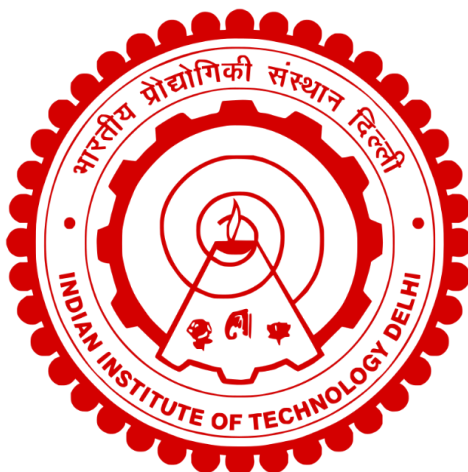


STUDY OF RESISTIVE SWITCHING PHENOMENON IN NANOSTRUCTURED MATERIALS AND THEIR NANOCOMPOSITES

AMAN SHARMA



**DEPARTMENT OF PHYSICS
INDIAN INSTITUTE OF TECHNOLOGY DELHI**

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STUDY OF RESISTIVE SWITCHING PHENOMENON IN NANOSTRUCTURED MATERIALS AND THEIR NANOCOMPOSITES

by

AMAN SHARMA

Department of Physics

Submitted

In fulfilment of the requirements of the degree of Doctor of Philosophy

to the



DEPARTMENT OF PHYSICS

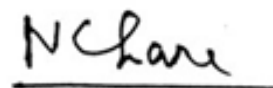
INDIAN INSTITUTE OF TECHNOLOGY DELHI

July 2025

Dedicated
to
My Family and Friends

CERTIFICATE

This is to certify that the thesis entitled “**Study of Resistive Switching Phenomenon in Nanostructured Materials and Their Nanocomposites**” being submitted by **Mr. Aman Sharma** to the Department of Physics, Indian Institute of Technology Delhi, for the award of the degree of ‘Doctor of Philosophy’ is a record of original and bonafide research work carried out by him under my supervision. He has fulfilled the requirements for the submission of this thesis, which is in my opinion has reached the requisite standard. The results contained in this thesis have not been submitted, in part or full, to any other university or institute for the award of any degree/diploma.



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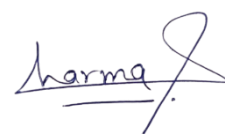
I would like to express my warm gratitude to my late brother-in-law, Shri Dharmendra Kumar (may his soul rest in peace), who played an important role in my early days of learning. His encouragement, guidance, and unwavering support laid the foundation for my academic journey, and his teachings continue to inspire me.

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Aman Sharma

Abstract

Memory devices are crucial for data storage and retrieval in modern computing systems, performing everything from basic operations to complex processing tasks. Resistive random-access memory (ReRAM) is an emerging non-volatile memory technology that has gained significant attention due to its promising advantages over traditional memory devices. Unlike conventional memories such as dynamic random-access memory (DRAM), flash and other memory devices, ReRAM operates on changing the resistance of a material to store data, offering faster switching speeds, lower power consumption and higher storage density which allows more data storage in a smaller footprint. Its endurance and retention capabilities are also superior, making it more reliable for long-term data storage. Furthermore, the simplicity of ReRAM's structure lends itself to easier fabrication and scalability, potentially leading to lower production costs and integration with advanced technologies like neuromorphic computing. The present thesis focuses on fabricating Zirconium oxide (ZrO_2) and Polyaniline (PANI) based nanocomposite devices and exploring their uses for resistive switching applications.

The ZrO_2 nanostructure powder is first synthesized by the hydrothermal method, after which the film is fabricated via the spray coating method. The film is used either as deposited or after being vacuum annealed and then the top contact is deposited by E-beam evaporation. The as-deposited film shows digital resistive switching and vacuum-annealed film shows analog resistive switching. The resistive switching measurement of the fabricated FTO/ ZrO_2 /Ag device depicts analog resistive switching in which the gradual ON and OFF states at 0.8 and -0.7 volts respectively. The fabricated device is tested for 100 cycles which showed uniform cycles with high resistance state (HRS) to low resistance state (LRS) resistance ratio $R_{\text{off}}/R_{\text{on}}$ of 1.86 at 0.35 volts. The switching mechanism in HRS and LRS is explained by I-V fitting model. In HRS, the device stays in the ohmic region at lower bias (till 0.23 volts) however at higher bias due to

filling of available traps the electrical transport is dominated by space charge limited conduction (SCLC). On the other hand, in a low resistance state (LRS), charge carriers are de-trapped, and the electrical conduction process is again governed by SCLC conduction.

We have investigated the resistive switching behaviour in as-deposited pristine ZrO_2 film without vacuum annealing. The pristine ZrO_2 sample shows digital switching at 1.8 V. The threshold voltage is found to decrease in the case of 1 wt% CNT- ZrO_2 nanocomposite device as it is 0.48 volts as compared to 1.8 volts for a pristine ZrO_2 device. The $R_{\text{off}}/R_{\text{on}}$ is also increased to 37 as compared to 21 for the pristine ZrO_2 device. The temperature-dependent resistance measurement is performed for the ZrO_2 -CNT resistive switching device to study the resistive switching behavior in both HRS and LRS respectively. The HRS of pristine ZrO_2 and 1wt% CNT- ZrO_2 shows semiconducting behaviour. However, HRS of 2wt% CNT- ZrO_2 and LRS of pristine ZrO_2 , 1 wt% CNT- ZrO_2 , 2wt% CNT- ZrO_2 sample shows metallic behaviour with the increase in resistance with an increase in temperature. The temperature dependent resistance coefficient (α) in LRS is increased from $3.1 \times 10^{-3} \text{ K}^{-1}$ for pristine ZrO_2 to $4.1 \times 10^{-2} \text{ K}^{-1}$ for 2wt% CNT- ZrO_2 which emphasizes that in pristine ZrO_2 the only oxygen vacancies are involved on the conduction process. However, for CNT- ZrO_2 composite device both oxygen vacancies as well as CNT filaments are involved in the process of conduction.

In order to see the effect of conducting silver nanoparticles (AgNP) on ZrO_2 nanocomposite device, the FTO/AgNP- ZrO_2 /Ag device is fabricated. The I-V measurement of pristine ZrO_2 film shows digital resistive switching at a threshold value of 1.8 volts. However, it is observed that with the increase of silver in the AgNP- ZrO_2 nanocomposite film, the threshold voltage becomes 1.53 volts for 0.5wt% AgNP- ZrO_2 device, and it came down to 0.38 volts for 1wt% AgNP- ZrO_2 device. The resistance ratio is also increased as it is 22 for pure ZrO_2 device and it

became 29 for 0.5wt% AgNP and 32 for 1wt% AgNP- ZrO₂ devices. The conduction mechanism is explained by the temperature-dependent resistivity measurement, which shows in HRS, all three devices (Pure ZrO₂, 0.5wt% and 1wt% AgNP- ZrO₂) show the semiconducting behaviour with a decrease of activation energy from 87.1 meV to 48.43 meV with an increase of AgNP content. In LRS, all the devices show a metallic-like conduction. It is also observed that the temperature coefficient of resistance (α) increases with an increase of AgNP from 3.54×10^{-3} to $5.15 \times 10^{-2} \text{ K}^{-1}$. The increase in the value of α for the AgNP-ZrO₂ composite device suggests that in pure ZrO₂, only oxygen vacancies take part in conduction; however, AgNP- ZrO₂ composite both oxygen vacancies as well as Ag metal nanoparticles are participating in the conduction process.

Additionally, we fabricated an FTO/CNT-PANI/Ag composite device. In the case of pristine PANI device, the digital switching is observed at 1.75 volts, however its behaviour is changed to analog resistive switching with voltage 0.85 volts for 0.5 wt% CNT-PANI device. The analog behaviour is verified by potentiation and depression measurement as there is no gap between the memresistance of the two states. Further, R-T measurements are performed in both states, which show semiconducting behaviour in HRS of pristine PANI with activation energy of 58 meV. The LRS of pristine PANI, HRS and LRS of 0.5 wt% CNT and 1wt% CNT-PANI show metallic behaviour with an increase of resistance with an increase in temperature. The α value increases to $3.1 \times 10^{-2} \text{ K}^{-1}$ for LRS of 1wt% CNT-PANI as compared to $5.1 \times 10^{-3} \text{ K}^{-1}$ for pristine PANI device. The increase in the value of α suggests that in pristine PANI only silver (Ag) ions take part in the conduction however in CNT-PANI composite device both CNT as well as Ag ions take part in the conduction process.

स्मृति (Memory) उपकरण आधुनिक कंप्यूटिंग प्रणालियों में डेटा संग्रहण और पुनर्प्राप्ति के लिए अत्यंत महत्वपूर्ण हैं, जो बुनियादी संचालन से लेकर जटिल प्रसंस्करण कार्यों तक सब कुछ संभालते हैं। रेजिस्टिव रैंडम-एक्सेस मेमोरी (ReRAM) एक उभरती हुई नॉन-वोलेटाइल मेमोरी तकनीक है, जिसने पारंपरिक मेमोरी उपकरणों पर अपने संभावित लाभों के कारण महत्वपूर्ण ध्यान आकर्षित किया है। पारंपरिक मेमोरी जैसे डायनामिक रैंडम-एक्सेस मेमोरी (DRAM), फ्लैश और अन्य उपकरणों के विपरीत, ReRAM डेटा संग्रहण के लिए सामग्री की प्रतिरोध को बदलने पर कार्य करता है, जिससे यह तेज स्विचिंग गति, कम ऊर्जा खपत और उच्च संग्रहण घनत्व प्रदान करता है, जिससे कम स्थान में अधिक डेटा संग्रहण संभव हो पाता है। इसकी एंड्यूरेंस और रिटेंशन क्षमताएँ भी उत्कृष्ट होती हैं, जिससे यह दीर्घकालिक डेटा संग्रहण के लिए अधिक विश्वसनीय बनता है। इसके अलावा, ReRAM की संरचना की सरलता इसे आसान निर्माण और स्केलेबिलिटी के लिए उपयुक्त बनाती है, जिससे उत्पादन लागत कम हो सकती है और न्यूरोमॉर्फिक कंप्यूटिंग जैसी उन्नत तकनीकों के साथ इसका एकीकरण संभव हो सकता है।

वर्तमान थीसिस में जिरकोनियम ऑक्साइड (ZrO_2) और पॉलीएनिलीन (PANI) आधारित नैनोकॉम्पोजिट डिवाइस का निर्माण और उनके रेजिस्टिव स्विचिंग अनुप्रयोगों के लिए उपयोग की खोज की गई है। ZrO_2 नैनोस्ट्रक्चर पाउडर को पहले हाइड्रोथर्मल विधि से संश्लेषित किया गया जिसके बाद फिल्म को स्प्रे कोटिंग विधि से तैयार किया गया। फिल्म को या तो डिपॉजिटेड अवस्था में या वैक्यूम ऐनीलिंग के बाद उपयोग किया गया और फिर शीर्ष संपर्क ई-बीम वाष्पीकरण द्वारा बनाया गया। डिपॉजिटेड फिल्म डिजिटल रेजिस्टिव स्विचिंग दिखाती है जबकि वैक्यूम ऐनीलड फिल्म एनालॉग रेजिस्टिव स्विचिंग दिखाती है। निर्मित FTO/ ZrO_2 /Ag डिवाइस का रेजिस्टिव स्विचिंग मापन 0.8 वोल्ट (ON) और -0.7 वोल्ट (OFF) पर एनालॉग स्विचिंग दिखाता है। डिवाइस का 100 चक्रों के लिए परीक्षण किया गया, जिसमें हाई रेसिस्टेंस स्टेट

(HRS) से लो रेसिस्टेंस स्टेट (LRS) के लिए प्रतिरोध अनुपात R_{off}/R_{on} 1.86 (0.35 वोल्ट पर) पाया गया। HRS और LRS में स्विचिंग तंत्र को I-V फिटिंग मॉडल से समझाया गया है। HRS में, डिवाइस कम बायस (0.23 वोल्ट तक) पर ओह्मिक क्षेत्र में रहता है, जबकि उच्च बायस पर उपलब्ध ट्रैप्स के भरने के कारण विद्युत परिवहन स्पेस चार्ज लिमिटेड कंडक्शन (SCLC) से नियंत्रित होता है। दूसरी ओर, LRS में चार्ज कैरियर्स डी-ट्रैप हो जाते हैं और विद्युत प्रवाह प्रक्रिया फिर से SCLC कंडक्शन द्वारा नियंत्रित होती है।

इसके बाद, बिना वैक्यूम ऐनीलिंग के डिपॉजिटेड प्रिस्टिन ZrO_2 फिल्म में रेजिस्टिव स्विचिंग व्यवहार की जांच की गई। प्रिस्टिन ZrO_2 नमूना 1.8 वोल्ट पर डिजिटल स्विचिंग दिखाता है। 1 wt% CNT- ZrO_2 नैनोकॉम्पोजिट डिवाइस के मामले में थ्रेशोल्ड वोल्टेज घटकर 0.48 वोल्ट पाया गया, जबकि प्रिस्टिन ZrO_2 डिवाइस के लिए यह 1.8 वोल्ट था। R_{off}/R_{on} अनुपात भी 21 (प्रिस्टिन ZrO_2) से बढ़कर 37 (1 wt% CNT- ZrO_2) हो गया। ZrO_2 -CNT रेजिस्टिव स्विचिंग डिवाइस के लिए तापमान-निर्भर प्रतिरोध मापन किया गया, जिससे HRS और LRS दोनों में रेजिस्टिव स्विचिंग व्यवहार का अध्ययन किया गया। प्रिस्टिन ZrO_2 और 1 wt% CNT- ZrO_2 का HRS सेमीकंडक्टिंग व्यवहार दिखाता है, जबकि 2 wt% CNT- ZrO_2 का HRS और प्रिस्टिन ZrO_2 , 1 wt% CNT- ZrO_2 , 2 wt% CNT- ZrO_2 का LRS मेटालिक व्यवहार दिखाता है, जिसमें तापमान बढ़ने पर प्रतिरोध बढ़ता है। LRS में तापमान-निर्भर प्रतिरोध गुणांक (α) प्रिस्टिन ZrO_2 के लिए $3.1 \times 10^{-3} K^{-1}$ से बढ़कर 2 wt% CNT- ZrO_2 के लिए $4.1 \times 10^{-2} K^{-1}$ हो गया, जो दर्शाता है कि प्रिस्टिन ZrO_2 में केवल ऑक्सीजन रिक्तियों की भूमिका होती है, जबकि CNT- ZrO_2 कॉम्पोजिट डिवाइस में ऑक्सीजन रिक्तियों के साथ-साथ CNT फिलामेंट्स भी प्रवाह प्रक्रिया में शामिल होते हैं।

चालक सिल्वर नैनोपार्टिकल्स (AgNP) के ZrO_2 नैनोकॉम्पोजिट डिवाइस पर प्रभाव को देखने के लिए, FTO/AgNP- ZrO_2 /Ag डिवाइस का निर्माण किया गया। प्रिस्टिन ZrO_2 फिल्म का I-V मापन

1.8 वोल्ट के थ्रेशोल्ड पर डिजिटल रेजिस्टिव स्विचिंग दिखाता है। हालांकि, यह देखा गया कि AgNP सामग्री की वृद्धि के साथ, थ्रेशोल्ड वोल्टेज 0.5 wt% AgNP-ZrO₂ डिवाइस के लिए 1.53 वोल्ट और 1 wt% AgNP-ZrO₂ डिवाइस के लिए 0.38 वोल्ट हो गया। प्रतिरोध अनुपात भी बढ़ा, जो प्रिस्टिन ZrO₂ डिवाइस के लिए 22 था और 0.5 wt% AgNP के लिए 29 और 1 wt% AgNP-ZrO₂ डिवाइस के लिए 32 हो गया। तापमान-निर्भर प्रतिरोधता मापन द्वारा प्रवाह तंत्र को समझाया गया, जिसमें HRS में सभी तीन डिवाइस (शुद्ध ZrO₂, 0.5 wt% और 1 wt% AgNP-ZrO₂) सेमीकंडक्टिंग व्यवहार दिखाते हैं, और सक्रियण ऊर्जा AgNP सामग्री बढ़ने के साथ 87.1 meV से घटकर 48.43 meV हो जाती है। LRS में सभी डिवाइस मेटालिक-जैसा प्रवाह दिखाते हैं। साथ ही, तापमान गुणांक (α) 3.54×10^{-3} से बढ़कर $5.15 \times 10^{-2} \text{ K}^{-1}$ हो जाता है। AgNP-ZrO₂ कॉम्पोज़िट डिवाइस के α के बढ़े हुए मान से संकेत मिलता है कि शुद्ध ZrO₂ में केवल ऑक्सीजन रिक्तियां प्रवाह में भाग लेती हैं, जबकि AgNP-ZrO₂ कॉम्पोज़िट में ऑक्सीजन रिक्तियों के साथ-साथ चांदी (Ag) नैनोकण भी प्रवाह प्रक्रिया में भाग लेते हैं।

अंत में, हमने FTO/CNT-PANI/Ag कॉम्पोज़िट डिवाइस का निर्माण किया। प्रिस्टिन PANI डिवाइस के मामले में, 1.75 वोल्ट पर डिजिटल स्विचिंग देखी गई, हालांकि 0.5 wt% CNT-PANI डिवाइस के लिए यह व्यवहार बदलकर 0.85 वोल्ट पर एनालॉग रेजिस्टिव स्विचिंग में बदल गया। एनालॉग व्यवहार को पोटेंशिएशन और डिप्रेशन मापन द्वारा सत्यापित किया गया क्योंकि दो स्टेटस की मेमरेसिस्टेंस के बीच कोई अंतराल नहीं था। इसके अलावा, दोनों अवस्थाओं में R-T मापन किया गया, जिसमें प्रिस्टिन PANI के HRS में 58 meV की सक्रियण ऊर्जा के साथ सेमीकंडक्टिंग व्यवहार देखा गया। प्रिस्टिन PANI के LRS, 0.5 wt% CNT और 1 wt% CNT-PANI के HRS और LRS मेटालिक व्यवहार दिखाते हैं, जिसमें तापमान बढ़ने पर प्रतिरोध में वृद्धि होती है। LRS के लिए α मान 1 wt% CNT-PANI के मामले में $3.1 \times 10^{-2} \text{ K}^{-1}$ तक बढ़ जाता

हैं, जबकि प्रिस्टिन PANI डिवाइस के लिए यह $5.1 \times 10^{-3} \text{ K}^{-1}$ था। α के बढ़े हुए मान से पता चलता है कि प्रिस्टिन PANI में केवल चांदी (Ag) आयन प्रवाह में भाग लेते हैं, जबकि CNT-PANI कॉम्पोजिट डिवाइस में CNT के साथ-साथ Ag आयन भी प्रवाह प्रक्रिया में भाग लेते हैं।

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