PVK **(d),** MoS_2 **(e),** and $MoSe_2$ **(f).**

3.3 Results and Discussion

I-V characteristics of the first cycle of flexible RRAM devices utilizing pristine switching layers including PVP, PVK, MoS_2, $MoSe_2$, and TiO_2 active layers were measured by applying a linear voltage sweep as shown in Figure 3.3(a) to (e) respectively. For the SET process, the voltage was swept from 0 → V_{max} → 0. In contrast, the RESET process involved sweeping the voltage from 0 → $-V_{max}$ → 0 without a compliance current limitation. It can be observed from the results both pristine polymer (PVP or PVK) and TiO_2 based RRAM devices show very narrow switching window in comparison of pristine 2 D materials (MoS_2 and $MoSe_2$). The SET and RESET switching voltages varied among the active layers. Devices with PVK exhibited analog switching with SET/RESET voltages of approximately 3 V and -3 V, respectively. For PVP, the device shows switching with SET/RESET voltages around 1.2 V and -1.4 V. TiO_2 based devices showed a combination of switching types, with digital switching in the positive voltage region (SET at 1.2 V) and analog switching in the negative voltage region (RESET at -3 V). Despite the differences in switching behavior, the I_{ON}/I_{OFF} was found to be slightly higher. The Ag/MoS_2/ITO device exhibited SET and RESET voltages of 1.34 V and -1.50 V, respectively, while the Ag/$MoSe_2$/ITO device demonstrated SET and RESET voltages of 0.8 V and -1.1 V.

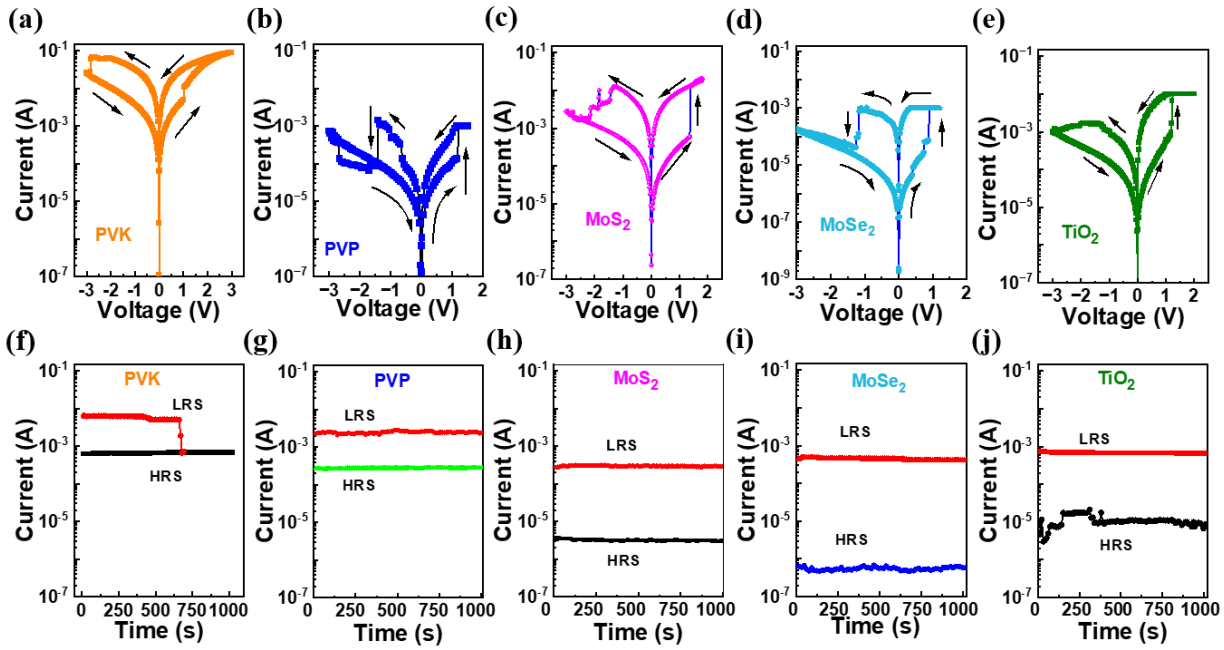


Figure 3.3 *I-V* Characteristics and corresponding retention time of pristine PVK **(a & f),** PVP **(b & g),** MoS_2 **(c & h),** and $MoSe_2$ **(d & i),** and TiO_2 **(e & j)** respectively. In retention time plots are carried out at read voltage of 0.2 V for both LRS and HRS.

Retention time plots for the LRS and HRS of flexible RRAM devices using pristine switching layers including PVP, PVK, MoS_2, $MoSe_2$, and TiO2 active layers at a read voltage of 0.2 V are shown in Figure 3.3(f)-(j) respectively. The results reveal that the LRS of the PVK switching layer remains stable for up to 650 seconds before degradation occurs. In the case of the PVP switching layer, both LRS and HRS maintain stability for up to 1000 seconds; however, the I_{ON}/I_{OFF} is less than 10. For TiO_2, the I_{ON}/I_{OFF} improves significantly to approximately 50, indicating better switching behavior compared to PVK and PVP. The retention plots for both pristine MoS_2 and $MoSe_2$ devices indicate stable I_{ON}/I_{OFF} over time, highlighting consistent performance and confirming their suitability for non-volatile flexible RRAM applications.

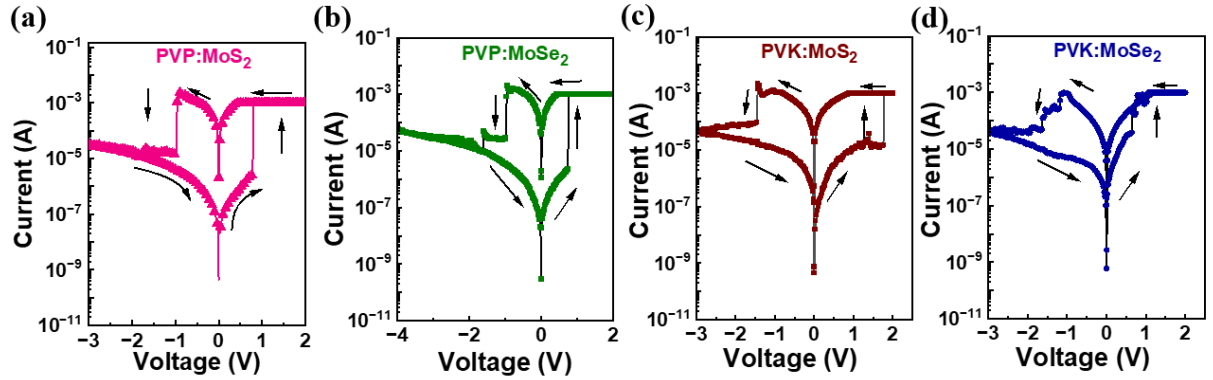


Figure 3.4 *I-V* Characteristics of composites of PVP:MoS_2 **(a),** PVP:$MoSe_2$ **(b),** PVK:MoS_2 **(c),** and PVP:$MoSe_2$ **(d)** switching layer RRAM device.

These results underscore the potential of MoS_2 and $MoSe_2$ as promising switching layer for flexible RRAM device. To further enhance the overall performance of RRAM devices, composites of polymer layers with 2D materials were employed as the switching layer. The incorporation of polymers like PVP or PVK improved the I_{ON}/I_{OFF} and SET and RESET voltages in composite RRAM devices. The composition of 2D materials (MoS_2 and $MoSe_2$) with PVP and PVK were studied for testing the behavior of the flexible RRAM device. The *I-V* characteristics for PVP:MoS_2, PVP:$MoSe_2$, PVK:MoS_2, and PVK:$MoSe_2$ flexible RRAM devices are shown in

Figure 3.4(a - d), respectively. Here it can be observed the overall switching performance including I_{ON}/I_{OFF} and SET and RESET voltages is improved.

Next, thin layer of TiO_2 (10 nm) was incorporated with PVP:$MoSe_2$ to form a bilayer structure in flexible RRAM devices, significantly enhancing the device's overall performance. The addition of TiO_2 introduces several advantages, such as improved charge transport, cycle to cycle repeatability, I_{ON}/I_{OFF}, and durability. TiO_2 is known for its high dielectric constant and the ability to generate oxygen vacancies, which play a crucial role in forming conductive filaments during the resistive switching process. When paired with the PVP:$MoSe_2$ composite, TiO_2 acts as a complementary layer, facilitating efficient charge trapping and release while improving the I_{ON}/I_{OFF} and maintaining device reliability.

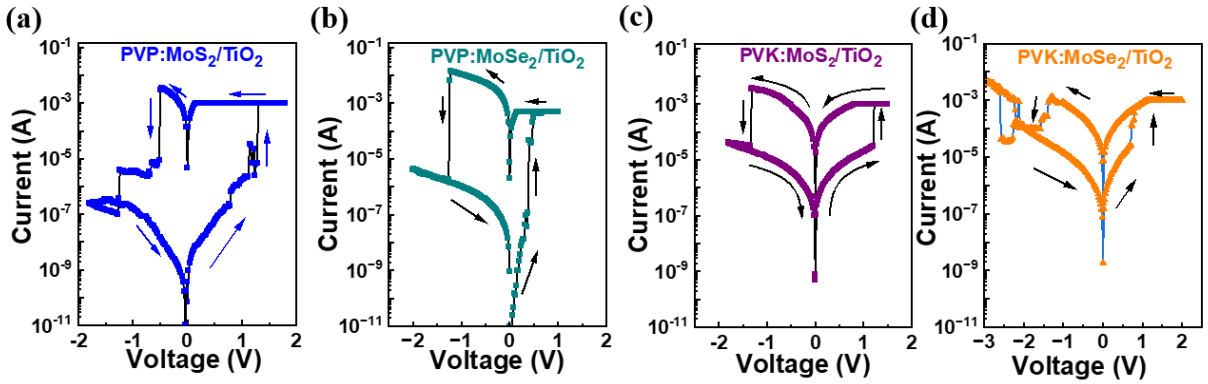


Figure 3.5 *I-V* Characteristics of bilayer of PVP:MoS_2/TiO_2 **(a),** PVP:$MoSe_2$/TiO_2 **(b),** PVK:MoS_2/TiO_2 **(c)** and PVP:$MoSe_2$/TiO_2 **(d)** switching layer RRAM device.

The *I-V* characteristics of PVP:MoS_2, PVP:$MoSe_2$, PVK:MoS_2, and PVK:$MoSe_2$ flexible RRAM devices with TiO_2 thin layer is shown in Figure 3.4(a - d). It can be seen from the results, the incorporation of TiO_2 enhances the device's I_{ON}/I_{OFF}, which is significantly higher than devices with only a single switching layer. This high I_{ON}/I_{OFF} ensures better distinction between the HRS and LRS, enabling reliable data storage and readout operations. Among these four combinations, PVK:$MoSe_2$ does not show a suitable resistive switching even after adding the TiO_2 layer. Thus, we did not explore PVK:$MoSe_2$ layer for further exploration, whereas rest of three PVP:MoS_2, PVP:$MoSe_2$, PVK:MoS_2 with TiO_2 are further explored for endurance, humidity, temperature, long term stability, and multi-level switching.

3.4 Conclusion

This chapter presented a comprehensive investigation into the resistive switching behavior of materials such as PVP, PVK, MoS_2, $MoSe_2$, TiO_2, and their composites, highlighting their potential as active layers in flexible RRAM devices. The unique properties of each material, including the flexibility and dielectric strength of PVP and PVK, the charge-trapping efficiency of MoS_2 and $MoSe_2$, and the stability and ionic mobility of TiO_2, were systematically analyzed. By integrating these materials in pristine, composite, and bilayer structures, significant improvements in device performance metrics, such as higher I_{ON}/I_{OFF}, lower operating voltages, and enhanced retention, were achieved. These advancements demonstrate the suitability of these materials and combinations for developing low-power, high-reliability, and scalable memory solutions. The findings underscore the importance of solution processed polymer and 2D material composites in enhancing the performance and durability of next-generation flexible electronic devices.

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