國立中山大學
材料與光電科學學系

博士論文 次世代電阻式記憶體之性能與物理機制研究 研究生 吳政憲 撰

國立中山大學材料與光電科學學系

博士論文

Department of Materials and Optoelectronic Science

National Sun Yat-sen University

Doctorate Dissertation

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Research on the Performance and Physical Mechanism of Next Generation Resistive Random Access Memory

研究生：吳政憲

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中華民國110年3月

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國立中山大學研究生學位論文審定書

本校材料與光電科學學系博士班

研究生吳政憲（學號：D043100003）所提論文

次世代電阻式記憶體之性能與物理機制研究
Research on the Performance and Physical Mechanism of Next Generation Resistive Random Access Memory

於中華民國 110 年 3 月 12 日經本委員會審查並舉行口試，符合博士學位論文標準。

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指導教授(蔡宗鳴) 蔡宗鳴 (簽名)

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吳政憲 謹識

摘要

隨著技術的進步，對電子產品的需求變得越來越重要，特別是在記憶體至關重要的可攜式產品領域。目前，非揮發式記憶體市場以快閃記憶體(flash memory)為主，但仍需減少寫入/抹除的時間並提高可靠性。隨著 flash memory 不斷的縮小，將達到嚴重的物理極限，因此開發次世代記憶體是當前的目標。在許多次世代記憶體中，電阻式隨機存取記憶體（RRAM）由於其出色的性能受到了廣泛的關注，期望作為次世代記憶體的解決方案。

然而，RRAM 仍存在一些量產上需要解決的問題，例如操作不穩定，操作電流大，物理機制不明確等。在這項研究中，新材料和新結構被用來改善元件性能。此外，還通過完善的電性量測，材料分析和模擬研究 RRAM 的切換機制。詳細說明如下：

在第三章中，我們提出了一種具有出色性能的 RRAM，方法是將摻有氮化硼的二氧化矽緩衝層（BN：SiO_2）插入氧化鉿(HfO_2)基底的 RRAM 中。 X 射線光電子能譜（XPS）證實六方氮化硼（h-BN）存在於 BN：SiO_2 層中，也觀察到 Pt/BN：SiO_2/HfO_2/BN：SiO_2/TiN 結構具有出色的操作次數（$> 10^{12}$ 次循環）和更高的穩定性。這可以歸因於成形(forming)過程中產生的氧離子被濺鍍機形成的 h-BN 結構侷限住。最後提出物理模型解釋插入 BN 層的 HfO_2 RRAM 之電阻切換行為。

在第四章中，展示了 Pt/In_2O_3/TiN 元件可以藉由 forming 過程所施加的偏壓，使切換層靠近在 Pt 電極或是 TiN 電極。這意味著氧化銦(In_2O_3)的 RRAM 可以在活性或者惰性電極上切換，且電流-電壓(I-V)曲線都具有良好的判讀窗口。透過材料和電性分析，發現在惰性電極切換的原因是 In_2O_3 材料富含氧空缺特性造成的，並提出物理模型進行解釋。

在第五章中，基於第四章的研究，本研究通過在 RRAM 的切換層中，沉積 In_2O_3 層作為氧離子存儲層，並探討元件的特性。透過比較 Pt / HfO_2 / TiN 元件和 Pt / HfO_2 / In_2O_3 / TiN 元件的電性結果，後者具有更好的性能，包括較低的 forming

電壓和 set/reset 電壓，具有較高電阻的低電阻狀態和高電阻狀態。通過擬合 I-V 曲線與變溫實驗驗證的傳導機制。最後，提出物理模型解釋實驗結果。

在第六章中，我們通過 reset 程度和 reset 脈衝時間的不同趨勢，來確定切換過程中電場分佈與強度的重要性。一般而言，較長的 reset 脈衝時間會形成較高的 reset 能量，較高的 reset 能量會導致較好的 reset 程度，如利用不同寬度的方波進行 reset 的實驗所示。但值得注意的是，使用三角波反而獲得相反的結果。當三角波的電壓上升時間較短，reset 能量較低，但 reset 程度卻更好。我們認為這是由於電場效應引起的：如果電壓上升的速度快於阻絲氧化的速度，則該元件在 reset 過程中會產生更大的電場，導致形成更高的電阻。為了進一步研究機制，透過快速量測手法去分析 reset 的電場效應，並透過 COMSOL 模擬進行驗證。

關鍵字：電阻式記憶體、電阻切換機制、氧化鉿、氮化硼、氧化銦、儲氧層、電場效應

Abstract

With advances in technology, the demand for electronic products has become increasingly important, especially in the field of portable products where memory is crucial. At present, the nonvolatile memory market is dominated by flash memories, despite the need to reduce write/erase time and improve reliability. With the continual scaling-down of devices, severe physical and material limitations will be reached, so development of next generation memory is a current target. Among many kind of the next-generation memories, resistive random access memory (RRAM) has attracted great attention as a next-generation memory solution due to its excellent features.

However, RRAM still has some issues that need to be solved for mass-production, such as operational instability, high operation current, unclear physical mechanism, and so on. In this research, the new material and new structure were used to improve the device characteristic. In addition, the switching mechanism in RRAM was investigated via the comprehensive electrical measurement, material analysis, and simulation. The detailed statement is as follow:

In chapter 3, we propose a resistive switching memory with outstanding comprehensive performance by inserting buffer layers of silicon dioxide doped with boron nitride (BN: SiO_2) into HfO_2 RRAM. X-ray photoelectron spectroscopy (XPS) spectra confirms that hexagonal boron nitride (h-BN) exists in the BN:SiO_2 layer. The

$Pt/BN{:}SiO_2/HfO_2/BN{:}SiO_2/TiN$ structure was observed to have superior switching endurance (> 10^{12} cycles) and higher stability. This can be attributed to the oxygen ions generated during the forming process being localized by h-BN flakes which are formed during the sputter process. A physical model is proposed to explain the resistive switching behavior of HfO_2 RRAM with the inserted BN-based layers.

In chapter 4, this study demonstrates a forming process technique which can control whether the switching layer of a $Pt/In_2O_3/TiN$ device is near the Pt electrode or the TiN electrode. This means that In_2O_3-based RRAM can be switched at either the active or inert electrode. The resistive switching current-voltage (I-V) curves for both electrodes exhibit stable memory windows. Through the material and electrical analysis, we find the reason for switching at the inert electrode is the oxygen vacancy-rich characteristic of the In_2O_3. Finally, a physical model is proposed to explain this phenomenon.

In chapter 5, based on the research in chapter 4, this study investigates an improvement in memory characteristics through depositing an In_2O_3 layer as an oxygen ion reservoir in the switching layer of resistive random access memory (RRAM). A comparison of experimental results for a $Pt/HfO_2/TiN$ device and a $Pt/HfO_2/In_2O_3/TiN$ device shows that the latter has better memory characteristics, including lower forming voltage and set/reset voltage, and higher resistances at low resistance state (LRS) and

high resistance state (HRS). The conduction mechanisms, verified through fitting I-V curves, correspond with the results of a varied temperature I-V experiment. Finally, we propose a physical model to explain our observations.

In chapter 6, we determine the importance of the electrical field distribution and strength during the switching process by demonstrating different trends in the degree of reset and the reset pulse time. In general, a longer reset pulse time results in a higher reset energy; a higher reset energy leads to a higher degree of reset, which we obtained by applying different width square waves. But quite notably, the opposite result was obtained using triangle waves, where a higher degree of reset occurred with a shorter rising time and a lower reset energy. We believe that this is due to the electric field effect: if the voltage rises faster than the filament oxidation, the device can produce a larger effective electric field and a higher resistance in the reset process. To further investigate the mechanism, the procedure of the reset process was analyzed in detail, and COMSOL simulation is also carried out for confirmation.

Keywords: Resistive Random Access Memory, Resistive Switching Mechanism, Hafnium Oxide, Boron Nitride, Indium Oxide, Oxygen Ion Reservoir, Electrical Field Effect

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