



國立中山大學物理學系

博士論文

Department of Physics

National Sun Yat-sen University

Doctorate Dissertation

先進記憶體元件之物理機制研究

Investigation on physical mechanism of advanced memory device

研究生：林志陽

Chih-Yang Lin

指導教授：張鼎張 博士

Dr. Ting-Chang Chang

中華民國 109 年 11 月

November 2020



國立中山大學物理學系

博士論文

Department of Physics

National Sun Yat-sen University

Doctorate Dissertation

先進記憶體元件之物理機制研究

Investigation on physical mechanism of advanced memory device

研究生：林志陽

Chih-Yang Lin

指導教授：張鼎張 博士

Dr. Ting-Chang Chang

中華民國 109 年 11 月

November 2020

# 國立中山大學研究生學位論文審定書

國立中山大學研究生學位論文審定書

本校物理學系博士班

研究生林志陽（學號：D042030006）所提論文

先進記憶體元件之物理機制研究

Investigation on physical mechanism of advanced memory device

於中華民國 109 年 10 月 31 日經本委員會審查並舉行口試，符合博士學位論文標準。

學位考試委員簽章：

召集人 王英郎

王英郎

委員 張鼎張

張鼎張

委員 李文熙

李文熙

委員 劉全璞

劉全璞

委員 葉文冠

葉文冠

委員

委員

委員

委員

委員

指導教授(張鼎張)

張鼎張

(簽名)



## 摘要

現行複雜結構的記憶體在微縮過程中逐漸面臨瓶頸，因此許多次世代記憶體正被開發與研究。其中，電阻式記憶體(RRAM)是最有潛力的記憶體，優點包含高可靠度、高密度、高速切換、節能、結構簡單等，使相同面積下記憶體的容量和操作速度能增長數千倍以上。目前許多公司與研究單位正在研究電阻式記憶體元件、將之應用於嵌入式記憶體，並於近期開始進行量產。

本論文的研究內容包含四個部分，第一部分為對銻錫氧化物(ITO)電極電阻式記憶體的研究，銻錫氧化物電阻式記憶體具有透明、可自我保護、快速切換等特性與優勢，此部分針對銻錫氧化物電極造成元件電性的改變進行進一步的分析與探討，藉由改變操作手法的方式使銻錫氧化物電阻式記憶體的物理模型更加明確。同時引入低介電質材料，使操作電場集中、進一步降低操作電壓與元件功耗。

基於第一部份研究的氧化物電極基礎，第二部分使用對電阻式記憶體進行電漿處理，將金屬電極表面氧化成氧儲存槽，使電極表面更能吸附氧離子，使元件操作電壓與阻態變穩定。此研究對於一般金屬電極形成氧儲存槽的部分進行分析、使用不同操作手法與驗證方式證明氧儲存槽的存在與其能改善元件電性的原因。

第三部份對於仿生記憶體進行研究，因人腦計算效率相較於現今處理器仍然高上許多，仿生記憶體的研究為現今次世代記憶體開發的重點之一。不同於現代電腦儲存記憶的方式，人腦並非靠 0 和 1 的數位兩階訊號來記憶，而是透過類比多階訊號來儲存記憶與傳遞訊息、記憶狀態也會隨著時間變弱，以降低整體消耗能量。

由於電阻式記憶體的三層結構與神經高度相似，因此本論文中使用將鋰(Li)摻雜至氧化矽中，製作出含有類似人腦離子傳導特性的電阻式記憶體，此元件具有良好的多位元(multi-bit)儲存功能、阻態能隨時間改變等高度類似神經元突觸的仿生特性，利用這種特性，仿效大腦學習的運作方式並進行圖形識別，未來有助於類神經網路、於記憶體中進行運算之元件(In-memory computing)及更高安全性之硬體圖形識別等科技的發展。

第四部份則對於選擇器(Selector)進行研究，由於電阻式記憶體在實際應用或導入量產時面臨一個很大的問題，當以最高密度的陣列製作成記憶體晶片時，會產生該判讀為高阻態卻判讀為低阻態的現象，導致判讀過程出現錯誤。為了解決此問題，選擇器是最受期待、而且被全世界廣泛研究的元件之一，其可以抑制未被選擇元件的初始漏電，使得目標元件被正確選擇並進行判讀與操作。本研究對於金屬絕緣體轉換(Metal-Insulator transition, MIT)特性進行研究，並將之應用於選擇器元件，首次整合釩金屬(Vanadium, V)至電阻式記憶體製程中，以傳統 RRAM 結構製作出可大幅抑制潛行電流的選擇器(Selector)元件。不但發現釩電極元件於相同結構下，可以藉由控制電壓極性決定元件特性為 Selector 或 RRAM。更進一步搭配銦錫氧化物(ITO)作為中間層，首次製作出僅使用 3 層 MIM 薄膜即可操作的 one-Selector-one-RRAM (1S1R)元件。除了氧化釩元件以外，也引入氧化鈮(niobium oxide, NbO)，藉由改變操作手法的方式製作出不需選擇器的記憶體元件。本研究建立金屬絕緣體轉換元件之 RRAM 及 Selector 的傳導機制及統整性物理模型(Universal Model)，

並將之應用於新操作方式、新結構、新材料與新製程技術。除了製作出更佳性能之 Selector 與 RRAM (1S1R)元件陣列以外，更能應用於新型圖像識別元件，促進次世代記憶體元件的實際應用與發展。

**關鍵詞：**電阻式記憶體、銦錫氧化物、電漿處理、仿生、氧化鉻、氧化鋇、選擇器

## **Abstract**

The existing complex structure of memory is gradually facing a bottleneck in the miniaturization process, so many generations of memory are being developed and researched. Among them, Resistive RAM (RRAM) is the most promising type of memory. The advantages of RRAM include high reliability, high density, high-speed switching, energy-saving, simple structure, etc., which can increase the capacity and operation speed of memory by thousands of times for the same area. Many companies and research institutes are currently investigating resistive memory devices for use in embedded memory and will begin mass production in the near future.

The first part is the studies about Indium Tin Oxide (ITO) electrode resistive memories. Indium Tin Oxide (ITO) resistive memories have features and advantages such as transparency, self-protection, fast switching, etc. This part further analyzes and discusses the changes in the electrical properties of components caused by Indium Tin Oxide (ITO) electrodes, and enables Indium Tin Oxide (ITO) resistive memories by changing the operation method. The physical model of memory has been clarified. Low dielectric materials are also introduced to concentrate the operating electric field and further reduce the operating voltage and power consumption of the components.

Based on the oxide electrode studied in the first part, the second part uses a plasma treatment on the resistive memory to oxidize the surface of the metal electrode to form an

oxygen storage tank, so that the surface of the electrode can better absorb oxygen ions and stabilize the operating voltage and resistance state of the device. This study analyzes the part of the metal electrode that forms an oxygen reservoir and uses different manipulation and verification methods to prove the existence of the oxygen reservoir and the reason why it can improve the electrical properties of the device.

The third part of the study is on bionic memory, which is one of the main focuses of next-generation memory development as the computational efficiency of the human brain is still much higher than that of today's processors. Unlike modern computers, the human brain does not rely on digital two-step signals of 0 and 1 to store memory but instead uses analog multi-step signals to store memory and transmit messages. Since the three-layer structure of resistive memory is highly similar to that of neurons, in this paper, Li is doped into silicon oxide to produce a resistive memory with ionic conduction properties similar to those of the human brain. In the future, the development of neural networks, in-memory computing, and more secure hardware graphics will be helpful.

The fourth part of the study is on the selector. A major problem with resistive memory is that when the highest density arrays are fabricated into memory chips, they may be interpreted as high resistance but low resistance, resulting in errors in the interpretation process. To solve this problem, selectors are one of the most desired and widely researched components in the world to suppress the initial leakage of unselected

components, so that the target components can be correctly selected and read and manipulated. This study investigates the characteristics of Metal-Insulator transition (MIT) and applies it to selector devices. For the first time, Vanadium (V) is integrated into a resistive memory process to produce a selector with a traditional RRAM structure that can significantly suppress latent currents. components. Not only has it been found that a V element can be characterized as either Selector or RRAM by controlling the voltage polarity of the element in the same structure, but it has also been taken one step further by using indium tin oxide (ITO) as an intermediate layer to produce for the first time one-Selector-one-RRAM (1S1R) elements which can be operated using only 3 MIM layers. In addition to VO components, Niobium oxide (NbO) is also introduced to enable the production of selector-less memory components by changing the operating method. This study establishes a universal physical model for the conductivity of RRAM and Selector for metal-insulator switching devices and applies it to new operating methods, new structures, new materials, and new process technologies. In addition to producing better performance Selector and RRAM (1S1R) device arrays, it can also be applied to new image recognition devices, promoting the practical application and development of next-generation memory devices.

**Keywords:** **RRAM, Indium tin oxide (ITO), Plasma treatment, Neuromorphic, Vanadium oxide, Niobium oxide, Selector.**

# Contents

國立中山大學研究生學位論文審定書 .....	i
博碩士論文公開授權書 .....	ii
致 謝 .....	iii
摘 要 .....	viii
Abstract.....	xi
Contents .....	xiv
Figure captions .....	xix
Table captions .....	xxxix
Symbolic representations.....	xl
Chapter 1 Introduction.....	1
1.1 Overview.....	1
1.2 Commercial Application and Development of Embedded memory .....	3
1.2.1 RRAM Market Application Objectives and Technical Future .....	3
1.3 The international situation of advanced embedded memory development and the current development in Taiwan.....	4
1.4 Value of Under Developing Embedded memory.....	5
Chapter 2 The Basic Principles of Advanced Memory Devices .....	7
2.1 Introduction of Advanced Memory devices .....	7

2.1.1	FeRAM.....	7
2.1.2	MRAM .....	11
2.1.3	PCRAM .....	15
2.1.4	RRAM .....	17
2.2	Carrier Conduction Mechanism for MIS/MIM devices .....	18
2.2.1	Ohmic Conduction .....	21
2.2.2	Schottky Emission.....	24
2.2.3	Poole-Frenkel Emission .....	28
2.2.4	Hopping Conduction .....	29
2.2.5	Tunneling Conduction .....	32
2.2.6	Space Charge Limited Current .....	34
2.2.7	Conclusion.....	35
Chapter 3	Mechanisms of Indium Tin Oxide Electrode RRAM .....	36
3.1	Modeling for self-compliance of ITO RRAM.....	37
3.1.1	Experimental .....	37
3.1.2	Results and Discussion.....	40
3.1.3	Conclusion.....	45
Chapter 4	Enhancing RRAM performance by introducing plasma treatment to the electrode.....	47

4.1	Analysis for plasma treatment to electrode on oxide-based RRAM .....	48
4.1.1	Experimental setup, Materials and Methods .....	48
4.1.2	Results and Discussion.....	52
4.1.3	Theory and Calculation .....	56
4.1.4	Conclusion.....	61
Chapter 5	Neuromorphic devices .....	62
5.1	Introduction to the relationship between neuron and RRAM.....	62
5.2	Adaptive Synaptic Memory via Lithium Ion Modulation in RRAM devices .....	66
5.2.1	Introduction .....	67
5.2.2	Experimental setup and material analysis .....	67
5.2.3	Multi-state memory for incremental set and reset.....	72
5.2.4	Lithium-driven multi-state STDP.....	73
5.2.5	Synaptic Pruning via Conductance Degradation.....	76
5.2.6	PPF based on self-pruning characteristics of lithium device .....	81
5.2.7	Conclusion.....	85
Chapter 6	Selector devices .....	87
6.1	A Comprehensive Study of Enhanced Characteristics with Localized Transition in Interface-type Vanadium-based Devices.....	89

6.1.1	Introduction .....	93
6.1.2	Experimental Measurements .....	94
6.1.3	Results and discussion.....	102
6.1.4	Conclusion.....	110
6.2	Attaining Resistive Switching Characteristics and Selector Properties by Varying Forming Polarities in a Single HfO <sub>2</sub> -based RRAM Device with Vanadium Electrode.....	111
6.2.1	Introduction .....	112
6.2.2	Experimental setup and material analysis .....	115
6.2.3	Results and Discussion.....	117
6.2.4	Conclusions .....	125
6.3	A High-Speed MIM Resistive Memory Cell with an Inherent Vanadium Selector .....	126
6.3.1	Introduction .....	128
6.3.2	Experimental Measurements .....	130
6.3.3	Results and discussion.....	137
6.3.4	Conclusion.....	144
6.4	Built-in Dual Selectors in Niobium Devices for Storage Applications .....	145
6.4.1	Introduction .....	146

6.4.2	Experimental Measurements .....	147
6.4.3	Results and discussion.....	152
6.4.4	Conclusion.....	159
Chapter 7 Conclusion .....		161
Reference .....		163
Publication .....		171
10 SCI First author papers .....		172
24 Refereed Paper (Co-Author) .....		173
10 International conferences .....		176
8 Patents .....		177
Curriculum Vitae .....		178
Education.....		178
Research Topics.....		178
Honors & Awards .....		178

