



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

Doctoral Dissertation

電阻式記憶體物理機制與超臨界流體技術應用於半導體
體元件之研究

Study on Physical Mechanism of Resistive Random Access

Memory Device and Supercritical Fluid Technique for

Semiconductor Device

研究生：林俊曲

Chun-Chu Lin

指導教授：蔡宗鳴 博士

Dr. Tsung-Ming Tsai

中華民國112年1月

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論文審定書

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

研究生林俊曲（學號：D053100012）所提論文

電阻式記憶體物理機制與超臨界流體技術應用於半導體元件之研究
Study on Physical Mechanism of Resistive Random Access Memory Device
and Supercritical Fluid Technique for Semiconductor Device

於中華民國 111 年 12 月 11 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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摘要

隨著科技的發展及進步，人們的日常生於與周遭環境中的電子 3C 產品將密不可分，因此物聯網(IoT)的概念將逐漸的受到重視，其中記憶元件的革新將主導著物聯網的發展，在許多新世代記憶元件蓬勃發展中，具有低功耗與高性能特點的電阻式記憶體(RRAM)非常有潛力成為新世代的主流記憶體。

此外，本研究開發新穎性的超臨界流體製程技術，可在低溫(RT~250°C)下改質電子元件與降低材料缺陷，大幅提升元件性能與可靠度。本研究將此技術應用於電致變色性能優化及增加酒精氣體感測器選擇比與抗水氣特性。

在第三章中，利用在銻錫氧化薄膜中共鍍了不同功率的釩實現透明電阻切換層，利用材料分析確認薄膜透明度與表面平整度，利用此薄膜作為電阻式記憶體元件的切換層，使記憶體有穩定的電阻切換特性。具有非常低的操作電壓與功耗。同時證明具有在透明元件上進行數據儲存的潛力。最後結合材料分析提出相關物理機制模型。

在第四章中，利用不同的機台限流使電阻式記憶體形成不同厚度的導通阻絲，同時實現單一元件具備單極操作與雙極操作之電阻切換特性，利用電性量測確認元件可靠度，最後結合材料分析提出相關物理機制模型。

在第五章中，利用高壓二氧化碳處理顯著提高電致變色元件性能和可靠性。中間層鋰鉬氧電解質在處理後形成結晶路徑，有效提升著色速率和退色透明度。利用高壓二氧化碳處理增加電致變色元件的特色能力與切換可靠度。利用高解析度穿透式電子顯微鏡證明結晶相形成。最後提出相關物理機制模型。

在第六章中，透過超臨界流體技術，改質氧化錫薄膜，藉由超臨界流體的高穿透性及高溶解性，將硫元素帶入形成鍵結。增加感測靈敏度，阻擋水氣影響，最後結合材料分析提出相關物理機制模型。

關鍵字：電阻式記憶體、銻錫氧化物、氧化鎳、超臨界流體技術、電致變色、氣體感測器

Abstract

With the fast development of technology, there have been so many electronic products in our daily lives. The concept of the Internet of things (IoT) get more and more attention because of the requirement of applications. The evolution of memory devices dominates the advancement, and among the next-generation memory devices, resistive random access memory (RRAM) has the most potential because of its advantages of low power-consumption and high performance.

In addition, this research develops a novel supercritical fluid (SCF) technology, which can modify electronic devices and reduce material defects at low temperatures (RT~250°C), greatly improving the performance and the reliability of electronic devices. In this study, this technology is applied to optimize the electrochromic performance and increase the selectivity and the moisture resistance of alcohol gas sensors.

In Chapter 3, the transparent resistive switching layer is realized by co-sputtering different powers of gadolinium on indium tin oxide thin film. Film transparency and surface flatness are verified by utilizing material analyses. Using this thin film as the switching layer of the RRAM enables the memory to have stable resistance switching characteristics and very low operating voltages and power consumption. Such RRAM also demonstrates the potential for data storage on transparent devices. Finally, a physical model is suggested on the basis of material analyses.

In Chapter 4, varying current compliances are utilized to control the thickness of conduction filaments in the RRAM, while also the resistance switching properties of a single RRAM device with both unipolar and bipolar operations is realized. The reliability of the device is confirmed by electrical measurements. Finally, a physical model is suggested on the basis of material analyses.

In Chapter 5, with the high-pressure carbon dioxide treatment, electrochromic element performance and dependability are significantly increased. After the treatment, the middle layer's lithium tantalum oxygen electrolyte crystallizes, which significantly boosts the bleaching transparency and the coloring rate. Electrochromic devices are treated with high pressure carbon dioxide to improve color retention and switching stability. High-resolution transmission electron microscopy is used to show how crystalline phase development occurs.

In Chapter 6, the supercritical-fluid (SCF) technique is used for changing the Tin oxide film. Sulfur element is drawn in to form bonds due to the high solubility and the penetration of supercritical fluid. Boost sensing sensitivity is enhanced, moisture influence is eliminated, and then suggest a model of the linked physical mechanism based on material analyses is proposed.

Keywords: Resistive Random Access Memory, Indium-Tin-Oxide, Nickel Oxide, Supercritical Fluid Technique, Electrochromic, Gas Sensor

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