Towards advanced flexible functional electrochemical metallization (ECM)-based reram devices

Qian, Kai

2018

Qian, K. (2018). Towards advanced flexible functional electrochemical metallization (ECM)-based reram devices. Doctoral thesis, Nanyang Technological University, Singapore.

<http://hdl.handle.net/10356/73421>

<https://doi.org/10.32657/10356/73421>

NANYANG
TECHNOLOGICAL
UNIVERSITY

**TOWARDS ADVANCED FLEXIBLE FUNCTIONAL
ELECTROCHEMICAL METALLIZATION (ECM)-BASED
RERAM DEVICES**

QIAN KAI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

2017

**TOWARDS ADVANCED FLEXIBLE FUNCTIONAL
ELECTROCHEMICAL METALLIZATION (ECM)-BASED
RERAM DEVICES**

QIAN KAI

SCHOOL OF MATERIALS SCIENCE AND ENGINEERING

A thesis submitted to the Nanyang Technological University
in partial fulfilment of the requirement for the degree of
Doctor of Philosophy

2017

Statement of Originality

I hereby certify that the work embodied in this thesis is the result of original research and has not been submitted for a higher degree to any other University or Institution.

.. 12/08/2017 ...
Date

Qian Kai
.....
Qian Kai

Abstract

Driven by the innovation and growing demand for the information technologies, new non-volatile memory devices are needed to be scalable and capable with excellent performances. The electrochemical metallization (ECM)-based resistive switching random access memory (ReRAM) device, which is the most promising candidate of the conventional Si-based Flash memory devices, has attracted tremendous attention due to its proven scalability potential, high-performance, and industrialization maturity.

Advanced flexible functional memories, which stand for lightweight and printability, are highly desirable for future wearable electronics. Besides the flexibility, the devices with other advanced functionalities such as transparency, portability, and stretchability also have significant advantages and added value in different areas for future electronics' applications. Therefore, to realize an integrated flexible functional circuit, a very important component of the circuitry elements-the advanced flexible functional memory unit is also in great demand. In this thesis, the research is focused on feasible approaches and decent materials for the realization of advanced flexible multi-functional ECM-based ReRAM devices with high performances.

To realize these, the research started from the design of memory devices structure. In the ECM-based ReRAM devices, the growth process of conductive filaments will be affected by the electric field. In order to realize the requirement of high electrical performance memory devices with low electroforming voltage and large ON/OFF ratio, Au nanoparticles (NPs) was inserted between amorphous Si switching layer and Au bottom electrode *via* facile self-assembly method at room temperature. The inserted Au NPs would modify the electric field distribution in the switching layer to affect the filaments growth, which was confirmed *via ex situ* TEM. The fabricated memory devices with Au NPs layer exhibited excellent electrical performances, *i.e.*, low electroforming voltage and large ON/OFF ratio on both flexible and rigid substrates at the same time. This work

offers a facile method and versatile structure for high electrical performance ECM-based ReRAM applications on both flexible and rigid substrates.

In order to realize flexible functional memory devices with excellent bending stability and switching endurance, the two dimensional (2D) hexagonal boron nitride (hBN) with inherent flexibility and excellent thermal stability was exploited as the switching layer for the first time. The ultrathin hBN (~3-5 nm) film was grown on the Cu foil substrate *via* scalable chemical vapor deposition (CVD) method, where Cu foil can act as both bottom electrode and substrate. The final fabricated Ag top electrode/hBN/Cu foil memory devices exhibited long retention time, reliable switching endurance, and excellent bending stability under bend conditions. This work promotes the 2D materials applications in the flexible ReRAM in future computing technology and wearable electronics.

Finally, the advanced flexible multi-functional ECM-based ReRAM devices were demonstrated, which possess flexibility, transparency, and portability. By utilizing the excellent properties of 2D hBN and graphene materials, the indium tin oxide (ITO) top electrode/hBN/Graphene memory devices was fabricated, which exhibited excellent performances in terms of transparency, ON/OFF ratio, retention time, and bending stability. The hBN/graphene film can be easily transferred onto different substrates for transferable memory devices fabrication, such as polyethylene terephthalate (PET) and soft polydimethylsiloxane (PDMS) substrates. The indium filaments were directly found for the first time *via ex situ* TEM, which broadens our understanding of the resistive switching mechanisms in the ECM-based memory device.

In conclusion, the thesis together with the herein encompassed approaches and mechanisms are believed to be able to provide some insightful ideas on the emerging topic of flexible memories and meanwhile it serve as a good guidance for the realization of advanced flexible functional ECM-based ReRAM for the future integrated flexible electronics applications.

Acknowledgements

The past 4-year Ph.D. study is a challenging journey and full of memorable experience. Fortunately, I was granted with lots of warm supports, patient guidance and help. First and foremost, I would like to extend my gratitude to my supervisor Prof. Lee Pooi See, for her great support and guidance throughout the duration of my PhD candidature. Certainly, her enthusiasm and dedication towards research have inspired me a lot as a good researcher. Sincerely, I would like to thank her for her creative ideas and providing me the opportunity to learn, without which this work would not have been achievable. I would also like to express my appreciation to my co-supervisor Assoc. Prof. Chen Tupei for sharing his vast knowledge on my research work and his team (Dr. Li Huakai and Zhang Jun) for helping me to fabricate devices during my candidature.

Thank Assoc. Prof. Teo Edwin Hang Tong and his team (Dr. Tay Roland Yingjie and Lin Jinjun) for their great supports to offer the essential experimental material of boron nitride for my research work. I extend my earnest gratitude to Assoc. Prof. Zhang Qichun and Assoc. Prof. Wang Junling for providing insightful recommendations as my thesis advisory committee members.

I would also like to express grateful acknowledgement to our group members: Dr. Yan Chaoyi, Dr. Yan Jian, Foo Ce Yao, Dr. Meng-Fang Lin, Dr. Wang Xu, Dr. Wang Jiangxin, Dr. Li Shaohui, Dr. Xiong Jiaqing, Dr. Cai Guofa, Dr. Cui Peng, Dr. Venkateswarlu Bhavanasi, Dr. Vipin Kumar, Dr. Kang Wenbin, Dr. Cui Mengqi, Dr. Kenji Chee Jianzhi, Dr. Nguyen Viet Cuong, Cheng Xing, Kaushik Parida, Chen Jingwei, Eh Lee See Alice, Tan Wei Ming Alvin, Gong Xuefei, Gao Dace, Ji Lin, Ciou Jing-Hao for their suggestions and invaluable help. I wish to thank the technical team in MSE for their efforts on providing professional guidance on those advanced characterization facilities. I also would like to thank the scholarships awarded by Nanyang Technological University.

Last but not least, I am thankful to my family for their constant love and support during all these years. Their immense love and support provide me the courage to make this dissertation possible.

Table of Contents

Abstract	i
Acknowledgements	iii
Table of Contents	v
Table Captions	xi
Figure Captions	xiii
Abbreviations	xxv
Chapter 1 Introduction	1
1.1 Problem Statement	2
1.2 Objectives and Scope	4
1.2.1 Develop strategies for enlarged memory window and reduced electroforming voltage ECM-based ReRAM	4
1.2.2 Realization of high performance flexible functional ECM-based ReRAM.....	5
1.2.3 Design for flexible, transparent, and transferable ECM-based ReRAM.....	6
1.3 Dissertation Overview	7
1.4 Findings and Outcomes.....	9
References	10
Chapter 2 Literature Review	15
2.1 Resistive Switching Random Access Memory (ReRAM).....	16

2.1.1 General feature	16
2.1.2 Materials	18
2.1.3 Switching mechanism for the ECM-based ReRAM	23
2.2 Flexible Functional ReRAM.....	29
2.2.1 Flexible ReRAM	30
2.2.2 Flexible transparent ReRAM	33
2.2.3 Flexible and transferable ReRAM.....	36
2.3 Challenges in Flexible Functional ECM-based ReRAM.....	38
2.4 PhD Studies in Context with Literature	39
References	41
 Chapter 3 Experimental Methodology.....	 49
3.1 Rationale for Materials Selection.....	50
3.1.1 Au NPs as interlayer in the ECM-based ReRAM	50
3.1.2 2D hBN as switching layer for flexible functional ECM-based ReRAM.....	51
3.1.3 ITO electrode for flexible transparent functional ECM-based ReRAM	52
3.2 Synthesis	53
3.2.1 Au NPs synthesis.....	53
3.2.2 2D hBN thin film preparation	53
3.3 Characterization	54
3.3.1 SEM.....	54
3.3.2 TEM	55
3.3.3 Focused ion beam (FIB)	57
3.3.4 Bending test station	58
3.3.5 Semiconductor characterization system	59

3.3.6 Electric field simulation	60
3.4 Device Fabrication	60
3.4.1 Au NPs-interlayer ECM-based ReRAM fabrication.....	60
3.4.2 Flexible hBN ECM-based ReRAM device fabrication.....	60
3.4.3 Flexible, transparent, and transferable multi-functional hBN-based ReRAM devices fabrication.....	62
3.4.4 Cross sectional TEM specimen preparation <i>via</i> FIB.....	63
3.5 Overview of Methodologies	64
References	65
 Chapter 4 Au NPs-Interlayer Amorphous Si ECM-Based ReRAM Devices on Flexible and Rigid substrates	71
4.1 Introduction.....	72
4.2 Experimental Methods	74
4.2.1 Fabrication of a-Si switching layer and Au NPs	74
4.2.2 Self-assembly Au NPs mono-layer formation on the substrates.....	74
4.2.3 Electric field simulation	75
4.2.4 Characterization	75
4.3 Results and Discussion	76
4.3.1 Structure of a-Si ECM-based ReRAM devices.....	76
4.3.2 Electroforming property evaluations of a-Si based memory devices with and without Au NPs interlayer on rigid substrate	76
4.3.3 Resistive switching characterization of a-Si based memories with and without Au NPs interlayer on inter Au BE (on rigid substrate)	81
4.3.4 <i>ex-situ</i> TEM characterization of a-Si based memories with and without Au NPs interlayer on rigid substrate	83

4.3.5 Electrical performances evaluations of a-Si based memories with and without Au NPs interlayer on rigid substrate	87
4.3.6 Electrical performances and bending stability evaluation of the a-Si memories with and without Au NPs interlayer on flexible substrate	88
4.4 Chapter Summary	91
References	92
 Chapter 5 Hexagonal Boron Nitride Thin Film for Flexible Functional ECM-Based ReRAM Applications	95
5.1 Introduction	96
5.2 Experimental Methods	98
5.2.1 Preparation of hBN films	98
5.2.2 Transfer hBN films onto ITO/PET	98
5.2.3 Characterization	99
5.3 Results and Discussion	99
5.3.1 Structure of hBN-based ReRAM devices	99
5.3.2 Resistive switching characterization of Ag TE/hBN/Cu foil devices	100
5.3.3 XPS characterization of hBN-based memory devices	101
5.3.4 Resistive switching characterization of Ag TE/hBN/ITO/PET memories...	104
5.3.5 CuO _x layer effect on the hBN-based memory devices	105
5.3.6 Resistive switching characterization of Au BE/hBN/Cu foil memories	105
5.3.7 <i>ex-situ</i> TEM characterization of Ag TE/hBN/Cu foil devices	108
5.3.8 Bending stability evaluation on the Ag TE/hBN/Cu foil devices	111
5.4 Chapter Summary	112
References	113

Chapter 6	Flexible, Transparent, and Transferable ECM-based ReRAM from Hexagonal Boron Nitride and Graphene	117
6.1	Introduction	118
6.2	Experimental Methods	120
6.2.1	hBN film preparation	120
6.2.2	PDMS substrate preparation	120
6.2.3	Flexible, transparent, and transferable multi-functional ECM-based ReRAM devices fabrication	121
6.2.4	Characterization	122
6.3	Results and Discussion	123
6.3.1	Electrical performance evaluation of ITO TE/hBN/FLG/PDMS memory	123
6.3.2	Transferability demonstration of hBN-based memory devices on ITO/PET substrate	124
6.3.3	Bending stability evaluation of ITO TE/hBN/FLG/PDMS device	125
6.3.4	Electrical performances evaluation of ITO TE/hBN/FLG/PDMS memory devices on different substrates	126
6.3.5	<i>ex-situ</i> TEM characterization of ITO TE/hBN/FLG/Cu foil at ON state	127
6.3.6	<i>ex-situ</i> TEM characterization of ITO TE/hBN/FLG/Cu foil at OFF state	130
6.4	Chapter Summary	132
	References	133
Chapter 7	Discussion and Future Work	137
7.1	Discussion	138
7.1.1	Au NPs-interlayer amorphous Si ECM-based ReRAM on flexible and rigid substrates	138
7.1.2	hBN thin film for flexible functional ECM-based ReRAM applications	139

7.1.3 Flexible, transparent, and transferable ECM-based ReRAM from hBN and graphene	140
7.2 Future Work	141
7.2.1 Stretchable ECM-based ReRAM for wearable electronics applications	141
7.2.2 <i>In-situ</i> observation of filaments in ECM-based ReRAM devices	142
References	144
Publication List	147
APPENDIX	149

Table Captions

Table 2.1 Different types of non-volatile memory devices comparison.^[2, 14]

Table 2.2 Summary of common inorganic materials-based ReRAM devices and corresponding electrical performances.^[1] Adapted from ref.1 with permission from Elsevier B.V.

Table 2.3 Summary of common organic materials-based ReRAM devices and corresponding electrical performances.^[1] Adapted from ref.1 with permission from Elsevier B.V.

Table 2.4 Summary of some typical organic, inorganic and 2D materials based ReRAM devices, corresponding to their performances in terms of switching endurance and bending cycles.

Figure Captions

Figure 2.1 (a) Schematic of the ReRAM devices architecture. Schematic of the two basic switching modes in ReRAM devices: (b) unipolar mode and (c) bipolar mode, respectively.^[1] Reproduced from ref. 1 with permission from Elsevier B.V.

Figure 2.2 (a-e) Schematic of the filament growth in an ECM-based memory cell.^[15] Reproduced from ref. 15 with permission from IOP Publishing.

Figure 2.3 The SET process in the Pt/H₂O/Ag cell: (a) I-t curve. SEM images of Ag filament growth when -1V bias was applied on Pt electrode: (b) 1 s, (c) 2s and (d) 4 s, respectively.^[67] Reproduced from ref. 67 with permission from AIP Publishing LLC.

Figure 2.4 Conductive filaments growth dynamics in Ag/SiO₂/Pt memory devices.^[68] (a) TEM image of planar Ag/SiO₂/Pt memory cell on SiN_x membrane. Inset: the memory cell structure. Scale bar, 200 nm. TEM images of the same Ag/SiO₂/Pt memory cell after the electroforming (b) and erasing (c) processes. Scale bar, 200 nm. (d) I-t curve for the electroforming process with 8V positive bias on Ag electrode, corresponding to the image in (b). (e) I-t curve for the RESET process with -10V positive bias on Ag electrode, corresponding to the image in (c). (f) Filaments growth dynamics of the Ag⁺ ions migration and reduction. (g) Diagram of the branched filament growth. (h) TEM images of another memory cell with large thickness after electroforming process. Scale bar, 200 nm. Zoomed-in image of the upper filament was shown in inset. Scale bar, 20 nm. (i) TEM image of the memory cell after RESET process, corresponding to same device of (h). Scale bar, 200nm. Inset: the same region as the inset in (h). Scale bar, 20nm. (j) I-t curve during the electroforming step with 10V positive bias on Ag electrode, corresponding to the image in (h). (k) I-t curve during the RESET step with -10V positive bias on Ag electrode, corresponding to the image in (i). Reproduced from ref. 68 with permission from Nature Publishing Group.

Figure 2.5 Ag filament growth dynamics observation *via in situ* TEM.^[62] (a) Schematic

of the *in situ* TEM experiment structure. (b-e) TEM images of the filaments growth dynamics in the Ag/SiO₂/W memory cell with 8V bias on the Ag electrode. Scale bar, 20 nm. (f-j) Schematics of the filament growth dynamics *via* splitting/merging process (f) Ag oxidation near the Ag electrode. (g) Ag clusters nucleate at the Ag electrode/SiO₂ interface, which serve as bipolar electrodes during the following filament growth. (h) Ag nanoclusters moved towards the inert electrode. (i) Void generation due to the Ag nanoclusters migration (highlighted by the dash line). (j) The continuous growth of filament *via* voids refilling step-by-step from the active electrode. Reproduced from ref.62 with permission from Nature Publishing Group.

Figure 2.6 (a) Schematic of the conductive-interlayer SiO_x-based ReRAM devices. (b) Four different inserted layers of multilayer graphene (MLG), carbon, Ti, and Pd, which were used in the SiO_x-based memory cells. (c) I-V characteristics of the one-Pd-interlayer SiO_x-based memory cell before and after bend with bending radius of 5 mm. Electroforming process was showed in the inset. (d) Switching endurance of the one-Pd-interlayer SiO_x cell. The top panel illustrated 1 cycle bend test.^[24] Adapted from ref. 24 with permission from American Chemical Society.

Figure 2.7 (a) Schematic of 1D-1R device on flexible PEN substrate. (b) Optical image of the 1D-1R devices on PEN substrate. Scale bar, 5 mm. (c) Illustration of the Al/PS:PCBM/Al/P3HT/Au/Al 1D-1R device. (d) Bis-FB-N₃ and P3HT chemical structure as diode material. (e) Bis-FB-N₃, PCBM, and PS chemical structure as active material for memory cell. (f) I-V characteristics of 1D-1R device before and after different mechanical deformations. (g) Endurance cycles of 1D-1R cell after different distortions. (h) I_{ON}/I_{OFF} ratio of the 1D-1R device during 10⁴ times bending cycles (bending radius, r=13 mm).^[86] Adapted from ref.86 with permission from Nature Publishing Group.

Figure 2.8 (a) Schematic of the Graphene (G)/SiO_x/ITO glass memory device on the left panel. Optical photography of Graphene/SiO_x/ITO glass memory device and its corresponding zoomed-in optical image on the top and bottom right panel, respectively.

Scale bar, 100 μm . (b) Transmittance spectra of the G/SiO_x/G devices. The green, blue and black curve corresponds to the monolayer G/ SiO_x/monolayer G, monolayer G/ SiO_x/bilayer G, and bilayer G/ SiO_x/ bilayer G structures transmittance, respectively. (c) I-V curves of G/SiO_x/ITO memory cell after electroforming process. The voltage sweep order was indicated by the number. (d) Switching endurance and (e) retention time of the G/SiO_x/ITO device. Both an ON and OFF state were measured with continuous +1V read voltage.^[85] Adapted from ref. 85 with permission from Nature Publishing Group.

Figure 2.9 Flexible transparent ReRAM device.^[85] (a) Schematic of the crossbar Graphene/SiO_x/Graphene device on PFA substrate (left panel) and its optical image (right panel). Scale bar, 20 μm . (b) Optical image of the Graphene/SiO_x/Graphene device, corresponding to its pillar structure in the inset. Scale bar, 100 μm . (c) Switching endurance from the crossbar device. (d) Bending endurance from a crossbar device. The bending radius is ~ 12 mm and the read voltage is +1V. The inset shows the actual flexible transparent pillar structure ReRAM. Reproduced from ref.85 with permission from Nature Publishing Group.

Figure 2.10 (a) Diagram of the organic memory device fabrication process. (b) The setup for the electrical measurement along with PMMA and P3HT chemical structures. (c) Optical image of the sticker-type memory device.^[82] Reproduced from ref. 82 with permission from John Wiley & Sons, Inc.

Figure 2.11 Demonstration of the sticker-type memory devices on kinds of substrates along with their corresponding I-V characteristics:^[82] (a) business card, (b) fake nail, (c) cylindrical vial (with a diameter of 20 mm), (d) medical wristband. The area of the memory device is about 1 cm². Reproduced from ref. 82 with permission from John Wiley & Sons, Inc.

Figure 3.1 Schematic diagram of a scanning electron microscopy (SEM).^[48] Reproduced from ref.48 with permission from Springer.

Figure 3.2 Schematic of a transmission electron microscopy (TEM).^[49] Reproduced from ref.49 with permission from Springer.

Figure 3.3 (a) Optical image of a FIB/SEM station. (b) Principle illustration of a FIB/SEM system.^[52] Reproduced from ref. 52 with permission from IOP Publishing.

Figure 3.4 Schematic of FIB system components.^[54] Reproduced from ref. 54 with permission from IOP Publishing, LTD.

Figure 3.5 Photographs of the home-make bend stage with a flexible ReRAM device under (a) flat and (b) bend condition, respectively.

Figure 3.6 Photographs of the test system (a) and (b) probe station for ReRAM devices measurements, respectively.

Figure 3.7 (a,b) Low and high magnification of the as-grown hBN domains SEM images onto a polycrystalline Cu substrate after 10 min of growth, respectively. (c) SEM images of continuous hBN films formed after 30 min and (d) 40 min of growth.^[60] Reproduced from ref. 60 with permission from John Wiley & Sons, Inc.

Figure 3.8 Flexible, transparent, and transferable hBN-based ReRAM device fabrication process.^[61] (a) hBN film with PMMA in DI water after removal of Cu foil substrate. (b) The transferred hBN film with PMMA onto graphene/Cu foil. The Hbn/PMMA film was highlighted by the red rectangle frame. (c) The transferred hBN/graphene film with PMMA in DI water after removal of Cu foil substrate. The hBN/PMMA film was highlighted by the red rectangle frame. (d) The hBN/graphene film with PMMA was transferred onto PDMS substrate. The hBN/graphene film was indicated by the red rectangle frame. (e) The transferred hBN film with PMMA onto ITO/PET substrate. After removal of PMMA using acetone, ITO top electrode was deposited on the hBN/ITO/PET to construct transparent and flexible ITO/hBN/ITO/PET memory device (f). Reproduced from ref. 61 with permission from the American Chemical Society.

Figure 3.9 (a) SEM image of the *ex-situ* TEM specimen in copper 3-post lift-out grid. The specimen was highlighted by the red rectangular box. (b) TEM image of a ReRAM device.

Figure 3.10 SEM images showing the *ex-situ* TEM specimen preparation *via* FIB.^[61] (a) ITO/hBN/graphene/Cu foil memory cell. (b) The memory cell was cut using a focused ion beam with a Ga ion beam at 30 kV beam energy. (c) FIB lift-out process (d) The memory cell was thinned down to ~ 100 nm and cleaned at 8 kV beam energy. Reproduced from ref. 61 with permission from the American Chemical Society.

Figure 4.1 (a) Schematic diagram for Au NPs assembling on 2-ATP-modified Au substrate. (b) SEM image of Au substrate coated with ~ 50 nm Au NPs monolayer, scale bar: 1 μm . (c) Size distribution by intensity spectra of ~ 50 nm Au NPs in water solution.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.2 The electroforming process in a pure a-Si memory device on rigid substrate with $V_{\text{forming}} \sim 11\text{V}$.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.3 (a) Schematic of the Ag/a-Si/Au NPs/Au device arrays and the setup for electrical characterization. (b) I-V curves for a-Si memory devices with and without Au NPs during the initial electroforming process. (c) Statistical histogram of the V_{forming} for 100 different cells in the a-Si memory devices. The fitting curves were obtained by Gaussian functions.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.4 (a) Simulation of electric field distribution along the X axis with different y coordinates away from the tip of Au NP by using CST EM studio for an Au NP. (b) Simulation of electric field distribution for multiple Au NPs according to the distance at the interface between Au NPs (or bottom electrode) surface and a-Si, and the distance

between Au NPs was defined as 10 nm. (c) Cross sectional TEM images of non-complete conducting filament in a-Si based device with Au NPs after electroforming process. Scale bar, 100 nm. The filament apparently grew from the active electrode (Ag TE). The region indicated by the red circle represented the filaments composed of Ag nanoparticles, and the blue rectangle area indicated the region without filaments. The simulation parameters are 95 nm-thick a-Si layer, 25 nm-radius Au NP and 1 V bias voltage. For (a) and (b), the distance from Au NPs surface to top electrode was kept as 95 nm, same with the planar region without Au NPs.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.5 TEM and EDS spot analyses for conducting filaments observation in a-Si memory with Au NPs-interlayer after electroforming process. (a) Cross sectional TEM image, and (b, c) TEM images corresponding to left and right red circle region of (a). (e, f) EDS spot analyses corresponding to (b) and (c), which indicates the filament is composed of Ag. Scale bar, 100nm.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.6 Resistive switching I-V curves of Ag/a-Si/Au (a) and Ag/a-Si/Au NPs/Au (b). A schematic illustration explaining the Ag filament change for the devices without (c) and with (d) Au NPs interlayer at OFF state, which cannot fully describe the CF shape in the device.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.7 (a-d) TEM images of the same device without Au NPs after 10 Set-Reset processes (OFF state). (e-g) TEM images of the same device with Au NPs after 10 Set-Reset processes (OFF state). The thinnest region and the dissolutions of the filaments took place at the a-Si and inert Au bottom electrode. The region indicated by the red arrows represented the longer Ag filaments, and the blue rectangle area indicated the region without filaments.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.8 (a) Line profile of EDS intensity of Ag, a-Si and Au elements along the red line, according to the **Figure 4.7d**. (b) EDS spectrum collected from the line region in (a). This indicates that the ruptured CF is composed of Ag element.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.9 TEM and EDS spot analyses for conducting filaments observation in a-Si memory with Au NPs-interlayer after erasing process. (a, c) Cross sectional TEM images. (b, d) EDS spot analyses corresponding to (a) and (c), which indicate the filament is composed of Ag and the nanoparticle onto the bottom electrode is Au. Scale bar, 100nm. This indicates that the ruptured CFs is composed of Ag element.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.10 I-V curves for a-Si memory devices without (a) and with (b) Au NPs during programming process. The multistep SET/RESET process is frequently observed in these devices, which might correspond to the formation/rupture of multifilaments (as shown in **Figure 4.7**) with different threshold voltage.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.11 Write endurance and retention time results by DC sweeping mode in the (a, c) Ag/a-Si/Au and (b, d) Ag/a-Si/Au NPs/Au cell (reading voltage, 0.1V).^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.12 I-V curves for a-Si memory devices without (a) and with (b) Au NPs during the initial electroforming process on the flexible PI substrate. The I-V characteristics of (c) Ag/a-Si/Au and (d) Ag/a-Si/Au NPs/Au memory devices on polyimide substrate.^[35] Adapted from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.13 (a) Illustration of the bending radius during the bending test. (b) Illustration of the bending test of the actual flexible Ag/a-Si/Au memory device on the polyimide (~200 μm) substrate, and the measured cells were near the middle of the device. Retention of both ON and OFF memory states (read at +0.1V) from the device of (a)

Ag/a-Si/Au/PI and (b) Ag/a-Si/Au NPs/Au/PI memory device.^[35] Adapted from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.14 SEM images of (a) the a-Si film on flexible Au/Cr/PI substrate and (b) Ag electrode on flexible a-Si/Au/Cr/PI substrate after 200 bending cycles with bend radius $R=10$ mm.

Figure 5.1 (a) Schematic of the Ag/hBN/Cu foil on PET substrate device arrays. (b) Cross-section TEM image of the Ag/hBN/Cu foil memory cell, and the thickness of hBN is about ~ 3 nm. (c) The electroforming process for hBN memory device with $V_{\text{forming}} = \sim 1.87$ V. (d) The switching characteristics for the hBN memory device after electroforming process.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.2 Characteristics of the flexible Ag TE/hBN/Cu foil memory device in terms of switching endurance (a) and retention time (b). The reading voltage is 0.1V.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.3 XPS characterization. (a) XPS survey spectra of hBN ultrathin film on the Cu foil. (b) B1s XPS peaks for the B-N bonding state, showing the presence of B-N (190.5 eV) and B-O (191.8 eV) bonds and (c) N1s XPS peak at 398.2 eV. (d) Cu 2p spectra, showing the presence of Cu₂O (932.65 eV), Cu⁰ (932.83 eV), CuO (933.64 eV) and Cu(OH)₂ (935.03 eV), and the atomic concentration of Cu was 15%.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.4 XPS characterization. (a) XPS survey spectra of hBN film on the SiO₂/Si substrate. (b) Cu 2p spectra, showing the presence of Cu₂O (932.65 eV), Cu⁰ (932.83 eV), and CuO (933.64 eV), and the atomic concentration of Cu was 0.3%.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.5 (a) Schematic of the Ag/hBN/ITO/PET memory device. (b) The electroforming process in the Ag/hBN/ITO/PET device with $V_{\text{forming}} \sim 1.9\text{V}$. The inset shows the transferred hBN film with PMMA onto ITO/PET substrate, indicated by the red rectangle frame. (c) The real flexible Ag/hBN/ITO/PET memory device. (d) The I-V characteristics of the Ag/hBN/ITO/PET memory device.^[43] Adapted from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.6 (a) Current (I) vs voltage (V) and (b) log (I) vs V curves of Ag TE/CuOx/Cu foil device. The hBN film was removed by using O_2 plasma, leaving with a possible CuOx layer during the hBN fabrication. Then, the Ag TE was deposited. It is clear that the possible CuOx layer cannot serve as the switching layer, indicating the possible CuOx layer has no significant influence on the key performance characteristics of hBN-based memory.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.7 (a) Schematic of the Au/hBN/Cu foil/PET device. (b) The electroforming process in the Au/hBN/ITO/PET device with $V_{\text{forming}} \sim 2\text{V}$. (c) The real flexible Au/hBN/Cu foil/PET memory devices. (d) The I-V characteristics of the Au/hBN/ITO/PET memory device. For this memory device, the I-V curves of (b, d) were measured under flat state. The Au electrode was grounded as the bottom electrode for electrical characterization.^[43] Adapted from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.8 (a) CAFM measurement and (b) I-V characteristic with a device configuration of diamond-coated tip/hBN/Cu foil device. The voltage sweep was $-2\text{V} \rightarrow 3\text{V} \rightarrow -2\text{V}$. (c) CAFM current maps of hBN-based memory at OFF state and (d) ON state with a 0.5V reading voltage, respectively. For (d), the region from 1.2 to 2.5 μm at the short edge, it was non-switched surface, and there was no voltage bias applied before reading its state.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.9 Observation of the conducting filaments in the same Ag TE/hBN/Cu foil device after SET process (ON state). (a) TEM image of a complete conducting filament.

The thinnest region of the filament is at the hBN/Cu foil interface. (b) STEM image of the ON-state sample, and the regions for EDS analyses are denoted by red circles. (c) EDS spectrum collected from the circle region “1” in the filament. (d) TEM image of a conducting filament which is not in complete contact with the Cu BE in the same device. (e) High resolution TEM image of Ag conducting filament corresponding to (d). The filament apparently starts growing from the Ag active electrode. (f) High resolution TEM image of non-complete Ag conducting filament (highlighted by the closed region), which clearly indicates the Ag filament starts growing from Ag TE. (g-i) Schematics of the filament growth for hBN-based resistive memory.^[43] Adapted from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.10 Characteristics of the flexible Ag TE/hBN/Cu foil on polyimide substrate (200 μm thick) memory device. (a) Illustration of 1 cycle during the bending test with bending radius $r=7$ mm, and the measured devices were near the middle of the sample. (b) Continuous bending experiment of the hBN-based device. The reading voltage is 0.1 V.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Figure 5.11 (a) SEM image of the Ag electrode/hBN/Cu foil on polyimide (200 μm thick) substrate after 750 bending cycles with bend radius $r=7$ mm. (b) SEM image of the hBN film, corresponding to the region marked in (a).

Figure 6.1 (a) Schematic of the ITO TE/hBN/FLG memory device fabrication process on any desired substrate. Chemical structures of (b) graphene and (c) hBN for bottom electrode and switching layer, respectively. (d) Schematic of ITO TE/hBN/FLG device on soft PDMS substrate. (e) Optical transmittance of ITO TE/hBN/FLG/PDMS device. The inset shows the actual memory device, indicating transparent characteristics.^[51] Reproduced from ref. 51 with permission from the American Chemical Society.

Figure 6.2 Electrical properties of the ITO TE/hBN/FLG/PDMS device. (a) A typical electroforming process with voltage of ~ 7.4 V in an ITO TE/hBN/FLG/PDMS memory device. (b) I-V characteristics after electroforming process. (c) 500 memory cycles and (d)

$\sim 5 \times 10^4$ s retention time from the memory device on flat condition, respectively. The readout voltage is + 0.1 V.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

Figure 6.3 (a) The transferred hBN film with PMMA onto ITO/PET substrate. (b) Transparent and flexible ITO/hBN/ITO/PET memory device. (c) Initial electroforming process for ITO TE/hBN/ITO/PET memory device with voltage of ~ 8.3 V. (d) Switching characteristics of ITO TE/hBN/ITO/PET memory device after electroforming process.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

Figure 6.4 (a, b) Illustration of 1 cycle bend test with bending radius of 14 mm. (c) Retention of the ON and OFF states during bending test. The inset showed the actual transparent flexible ITO TE/hBN/FLG/PDMS device on PET substrate. The readout voltage is + 0.1 V.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

Figure 6.5 Demonstration of the ITO TE /hBN/FLG/PDMS memory labels tagged on (a) a rough and soft wallet, (b) a centrifuge tube ($r \approx 8$ mm), and (c) device attached onto fingers with their corresponding switching characteristics. The memory device is easy to attach onto various curved objects' surfaces and exhibits excellent flexibility.^[51] Reproduced from ref. 51 with permission from the American Chemical Society.

Figure 6.6 Observation of conductive filaments in ITO TE /hBN/FLG/Cu foil memory cell at ON state. TEM images of (a) a non-complete and (b) a complete conducting filament in the same memory cell (highlighted by the closed regions), indicating the filament commences growth from ITO TE. (c) EDS elemental mapping result of the memory cell in STEM mode, corresponding to (b). (d) STEM image of the ITO TE /hBN/FLG device. (e) Line profile of the EDS intensity of Cu, In, and Sn elements along the red line in (a) from Cu foil to ITO TE. (f) EDS spectrum of the filament in region “1” of (d). The intensity of Cu, In, and Sn were shown in the insert table. It indicated the

filament was primarily composed of In.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

Figure 6.7 (a) Initial electroforming process of Ag TE/hBN/FLG/Cu foil memory device with voltage of ~ 3.5 V. (b) Initial electroforming process for ITO/hBN/FLG/Cu foil memory device. During the electroforming process, the positive voltage was applied on the graphene/Cu foil electrode, while the ITO electrode was grounded. It is clear that there was no resistive switching even with a high voltage, indicating the Cu foil which was isolated by few-layer graphene cannot contribute the resistive switching.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

Figure 6.8 Observation of conductive filaments in ITO TE /hBN/FLG/Cu foil memory cell at OFF state. (a) TEM image of a non-complete filament in the memory cell (highlighted by the closed regions), indicating the filament ruptured at the thinnest part of the filament at the hBN/graphene interface, leading to the OFF state. (b) STEM image of the ITO TE /hBN/FLG device, corresponding to (a). (c) EDS spectrum of the filament in region “1” of (b). (d-f) Schematic illustration of the In filament growth in the ITO TE /hBN/FLG memory device.^[51] Reproduced from ref. 51 with permission from the American Chemical Society.

Figure 7.1 Schematic structure and fabrication process for the stretchable 2D materials ReRAM device. (a) Ag TE/ hBN/Graphene BE on the pre-strained PDMS substrate. (b) Rippled Ag TE/ hBN/Graphene/PDMS ReRAM device after releasing the strain.

Figure 7.2 (a) SEM image of the Molybdenum 3-post lift-out grid for *in situ* TEM experiment. (b) Schematic of the *in situ* TEM measurement system. (c) TEM specimen in the center of the grid B. (d) The memory structure for *in situ* TEM experiment, consisting Pt layer/Au TE/hBN film/Cu foil.

Abbreviations

ReRAM	Resistive Switching Random Access Memory
ECM	Electrochemical Metallization
2D	Two dimensional
a-Si	Amorphous Si
NPs	Nanoparticles
PI	Polyimide
hBN	Hexagonal Boron Nitride
PET	Polyethylene terephthalate
2-ATP	2-Aminothiophenol
ITO	Indium Tin Oxide
APS	Ammonium Persulfate
PMMA	Poly(methylmethacrylate)
PDMS	Polydimethylsiloxane
TE	Top Electrode
BE	Bottom Electrode
CC	Compliance Current
CF	Conducting Filament
I-V	Current-Voltage
CVD	Chemical Vapor Deposition
FIB	Focused Ion Beam
EDS	Energy Dispersive Spectroscopy
XPS	X-ray Photoelectron Spectroscopy
XRD	X-ray Diffraction
TEM	Transmission Electron Microscopy
STEM	Scanning Transmission Electron Microscopy
UV-Vis	Ultraviolet Visible Spectroscopy
CAFM	Conductive Atomic Force Microscopy
FESEM	Field Emission Scanning Electron Microscopy

Chapter 1

Introduction

In this chapter, a brief introduction on the current progress of flexible functional resistive switching random access memory (ReRAM) devices is presented. The issues that limit the performance of flexible functional ReRAM devices are identified (such as complicated fabrication procedures, limited mechanical stability and thermal stability) and the corresponding strategies to solve the problems are briefed. Finally, the organization of the whole dissertation was described with the major findings summarized in the end. This chapter serves as a guidance to lay the objective of the current research and the approaches and strategies to accomplish the target.

1.1 Problem Statement

Resistive random access memory (ReRAM) devices, which can store and process information, are constituted of an electrode/insulator (or semiconductor)/electrode sandwich structure. The resistive switching phenomenon in ReRAM was found two centuries ago, however, its theoretical inception can only be dated back 40 years ago.^[1, 2] Then, the link between experiment and theory in ReRAM was established by Dmitri B. Strukov *et al.* in 2008.^[3] The ReRAM devices possess outstanding potential of miniaturization down to less than 10 nm and exhibit high endurance, fast switching, and low-energy consumption, which can fulfil the requirements of scalability and capability of new computing technologies.^[4, 5] Consequently, ReRAM device, which has attracted extensive attention from academic and industrial communities, is the best potential candidate for the replacement of the conventional silicon-based Flash memories.^[3-12] Especially, the electrochemical metallization (ECM)-based memory device, one of the major types of ReRAM devices, has attracted tremendous attention because of their proven scalability potential, high-performance, and industrialization maturity.^[13]

It is no longer the only criteria to reduce the cost of the electronic devices for the emerging technological needs. The devices with advanced functionalities such as flexibility, transparency, stretchability, and environmental robustness have significant advantages and value-add in different areas for future electronics applications.^[14-19] For the fully integrated electronic systems, the functional memory units- one of the critical and fundamental components for information storage and process, are essential and indispensable.^[11, 20-32]

In ECM-based ReRAM devices, the pristine memory cells are usually needed to be activated into switching states *via* electroforming process with a high voltage,^[5, 33] which may limit the integration potential in advanced crossbar structures or damage the memory cells permanently, leading to low switching performance and device yield.^[33-35] On the other hand, a large memory window, *i.e.*, ON/OFF ratio, is also desirable for the high density data storage realization in ReRAM devices to avoid misreading during multilevel

switching operation.^[36-39] To reduce the electroforming voltage (V_{forming}) of ECM-based ReRAM devices, several relatively complex fabrication approaches^[33, 40] or heat treatment methods with high temperature^[41, 42] were introduced, which may limit the stackable integration of electronic devices.^[43, 44] Especially, the high temperature process may damage the plastic flexible substrates with poor thermal stability, limiting the advanced flexible functional ReRAM devices fabrication.^[45, 46] On the other hand, to increase the memory window of ReRAM devices, several complicated approaches also have been proposed,^[34, 47-50] which are difficult to control. Therefore, a delicate design, which can realize the low electroforming voltage and large memory window in ReRAM devices at the same time on both flexible and rigid substrates, is imperative.

Generally speaking, in terms of switching endurance, inorganic-based ReRAM has significant advantages over organic ones, while organic-based memory devices prevail in high-mechanical flexibility.^[5] For flexible inorganic-based ReRAM devices, their flexibility and switching performances always suffer from the brittle nature of common inorganic switching materials (*e.g.* oxides, chalcogenides). It is still a big challenge for these memories to be flexible.^[11, 51, 52] For flexible organic-based ReRAM devices, however, their switching performances always suffer from the degradation of organic switching layers under high temperature.^[5, 51, 53] Therefore, further efforts are required to explore decent materials to realize both excellent mechanical and electrical performances flexible functional ReRAM devices.

In addition, fully integrated visibly transparent electronics have also received tremendous attention promising applications ranging from display, consumer products to industrial equipment,^[19, 54] as well as transferable electronics which can be transferred onto nonconventional substrates (*e.g.* soft or nonplanar ones).^[25, 55] Although a delightful picture was depicted, there are few reports about multifunctional ReRAM devices. For instance, flexible multifunctional ReRAM, *i.e.*, flexible, transparent, and transferable memory devices, which requires excellent electrical, mechanical and optical properties, is much more challenging to achieve these at the same time. Especially, the electrochemical active electrodes (*e.g.* Ag, Cu) which can generate conducting filaments under electric

filed in the ECM-based ReRAM are not suitable for transparent memory devices due to their mirror reflection. Therefore, a transparent electrode which can generate conducting filaments under electric filed is necessary for fully transparent ECM-based ReRAM devices. The development in this field is still in its cradle.

1.2 Objectives and Scope

1.2.1 Develop strategies for enlarged memory window and reduced electroforming voltage ECM-based ReRAM

As described earlier, to realize large memory window and low electroforming voltage on both flexible and rigid substrates, a versatile fabrication process should be proposed at a relatively low temperature, which can cater to stackable integration on thermal instability flexible substrates. In ECM-based ReRAM devices, the increase of electric field in the switching layer will lead to increases in the ionic current density and drift velocity.^[7, 56, 57] Hence, the front of the ruptured filaments has the highest electric field, where the cations would preferably diffuse and become reduced during subsequent SET process.^[58] Therefore, it is possible to improve the electrical performances of ECM-based ReRAM devices in terms of low electroforming voltage and large memory window *via* tuning the electric filed, which can control the filament growth.

Hypothesis 1: *In the ECM-based ReRAM device with Au nanoparticles (NPs)-interlayer, the electric filed intensity at the tip of the metal NPs can be enhanced, which would directly affect the dynamic transport of the Ag^+ ions and direct the conductive filaments growth to improve the memory device performances.*

Approach: Metal NPs-enhanced electric field is proposed to induce higher electric field, and the cations will preferably gather around the NPs site during electroforming process, promoting the growth of the conductive filament and leading to the lower electroforming voltage; Meanwhile, the cations would drift faster during RESET process to generate wider gap between ruptured the filament tip and electrode, leading to high resistance at

the OFF state and large ON/OFF ratio. Therefore, it could be promising to realize large memory window and low electroforming voltage by inserting metal NPs in ECM-based ReRAM devices at the same time. The Ag active electrode/amorphous Si (a-Si)/Au bottom electrode structure was employed for the effect of metal NPs demonstration in ECM-based ReRAM devices. This configuration is deemed to provide good imaging contrast under TEM analyses for the investigation of Ag metal filament formation in the a-Si switching layer. Here the Au NPs could be inserted between the inert Au bottom electrode and a-Si switching layer, which will not involve the Ag filaments formation/rupture in the Ag top electrode/a-Si/Au bottom electrode memory devices.

Herein, the task is to develop a simple method to enhance the electric performances of ECM-based ReRAM on both flexible and rigid substrates. The Au NPs can be prepared *via* solution synthesis, of which their sizes can be precisely controlled.^[59] Then the Au NPs will be inserted between Au bottom electrode and a-Si layer via self-assembly technology at room temperature to form a uniform monolayer. This synthesis method at room temperature is suitable for ReRAM devices fabrication on both flexible and rigid substrates.

1.2.2 Realization of high performance flexible functional ECM-based ReRAM

Flexible ReRAM devices, which offer mechanical versatility in data storage, provide great advantages of being foldable, lightweight, and printable for future electronics application.^[20, 24] Some electronics manufactures also show a growing interest in flexible display consumer electronics, such as TVs, E-readers, and mobile phones.^[60] However, for the flexible ReRAM devices, the bending stability under mechanical deformation conditions and switching endurance is an urgent and main barrier for flexible ReRAM applications. The objective for this research is to realize high performance flexible ECM-based ReRAM devices with excellent bending stability and switching endurance under bend condition.

Hypothesis 2: *In the ECM-based ReRAM device, 2D hexagonal boron nitride material with unique physical properties (e.g., high thermal stability, inherent flexibility) may lead to excellent switching endurance and bending stability ReRAM with small bending radius.*

Approach: Two dimensional (2D) hexagonal boron nitride (hBN) film, of which structure is similar to graphene with a bandgap of ~ 5.9 eV, has aroused great research interest due to its unique properties, such as high thermal conductivity, excellent thermal stability (1000 °C), chemical inertness, high transparency, exceptional mechanical and electrical properties.^[61-64] In addition, compare to other 2D materials (e.g., graphene), hBN does not require any transfer process to build a ReRAM device. hBN film can be grown on a metallic substrate (which can act as electrode and substrate) using scalable chemical vapor deposition (CVD) technique, and the top electrodes can be easily evaporated on it to form the metal/insulator/metal cells. This approach can avoid the generation of cracks and contaminants during 2D material manipulation. Moreover, during the CVD growth process, the defective grain boundaries (from one atom thick to few atoms thick) will form across the layered hBN thin film.^[65, 66] The grain boundaries in CVD-grown hBN sheets would allow easy metallic ion penetration, which can assist the conductive metal filaments formation. Therefore, the 2D hBN material is a good candidate for future flexible ReRAM applications.

1.2.3 Design for flexible, transparent, and transferable ECM-based ReRAM

Electronic modules have been going through extensive innovations to meet the ever-increasing technological demands with multiple functionalities, such as flexibility transparency, and portability.^[67] The objective here is to accomplish flexible, transparent, and transferable multi-functional ECM-based ReRAM devices. For making the transferable electrodes, graphene, an excellent choice as electrode for wearable electronics, can be efficiently transferred onto other different substrates.^[68-70] In addition to the high conductivity of the monolayer and few layer graphene, graphene also offers advantages of the optical transparency and flexibility. On the other hand, like layered structure of graphene sheets, the 2D hBN film also can be easily transferred to foreign

substrate via a conventional wet transfer approach.^[71] Therefore, it is possible to realize the flexible and transferable ReRAM device *via* combining 2D hBN and graphene materials. However, graphene electrode is unable to provide filament growth, therefore we explore the use of transparent electrode like ITO and its roles in resistive switching.

Hypothesis 3: *In the ECM-based ReRAM device, the indium ions (In^{3+}) in ITO electrode may be reduced to indium filament for the resistive switching, indicating that ITO can be used to construct transparent ECM-based ReRAM device.*

Approach: The indium tin oxide (ITO), which serves as both conducting electrode and switching active material, can exhibit resistive switching behaviors due to the oxygen migration under electric field.^[72] Based on electrochemical metallization theory,^[7] the ITO electrode may form the conductive filaments under electric field for the ECM-based ReRAM operation. Therefore, to realize fully transparent, flexible, and transferable ECM-based ReRAM devices, ITO electrode will be employed.

1.3 Dissertation Overview

Flexible functional ReRAM devices have stimulated extensive interests in the field of information technology, which has a great potential for next-generation flexible functional electronics that needs urgent development. The thesis herein addresses the current issues that limit the performances of such flexible functional ECM-base ReRAM devices for feasible applications. Efforts were made toward device structural design, novel switching materials, and switching mechanism study for high-performance flexible functional ECM-based ReRAM devices.

Chapter 1 explains the importance of the current study with a brief introduction of the current progress of the flexible functional ECM-based ReRAM devices. Problems that limit the high-performance of flexible ECM-based ReRAM and multi-functional flexible memory devices realization for potential practical devices are identified. The feasible approaches to realize the objectives of flexible functional ECM-based ReRAM devices

are outlined.

Chapter 2 reviews the basic concepts and progress on flexible functional ReRAM devices. Firstly, the electrode and switching layer materials selection and the switching mechanism of ECM-based ReRAM are discussed. Subsequently, the reported work on flexible functional memory devices and related techniques to achieve flexible functional memory devices are reviewed. Challenges in the high-performance flexible functional ECM-based memory devices realization are discussed.

Chapter 3 presents rationales for the materials selection to fabricate flexible functional ECM-based ReRAM devices in the thesis. The synthesis procedure as well as the mechanism is then described to gain a solid understanding of the selected material and fabrication approaches. The working principles of characterization tools like SEM, TEM, FIB, etc. were also included in this chapter. Finally, the device fabrication procedures along with the schematics were presented for a good perception of the device configuration.

Chapter 4 presents the strategy for the realization of high electrical performance ECM-based ReRAM devices on both flexible and rigid substrates. The Au NPs monolayer is inserted between the a-Si switching layer and the Au bottom electrode (BE) *via* a simple self-assembly method. Compared with the Ag TE/a-Si/Au BE devices, the Ag TE/a-Si/Au NPs-interlayer/Au BE ECM-based memory devices exhibit lower electroforming voltage and larger memory window on both flexible and rigid substrates. For this phenomenon, *ex situ* TEM was employed to gain insight into the mechanism of the performance change.

Chapter 5 presents the approach to realize a high-performance flexible ECM-based ReRAM devices. To improve the bending stability of flexible memory devices, the CVD-grown ultrathin 2D hBN material (~3-5 nm) was introduced for the first time for the flexible ECM-based memory device, which was sandwiched between Cu foil and Ag electrodes. The final hBN-based memory device features excellent bending stability

under bend condition (bending radius, 7 mm) as well as long retention time and good switching endurance. The switching mechanism was carefully studied *via ex situ* TEM.

Chapter 6 described the strategy for the accomplishment of flexible, transparent, and transferable multi-functional ECM-based ReRAM devices, where the 2D hBN (~5 nm) film was sandwiched between ITO top electrode and 2D graphene bottom electrode. Due to the excellent mechanical property of 2D materials, the 2D hBN and graphene materials were easily transferred onto different substrates (e.g. PET, PDMS) with the assistant of PMMA. The direct observation of indium filaments in ITO/hBN/Graphene ECM-based memory device was found for the first time *via ex situ* TEM, which is responsible for the resistive switching.

Chapter 7 concludes the established techniques for the realization of advanced flexible functional ECM-based ReRAM devices. Suggestion on the more advanced flexible functional ECM-based memory device and the related studies on the switching mechanism are provided in the future work.

1.4 Findings and Outcomes

This thesis is dedicated to realizing high-performance flexible ECM-based ReRAM devices and multi-functional flexible ECM-based memory devices together with the switching mechanism study. The research led to several novel outcomes:

1. High electrical performance ECM-based ReRAM devices with low electroforming voltage and large ON/OFF ratio were demonstrated by inserting Au NPs mono-layer on both flexible and rigid substrates. The Au NPs layer will affect the filaments growth, which was confirmed *via ex situ* TEM. A simple method was developed to insert the Au NPs mono-layer *via* self-assembly technology under ambient conditions for flexible memory devices fabrication, which offers a versatile structure for high electrical performance ECM-based ReRAM applications on both flexible and rigid substrates.

2. High electrical and mechanical performances flexible ECM-based ReRAM devices with CVD-grown ultrathin 2D hBN material (~3-5 nm) were presented for the first time. The excellent properties of hBN allow the flexible hBN-based memory device to exhibit good bending stability and switching endurance under bend conditions. The transferability of the hBN film was also demonstrated in the Ag TE/hBN/ITO/PET memory devices. This work promotes and expands the 2D materials application in the flexible ReRAM in future wearable electronics and information technology.
3. Flexible, transparent, and transferable multi-functional ECM-based ReRAM devices were demonstrated for the first time. By utilizing the superior optical, mechanical, and electrical properties of the 2D materials, the advanced flexible hBN-based memory device was fabricated with ITO top electrode and graphene bottom electrode on PET or soft PDMS substrates (ITO TE/hBN/graphene/PDMS or PET). More importantly, for the first time, the indium filaments were found to be responsible for the resistive switching *via ex situ* TEM, which broadens the understanding of the resistive switching mechanism for the ECM-based memory devices.

References

- [1] L. O. Chua, *IEEE Trans. Circuit theory* **1971**, 18, 507-519.
- [2] L. O. Chua, S. M. Kang, *Proc. IEEE* **1976**, 64, 209-223.
- [3] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, *Nature* **2008**, 453, 80-83.
- [4] J. J. S. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nanotechnol.* **2013**, 8, 13-24.
- [5] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Mater. Sci. Eng., R* **2014**, 83, 1-59.
- [6] J. Shang, G. Liu, H. L. Yang, X. J. Zhu, X. X. Chen, H. W. Tan, B. L. Hu, L. Pan, W. H. Xue, R. W. Li, *Adv. Funct. Mater.* **2014**, 24, 2171-2179.
- [7] R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* **2009**, 21, 2632-2663.
- [8] C. S. Hwang, *Adv. Electron. Mater.* **2015**, 1.
- [9] I. Valov, W. D. Lu, *Nanoscale* **2016**, 8, 13828-13837.

- [10] M. Wang, C. Bi, L. Li, S. B. Long, Q. Liu, H. B. Lv, N. H. Lu, P. X. Sun, M. Liu, *Nat. Commun.* **2014**, 5, 4598.
- [11] J. Yao, J. Lin, Y. H. Dai, G. D. Ruan, Z. Yan, L. Li, L. Zhong, D. Natelson, J. M. Tour, *Nat. Commun.* **2012**, 3, 1101.
- [12] H. Wang, F. B. Meng, B. W. Zhu, W. R. Leow, Y. Q. Liu, X. D. Chen, *Adv. Mater.* **2015**, 27, 7670-7676.
- [13] I. Valov, R. Waser, J. R. Jameson, M. N. Kozicki, *Nanotechnology* **2011**, 22.
- [14] Y. S. Chen, M. Y. Hong, G. S. Huang, *Nat. Nanotechnol.* **2012**, 7, 197-203.
- [15] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, 335, 1326-1330.
- [16] S.-W. Hwang, H. Tao, D.-H. Kim, H. Cheng, J.-K. Song, E. Rill, M. A. Brenckle, B. Panilaitis, S. M. Won, Y.-S. Kim, *Science* **2012**, 337, 1640-1644.
- [17] J. J. Liang, L. Li, X. F. Niu, Z. B. Yu, Q. B. Pei, *Nat. Photonics* **2013**, 7, 817-824.
- [18] J. A. Rogers, T. Someya, Y. G. Huang, *Science* **2010**, 327, 1603-1607.
- [19] J. F. Wager, *Science* **2003**, 300, 1245-1246.
- [20] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, *Nat. Mater.* **2015**, 14, 199-204.
- [21] S. T. Han, Y. Zhou, V. Roy, *Adv. Mater.* **2013**, 25, 5425-5449.
- [22] X. He, J. Zhang, W. Wang, W. Xuan, X. Wang, Q. Zhang, C. G. Smith, J. Luo, *ACS Appl. Mater. Interfaces* **2016**, 8, 10954-10960.
- [23] N. R. Hosseini, J. S. Lee, *Adv. Funct. Mater.* **2015**, 25, 5586-5592.
- [24] Y. Ji, D. F. Zeigler, D. S. Lee, H. Choi, A. K. Y. Jen, H. C. Ko, T. W. Kim, *Nat. Commun.* **2013**, 4, 2707.
- [25] Y. C. Lai, F. C. Hsu, J. Y. Chen, J. H. He, T. C. Chang, Y. P. Hsieh, T. Y. Lin, Y. J. Yang, Y. F. Chen, *Adv. Mater.* **2013**, 25, 2733-2739.
- [26] Y. C. Lai, Y. C. Huang, T. Y. Lin, Y. X. Wang, C. Y. Chang, Y. X. Li, T. Y. Lin, B. W. Ye, Y. P. Hsieh, W. F. Su, Y. J. Yang, Y. F. Chen, *NPG Asia Mater.* **2014**, 6, e87.
- [27] Y. Liu, H. Wang, W. Shi, W. Zhang, J. Yu, B. K. Chandran, C. Cui, B. Zhu, Z. Liu, B. Li, *Angew. Chem., Int. Ed.* **2016**, 128, 9030-9034.
- [28] H. W. Tan, G. Liu, X. J. Zhu, H. L. Yang, B. Chen, X. X. Chen, J. Shang, W. D. Lu, Y. H. Wu, R. W. Li, *Adv. Mater.* **2015**, 27, 2797-2803.

- [29] B. Zhu, H. Wang, Y. Liu, D. Qi, Z. Liu, H. Wang, J. Yu, M. Sherburne, Z. Wang, X. Chen, *Adv. Mater.* **2016**, 28, 1559-1566.
- [30] D. Son, J. Lee, S. Qiao, R. Ghaffari, J. Kim, J. E. Lee, C. Song, S. J. Kim, D. J. Lee, S. W. Jun, S. Yang, M. Park, J. Shin, K. Do, M. Lee, K. Kang, C. S. Hwang, N. S. Lu, T. Hyeon, D. H. Kim, *Nat. Nanotechnol.* **2014**, 9, 397-404.
- [31] K. Qian, V. C. Nguyen, T. P. Chen, P. S. Lee, *J. Mater. Chem. C* **2016**, 4, 9637-9645.
- [32] D. H. Lien, Z. K. Kao, T. H. Huang, Y. C. Liao, S. C. Lee, J. H. He, *ACS Nano* **2014**, 8, 7613-7619.
- [33] G. Wang, A. R. O. Raji, J. H. Lee, J. M. Tour, *ACS Nano* **2014**, 8, 1410-1418.
- [34] S. H. Jo, W. Lu, *Nano Lett.* **2008**, 8, 392-397.
- [35] G. Bersuker, Y. Jeon, H. R. Huff, *Microelectron. Reliab.* **2001**, 41, 1923-1931.
- [36] S. J. Choi, G. S. Park, K. H. Kim, S. Cho, W. Y. Yang, X. S. Li, J. H. Moon, K. J. Lee, K. Kim, *Adv. Mater.* **2011**, 23, 3272-3277.
- [37] M. J. Rozenberg, I. H. Inoue, M. J. Sanchez, *Phys. Rev. Lett.* **2004**, 92, 178302.
- [38] S. Balatti, S. Larentis, D. C. Gilmer, D. Ielmini, *Adv. Mater.* **2013**, 25, 1474-1478.
- [39] B. L. Hu, X. J. Zhu, X. X. Chen, L. Pan, S. S. Peng, Y. Z. Wu, J. Shang, G. Liu, Q. Yan, R. W. Li, *J. Am. Chem. Soc.* **2012**, 134, 17408-17411.
- [40] B. K. You, W. I. Park, J. M. Kim, K. I. Park, H. K. Seo, J. Y. Lee, Y. S. Jung, K. J. Lee, *ACS Nano* **2014**, 8, 9492-9502.
- [41] J. Yao, Z. Z. Sun, L. Zhong, D. Natelson, J. M. Tour, *Nano Lett.* **2010**, 10, 4105-4110.
- [42] Y. F. Chang, P. Y. Chen, Y. T. Chen, F. Xue, Y. Z. Wang, F. Zhou, B. Fowler, J. C. Lee, *Appl. Phys. Lett.* **2012**, 101, 052111.
- [43] M. J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y. B. Kim, C. J. Kim, D. H. Seo, S. Seo, U. I. Chung, I. K. Yoo, K. Kim, *Nat. Mater.* **2011**, 10, 625-630.
- [44] M. J. Lee, S. Seo, D. C. Kim, S. E. Ahn, D. H. Seo, I. K. Yoo, I. G. Baek, D. S. Kim, I. S. Byun, S. H. Kim, I. R. Hwang, J. S. Kim, S. H. Jeon, B. H. Park, *Adv. Mater.* **2007**, 19, 73-76.
- [45] S. Park, G. Wang, B. Cho, Y. Kim, S. Song, Y. Ji, M. H. Yoon, T. Lee, *Nat. Nanotechnol.* **2012**, 7, 438-442.

- [46] N. Gergel-Hackett, J. L. Tedesco, C. A. Richter, *Proc. IEEE* **2012**, 100, 1971-1978.
- [47] S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn, K. J. Lee, T. Lee, S. O. Kim, *Nano Lett.* **2012**, 12, 2217-2221.
- [48] H. W. Zhang, L. F. Liu, B. Gao, Y. J. Qiu, X. Y. Liu, J. Lu, R. Q. Han, J. F. Kang, B. Yu, *Appl. Phys. Lett.* **2011**, 98, 042105.
- [49] Y. C. Yang, F. Pan, Q. Liu, M. Liu, F. Zeng, *Nano Lett.* **2009**, 9, 1636-1643.
- [50] H. Y. Lee, Y. S. Chen, P. S. Chen, T. Y. Wu, F. Chen, C. C. Wang, P. J. Tzeng, M. J. Tsai, C. Lien, *IEEE Electron Device Lett.* **2010**, 31, 44-46.
- [51] Y. Yang, G. Yuan, Z. Yan, Y. Wang, X. Lu, J. M. Liu, *Adv. Mater.* **2017**, 29, 1700425.
- [52] J. Jang, F. Pan, K. Braam, V. Subramanian, *Adv. Mater.* **2012**, 24, 3573-3576.
- [53] S. Menzel, M. Waters, A. Marchewka, U. Bottger, R. Dittmann, R. Waser, *Adv. Funct. Mater.* **2011**, 21, 4487-4492.
- [54] G. Thomas, *Nature* **1997**, 389, 907-908.
- [55] Q. N. Thanh, H. Jeong, J. Kim, J. W. Kevek, Y. H. Ahn, S. Lee, E. D. Minot, J. Y. Park, *Adv. Mater.* **2012**, 24, 4499-4504.
- [56] J. J. O'Dwyer, *The theory of electrical conduction and breakdown in solid dielectrics*, Clarendon Press, **1973**.
- [57] S. Kim, S. Choi, J. Lee, W. D. Lu, *ACS Nano* **2014**, 8, 10262-10269.
- [58] Y. C. Yang, P. Gao, S. Gaba, T. Chang, X. Q. Pan, W. Lu, *Nat. Commun.* **2012**, 3, 732.
- [59] G. Frens, *Nature* **1973**, 241, 20-22.
- [60] S. T. Han, Y. Zhou, V. A. L. Roy, *Adv. Mater.* **2013**, 25, 5425-5449.
- [61] Z. Liu, Y. J. Gong, W. Zhou, L. L. Ma, J. J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou, P. M. Ajayan, *Nat. Commun.* **2013**, 4, 2541.
- [62] L. Britnell, R. V. Gorbachev, R. Jalil, B. D. Belle, F. Schedin, A. Mishchenko, T. Georgiou, M. I. Katsnelson, L. Eaves, S. V. Morozov, N. M. R. Peres, J. Leist, A. K. Geim, K. S. Novoselov, L. A. Ponomarenko, *Science* **2012**, 335, 947-950.
- [63] M. Bokdam, P. A. Khomyakov, G. Brocks, Z. C. Zhong, P. J. Kelly, *Nano Lett.* **2011**, 11, 4631-4635.

- [64] H. Wang, F. C. Liu, W. Fu, Z. Y. Fang, W. Zhou, Z. Liu, *Nanoscale* **2014**, 6, 12250-12272.
- [65] C. B. Pan, Y. F. Ji, N. Xiao, F. Hui, K. C. Tang, Y. Z. Guo, X. M. Xie, F. M. Puglisi, L. Larcher, E. Miranda, L. L. Jiang, Y. Y. Shi, I. Valov, P. C. McIntyre, R. Waser, M. Lanza, *Adv. Funct. Mater.* **2017**, 27, 1604811.
- [66] A. L. Gibb, N. Alem, J. H. Chen, K. J. Erickson, J. Ciston, A. Gautam, M. Linck, A. Zettl, *J. Am. Chem. Soc.* **2013**, 135, 6758-6761.
- [67] D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. Z. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. G. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, 333, 838-843.
- [68] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, 5, 574-578.
- [69] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, 457, 706-710.
- [70] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, 3, 270-274.
- [71] L. Song, L. J. Ci, H. Lu, P. B. Sorokin, C. H. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, P. M. Ajayan, *Nano Lett.* **2010**, 10, 3209-3215.
- [72] J. S. Huang, Y. C. Lin, H. W. Tsai, W. C. Yen, C. W. Chen, C. Y. Lee, T. S. Chin, Y. L. Chueh, *Adv. Electron. Mater.* **2015**, 1, 1500061.

Chapter 2

Literature Review

The resistive switching random access memory (ReRAM) device, which is the best potential candidate of the conventional silicon-based Flash memories for data storage and processing, has attracted immense interest due to its fast switching, high endurance, low-energy consumption, simple structure, and scalability. In particular, the scalability potential and maturity of industrialization have been proven for the electrochemical metallization (ECM)-based ReRAM. On one hand, excellent electrical performances are needed (e.g., low electroforming voltage, large memory window) to realize high yield and high density data storage and avoid misreading during the device operation. On the other hand, the devices with advanced functionalities such as flexibility, transparency, and portability as well as superior mechanical and electrical performances are expected for future electronics applications in different areas. In this chapter, techniques to realize high electrical performance flexible memory devices (i.e. low electroforming voltage, large memory window) and flexible multi-functional ReRAM devices (e.g. flexibility, transparency, and portability) are reviewed to understand the current progress and issues to resolve in this field.

2.1 Resistive Switching Random Access Memory (ReRAM)

ReRAM device is two-terminal capacitor-like structure, which consists of electron conductor/resistive material/electron conductor layers. The internal resistance state can freely switch between high and low states under electrical stimuli, which also can maintain for a long time without power applied. Due to its excellent performances, ReRAM will be a great potential candidate to replace the current main silicon-based Flash memories.^[1-4]

2.1.1 General feature

The original theoretical description of ReRAM switching behavior can be traced back 40 years ago.^[5, 6] Then, the link between experiment and theory in ReRAM was established by Dmitri B. Strukov *et al.* in 2008.^[7] It has been demonstrated that ReRAM devices possess outstanding potential of miniaturization less than 10 nm^[8] and exhibit sub-ns operation speed,^[9, 10] low power consumption (<0.1 pJ),^[11, 12] and excellent switching endurance (>10¹² cycles)^[13]. The conventional silicon-based Flash memory, which represents the current main nonvolatile memory due to its low cost and high density data storage, is suffering from low endurance (10⁶ switching cycles), poor switching speed (write/erase time: 1 ms/0.1 ms) and high write voltage.^[1] In addition, in the near future, Flash memories are expected to run into their physical limits such as large leakage current.^[1] To overcome the Flash memory's drawbacks, besides the ReRAM, the phase-change RAM (PCM), magnetic RAM (MRAM), and ferroelectric RAM (FeRAM) devices also have been proposed. However, these three types of memory devices are also facing the miniaturization issue due to their large cell size, as shown in **Table 2.1**.^[2, 14] Therefore, compared to these different memory devices, ReRAM would be the most promising candidate as next generation non-volatile memories.^[1-4] Normally, there are three types of ReRAM devices, which are thermochemical mechanism (TCM) -based memory, valence change mechanism (VCM)-based memory, and electrochemical metallization (ECM, *i.e.* metal filaments formation/rupture)-based memory devices, respectively.^[15] Among of these, the ECM-based ReRAM, sometimes referred as

conductive-bridge random access memory,^[15, 16] has aroused tremendous attention due to its proven scalability potential, high-performance, and industrialization maturity.^[15]

Table 2.1 Different types of non-volatile memory devices comparison.^[2, 14]

	Flash	ReRAM	PCM	MRAM	FeRAM
Feature size F, nm	22	5	45	65	180
Cell Area	4F ²	4F ²	4F ²	20F ²	22F ²
Read Time	0.1 ms	<10 ns	12 ns	35 ns	40 ns
Write/Erase Time	1/0.1 ms	~10 ns	100 ns	35 ns	65 ns
Write Cycles	1E4	1E12	1E9	>1E12	1E14
Write Voltage (V)	15	0.6/-0.2	3	1.8	1.3-3.3
Read Voltage	1.8	0.15	1.2	1.8	1.3-3.3
Retention Time (year)	10 y	>10 y	>10 y	>10 y	10 y

Figure 2.1 shows the basic structure of ReRAM device, where the resistive switching layer was sandwiched between two electron conductors. The intrinsic mechanism for all ReRAM devices is resistive switching under electric field, of which resistance state can be freely transformed between high resistance state (OFF state or HRS) and low resistance state (ON state or LRS). To program the fresh ReRAM device into switching state, an electroforming process is always required ahead of the first write operation to create an easy transport channel for the ions transport.^[3, 17] This electroforming step normally requires a high voltage, which may damage the memory cells permanently, leading to low switching performance and device yield.^[18-20] On the other hand, the electrical properties of the diode or selector could be adversely affected by the high electroforming voltage, which would limit the advanced crossbar structures (*e.g.* one selector-one resistive memory, one diode-one resistive memory) applications.^[21, 22] In order to improve the ReRAM performances *via* reducing the electroforming voltage, several relatively complex fabrication approaches^[23, 24] or heat treatment methods with high temperature^[25, 26] were introduced, which would limit the stackable integration of electronic devices.^[27, 28] Especially, the high temperature process may damage the plastic flexible substrates with poor thermal stability, limiting the advanced flexible functional

ReRAM devices fabrication.^[29, 30] For example, Gunuk Wang *et al.* reported a conducting-interlayer ReRAM device, where several conducting layers were inserted in the SiO_x switching layer one by one *via* electron beam evaporation to reduce the electroforming voltage.^[24] Goux *et al.* introduced oxygen-deficient NiO based memory devices, where the optimized oxidation process was carried out at 500 °C.^[31]

Normally, the logic “0” state and “1” state are assigned to the OFF and ON states, respectively. To program the ReRAM devices from HRS to LRS, SET process is required. In contrast, RESET process is needed to switch the ReRAM devices from LRS to HRS state. As shown in **Figure 2.1b** and c, based on the resistive switching behaviors, ReRAM devices operation could be categorized into unipolar and bipolar switching mode. For the unipolar mode (**Figure 2.1b**), the resistive switching can be realized by applying the same electrical polarity. While for the bipolar mode (**Figure 2.1c**), the resistive switching between LRS and HRS requires opposite electrical polarities. Generally, a current compliance (I_{comp}) needs to be applied during the resistive switching to optimize the operation and avoid the breakdown damage of the ReRAM cells. In order to read the memory state without detectable change during detection process, a small voltage magnitude is employed on the read operation. In the ReRAM devices, a large memory window, *i.e.*, ON/OFF ratio, is desirable for the high density data storage realization in ReRAM devices to avoid misreading during multilevel switching operation.^[32-35] To increase the memory window of ReRAM devices, several complicated approaches also have been proposed,^[18, 36-39] which are difficult to control. For instance, Yang *et al.* reported a manganese (Mn) -doped ZnO based ReRAM device, where the 3% Mn dopants in ZnO film can increase the resistivity of the HRS state.^[38]

2.1.2 Materials

ReRAM device is consisted of a resistive switching layer and two electrodes. Therefore, the material in ReRAM devices could be simply categorized into resistive switching layer and electrode materials.

Figure 2.1 (a) Schematic of the ReRAM devices architecture. Schematic of the two basic switching modes in ReRAM devices: (b) unipolar mode and (c) bipolar mode, respectively.^[1] Reproduced from ref. 1 with permission from Elsevier B.V.

Resistive switching layer materials. So far, various switching layer media have been exploited in ReRAM devices, which normally can be simply grouped into organic and inorganic materials. For ReRAM device, it requires insulating and conductive phases for the resistive switching. To obtain reliable switching, the reaction between these two phases should not occur even at high temperature.^[2] Joule heating, which would induce high temperature for the possible chemical interactions, is not avoidable and should be seriously considered for the materials selection in memory devices.^[2, 40, 41]

Generally speaking, in terms of switching endurance, inorganic-based ReRAM devices have a significant advantage over organic ones due to their excellent thermal stability, while organic-based memory devices prevail in high-mechanical flexibility and simple fabrication.^[4] Inorganic switching materials for ReRAM can be simply categorized into oxide insulators, such as complex oxides (*e.g.* $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$), metal oxides (*e.g.* TiO_x),

non-metal oxides (*e.g.* SiO_x), and non-oxides, such as tellurides (*e.g.* ZnTe), amorphous Si, nitrides (*e.g.* AlN), which have been summarized in **Table 2.2**.^[1]

Table 2.2 Summary of common inorganic materials-based ReRAM devices and corresponding electrical performances.^[1] Adapted from ref. 1 with permission from Elsevier B.V.

Storage medium	Switching mode	ON/OFF ratio	Operation speed	Endurance (cycles)
<i>Binary oxides</i>				
MgO _x	Unipolar, bipolar	>10 ⁵	–	>4 × 10 ²
AlO _x	Unipolar, bipolar	>10 ⁶	<10 ns; <10 ns	>10 ⁴
SiO _x	Unipolar, bipolar	>10 ⁷	<100 ps; <100 ps	>10 ⁸
TiO _x	Unipolar, bipolar	>10 ⁵	<5 ns; <5 ns	>2 × 10 ⁶
CrO _x	Bipolar	>10 ²	<4 μs; <5 μs	>6 × 10 ⁴
MnO _x	Unipolar, bipolar	>10 ⁴	<100 ns; <200 ns	>10 ⁵
FeO _x	Bipolar	>10 ²	<10 ns; <10 ns	>6 × 10 ⁴
CoO _x	Unipolar, bipolar	>5 × 10 ³	<20 ns; <20 ns	>10 ³
NiO _x	Unipolar, bipolar	>10 ⁶	<10 ns; <20 ns	>10 ⁶
CuO _x	Unipolar, bipolar	>10 ⁵	<50 ns; <50 ns	>1.2 × 10 ⁴
ZnO _x	Unipolar, bipolar	>10 ⁷	<5 ns; <5 ns	>10 ⁶
CaO _x	Bipolar	>10 ²	<400 ns; <600 ns	>10 ⁴
GeO _x	Unipolar, bipolar	>10 ⁹	<20 ns; <20 ns	>10 ⁶
ZrO _x	Unipolar, bipolar	>10 ⁶	<10 ns; <10 ns	>10 ⁴
NbO _x	Unipolar, bipolar	>10 ⁸	<100 ns; <100 ns	>10 ⁷
MoO _x	Unipolar, bipolar	>10	<1 μs; <1 μs	>10 ⁶
HfO _x	Unipolar, bipolar	>10 ⁵	<300 ps; <300 ps	>10 ¹⁰
TaO _x	Unipolar, bipolar	>10 ⁹	<105 ps; <120 ps	>10 ¹²
WO _x	Unipolar, bipolar	>10 ⁴	<300 ns; <50 ns	>10 ⁸
CeO _x	Unipolar, bipolar	>10 ⁵	<1 μs; <200 ns	>10 ⁴
GdO _x	Unipolar, bipolar	>5 × 10 ⁵	<1 ns; <1 ns	>10 ⁷
YbO _x	Unipolar, bipolar	>10 ⁵	–	>10 ⁵
LuO _x	Unipolar, bipolar	>10 ⁴	<10 ns; <30 ns	>8 × 10 ³
<i>Ternary and more complex oxides</i>				
LaAlO ₃	Bipolar	>10 ⁴	–	>10 ²
SrTiO ₃	Bipolar	>10 ⁵	<5 ns; <5 ns	>10 ⁶
BaTiO ₃	Unipolar, bipolar	>10 ⁴	<10 ns; <70 ns	>10 ⁵
LC(or S)MO	Bipolar	>10 ³	<25 ns; <25 ns	>10 ³
PCMO	Bipolar	>10 ³	<8 ns; <8 ns	>10 ¹⁰
BiFeO ₃	Unipolar, bipolar	>10 ⁵	<50 ns; <100 μs	>10 ³
<i>Chalcogenides</i>				
Cu ₂ S	Bipolar	>10 ⁶	<100 μs; <100 μs	>10 ⁵
GeS _x	Bipolar	>10 ⁵	<50 ns; <50 ns	>7.5 × 10 ⁶
Ag ₂ S	Bipolar	>10 ⁶	<200 ns; <200 ns	–
Ge _x Se _y	Bipolar	>10 ⁶	<100 ns; <100 ns	>3.2 × 10 ¹⁰
<i>Nitrides</i>				
AlN	Unipolar, bipolar	>10 ³	<10 ns; <10 ns	>10 ⁸
SiN	Unipolar, bipolar	>10 ⁷	<100 ns; <100 ns	>10 ⁹
<i>Others</i>				
a-C	Unipolar, bipolar	>3 × 10 ²	<50 ns; <10 ns	>10 ³
a-Si	Bipolar	>10 ⁷	<5 ns; <10 ns	>10 ⁸
AgI	Bipolar	>10 ⁶	<50 ns; <150 ns	>4 × 10 ⁵

Organic switching materials for ReRAM devices can be loosely classified into polymers (*e.g.* poly(methylmethacrylate) (PMMA))^[42] and small molecules (*e.g.* tris(8-hydroxyquinoline) aluminum (Alq3))^[43], which have been summarized in **Table 2.3** with their corresponding performances. Although the switching characteristics of most of organic-based ReRAM cannot be comparable to those in inorganic-based memory devices, organic switching materials with high-mechanical flexibility have attracted great interest due to its tremendous potential in the future flexible functional integrated electronics.^[1]

Table 2.3 Summary of common organic materials-based ReRAM devices and corresponding electrical performances.^[1] Adapted from ref. 1 with permission from Elsevier B.V.

Storage medium	Switching mode	ON/OFF ratio	Operation speed	Endurance (cycles)
<i>Small molecules</i>				
AIDCN	Bipolar	$>10^4$	<10 ns; <40 ns	–
Alq ₃	Unipolar, bipolar	$>10^6$	–	$>2 \times 10^4$
Cu:TCNQ	Bipolar	$>10^4$	<10 ns; –	$>10^4$
NPB	Bipolar	$>10^2$	–	$>10^6$
Rose bengal	Bipolar	$>10^5$	<500 ns; <50 ms	$>7.2 \times 10^7$
<i>Polymers</i>				
MEH-PPV	Unipolar, bipolar	$>10^4$	<1 μ s; –	$>5 \times 10^1$
P3HT	Unipolar, bipolar	$>10^4$	<300 ns; <300 ns	$>3 \times 10^4$
PARA	Unipolar, bipolar	$>10^5$	<80 ns; <1 μ s	$>10^3$
Parylene-C	Bipolar	$>10^7$	<15 ns; <15 ns	$>2.5 \times 10^2$
PEDOT:PSS	Unipolar, Bipolar	$>10^5$	<500 ns; <500 ns	$>10^4$
PFN-C	Unipolar	$>10^7$	<300 ns; <500 ns	$>4 \times 10^3$
PFO	Unipolar	$>10^3$	–	$>5 \times 10^3$
PI	Unipolar, bipolar	$>10^8$	<200 ns; <200 ns	$>10^5$
PMMA	Bipolar	$>10^7$	–	$>1.5 \times 10^5$
PS	Unipolar, bipolar	$>10^4$	<100 ns; <100 ns	$>10^2$
PVA	Bipolar	$>10^7$	–	$>10^2$
PVK	Unipolar, bipolar	$>5 \times 10^9$	<5 ms; <30 ms	$>10^3$
PVP	Bipolar	$>4 \times 10^3$	<10 ns; <10 ns	–
WPF-oxy-F	Bipolar	$>10^5$	<10 μ s; <100 μ s	$>10^4$
<i>Others</i>				
Graphene oxide	Bipolar	$>10^4$	<5 ns; <5 ns	$>10^3$

Mechanical flexibility is a key issue for flexible ReRAM devices, thus the memory devices at various bending states need to be carefully explored and understood for future applications. To explain the stable flexible memory devices under bending condition, the bending strain ε_{top} for the top film layer that is placed onto a substrate is an important parameter and needs to be analyzed. When the substrate is bent, the top surface layer is in tension, which can be stretched by the bending strain ε_{top} .^[44] The estimated bending strain ε_{top} induced on the surface of a substrate by bending the substrate into a radius of R is given by the following equation 1:

$$\varepsilon_{top} = \left(\frac{d_f + d_s}{2R} \right) \frac{(1 + 2\eta + \chi\eta^2)}{(1 + \eta)(1 + \chi\eta)} \quad (1)$$

Where $\eta = d_f/d_s$ (d_f and d_s are the thickness of the film layer and the substrate, respectively) and $\chi = Y_f/Y_s$ (Y_f and Y_s are the Young's modulus of the film layer and the substrate, respectively). Simply ε_{top} can be expressed as $d_s/2R$.^[45, 46] Therefore, with a fixed thickness of the substrate, the bending strain of the active layer on the substrate will greatly affect the flexible ReRAM devices performances. Due to the unique physical and electrical properties, ultrathin two-dimensional (2D) nanomaterials (*e.g.* MoO_x thin film, ultrathin WO₃ · H₂O nanosheets), which exhibited both excellent electrical and mechanical properties in the memory devices, have stimulated more and more interest in the past few years for ReRAM applications.^[47-49] For example, Liang *et al.* demonstrated

2D ultrathin $\text{WO}_3 \cdot \text{H}_2\text{O}$ nanosheets-based ReRAM devices, which exhibited excellent bending endurance more than 2000 cycles with bending radius of 8 mm.^[48] For the $\text{WO}_3 \cdot \text{H}_2\text{O}$ bulk-based memory device, the bending cycles was only about ~100 with bending radius of 12 mm on the same ITO/PET substrate. However, the synthesis process of 2D $\text{WO}_3 \cdot \text{H}_2\text{O}$ nanosheets involves with liquid phase exfoliation, which is not compatible with the semiconductor industry. The same applies to graphene oxide and MoS_2 , which furthermore are not excellent insulators, meaning that they are not able to provide large ON/OFF ratios in ReRAM devices.^[50, 51] Therefore, novel 2D materials which are compatible with the semiconductor industry and excellent insulator will be highly desirable for the future flexible ReRAM applications. In addition, with the raising concerns for the environment, fabrication of environmentally friendly materials (such as crab shell-based chitosan, egg albumen, sericin, and silk protein), biocompatible and biodegradable ReRAM devices also arouse great interests.^[52-55]

Electrode materials. In ReRAM devices, the electrodes are not only acting as electron transport paths, they would also have a major impact on the switching behaviors. For instance, the bipolar switching behavior in the Cu/P3HT:PCBM/ITO memory device will disappear when the Cu electrode was displaced by a Pt electrode.^[56] Normally, according to the contribution of electrodes to the switching behaviors, there are three kinds of electrode materials in the memory devices. First, the electrodes don't affect the resistive switching, which only serve as carriers transport path, such as inert Pd^[57] and Pt^[58] electrodes. Second, in the anion migration-based memory (*i.e.* valence change memories (VCM)) devices, the electrodes have significant impact on the anion vacancies migration and accumulation for the conductive filaments formation.^[59, 60] Therefore, in order to obtain the stable resistive switching behaviors in certain switching materials, a proper electrode is required. For instance, the Ta_2O_5 -based memory devices exhibited significantly different switching characteristics with various metal electrodes (*e.g.* Hf, Ti, Al, Ni) due to their variant attraction for oxygen ions.^[59] Third, in the ECM-based ReRAM devices, the electrodes account for the resistive switching, which are involved in the conducting filaments formation and rupture.^[2, 20, 61] In these ECM-based memory devices, the electrochemically active electrodes (*e.g.* Ag, Cu) would generate the

conductive filaments *via* electrochemical metallization under electric field. For instance, the Ag filament dynamics were unambiguously confirmed in Ag/ Si/tungsten (W) ECM-based memory device *via in situ* TEM technique.^[62]

2.1.3 Switching mechanism for the ECM-based ReRAM

As mentioned above, both the electrode and switching materials would affect the switching behaviors of the ReRAM devices. As a result, the resistive switching mechanism, which mainly involve ion (cation or anion) migration, charge trapping/de-trapping, tunneling effect, intermolecular charge transfer, *etc.*^[1, 2, 63] due to the possible chemical interactions in the memory devices under a high Joule heating or electric field,^[64, 65] is still not clearly understood. Among these different switching mechanisms-based memories, the ECM-based ReRAM, of which resistive switching operation stems from the electrochemical dissolution/deposition of the active electrodes, exhibits the proven scalability potential, high-performance, and industrialization maturity for future memory devices application.^[15] Here the microscopic understanding of the switching process will be focused in the ECM-based ReRAM.

The ECM-based memory cell normally consists of an electrochemically inert electrode (*e.g.* W or Pt) and active conductor (*e.g.* Ag, Cu).^[15] In ECM-based ReRAM devices, the conducting filaments would be generated from the electrochemically active electrodes due to electrochemical metallization under electric field, leading to the transition between OFF and ON states.^[3, 62] As shown in **Figure 2.2 A**, there is no electrodeposited metal onto the Pt electrode, indicating the OFF state. Then the SET operation would occur with a sufficient forward bias application on the active Ag electrode. There are three steps in the SET process:

(i) anodic dissolution of active Ag electrode under electric field

where Ag^+ means the metal cation in the switching material;

(ii) migration of Ag^+ cations across the switching layer to the inert counter electrode under electric field;

Figure 2.2 (A-E) Schematic of the filament growth in an ECM-based memory cell.^[15] Reproduced from ref. 15 with permission from IOP Publishing.

(iii) reduction of Ag^+ cations and electro-crystallization of Ag conducting filament

In typical electrolytes-based memory devices (e.g. GeS_x and GeSe_x),^[3, 66] the metal filaments would preferentially grow towards the active electrode (**Figure 2.2 C**) due to the electric-field-enhanced electro-crystallization process. Then the memory cell will be switched to ON state when the Ag filament reaches the anode (**Figure 2.2 D**). This ON-state can keep unless a sufficient negative bias was applied on the active anode, which would electrochemically dissolve the Ag filament to RESET the cell, leading to an OFF state (**Figure 2.2 E**). During the initial RESET process, the metal filament will dissolve under the action of electrochemical current (*i.e.* Faradaic current) and electronic current.^[15] In addition, the kinetics of (i) - (iii) processes would mainly determine the SET switching speed in the ECM-based memory device. Therefore, more attentions should be paid to analyze and control the overall filament growth kinetics.

In order to well understand the switching mechanism, the conducting filament growth

was demonstrated in the Ag/H₂O/Pt memory cell (**Figure 2.3**).^[67] During SET switching, a positive bias was applied on the active Ag electrode, which was oxidized into Ag⁺ cations under electric field. Subsequently, the Ag⁺ cations migrated through the electrolyte towards the inert cathode Pt electrode. Thereafter, the Ag⁺ cations would be electrochemically reduced to Ag atoms and deposited on the inert Pt electrode (**Figure 2.3 b**). With this repeated redox reaction and migration processes, the Ag filament, of which wide base was at the H₂O/Pt electrode interface and thinnest part was located at the Ag/H₂O interface, will gradually grow from the inert Pt electrode to Ag anode, leading to the ON state (**Figure 2.3 c and d**). Application of negative bias on Ag electrode would switch the memory cell to OFF state, leading to the anodic dissolution of Ag filament at the interface of Ag anode/H₂O switching medium where the large voltage drop was located.

Figure 2.3 The SET process in the Pt/H₂O/Ag cell: (a) I-t curve. SEM images of Ag filament growth when -1V bias was applied on Pt electrode: (b) 1 s, (c) 2s and (d) 4 s, respectively.^[67] Reproduced from ref. 67 with permission from AIP Publishing LLC.

Normally, the electric field distribution and inhomogeneity in the switching layer and its electrochemical and structural environment would affect the filament growth process (*i.e.* redox and migration processes), indicating the dynamic process of filament growth is

stochastic in nature.^[62] To obtain superior performance ECM-based ReRAM devices, it is necessary and important to uncover the microscopic origin of filaments growth dynamic to control the memory operations *via* tuning the filament growth. Generally speaking, in ECM-based memory device, the filament's geometry depends on the redox rates, while the direction and nucleation sites of the filaments growth are determined by the ion mobility in the switching layer.^[62]

For example, when the redox rates are low while ion mobility is high, the filaments with branched structure would commence growing towards the active electrode.^[62] For the Ag/sputtered SiO₂/Pt ECM-based memory device, which has high ion mobility due to the high density of grain boundaries in the SiO₂ layer and low redox rates, the branched filaments would grow towards active Ag electrode with thinnest part near the inert Pt electrode (**Figure 2.4b, h**).^[68] After electroforming process with positive bias on active Ag electrode, as shown in **Figure 2.4b**, several conical shape conductive filaments can be observed in the SiO₂ layer. It is clear that the filaments commenced growing from inert Pt electrode, which well agreed with the observation in ECM-based memory cells.^[3, 66]

However, as shown in **Figure 2.4b**, the wide base of the filament was located at the interface of Ag electrode/SiO₂ film, and the thinnest part was near the Pt electrode/SiO₂ film interface, which was not consistent with conventional ECM-based ReRAM device (*e.g.* **Figure 2.3** above).^[3, 66] In addition, there were also some incomplete branched filaments in the SiO₂ switching layer in **Figure 2.4b** and h. During the subsequent RESET/SET process, the rupture/formation of filament would occur at the narrowest part of the filaments.^[67] Therefore, in the filament/Pt electrode interface, it is clear that the filament would first break in **Figure 2.4c** and i. However, for typical electrolytes-based memory devices (*e.g.* GeS_x and GeSe_x), during SET process, the wider base of the Ag filaments would locate at the switching layer/inert electrode interface due to the reduction of abundant Ag⁺ ions with high mobility at the inert electrode.^[3, 66]

For the non-typical switching materials (*e.g.* SiO₂) ECM-based ReRAM devices, the cation supply would affect the filament growth. As shown in **Figure 2.4f**, the Ag

filaments still started growing towards the active anode. However, the limited amount of Ag ions would preferably migrate to and be reduced in the front of the existing filaments where the electric field is the highest. Thereafter, due to the distorted electric field lines (**Figure 2.4g**), the branched filaments would form in the switching layer. As a result, the narrowest part of the filaments would locate at the switching layer/inert electrode interface, which is most crucial to the continued ECM-based memory devices optimization.

Figure 2.4 Conductive filaments growth dynamics in Ag/SiO₂/Pt memory devices.^[68] (a) TEM image of planar Ag/SiO₂/Pt memory cell on SiN_x membrane. Inset: the memory cell structure. Scale bar, 200 nm. TEM images of the same Ag/SiO₂/Pt memory cell after the electroforming (b) and erasing (c) processes. Scale bar, 200 nm. (d) I-t curve for the electroforming process with 8V positive bias on Ag electrode, corresponding to the image in (b). (e) I-t curve for the RESET process with -10V positive bias on Ag electrode, corresponding to the image in (c). (f) Filaments growth dynamics of the Ag⁺ ions migration and reduction. (g) Diagram of the branched filament growth. (h) TEM images of another memory cell with large thickness after electroforming process. Scale bar, 200 nm. Zoomed-in image of the upper filament was shown in inset. Scale bar, 20 nm. (i) TEM image of the memory cell after RESET process, corresponding to same device of (h). Scale bar, 200nm. Inset: the same region as the inset in (h). Scale bar, 20nm. (j) I-t curve during the electroforming step with 10V positive bias on Ag electrode, corresponding to the image in (h). (k) I-t curve during the RESET step with -10V positive bias on Ag electrode, corresponding to the image in (i). Reproduced from ref. 68 with permission from Nature Publishing Group.

On the other hand, when both the ion mobility and redox rate are extremely low, the filaments would commence growing towards the inert electrode *via* repeated splitting and merging processes.^[62] For example, to compare with the sputtered SiO₂-based memory device (**Figure 2.4**), *in situ* TEM was employed to observe the filaments growth dynamics in the evaporated SiO₂-based memory device, which has low ion mobility due to less defects, and low redox rate.^[62] The overall filament growth dynamics, which could be regarded as the step-by-step movement of Ag cluster, were illustrated by **Figure 2.5**. As shown in **Figure 2.5a**, the Ag wire directly connected the W probe coated with ~40 nm-thick evaporated SiO₂ film. When 8V positive bias was applied on the Ag electrode, several Ag clusters firstly appeared at the SiO₂ layer/active Ag electrode interface after ~3 min (**Figure 2.5b**). Then during the subsequent growth, the Ag clusters would act as bipolar electrodes (**Figure 2.5g**). Thereafter, these clusters would undergo the splitting and merging processes to move towards the inert electrode (**Figure 2.5h**). Because of the high concentration Ag⁺ ions near the Ag electrode, the Ag clusters would nucleate at the Ag electrode/SiO₂ interface, leading to a conical shape filament with the repeated nucleation and growth processes (**Figure 2.5d**). As shown in **Figure 2.5e, i**, the Ag filament wider base was located at the Ag/SiO₂ interface, growing towards the inert W electrode. In addition, during the Ag clusters movement process, a void would be left at the SiO₂/Ag interface region (**Figure 2.5d, e**), which was induced by the increased mechanical stress, indicating the plastic deformation of the storage medium. The existence of void would offer space to facilitate the ion diffusion and Ag clusters movement (**Figure 2.5d, e**). When the existing Ag clusters move out, the remain voids will have lower strain energy, which would facilitate the new clusters to fill in and filament growth towards the counter electrode. In practice, in the same memory device, it is possible that different filament growth modes may coexist simultaneously due to the variations in the local ion mobility and redox rate, which both are affected by the local electrochemical potential, local defect energy profile and densities.^[62] Therefore, it is very challenging to identify the exact dynamic process of filaments growth.

Figure 2.5 Ag filament growth dynamics observation *via in situ* TEM.^[62] (a) Schematic of the *in situ* TEM experiment structure. (b-e) TEM images of the filaments growth dynamics in the Ag/SiO₂/W memory cell with 8V bias on the Ag electrode. Scale bar, 20 nm. (f-j) Schematics of the filament growth dynamics *via* splitting/merging process (f) Ag oxidation near the Ag electrode. (g) Ag clusters nucleate at the Ag electrode/SiO₂ interface, which serve as bipolar electrodes during the following filament growth. (h) Ag nanoclusters moved towards the inert electrode. (i) Void generation due to the Ag nanoclusters migration (highlighted by the dash line). (j) The continuous growth of filament *via* voids refilling step-by-step from the active electrode. Reproduced from ref. 62 with permission from Nature Publishing Group.

2.2 Flexible Functional ReRAM

The advancement of electronics has greatly changed the world in all ways, from space exploration to our daily life. Emerging electronic devices, which are anticipated to realize multiple advanced functionalities such as flexibility, stretchability, wearability, environmental friendly, transparency, and environmental robustness, have attracted tremendous attention from both academic and industrial communities. Among these functionalities, flexibility, which enables thin and lightweight device on a bendable substrate, is the most desirable function for future wearable electronics applications. These wide applications push the advances in electronic transistors, sensors, triboelectric nanogenerators, supercapacitors, electrochromics, organic light-emitting diodes (OLED), and electroluminescent devices for future electronics applications.^[69-79] To realize a fully flexible integrated electronic system, the flexible functional ReRAM devices which can store and process information are essential and indispensable.

2.2.1 Flexible ReRAM

Flexible ReRAM devices, which offer mechanical versatility in data storage, provide great advantages of being foldable, lightweight, and printable for future electronics application.^[45, 47, 48, 80-88] For example, some electronics manufactures show great interests in flexible consumer electronics, such as TVs, E-readers, and mobile phones.^[45] So far, various inorganic materials have been demonstrated for flexible RRAM applications, such as oxide insulator, amorphous silicon, and solid electrolyte.^[24, 80, 89, 90]

Figure 2.6 (a) Schematic of the conductive-interlayer SiO_x-based ReRAM devices. (b) Four different inserted layers of multilayer graphene (MLG), carbon, Ti, and Pd, which were used in the SiO_x-based memory cells. (c) I-V characteristics of the one-Pd-interlayer SiO_x-based memory cell before and after bend with bending radius of 5 mm. Electroforming process was showed in the inset. (d) Switching endurance of the one-Pd-interlayer SiO_x cell. The top panel illustrated 1 cycle bend test.^[24] Adapted from ref. 24 with permission from American Chemical Society.

For example, Wang et al. demonstrated the flexible SiO_x memory devices on polyimide (PI) substrate which also exhibited lower electroforming voltage with different conductive interlayers (*i.e.* Pd, Ti, carbon, multilayer graphene) at room temperature.^[24]

Figure 2.6a, b showed the structure of the conducting-interlayer SiO_x ReRAM device. Each 30 nm-thick SiO_x layer was deposited *via* electron beam evaporation and each conducting interlayer was 5 nm. As shown in **Figure 2.6c**, after 100 times repeated bending cycles with bending radius of 5 mm, the one-Pd-interlayer SiO_x memory device exhibited similar I-V curve to the one before bending. Also, the memory window maintained at $\sim 10^3$ during 150 switching cycles after 100 bend cycles, which was similar to the one under flat condition (**Figure 2.6d**). However, due to the brittle nature of these oxides that are ceramics, it is very difficult to demonstrate good switching stability under mechanical bend condition.

Flexible organic-based RRAM devices also have been intensively investigated due to their outstanding features of light weight, mechanical elasticity and roll-to-roll printability.^[42, 82, 83, 86, 91, 92] By utilizing the excellent mechanical properties of both organic materials (poly(3-butylthiophene) (P3HT) and poly(methyl methacrylate) (PMMA)) and graphene electrode, Lai and coworkers demonstrated transferable and flexible label-like RRAM devices which showed excellent performances and a good stability.^[82, 83] In the work by Ji and coworkers, twistable and flexible all-organic 64-bit ReRAM device consisting of one diode-one resistor (1D-1R) structures without cross-talk were demonstrated.^[86] A compound of polystyrene (PS) and 6-phenyl-C61 butyric acid methyl ester (PCBM) and poly(3-hexylthiophene) (P3HT) were employed as the memory and diode active materials on polyethylene naphthalate (PEN) substrate, respectively (**Figure 2.7**). The all-organic memory device exhibited excellent switching endurances, even during and after various mechanical deformations (e.g. bending, twisted, rolled, **Figure 2.7f**). In addition, the 64-bit 1D-1R memory cells featured large memory window (I_{ON}/I_{OFF} ratio ~ 1000), long retention time (10^4 s) and reliable switching endurance cycles (100 cycles, **Figure 2.7g**) even after substrate deformation up to 10^4 bending cycles (**Figure 2.7h**). However, for the organic-based ReRAM devices, they always show a poor endurance due to their easy degradation with the time under high temperature induce by the Joule heating.

Figure 2.7 (a) Schematic of 1D-1R device on flexible PEN substrate. (b) Optical image of the 1D-1R devices on PEN substrate. Scale bar, 5 mm. (c) Illustration of the Al/PS:PCBM/Au/P3HT/Au/Al 1D-1R device. (d) Bis-FB-N₃ and P3HT chemical structure as diode material. (e) Bis-FB-N₃, PCBM, and PS chemical structure as active material for memory cell. (f) I-V characteristics of 1D-1R device before and after different mechanical deformations. (g) Endurance cycles of 1D-1R cell after different distortions. (h) I_{ON}/I_{OFF} ratio of the 1D-1R device during 10⁴ times bending cycles (bending radius, r=13 mm).^[86] Adapted from ref. 86 with permission from Nature Publishing Group.

To solve these problems (i.e. poor bending stability in inorganic-based memory devices and poor switching endurance in organic-based memory devices), one promising methodology is to replace the metallic or insulating films in the ReRAM cells by other materials with advanced capabilities. Besides the unique electronic structures, the emergence of two-dimensional (2D) materials with excellent mechanical properties (*e.g.* elastic constant of 180±60 N m⁻¹, breaking strength of 15±3 N m⁻¹ (23 ±4.6 GPa) and failure strain between 6 and 11% for MoS₂ material^[93]; elastic constant of 340 N m⁻¹, breaking strength of 42 N m⁻¹ (125.3 GPa), and failure strain >10% for graphene^[94]) brings a new dawn for the future flexible electronics applications.^[48, 95-97] It has been demonstrated that the 2D materials based ReRAM devices exhibited excellent switching

endurances and bending stability, such as 2D MoO_x thin film and ultrathin $\text{WO}_3 \cdot \text{H}_2\text{O}$ nanosheets.^[47, 48] In order to compare with the 2D materials-based memory devices in terms of switching endurance and bending stability, the summary of some typical inorganic and organic materials-based memory devices is provided in **Table 2.4**. One can see that the 2D material-based memory devices exhibited excellent performances in terms of switching endurance and bending stability and consequently may be the most promising switching materials for the flexible functional ReRAM in the near future. However for common 2D materials (e.g., graphene oxide, $\text{WO}_3 \cdot \text{H}_2\text{O}$ nanosheets), their synthesis process usually involves with the liquid phase exfoliation and Hummers method,^[48, 98] which is not compatible with the semiconductor industry and scalable for manufacturing. Therefore, a novel 2D material, which can be prepared *via* scalable method for manufacturing, is important and necessary for the future flexible ReRAM devices applications.

Table 2.4 Summary of some typical organic, inorganic and 2D materials based ReRAM devices, corresponding to their performances in terms of switching endurance and bending cycles.

switching layer type	switching material	switching endurance (#)	bending cycles (#)	bending radius (mm)
inorganic	SiO_x ^[85]	400	300	12
	Ag_2Se ^[89]	10^4	100	16
	$\text{WO}_3 \cdot \text{H}_2\text{O}$ bulk ^[48]	5×10^3	100	12
	HfO_x ^[99]	10^8	1200	6
organic	PS:PCBM ^[86]	100	10^4	13
	pEGDMA ^[100]	500	10^3	4
	PS+BCNT ^[101]	100	500	<7
2D materials	$\text{WO}_3 \cdot \text{H}_2\text{O}$ nanosheet ^[48]	5×10^3	2×10^3	8
	MoO_x ^[47]	10^4	10^4	7

2.2.2 Flexible transparent ReRAM

Fully integrated visibly transparent circuits have received tremendous attention promising applications ranging from display, consumer products to industrial equipment.^[102, 103] The transparent memory unit is one of the essential circuitry elements.^[85] Transparent

ReRAM, possessing the advantages of both invisible electronics and RRAM, would be useful in integrated visually transparent electronics and has aroused great interests in recent years.^[85, 104-107] To realize highly transparent ReRAM device, both transparent conductive electrodes and storage mediums with large band-gap (>3.1 eV) are required.^[85, 102]

Figure 2.8 (a) Schematic of the Graphene (G)/SiO_x/ITO glass memory device on the left panel. Optical photography of Graphene/SiO_x/ITO glass memory device and its corresponding zoomed-in optical image on the top and bottom right panel, respectively. Scale bar, 100 μ m. (b) Transmittance spectra of the G/SiO_x/G devices. The green, blue and black curve corresponds to the monolayer G/ SiO_x/monolayer G, monolayer G/ SiO_x/bilayer G, and bilayer G/ SiO_x/ bilayer G structures transmittance, respectively. (c) I-V curves of G/SiO_x/ITO memory cell after electroforming process. The voltage sweep order was indicated by the number. (d) Switching endurance and (e) retention time of the G/SiO_x/ITO device. Both an ON and OFF state were measured with continuous +1V read voltage.^[85] Adapted from ref. 85 with permission from Nature Publishing Group.

Yao *et al.* presented a route to construct highly transparent SiO_x (bandgap, ~ 9 eV) memory devices with indium tin oxide (ITO) and graphene (G) electrodes.^[85] The ultrathin 2D graphene is a great promising material for transparent wearable electronics due to its low absorption (2.3% per layer) in the visible region,^[108, 109] whereas ITO stands for the state-of-the-art transparent electrode material. Briefly, the SiO_x layer ($\sim 70\text{nm}$ thick) was deposited on the ITO/glass bottom electrode via physical vapour deposition, then, the bilayer graphene top electrodes was transferred onto the switching layer (**Figure 2.8a**). The graphene/ SiO_x /ITO transparent ReRAM devices exhibited unipolar switching characteristics (**Figure 2.8 c**) with good switching endurance (**Figure 2.8 d**) and long data retention time (**Figure 2.8 e**). In addition, the SiO_x layer also can be deposited on the bilayer graphene/glass substrate to construct a bilayer graphene/ SiO_x /bilayer graphene memory device, which exhibited high transmittance of $\sim 90\%$ in the visible region (**Figure 2.8b**). In addition, the transmittance of the SiO_x based memory can be further increased to $\sim 95\%$ by using all monolayer graphene electrodes (blue curve, **Figure 2.8b**). The graphene/ SiO_x / graphene memory device also exhibited similar switching performances to those of graphene/ SiO_x /ITO memory cell in **Figure 2.8c**.

Besides the inherent transparency of graphene film, the graphene/ SiO_x /graphene memory device would be fabricated on the flexible transparent PFA (fluoropolymer) substrate due to the transferability and flexibility of graphene film^[102] (**Figure 2.9 a, b**). The flexible transparent memory device exhibited the similar switching characteristics (**Figure 2.9 c**) to those from device on rigid substrate (**Figure 2.8d**). In addition, unlike the rigid substrate, the Graphene/ SiO_x /Graphene devices on flexible substrates demonstrated the feasibility for the future flexible transparent functional ReRAM applications (**Figure 2.9d**). However, the G/ SiO_x /G memory device can only exhibited fair good mechanical durability without significant memory-state degradation during 300 bending cycles due to the brittle nature of ceramics (**Figure 2.9d**).

Figure 2.9 Flexible transparent ReRAM device.^[85] (a) Schematic of the crossbar Graphene/SiO_x/Graphene device on PFA substrate (left panel) and its optical image (right panel). Scale bar, 20 μm. (b) Optical image of the Graphene/SiO_x/Graphene device, corresponding to its pillar structure in the inset. Scale bar, 100 μm. (c) Switching endurance from the crossbar device. (d) Bending endurance from a crossbar device. The bending radius is ~12 mm and the read voltage is +1V. The inset shows the actual flexible transparent pillar structure ReRAM. Reproduced from ref. 85 with permission from Nature Publishing Group.

2.2.3 Flexible and transferable ReRAM

Due to the established process for semiconductor fabrication, electronics are normally fabricated on flat and rigid substrates.^[110] However, with the growing technological demands of multi-functionalities (e.g. portability, flexibility), the electronics fabrication on non-conventional substrates have attracted more and more interest for different applications, such as nonplanar and soft substrates.^[69, 83, 111] Therefore, the fabrication processes for future electronics on non-conventional substrates need to be established. Among the various switching mediums, the organic-based ReRAM devices, which possess superior advantages of solution-printability, flexibility, and low-cost, have aroused great interest.^[112-114] As a typical example, Lai *et al.* demonstrated a flexible transferable sticker-type organic ReRAM with graphene as the bottom electrode on

different substrates.^[82] The sticker-type ReRAM device consisted of graphene bottom electrode, poly(methylmethacrylate) (PMMA): poly (3-hexylthiophene) (P3HT) switching layer, and Al top electrode. As shown in Figure 2.10, the PMMA:P3HT composite was spin-coated on the graphene/Cu foil. When the Cu substrate was removed, this sticker-type ReRAM would be transferred easily onto arbitrary substrates, such as on the PET substrate (Figure 2.10c).

Figure 2.10 (a) Diagram of the organic memory device fabrication process. (b) The setup for the electrical measurement along with PMMA and P3HT chemical structures. (c) Optical image of the sticker-type memory device.^[82] Reproduced from ref. 82 with permission from John Wiley & Sons, Inc.

On the other hand, the sticker-type memory devices were also transferred to other different nonconventional substrates to broaden their applications (**Figure 2.11**), such as fake nail, cylindrical vial, business card, and medical wristband, respectively. Based on the corresponding results of the electrical measurements, it was demonstrated that this sticker-type memory devices can work well regardless of the substrates, which greatly expand the ReRAM applications on various kinds of substrates. In addition, the organic-based memory device exhibited high ON/OFF ratio ($\sim 10^5$), and more than 15 hours retention time. However, the write endurance (~ 80 cycles) is not good due to the easy degradation of organic materials under high temperature induced by the Joule heating.

Figure 2.11 Demonstration of the sticker-type memory devices on kinds of substrates along with their corresponding I-V characteristics: ^[82] (a) business card, (b) fake nail, (c) cylindrical vial (with a diameter of 20 mm), (d) medical wristband. The area of the memory device is about 1 cm². Reproduced from ref. 82 with permission from John Wiley & Sons, Inc.

2.3 Challenges in Flexible Functional ECM-based ReRAM

As discussed in the review, future ReRAM is expected to retain multi-functionalities such as flexibility, transparency, and portability as well as superior mechanical and electrical performances. However, there are still several challenges to realize advanced flexible functional ECM-based ReRAM with excellent electrical and mechanical performances.

Firstly, as discussed in **2.1.1**, in order to obtain high electrical performance ReRAM devices in terms of lower electroforming voltage or large ON/OFF ratio, several methods have been proposed. To reduce the electroforming voltage (V_{forming}) of ECM-based ReRAM devices, several relatively complex fabrication approaches^[23, 24] or heat treatment methods with high temperature^[25, 26] were introduced, which may limit the stackable integration of electronic devices.^[27, 28] Especially, the high temperature process may damage the plastic flexible substrates with poor thermal stability, limiting the advanced flexible functional ReRAM devices fabrication.^[29, 30] On the other hand, to increase the memory window of ReRAM devices, several complicated approaches also have been proposed,^[18, 36-39] which are difficult to control. Therefore, it is quite

challenging for a good design that can meet these desirable requirements of lower electroforming voltage and large ON/OFF ratio at the same time especially on flexible substrate.

Secondly, in ReRAM device, the material selection for the switching layer can be quite versatile. However, for flexible functional ReRAM, the conventional inorganic-based memory devices always exhibit poor bending stability due to their brittle nature. For organic-based memory devices, they always showed poor endurance due to the easy degradation of organic materials with the time under high temperature induced by Joule heating. Therefore, the switching material possessing both excellent mechanical and electrical properties and thermal stability is a major challenge for flexible functional ReRAM.

Thirdly, to construct excellent performances ReRAM devices with multi-functionality, *i.e.* flexibility, transferability, and transparency, the switching layer with excellent mechanical property like graphene and thermal stability is required. On the other hand, wide band-gap switching materials (>3.1 eV) sandwiched between transparent conductive electrodes (e.g. ITO, graphene) are necessary. In addition, it should be noted that for ECM-based ReRAM, the active electrodes (e.g. Ag, Cu) are not suitable for transparent ReRAM due to the mirror reflection property. Hence, transparent electrodes which can generate filaments are also required for some certain ECM-based non-oxides (e.g. hexagonal boron nitride) ReRAM devices. Therefore, a critical challenge in the multifunctional ReRAM is to realize their flexibility, transparency and transferability at the same time along with excellent performances onto various substrates and under strain.

2.4 PhD Studies in Context with Literature

As mentioned earlier, the realization of ECM-based functional ReRAM with excellent performances requires a systematic study from the device structure and materials to working mechanisms. In this thesis, the device structure design, materials exploitation,

and mechanisms study will be investigated to enable advanced flexible functional ECM-based ReRAM, aiming to resolve the challenges as discussed above.

In order to lower the electroforming voltage and enlarge the ON/OFF ratio at the same time, a simple self-assembly approach to fabricate the Au NPs-interlayer amorphous Si ECM-based ReRAM on both flexible and rigid substrates at room temperature was demonstrated. The electric field distribution and intensity in the switching medium can be effectively modified by the Au NPs-interlayer, which would tune the filament growth/rupture, leading to low electroforming voltage and large memory window at the same time. This method would satisfy the ECM-based ReRAM applications with electric performances enhancement on both flexible and rigid substrates.

In order to improve both switching endurance and bending stability in flexible functional ECM-based ReRAM, a novel flexible 2D layered hexagonal boron nitride (hBN) –based memory device was demonstrated for the first time. The ultrathin (~3-5 nm) hBN film was fabricated on Cu foil *via* chemical vapor deposition technique which is scalable for manufacturing. On the one hand, hBN film, which is also called as “white graphene” with a band gap of ~5.9 eV, exhibits high temperature stability, large thermal conductivity, and exceptional mechanical properties, which would favor the excellent performances of hBN-based memory device under high temperature and bend condition. Therefore, the hBN-based ReRAM exhibited excellent switching endurance and bending stability under bend condition.

For the flexible, transparent, and transferable functional ReRAM, the hBN-based memory device with ITO and graphene electrodes was fabricated on soft PDMS substrate. On the one hand, based on the inherent excellent mechanical properties of 2D hBN and graphene materials, the hBN-based memory device can be transferred freely to various substrates. On the other hand, the indium filament in the ITO/hBN/graphene device was found for the first time, which provides critical insight on the complex resistive switching mechanisms for the ECM-based ReRAM. The ITO/hBN/graphene/PDMS memory device not only exhibits excellent performance in

terms of optical transmittance ($\sim 85\%$ in the visible wavelength), ON/OFF ratio (~ 400), retention time ($\sim 5 \times 10^4$) but also shows robust flexibility under bend condition and stable operation on arbitrary substrates.

References

- [1] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Mater. Sci. Eng., R* **2014**, 83, 1-59.
- [2] J. J. S. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nanotechnol.* **2013**, 8, 13-24.
- [3] R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* **2009**, 21, 2632-2663.
- [4] D. S. Jeong, R. Thomas, R. S. Katiyar, J. F. Scott, H. Kohlstedt, A. Petraru, C. S. Hwang, *Rep. Prog. Phys.* **2012**, 75, 076502.
- [5] L. O. Chua, *IEEE Trans. Circuit theory* **1971**, 18, 507-519.
- [6] L. O. Chua, S. M. Kang, *Pro. IEEE* **1976**, 64, 209-223.
- [7] D. B. Strukov, G. S. Snider, D. R. Stewart, R. S. Williams, *Nature* **2008**, 453, 80-83.
- [8] C. Ho, C.-L. Hsu, C.-C. Chen, J.-T. Liu, C.-S. Wu, C.-C. Huang, C. Hu, F.-L. Yang, "9nm half-pitch functional resistive memory cell with $< 1\mu\text{A}$ programming current using thermally oxidized sub-stoichiometric WO_x film", presented at *Electron Devices Meeting (IEDM), 2010 IEEE International*, 2010.
- [9] B. J. Choi, A. C. Torrezan, K. J. Norris, F. Miao, J. P. Strachan, M. X. Zhang, D. A. A. Ohlberg, N. P. Kobayashi, J. J. Yang, R. S. Williams, *Nano Lett.* **2013**, 13, 3213-3217.
- [10] A. C. Torrezan, J. P. Strachan, G. Medeiros-Ribeiro, R. S. Williams, *Nanotechnology* **2011**, 22, 485203.
- [11] B. Govoreanu, G. Kar, Y. Chen, V. Paraschiv, S. Kubicek, A. Fantini, I. Radu, L. Goux, S. Clima, R. Degraeve, " $10 \times 10 \text{nm}^2$ Hf/HfO_x crossbar resistive RAM with excellent performance, reliability and low-energy operation", presented at *Electron Devices Meeting (IEDM), 2011 IEEE International*, 2011.
- [12] C. H. Cheng, C. Y. Tsai, A. Chin, F. S. Yeh, *Electron Devices Meeting* **2010**, IEEE International.

- [13] M.-J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y.-B. Kim, C.-J. Kim, D. H. Seo, S. Seo, *Nat. Mater.* **2011**, 10, 625-630.
- [14] I. R. Committee, *Semiconductor Industry Association*, [http://www. itrs. net/Links/2011ITRS/2011Chapters/2011ExecSum. pdf](http://www.itrs.net/Links/2011ITRS/2011Chapters/2011ExecSum.pdf) **2011**.
- [15] I. Valov, R. Waser, J. R. Jameson, M. N. Kozicki, *Nanotechnology* **2011**, 22, 254003.
- [16] H.-S. P. Wong, H.-Y. Lee, S. Yu, Y.-S. Chen, Y. Wu, P. S. Chen, B. Lee, F. T. Chen, M.-J. Tsai, *Pro. IEEE* **2012**, 100, 1951-1970.
- [17] K. M. Kim, D. S. Jeong, C. S. Hwang, *Nanotechnology* **2011**, 22, 254002.
- [18] S. H. Jo, W. Lu, *Nano Lett.* **2008**, 8, 392-397.
- [19] J. Yao, L. Zhong, D. Natelson, J. M. Tour, *Sci. Rep.* **2012**, 2, 242.
- [20] K. Qian, V. C. Nguyen, T. P. Chen, P. S. Lee, *Adv. Electron. Mater.* **2016**, 2, 1500370.
- [21] J. H. Yoon, S. J. Song, I. H. Yoo, J. Y. Seok, K. J. Yoon, D. E. Kwon, T. H. Park, C. S. Hwang, *Adv. Funct. Mater.* **2014**, 24, 5086-5095.
- [22] G. Bersuker, Y. Jeon, H. R. Huff, *Microelectron. Reliab.* **2001**, 41, 1923-1931.
- [23] B. K. You, W. I. Park, J. M. Kim, K. I. Park, H. K. Seo, J. Y. Lee, Y. S. Jung, K. J. Lee, *ACS Nano* **2014**, 8, 9492-9502.
- [24] G. Wang, A. R. O. Raji, J. H. Lee, J. M. Tour, *ACS Nano* **2014**, 8, 1410-1418.
- [25] J. Yao, Z. Z. Sun, L. Zhong, D. Natelson, J. M. Tour, *Nano Lett.* **2010**, 10, 4105-4110.
- [26] Y. F. Chang, P. Y. Chen, Y. T. Chen, F. Xue, Y. Z. Wang, F. Zhou, B. Fowler, J. C. Lee, *Appl. Phys. Lett.* **2012**, 101, 052111.
- [27] M. J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y. B. Kim, C. J. Kim, D. H. Seo, S. Seo, U. I. Chung, I. K. Yoo, K. Kim, *Nat. Mater.* **2011**, 10, 625-630.
- [28] M. J. Lee, S. Seo, D. C. Kim, S. E. Ahn, D. H. Seo, I. K. Yoo, I. G. Baek, D. S. Kim, I. S. Byun, S. H. Kim, I. R. Hwang, J. S. Kim, S. H. Jeon, B. H. Park, *Adv. Mater.* **2007**, 19, 73-76.
- [29] S. Park, G. Wang, B. Cho, Y. Kim, S. Song, Y. Ji, M. H. Yoon, T. Lee, *Nat. Nanotechnol.* **2012**, 7, 438-442.
- [30] N. Gergel-Hackett, J. L. Tedesco, C. A. Richter, *Pro. IEEE* **2012**, 100, 1971-1978.

- [31] L. Goux, J. G. Lisoni, X. P. Wang, M. Jurczak, D. J. Wouters, *IEEE Trans. Electron. Devices* **2009**, 56, 2363-2368.
- [32] S. J. Choi, G. S. Park, K. H. Kim, S. Cho, W. Y. Yang, X. S. Li, J. H. Moon, K. J. Lee, K. Kim, *Adv. Mater.* **2011**, 23, 3272-3277.
- [33] M. J. Rozenberg, I. H. Inoue, M. J. Sanchez, *Phys. Rev. Lett.* **2004**, 92.
- [34] S. Balatti, S. Larentis, D. C. Gilmer, D. Ielmini, *Adv. Mater.* **2013**, 25, 1474-1478.
- [35] B. L. Hu, X. J. Zhu, X. X. Chen, L. Pan, S. S. Peng, Y. Z. Wu, J. Shang, G. Liu, Q. Yan, R. W. Li, *J. Am. Chem. Soc.* **2012**, 134, 17408-17411.
- [36] S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn, K. J. Lee, T. Lee, S. O. Kim, *Nano Lett.* **2012**, 12, 2217-2221.
- [37] H. W. Zhang, L. F. Liu, B. Gao, Y. J. Qiu, X. Y. Liu, J. Lu, R. Q. Han, J. F. Kang, B. Yu, *Appl. Phys. Lett.* **2011**, 98, 042105.
- [38] Y. C. Yang, F. Pan, Q. Liu, M. Liu, F. Zeng, *Nano Lett.* **2009**, 9, 1636-1643.
- [39] H. Y. Lee, Y. S. Chen, P. S. Chen, T. Y. Wu, F. Chen, C. C. Wang, P. J. Tzeng, M. J. Tsai, C. Lien, *IEEE Electron Device Lett.* **2010**, 31, 44-46.
- [40] J. J. Yang, M. X. Zhang, J. P. Strachan, F. Miao, M. D. Pickett, R. D. Kelley, G. Medeiros-Ribeiro, R. S. Williams, *Appl. Phys. Lett.* **2010**, 97, 232102.
- [41] U. Russo, D. Ielmini, C. Cagli, A. L. Lacaita, *IEEE Trans. Electron. Devices* **2009**, 56, 186-192.
- [42] D. I. Son, T. W. Kim, J. H. Shim, J. H. Jung, D. U. Lee, J. M. Lee, W. I. Park, W. K. Choi, *Nano Lett.* **2010**, 10, 2441-2447.
- [43] M. Lauters, B. McCarthy, D. Sarid, G. Jabbour, *Appl. Phys. Lett.* **2005**, 87, 231105.
- [44] Z. Suo, E. Y. Ma, H. Gleskova, S. Wagner, *Appl. Phys. Lett.* **1999**, 74, 1177-1179.
- [45] S. T. Han, Y. Zhou, V. A. L. Roy, *Adv. Mater.* **2013**, 25, 5425-5449.
- [46] Y. Zhou, S. T. Han, Z. X. Xu, V. A. L. Roy, *J. Mater. Chem.* **2012**, 22, 4060-4065.
- [47] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, *Nat. Mater.* **2015**, 14, 199-204.
- [48] L. Liang, K. Li, C. Xiao, S. J. Fan, J. Liu, W. S. Zhang, W. H. Xu, W. Tong, J. Y. Liao, Y. Y. Zhou, B. J. Ye, Y. Xie, *J. Am. Chem. Soc.* **2015**, 137, 3102-3108.
- [49] C. Tan, Z. Liu, W. Huang, H. Zhang, *Chem. Soc. Rev.* **2015**, 44, 2615-2628.

- [50] F. Zhuge, B. L. Hu, C. L. He, X. F. Zhou, Z. P. Liu, R. W. Li, *Carbon* **2011**, 49, 3796-3802.
- [51] P. F. Cheng, K. Sun, Y. H. Hu, *Nano Lett.* **2016**, 16, 572-576.
- [52] X. He, J. Zhang, W. Wang, W. Xuan, X. Wang, Q. Zhang, C. G. Smith, J. Luo, *ACS Appl. Mater. Interfaces* **2016**, 8, 10954-10960.
- [53] H. Wang, B. Zhu, X. Ma, Y. Hao, X. Chen, *Small* **2016**, 12, 2715-2719.
- [54] H. Wang, F. Meng, Y. Cai, L. Zheng, Y. Li, Y. Liu, Y. Jiang, X. Wang, X. Chen, *Adv. Mater.* **2013**, 25, 5498-5503.
- [55] N. R. Hosseini, J. S. Lee, *Adv. Funct. Mater.* **2015**, 25, 5586-5592.
- [56] S. Gao, C. Song, C. Chen, F. Zeng, F. Pan, *J. Phys. Chem. C* **2012**, 116, 17955-17959.
- [57] Y. C. Yang, P. Sheridan, W. Lu, *Appl. Phys. Lett.* **2012**, 100, 203112.
- [58] C. Chen, Y. C. Yang, F. Zeng, F. Pan, *Appl. Phys. Lett.* **2010**, 97, 083502.
- [59] C. Chen, S. Gao, F. Zeng, G. S. Tang, S. Z. Li, C. Song, H. D. Fu, F. Pan, *J. Appl. Phys.* **2013**, 114, 014502.
- [60] Y. S. Lin, F. Zeng, S. G. Tang, H. Y. Liu, C. Chen, S. Gao, Y. G. Wang, F. Pan, *J. Appl. Phys.* **2013**, 113, 064510.
- [61] K. Qian, R. Y. Tay, V. C. Nguyen, J. X. Wang, G. F. Cai, T. P. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.
- [62] Y. C. Yang, P. Gao, L. Z. Li, X. Q. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, 5, 4232.
- [63] Q.-D. Ling, D.-J. Liaw, C. Zhu, D. S.-H. Chan, E.-T. Kang, K.-G. Neoh, *Prog. Polym. Sci.* **2008**, 33, 917-978.
- [64] J. J. Yang, J. P. Strachan, F. Miao, M. X. Zhang, M. D. Pickett, W. Yi, D. A. A. Ohlberg, G. Medeiros-Ribeiro, R. S. Williams, *Appl. Phys. A* **2011**, 102, 785-789.
- [65] J. J. Yang, J. P. Strachan, Q. F. Xia, D. A. A. Ohlberg, P. J. Kuekes, R. D. Kelley, W. F. Stickle, D. R. Stewart, G. Medeiros-Ribeiro, R. S. Williams, *Adv. Mater.* **2010**, 22, 4034-4038.
- [66] R. Waser, M. Aono, *Nat. Mater.* **2007**, 6, 833-840.
- [67] X. Guo, C. Schindler, *Appl. Phys. Lett.* **2007**, 91, 133513.

- [68] Y. C. Yang, P. Gao, S. Gaba, T. Chang, X. Q. Pan, W. Lu, *Nat. Commun.* **2012**, 3, 732.
- [69] D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. Z. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. G. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, 333, 838-843.
- [70] L. Wang, M. H. Yoon, G. Lu, Y. Yang, A. Facchetti, T. J. Marks, *Nat. Mater.* **2006**, 5, 893-900.
- [71] S. Lee, W. Kim, K. Yong, *Adv. Mater.* **2011**, 23, 4398-4402.
- [72] G. Cai, P. Darmawan, M. Cui, J. Wang, J. Chen, S. Magdassi, P. S. Lee, *Adv. Energy Mater.* **2015**, 6, 1501882.
- [73] J. X. Wang, C. Y. Yan, G. F. Cai, M. Q. Cui, A. L. S. Eh, P. S. Lee, *Adv. Mater.* **2016**, 28, 4490-4496.
- [74] C. Y. Yan, J. X. Wang, W. B. Kang, M. Q. Cui, X. Wang, C. Y. Foo, K. J. Chee, P. S. Lee, *Adv. Mater.* **2014**, 26, 2022-2027.
- [75] W. B. Kang, C. Y. Yan, C. Y. Foo, P. S. Lee, *Adv. Funct. Mater.* **2015**, 25, 4203-4210.
- [76] H. L. Zhu, Z. G. Xiao, D. T. Liu, Y. Y. Li, N. J. Weadock, Z. Q. Fang, J. S. Huang, L. B. Hu, *Energy Environ. Sci.* **2013**, 6, 2105-2111.
- [77] H. Y. Guo, Z. Wen, Y. L. Zi, M. H. Yeh, J. Wang, L. P. Zhu, C. G. Hu, Z. L. Wang, *Adv. Energy Mater.* **2016**, 6, 1501593.
- [78] J. Y. Jeon, T. J. Ha, *ACS Appl. Mater. Interfaces* **2016**, 8, 2866-2871.
- [79] Y. S. Chen, M. Y. Hong, G. S. Huang, *Nat. Nanotechnol.* **2012**, 7, 197-203.
- [80] D. H. Lien, Z. K. Kao, T. H. Huang, Y. C. Liao, S. C. Lee, J. H. He, *ACS Nano* **2014**, 8, 7613-7619.
- [81] K. Qian, R. Y. Tay, V. C. Nguyen, J. Wang, G. Cai, T. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.
- [82] Y. C. Lai, Y. X. Wang, Y. C. Huang, T. Y. Lin, Y. P. Hsieh, Y. J. Yang, Y. F. Chen, *Adv. Funct. Mater.* **2014**, 24, 1430-1438.
- [83] Y. C. Lai, F. C. Hsu, J. Y. Chen, J. H. He, T. C. Chang, Y. P. Hsieh, T. Y. Lin, Y. J. Yang, Y. F. Chen, *Adv. Mater.* **2013**, 25, 2733-2739.

- [84] J. Q. Liu, Z. Y. Yin, X. H. Cao, F. Zhao, L. H. Wang, W. Huang, H. Zhang, *Adv. Mater.* **2013**, 25, 233-238.
- [85] J. Yao, J. Lin, Y. H. Dai, G. D. Ruan, Z. Yan, L. Li, L. Zhong, D. Natelson, J. M. Tour, *Nat. Commun.* **2012**, 3, 1101.
- [86] Y. Ji, D. F. Zeigler, D. S. Lee, H. Choi, A. K. Y. Jen, H. C. Ko, T. W. Kim, *Nat. Commun.* **2013**, 4, 2707.
- [87] Y. Ji, S. Lee, B. Cho, S. Song, T. Lee, *ACS Nano* **2011**, 5, 5995-6000.
- [88] H. Y. Jeong, J. Y. Kim, J. W. Kim, J. O. Hwang, J. E. Kim, J. Y. Lee, T. H. Yoon, B. J. Cho, S. O. Kim, R. S. Ruoff, S. Y. Choi, *Nano Lett.* **2010**, 10, 4381-4386.
- [89] J. Jang, F. Pan, K. Braam, V. Subramanian, *Adv. Mater.* **2012**, 24, 3573-3576.
- [90] K. Qian, V. C. Nguyen, T. Chen, P. S. Lee, *Adv. Electron. Mater.* **2016**, 2, 1500370.
- [91] Y. Yang, J. Ouyang, L. P. Ma, R. J. H. Tseng, C. W. Chu, *Adv. Funct. Mater.* **2006**, 16, 1001-1014.
- [92] J. C. Scott, L. D. Bozano, *Adv. Mater.* **2007**, 19, 1452-1463.
- [93] S. Bertolazzi, J. Brivio, A. Kis, *ACS Nano* **2011**, 5, 9703-9709.
- [94] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science* **2008**, 321, 385-388.
- [95] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, 335, 1326-1330.
- [96] T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y. J. Kim, A. Gholinia, S. J. Haigh, O. Makarovskiy, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, A. Mishchenko, *Nat. Nanotechnol.* **2013**, 8, 100-103.
- [97] S. P. Koenig, N. G. Boddeti, M. L. Dunn, J. S. Bunch, *Nat. Nanotechnol.* **2011**, 6, 543-546.
- [98] X. R. Li, F. Y. Kong, J. Liu, T. M. Liang, J. J. Xu, H. Y. Chen, *Adv. Funct. Mater.* **2012**, 22, 1981-1988.
- [99] J. Shang, W. Xue, Z. Ji, G. Liu, X. Niu, X. Yi, L. Pan, Q. Zhan, X.-H. Xu, R.-W. Li, *Nanoscale* **2017**, 9, 7037-7046.
- [100] B. H. Lee, H. Bae, H. Seong, D. I. Lee, H. Park, Y. J. Choi, S. G. Im, S. O. Kim, Y. K. Choi, *ACS Nano* **2015**, 9, 7306-7313.
- [101] S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn, K. J. Lee, T. Lee, S. O. Kim, *Nano Lett.* **2012**, 12, 2217-2221.

- [102] G. Thomas, *Nature* **1997**, 389, 907-908.
- [103] J. F. Wager, *Science* **2003**, 300, 1245-1246.
- [104] J. Shang, G. Liu, H. L. Yang, X. J. Zhu, X. X. Chen, H. W. Tan, B. L. Hu, L. Pan, W. H. Xue, R. W. Li, *Adv. Funct. Mater.* **2014**, 24, 2171-2179.
- [105] S. Jung, J. Kong, S. Song, K. Lee, T. Lee, H. Hwang, S. Jeon, *J. Electrochem. Soc.* **2010**, 157, H1042-H1045.
- [106] J. Lee, O. Kim, *Jpn J. Appl. Phys.* **2011**, 50, 06GF01.
- [107] C. Y. Huang, Y. T. Ho, C. J. Hung, T. Y. Tseng, *IEEE Trans. Electron. Devices* **2014**, 61, 3435-3441.
- [108] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, 5, 574-578.
- [109] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, *Science* **2008**, 320, 1308-1308.
- [110] O. Hayden, R. Agarwal, W. Lu, *Nano Today* **2008**, 3, 12-22.
- [111] Q. N. Thanh, H. Jeong, J. Kim, J. W. Kevek, Y. H. Ahn, S. Lee, E. D. Minot, J. Y. Park, *Adv. Mater.* **2012**, 24, 4499-4504.
- [112] J. Y. Ouyang, C. W. Chu, C. R. Szmada, L. P. Ma, Y. Yang, *Nat. Mater.* **2004**, 3, 918-922.
- [113] R. J. Tseng, C. L. Tsai, L. P. Ma, J. Y. Ouyang, *Nat. Nanotechnol.* **2006**, 1, 72-77.
- [114] B. Cho, S. Song, Y. Ji, T. W. Kim, T. Lee, *Adv. Funct. Mater.* **2011**, 21, 2806-2829.

Chapter 3

Experimental Methodology

In order to realize high performance flexible functional electrochemical metallization (ECM)-based resistive switching random access memory (ReRAM) devices, material and device structure designs are very important. This chapter first presents the rationale for the materials selection to achieve high performance flexible functional ReRAM devices. The important experimental techniques for in-depth characterizations of the samples and devices (e.g. morphology, electrical properties) are then introduced with their corresponding working principles. Lastly, the processes for flexible functional ReRAM devices fabrication are elaborated.

3.1 Rationale for Materials Selection

3.1.1 Au NPs as interlayer in the ECM-based ReRAM

As discussed in **Chapter 2**, high electroforming voltage may limit the integration potential in advanced crossbar structures or damage the memory cells permanently, leading to low switching performance and device yield.^[1-3] Large ON/OFF ratio is required to realize high density data storage and avoid misreading during the device operation.^[4-6] Therefore, a simple method, which is suitable for ReRAM devices fabrication on both flexible and rigid substrates, is desired to meet these two requirements at the same time.

As already discussed in **Chapter 2**, the resistive switching in ECM-based ReRAM devices involves the metal cations M^{z+} (e.g. Ag^+ , Cu^{2+}) transport in switching layer and its redox reactions. In the conducting filament growth process, the electric field strength E is the driving force for the M^{z+} ions migration inside the switching layer. The M^{z+} ionic current density would be described by Mott and Curney's equation 1:^[7]

$$i = 2ze c a v \exp(-W_a^0/kT) \sinh(azeE/2kT) \quad (1)$$

where c is the concentration of mobile M^{z+} ions, a is the ions jump distance, v is a frequency factor, W_a is the energy barrier for ion hopping, T is the absolute temperature, k is Boltzmann's constant, and E is electric field. As shown in equation 1, the increase of electric field strength would lead to the ionic current density increase. In addition, during SET process, it has been demonstrated that the metal ions will preferably migrate towards the existing filament and would be reduced at the end of it, where the front of the ruptured filament has the highest electrochemical deposition rate of M atoms due to its high electric field.^[8, 9] Therefore, it is possible to control the filament growth by tuning the electric field to enlarge the ON/OFF ratio and lower the electroforming voltage at the same time.

Compared with the other planar region of the bottom electrode, the electric field strength at the tip of the NPs location would be higher when a metal nanoparticles (NPs) layer was

inserted between switching layer and bottom electrode. It is hypothesized that the higher NPs-enhanced electric field strength would facilitate the aggregation of more M^{z+} ions around the NPs location and greatly increase the M atoms nucleation probability around these nanoparticles sites,^[10, 11] which could promote the conductive filament growth and electroforming voltage reduction. In addition, during RESET process, the NPs-enhanced electric field will allow the metal cations to drift faster and lead to wider depleted gap between the remnant filament and electrode, resulting in high resistance at OFF state and large ON/OFF ratio.

Au material is usually employed as inert electrode in the ReRAM devices, which will not involve the redox reaction in the ECM-based ReRAM devices. Therefore, Au NPs would be good candidate as inserting layer. On the other hand, the Au NPs layer can be easily assembled on substrates, such as spin-coating and self-assembly methods, which can deliver simple fabrication technique at room temperature on flexible substrate for flexible functional ECM-based ReRAM devices applications.

3.1.2 2D hBN as switching layer for flexible functional ECM-based ReRAM

As discussed in Chapter 2, the traditional inorganic (*e.g.* transition metal oxides, complex oxides, chalcogenide) based ReRAM devices show poor bending stability due to their brittle nature, while the organic based ReRAM devices exhibit poor switching stability due to the easy degradation under high temperature.^[12, 13] To solve these problems, one promising approach is to replace these switching layers with other materials with advanced capabilities. The emergence of two-dimensional (2D) materials with unique physical (*e.g.* high transparency, excellent flexibility) and electrical properties bring a new dawn for future flexible functional electronics applications.^[13-18] 2D materials such as hBN and graphene have been attracting more and more research interest due to the unique properties, such as high transparency, excellent thermal and mechanical stability, chemical inertness and so on due to their sp^2 -bonded character.^[19, 20] hBN exhibits the same sp^2 honeycomb structure with graphene, which is excellent insulator with large

bandgap ($> 5\text{eV}$), holding great promising applications from neutron shielding, transistor, to coating material at high temperature against oxidation, and so on.^[21-24]

Firstly, compared to other 2D conductive and semiconducting materials, hBN does not require any transfer process to build an ReRAM, as it can be grown on a metallic substrate (which acts as bottom electrode) using scalable chemical vapor deposition (CVD) technique, and the top electrodes can be easily evaporated on it to form the metal/insulator/metal cells. This strongly simplifies the fabrication process, as well as it avoids the generation of cracks during 2D material manipulation^[25] and the presence of contaminants from polymer scaffolds.^[26] Secondly, the insulating nature of hBN with bandgap over 5eV should result in a large current ON/OFF ratio in ECM-based ReRAM devices. Thirdly, the superior chemical stability of hBN may inhibit interaction with adjacent layers, and its large thermal conductivity (2000 WmK^{-1}) and high thermal stability ($1000\text{ }^{\circ}\text{C}$) could favor heat dissipation in ReRAM devices.^[27-29] Moreover, hBN shows better reliability than HfO_2 when exposed to electrical stresses,^[30] which may lead to excellent switching endurance in ReRAM devices. Finally, 2D hBN material has excellent mechanical (*e.g.* elastic constant of 503 N m^{-1} and breaking strength of 15.7 N m^{-1})^[31] and optical properties^[32], motivating fabrication of functional ReRAM devices with excellent bending stability and transparency.

In summary, the hBN material with excellent mechanical, optical, and electric properties possesses great potential to enable multi-functional ReRAM devices with excellent electrical and mechanical performances.

3.1.3 ITO electrode for flexible transparent functional ECM-based ReRAM

In order to obtain superior performance, a complete understanding of the switching mechanism is necessary to effectively tune the switching behaviors in the ReRAM devices.^[33-37] For the transparent ReRAM devices with ITO electrode, the oxygen vacancies migration or other switching mechanisms were normally identified to occur in the switching layer for the resistance change, which are not related to the ITO

electrode.^[38-42] In fact, the oxygen vacancies migration can also happen in the ITO material under high electric field, leading to the resistive switching behaviors.^[43] Therefore, a clear switching mechanism for the resistance change in ReRAM devices needs to be identified. Especially, with the limitation on opacity of the conducting metal electrodes, such as Ag and Cu, it is urgent and necessary to identify potential candidate for transparent electrode material which can induce resistive switching behavior for transparent functional ECM-based ReRAM application. The proposed transparent conducting electrode is ITO and the device stack will be ITO top electrode/hBN/Graphene sandwich structure device. Based on the ECM theory, the ITO electrode may form the conductive filaments under electric field for the ECM-based ReRAM operation.

3.2 Synthesis

3.2.1 Au NPs synthesis

Au NPs were synthesized *via* conventional hydrothermal method as follows.^[44] Chloroauric acid ($\text{AuCl}_3 \cdot \text{HCl} \cdot 4\text{H}_2\text{O}$), trisodium citrate dihydrate ($\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$), 2-aminothiophenol (2-ATP) were used without further purification purchased, which are also from Sigma-Aldrich. Solutions are prepared from HAuCl_4 (solution i, 10^{-2} % by weight,) and $\text{C}_6\text{H}_5\text{Na}_3\text{O}_7 \cdot 2\text{H}_2\text{O}$ (solution ii, 1% by weight). Briefly, solution ii (0.8 ml) is added to 100 ml boiled solution i with high-speed mixing. After about 20 min, the mixed solution will change into brilliant red, indicating the formation of spherical Au NPs with ~50 nm diameter.

3.2.2 2D hBN thin film preparation

Few-layer h-BN films were grown on 25 μm thick Cu foils (Alfa Aesar, 99.8%) by atmospheric pressure (AP) chemical vapor deposition (CVD), which was carried out by our collaborator, Roland Yingjie Tay. Prior to growth, the Cu foil was dipped in dilute nitric acid for a few seconds and washed in deionized (DI) water. The Cu foil was then

inserted into a 2 inch quartz tube and was positioned within the heating zone of the furnace. A constant flow of 200 sccm of Ar and 20 sccm of H₂ was used as the carrier gas. 10 mg of ammonia borane (NH₃-BH₃) was placed in a ceramic boat upstream of the quartz tube away from the heating zone. The temperature of the furnace was raised from room temperature to 1020 °C in 40 min and was kept at 1020 °C for another 2 h for annealing. During growth, ammonia borane was heated at ~85 °C using a flexible heat belt. After growth, the lid of the furnace was lifted for fast cooling.^[29, 45]

3.3 Characterization

The materials prepared for ReRAM devices were thoroughly characterized via kinds of characterization tools, depending on the specific requirement.

3.3.1 SEM

SEM is used to evaluate the morphologies of the as prepared materials. Compared to optical microscopy that uses light to produce images, SEM, which uses electrons to produce largely magnified images, is utilized for nanostructure and morphology analysis. This is because the resolution of SEM determined from the minimum distinguishable distance could be very high as predicted from Abbe's equation:^[46]

$$d = 0.612 \lambda / NA$$

d is the resolution, λ is the radiation wavelength of the travelling electron, and NA is called numerical aperture which is an equipment constant. As shown in **Figure 3.1**, the electron gun will produce a beam of electrons, which can be accelerated under potentials and pass through the condenser lens in the vacuum. Then the objective lens focuses the beam onto the sample. Subsequently, the electron beam strikes on the sample surface and interact with the sample to eject the electrons and X-rays. Normally, secondary electrons and backscattered electrons are typically the most useful electrons that results in the contrast. Secondary electrons are generated from inelastic collision between the electron beam and the shell electron of the sample, which are employed to show the sample's topography and morphology. Backscattered electrons come from the collision between

the sample atom nucleus and the primary electron beam. The back scattered electrons are thus sensitively affected by the sample density or atomic weight and will bring a large contrast between samples of different compositions.^[47] The secondary electrons and backscattered electrons will be collected and converted into a signal by the detector. Finally, the final image would be produced when these signals are sent to the screen.

Figure 3.1 Schematic diagram of a scanning electron microscopy (SEM).^[48] Reproduced from ref. 48 with permission from Springer.

3.3.2 TEM

TEM was used to investigate the detailed morphology and structure analysis of the as-prepared ReRAM device. When electrons with high energy pass through a sample, then

the sample information, such as grain boundaries, dislocations, and crystal structure, can be obtained based on the interactions between the sample atoms and electrons. In addition, the chemical composition can be analyzed *via* the equipped energy disperse spectrometer (EDS). The basic principle for the TEM operation is same with the light microscope which uses light to produce images. To obtain high resolution images, the electrons with much smaller wavelength are employed for TEM observation, which even can acquire the monatomic internal structures.

Figure 3.2 Schematic of a transmission electron microscopy (TEM).^[49] Reproduced from ref. 49 with permission from Springer.

As shown in **Figure 3.2**, the electron gun will produce a beam of electrons, which can be accelerated under potentials and pass through the condenser lens in the vacuum. Then the condenser lens focuses the beam into a coherent and small beam, of which high angle electrons would be excluded by the condenser aperture. Subsequently, part of the beam will strike and transmit the specimen based on its electron transparency and thickness. Then the objective lens focuses the transmitted portion electrons into an image which can

be enlarged by the next projector and intermediate lenses. The high-angle diffracted electrons can be blocked by the optional objective apertures to enhance the contrast. Finally, the user could see the detailed morphology of the specimen when the image strikes the fluorescent screen to generate light. In the TEM image, it will exhibit darker area if fewer electrons can transmit through the specimen. In contrast, it would exhibit lighter area when the specimen can be transmitted through by more electrons.

3.3.3 Focused ion beam (FIB)

FIB system plays a significantly important role in semiconductor industry, by means of TEM sample preparation and cross-sectional observation on integrated circuit.^[50, 51] Especially for ECM-based ReRAM devices, in order to observe and characterize the conducting filaments inside ReRAM devices, FIB is necessary for the TEM specimen preparation. FIB system is usually integrated with a SEM, allowing *in situ* observation and real-time monitoring of FIB process (**Figure 3.3**).

Figure 3.3 (a) Optical image of a FIB/SEM station. (b) Principle illustration of a FIB/SEM system.^[52] Reproduced from ref. 52 with permission from IOP Publishing.

A FIB system is mainly consisting of an ion source, an ion beam column, a beam deflector and a sample stage in sequence, as shown in **Figure 3.4**. Gallium is commonly selected as the liquid metal ion source (LIMS) with advantages of low melting point, volatility and vapor pressure but high discriminability from other elements.^[53] The gallium ions (Ga^+) are extracted from the liquid source tip and then collimated by an

upper lens into a parallel beam. A following optic column beneath the source filters out the ions of undesired mass-charge ratio or deviated to the vertical direction.^[54] The lower lens with a deflector is critical to further focus the beam and then defines the final landing position onto the substrate.^[50] A multi-channel plate (MCP) is right above the projected substrate surface to collect the ion-induced secondary electrons emitted from sample for imaging.^[55] In addition, there is an auxiliary gas nozzle quite closed to the substrate delivering gases which are reactive to the incident ions, to allow either deposition or accelerated etching.

Figure 3.4 Schematic of FIB system components.^[54] Reproduced from Ref. 54 with permission from IOP Publishing, LTD.

3.3.4 Bending test station

A home-made linear translation stage was employed for the ReRAM devices bend test. The translation stage was controlled by a CL-01A stepper motor controller, which could be programmed to achieve different translation operations on the stage. Performance of the devices under bend radii was measured by compressing the devices to corresponding positions on the stage. The bending stability measurements of the ReRAM devices were

carried out by programming the controller for repetitive translations between the strained and relaxed positions. **Figure 3.5a** is a photograph of the bending stage with a flat ReRAM device. **Figure 3.5b** shows a flexible ReRAM device under bending test.

Figure 3.5 Photographs of the home-make bend stage with a flexible ReRAM device under (a) flat and (b) bend condition, respectively.

3.3.5 Semiconductor characterization system

For the I - V measurements of two-terminal ReRAM devices, Keithley 4200 semiconductor characterization system (**Figure 3.6a**) was employed, which also was equipped with probe station (**Figure 3.6b**). The two probes will connect the top and bottom electrodes of the memory devices, respectively (**Figure 3.6b**). In the characterization system, the voltage and current can be tuned according to the memory devices requirements.

Figure 3.6 Photographs of the test system (a) and (b) probe station for ReRAM devices measurements, respectively.

3.3.6 Electric field simulation

In order to study the impact of the electric field on the conducting filament growth process, the electric field distribution in the amorphous Si switching layer was systematically investigated. The simulation modeling was built in CST EM Studio and the electrostatics template was selected for the simulation. The boundary conditions of the proposed materials are open in horizontal directions. The electrical potential was set to 1 V on the top electrode, and the bottom electrode was grounded. Here the electrodes were assumed as perfect conductor, which have no voltage drop. The parameters in this simulation model include the diameter of Au NPs, the thickness and permittivity of the amorphous Si switching layer.

3.4 Device Fabrication

3.4.1 Au NPs-interlayer ECM-based ReRAM fabrication

Firstly, the ~150 nm thick Au/Cr (adhesive layer, ~5nm) bottom electrode (BE) was grown *via* electron beam evaporation on a flexible polyimide (PI) or rigid SiO₂/Si substrate. Secondly, the mono-layer Au NPs (diameter, ~50 nm) was self-assembled on the bottom electrodes on the flexible substrate and rigid substrate. Thirdly, the a-Si switching layer was deposited on the Au NPs layer *via* plasma enhanced chemical vapor deposition (PECVD). During PECVD, a mixture of N₂ (150 sccm) N₂O (50 sccm), and SiH₄ (10 sccm) gas was employed with deposition rate is of ~1 nm per second (Pressure=400 mTorr, RF Power=20W, Temperature=200 °C, Model: Cello AEGIS20). The deposition time is 95 seconds. Finally, the Ag circular top electrode (TE, ~150 nm thick and ~250 μm diameter) was deposited on the a-Si layer with shadow mask *via* electron beam evaporation.

3.4.2 Flexible hBN ECM-based ReRAM device fabrication

Firstly, in the hBN growth process, the size of the hBN domains are typically less than 10 μm on Cu foil substrate, where the Cu foil also served as bottom electrode. The as-grown

hBN domains were shown in **Figure 3.7a, b** during the initial stage of growth with a growth time of 10 min. The growth of hBN begins by nucleation in the form of triangles and the neighboring domains merge together to form a partially continuous film. It should be noted that the orientations of these domains are not align and this leads to grain boundary defects when the domains merge.^[56] When the growth time is extended to 30 min, a continuous film covering over centimeters range is formed (**Figure 3.7c**). Characteristic wrinkles on the film can be observed because of the thermal expansion (CTE) coefficient difference between hBN and the underlying Cu foil.^[57] The presences of few-layers islands on the film, which are triangular in shape, indicate that the growth is not self-limited.^[58] When the growth time is further extended to 40 min (sample used for the memory device, the thickness is ~3-5 nm), the film grows in thickness and multilayer regions often occurs along the surface defects and grain boundaries of the hBN film (**Figure 3.7d**).^[59] So it is clearly possible for the Ag filament growth along the grain boundary in the hBN-based memory device.

Figure 3.7 (a,b) Low and high magnification of the as-grown hBN domains SEM images onto a polycrystalline Cu substrate after 10 min of growth, respectively. (c) SEM images of continuous hBN films formed after 30 min and (d) 40 min of growth.^[60] Reproduced from ref. 60 with permission from John Wiley & Sons, Inc.

Finally, the Ag circular top electrode (TE, ~ 150 nm thick and ~ 250 μm diameter) was directly deposited on the hBN/Cu foil with shadow mask *via* electron beam evaporation to make a flexible Ag TE/hBN/Cu foil ECM-based ReRAM device.

3.4.3 Flexible, transparent, and transferable multi-functional hBN-based ReRAM devices fabrication

Figure 3.8 Flexible, transparent, and transferable hBN-based ReRAM device fabrication process.^[61] (a) hBN film with PMMA in DI water after removal of Cu foil substrate. (b) The transferred hBN film with PMMA onto graphene/Cu foil. The Hbn/PMMA film was highlighted by the red rectangle frame. (c) The transferred hBN/graphene film with PMMA in DI water after removal of Cu foil substrate. The hBN/PMMA film was highlighted by the red rectangle frame. (d) The hBN/graphene film with PMMA was transferred onto PDMS substrate. The hBN/graphene film was indicated by the red rectangle frame. (e) The transferred hBN film with PMMA onto ITO/PET substrate. After removal of PMMA using acetone, ITO top electrode was deposited on the hBN/ITO/PET to construct transparent and flexible ITO/hBN/ITO/PET memory device (f). Reproduced from ref. 61 with permission from the American Chemical Society.

Figure 3.8 illustrated the schematic fabrication processes of the flexible, transparent, and transferable ITO TE /hBN/graphene memory device. Firstly, PMMA layer was coated on the chemical vapor deposition (CVD)-hBN film, then the Cu substrate was etched away using ammonium persulfate (APS) solution, leaving the PMMA/hBN in the DI water

(**Figure 3.8a**). Subsequently, the PMMA/hBN was transferred on graphene/Cu foil substrate via a conventional wet transfer approach (**Figure 3.8a and b**).^[36] Then, another layer of PMMA was coated on hBN/graphene/Cu foil. The PMMA/hBN/graphene can be easily transferred to any desired substrates (e.g. soft PDMS substrate) after the Cu foil was etched away using APS solution (**Figure 3.8c and d**). Or the hBN film with PMMA (**Figure 3.8a**) can be directly transferred to ITO/PET substrate (**Figure 3.8e**). When the PMMA layer was dissolved using acetone solution, the transparent ITO TE was then deposited on the hBN layer to construct transparent and flexible ReRAM device (**Figure 3.8f**).

3.4.4 Cross sectional TEM specimen preparation via FIB

In order to observe the conducting filaments inside the switching layer, *ex situ* TEM was employed. The TEM specimen was mounted on a copper 3-post lift-out grid (**Figure 3.9a**) by using FIB system. The length and width of the TEM specimen is about $\sim 10\ \mu\text{m}$ and $\sim 5\ \mu\text{m}$, respectively (**Figure 3.9b**). In order to clearly observe the change inside the switching layer, the thickness of the TEM specimen is about $\sim 70\text{-}100\ \text{nm}$.

Figure 3.9. (a) SEM image of the *ex-situ* TEM specimen in copper 3-post lift-out grid. The specimen was highlighted by the red rectangular box. (b) TEM image of a ReRAM device.

Briefly, the cross-sectional TEM specimens (**Figure 3.10a**) were cut *via* a dual beam focused ion beam (FIB, FEI Helios 600i) with a Ga ion beam at 30kV beam energy (**Figure 3.10b**). The Ga^+ ion source provides the bombardment of selected area down to 5 nm resolution levels for TEM sample preparation. During TEM specimen preparation, a $\sim 100\ \text{nm}$ thick Pt layer was coated on the top electrode to avoid ions radiation damage

before cut. Subsequently, the memory cell was cut using a FIB with the Ga ion (**Figure 3.10b**), followed by lift out with a fine tungsten pin (**Figure 3.10c**). Finally, the specimen was thinned down to ~70-100 nm and cleaned at 8 kV beam energy for TEM observation (**Figure 3.10d**).

Figure 3.10 SEM images showing the ex-situ TEM specimen preparation via FIB.^[61] (a) ITO/hBN/graphene/Cu foil memory cell. (b) The memory cell was cut using a focused ion beam with a Ga ion beam at 30 kV beam energy. (c) FIB lift-out process (d) The memory cell was thinned down to ~ 100 nm and cleaned at 8 kV beam energy. Reproduced from ref. 61 with permission from the American Chemical Society.

3.5 Overview of Methodologies

In summary, this chapter starts by discussing the importance of lower electroforming voltage and large memory window and the factor which may affect the conductive filaments growth. A simple method was proposed to achieve low electroforming voltage as well as large memory window, which is suitable for flexible functional ECM-based ReRAM fabrication on plastic substrate at room temperature. Subsequently, the drawbacks of common inorganic (*e.g.* transition metal oxides, chalcogenide) and organic

materials for flexible functional ReRAM were reviewed, indicating the exploration of new materials for ReRAM is urgent and necessary. The 2D hBN may be a good choice for flexible functional memory devices due to its superior properties, which is possible to show great potential for multi-functional ReRAM applications. In addition, in order to realize multi-functional (*e.g.* transparency, flexibility, and transferability) memory devices, graphene film was employed as bottom electrode due to its excellent electrical and mechanical properties together with 2D hBN material. Based on the ECM theory, ITO was employed as transparent top electrode for the multi-functional ReRAM fabrication, which may form the conductive filaments for the hBN-based memory device operation.

Principles underlying technique such as SEM, TEM, and FIB were presented, which provide useful information about these characterizations for the memory devices.

The ReRAM fabrication with self-assembly mono-layer Au NPs on both flexible and rigid substrates was presented. Then, the use of 2D CVD-grown hBN material for flexible functional ReRAM fabrication was introduced for the first time. Finally, the integration approach of the flexible, transparent, and transferable multi-functional ReRAM were introduced by employing the graphene and ITO as electrodes.

With the reasonable selection of device structure and materials discussed, synthesis mechanism studied, characterization and devices fabrication methods presented, this chapter provides the fundamental understanding and clarification of the analytical techniques employed and approaches for the realization of the advanced flexible functional ECM-based ReRAM devices.

References

- [1] G. Wang, A. R. O. Raji, J. H. Lee, J. M. Tour, *ACS Nano* **2014**, 8, 1410-1418.
- [2] S. H. Jo, W. Lu, *Nano Lett.* **2008**, 8, 392-397.
- [3] G. Bersuker, Y. Jeon, H. R. Huff, *Microelectron. Reliab.* **2001**, 41, 1923-1931.

- [4] S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn, K. J. Lee, T. Lee, S. O. Kim, *Nano Lett.* **2012**, 12, 2217-2221.
- [5] K. Nagashima, T. Yanagida, K. Oka, M. Taniguchi, T. Kawai, J. S. Kim, B. H. Park, *Nano Lett.* **2010**, 10, 1359-1363.
- [6] B. L. Hu, X. J. Zhu, X. X. Chen, L. Pan, S. S. Peng, Y. Z. Wu, J. Shang, G. Liu, Q. Yan, R. W. Li, *J. Am. Chem. Soc.* **2012**, 134, 17408-17411.
- [7] J. J. O'Dwyer, The theory of electrical conduction and breakdown in solid dielectrics, Clarendon Press, 1973.
- [8] Y. C. Yang, P. Gao, S. Gaba, T. Chang, X. Q. Pan, W. Lu, *Nat. Commun.* **2012**, 3, 732.
- [9] Q. Liu, C. M. Dou, Y. Wang, S. B. Long, W. Wang, M. Liu, M. H. Zhang, J. N. Chen, *Appl. Phys. Lett.* **2009**, 95, 023501.
- [10] C. Schindler, G. Staikov, R. Waser, *Appl. Phys. Lett.* **2009**, 94, 072109.
- [11] Q. Liu, S. Long, H. Lv, W. Wang, J. Niu, Z. Huo, J. Chen, M. Liu, *ACS Nano* **2010**, 4, 6162-6168.
- [12] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Mater. Sci. Eng., R* **2014**, 83, 1-59.
- [13] L. Liang, K. Li, C. Xiao, S. J. Fan, J. Liu, W. S. Zhang, W. H. Xu, W. Tong, J. Y. Liao, Y. Y. Zhou, B. J. Ye, Y. Xie, *J. Am. Chem. Soc.* **2015**, 137, 3102-3108.
- [14] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, *Nat. Mater.* **2015**, 14, 199-204.
- [15] C. X. Hao, F. S. Wen, J. Y. Xiang, S. J. Yuan, B. C. Yang, L. Li, W. H. Wang, Z. M. Zeng, L. M. Wang, Z. Y. Liu, Y. J. Tian, *Adv. Funct. Mater.* **2016**, 26, 2016-2024.
- [16] P. F. Cheng, K. Sun, Y. H. Hu, *Nano Lett.* **2016**, 16, 572-576.
- [17] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, 335, 1326-1330.
- [18] T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y. J. Kim, A. Gholinia, S. J. Haigh, O. Makarovskiy, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, A. Mishchenko, *Nat. Nanotechnol.* **2013**, 8, 100-103.
- [19] A. K. Geim, K. S. Novoselov, *Nat. Mater.* **2007**, 6, 183-191.
- [20] C. N. R. Rao, A. K. Sood, K. S. Subrahmanyam, A. Govindaraj, *Angew. Chem., Int. Edit.* **2009**, 48, 7752-7777.
- [21] D. Pacile, J. C. Meyer, C. O. Girit, A. Zettl, *Appl. Phys. Lett.* **2008**, 92, 133107.

- [22] D. Golberg, Y. Bando, Y. Huang, T. Terao, M. Mitome, C. C. Tang, C. Y. Zhi, *ACS Nano* **2010**, 4, 2979-2993.
- [23] Z. Liu, Y. J. Gong, W. Zhou, L. L. Ma, J. J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou, P. M. Ajayan, *Nat. Commun.* **2013**, 4, 2541.
- [24] G. H. Lee, Y. J. Yu, X. Cui, N. Petrone, C. H. Lee, M. S. Choi, D. Y. Lee, C. Lee, W. J. Yoo, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, J. Hone, *ACS Nano* **2013**, 7, 7931-7936.
- [25] M. Lanza, Y. Wang, T. Gao, A. Bayerl, M. Porti, M. Nafria, Y. B. Zhou, G. Y. Jing, Y. F. Zhang, Z. F. Liu, D. P. Yu, H. L. Duan, *Nano Res.* **2013**, 6, 485-495.
- [26] J. D. Wood, G. P. Doidge, E. A. Carrion, J. C. Koepke, J. A. Kaitz, I. Datye, A. Behnam, J. Hewaparakrama, B. Aruin, Y. F. Chen, H. Dong, R. T. Haasch, J. W. Lyding, E. Pop, *Nanotechnology* **2015**, 26, 055302.
- [27] K. K. Kim, A. Hsu, X. T. Jia, S. M. Kim, Y. M. Shi, M. Dresselhaus, T. Palacios, J. Kong, *ACS Nano* **2012**, 6, 8583-8590.
- [28] C. B. Pan, Y. F. Ji, N. Xiao, F. Hui, K. C. Tang, Y. Z. Guo, X. M. Xie, F. M. Puglisi, L. Larcher, E. Miranda, L. L. Jiang, Y. Y. Shi, I. Valov, P. C. McIntyre, R. Waser, M. Lanza, *Adv. Funct. Mater.* **2017**, 27, 10.
- [29] R. Y. Tay, X. L. Wang, S. H. Tsang, G. C. Loh, R. S. Singh, H. Li, G. Mallick, E. H. T. Teo, *J. Mater. Chem. C* **2014**, 2, 1650-1657.
- [30] Y. F. Ji, C. B. Pan, M. Y. Zhang, S. B. Long, X. J. Lian, F. Miao, F. Hui, Y. Y. Shi, L. Larcher, E. Wu, M. Lanza, *Appl. Phys. Lett.* **2016**, 108, 012905.
- [31] L. Song, L. J. Ci, H. Lu, P. B. Sorokin, C. H. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, P. M. Ajayan, *Nano Lett.* **2010**, 10, 3209-3215.
- [32] Z. Remes, M. Nesladek, K. Haenen, K. Watanabe, T. Taniguchi, *Phys. Status Solidi A* **2005**, 202, 2229-2233.
- [33] Y. C. Yang, P. Gao, L. Z. Li, X. Q. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, 5, 4232.
- [34] J. J. S. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nanotechnol.* **2013**, 8, 13-24.
- [35] D. J. Wouters, R. Waser, M. Wuttig, *Pro. IEEE* **2015**, 103, 1274-1288.
- [36] K. Qian, R. Y. Tay, V. C. Nguyen, J. Wang, G. Cai, T. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.

- [37] K. Qian, V. C. Nguyen, T. Chen, P. S. Lee, *Adv. Electron. Mater.* **2016**, 2, 1500370.
- [38] M. Ismail, A. M. Rana, I. Talib, T. L. Tsai, U. Chand, E. Ahmed, M. Y. Nadeem, A. Aziz, N. A. Shah, M. Hussain, *Solid State Commun.* **2015**, 202, 28-34.
- [39] C. Y. Huang, Y. T. Ho, C. J. Hung, T. Y. Tseng, *IEEE Trans. Electron. Devices* **2014**, 61, 3435-3441.
- [40] J. Shang, G. Liu, H. L. Yang, X. J. Zhu, X. X. Chen, H. W. Tan, B. L. Hu, L. Pan, W. H. Xue, R. W. Li, *Adv Funct Mater* **2014**, 24, 2171-2179.
- [41] P. K. Yang, C. H. Ho, D. H. Lien, J. R. D. Retamal, C. F. Kang, K. M. Chen, T. H. Huang, Y. C. Yu, C. I. Wu, J. H. He, *Scientific Reports* **2015**, 5, 15087.
- [42] H. D. Kim, H. M. An, Y. Seo, T. G. Kim, *IEEE Electron Device Lett.* **2011**, 32, 1125-1127.
- [43] J. S. Huang, Y. C. Lin, H. W. Tsai, W. C. Yen, C. W. Chen, C. Y. Lee, T. S. Chin, Y. L. Chueh, *Adv. Electron. Mater.* **2015**, 1, 1500061.
- [44] G. Frens, *Nature* **1973**, 241, 20-22.
- [45] R. Y. Tay, M. H. Griep, G. Mallick, S. H. Tsang, R. S. Singh, T. Tumlin, E. H. T. Teo, S. P. Karna, *Nano Lett.* **2014**, 14, 839-846.
- [46] W. Zhou, Z. L. Wang, *Scanning microscopy for nanotechnology: techniques and applications*, Springer science & business media, **2007**.
- [47] D. J. Stokes, *Principles and Practice of Variable Pressure/Environmental Scanning Electron Microscopy (VP-ESEM)*, 17-62.
- [48] W. Zhou, R. Apkarian, Z. L. Wang, D. Joy, in *Scanning microscopy for nanotechnology*, Springer, **2006**, 1-40.
- [49] L. C. Sawyer, D. T. Grubb, in *Polymer microscopy*, Springer, **1996**, 17-47.
- [50] A. A. Tseng, *Small* **2005**, 1, 924-939.
- [51] L. A. Giannuzzi, F. A. Stevie, *Micron* **1999**, 30, 197-204.
- [52] J. Gierak, *Semiconductor Science and Technology* **2009**, 24.
- [53] N. Yao, *Focused ion beam systems: basics and applications*, Cambridge University Press, **2007**.
- [54] A. A. Tseng, *J. Micromech. Microeng.* **2004**, 14, R15-R34.
- [55] S. Reyntjens, R. Puers, *J. Micromech. Microeng.* **2001**, 11, 287-300.

- [56] A. L. Gibb, N. Alem, J. H. Chen, K. J. Erickson, J. Ciston, A. Gautam, M. Linck, A. Zettl, *J. Am. Chem. Soc.* **2013**, 135, 6758-6761.
- [57] B. Yates, M. J. Overy, O. Pirgon, *Philosophical Magazine* **1975**, 32, 847-857.
- [58] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, J. Kong, *Nano Lett.* **2012**, 12, 161-166.
- [59] M. S. Bresnehan, G. R. Bhimanapati, K. Wang, D. W. Snyder, J. A. Robinson, *ACS Appl. Mater. Interfaces* **2014**, 6, 16755-16762.
- [60] K. Qian, R. Y. Tay, V. C. Nguyen, J. X. Wang, G. F. Cai, T. P. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.
- [61] K. Qian, R. Y. Tay, M. F. Lin, J. W. Chen, H. K. Li, J. J. Lin, J. X. Wang, G. F. Cai, V. C. Nguyen, E. H. T. Teo, T. P. Chen, P. S. Lee, *ACS Nano* **2017**, 11, 1712-1718.

Chapter 4*

Au NPs-Interlayer Amorphous Si ECM-Based ReRAM Devices on Flexible and Rigid substrates

The strategies to realize electrochemical metallization (ECM)-based resistive switching random access memory (ReRAM) devices with great improvements in switching performances on both flexible and rigid substrates at room temperature are discussed in this chapter. Specifically, the amorphous Si (a-Si) based ReRAM with a gold nanoparticles (Au NPs) mono-layer between a-Si and bottom electrode realized excellent performances with low electroforming voltage and large ON/OFF ratio at the same time, as compared to a pure a-Si memory device. The mechanism for this phenomenon is due to the modified electric field distribution with the insertion of Au NPs, which can directly affect the dynamic transport of ions and lead to the change of filament growth. Ex-situ transmission electron microscopy (TEM) is used to directly capture the filaments growth process in these two types of memory devices to verify the evolution of conductive filament (CF). This facile fabrication approach offers a versatile structural platform to enhance the electrical performances for future ReRAM application.

*This section published substantially as “Kai Qian, Viet Cuong Nguyen, Tupei Chen, and Pooi See Lee *, Advanced Electronic Materials, **2016**, 2, 1500370.”

4.1 Introduction

With the rapid development of the Internet of Things (IoT) and the ever-growing concerns about human health monitoring, the flexible ReRAM chips are required for the wearable electronics and have attracted more and more interest due to its excellent performance.^[1-4] For the ReRAM device, electroforming voltage and memory window are two important parameters, which are needed to be optimized for the electrical performance enhancement.

In order to activate the fresh ECM-based memory devices into switching states, the electroforming process with a higher voltage than the usual operation voltage is needed.^[5-7] However, the high electroforming voltage may limit the integration potential in advanced crossbar structures (e.g., one resistor-one selector and one resistor-one diode) or damage the memory cells permanently, leading to low switching performance and device yield.^[5, 7-11] Normally the electrical properties of the oxide-based selector and diode would be adversely affected by the high voltage.^[12, 13] The high electrical stress will induce the molecular-bond breaking, which is responsible for dielectric film degradation.^[9] Under high electric stress, the oxide will be degraded *via* the electron traps formation and accompanied physical changes in the oxide structure, which will induce the bond breaking and re-arrangement and lead to destructive breakdown.^[9, 12] For example, for the oxide-based Schottky-diodes, they always suffer from the relatively low breakdown voltage, such as VO₂ and CuO/InZnO-based diodes.^[14-16] In the vertical one diode-one resistor SiO_x-based ReRAM devices, the electroforming voltage is more than 10 V, which degrades the diode performance and results in low integrated devices yield (< 70%).^[14, 17] On the other hand, the high electroforming voltage may also damage the switching material itself, leading to low device yield.^[5, 8] For instance, in the Ni/a-Si/Ni ReRAM devices, a high electroforming voltages > 10 V are required, leading to low device yield < 40%.^[8] In order to reduce the electroforming voltage, several methods have been proposed to decrease the initial resistance, which are associated with high temperature treatments or complicated fabrication process.^[7, 18-21] Yao *et al.* presented an annealing-assisted approach to reduce the electroforming voltages *via* increasing initial

conduction.^[19] Before annealing process, the electroforming voltages of the as-fabricated devices were about ~22 V. For the devices which were annealed at 600 °C for 10 min in vacuum, the electroforming voltages will be reduced to ~ 15V due to more defects introduced. However, the thermal annealing treatment is not suitable for the ReRAM applications on flexible substrates with poor thermal stability.

On the other hand, increasing demand for high density data storage with continuous downscaling has triggered research attention towards multilevel ReRAM which offers an opportunity to store more than 2-bits in a single cell.^[22-24] The actual value of the ON-state depends on the compliance currents or the magnitude of the SET/RESET voltages.^[22, 25] In the ReRAM devices, the stochastic rupture and regeneration of the conductive filaments would cause fluctuations of the resistance at ON- and OFF-state.^[26] Therefore, a large ON/OFF ratio of different resistive states is generally required to keep the stable operation of multilevel switching,^[27-29] which is also an important feature for the resistive memory to avoid misreading during the device operation. To increase the ON/OFF ratio, several methods also have been developed to increase the initial resistance.^[8, 27, 30-32] For instance, Yang *et al.* reported a manganese (Mn) -doped ZnO based ReRAM device, where the 3% Mn dopants in ZnO film can increase the resistivity of the HRS state to enlarge the memory window.^[31] Because Mn is a deep donor in ZnO and can significantly depress the intrinsic donors concentration such as oxygen vacancies or interstitial zins. However, these fabrication processes are also complicated and not easy to control. Based on the aforementioned analysis, it is difficult to realize the reduced electroforming voltage and enlarged memory window at the same time.

In order to meet the desirable requirements of a) lowering the electroforming voltage (V_{forming}) and b) enhancing the ON/OFF ratio, a simple approach which should be suitable for flexible ReRAM fabrication need to be proposed. In this work, the self-assembled Au NPs monolayer was inserted at the interface between the resistive switching (RS) material (a-Si) and the Au bottom electrode to lower the electroforming voltage as well as enhance the ON/OFF ratio. The self-assembled Au NPs in a-Si based memory can extensively modify the electric field distribution and enhance the electric field intensity

around the Au NPs sites, leading to the growth of Ag filaments from Ag TE to the Au NPs location. These analyses were carried out through a carefully designed experimental procedure and verified with simulation. Detailed ex-situ TEM reveals the role of Au NPs in the memory device. In addition, the Au NPs-interlayer a-Si memory also can be fabricated on flexible substrates with low V_{forming} and high ON/OFF ratio and they can operate under mechanical stressed conditions. This study offers a useful and versatile structure platform for next-generation memory applications for enhancement of the switching properties.

4.2 Experimental Methods

4.2.1 Fabrication of a-Si switching layer and Au NPs

For the a-Si layer, it was deposited by plasma enhanced chemical vapor deposition (PECVD). For the Au NPs synthesis (diameter, ~50 nm), there is a standard procedure by sodium citrate reduction.^[33] Detailed preparation on a-Si layer and Au NPs can be found in **Chapter 3**.

4.2.2 Self-assembly Au NPs mono-layer formation on the substrates

For the formation of Au NPs mono-layer, the Au substrate was modified by self-assembled Au NPs through 2-aminothiophenol (2-ATP), as schematically illustrated in **Figure 4.1a**. The Au substrate was immersed in 2-ATP ethanol solution (1 mM) for about 1 hour. Subsequently, the Au electrode surface was coated with 2-ATP due to formation of Au-S bonds and the electrostatic affinity between amino groups and Au NPs which are coated with negative citrate ions.^[34] Thereafter, the substrate was fully rinsed with ethanol and water and dried with a stream of nitrogen. Finally, this modified Au substrate was immersed in Au NPs solution, and Au substrate coated with Au NPs can be obtained after a period of time. As shown in **Figure 4.1b**, the distribution of Au NPs onto the Au substrate was uniform and monolayer. In addition, based on the size distribution spectra, the diameter of the Au NPs is mainly about ~ 50 nm (**Figure 4.1c**).

Figure 4.1 (a) Schematic diagram for Au NPs assembling on 2-ATP-modified Au substrate. (b) SEM image of Au substrate coated with ~50 nm Au NPs monolayer, scale bar: 1 μm. (c) Size distribution by intensity spectra of ~50 nm Au NPs in water solution.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

4.2.3 Electric field simulation

The models were built in CST EM Studio and the electrostatics template was selected for the simulation of resistive switching behavior in the memory device.^[36] The electrodes were assumed as perfect conductor, which has no voltage drop. The simulation parameters are 95 nm-thick a-Si (permittivity, 11.9) layer, 25 nm-radius Au NP and 1V bias voltage. The 1V bias was applied on the top electrode, while the bottom electrode surface was selected as the ground. The electric field was solved by the following equations assuming that no charges are present at atmospheric temperature (25 °C):

$$\nabla^2 V = 0 \quad (1)$$

$$E = -\nabla V \quad (2)$$

where V is the electric potential.

4.2.4 Characterization

The SEM image was carried out using field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F). The nanoparticles size distribution was measured on a

Malvin Zetasizer Nano Series 90 at room temperature. Sample for cross sectional TEM was prepared by using a dual beam focused ion beam (FIB) (FEI Helios 450S). TEM and energy disperse spectrometer (EDS) analyses were performed with a JEOL JEM-2100 electron microscope (200kV) and a JEOL JED 2300T. The current-voltage (I-V) characteristics of these resistive memory devices were conducted in an ambient atmosphere and dark room on Keithley 4200 semiconductor analyzer in DC voltage sweeping mode (sweep rate, 0.01V/s).

4.3 Results and Discussion

4.3.1 Structure of a-Si ECM-based ReRAM devices

The device structure consists of a top electrode (TE), self-assembled Au nanoparticles (Au NPs), resistive switching (RS) material (a-Si), and a bottom electrode (BE), as schematically illustrated in **Figure 4.3a**. Both the BE (Au/Cr) and the TE (Ag, $200 \times 200 \mu\text{m}^2$) were deposited by electron beam evaporation (Edwards Auto 306 Turbo) on a SiO_2/Si substrate. The RS material (a-Si, $\sim 95 \text{ nm}$) was fabricated by PECVD.

4.3.2 Electroforming property evaluations of a-Si based memory devices with and without Au NPs interlayer on rigid substrate

To evaluate and compare the performances of the devices, direct current (DC) voltage sweeping (sweep rate, 0.01V/s) was applied to the Ag TE. Before repeating the voltage sweeping, electroforming process was performed under a compliance current (CC) of $1 \mu\text{A}$ avoiding the memory cell breakdown. Typically, the electroforming process for the fabricated a-Si memory can be achieved by voltage sweeps to a certain high value where the conductance suddenly increases, which is referred to as the V_{forming} (the first sweep in **Figure 4.2**).^[37, 38] Before the reproducible switching I-V behaviors, the voltages for the increase in conductance and the current fluctuation gradually moved to the lower voltage region in the subsequent voltage sweep (**Figure 4.2**). The phenomenon of steep increase in current in the memory devices (**Figure 4.2**), which occurred at the threshold bias of the

electroforming process, is induced by the ultrahigh switching speed of the resistance change. For this ultrahigh speed, one reason is that the distance for the ionic species to move during switching is fairly short (nanometer scale). The other key reason is that the nanoscale switching layer is under very high electric field for enhanced ion mobility and is heated up during switching Joule heat, which greatly increase the mobility of the ionic species and enables fast switching.^[39] On the other hand, in order to realize reliable resistive switching behaviors, several continuous voltage sweeps (**Figure 4.2**) are normally required to obtain complete electroforming process.^[19] That is because during the first voltage sweep for the electroforming process, the strong filaments cannot be formed in the switching layer for the subsequent resistive switching events. Therefore, during the subsequent electroforming processes, the steep increase in current will still occur at the threshold voltage.

Figure 4.2 The electroforming process in a pure a-Si memory device on rigid substrate with $V_{\text{forming}} \sim 11\text{ V}$.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.3b showed representative initial I-V curves (*i.e.*, the first sweep) for the devices with and without Au NPs-interlayer during the electroforming process. As shown in **Figure 4.3b**, the V_{forming} was significantly decreased when the Au NPs-interlayer was inserted. **Figure 4.3c** showed the statistical histogram of V_{forming} for a-Si memory systems (100 cells, respectively) with the fitting curves by Gaussian functions. The V_{forming} values were found to be 5.8 ± 1 and $11.7 \pm 1.1\text{ V}$ for the a-Si memory devices with and without Au NPs-interlayer. A significant reduction in the electroforming voltage has been achieved

with the Au NPs-interlayer. The observed phenomenon in these devices can be explained by electric-enhanced, redox-based ion-migration mechanism.^[38, 40]

Figure 4.3 (a) Schematic of the Ag/a-Si/Au NPs/Au device arrays and the setup for electrical characterization. (b) I-V curves for a-Si memory devices with and without Au NPs during the initial electroforming process. (c) Statistical histogram of the V_{forming} for 100 different cells in the a-Si memory devices. The fitting curves were obtained by Gaussian functions.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Based on the electrochemical metallization theory, in the CF growth process, the electric field strength will affect the electromigration of Ag^+ cations, and the Ag^+ ionic current density can be defined by Mott and Gurney's eq 1:^[40, 41]

$$i = 2ecav \exp(-W_a^0/kT) \sinh(aeE/2kT) \quad (3)$$

where c is the mobile cations concentration, a is the jump distance of the ions, v is a frequency factor, W_a is the energy barrier for ion hopping, E is electric field, k is Boltzmann's constant, and T is the absolute temperature. From eq 3, it is clear that the ionic current density i will increase with the increase of electric field E . To study the impact of the Au NPs on the electric field, we systematically investigated the electric field distribution in the a-Si matrix by using CST EM studio. As shown in **Figure 4.4a**, the intensity of electric field is obviously high at the tip of Au NPs, and the intensity decreases with the increasing of distance away from Au NP tip. The simulation results also demonstrated that the intensity of the electric field at the tip of the NPs greatly

exceeds that of the planar region ($E=1V/95nm\approx 10.53$ MV/m), which is 2.61 times of the planar region (**Figure 4.4a**). On the other hand, the intensity of electric field was also considerably enhanced between Au NPs, which is 1.58 times of the planar region (**Figure 4.4b**). While the highest electric field intensity of multiple Au NPs will decrease a little due to the interaction and mutual influences of the electric field distribution. It is noteworthy that the electrical field intensity at the column region above the Au NPs location is higher compared with the region without Au NPs.

Figure 4.4 (a) Simulation of electric field distribution along the X axis with different y coordinates away from the tip of Au NP by using CST EM studio for an Au NP. (b) Simulation of electric field distribution for multiple Au NPs according to the distance at the interface between Au NPs (or bottom electrode) surface and a-Si, and the distance between Au NPs was defined as 10 nm. (c) Cross sectional TEM images of non-complete conducting filament in a-Si based device with Au NPs after electroforming process. Scale bar, 100 nm. The filament apparently grew from the active electrode (Ag TE). The region indicated by the red circle represented the filaments composed of Ag nanoparticles, and the blue rectangle area indicated the region without filaments. The simulation parameters are 95 nm-thick a-Si layer, 25 nm-radius Au NP and 1V bias voltage. For (a) and (b), the distance from Au NPs surface to top electrode was kept as 95 nm, same with the planar region without Au NPs.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

To verify that the growth of the CFs is controlled by the Au NPs, TEM was used to directly capture the CF growth process in the memory cell. **Figure 4.4c** shows the TEM

images of the non-complete conducting filaments in the a-Si-based device with Au NPs-interlayer. After electroforming process, it is clear that the non-complete conducting filaments appeared on the top of Au NPs region (as shown in the red circle region of **Figure 4.4c** and **Figure 4.5a**), where the electric field intensity is higher compared with the region without Au NPs. In addition, the non-complete filaments were composed of nanoparticles, not the compact wire. The filament component is proved to be Ag from spot analysis of energy dispersive spectroscopy (EDS) (**Figure 4.5e, f**). More importantly, there was no conducting filament at the region without Au NPs, which was marked by the blue rectangle (**Figure 4.4c** and **Figure 4.5a**). Because of the Au NPs-enhanced electric field, around the NPs location, more Ag^+ ions will be converged than other planar regions, leading to enhanced nucleation probability of Ag atoms.^[40, 42] This will promote the growth of the Ag CFs towards to the Au NPs location and consequently result in a reduction of the electroforming voltage. Furthermore, the filament started growing from the active Ag electrode (anode) instead. This phenomenon is different from the conventional electrochemical metallization (ECM) theory, which indicates the cations should be reduced at the negatively charged cathode side and start growing from cathode.^[41] Here, because the a-Si offers very low cation mobility, the Ag cations move very slowly and may be reduced after a short distance by capturing free electrons.^[38]

Figure 4.5 TEM and EDS spot analyses for conducting filaments observation in a-Si memory with Au NPs-interlayer after electroforming process. (a) Cross sectional TEM image, and (b, c) TEM images corresponding to left and right red circle region of (a). (e, f) EDS spot analyses corresponding to (b) and (c), which indicates the filament is composed of Ag. Scale bar, 100nm.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

In addition, it is noteworthy that the current level of the devices with Au NPs abruptly increases at a lower current of about 2×10^{-8} A at ~ 5.5 V (**Figure 4.3b**). However, for the devices without Au NPs, the rapid increase of current happens at about 3×10^{-7} A at ~ 10.8 V (**Figure 4.3b**). That means the Ag filaments can be nucleated and propagated easily and quickly in the Au NPs-interlayer a-Si memory, which further verifies that the filament growth is facilitated by the enhanced electric field, in agreement with the hypothesis of electric field-assisted ion transport inside the a-Si active material.^[38, 43]

4.3.3 Resistive switching characterization of a-Si based memories with and without Au NPs interlayer on inter Au BE (on rigid substrate)

Figure 4.6 Resistive switching I-V curves of Ag/a-Si/Au (a) and Ag/a-Si/Au NPs/Au (b). A schematic illustration explaining the Ag filament change for the devices without (c) and with (d) Au NPs interlayer at OFF state, which cannot fully describe the CF shape in the device.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Furthermore, the electrical switching performances after electroforming process were investigated, as shown in **Figure 4.6**. Here the current compliance was limited by 1 mA

to avoid the memory cell breakdown. One noticeable difference can be found that the current level at the OFF state decreases a lot when Au NPs interlayer was inserted. This different switching behavior indicates that the formation/rupture of the Ag CFs is modulated by the Au NPs interlayer. For the device without Au NPs (**Figure 4.6a**), the current increased gradually at about ~ 0.75 V, indicating the SET process (stage 1) from high resistance state (HRS, defined as OFF state) to a low resistance state (LRS, defined as ON state). During the subsequent voltage sweep, the LRS state can be maintained (stage 2) even if the power is turned off. When a reverse voltage was swept on Ag TE, the current decreased gradually, indicating the RESET process from LRS to HRS (stage 3 and 4) due to the rupture or dissolution of the conductive filaments which results from reversed electrochemical reaction^[38, 44] or thermally assisted electrochemical reaction.^[45] For the device with Au NPs (**Figure 4.6b**), during the OFF state to ON state process, the current increased abruptly to 1 mA at about ~ 0.67 V. When a reverse voltage was applied on Ag TE, the current decreased abruptly at about -0.35 V, indicating the HRS state was recovered (stage 3, 4). In addition, as shown in the I-V curves of **Figure 4.6a** and **b**, the characteristics of loss process and asymmetry can be observed. For this phenomenon, it always happens in the filament-based resistive switching memories.^[46, 47] In the filament-based memory devices, the uncontrollable or random rupture/growth of the filament accompanied with joule heating deteriorates the resistive switching devices performances, which would cause large fluctuations of resistances and switching voltages and lead to the phenomena of loss process and asymmetry in the I-V curves.^[21, 48]

Compared with device without Au NPs (**Figure 4.6a**, stage 3), the current changes abruptly and quickly due to the Au NPs-enhanced electric field. For the device without Au NPs (**Figure 4.6a**), the ON/OFF current ratio was about 16, while the ON/OFF ratio was about 3821 for the device with Au NPs which has more resistance HRS (**Figure 4.6b**). The ON/OFF ratio was highly enhanced by inserting Au NPs in the device, which made it very easy to distinguish the storage information ("1" or "0") due to the high memory margin and is beneficial to the multilevel switching resistive memory for high density data storage. In the ReRAM devices (**Figure 4.6c** and **d**), the evolution of the depleted gap between the conductive filament tip and electrode during switching can

explain the difference resistances in OFF state: a narrower/wider depleted gap length between the electrode and CF tip leads to higher/lower current at the OFF state.^[49, 50]

4.3.4 *ex-situ* TEM characterization of a-Si based memories with and without Au NPs interlayer on rigid substrate

Figure 4.7 (a-d) TEM images of the same device without Au NPs after 10 Set-Reset processes (OFF state). (e-g) TEM images of the same device with Au NPs after 10 Set-Reset processes (OFF state). The thinnest region and the dissolutions of the filaments took place at the a-Si and inert Au bottom electrode. The region indicated by the red arrows represented the longer Ag filaments, and the blue rectangle area indicated the region without filaments.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

To verify that the evolution of the CFs is controlled by the Au NPs, TEM was used to directly capture the CF growth process in the memory cell. **Figure 4.7a-d** showed the cross section TEM images of a same device without Au NPs at OFF state after 10 repetitive Set-Reset processes. One can see several ruptured longer protrusion-like regions as marked by arrows therein. Indeed, these images taken after the erasing process clearly revealed well-defined conducting filaments (highlighted by the 1-4 arrows in **Figure 4.7a-d**) with a typical conical shape. To determine the nature of the ruptured bridge-like filaments, further chemical analysis along the ruptured filament axis (the one in **Figure 4.7d**) was carried out via EDS line profiling. As shown in **Figure 4.8**, these detailed studies verified that the ruptured CFs is composed Ag element. These filaments were localized with a wider base, and the thinnest part of the ruptured filaments (~8 nm lateral size) is apparently near the inert Au electrode interface, and the gap between the filaments tip and Au BE is about ~10 nm (**Figure 4.7a-d**). During SET/RESET process, the dissolution and formation of the Ag filaments will take place at the interface between a-Si and Au BE where the thinnest part of Ag CFs is.^[38, 44]

Figure 4.8 (a) Line profile of EDS intensity of Ag, a-Si and Au elements along the red line, according to the **Figure 4.7d**. (b) EDS spectrum collected from the line region in (a). This indicates that the ruptured CF is composed of Ag element.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.7e-g showed the cross section TEM images of a same device with Au NPs after 10 repetitive Set-Reset processes, which also has been switched to OFF state. Several long ruptured conical shape filaments were marked by arrows therein. To determine the nature of the ruptured filaments (the one in **Figure 4.7f**), further chemical analysis was

carried out via EDS. As shown in **Figure 4.9b**, the detailed studies verified that the ruptured CFs is composed Ag element. In addition, the nanoparticle on the bottom electrode is Au NP (**Figure 4.9c, d**).

Figure 4.9 TEM and EDS spot analyses for conducting filaments observation in a-Si memory with Au NPs-interlayer after erasing process. (a, c) Cross sectional TEM images. (b, d) EDS spot analyses corresponding to (a) and (c), which indicate the filament is composed of Ag and the nanoparticle onto the bottom electrode is Au. Scale bar, 100nm. This indicates that the ruptured CFs is composed of Ag element.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

It is evidently found that the remnant Ag filaments (**Figure 4.7e-g**) are shorter than those in the device without Au NPs (**Figure 4.7a-d**), which means the gap between filaments tip and Au BE or Au NPs is wider in the device with Au NPs, leading to the lower current at the OFF state. In addition, as shown **Figure 4.3b** and **Figure 4.6b**, the Au NPs inserted devices show faster resistance transitions during electroforming and reset processes, which indicate faster Ag^+ ions drift process. These results thus suggest that Au NPs interlayer allows the Ag ions to drift faster under the Au NPs enhanced electric field during electroforming and RESET processes, leading to lower electroforming voltage and higher HRS resistance. Therefore, the different RS behavior *via* Au NPs inserted can be understood by the faster Ag ions drift process due to Au NPs enhanced electric field: during electroforming process, the Ag ions can be easily supplied from the Ag TE,

leading to the nucleation and formation of Ag CFs easily and lower electroforming voltage. During RESET process, the positive voltage was applied on the Au bottom electrode, the electric field strength around Au NPs will be enhanced (like the one shown in **Figure 4a**), the Ag^+ cations drift faster and are easily depleted, as a result, the current decreased abruptly (**Figure 4.6b**), leading to a wider gap and a more resistive HRS, as shown in **Figure 4.7e-g**. However, for the device without Au NPs, during RESET process, the current decreased gradually when reverse voltage was applied as shown **Figure 4.6a**, which meant the Ag filaments dissolved gradually and slowly, leading to the longer length of the ruptured filaments (**Figure 4.7a-d**) inside the a-Si matrix and high current level at HRS. Furthermore, as shown in **Figure 4.7**, it is revealed that a substantial number of Ag filaments still exist in the a-Si film after erasing process, which can facilitate subsequent filament growth. This effect explains why the set voltage is lower compared with the one during the initial electroforming process. On the other hand, the leakage current of the device in the OFF state may increase due to the existence of the residual Ag atoms in the a-Si film (**Figure 4.7**), which explains the resistance of the device did not return to the initial state level after RESET process.

Figure 4.10 I-V curves for a-Si memory devices without (a) and with (b) Au NPs during programming process. The multistep SET/RESET process is frequently observed in these devices, which might correspond to the formation/rupture of multifilaments (as shown in **Figure 4.7**) with different threshold voltage.^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

In addition, the multistep SET/ RESET process is frequently observed in these devices. As shown in **Figure 4.10a** and **b**, there are multi-steps during SET process, where the current will suddenly increase, indicating more filaments formation and high current level. During the SET process, the voltage sweeps to a certain value where the conductance of the memory cell suddenly increases, which is referred to as threshold voltage (V_{th}). During RESET process, there are also some multi-steps, where the current suddenly decreases, indicating part of the filaments break and lowers the current level. Therefore, for this phenomena, it might correspond to the formation/rupture of multi-filaments with different V_{th} .^[31, 40] As shown in **Figure 4.7**, several ruptured Ag CFs have been observed, it can be rationalized that when the cell was switched to ON state, these gaps will be filled with Ag. This phenomenon implies a potential that multilevel data storage could be realized by effective control of V_{th} to increase the data storage density.

4.3.5 Electrical performances evaluations of a-Si based memories with and without Au NPs interlayer on rigid substrate

Figure 4.11 showed the write endurance and retention time of the devices without and with Au NPs, respectively. These characteristics were measured using the DC sweep mode at a reading voltage of 0.1V. For the device without Au NPs (**Figure 4.11a**), the ON/OFF current ratio was about 10~200 during the repeated 100 cycles. In contrast, the ON/OFF ratio of the device with Au NPs was increased to about $\sim 5 \times 10^2 - 4 \times 10^3$ during the repeated 100 cycles (**Figure 4.11b**) due to the high resistance of OFF state. Furthermore, in terms of retention time (**Figure 4.11c** and **d**), the pure and Au NPs-inserted devices all remained stable without any obvious electrical degradation within about 2500s, respectively. These results demonstrate the competitive switching stability of the Au NPs-inserted a-Si memory device.

Figure 4.11 Write endurance and retention time results by DC sweeping mode in the (a, c) Ag/a-Si/Au and (b, d) Ag/a-Si/Au NPs/Au cell (reading voltage, 0.1V).^[35] Reproduced from ref. 35 with permission from John Wiley & Sons, Inc.

4.3.6 Electrical performances and bending stability evaluation of the a-Si memories with and without Au NPs interlayer on flexible substrate

The Au NPs-interlayer a-Si (~95 nm thick) memory was also fabricated and characterized on a polyimide (PI) (~200 μm thick) flexible substrate (the top panel of **Figure 4.12**). The flexible devices fabrication process was similar to that used for rigid device. Here the PI was chosen as the plastic substrate for its low surface roughness and comparatively high thermal stability (up to 520K), which prevents substrate deformation during the fabrication process and sustains the current local heating involved during the initial electroforming process.^[51, 52] The devices showed the similar memory switching characteristics as those devices on rigid substrates. The V_{forming} of the flexible devices without and with Au NPs was found to be ~12 and ~6 V (**Figure 4.12a, b**), which demonstrated the substrate-independent V_{forming} .

Figure 4.12 I-V curves for a-Si memory devices without (a) and with (b) Au NPs during the initial electroforming process on the flexible PI substrate. The I-V characteristics of (c) Ag/a-Si/Au and (d) Ag/a-Si/Au NPs/Au memory devices on polyimide substrate. ^[35] Adapted from ref. 35 with permission from John Wiley & Sons, Inc.

Also, the switching I-V curves after electroforming process were similar to that of the devices on rigid substrates (**Figure 4.12c, d**). For the device without Au NPs, the current increased or decreased slowly and gradually to switch the device to ON state (at $\sim 1.4\text{V}$) or OFF state (at $\sim -0.93\text{V}$) with a low ON/OFF ratio, respectively (**Figure 4.12c**). While for the device with Au NPs, the abrupt increase (at $\sim 0.4\text{V}$) or decrease (at $\sim -0.28\text{V}$) of current happened with the high ON/OFF ratio due to the fast drift of Ag^+ cations caused by Au NPs-enhanced electric field (**Figure 4.12d**).

Figure 4.13 (a) Illustration of the bending radius during the bending test. (b) Illustration of the bending test of the actual Ag/a-Si/Au memory device on the polyimide (~ 200 μm) substrate, and the measured cells were near the middle of the device. Retention of both ON and OFF memory states (read at $+0.1\text{V}$) from the device of (a) Ag/a-Si/Au/PI and (b) Ag/a-Si/Au NPs/Au/PI memory device.^[35] Adapted from ref. 35 with permission from John Wiley & Sons, Inc.

Figure 4.13c and **d** showed the ON/OFF ratios of flexible devices varied before bending (defined as the bending radius $R = \infty$) and after repeated bending cycles at $R = 10$ mm. The flexible device without Au NPs showed a low ON/OFF ratio (< 300) after 200 repeated bending cycles (**Figure 4.13c**). On the other hand, the flexible device with Au NPs still maintains high ON/OFF ratio (> 1000) (**Figure 4.13d**). These results showed that the Au NPs-interlayer a-Si memory can be fabricated on a flexible substrate, and it also delivers lower V_{forming} and higher ON/OFF ratio under mechanical bending conditions.

Figure 4.14 SEM images of (a) the a-Si film on flexible Au/Cr/PI substrate and (b) Ag electrode on flexible a-Si/Au/Cr/PI substrate after 200 bending cycles with bend radius $R = 10$ mm.

However, here the a-Si-based ReRAM devices suffer severely from limited bendability at large strain due to the low failure strain of a-Si film ($\sim 0.5\text{-}2\%$),^[53] leading to the film crack upon repeated bending operation. As shown in **Figure 4.14**, for the flexible a-Si-based ReRAM device on PI substrate, after 200 bending cycles with bend radius $R=10$ mm, part of the memory cells cannot work due to the existence of cracks on both a-Si film and Ag electrode induced by the strain.

4.4 Chapter Summary

In summary, the Au NPs-interlayer a-Si nonvolatile memory devices were fabricated *via* self-assembly method. When compared to a pure a-Si memory device without Au NPs, the Au NPs-interlayer a-Si memory device delivers great improvements in lowering the electroforming voltage as well as enhancing the ON/OFF ratio. The simulation results and ex-situ TEM analyses confirm that the Au NPs-interlayer provides practical capability to modify the electric field distribution and enhances the electric field intensity at the column region above the Au NPs location, which facilitates the CF nucleation and leads to the lower electroforming voltage. On the other hand, the remnant Ag CFs will be shorter for the device with Au NPs due to the Au NPs-enhanced electric field which allows the Ag cations to drift faster and be easily depleted, leading to more resistant HRS and high ON/OFF ratio. In addition, the Au NPs-interlayer a-Si flexible memory devices also show low V_{forming} and high ON/OFF ratio. The Au NPs-interlayer a-Si memory system is promising to satisfy the prerequisite conditions for future nonvolatile memory applications in terms of the enhancement of the switching properties and facile fabrication versatility. However, due to the brittle nature of the a-Si film, the flexible a-Si-based memory devices showed poor bending stability during the bending test. Therefore, it is important and necessary to exploit a novel material for flexible ReRAM application with both high bending stability and good electrical performance.

References

- [1] J. Shang, W. Xue, Z. Ji, G. Liu, X. Niu, X. Yi, L. Pan, Q. Zhan, X.-H. Xu, R.W. Li, *Nanoscale* **2017**, 9, 7037-7046.
- [2] Y. Yang, G. Yuan, Z. Yan, Y. Wang, X. Lu, J. M. Liu, *Adv. Mater.* **2017**, 29, 1700425.
- [3] B. H. Lee, H. Bae, H. Seong, D. I. Lee, H. Park, Y. J. Choi, S. G. Im, S. O. Kim, Y. K. Choi, *ACS Nano* **2015**, 9, 7306-7313.
- [4] S. T. Han, Y. Zhou, V. A. L. Roy, *Adv. Mater.* **2013**, 25, 5425-5449.
- [5] J. Yao, L. Zhong, D. Natelson, J. M. Tour, *Sci. Rep.* **2012**, 2.
- [6] K. M. Kim, D. S. Jeong, C. S. Hwang, *Nanotechnology* **2011**, 22.
- [7] G. Wang, A. R. O. Raji, J. H. Lee, J. M. Tour, *ACS Nano* **2014**, 8, 1410-1418.
- [8] S. H. Jo, W. Lu, *Nano Lett.* **2008**, 8, 392-397.
- [9] G. Bersuker, Y. Jeon, H. R. Huff, *Microelectron. Reliab.* **2001**, 41, 1923-1931.
- [10] J. H. Yoon, S. J. Song, I. H. Yoo, J. Y. Seok, K. J. Yoon, D. E. Kwon, T. H. Park, C. S. Hwang, *Adv. Funct. Mater.* **2014**, 24, 5086-5095.
- [11] J. Y. Seok, S. J. Song, J. H. Yoon, K. J. Yoon, T. H. Park, D. E. Kwon, H. Lim, G. H. Kim, D. S. Jeong, C. S. Hwang, *Adv. Funct. Mater.* **2014**, 24, 5316-5339.
- [12] J. McPherson, J. Y. Kim, A. Shanware, H. Mogul, *Appl. Phys. Lett.* **2003**, 82, 2121-2123.
- [13] G. Wang, A.-R. O. Raji, J.-H. Lee, J. M. Tour, *ACS Nano* **2014**, 8, 1410-1418.
- [14] L. Ji, Y. F. Chang, B. Fowler, Y. C. Chen, T. M. Tsai, K. C. Chang, M. C. Chen, T. C. Chang, S. M. Sze, E. T. Yu, J. C. Lee, *Nano Lett.* **2014**, 14, 813-818.
- [15] S. H. Chang, S. B. Lee, D. Y. Jeon, S. J. Park, G. T. Kim, S. M. Yang, S. C. Chae, H. K. Yoo, B. S. Kang, M. J. Lee, T. W. Noh, *Adv. Mater.* **2011**, 23, 4063-4067.
- [16] M. J. Lee, S. I. Kim, C. B. Lee, H. Yin, S. E. Ahn, B. S. Kang, K. H. Kim, J. C. Park, C. J. Kim, I. Song, *Adv. Funct. Mater.* **2009**, 19, 1587-1593.
- [17] G. Wang, A. C. Lauchner, J. Lin, D. Natelson, K. V. Palem, J. M. Tour, *Adv. Mater.* **2013**, 25, 4789-4793.
- [18] Y. F. Wang, X. Y. Qian, K. J. Chen, Z. H. Fang, W. Li, J. Xu, *Appl. Phys. Lett.* **2013**, 102, 042103.

- [19] J. Yao, Z. Z. Sun, L. Zhong, D. Natelson, J. M. Tour, *Nano Lett.* **2010**, 10, 4105-4110.
- [20] Y. F. Chang, P. Y. Chen, Y. T. Chen, F. Xue, Y. Z. Wang, F. Zhou, B. Fowler, J. C. Lee, *Appl. Phys. Lett.* **2012**, 101, 052111.
- [21] B. K. You, W. I. Park, J. M. Kim, K. I. Park, H. K. Seo, J. Y. Lee, Y. S. Jung, K. J. Lee, *ACS Nano* **2014**, 8, 9492-9502.
- [22] A. Beck, J. G. Bednorz, C. Gerber, C. Rossel, D. Widmer, *Appl. Phys. Lett.* **2000**, 77, 139-141.
- [23] M. J. Rozenberg, I. H. Inoue, M. J. Sanchez, *Phys. Rev. Lett.* **2004**, 92, 178302.
- [24] S. Balatti, S. Larentis, D. C. Gilmer, D. Ielmini, *Adv. Mater.* **2013**, 25, 1474-1478.
- [25] Y. T. Lu, S. B. Long, Q. Liu, Q. Wang, M. H. Zhang, H. B. Lv, L. B. Shao, Y. Wang, S. Zhang, Q. Y. Zuo, S. Liu, M. Liu, *Phys. Status Solidi RRL* **2010**, 4, 124-126.
- [26] J. Shang, W. H. Xue, Z. H. Ji, G. Liu, X. H. Niu, X. H. Yi, L. Pan, Q. F. Zhan, X. H. Xu, R. W. Li, *Nanoscale* **2017**, 9, 7037-7046.
- [27] S. K. Hwang, J. M. Lee, S. Kim, J. S. Park, H. I. Park, C. W. Ahn, K. J. Lee, T. Lee, S. O. Kim, *Nano Lett.* **2012**, 12, 2217-2221.
- [28] K. Nagashima, T. Yanagida, K. Oka, M. Taniguchi, T. Kawai, J. S. Kim, B. H. Park, *Nano Lett.* **2010**, 10, 1359-1363.
- [29] B. L. Hu, X. J. Zhu, X. X. Chen, L. Pan, S. S. Peng, Y. Z. Wu, J. Shang, G. Liu, Q. Yan, R. W. Li, *J. Am. Chem. Soc.* **2012**, 134, 17408-17411.
- [30] H. W. Zhang, L. F. Liu, B. Gao, Y. J. Qiu, X. Y. Liu, J. Lu, R. Q. Han, J. F. Kang, B. Yu, *Appl. Phys. Lett.* **2011**, 98, 042105.
- [31] Y. C. Yang, F. Pan, Q. Liu, M. Liu, F. Zeng, *Nano Lett.* **2009**, 9, 1636-1643.
- [32] H. Y. Lee, Y. S. Chen, P. S. Chen, T. Y. Wu, F. Chen, C. C. Wang, P. J. Tzeng, M. J. Tsai, C. Lien, *IEEE Electron Device Lett.* **2010**, 31, 44-46.
- [33] G. Frens, *Nature Phys. Sci.* **1973**, 241, 20-22.
- [34] K. Qian, H. L. Liu, L. B. Yang, J. H. Liu, *Analyst* **2012**, 137, 4644-4646.
- [35] K. Qian, V. C. Nguyen, T. P. Chen, P. S. Lee, *Adv. Electron. Mater.* **2016**, 2, 1500370.
- [36] M. Studio, *Bad Nuheimer Str.* **2008**, 19, 64289.
- [37] S. H. Jo, K. H. Kim, W. Lu, *Nano Lett.* **2009**, 9, 870-874.

- [38] Y. C. Yang, P. Gao, S. Gaba, T. Chang, X. Q. Pan, W. Lu, *Nat. Commun.* **2012**, 3, 732.
- [39] R. Waser, D. Ielmini, H. Akinaga, H. Shima, H. S. P. Wong, J. J. Yang, S. Yu, *Resistive Switching: From Fundamentals of Nanoionic Redox Processes to Memristive Device Applications*. John Wiley & Sons, **2015**, 1-30.
- [40] Q. Liu, S. B. Long, H. B. Lv, W. Wang, J. B. Niu, Z. L. Huo, J. N. Chen, M. Liu, *ACS Nano* **2010**, 4, 6162-6168.
- [41] R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* **2009**, 21, 2632-2663.
- [42] C. Schindler, G. Staikov, R. Waser, *Appl. Phys. Lett.* **2009**, 94, 072109.
- [43] S. H. Jo, K. H. Kim, W. Lu, *Nano Lett.* **2009**, 9, 496-500.
- [44] X. Guo, C. Schindler, *Appl. Phys. Lett.* **2007**, 91, 133513.
- [45] W. H. Guan, M. Liu, S. B. Long, Q. Liu, W. Wang, *Appl. Phys. Lett.* **2008**, 93, 223506.
- [46] D. H. Lien, Z. K. Kao, T. H. Huang, Y. C. Liao, S. C. Lee, J. H. He, *ACS Nano* **2014**, 8, 7613-7619.
- [47] M. J. Lee, C. B. Lee, D. Lee, S. R. Lee, M. Chang, J. H. Hur, Y. B. Kim, C. J. Kim, D. H. Seo, S. Seo, U. I. Chung, I. K. Yoo, K. Kim, *Nat. Mater.* **2011**, 10, 625-630.
- [48] Y. B. Zhu, K. Zheng, X. Wu, L. K. Ang, *Sci. Rep.* **2017**, 7, 43664.
- [49] S. Ambrogio, S. Balatti, D. C. Gilmer, D. Ielmini, *IEEE Trans. Electron. Devices* **2014**, 61, 2378-2386.
- [50] S. Kim, S. Choi, J. Lee, W. D. Lu, *ACS Nano* **2014**, 8, 10262-10269.
- [51] S. Park, G. Wang, B. Cho, Y. Kim, S. Song, Y. Ji, M. H. Yoon, T. Lee, *Nat. Nanotechnol.* **2012**, 7, 438-442.
- [52] J. Yao, J. Lin, Y. H. Dai, G. D. Ruan, Z. Yan, L. Li, L. Zhong, D. Natelson, J. M. Tour, *Nat. Commun.* **2012**, 3, 1101.
- [53] H. Gleskova, S. Wagner, Z. Suo, *Appl. Phys. Lett.* **1999**, 75, 3011-3013.

Chapter 5*

Hexagonal Boron Nitride Thin Film for Flexible Functional ECM-Based ReRAM Applications

The two-dimensional (2D) hexagonal boron nitride (hBN), which has attracted a lot of attention due to its fascinating physical properties (e.g., high thermal stability and superior mechanical properties), would exhibit excellent switching endurance and bending stability with small bending radius for flexible resistive switching random access memory (ReRAM) applications. Here, the ultrathin (~3-5 nm) flexible chemical vapor deposition (CVD)-grown hBN-based ReRAM was demonstrated for the first time, of which switching mechanism was investigated via ex-situ transmission electron microscopy (TEM) and conductive atomic force microscopy (CAFM). The hBN-based ReRAM featured excellent switching endurance (~550 cycles) and acceptable memory window (~150). Especially, it can operate under extreme bend condition (bending radius, 7 mm) without large variation of memory window, even after 750 bending cycles. This work would provide an important step to broaden and deepen the understanding on the switching mechanism in 2D hBN-based ReRAM and impel the 2D materials applications for the future flexible integrated electronics.

This section published substantially as “Kai Qian, Roland Yingjie Tay, Viet Cuong Nguyen, Jiangxin Wang, Guofa Cai, Tupei Chen, Edwin Hang Tong Teo, and Pooi See Lee, *Advanced Functional Materials*, **2016**, 26, 2176-2184.”

5.1 Introduction

Future electronic modules are expected to possess more advanced functionalities such as flexibility and wearability.^[1-4] Hence, resistive switching memories, which can be scaled down to less than 10 nm and offer high write/erase speed, high endurance, low power consumption,^[5-7] have emerged as excellent candidates which are driven by the ever-growing demand for potential applications in the field of next-generation flexible electronics.^[8-10]

Recently the organic-based ReRAM devices have been attracting more and more interest due to their potential advantages over common inorganic memory devices, such as their flexibility, light weight, and mechanical elasticity.^[8, 11-15] However, compared with inorganic memories, the thermal stability of organic switching layer is worse at high temperature induced by the Joule heating, leading to poor switching endurance of organic-based ReRAM (refer to **Table 2.2, 2.3 and 2.4, Chapter 2**).^[16-18] For the common inorganic switching layer, like the a-Si based ReRAM devices fabricated in **Chapter 4**, their bending stability is poor due to the low failure strain (~0.5-2%) of a-Si film during the bending test. In addition, although many oxide ReRAM devices have better endurance of writing/erasing cycles and better temperature stability than those of organic memory devices, it is still a big challenge for these oxide memories to be flexible. These brittle oxides also suffer severely from limited bendability to large strain upon repeated bending or stretching operations due to their low failure strain (~1-2%) (refer to **Table 2.4, Chapter 2**).^[17, 19, 20] Therefore, further efforts are required to explore decent materials to realize high-performance flexible functional ReRAM devices with excellent bending stability and switching endurance.

Recently, the emergence of 2D materials which possess fascinating physical properties (*e.g.* high mechanical strength and thermal stability) have been attracting more and more interests and have a great potential in the flexible electronics applications.^[21-26] For example, in terms of mechanical properties, for graphene, the elastic constant, breaking strength, and failure strain are $\sim 340 \text{ N m}^{-1}$, $\sim 42 \text{ N m}^{-1}$, and $>10\%$, respectively.^[25] For

MoS₂, its elastic constant, breaking strength, and failure strain are $\sim 180 \pm 60 \text{ N m}^{-1}$, $\sim 15 \pm 3 \text{ N m}^{-1}$, and $\sim 6\text{-}11\%$, respectively.^[26] However, graphene is conductive and needs to be complemented by an insulator which is not suitable as a switching layer. Son *et al.* reported an organic ReRAM device fabricated with graphene sandwiched between two insulating poly(methyl methacrylate) (PMMA) polymer layers.^[27] Here the difficult graphene transfer process was required for the Al/PMMA/graphene/PMMA/ITO/PET memory fabrication. MoS₂ is not good insulator and therefore unable to provide high resistance at OFF state to realize large memory window with low current compliance.^[28] The current level of MoS₂-based memory cell at OFF state was at $\sim 0.5 \text{ mA}$. On the other hand, its liquid phase exfoliation synthesis process is not compatible with the semiconductor industry, as well as WO₃ · H₂O nanosheets-based ReRAM.^[29, 30] In addition, like graphene oxide (GO), which is also not an excellent insulator, it can be easily degraded with the time, and for this reason GO-based ReRAM devices showed a poor endurance < 100 cycles.^[31, 32]

The CVD-grown hBN, which has a similar structure to graphene, has also gained significant amount of attention due to its own unique properties such as electrical insulator with a wide band gap of $\sim 5.9 \text{ eV}$, high thermal conductivity, and high temperature stability (1000°C).^[33-37] Due to its strong covalent B-N bonds, hBN exhibits exceptional mechanical properties with a significant elastic constant (503 N m^{-1}), breaking strength (15.7 N m^{-1}), and large failure strain ($> 10\%$), indicating a great potential in flexible electronics applications.^[21, 22, 38, 39] However, the use of the hBN material as an active material for electronics is still in nascent stage, extensive work on the related strategies and mechanisms are required.

In this chapter, a novel flexible resistive memory device comprising an ultrathin hBN ($\sim 3\text{-}5 \text{ nm}$) active layer sandwiched between Ag top electrode (TE) and Cu foil bottom electrode (BE) on a polyethylene terephthalate (PET) substrate (**Figure 1a**) was demonstrated. In order to exclude the effect of the Cu foil, a similar structure with indium tin oxide (ITO)/PET substrate (**Figure 3a**) in replacement of Cu foil BE was further investigated. The as-fabricated Ag TE/hBN/Cu foil memory device showed excellent

performance in various important aspects including ON/OFF ratio (~ 150), write/erase cycling (~ 550), retention time ($\sim 3 \times 10^3$ s) and bending endurance (~ 750 cycles). To investigate the underlying switching mechanism of the hBN-based memory device, CAFM and ex-situ TEM were used to capture the details of CFs growth process. It is observed that the Ag CFs starts growing from anode towards cathode and the narrowest region of the filament is near the hBN/cathode interface.

5.2 Experimental Methods

5.2.1 Preparation of hBN films

Few-layer h-BN films with thickness ~ 3 -5 nm were grown on 25 μm thick Cu foils (Alfa Aesar, 99.8%) by atmospheric pressure (AP) chemical vapor deposition (CVD) similar to previous reports.^[40, 41] Detailed preparation on h-BN films can be found in **Chapter 3**. The growth time is 40 mins for the hBN samples used for flexible hBN-based memory devices in this chapter (**Figure 3.7d** in **Chapter 3**).

5.2.2 Transfer hBN films onto ITO/PET

The as-grown h-BN film on Cu was transferred onto the ITO/PET substrate using a conventional wet transfer approach.^[42] A layer of poly(methyl methacrylate) (PMMA) was first spin coated onto the h-BN/Cu at 3000 rpm for 30 s. The PMMA/h-BN/Cu was then placed on ammonia persulfate (APS) solution for several hours to etch away the Cu. After etching the Cu, the floating PMMA/h-BN film was extracted and placed onto DI water to rinse away the APS residues. This process was repeated twice. The cleaned PMMA/h-BN film was extracted onto an ITO/PET substrate and baked at 50 °C for several minutes until it is dried. Finally, the PMMA was removed by submerging the sample in acetone. For the transferred Ag/hBN/ITO/PET memory, the device yield is about $\sim 40\%$. For the Ag/hBN/Cu foil memory which does not require transfer process for hBN film, the device yield is about $\sim 80\%$.

5.2.3 Characterization

The SEM image was carried out using field emission scanning electron microscopy (FESEM, JEOL, JSM-7600F). Sample for transmission electron microscopy (TEM) observations was fabricated by using a dual beam focused ion beam (FIB) (FEI Helios 450S). TEM and energy disperse spectrometer (EDS) analyses were performed with a JEOL JEM-2100 electron microscope (200kV) and a JEOL JED 2300T, respectively. The X-ray photoelectron spectroscopy (XPS) was conducted with VG ESCALab 220i-XL. An atomic force microscopy (NT-MDT) equipped with a conducting cantilever coated diamond was employed for the CAFM measurements of the device. The current-voltage (I-V) characteristics of these resistive memory devices were conducted in an ambient atmosphere and dark room on Keithley 4200 semiconductor analyzer in DC voltage sweeping mode.

5.3 Results and Discussion

5.3.1 Structure of hBN-based ReRAM devices

The device structure consists of a top electrode (TE), resistive switching (RS) material (h-BN), and a bottom electrode (BE) Cu foil on the PET substrate, as schematically illustrated in **Figure 5.1a**. The Ag TE (~150 nm thick) was deposited by electron beam evaporation (Edwards Auto 306 Turbo), and the RS material hBN with ~3-5 nm thick (**Figure 5.1b**) was fabricated by CVD. **Figure 5.1b** shows the TEM image of a real memory cell with ~ 3-5 nm thick ultrathin hBN film sandwiched between Ag top electrode and Cu foil.

5.3.2 Resistive switching characterization of Ag TE/hBN/Cu foil devices

Figure 5.1 (a) Schematic of the Ag/hBN/Cu foil on PET substrate device arrays. (b) Cross-section TEM image of the Ag/hBN/Cu foil memory cell, and the thickness of hBN is about ~3 nm. (c) The electroforming process for hBN memory device with $V_{\text{forming}} = \sim 1.87$ V. (d) The switching characteristics for the hBN memory device after electroforming process.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

To evaluate the performances of the device, direct current (DC) voltage sweeping (sweep rate 0.01 V/s) was applied to the Ag TE (anode), while the Cu foil BE (cathode) was grounded. It is observed that the hBN film was in the initial high resistance state, and electroforming process under a compliance current (CC) of 0.1 mA is required to transform the pristine resistive memory into switching state. The electroforming process for hBN memory can be achieved by voltage sweeps to a certain high value (~ 1.87 V) where the conductance suddenly increases, which is referred to as the V_{forming} (**Figure 5.1c**). Finally, the reproducible switching current-voltage (I-V) behaviors were attained under a compliance current of 1 mA after electroforming process. The hBN based memory exhibited a typical hysteresis loop in the I-V curve at forward and reverse voltages with acceptable ON/OFF ratio of ~ 150 (**Figure 5.1d**). When a forward bias

applied to Ag TE exceeds the SET voltage (V_{set} , $\sim 0.72\text{V}$), the current of the device rapidly increases and the devices transit from the OFF-state to the ON-state. Subsequently, the devices abruptly returned to the OFF-state at a RESET voltage (V_{reset} , $\sim -0.37\text{V}$) when a reverse voltage was applied to the Ag TE, suppressing the current flow at lower reset voltages.

Figure 5.2 Characteristics of the flexible Ag TE/hBN/Cu foil memory device in terms of switching endurance (a) and retention time (b). The reading voltage is 0.1V .^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

Furthermore, the electrical switching properties of the flexible Ag TE/hBN/Cu foil memory device in terms of write cycling and retention time at room temperature were monitored, as shown in **Figure 5.2**. The resistance values were read out at 0.1 V . The device write cycles (**Figure 5.2a**) were demonstrated with steady operation for 550 cycles. Although the resistance values of both the HRS and LRS showed slight fluctuations, a $100\times$ memory window between the ON and OFF state was obtained without any noticeable degradation during the 550 cycles, and both states showed no disturbance for around $3\times 10^3\text{ s}$ (**Figure 5.2b**).

5.3.3 XPS characterization of hBN-based memory devices

As there is a possibility that the Cu foil may be mildly oxidized leading to the formation of a continuous thin film at the interface between hBN and Cu foil, XPS was utilized to determine the oxidation state of the Cu foil as well as the chemical composition of the hBN. **Figure 5.3a** shows the XPS survey spectrum of the hBN/Cu foil containing B, N, Cu, O, and some traces of C elements.

Figure 5.3 XPS characterization. (a) XPS survey spectra of hBN ultrathin film on the Cu foil. (b) B1s XPS peaks for the B-N bonding state, showing the presence of B-N (190.5 eV) and B-O (191.8 eV) bonds and (c) N1s XPS peak at 398.2 eV. (d) Cu 2p spectra, showing the presence of Cu₂O (932.65 eV), Cu⁰ (932.83 eV), CuO (933.64 eV) and Cu(OH)₂ (935.03 eV), and the atomic concentration of Cu was 15%.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

In the hBN film, the B-N bonding is determined by the distinctive B 1s and N 1s peaks located at 190.5 and 398.2 eV, as shown in **Figure 5.3b, c**, respectively, which is in agreement with previous reported results.^[40, 44] Some traces of boron oxide were also observed at 191.8 eV due to the oxidation of boron during the fabrication process.^[45, 46] The hBN film has exceptional chemical stabilities, which will not form the boron oxide even at high temperature up to 1100 °C in oxygen-rich atmospheres.^[47] Therefore, it is rationally concluded that the formed boron oxide was from the oxidation of excess boron in the furnace. **Figure 5.3d** shows the deconvoluted Cu 2p peaks composing of Cu₂O (932.65 eV), Cu⁰ (932.83 eV), CuO (933.64 eV) and Cu(OH)₂ (935.03 eV),^[48] indicating the presence of copper oxide. The extracted atomic concentration of Cu from the XPS

scan is 15%. Hence, the copper oxide layer may have partially contributed as the resistive layer for resistive memory.^[49] Lv *et al.* demonstrated that the Al/CuO_x/Cu device exhibited bipolar resistive switching,^[49] indicating that the CuO_x can serve as switching layer.

Figure 5.4 XPS characterization. (a) XPS survey spectra of hBN film on the SiO₂/Si substrate. (b) Cu 2p spectra, showing the presence of Cu₂O (932.65 eV), Cu⁰ (932.83 eV), and CuO (933.64 eV), and the atomic concentration of Cu was 0.3%.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

In order to verify that the resistive switching in the samples are governed primarily by the ultrathin hBN layer, while the Cu BE has no significant influence on the key performance characteristics, transfer of hBN film to exclude the contributions of Cu was carried out. The characteristics of a transferred hBN film on SiO₂/Si substrate were determined by using XPS. **Figure 5.4a** shows the survey spectrum of the transferred hBN film on SiO₂/Si substrate. As compared to the hBN films on Cu foil, it is observed that the intensity of Cu 2p peak (highlighted by the red rectangle) is significantly reduced and the extracted atomic concentration drops to 0.3%, indicating the Cu element mainly existed on the surface of Cu foil. **Figure 5.4b** shows the Cu 2p peak deconvolution into Cu₂O (932.65 eV), Cu⁰ (932.83 eV), and CuO (933.64 eV), indicating the presence of residual Cu and Cu oxide. For the transferred hBN films, it is expected to have a small amount of residual Cu during the Cu wet etching process. However, the effect of Cu element in the resistive switching performance should be at most minimal for transferred hBN films.

5.3.4 Resistive switching characterization of Ag TE/hBN/ITO/PET memories

Figure 5.5 (a) Schematic of the Ag/hBN/ITO/PET memory device. (b) The electroforming process in the Ag/hBN/ITO/PET device with $V_{\text{forming}} \sim 1.9\text{V}$. The inset shows the transferred hBN film with PMMA onto ITO/PET substrate, indicated by the red rectangle frame. (c) The real flexible Ag/hBN/ITO/PET memory device. (d) The I-V characteristics of the Ag/hBN/ITO/PET memory device.^[43] Adapted from ref. 43 with permission from John Wiley & Sons, Inc.

As shown in **Figure 5.5a**, the hBN film was transferred onto ITO/PET substrates (the inset in **Figure 5.5b**) using a conventional wet transfer approach,^[42] then the Ag TE was deposited on it. After the electroforming process (**Figure 5.5b**), the I-V characteristic of the Ag/hBN/ITO/PET memory device was studied (**Figure 5.5d**). DC voltage sweeping was applied to the Ag TE, and the ITO/PET was grounded. It is observed when a positive voltage applied to Ag TE, the current increases abruptly at $\sim 0.7\text{ V}$, indicating that the device transits from the OFF-state to the ON-state. Subsequently, when a reverse voltage was applied on Ag TE, the device reverts back to the OFF-state. It is obvious that the Ag/hBN/ITO/PET showed similar switching characteristics to the Ag/hBN/Cu foil, confirming that the copper oxide at the interface of the Ag/hBN/Cu foil is not a major contributing factor towards the resistive switching performances of the memory device.

5.3.5 CuO_x layer effect on the hBN-based memory devices

Figure 5.6 (a) Current (I) vs voltage (V) and (b) log (I) vs V curves of Ag TE/CuO_x/Cu foil device. The hBN film was removed by using O₂ plasma, leaving with a possible CuO_x layer during the hBN fabrication. Then, the Ag TE was deposited. It is clear that the possible CuO_x layer cannot serve as the switching layer, indicating the possible CuO_x layer has no significant influence on the key performance characteristics of hBN-based memory.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

To further investigate whether the possible copper oxide layer between hBN and Cu foil may affect the hBN-based memory performance, the hBN was etched by using O₂ plasma, leaving with a possible CuO_x layer. Then, the Ag TE was deposited on the exposed Cu foil to fabricate the Ag/CuO_x/Cu foil memory device. When the positive voltage was applied on the Ag TE, it showed the quasi-Ohmic contact without obvious hysteresis loop in the I-V curve (**Figure 5.6**), indicating that the possible CuO_x layer at the interface will not affect the hBN-based memory performance significantly. From these findings, it is clear that the resistive switching characteristics are governed by the ultrathin hBN layer, and the Cu foil BE materials used have no significant influence on the key performance characteristics

5.3.6 Resistive switching characterization of Au BE/hBN/Cu foil memories

It is reckoned that the Cu foil can serve also as the active electrode like Ag electrode,^[50, 51] so the hBN/Cu foil with Au acting as the BE deposited on it was investigated. The positive voltage was applied on the Cu foil, and Au electrode was grounded during the SET process. As shown in **Figure 5.7**, this Au BE/hBN/Cu foil device with lower

ON/OFF ratio also exhibited a similar typical hysteresis loop in the I-V curve to the Ag/hBN/Cu foil device (**Figure 5.1d**). After electroforming process (**Figure 5.7b**), application of a forward bias on the Cu foil causes a shift from HRS to a LRS, and a reverse bias switches the device back to the LRS (**Figure 5.7d**).

Figure 5.7 (a) Schematic of the Au/hBN/Cu foil/PET device. (b) The electroforming process in the Au/hBN/ITO/PET device with $V_{\text{forming}} \sim 2\text{V}$. (c) The real flexible Au/hBN/Cu foil/PET memory devices. (d) The I-V characteristics of the Au/hBN/ITO/PET memory device. For this memory device, the I-V curves of (b, d) were measured under flat state. The Au electrode was grounded as the bottom electrode for electrical characterization.^[43] Adapted from ref. 43 with permission from John Wiley & Sons, Inc.

In order to verify the resistive switching mechanism, CAFM was conducted to capture the ON and OFF states CAFM images using the diamond coated tip as electrode instead of Au BE (**Figure 5.8a**). DC voltage sweeping was applied to the Cu foil, and the diamond-coated tip was grounded. It showed typical hysteresis loop in the I-V curve at positive and negative voltage (**Figure 5.8b**). It is observed that there is no current change during the first voltage sweep 1 ($-2\text{V} \rightarrow 0\text{V}$), and the current abruptly increased at $\sim 1.3\text{V}$ during the second voltage sweep ($0 \rightarrow 3\text{V}$), indicating that the transition from high resistance to low resistance was related to Cu electrode. **Figure 5.8c** shows the three-dimensional (3D) image of CAFM scan, and the hBN-based memory was switched to OFF state. Here the reading voltage of 0.5V was used at the CAFM tip to prevent the

disturbance of switching state. It was clear that there was no obvious current signal in this image, indicating the memory was at high resistance state (**Figure 5.8c**). During the ON state, the CAFM current maps of the hBN-based memory were shown in **Figure 5.8d**. Current “spikes” which are distributed unevenly on the hBN film surface can be observed, indicating the presence of CFs in the hBN film. Moreover, for the region from 1.2 to 2.5 μm at the short edge (**Figure 5.8d**), it was non-switched surface without voltage bias applied before reading its state. There was no (or very low) leakage current in the CAFM image (**Figure 5.8d**), indicating the relatively good quality ultra-thin hBN film is beneficial to resistive switching memory in CMOS.^[52] Therefore, from this CAFM study, it is concluded that the switching mechanism is due to the formation/rupture of CFs which composed of active Cu element,^[51] which supports well the filament model as switching mechanism of resistive memory.

Figure 5.8 (a) CAFM measurement and (b) I-V characteristic with a device configuration of diamond-coated tip/hBN/Cu foil device. The voltage sweep was $-2\text{V} \rightarrow 3\text{V} \rightarrow -2\text{V}$. (c) CAFM current maps of hBN-based memory at OFF state and (d) ON state with a 0.5V reading voltage, respectively. For (d), the region from 1.2 to 2.5 μm at the short edge, it was non-switched surface, and there was no voltage bias applied before reading its state.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

5.3.7 *ex-situ* TEM characterization of Ag TE/hBN/Cu foil devices

Figure 5.9 Observation of the conducting filaments in the same Ag TE/hBN/Cu foil device at ON state. (a) TEM image of a complete conducting filament. The thinnest region of the filament is at the hBN/Cu foil interface. (b) STEM image of the ON-state sample, and the regions for EDS analyses are denoted by red circles. (c) EDS spectrum collected from the circle region "1" in the filament. (d) TEM image of a conducting filament which is not in complete contact with the Cu BE in the same device. (e) High resolution TEM image of Ag conducting filament corresponding to (d). (f) High resolution TEM image of non-complete Ag conducting filament (highlighted by the closed region), which clearly indicates the Ag filament starts growing from Ag TE. (g-i) Schematics of the filament growth for hBN-based resistive memory.^[43] Adapted from ref. 43 with permission from John Wiley & Sons, Inc.

In the Ag TE/hBN/Cu BE memory device, both the Ag and Cu electrodes are active electrode, which all can form the CFs.^[50] However, the filament composition and growth direction in the Ag TE/hBN/Cu BE memory device cannot be determined by CAFM, therefore, the cross sectional TEM was necessary tool to verify the resistive switching mechanism. Prior to TEM, a Ag TE/hBN/Cu BE memory cell with $\sim 200\ \mu\text{m}$ diameter was set to the ON-state with positive voltage on the Ag electrode through three repetitive switching cycles. At this point, a TEM specimen (ON-state sample, width: $\sim 15\ \mu\text{m}$, depth: $\sim 10\ \mu\text{m}$, thickness: $\sim 100\ \text{nm}$) was prepared by using a dual-beam FIB. **Figure 5.9** shows the cross-sectional TEM image of this ON state specimen. Indeed, images taken after the SET operation clearly revealed a well-defined conducting filament (highlighted by the dash dot line in **Figure 5.9a**, d with a typical conical shape. And the filament bridges the Ag TE and the Cu foil BE across the hBN layer, which is localized with wider base near the Ag TE and thinner part near the Cu foil BE (**Figure 5.9a**). To investigate this further, the chemical composition of the conducting filament was characterized by EDS compositional analysis in scanning TEM (STEM) mode. As shown in **Figure 5.9c**, the Ag element concentration in the middle of hBN film is much larger (circle region labeled “1” in **Figure 5.9b**). Note that the EDS intensity associated with elemental Cu includes the distribution from the Cu TEM grid supporting the sample and Cu foil bottom electrode.

To further study the composition of the CF, a HRTEM was used to analyze the non-complete CF in the same ON state memory cell (**Figure 5.9e**, corresponding to **Figure 5.9d**). At the wider base, it is clear the filament has the same lattice fringes with the Ag TE, and the lattice fringes in the filament grow along the one in the Ag TE (**Figure 5.9e**, the region indicated by the right two long red lines). In addition, **Figure 5.9e** clearly shows d-spacing of 0.23 and 0.20 nm measured in the TE region, corresponding to the Ag (111) and Ag (200) plane, respectively. **Figure 5.9e** also shows d-spacing of 0.20 nm measured in the CF region, corresponding to the Ag (200) plane. These results suggest that Ag is the primary elemental component of the CF in the Ag/hBN/Cu foil memory device. More importantly, as shown in **Figure 5.9f**, it is clear that the non-complete filament (highlighted by the closed region) starts growing from the active Ag TE instead,

and the observed CF shape also was different from the conventional ECM theory.^[6] In this ECM theory, a key hypothesis is that the M^{z+} will be reduced to M atoms at the cathode which has enough electrons, and cannot capture electrons for reduction during the drift process in the switching layer, which is reasonable for traditional solid state electrolyte materials with high solubility and diffusion coefficients of the M^{z+} (Ag^+ or Cu^{2+}).^[53] For this ECM theory, it has been confirmed by visual evidence, such as in the $Ag/H_2O/Pt$ and $Ag/SiO_2/Pt$ structure.^[54, 55] However, for those switching materials which offer lower cation mobility, the phenomena of the filament growth from the anode to the cathode also has been demonstrated in the $Cu/ZrO_2/Pt$ and $Ag/amorphous\ Si/Pt$ memory devices.^[50, 53, 54] Here for the $Ag\ TE/hBN/Cu$ foil device, the hBN film may offer much lower Ag^+ ions mobility than those of traditional solid-state electrolytes. Therefore, the Ag^+ cations may only travel a short distance before they are reduced back to Ag atoms inside hBN film by capturing the free electrons injected from Cu foil cathode, as shown in **Figure 5.9f**. In fact, even for switching materials with high cation mobility, the electronic current is still the main component of the programming current instead of the ionic current,^[56] so it is clearly possible for the cation reduction in hBN through the ample electron injected from Cu foil BE.

Based on the above analysis, the CF growth process in the hBN-based memory is illustrated in **Figure 5.9g-i** which can be depicted as follows. When a forward bias is applied to the active Ag TE, the Ag atoms undergo oxidation to form Ag^+ ions (**Figure 5.9g**). The Ag^+ ions are then migrated to the Cu foil cathode under the electric field. However, due to the low cation mobility that the hBN film offers, the Ag^+ ions may only travel a short distance before they are reduced to Ag atoms by capturing the free electrons injected from Cu foil cathode (**Figure 5.9f** and **h**). These Ag clusters then behave as bipolar electrodes during the subsequent filament growth and follow the splitting and merging processes,^[50] leading to the clusters migration to the Cu foil cathode (**Figure 5.9h**). As this oxidation/reduction processes continue, the Ag filaments will gradually grow from the Ag anode to the Cu foil cathode (**Figure 5.9d** and **i**) until it reaches the cathode, switching the memory to ON state (**Figure 5.9a**, and **Figure 5.1d**, SET). It should be noted that the synthesis of hBN films by CVD on polycrystalline Cu substrates

often leads to the formation of many grain boundaries or other defects.^[40, 57] Therefore, the CF may grow along the hBN domain grain boundaries or other defective sites where the filament concentrates easily.^[58-60] During the RESET process, when reverse bias was applied on the Ag TE, the CF will dissolve at the thinnest part near the hBN/Cu foil BE interface. Because when RESET voltage is applied, the thinnest part of filament suffers a drastic voltage drop,^[55] and the neck region has the highest current density resulting in high temperature to accelerate the oxidation reaction,^[53] leading to the CF first rupture near the cathode. In this case, the device will be switched back to the OFF-state (**Figure 5.1d**, RESET).

5.3.8 Bending stability evaluation on the Ag TE/hBN/Cu foil devices

Figure 5.10 Characteristics of the flexible Ag TE/hBN/Cu foil on polyimide substrate (200 μm thick) memory device. (a) Illustration of 1 cycle during the bending test with bending radius $r=7$ mm, and the measured devices were near the middle of the sample. (b) Continuous bending experiment of the hBN-based device. The reading voltage is 0.1V.^[43] Reproduced from ref. 43 with permission from John Wiley & Sons, Inc.

In order to confirm the feasibility of the hBN-based device for flexible memory application, bending tests were carried out under repeated cycles (750 times) as shown in **Figure 5.10** a and b. It is observed that the ON/OFF ratios did not change much (**Figure 5.10d**) when a bending radius (r) of 7 mm was applied to the devices. Especially, compared to the flexible a-Si-based ReRAM device which only exhibited ~ 200 bending cycles (bending radius, $r=10$ mm) due to the low failure strain of a-Si film (**Figure 4.13**, **Chapter 4**), the Ag TE/hBN/Cu foil device showed excellent bending stability and has a great potential in the future flexible nonvolatile memory application.

Figure 5.11 (a) SEM image of the Ag electrode/hBN/Cu foil on polyimide (200 μm thick) substrate after 750 bending cycles with bend radius $r=7$ mm. (b) SEM image of the hBN film, corresponding to the region marked in (a).

As shown in **Figure 5.11a**, after 750 repeated bending cycles, part of the Ag electrodes detached from the hBN film, leading to the failure of the Ag electrode/hBN/Cu foil memory devices. However, due to the large failure strain of the hBN film, there was no crack in the hBN switching layer (**Figure 5.11b**), indicating a promising application of 2D hBN material for future flexible electronics.

5.4 Chapter Summary

In summary, here a layered 2D material was introduced for creating flexible resistive switching memory devices with the configuration of Ag TE/hBN/Cu foil, which features excellent performances in terms of retention time, write cycles and bending endurance. The underlying mechanism is the formation/rupture of Ag filament that commences its growth from the anode (Ag TE) with narrowest region near the hBN/Cu foil BE interface *via ex-situ* TEM. This phenomenon, which is different from the traditional ECM theory, results from the low cation mobility offered by the hBN thin film. This study deepens and broadens the understanding of the switching mechanism in filament-based resistive memories and exploits 2D materials for use as resistive memory device in future computing systems.

References

- [1] T. Sekitani, T. Yokota, U. Zschieschang, H. Klauk, S. Bauer, K. Takeuchi, M. Takamiya, T. Sakurai, T. Someya, *Science* **2009**, 326, 1516-1519.
- [2] T. Sekitani, U. Zschieschang, H. Klauk, T. Someya, *Nat. Mater.* **2010**, 9, 1015-1022.
- [3] C. Y. Yan, J. X. Wang, W. B. Kang, M. Q. Cui, X. Wang, C. Y. Foo, K. J. Chee, P. S. Lee, *Adv. Mater.* **2014**, 26, 2022-2027.
- [4] C. Y. Yan, W. B. Kang, J. X. Wang, M. Q. Cui, X. Wang, C. Y. Foo, K. J. Chee, P. S. Lee, *ACS Nano* **2014**, 8, 316-322.
- [5] J. J. S. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nanotechnol.* **2013**, 8, 13-24.
- [6] R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* **2009**, 21, 2632-2663.
- [7] J. J. Yang, M. D. Pickett, X. M. Li, D. A. A. Ohlberg, D. R. Stewart, R. S. Williams, *Nat. Nanotechnol.* **2008**, 3, 429-433.
- [8] Y. Ji, D. F. Zeigler, D. S. Lee, H. Choi, A. K. Y. Jen, H. C. Ko, T. W. Kim, *Nat. Commun.* **2013**, 4, 2707.
- [9] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, *Nat. Mater.* **2015**, 14, 199-204.
- [10] J. Q. Liu, Z. Y. Yin, X. H. Cao, F. Zhao, L. H. Wang, W. Huang, H. Zhang, *Adv. Mater.* **2013**, 25, 233-238.
- [11] F. Pan, S. Gao, C. Chen, C. Song, F. Zeng, *Mater. Sci. Eng., R* **2014**, 83, 1-59.
- [12] Y. C. Lai, F. C. Hsu, J. Y. Chen, J. H. He, T. C. Chang, Y. P. Hsieh, T. Y. Lin, Y. J. Yang, Y. F. Chen, *Adv. Mater.* **2013**, 25, 2733-2739.
- [13] Y. C. Lai, Y. X. Wang, Y. C. Huang, T. Y. Lin, Y. P. Hsieh, Y. J. Yang, Y. F. Chen, *Adv. Funct. Mater.* **2014**, 24, 1430-1438.
- [14] Y. C. Lai, Y. C. Huang, T. Y. Lin, Y. X. Wang, C. Y. Chang, Y. X. Li, T. Y. Lin, B. W. Ye, Y. P. Hsieh, W. F. Su, Y. J. Yang, Y. F. Chen, *Npg Asia Mater.* **2014**, 6, e87.
- [15] J. T. Wang, K. Saito, H. C. Wu, H. S. Sun, C. C. Hung, Y. G. Chen, T. Isono, T. Kakuchi, T. Satoh, W. C. Chen, *Npg Asia Mater.* **2016**, 8, e298.
- [16] S. Menzel, M. Waters, A. Marchewka, U. Bottger, R. Dittmann, R. Waser, *Adv. Funct. Mater.* **2011**, 21, 4487-4492.

- [17] Y. Yang, G. Yuan, Z. Yan, Y. Wang, X. Lu, J. M. Liu, *Adv. Mater.* **2017**, 29, 1700425.
- [18] M. Fang, J. H. Chen, X. L. Xu, P. H. Yang, H. F. Hildebrand, *Int. J. Antimicrob. Agents* **2006**, 27, 513-517.
- [19] J. Shang, W. H. Xue, Z. H. Ji, G. Liu, X. H. Niu, X. H. Yi, L. Pan, Q. F. Zhan, X. H. Xu, R. W. Li, *Nanoscale* **2017**, 9, 7037-7046.
- [20] D. Son, J. Lee, S. Qiao, R. Ghaffari, J. Kim, J. E. Lee, C. Song, S. J. Kim, D. J. Lee, S. W. Jun, S. Yang, M. Park, J. Shin, K. Do, M. Lee, K. Kang, C. S. Hwang, N. S. Lu, T. Hyeon, D. H. Kim, *Nat. Nanotechnol.* **2014**, 9, 397-404.
- [21] G. H. Lee, Y. J. Yu, X. Cui, N. Petrone, C. H. Lee, M. S. Choi, D. Y. Lee, C. Lee, W. J. Yoo, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, J. Hone, *ACS Nano* **2013**, 7, 7931-7936.
- [22] G. Shi, Y. Hanlumuayang, Z. Liu, Y. J. Gong, W. L. Gao, B. Li, J. Kono, J. Lou, R. Vajtai, P. Sharma, P. M. Ajayan, *Nano Lett.* **2014**, 14, 1739-1744.
- [23] M. F. El-Kady, V. Strong, S. Dubin, R. B. Kaner, *Science* **2012**, 335, 1326-1330.
- [24] T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y. J. Kim, A. Gholinia, S. J. Haigh, O. Makarovskiy, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, A. Mishchenko, *Nat. Nanotechnol.* **2013**, 8, 100-103.
- [25] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science* **2008**, 321, 385-388.
- [26] S. Bertolazzi, J. Brivio, A. Kis, *ACS Nano* **2011**, 5, 9703-9709.
- [27] D. I. Son, T. W. Kim, J. H. Shim, J. H. Jung, D. U. Lee, J. M. Lee, W. I. Park, W. K. Choi, *Nano Lett.* **2010**, 10, 2441-2447.
- [28] P. F. Cheng, K. Sun, Y. H. Hu, *Nano Lett.* **2016**, 16, 572-576.
- [29] C. B. Pan, Y. F. Ji, N. Xiao, F. Hui, K. C. Tang, Y. Z. Guo, X. M. Xie, F. M. Puglisi, L. Larcher, E. Miranda, L. L. Jiang, Y. Y. Shi, I. Valov, P. C. McIntyre, R. Waser, M. Lanza, *Adv. Funct. Mater.* **2017**, 27, 1604811.
- [30] L. Liang, K. Li, C. Xiao, S. J. Fan, J. Liu, W. S. Zhang, W. H. Xu, W. Tong, J. Y. Liao, Y. Y. Zhou, B. J. Ye, Y. Xie, *J. Am. Chem. Soc.* **2015**, 137, 3102-3108.
- [31] F. Zhuge, B. L. Hu, C. L. He, X. F. Zhou, Z. P. Liu, R. W. Li, *Carbon* **2011**, 49, 3796-3802.

- [32] C. L. He, F. Zhuge, X. F. Zhou, M. Li, G. C. Zhou, Y. W. Liu, J. Z. Wang, B. Chen, W. J. Su, Z. P. Liu, Y. H. Wu, P. Cui, R. W. Li, *Appl. Phys. Lett.* **2009**, 95, 232101.
- [33] S. Park, J. Lee, H. S. Kim, J. B. Park, K. H. Lee, S. A. Han, S. Hwang, S. W. Kim, H. J. Shin, *ACS Nano* **2015**, 9, 633-638.
- [34] S. A. Han, K. H. Lee, T. H. Kim, W. Seung, S. K. Lee, S. Choi, B. Kumar, R. Bhatia, H. J. Shin, W. J. Lee, S. Kim, H. S. Kim, J. Y. Choi, S. W. Kim, *Nano Energy* **2015**, 12, 556-566.
- [35] K. H. Lee, H. J. Shin, J. Lee, I. Y. Lee, G. H. Kim, J. Y. Choi, S. W. Kim, *Nano Lett.* **2012**, 12, 714-718.
- [36] H. Wang, F. C. Liu, W. Fu, Z. Y. Fang, W. Zhou, Z. Liu, *Nanoscale* **2014**, 6, 12250-12272.
- [37] Z. Liu, L. Song, S. Z. Zhao, J. Q. Huang, L. L. Ma, J. N. Zhang, J. Lou, P. M. Ajayan, *Nano Lett.* **2011**, 11, 2032-2037.
- [38] L. Song, L. J. Ci, H. Lu, P. B. Sorokin, C. H. Jin, J. Ni, A. G. Kvashnin, D. G. Kvashnin, J. Lou, B. I. Yakobson, P. M. Ajayan, *Nano Lett.* **2010**, 10, 3209-3215.
- [39] J. T. Wu, B. L. Wang, Y. J. Wei, R. G. Yang, M. Dresselhaus, *Mater. Res. Lett.* **2013**, 1, 200-206.
- [40] R. Y. Tay, M. H. Griep, G. Mallick, S. H. Tsang, R. S. Singh, T. Tumlin, E. H. T. Teo, S. P. Karna, *Nano Lett.* **2014**, 14, 839-846.
- [41] R. Y. Tay, X. L. Wang, S. H. Tsang, G. C. Loh, R. S. Singh, H. Li, G. Mallick, E. H. T. Teo, *J. Mater. Chem. C* **2014**, 2, 1650-1657.
- [42] X. S. Li, Y. W. Zhu, W. W. Cai, M. Borysiak, B. Y. Han, D. Chen, R. D. Piner, L. Colombo, R. S. Ruoff, *Nano Lett.* **2009**, 9, 4359-4363.
- [43] K. Qian, R. Y. Tay, V. C. Nguyen, J. X. Wang, G. F. Cai, T. P. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.
- [44] K. S. Park, D. Y. Lee, K. J. Kim, D. W. Moon, *Appl. Phys. Lett.* **1997**, 70, 315-317.
- [45] D. D. Shao, J. X. Li, X. L. Tan, Z. S. Yang, K. Okuno, Y. Oya, *J. Nucl. Mater.* **2015**, 457, 118-123.
- [46] J. S. Park, J. M. Lee, S. K. Hwang, S. H. Lee, H. J. Lee, B. R. Lee, H. I. Park, J. S. Kim, S. Yoo, M. H. Song, S. O. Kim, *J. Mater. Chem.* **2012**, 22, 12695-12700.

- [47] Z. Liu, Y. J. Gong, W. Zhou, L. L. Ma, J. J. Yu, J. C. Idrobo, J. Jung, A. H. MacDonald, R. Vajtai, J. Lou, P. M. Ajayan, *Nat. Commun.* **2013**, 4, 2541.
- [48] M. C. Biesinger, L. W. M. Lau, A. R. Gerson, R. S. C. Smart, *Appl. Surf. Sci.* **2010**, 257, 887-898.
- [49] H. B. Lv, M. Wang, H. J. Wan, Y. L. Song, W. J. Luo, P. Zhou, T. G. Tang, Y. Y. Lin, R. Huang, S. Song, J. G. Wu, H. M. Wu, M. H. Chi, *Appl. Phys. Lett.* **2009**, 94, 213502.
- [50] Y. C. Yang, P. Gao, L. Z. Li, X. Q. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, 5, 4232.
- [51] S. J. Choi, G. S. Park, K. H. Kim, S. Cho, W. Y. Yang, X. S. Li, J. H. Moon, K. J. Lee, K. Kim, *Adv. Mater.* **2011**, 23, 3272-3277.
- [52] D. S. Jeong, R. Thomas, R. S. Katiyar, J. F. Scott, H. Kohlstedt, A. Petraru, C. S. Hwang, *Rep. Prog. Phys.* **2012**, 75, 076502.
- [53] Q. Liu, J. Sun, H. B. Lv, S. B. Long, K. B. Yin, N. Wan, Y. T. Li, L. T. Sun, M. Liu, *Adv. Mater.* **2012**, 24, 1844-1849.
- [54] Y. C. Yang, P. Gao, S. Gaba, T. Chang, X. Q. Pan, W. Lu, *Nat. Commun.* **2012**, 3, 732.
- [55] X. Guo, C. Schindler, *Appl. Phys. Lett.* **2007**, 91, 133513.
- [56] C. Schindler, I. Valov, R. Waser, *Phys. Chem. Chem. Phys.* **2009**, 11, 5974-5979.
- [57] K. K. Kim, A. Hsu, X. Jia, S. M. Kim, Y. Shi, M. Hofmann, D. Nezich, J. F. Rodriguez-Nieva, M. Dresselhaus, T. Palacios, J. Kong, *Nano Lett.* **2012**, 12, 161-166.
- [58] M. J. Lee, S. Han, S. H. Jeon, B. H. Park, B. S. Kang, S. E. Ahn, K. H. Kim, C. B. Lee, C. J. Kim, I. K. Yoo, D. H. Seo, X. S. Li, J. B. Park, J. H. Lee, Y. Park, *Nano Lett.* **2009**, 9, 1476-1481.
- [59] J. Y. Son, Y. H. Shin, *Appl. Phys. Lett.* **2008**, 92, 222106.
- [60] G. Bersuker, D. C. Gilmer, D. Veksler, J. Yum, H. Park, S. Lian, L. Vandelli, A. Padovani, L. Larcher, K. McKenna, A. Shluger, V. Iglesias, M. Porti, M. Nafria, W. Taylor, P. D. Kirsch, R. Jammy, *IEDM Tech. Dig.* **2010**, 456-459.

Chapter 6*

Flexible, Transparent, and Transferable ECM-based ReRAM from Hexagonal Boron Nitride and Graphene

Electronics with multi-functionalities such as transparency, portability, and flexibility are anticipated for future circuitry development. Flexible memory is one of the indispensable elements in hybrid electronics integrated circuit as the information storage device. Herein, a transparent, flexible, and transferable hexagonal boron nitride (hBN)-based resistive switching memories with indium tin oxide (ITO) and graphene electrodes was demonstrated on soft polydimethylsiloxane (PDMS) substrate. The ITO/hBN/graphene/PDMS memory device not only exhibits excellent performances in terms of optical transmittance ($\sim 85\%$ in the visible length), ON/OFF ratio (~ 400), retention time ($\sim 5 \times 10^4$ s), but also shows robust flexibility under bending conditions and stable operation on arbitrary substrates. More importantly, direct observation of indium filaments in ITO/hBN/graphene device is found for the first time via ex-situ transmission electron microscopy (TEM), which broadens the understanding of the resistive switching mechanisms in the electrochemical metallization (ECM)-based resistive switching random access memory (ReRAM).

This section published substantially as “Kai Qian, Roland Yingjie Tay, Mengfang Lin, Jingwei Chen, Huakai Li, Jinjun Lin, Jiangxin Wang, Guofa Cai, Viet Cuong Nguyen, Edwin Hang Tong Teo, Tupei Chen, and Pooi See Lee, ACS Nano, **2017**, *11*, 1712-1718.”

6.1 Introduction

Electronic modules have been going through extensive innovations to meet the ever-increasing technological demands with multiple functionalities, such as flexibility, transparency, and portability.^[1] Most electronic devices are fabricated on conventional substrates (*e.g.* flat, rigid and smooth SiO₂/Si and plastics) due to the well-established semiconducting fabrication processes and difficult handling requirements on arbitrary non-conventional substrates (*e.g.* soft or nonplanar ones).^[2, 3] Recent progress has been made to construct transparent flexible electronic devices in various areas, such as transistors,^[4, 5] charge-trap memory,^[6] photodetector,^[7, 8] electrochromics,^[9, 10] and triboelectric nanogenerator.^[11] With the growing interest in the field of flexible or implantable electronics applications on non-conventional substrates, it is an urgent task to establish fabrication strategies for functional electronics on desired arbitrary substrates.^[1, 12, 13] Resistive random access memory (ReRAM), which can store and process information, is considered one of the most promising candidates for next generation memory due to its excellent storage capability and scalability.^[14-18] Therefore, efforts to obtain multi-functional ReRAM have also aroused great interest.^[3, 19-25]

The use of two-dimensional (2D) materials (*e.g.* WO₃·H₂O, and MoO_x) in flexible ReRAM devices has the potential to outperform conventional oxides in terms of bending stability (refer to **Table 2.4, Chapter2**).^[17, 26-28] The 2D hBN-based flexible ReRAM devices were also demonstrated in **Chapter 4**, which also exhibited excellent performances in terms of bending stability and switching endurance. Besides of the excellent mechanical properties of these 2D materials, their other fascinating properties (*e.g.* high transparency)^[4, 17, 29-31] will also offer a new opportunity for the development of future multi-functional electronics. For example, Lee *et al.* reported a 2D materials-based transistor with graphene electrodes, MoS₂ channels, and hBN dielectric.^[29] The MoS₂-based transistor exhibited highly flexible due to the excellent mechanical properties of 2D materials (*e.g.*, elastic constant of 180±60 N m⁻¹ and breaking strength of 15±3 N m⁻¹ (23±4.6 GPa) for MoS₂)^[32] and transparent with ~ 80 % transmittance in the visible region due to the low absorption of each material (2-5 % for monolayer MoS₂).^[29]

negligible for hBN in visible range,^[33] and 2.3% per graphene layer^[34]). In addition, graphene, an excellent choice as electrode for wearable electronics due to its excellent mechanical properties (elastic constant of 340 N m^{-1} , and breaking strength of 42 N m^{-1} (125.3 GPa)),^[35-38] it can be efficiently transferred to other arbitrary substrates with large area after removal of the supporting metal.^[3, 39] For example, Lai *et al.* presented a transferable macromolecular memory with CVD grown-graphene electrode on arbitrary substrates after removal of the Cu foil, such as a medical wristband, glove, and cylindrical vial substrate.^[3] Thus, it is rational to suggest that 2D materials would be an attractive solution for multi-functional ReRAM applications.

In order to obtain excellent memory performances, a thorough understanding of the switching mechanism is necessary to effectively control the switching characteristics.^[14, 16-18, 40] For the transparent ReRAM devices with indium tin oxide (ITO) electrodes, the resistive switching behaviors were always associated with the oxygen ions migration mechanism or other switching mechanisms, which are not related to the migration of ITO electrodes.^[41-45] For instance, in the transparent ITO/HfO_x/ITO ReRAM device, the formation/annihilation of the metallic hafnium-rich filament due to the oxygen ions migration under an electric field was responsible for the bipolar resistive switching.^[43] For the transparent ITO/AlN/ITO ReRAM device, the electron trapping and detrapping processes in the AlN switching layer-related electron traps were thought to account for the bipolar resistive switching.^[46]

However, the ITO based device, which can serve as both conducting electrode and switching active material, can also exhibit resistive switching behaviors due to the oxygen ions migration induced by the electric field.^[47] Therefore, to confirm the role of ITO electrodes in ReRAM devices, microscopic experiments that can provide the direct observation of the resulting physical and chemical changes are essential to thoroughly understand the resistive switching mechanism. In order to exclude the influence of oxygen present in the active layer, selecting the active materials without oxygen is necessary, such as the 2D hBN material.

Herein, a novel flexible, transparent, and transferable ReRAM device based on ultrathin hBN (≈ 5 nm) switching layer with ITO top electrode (TE) and few-layer graphene (FLG) bottom electrode (BE) was demonstrated on a soft polydimethylsiloxane (PDMS) substrate (**Figure 6.1d**). The as-fabricated ITO/hBN/FLG/PDMS memory device featured high transmittance of $\sim 85\%$ in the visible region, long retention time ($\sim 5 \times 10^4$ s), stable memory characteristics ($R_{\text{OFF}}/R_{\text{ON}}$ ratio ~ 400) on different substrates, and reliable flexibility after substrate deformation. More importantly, the direct observation of indium (In) filaments is reported for the first time via ex-situ transmission electron microscopy (TEM) to account for the stable resistive switching of the ITO/hBN/FLG/PDMS memory device. This new finding undoubtedly contributes to the understanding of the switching mechanism in 2D materials for the rapid development of ReRAM.

6.2 Experimental Methods

6.2.1 hBN film preparation

hBN films with thickness ~ 5 nm were grown by chemical vapor deposition (CVD) on Cu substrates as reported previously.^[17, 48, 49] Detailed preparation on h-BN films can be found in **Chapter 3**.

6.2.2 PDMS substrate preparation

The PDMS substrate was fabricated by mixing the PDMS curer and base (Sylgard 184, Dow Corning, USA) at a weight ratio of 1/10, which was then diluted with n-hexane and poured into a glass petri dish. Finally, the solidified PDMS substrate was peeled off from the petri dish after curing at 80°C for 2 hours. The PDMS substrate thickness was about ~ 220 μm .

6.2.3 Flexible, transparent, and transferable multi-functional ECM-based ReRAM devices fabrication

A conventional wet transfer approach was employed to transfer hBN and graphene films from Cu foil substrate to other foreign substrates.^[50] The device structure (**Figure 6.1d**) was composed of an ITO TE, chemical vapor deposition (CVD)-grown hBN switching layer,^[17] and a few-layer graphene film (Graphenea, Spain) bottom electrode. ITO TE with ~ 250 μm diameter was deposited onto the hBN switching layer with a hard shadow mask without annealing process. The resistance of the ITO electrode is about ~ 600 - 800 Ω . The ITO TE/hBN/graphene memory device can be transferred to different substrates, such as PDMS (**Figure 6.1d**) and PET (polyethylene terephthalate) (**Figure 6.3b**). Detailed transfer process of hBN and graphene films and ReRAM devices fabrication can be found in **Chapter 3**.

Figure 6.1 (a) Schematic of the ITO TE/hBN/FLG memory device fabrication process on any desired substrate. Chemical structures of (b) graphene and (c) hBN for bottom electrode and switching layer, respectively. (d) Schematic of ITO TE/hBN/FLG device on soft PDMS substrate. (e) Optical transmittance of ITO TE/hBN/FLG/PDMS device. The inset shows the actual memory device, indicating transparent characteristics.^[51] Reproduced from ref. 51 with permission from the American Chemical Society.

Figure 6.1a illustrated the schematic fabrication processes of the transparent, flexible, and transferable ITO TE /hBN/ few layer graphene (FLG) memory device. In short, a layer of poly(methyl methacrylate) (PMMA) was first coated on the chemical vapor deposition (CVD)-hBN film, which was then transferred on graphene/copper (Cu) foil substrate via a conventional wet transfer approach.^[17] Subsequently, another layer of PMMA was coated on hBN/graphene/Cu foil. Then, the PMMA/hBN/graphene can be easily transferred to any desired substrates after the Cu foil was etched away using ammonia persulfate (APS) solution. Finally, after removal of the PMMA layer using acetone, the ITO was deposited on the hBN/graphene film as the TE (**Figure 6.1d**).

To meet the high transparency of the memory device without sacrificing the electrical conductivity of graphene bottom electrode during the transfer process, few-layer graphene was employed to construct ITO TE/hBN/FLG on soft PDMS or flexible ITO/PET (**Figure 6.3a, b**) substrates for the electrical switching behaviors measurement. This as-fabricated ITO TE/hBN/FLG/PDMS memory device shows good transmittance of ~85% over the visible wavelength range (**Figure 6.1e**).

6.2.4 Characterization

The transmission spectra of the device were measured over the wavelength range from 300 to 900 nm with UV-Vis-NIR spectrometer (Cary 5000 and DRA 2500, Agilent Technologies). Electrical characterizations were conducted via Keithley 4200 semiconductor analyzer at a DC voltage sweep rate of 0.01V/s. The ON state resistive memory sample for TEM observation was prepared via a dual beam FIB (FEI Helios 450S). JEOL JEM-2100 electron microscope (200 kV) and JEOL JED 2300T EDS were employed for TEM/EDS analyses, respectively.

6.3 Results and Discussion

6.3.1 Electrical performance evaluation of ITO TE/hBN/FLG/PDMS memory

Figure 6.2 Electrical properties of the ITO TE/hBN/FLG/PDMS device. (a) A typical electroforming process with voltage of ~ 7.4 V in an ITO TE/hBN/ FLG /PDMS memory device. (b) I-V characteristics after electroforming process. (c) 500 memory cycles and (d) $\sim 5 \times 10^4$ s retention time from the memory device on flat condition, respectively. The readout voltage is + 0.1 V.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

The electrical performances of the ITO TE/hBN/FLG/PDMS device were conducted both on flat condition. To avoid damaging the graphene BE when the electrical probe approached during measurement, a contact ITO thin film was pre-deposited to partially contact with the graphene BE on PDMS substrate. **Figure 6.2b** showed the current-voltage (I-V) curve from the ITO TE /hBN/FLG/PDMS device after the initial electroforming process with a relatively high voltage of ~ 7.4 V (**Figure 6.2a**). Application of a positive voltage on ITO TE switched the memory device from OFF state (i.e. high resistance) to ON state (i.e. low resistance) at ~ 0.66 V, which was defined as SET process. Afterward, the device returned to OFF state when a reverse bias (~ -0.9 V) was applied, which was called RESET process. The ITO TE /hBN/FLG memory device

exhibited bipolar switching mode and an acceptable ON/OFF ratio above ~ 400 . Furthermore, the other electrical switching behaviors were also investigated using the reading voltage of 0.1 V, such as write cycles and retention time. The ON and OFF states of the devices were demonstrated with steady operation during the 500 write cycles (**Figure 6.2c**), showing no noticeable degradation after 5×10^3 s (**Figure 6.2d**). For the Ag TE/hBN/Cu foil memory devices in **Chapter 5**, their SET/RESET voltage, retention time, switching endurance, and memory window was $\sim 0.72/-0.37$ V, ~ 3500 s, ~ 550 cycles, and ~ 155 , respectively. For these two different hBN-based memory devices, they exhibited the same order of magnitude in terms of the electrical performances, despite that the different quality of the different batch of hBN film, the random formation/rupture of filaments, both of these factors will affect the electrical performances of the memory devices.

6.3.2 Transferability demonstration of hBN-based memory devices on ITO/PET substrate

Figure 6.3 (a) The transferred hBN film with PMMA onto ITO/PET substrate. (b) Transparent and flexible ITO/hBN/ITO/PET memory device. (c) Initial electroforming process for ITO TE/hBN/ITO/PET memory device with voltage of ~ 8.3 V. (d) Switching characteristics of ITO TE/hBN/ITO/PET memory device after electroforming process.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

In order to demonstrate the transferability hBN-based memory device, ITO TE /hBN/ITO/PET memory device was demonstrated. As shown in **Figure 6.3a**, the hBN film with PMMA was transferred onto ITO/PET substrate. After removal of PMMA using acetone, ITO top electrode was deposited on the hBN/ITO/PET to construct transparent and flexible ITO/hBN/ITO/PET memory device (**Figure 6.3a**). Compared with ITO TE /hBN/FLG/PDMS device, the ITO/hBN/ITO/PET memory device also exhibited similar switching behaviors (**Figure 6.3c** and d). For the ITO TE/hBN/ITO/PET device which only needs one time transfer process for hBN film, the device yield is ~40%. For the ITO TE/hBN/FLG/PDMS which needs two times transfer processes for hBN and graphene film, the device yield is ~15%.

6.3.3 Bending stability evaluation of ITO TE/hBN/FLG/PDMS device

Figure 6.4 (a, b) Illustration of 1 cycle bend test with bending radius of 14 mm. (c) Retention of the ON and OFF states during bending test. The inset showed the actual transparent flexible ITO TE/hBN/FLG/PDMS device on PET substrate. The readout voltage is + 0.1 V.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

To evaluate the feasibility of the ITO TE /hBN/FLG/PDMS (~220 μm thick) device on PET substrate (~100 μm thick) for flexible memory applications, the switching behaviors of the memory device were examined under bending condition ($r=14 \text{ mm}$, **Figure 6.4a**

and b). The memory window maintained 100X and did not change much during 850 times continuous bending cycles (**Figure 6.4d**), indicating excellent bending stability and a great potential for nonvolatile memory applications in transparent flexible electronics. For this work, due to the large thickness of the substrate ($\sim 320\ \mu\text{m}$ thick) and the brittle nature of the ITO electrode which is easy to break under large strain, the large bending radius was adopted here. For the flexible Ag TE/hBN/Cu foil ($\sim 25\ \mu\text{m}$ thick)/polyimide ($\sim 220\ \mu\text{m}$) memory device in **Chapter 5**, it exhibited more excellent bending endurance (~ 750 cycles) with small bending radius ($r=7\ \text{mm}$) due to the large failure strain of hBN and excellent ductility of metal electrodes. Compared with the flexible Ag TE/hBN/Cu foil memory device in **Chapter 5**, more importantly, in this chapter, the flexible multi-functional ITO TE /hBN/FLG memory devices were realized with transparent ITO and graphene electrodes, which are transparent, transferable, and can conform to various objects with robust operation and reliable switching characteristics on arbitrary substrates (**Figure 6.5**).

6.3.4 Electrical performances evaluation of ITO TE/hBN/FLG/PDMS memory devices on different substrates

In order to broaden the memory device for more realistic applications, ITO TE /hBN/FLG/PDMS device was further characterized as a label on arbitrary surfaces. The corresponding I-V characteristics of these memory devices were conducted when it was tagged on different objects (**Figure 6.5**). Firstly, **Figure 6.5a** and **b** showed the I-V characteristics of the ITO TE /hBN/FLG/PDMS memory device labelled on different surfaces: a rough and soft wallet (flat surface, $r = \infty$, **Figure 6.5a**), and a centrifuge tube ($r \approx 8\text{mm}$, **Figure 6.5b**). As the voltage bias was applied, they exhibited similar switching behaviors. The results indicated that the ITO TE /hBN/MGL/PDMS device can function consistently on both planar and non-planar surfaces with stable switching properties. As shown in **Figure 6.5c**, the ITO TE /hBN/MGL/PDMS device was further demonstrated as on-skin label conforming to the back of the hand, which was still completely switchable and operated normally. These tests demonstrated that the ITO TE /hBN/FLG/PDMS memory device can conform to various objects with robust operation

and reliable switching characteristics on arbitrary substrates, promising an exciting opportunity for epidermal electronics applications.

Figure 6.5 Demonstration of the ITO TE /hBN/FLG/PDMS memory labels tagged on (a) a rough and soft wallet, (b) a centrifuge tube ($r \approx 8\text{mm}$), and (c) device attached onto fingers with their corresponding switching characteristics. The memory device is easy to attach onto various curved objects' surfaces and exhibits excellent flexibility.^[51] Reproduced from ref. 51 with permission from the American Chemical Society.

6.3.5 *ex-situ* TEM characterization of ITO TE/hBN/FLG/Cu foil at ON state

The switching mechanism is essential for the design of memory devices in terms of reproducibility and comprehensive modeling.^[18, 52] Understanding the switching behavior is thus of vital importance for device optimization. Therefore, to reveal the switching mechanism of ITO TE /hBN/FLG memory device, *ex-situ* TEM and EDS analyses were employed for further analyses. The ITO TE/hBN/FLG on Cu foil substrate was fabricated for the investigation of resistive switching mechanism. First, the specimen for TEM measurements was prepared via focused ion beam (FIB) after being subjected to more than 20 repetitive write cycles to ON state. As shown in **Figure 6.6a**, a non-complete conductive filament clearly starts growing from the ITO TE. In addition, there is a complete cone-shaped filament with a clearly different contrast from the background hBN/FLG film in the memory cell (**Figure 6.6b**). The hBN/FLG film has low contrast, while the conducting filament which has relative high contrast can be seen to clearly connect the ITO TE and graphene BE, leading to the memory cell to ON state.

Figure 6.6 Observation of conductive filaments in ITO TE /hBN/FLG/Cu foil memory cell at ON state. TEM images of (a) a non-complete and (b) a complete conducting filament in the same memory cell (highlighted by the closed regions), indicating the filament commences growth from ITO TE. (c) EDS elemental mapping result of the memory cell in STEM mode, corresponding to (b). (d) STEM image of the ITO TE /hBN/FLG device. (e) Line profile of the EDS intensity of Cu, In, and Sn elements along the red line in (a) from Cu foil to ITO TE. (f) EDS spectrum of the filament in region "1" of (d). The intensity of Cu, In, and Sn were shown in the insert table. It indicated the filament was primarily composed of In.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

Therefore, it is rationally concluded that the upper region separated by the white dash line was hBN switching layer where filaments existed, while the lower region was few-layer graphene BE. The thinnest region and wider base of the filament are located at the hBN/FLG interface and the ITO TE/hBN interface, respectively. To confirm the chemical composition of the complete filament, the EDS analysis was conducted in scanning TEM (STEM) mode. **Figure 6.6c** presented the filament EDS mapping result of the ITO TE /hBN/FLG/Cu foil memory cell, corresponding to **Figure 6.6b**. It is clear that the filament has an In-rich stoichiometry (**Figure 6.6c**), indicating the conducting filaments are primarily composed of In element in ITO TE /hBN/FLG memory device. Here in the ITO TE /hBN/FLG memory device, due to the low ion mobility the hBN film offered,^[17, 18] the conductive filaments started growing from the ITO anode (**Figure 6.6a**), leading to the inverted cone shaped Indium filament with wider base near the ITO TE/hBN interface

(**Figure 6.6b**). It exhibited the same phenomenon with the one in the Ag TE/hBN/Cu foil memory devices in **Chapter 5**. In the Ag TE/hBN/Cu foil device, the cone-shaped Ag filaments also commenced growing from the anode (Ag top electrode) with wider base near the Ag TE/hBN interface due to the low ion mobility the hBN film offered.

To further investigate the chemical composition of the conductive filaments, EDS profiling analysis was carried out along the filament (**Figure 6.6d** and **e**). Despite the semi-quantitative nature of EDS analysis, in the filament region (**Figure 6.6e**), it is clear that the In intensity was higher than tin (Sn) intensity. On the other hand, the filament composition was also further studied via EDS point analysis (circle region 1 in **Figure 6.6d**). As shown in **Figure 6.6f**, there was no Sn element in the filament which may be due to the low Sn content, indicating the filament is mainly consisted of In element. Therefore, the ITO electrode, which was similar to other active electrodes (*e.g.* Ag, Cu) in the RERAM, can also form the In conductive filaments upon applied high electric field. This finding is critically important for the deep understanding of the complex resistive switching mechanism in the transparent RERAM with ITO electrodes, which will be beneficial to the continued optimization of this important class of transparent memories. It is noteworthy that a higher electric field ($\sim 14.8 \text{ MV cm}^{-1}$) was required for the In evolution and migration in the hBN film during the electroforming process (**Figure 6.2a**). While in the Ag TE/hBN/FLG memory device, a lower electric field ($\sim 7 \text{ MV cm}^{-1}$) (**Figure 6.7a**) was required for the Ag movement due to the high electrochemical activity of Ag electrode.^[18] Moreover, in order to produce the indium ions, In-O bonds in the ITO electrode need to be broken with a high electric field, of which bond dissociation energy is $346 \pm 30 \text{ kJ/mol}$.^[53]

In addition, the Cu element intensity (**Figure 6.6f**) can be associated with the Cu foil and Cu TEM grid supporting the device. It is noteworthy that the Cu foil does not contribute the resistive switching, which was isolated by few-layer graphene BE. During the electroforming process, when a high positive voltage was applied on the graphene electrode (FLG/Cu electrode) while ITO was grounded, the ITO TE/hBN/FLG/Cu foil device did not show resistive switching (**Figure 6.7b**).

Figure 6.7 (a) Initial electroforming process of Ag TE/hBN/FLG/Cu foil memory device with voltage of ~ 3.5 V. (b) Initial electroforming process for ITO/hBN/FLG/Cu foil memory device. During the electroforming process, the positive voltage was applied on the graphene/Cu foil electrode, while the ITO electrode was grounded. It is clear that there was no resistive switching even with a high voltage, indicating the Cu foil which was isolated by few-layer graphene cannot contribute the resistive switching.^[51] Adapted from ref. 51 with permission from the American Chemical Society.

6.3.6 *ex-situ* TEM characterization of ITO TE/hBN/FLG/Cu foil at OFF state

The memory cell was reset to the OFF-state through more than 20 repetitive switching cycles for the *ex-situ* TEM measurements. **Figure 6.8a** showed a cross-sectional TEM image of the OFF-state sample after RESET process. The OFF-state filament (**Figure 6.8a**) with a wider base at the ITO/hBN interface and thinner part at the hBN/graphene interface is similar to the one at ON-state (**Figure 6.6b**). It is clear that the dissolution of the filament occurred at the hBN/graphene interface where the thinnest part of filament was, leading to the OFF state. To determine the nature of the ruptured filament, the filament composition was studied *via* EDS point analysis (region 1 in **Figure 6.8b**). As shown in **Figure 6.8c**, the detailed studies verified that the ruptured filament is mainly composed of In element.

Figure 6.8 Observation of conductive filaments in ITO TE /hBN/FLG/Cu foil memory cell at OFF state. (a) TEM image of a non-complete filament in the memory cell (highlighted by the closed regions), indicating the filament ruptured at the thinnest part of the filament at the hBN/graphene interface, leading to the OFF state. (b) STEM image of the ITO TE /hBN/FLG device, corresponding to (a). (c) EDS spectrum of the filament in region “1” of (b). (d-f) Schematic illustration of the In filament growth in the ITO TE /hBN/FLG memory device.^[51] Reproduced from ref. 51 with permission from the American Chemical Society.

On the basis of the above analysis, the indium filament growth process was illustrated in **Figure 6.8d-f** and depicted as follows. Upon forward bias applied on the ITO TE, the In-O bond was broken, and the In^{3+} ions migrated towards the cathode. Then these In^{3+} ions will be reduced to In atom to form the In nanoclusters and nucleate near the active ITO TE (**Figure 6.8d** and **Figure 6.6a**) due to the low ion mobility the hBN film offered.^[17, 18] These In clusters then behave as bipolar electrodes during the subsequent filament growth and follow the splitting to merging processes,^[18] leading to the clusters migration to the graphene cathode (**Figure 6.8e**). In addition, due to the high concentration of In^{3+} ions near the anode and therefore abundant In clusters will be nucleated near the ITO TE. With the repeated In clusters nucleation, migration inside hBN film, the conducting filament will gradually grow from the ITO TE to graphene bottom electrode (**Figure 6.8f**), leading to the formation of a cone shaped filament with its thinnest region at the hBN/graphene BE interface and switching the memory to ON state (**Figure 6.6b**). During the RESET process, due to the major voltage drop is located at the neck of the filament,^[54] the thinnest part of conductive filament with high current density at the

hBN/graphene interface (**Figure 6.8a**) will be first to dissolve upon reverse bias applied, leading to the OFF state.

Compared with the work (Ag TE/hBN/Cu foil) in **Chapter 5**, the ITO and graphene electrodes were used in this chapter to take place of the Ag and Cu electrodes, realizing the flexible, transparent, and portable multi-functional hBN-based ReRAM. In addition, the finding of the In filaments deserves the attention to confirm the actual switching mechanism in the transparent ReRAM devices with ITO electrodes for continued devices optimization. For example, in the transparent ITO/AlN/ITO memory device,^[46] it is possible that the formation/rupture of the In filaments would account for the bipolar resistive switching.

6.4 Chapter Summary

In summary, a flexible, transparent, and transferable ECM-based ITO TE/hBN/graphene resistive memory device has been successfully demonstrated on soft PDMS substrate with a clear switching mechanism: the formation and annihilation of indium filaments. Based on the inherent excellent mechanical properties of 2D hBN and graphene materials, the as-fabricated hBN-based memory device can be transferred freely to different substrates with stable switching characteristics, which is beneficial to future multifunctional soft electronic applications. The ITO TE/hBN/graphene/PDMS memory devices featured high transmittance (~85%) over the visible region, long retention time (5×10^4 s), large memory window (ON/OFF ratio, ~400), and excellent stability under bending conditions. More importantly, the indium filaments were confirmed here for the first time *via ex-situ* TEM, which is responsible for the resistive switching. In general, it is of fundamental interest for the community that a material like ITO, which was expected to serve as an electrode, is found to involve in filaments formation/rupture in ReRAM. This finding of the existence of In filaments definitely broadens the understanding of the switching mechanism in ECM-based ReRAM with ITO electrodes and deserves particular attention for the optimization of the transparent memory devices with ITO electrodes.

References

- [1] D. H. Kim, N. S. Lu, R. Ma, Y. S. Kim, R. H. Kim, S. D. Wang, J. Wu, S. M. Won, H. Tao, A. Islam, K. J. Yu, T. I. Kim, R. Chowdhury, M. Ying, L. Z. Xu, M. Li, H. J. Chung, H. Keum, M. McCormick, P. Liu, Y. W. Zhang, F. G. Omenetto, Y. G. Huang, T. Coleman, J. A. Rogers, *Science* **2011**, 333, 838-843.
- [2] Q. N. Thanh, H. Jeong, J. Kim, J. W. Kevek, Y. H. Ahn, S. Lee, E. D. Minot, J. Y. Park, *Adv. Mater.* **2012**, 24, 4499-4504.
- [3] Y. C. Lai, F. C. Hsu, J. Y. Chen, J. H. He, T. C. Chang, Y. P. Hsieh, T. Y. Lin, Y. J. Yang, Y. F. Chen, *Adv. Mater.* **2013**, 25, 2733-2739.
- [4] T. Georgiou, R. Jalil, B. D. Belle, L. Britnell, R. V. Gorbachev, S. V. Morozov, Y. J. Kim, A. Gholinia, S. J. Haigh, O. Makarovskiy, L. Eaves, L. A. Ponomarenko, A. K. Geim, K. S. Novoselov, A. Mishchenko, *Nat. Nanotechnol.* **2013**, 8, 100-103.
- [5] K. Nomura, H. Ohta, A. Takagi, T. Kamiya, M. Hirano, H. Hosono, *Nature* **2004**, 432, 488-492.
- [6] S. M. Kim, E. B. Song, S. Lee, J. F. Zhu, D. H. Seo, M. Mecklenburg, S. Seo, K. L. Wang, *ACS Nano* **2012**, 6, 7879-7884.
- [7] Z. Zheng, L. Gan, H. Q. Li, Y. Ma, Y. Bando, D. Golberg, T. Y. Zhai, *Adv. Funct. Mater.* **2015**, 25, 5885-5894.
- [8] J. X. Wang, C. Y. Yan, M. F. Lin, K. Tsukagoshi, P. S. Lee, *J. Mater. Chem. C* **2015**, 3, 596-600.
- [9] W. B. Kang, C. Y. Yan, C. Y. Foo, P. S. Lee, *Adv. Funct. Mater.* **2015**, 25, 4203-4210.
- [10] G. Cai, P. Darmawan, M. Cui, J. Wang, J. Chen, S. Magdassi, P. S. Lee, *Adv. Energy Mater.* **2015**, 6, 1501882.
- [11] B. N. Chandrashekar, B. Deng, A. S. Smitha, Y. B. Chen, C. W. Tan, H. X. Zhang, H. L. Peng, Z. F. Liu, *Adv. Mater.* **2015**, 27, 5210-5216.
- [12] K. Chung, C. H. Lee, G. C. Yi, *Science* **2010**, 330, 655-657.
- [13] S. H. Chae, W. J. Yu, J. J. Bae, D. L. Duong, D. Perello, H. Y. Jeong, Q. H. Ta, T. H. Ly, Q. A. Vu, M. Yun, X. F. Duan, Y. H. Lee, *Nat. Mater.* **2013**, 12, 403-409.
- [14] J. J. S. Yang, D. B. Strukov, D. R. Stewart, *Nat. Nanotechnol.* **2013**, 8, 13-24.

- [15] R. Waser, M. Aono, *Nat. Mater.* **2007**, 6, 833-840.
- [16] K. Qian, V. C. Nguyen, T. Chen, P. S. Lee, *Adv. Electron. Mater.* **2016**, 2, 1500370.
- [17] K. Qian, R. Y. Tay, V. C. Nguyen, J. Wang, G. Cai, T. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.
- [18] Y. C. Yang, P. Gao, L. Z. Li, X. Q. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, 5, 4232.
- [19] N. Gogurla, S. P. Mondal, A. K. Sinha, A. K. Katiyar, W. Banerjee, S. C. Kundu, S. K. Ray, *Nanotechnology* **2013**, 24, 345202.
- [20] N. R. Hosseini, J. S. Lee, *Adv. Funct. Mater.* **2015**, 25, 5586-5592.
- [21] J. W. Seo, J. W. Park, K. S. Lim, S. J. Kang, Y. H. Hong, J. H. Yang, L. Fang, G. Y. Sung, H. K. Kim, *Appl. Phys. Lett.* **2009**, 95, 133508.
- [22] J. Yao, J. Lin, Y. H. Dai, G. D. Ruan, Z. Yan, L. Li, L. Zhong, D. Natelson, J. M. Tour, *Nat. Commun.* **2012**, 3, 1101.
- [23] Y. C. Lai, Y. X. Wang, Y. C. Huang, T. Y. Lin, Y. P. Hsieh, Y. J. Yang, Y. F. Chen, *Adv. Funct. Mater.* **2014**, 24, 1430-1438.
- [24] K. Qian, G. Cai, V. C. Nguyen, T. Chen, P. S. Lee, *ACS Appl. Mater. Interfaces* **2016**, 8, 27885.
- [25] K. Qian, V. C. Nguyen, T. Chen, P. S. Lee, *J. Mater. Chem. C* **2016**, 4, 9637-9645.
- [26] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, *Nat. Mater.* **2015**, 14, 199-204.
- [27] C. L. Tan, Z. D. Liu, W. Huang, H. Zhang, *Chem. Soc. Rev.* **2015**, 44, 2615-2628.
- [28] L. Liang, K. Li, C. Xiao, S. J. Fan, J. Liu, W. S. Zhang, W. H. Xu, W. Tong, J. Y. Liao, Y. Y. Zhou, B. J. Ye, Y. Xie, *J. Am. Chem. Soc.* **2015**, 137, 3102-3108.
- [29] G. H. Lee, Y. J. Yu, X. Cui, N. Petrone, C. H. Lee, M. S. Choi, D. Y. Lee, C. Lee, W. J. Yoo, K. Watanabe, T. Taniguchi, C. Nuckolls, P. Kim, J. Hone, *ACS Nano* **2013**, 7, 7931-7936.
- [30] H. Wang, F. C. Liu, W. Fu, Z. Y. Fang, W. Zhou, Z. Liu, *Nanoscale* **2014**, 6, 12250-12272.
- [31] S. Z. Butler, S. M. Hollen, L. Y. Cao, Y. Cui, J. A. Gupta, H. R. Gutierrez, T. F. Heinz, S. S. Hong, J. X. Huang, A. F. Ismach, E. Johnston-Halperin, M. Kuno, V. V.

- Plashnitsa, R. D. Robinson, R. S. Ruoff, S. Salahuddin, J. Shan, L. Shi, M. G. Spencer, M. Terrones, W. Windl, J. E. Goldberger, *ACS Nano* **2013**, 7, 2898-2926.
- [32] S. Bertolazzi, J. Brivio, A. Kis, *ACS Nano* **2011**, 5, 9703-9709.
- [33] Z. Remes, M. Nesladek, K. Haenen, K. Watanabe, T. Taniguchi, *Phys. Status Solidi A* **2005**, 202, 2229-2233.
- [34] R. R. Nair, P. Blake, A. N. Grigorenko, K. S. Novoselov, T. J. Booth, T. Stauber, N. M. R. Peres, A. K. Geim, *Science* **2008**, 320, 1308-1308.
- [35] S. Bae, H. Kim, Y. Lee, X. F. Xu, J. S. Park, Y. Zheng, J. Balakrishnan, T. Lei, H. R. Kim, Y. I. Song, Y. J. Kim, K. S. Kim, B. Ozyilmaz, J. H. Ahn, B. H. Hong, S. Iijima, *Nat. Nanotechnol.* **2010**, 5, 574-578.
- [36] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, 457, 706-710.
- [37] G. Eda, G. Fanchini, M. Chhowalla, *Nat. Nanotechnol.* **2008**, 3, 270-274.
- [38] C. Lee, X. D. Wei, J. W. Kysar, J. Hone, *Science* **2008**, 321, 385-388.
- [39] A. Reina, X. T. Jia, J. Ho, D. Nezich, H. B. Son, V. Bulovic, M. S. Dresselhaus, J. Kong, *Nano Lett.* **2009**, 9, 30-35.
- [40] D. J. Wouters, R. Waser, M. Wuttig, *Pro. IEEE* **2015**, 103, 1274-1288.
- [41] M. Ismail, A. M. Rana, I. Talib, T. L. Tsai, U. Chand, E. Ahmed, M. Y. Nadeem, A. Aziz, N. A. Shah, M. Hussain, *Solid State Commun.* **2015**, 202, 28-34.
- [42] C. Y. Huang, Y. T. Ho, C. J. Hung, T. Y. Tseng, *IEEE Trans. Electron. Devices* **2014**, 61, 3435-3441.
- [43] J. Shang, G. Liu, H. L. Yang, X. J. Zhu, X. X. Chen, H. W. Tan, B. L. Hu, L. Pan, W. H. Xue, R. W. Li, *Adv. Funct. Mater.* **2014**, 24, 2171-2179.
- [44] P. K. Yang, C. H. Ho, D. H. Lien, J. R. D. Retamal, C. F. Kang, K. M. Chen, T. H. Huang, Y. C. Yu, C. I. Wu, J. H. He, *Sci. Rep.* **2015**, 5, 15087.
- [45] H. D. Kim, H. M. An, Y. Seo, T. G. Kim, *IEEE Electron Device Lett.* **2011**, 32, 1125-1127.
- [46] H. D. Kim, H. M. An, Y. Seo, T. G. Kim, *IEEE Electron Device Lett.* **2011**, 32, 1125-1127.
- [47] J. S. Huang, Y. C. Lin, H. W. Tsai, W. C. Yen, C. W. Chen, C. Y. Lee, T. S. Chin, Y. L. Chueh, *Adv Electron Mater* **2015**, 1, 1500061.

- [48] R. Y. Tay, M. H. Griep, G. Mallick, S. H. Tsang, R. S. Singh, T. Tumlin, E. H. T. Teo, S. P. Karna, *Nano Lett.* **2014**, 14, 839-846.
- [49] R. Y. Tay, X. L. Wang, S. H. Tsang, G. C. Loh, R. S. Singh, H. Li, G. Mallick, E. H. T. Teo, *J. Mater. Chem. C* **2014**, 2, 1650-1657.
- [50] X. S. Li, Y. W. Zhu, W. W. Cai, M. Borysiak, B. Y. Han, D. Chen, R. D. Piner, L. Colombo, R. S. Ruoff, *Nano Lett.* **2009**, 9, 4359-4363.
- [51] K. Qian, R. Y. Tay, M. F. Lin, J. W. Chen, H. K. Li, J. J. Lin, J. X. Wang, G. F. Cai, V. C. Nguyen, E. H. T. Teo, T. P. Chen, P. S. Lee, *ACS Nano* **2017**, 11, 1712-1718.
- [52] B. H. Lee, H. Bae, H. Seong, D. I. Lee, H. Park, Y. J. Choi, S. G. Im, S. O. Kim, Y. K. Choi, *ACS Nano* **2015**, 9, 7306-7313.
- [53] Y.R. Luo, *Handbook of bond dissociation energies in organic compounds*, CRC press, **2002**.
- [54] X. Guo, C. Schindler, *Appl. Phys. Lett.* **2007**, 91, 133513.

Chapter 7

Discussion and Future Work

Resistive switching random access memory (ReRAM) devices with advanced functionalities have significant advantages and added value in different areas, which are essential for future electronics' applications. In this chapter, the threads of the whole thesis were drawn together with a general discussion on the achieved results which correspond to the initial hypotheses. Based on this, the accomplishments as well as the potential issues for flexible functional electrochemical metallization (ECM)-based ReRAM devices are identified and addressed to achieve better functional memory devices. The insights and suggestions for the flexible functional ECM-based ReRAM devices are provide as future work at the end.

7.1 Discussion

This thesis is dedicated to addressing the involved issues and overcoming related challenges for the flexible functional ECM-based ReRAM devices realization with excellent performances. In order to accomplish the target, we focus on designing the suitable device configuration and exploring decent materials as well as the switching mechanisms. Specific discussions and achievements for these points are further described in the following sections.

7.1.1 Au NPs-interlayer amorphous Si ECM-based ReRAM on flexible and rigid substrates

The objective for this study is to realize low electroforming voltage and large ON/OFF ratio ECM-based ReRAM devices on both flexible and rigid substrates. The identified difficulty to achieve such task is how to meet these two requirements at the same time at room temperature *via* a facile method.

In the ECM-based ReRAM devices, the electric field will affect the conducting filaments growth.^[1, 2] This thesis has shown that in the Ag TE/amorphous Si/Au BE ECM-based ReRAM, the metallic Au nanoparticles layer, which was inserted between amorphous Si and Au BE, can modify the electric field distribution and intensity to tune the Ag filaments growth. The Au NPs were synthesized using simple aqueous solution method. Then, the Au NPs were inserted in the memory devices via facile self-assembly technology on both flexible and rigid substrates at room temperature. Compared with the filaments in Ag TE/a-Si/Au BE memory devices, the change of filaments in Ag TE/a-Si/Au NPs-layer/Au BE memory devices was studied *via ex-situ* TEM. For the ECM-based memory devices on both flexible and rigid substrates, the electric field intensity and distribution can be tuned through Au NPs-interlayer, which will facilitate the conducting filaments growth and result in low electroforming voltage; In addition, due to the Au NPs-enhanced electric field, the Ag filaments would be easily depleted because of the fast drift of Ag ions during RESET process, leading to shorter remnant Ag filaments

and high ON/OFF ratio. In conclusion, the objective to realize low electroforming voltage and large memory window ECM-based ReRAM devices at the same time on both flexible and rigid substrates has been achieved. However, the flexibility of the amorphous Si-based memory devices is not satisfactory due to the brittle nature of the amorphous Si switching layer. Therefore, the bending stability of the flexible ECM-based ReRAM devices needs to be improved by exploring novel materials as switching layer.

7.1.2 hBN thin film for flexible functional ECM-based ReRAM applications

As discussed in 7.1.1, to improve the bending stability of the ReRAM devices, a novel material needs to be explored as switching layer. It has been demonstrated that the 2D materials based ReRAM devices exhibited excellent switching endurance and bending stability.^[3,4] The hBN 2D material is an excellent candidate for the flexible ECM-based ReRAM devices. In this study, the ~3-5 nm CVD-grown hBN films were employed to fabricate flexible ECM-based ReRAM devices with Cu foil and Ag electrodes. The switching mechanism (*i.e.*, Ag filaments formation and rupture) was studied carefully and confirmed *via ex situ* TEM, which was the conducting Ag filaments formation and rupture. The hBN ECM-based ReRAM devices feature good write/erase endurance, long retention time and acceptable memory window. Especially, the memory device can operate under extreme bending conditions (bending radius, $r=7$ mm) without large variation of memory window, even after 750 bending cycles. Compared with the previous amorphous-Si ECM-based ReRAM devices, the Ag TE/hBN/Cu foil memory devices exhibited better bending stability under bent condition. In addition, as shown in **Table 2.4** in **Chapter 2**, compared with the flexible conventional inorganic materials-based memory devices (*e.g.* SiO_x (300 bending cycles at $r=12$ mm),^[5] Ag₂Se (100 bending cycles at $r=16$ mm),^[6] and WO₃ (100 bending cycles at $r=12$ mm)^[3]), the hBN-based memory devices showed more excellent bending endurance. Compared to the flexible conventional organic materials-based memory devices (*e.g.* PS:PCBM, switching endurance: 100 cycles^[7]), the hBN-based memory devices also exhibited more excellent switching endurance (~550 cycles). This work expands the application of 2D material in ReRAM devices in future wearable electronics and information technology.

7.1.3 Flexible, transparent, and transferable ECM-based ReRAM from hBN and graphene

The objective for this study is to realize multifunctional - flexible, transparent, and transferable ECM-based ReRAM memory devices. In order to develop fully transparent ECM-based ReRAM devices, both transparent top and bottom electrodes are required. The layered structure of graphene film, which can be easily transferred onto foreign substrates, is a good choice as bottom electrode due to its excellent optical and mechanical properties.^[8, 9] For the top electrode, the active electrodes (*e.g.* Ag, Cu) are not suitable for transparent ReRAM due to their mirror reflection property. In addition, due to the filaments formation/rupture mechanism in the hBN ECM-based memory devices, the graphene also cannot be employed as top electrode. Therefore, a top electrode which is inherently transparent and can generate conducting filament is necessary. In this study, the ~3-5 nm CVD-grown hBN films, which were sandwiched between ITO top electrode and graphene film bottom electrode, were employed to fabricate flexible, transparent, and transferable ECM-based ReRAM devices. The indium filaments were confirmed here for the first time *via ex-situ* TEM, which is responsible for the resistive switching. Due to the inherent excellent mechanical properties of 2D hBN and graphene materials, the hBN ECM-based memory device can be transferred freely to different substrates with stable switching characteristics. The objective for a multifunctional- flexible, transparent, and transferable ECM-based ReRAM memory device was successfully accomplished. The ITO TE/hBN/graphene/PDMS memory devices featured high transmittance (~85%) over the visible region, long retention time (5×10^4 s), large memory window (ON/OFF ratio, ~400), and excellent switching endurance (~500 cycles) and bending stability (~850 repeated bending cycles at $r=14$ mm). Compared with the flexible and transferable organic PMMA:P3HT -based ReRAM devices which exhibited bipolar switching with switching endurance of ~80 cycles,^[10] the ITO TE/hBN/graphene/PDMS memory device exhibited both excellent switching endurance (~500 cycles) and high transparency. Compared to the flexible and transparent SiO_x-based memory device (switching endurance: 400 cycles, bending endurance: 300 cycles at $r=12$ mm),^[5] the ITO TE/hBN/graphene/PDMS memory devices exhibited

excellent bending stability and unique portability which can conform to arbitrary substrates with reliable switching characteristics.

7.2 Future Work

7.2.1 Stretchable ECM-based ReRAM for wearable electronics applications

With the previous discussions on the realization of advanced flexible functional ECM-based ReRAM devices, such as flexible amorphous Si (**Chapter 4**) and hBN (**Chapter 5**) memory devices, flexible, transparent, and transferable hBN memory devices (**Chapter 6**), the achievements were elaborated. However, for realization of the wearable functional electronics, the ultimate form of electronics should be not only flexible, but also stretchable to retain stable electrical performance under deformation.^[11, 12] The latest progress on the development of stretchable ReRAM devices demonstrates their potential applicability for future wearable electronics applications.^[13-15] 2D hBN and graphene materials, which both exhibit superior mechanical properties (*i.e.* flexibility and elasticity), are excellent candidates for next-generation wearable electronics.^[16-18] Especially, the elastic and wrinkled graphene film has exhibited a great potential application in different stretchable electronics.^[14, 19] To obtain stretchable and wearable ReRAM devices with excellent stability and practicability, the feasible approach is herein suggested for future studies.

The stretchable ECM-based ReRAM device can be demonstrated with wrinkled structure. The stretchable ReRAM device will be consisted of Ag top electrode (TE), hBN switching layer, and graphene bottom electrode (BE) onto a PDMS elastomer substrate (**Figure 7.1**). First, the PMMA/hBN will be transferred onto graphene/Cu foil substrate. Then the supporting Cu foil can be etched via ammonium sulfate (APS) solution to obtain substrate-free PMMA/hBN/Graphene membrane. Thereafter, the PMMA/hBN/Graphene film will be transferred to a pre-strained elastic PDMS substrate. The PMMA can be dissolved with acetone, then, the Ag TE will be deposited on the pre-strained hBN/Graphene/PDMS substrate (**Figure 7.1a**). Subsequently, the Ag TE/hBN/graphene ECM-based ReRAM device would spontaneously form the buckled structure when it is

released from the pre-strained state to nature state (**Figure 7.1b**). Finally, the stretchability can be realized in the resultant waved 2D hBN-based ReRAM device *via* the conversion between the planar strain and vertical displacement.

Figure 7.1 Schematic structure and fabrication process for the stretchable 2D materials ReRAM device. (a) Ag TE/ hBN/Graphene BE on the pre-strained PDMS substrate. (b) Rippled Ag TE/ hBN/Graphene/PDMS ReRAM device after releasing the strain.

7.2.2 *In-situ* observation of filaments in ECM-based ReRAM devices

Based on the previous discussions on the amorphous Si and hBN-based ECM-based ReRAM devices, the resistive switching effect has been studied and confirmed *via ex-situ* TEM technology, which is caused by the formation/rupture of conducting filaments.^[20-22] Although part of filaments can be observed visually at ON- or OFF state *via* cross-sectional TEM, it is still possible that some crucial filaments may be missed during the TEM specimen fabrication *via* focused ion beam (FIB). In particular, the memory cell would be completely damaged during the thinning down process, which would prevent detailed studies of the switching behavior at ON- and OFF states in the same device. On the other hand, there are still some crucial questions remain unclear in different memory devices systems,^[23, 24] such as how the filaments migrate inside switching layer, where the filaments start to rupture and grow under electric field, indicating the controversial issues in the switching mechanisms.^[25-27] Therefore, it is essential to completely understand the filament dynamics and switching behaviors in ECM-based memory devices to optimize the performances.^[1, 28, 29] Recently, with the rapid development of *in situ* TEM system, the real-time measurements with rapid imaging technique have been realized for the characterizations of electrical properties.^[30] Therefore, the direct

observation of filament dynamics in the ECM-based ReRAM devices has stimulated great interest *via in situ* TEM technology, which can study the switching behaviors from the same cell.^[23, 24, 29, 31, 32]

Figure 7.2 (a) SEM image of the Molybdenum 3-post lift-out grid for *in situ* TEM experiment. (b) Schematic of the *in situ* TEM measurement system. (c) TEM specimen in the center of the grid B. (d) The Pt layer/Au TE/hBN film/Cu foil memory structure for *in situ* TEM experiment.

In the case of 2D materials ReRAM devices, the dynamic observation of conducting filaments growth under electric field was not reported previously. To guide the design of 2D hBN ECM-based ReRAM device with desirable properties, *in situ* TEM technology was employed to observe the dynamic filaments growth in hBN switching layer. As shown in **Figure 7.2a**, the Molybdenum 3-post lift-out grid was used as the supporting substrate and electrode. The schematic of the *in situ* TEM measurement system was shown in **Figure 7.2b**. The memory device was consisted of Au top electrode layer, ~10 nm hBN switching layer, and Cu foil bottom electrode layer (**Figure 7.2d**). The Pt protective layer was deposited on Au top electrode. Then the Au TE/hBN/Cu foil cell was cut *via* focused ion beam technology and put on the center of the grid (**Figure 7.2c**). For this *in situ* TEM measurement, a movable W probe will connect the external circuit and Pt layer, respectively, while the Cu foil/molybdenum grid is grounded (**Figure 7.2b**).

In addition, for different metal electrodes, their ions have different sizes and charge numbers, such as Ag^+ , Cu^{2+} , and In^{3+} , which may affect the filaments growth.^[24] In order to guide the ECM-based ReRAM performances optimization, the switching layer (*e.g.* amorphous Si, hBN) will be fixed with different electrodes (*e.g.* Ag, Cu, ITO) to check the filament dynamics in the switching layer *via in situ* TEM.

References

- [1] R. Waser, R. Dittmann, G. Staikov, K. Szot, *Adv. Mater.* **2009**, 21, 2632-2663.
- [2] Q. Liu, S. Long, H. Lv, W. Wang, J. Niu, Z. Huo, J. Chen, M. Liu, *ACS Nano* **2010**, 4, 6162-6168.
- [3] L. Liang, K. Li, C. Xiao, S. J. Fan, J. Liu, W. S. Zhang, W. H. Xu, W. Tong, J. Y. Liao, Y. Y. Zhou, B. J. Ye, Y. Xie, *J. Am. Chem. Soc.* **2015**, 137, 3102-3108.
- [4] A. A. Bessonov, M. N. Kirikova, D. I. Petukhov, M. Allen, T. Ryhanen, M. J. A. Bailey, *Nat. Mater.* **2015**, 14, 199-204.
- [5] J. Yao, J. Lin, Y. H. Dai, G. D. Ruan, Z. Yan, L. Li, L. Zhong, D. Natelson, J. M. Tour, *Nat. Commun.* **2012**, 3, 1101.
- [6] J. Jang, F. Pan, K. Braam, V. Subramanian, *Adv. Mater.* **2012**, 24, 3573-3576.
- [7] Y. Ji, D. F. Zeigler, D. S. Lee, H. Choi, A. K. Y. Jen, H. C. Ko, T. W. Kim, *Nat. Commun.* **2013**, 4, 2707.
- [8] K. Chung, C. H. Lee, G. C. Yi, *Science* **2010**, 330, 655-657.
- [9] K. S. Novoselov, V. I. Fal'ko, L. Colombo, P. R. Gellert, M. G. Schwab, K. Kim, *Nature* **2012**, 490, 192-200.
- [10] Y. C. Lai, Y. X. Wang, Y. C. Huang, T. Y. Lin, Y. P. Hsieh, Y. J. Yang, Y. F. Chen, *Adv. Funct. Mater.* **2014**, 24, 1430-1438.
- [11] J. X. Wang, C. Y. Yan, G. F. Cai, M. Q. Cui, A. L. S. Eh, P. S. Lee, *Adv. Mater.* **2016**, 28, 4490-4496.
- [12] J. A. Rogers, T. Someya, Y. G. Huang, *Science* **2010**, 327, 1603-1607.
- [13] D. Son, J. Lee, S. Qiao, R. Ghaffari, J. Kim, J. E. Lee, C. Song, S. J. Kim, D. J. Lee, S. W. Jun, S. Yang, M. Park, J. Shin, K. Do, M. Lee, K. Kang, C. S. Hwang, N. S. Lu, T. Hyeon, D. H. Kim, *Nat. Nanotechnol.* **2014**, 9, 397-404.

- [14] Y. C. Lai, Y. C. Huang, T. Y. Lin, Y. X. Wang, C. Y. Chang, Y. X. Li, T. Y. Lin, B. W. Ye, Y. P. Hsieh, W. F. Su, Y. J. Yang, Y. F. Chen, *Npg Asia Mater.* **2014**, 6, e87.
- [15] J. T. Wang, K. Saito, H. C. Wu, H. S. Sun, C. C. Hung, Y. G. Chen, T. Isono, T. Kakuchi, T. Satoh, W. C. Chen, *Npg Asia Mater.* **2016**, 8, e298.
- [16] K. S. Kim, Y. Zhao, H. Jang, S. Y. Lee, J. M. Kim, K. S. Kim, J. H. Ahn, P. Kim, J. Y. Choi, B. H. Hong, *Nature* **2009**, 457, 706-710.
- [17] M. Topsakal, S. Ciraci, *Phys. Rev. B* **2010**, 81, 024107.
- [18] N. Izyumskaya, D. O. Demchenko, S. Das, Ü. Özgür, V. Avrutin, H. Morkoç, *Adv. Electron. Mater.* **2017**, 3, 1600485.
- [19] Y. Wang, R. Yang, Z. W. Shi, L. C. Zhang, D. X. Shi, E. Wang, G. Y. Zhang, *ACS Nano* **2011**, 5, 3645-3650.
- [20] K. Qian, V. C. Nguyen, T. P. Chen, P. S. Lee, *Adv. Electron. Mater.* **2016**, 2, 1500370.
- [21] K. Qian, R. Y. Tay, M. F. Lin, J. W. Chen, H. K. Li, J. J. Lin, J. X. Wang, G. F. Cai, V. C. Nguyen, E. H. T. Teo, T. P. Chen, P. S. Lee, *ACS Nano* **2017**, 11, 1712-1718.
- [22] K. Qian, R. Y. Tay, V. C. Nguyen, J. X. Wang, G. F. Cai, T. P. Chen, E. H. T. Teo, P. S. Lee, *Adv. Funct. Mater.* **2016**, 26, 2176-2184.
- [23] Y. C. Yang, P. Gao, S. Gaba, T. Chang, X. Q. Pan, W. Lu, *Nat. Commun.* **2012**, 3, 732.
- [24] Y. C. Yang, P. Gao, L. Z. Li, X. Q. Pan, S. Tappertzhofen, S. Choi, R. Waser, I. Valov, W. D. Lu, *Nat. Commun.* **2014**, 5, 4232.
- [25] S. Gao, C. Song, C. Chen, F. Zeng, F. Pan, *J. Phys. Chem. C* **2012**, 116, 17955-17959.
- [26] S. Gao, C. Song, C. Chen, F. Zeng, F. Pan, *J. Phys. Chem. C* **2013**, 117, 11881-11882.
- [27] I. Valov, R. Waser, *J. Phys. Chem. C* **2013**, 117, 11878-11880.
- [28] R. Waser, M. Aono, *Nat. Mater.* **2007**, 6, 833-840.
- [29] G.S. Park, Y. B. Kim, S. Y. Park, X. S. Li, S. Heo, M.-J. Lee, M. Chang, J. H. Kwon, M. Kim, U.-I. Chung, *Nat. Commun.* **2013**, 4, 2382.
- [30] B. C. Regan, S. Aloni, R. O. Ritchie, U. Dahmen, A. Zettl, *Nature* **2004**, 428, 924-927.

- [31] S. J. Choi, G. S. Park, K. H. Kim, S. Cho, W. Y. Yang, X. S. Li, J. H. Moon, K. J. Lee, K. Kim, *Adv. Mater.* **2011**, 23, 3272-3277.
- [32] Q. Liu, J. Sun, H. B. Lv, S. B. Long, K. B. Yin, N. Wan, Y. T. Li, L. T. Sun, M. Liu, *Adv. Mater.* **2012**, 24, 1844-1849.

Publication List

1. **Kai Qian**, Roland Yingjie Tay, Meng-Fang Lin, Jingwei Chen, Huakai Li, Jinjun Lin, Jiangxin Wang, Guofa Cai, Viet Cuong Nguyen, Edwin Hang Tong Teo, Tupei Chen, Pooi See Lee. “Direct Observation of Indium Conductive Filaments in Transparent Flexible, and Transferable Resistive Switching Memory”, *ACS Nano*, **2017**, *11*, 1712.
2. **Kai Qian**, Roland Yingjie Tay, Viet Cuong Nguyen, Jiangxin Wang, Guofa Cai, Tupei Chen, Edwin Hang Tong Teo, Pooi See Lee. “Hexagonal Boron Nitride Thin Film for Flexible Resistive Memory Applications” *Adv. Funct. Mater.* **2016**, *26*, 2176.
3. **Kai Qian**, Guofa Cai, Viet Cuong Nguyen, Tupei Chen, Pooi See Lee. “Direct Observation of Conducting Filaments in Tungsten Oxide Based Transparent Resistive Switching Memory”, *ACS Appl. Mater. Interfaces* **2016**, *8*, 27885.
4. **Kai Qian**, Viet Cuong Nguyen, Tupei Chen, Pooi See Lee. “Novel Concepts in Functional Resistive Switching Memories”, *J. Mater. Chem. C*, **2016**, *4*, 9637.
5. **Kai Qian**, Viet Cuong Nguyen, Tupei Chen, Pooi See Lee. “Amorphous-Si-Based Resistive Switching Memories with Highly Reduced Electroforming Voltage and Enlarged Memory Window” *Adv. Electron. Mater.* **2016**, 1500370.
6. Guofa Cai, Mengqi Cui, Vipin Kumar, Peter Darmawan, Jiangxin Wang, Xu Wang, Alice Lee-Sie Eh, **Kai Qian**, Pooi See Lee, “Ultra-large optical modulation of electrochromic porous WO₃ film and the local monitoring of redox activity”, *Chemical Science*, **2016**, *7*, 1373-1382.
7. Guofa Cai, Jiangxin Wang, **Kai Qian**, Jingwei Chen, Shaohui Li, Pooi See Lee, “Extremely Stretchable Strain Sensors Based on Conductive Self-Healing Dynamic Cross-Links Hydrogels for Human-Motion Detection”, *Advanced Science*, **2016**, 10.1002/advs.201600190.
8. Benlin Hu, Chengyuan Wang, Jing Zhang, **Kai Qian**, Pooi See Lee, Qichun Zhang, “Organic memory effect from donor–acceptor polymers based on 7-perfluorophenyl-6 H-[1, 2, 5] thiadiazole [3, 4-g] benzoimidazole”, *RSC Advances*, **2015**, *5*, 77122-77129.

9. Benlin Hu, Chengyuan Wang, Jing Zhang, **Kai Qian**, Wangqiao Chen, Pooi See Lee, Qichun Zhang, “Water-soluble conjugated polymers as active elements for organic nonvolatile memories”, *RSC Advances*, **2015**,5, 30542-30548

APPENDIX

Table 1 Materials used in the thesis.

Materials	Quality	Supplier	Product number
Chloroauric acid	99.999%	Sigma-Aldrich	254169
2-aminothiophenol	99%	Sigma-Aldrich	274240
Trisodium citrate dihydrate	N.A.	Sigma-Aldrich	S1804
PMMA	Analytical standard	Sigma-Aldrich	81489
PDMS	N.A.	Dow Corning	Sylgard 184
Ammonium persulfate	$\geq 98.0\%$	Sigma-Aldrich	248614
Ammonia borane	97.0%	Sigma-Aldrich	682098