Flexible Resistive Memory Devices with Solution Processed Polymer:2D Material Composites as Switching Layer

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7
Conclusion and Future Work

Despite the extensive investigation and achievement of numerous objectives related to the fabrication methods and performance of flexible resistive memory devices using solution-processed polymer:2D material composites as the switching layer, significant progress has been made. However, there remains considerable potential for further innovative research before these flexible resistive memory devices can be practically implemented and widely adopted in society. This chapter provides a concise summary of the thesis findings and outlines potential areas for future research.

7.1 SUMMARY

The research conducted for this thesis emphasizes on potential of solution-processed polymer:2D material composites as the switching layer is a suitable candidate for flexible electronics applications reliable, multi-level data storage with high mechanical stability upon bending. The objective of the thesis is included with low V_{SET} and V_{RESET}, high endurance, excellent retention time with enhanced switching. Various experimental investigations were conducted with these goals in mind, and the resulting conclusion are as follows;

I. To enhance the performance of RRAM devices various solution-processed polymer and 2D material composites are demonstrated with ITO as BE and Ag as TE. All devices showed excellent stability in electrical performance upon bending.

II. 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.

III. RRAM devices with Ag/(PVP:MoS_2)/TiO_2/ITO hybrid structure on both rigid and flexible substrate have shown reliable resistive switching with low values of V_{SET} and V_{RESET} for rigid (1.0 V, −1.2 V) and flexible (1.5 V, −0.7 V) devices. Non volatile memory behavior with excellent retention up to 10000 seconds and decent I_{ON}/I_{OFF} more than 10^3 was achieved. The endurance of more than 200 DC cycles indicates the good repeatability of the device. Log (V) versus log (I) graph showed dominating ohmic conduction and SCLC mechanism in the devices. Bending stability up to 7 mm indicate that these bilayers with 2D material and polymers can be excellent alternatives for switching layer in RRAM devices for polymer and flexible electronics.

IV. High-performance flexible Ag/PVK:MoS_2/TiO_2/ITO RRAM devices were investigated. The novel combination of PVK:MoS_2/TiO_2 as an active layer helped the devices to show reliable resistive switching with low values of V_{SET} (1.2 V) and V_{RESET} (−1.5 V) voltages. Nonvolatile memory behavior with excellent retention

more than 10000 seconds and a decent I_{ON}/I_{OFF} of over 10^2 was achieved. Ohmic conduction and SCLC mechanism in the devices were indicated by a double log *I–V* plot. Moreover, these devices exhibited high stability in performance upon bending and high endurance over 1000 cycles. These devices were further comprehensively investigated for their shelf life and stability for long duration. These devices were able to exhibit excellent switching behavior with a maximum V_{SET} of ~1.5 V and lowest V_{RESET} of ~−1.6 V, upon systematic characterization for memory performance for 20 months. These devices exhibited excellent shelf life, low values of and V_{SET} and V_{RESET} with high retention for more than 10^4 seconds. Moreover, the switching performance was intact upon exposure to decent humidity levels and upon heating. Although the devices exhibited almost unchanged V_{SET} and V_{RESET} values upon the variation of humidity exposure from RH of ~42% to ~99%, the magnitude of V_{SET} and V_{RESET} increased upon heating at 100 ˚C, with decay in I_{ON}/I_{OFF}. These results indicate that the proposed hybrid bilayer (PVK:MoS_2/TiO_2) can be a suitable switching layer candidate for flexible RRAM devices for realistic applications.

V. Finally, high-performance, forming-free, and flexible Ag/PVP:$MoSe_2$/ITO RRAM devices with multibit data storage capability are demonstrated in this work. The novel composite of PVP and $MoSe_2$ as an active layer has shown a reliable resistive switching behavior with low V_{SET} and V_{RESET} (0.7 V/~−1 V). Multilevel switching (2-bit storage) with excellent retention of around 10^4 seconds was achieved along with the endurance of more than 1000 cycles, which indicates excellent stability and repeatability with very low current operation, i.e., 100 µA. Weibull's distributions of currents and switching voltages have confirmed that the device has very low cycle-to-cycle variation and thus better reliability. Moreover, these devices have shown high mechanical stability upon bending with up to a 7 mm bending radius. These performance parameters strongly suggest that the PVP:$MoSe_2$ composite can be an excellent choice for an active switching layer in flexible RRAM devices and can be further explored for flexible large-area electronics applications.

For more clarification the performance parameters of fabricated devices are compared as shown in table 7.1.

Table 7.1: Comparison of Switching Parameters of Flexible RRAM Devices with Different Solution Processed Polymer:2D Material Composites Switching Layer

Device Structure	**Substrate**	**V_{SET} / V_{RESET} (V)**	**I_{ON}/I_{OFF}**	***Endur.***	**Ret. (s)**	**P_{SET} (mW)**	**P_{RESET} (µW)**	**Remarks**
Ag/PVP:MoS_2/TiO_2/ITO	PEN/Flexible	1.5/-0.68	10^3	200	10^4	1.1	5	Low power
Ag/PVK:MoS_2/TiO_2/ITO	PEN/Flexible	1.2/-1.5	10^2	1000	10^4	1.27	50	Shelf life stability
Ag/PVP:$MoSe_2$/ITO	PET/Flexible	0.7/-1	10^3	1150	10^4	0.73	28	Multilevel resistive switching

Based on the parameter comparison of different flexible RRAM devices, it is evident that the choice of polymer matrix and 2D material composition significantly influences device performance. The Ag/PVP:$MoSe_2$/ITO device demonstrated the best overall performance, with the lowest switching voltages (0.7 V / -1.0 V), a high I_{ON}/I_{OFF} (~10^3), and the highest endurance of 1150 cycles, while maintaining a stable retention time of ~10^4 seconds. It also exhibited the lowest power consumption, making it highly suitable for low-power memory applications. In contrast, the Ag/PVK:MoS_2/TiO_2/ITO device showed moderate performance with a lower I_{ON}/I_{OFF} (~10^2)

and excellent shelf-life stability. The Ag/PVP:MoS_2/TiO_2/ITO device, while offering a higher I_{ON}/I_{OFF} with low RESET power (P_{RESET}) and moderate SET power (P_{SET}), required slightly higher set voltage. Overall, the Ag/PVP:$MoSe_2$/ITO device outperformed the others in terms of power, endurance, and multilevel resistive switching capability, indicating its strong potential for future flexible non-volatile memory technologies.

7.2 Scope for Extension and Material Selection Guidelines for Future Flexible RRAM Devices

The methods and materials developed in this thesis for flexible resistive RRAM devices using polymer:2D material composites, particularly with MoS_2, $MoSe_2$ with PVP and PVK, can be extended to other TMDs or 2D materials. Here are some key points regarding their applicability and guidelines for selecting appropriate materials:

Versatility of TMDs: The thesis highlights the potential of TMDs like MoS_2 and $MoSe_2$ as switching layers in flexible RRAM devices. Other 2D materials such as WS_2, WSe_2, and MXenes have shown promise in similar applications due to their mechanical strength and tunable properties, making them suitable candidates for flexible composite RRAM arrays.

Material Combinations: The successful demonstration of MoS_2 and $MoSe_2$ with PVP or PVK polymers suggests that other combinations of TMDs with various polymers could yield beneficial results. For instance, polymers like PMMA and PVA have been explored with TMDs, indicating that the choice of polymer can significantly influence the performance of the composite.

Mechanical Flexibility: Selection of 2D materials and polymers that exhibit high mechanical flexibility to ensure the durability of the device under bending conditions. This is crucial for applications in flexible electronics.

Dielectric Properties: Materials with favorable dielectric constants to enhance the performance of the memory devices. For example, PVP is noted for its high dielectric constant, which is advantageous in composite formulations.

Chemical Compatibility: Good dispersion and interfacial interaction with the polymer materials are essential.

Synthesis Complexity: Consider the ease of synthesis and processing of the materials. Solution processed materials are advantageous due to low temperature process technique.

7.3 CONCLUSION

This thesis highlights the potential of solution-processed polymer:2D material composites as switching layers in flexible RRAM devices, emphasizing their reliability, multilevel data storage capabilities, and high mechanical stability. A variety of solution-processed composites, such as PVP, PVK, MoS_2, $MoSe_2$, TiO_2, and their combinations, were systematically investigated for their resistive switching properties using ITO as a BE and Ag as a TE. These materials demonstrated unique advantages, including the dielectric strength of PVP and PVK, the charge-trapping efficiency of MoS_2 and $MoSe_2$, and the stability of TiO_2, enabling enhanced performance metrics like high I_{ON}/I_{OFF} ratios, low operating voltages, and excellent retention times. Hybrid structures, such as Ag/(PVP:MoS_2)/TiO_2/ITO, exhibited reliable switching behavior with low SET/RESET voltages (e.g., 1.5 V/−0.7 V for flexible devices) and excellent retention up to 10,000 seconds, coupled with endurance exceeding 200 cycles. Advanced bilayers like Ag/PVK:MoS_2/TiO_2/ITO achieved high endurance over 1,000 cycles, exceptional stability upon bending, and consistent performance under varying humidity and temperatures. Additionally, forming-free Ag/PVP:$MoSe_2$/ITO devices showcased multilevel data storage capabilities with low power operation, retention of 10^4 seconds, and mechanical stability at bending radii of up to 7 mm. These findings underscore the suitability of polymer:2D material composites for flexible

RRAM applications, offering promising avenues for scalable, durable, and high-performance flexible electronics.

7.4 Future Scope

The future research in 2D materials-based RRAM devices should focus on addressing current challenges and advancing the field toward scalable, reliable, and high-performance flexible memory solutions. Key areas of investigation are outlined below:

1. **Improvement in Fabrication Technology:**
   The synthesis and direct integration of 2D materials need significant advancements to eliminate the transferring step, which introduces defects and compromises device reliability. Future fabrication processes should aim for rapid, cost-effective, high-throughput production methods compatible with industrial standards, such as roll-to-roll or additive manufacturing. Integration of such processes with flexible substrates will pave the way for scalable fabrication of flexible RRAM devices.
2. **Crack Reduction and Structural Optimization:**
   Addressing crack formation in 2D material layers is crucial for enhancing electrical characteristics such as endurance, retention, and switching ratios. Research should explore reducing device dimensions and employing multilayered 2D material architectures to mitigate crack-induced variability. Optimization of device structures, including sandwich and planar configurations, and systematic selection of active layer materials will be essential for performance improvements.
3. **Understanding Conduction Mechanisms:**
   While various conduction mechanisms have been proposed, there remains a need for in-depth exploration of resistive switching behavior in 2D materials. Advanced experimental and theoretical studies should aim to uncover the underlying mechanisms, such as filamentary conduction and charge trapping, to enable precise control over device performance.
4. **Advanced Characterization Techniques:**
   Developing state-of-the-art nanoscale characterization tools will facilitate a deeper understanding of material interfaces, defect dynamics, and switching phenomena. Techniques such as in-situ electron microscopy, near-field scanning optical microscopy, and synchrotron-based analysis could provide valuable insights into the physical and chemical processes governing device operation.
5. **Predictive Simulations:**
   Computational modeling and simulations should be leveraged to predict the behavior of 2D materials-based RRAM devices under varying parameters, such as material composition, device geometry, and environmental conditions. Such simulations can reduce material wastage and fabrication costs while guiding experimental efforts toward optimal device designs.
6. **Flexibility Without Compromise:**
   Enhancing mechanical endurance while maintaining or improving electrical performance is paramount. Future research should explore methods to universalize flexibility across 2D material-based RRAM devices by tailoring material properties and layer combinations. Special attention should be paid to maintaining stability under extreme bending, twisting, and other mechanical stresses.
7. **Environmentally Stable Designs:**
   Long-term environmental stability, including resistance to humidity and temperature variations, is critical for real-world applications. Investigations should focus on designing encapsulation layers and optimizing material properties to ensure consistent device performance over extended periods, as demonstrated in PVK:MoS_2/TiO_2 bilayers.
8. **Multilevel and High-Density Storage:**

Multibit resistive switching, as shown by PVP:$MoSe_2$ devices, holds significant potential for increasing data density in flexible RRAM devices. Further research should explore novel material combinations and strategies, such as compliance current tuning and multilayer stacking, to achieve reliable multilevel data storage.

9. **Integration with Flexible Electronics:**
   As the future of electronics shifts toward flexible and wearable systems, integrating RRAM devices with sensors, processors, and communication modules is crucial. Exploring hybrid systems that combine memory, sensing, and computation on flexible substrates will be a key area of innovation.
10. **Exploration of New Material Combinations:**
    Rarely explored 2D materials like $MoSe_2$, combined with polymers such as PVP, have demonstrated promising resistive switching characteristics. Future research should investigate other unique material combinations for active layers to achieve high-density, low-power, and scalable memory devices.

By addressing these directions, the field of 2D materials-based flexible RRAM devices will progress toward practical applications in next-generation electronics, contributing to advancements in wearable technologies, IoT systems, and high-density memory storage solutions.

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