

Fabrication of ceria thin films for high performance resistive random access memory applications

Author:

Zhang, Lepeng

Publication Date:

2016

DOI:

<https://doi.org/10.26190/unsworks/19027>

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Fabrication of Ceria Thin Films for High Performance Resistive Random Access Memory Applications

Lepeng Zhang

A thesis in fulfilment of the requirements for the degree of

Master of Engineering (Research)



School of Materials Science & Engineering

Faculty of Science

University of New South Wales

April 2016

PLEASE TYPE
THE UNIVERSITY OF NEW SOUTH WALES

Thesis/Dissertation Sheet

Surname or Family name: **Lepeng**

First name: **Zhang**

Other name/s:

Abbreviation for degree as given in the University calendar: **Master
of Engineering**

School: **School of Materials Science & Engineering**

Faculty: **Faculty of Science**

Title:
Fabrication of Ceria Thin Films For High Performance Resistive
Random Access Memory Applications

Abstract 350 words maximum: (PLEASE TYPE)

Resistive random access memories (RRAMs) have attracted much attention because of their unique advantages, such as simpler structure, faster reading and writing speed, smaller bit size and lower power consumption. Metal oxide thin films are potential candidates for RRAMs owing to their tunable physical properties, e.g. oxygen vacancy concentration. In this dissertation, solution processed metal oxide thin films with tunable resistive switching properties have been explored.

First, sputtered CeO_2 ceria thin films were fabricated by implementing different sputtering (temperatures and powers) conditions. The films deposited at low temperatures were found to have random crystal orientation and dense structure. The effects of deposition conditions on resistive switching characteristics were investigated. Improved and stable resistive switching behaviours were achieved at low deposition temperatures. In addition, the possible switching mechanism was explained on the basis of quantitative analysis.

Furthermore, indium doped CeO_2 nanocrystalline films were directly grown by a one-step template-free electrochemical deposition process. The Au/In- CeO_2 /FTO capacitor exhibits stable bipolar resistive switching behavior, and the resistive switching behavior may be related to the oxygen vacancies, giving rise to the formation of straight and extensible conducting filaments along the electric fields. Superior stability in resistive switching characteristics was also observed, indicating that CeO_2 is a potential material for next-generation nonvolatile memory applications.

Finally, different elements were doped into CeO_2 for investigating doping effects on the resistive switching properties of CeO_2 .

The studies in this dissertation demonstrate the great potential of fabricating novel CeO_2 based RRAM devices by both physical and chemical approaches. Doping indium or gadolinium into ceria can enhance the performances of the resistive switching behaviour by introducing more oxygen vacancies. This study presents a potential research direction towards developing new approaches to fabricate next generation nanoelectronic devices.

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ACKNOWLEDGEMENTS

I would like to express my sincere gratitude and appreciation to my supervisors Professor Sean Li, Dr. Adnan Younis and Dr. Dewei Chu for their endless help to finish this thesis. Their encouragement helped me remain enthusiastic and concentration on research. Their guidance and advice also inspire me to be a good researcher and to critically think about the research. I am deeply grateful for their suggestions that lead me in the right research direction.

Special thanks to Material Science and Engineering UNSW Australia for providing such an excellent environment. Finally, I express my deepest gratitude to my parents who supported me to finish this master degree.

LIST OF PUBLICATIONS

1. Adnan Younis, **Lepeng Zhang**, Dewei Chu, and Sean Li, Probing complementary memristive characteristics in oxide based memory device via non-conventional chronoamperometry approach, Applied Physics Letters 108, 033506 (2016)。
2. **Lepeng Zhang**, A.Younis, D.Chu, S.Li. Impact of Deposition Parameters on the Performance of Ceria Based Resistive Switching Memories, Journal of Physics D: Applied Physics (In Press-2016)

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Abstract

Many studies have investigated Resistive random access memories (RRAMs) because of their unique advantages compared with current memory technology, such as simpler structure, faster reading and writing speed, smaller bit size, lower power consumption. Metal oxides have shown superior resistive switching properties such as larger ON/OFF ratio, faster response speed and scalability compared with other materials. Therefore, this dissertation is focused on the development of high quality metal oxide thin films for RRAM applications with different deposition approaches.

Ceria based resistive memory stacks were fabricated by implementing different sputter (temperatures and powers) conditions. The films deposited at low temperatures were found to have random grains orientations, lower porosity and dense structure. The effects of deposition conditions on resistive switching characteristics were also investigated. Improved and reliable resistive switching behaviours were achieved for the memory device occupying less porous and dense structures prepared at low temperatures. Finally, the underlying switching mechanism was also explained on the basis of quantitative analysis.

Furthermore, indium doped CeO_2 nanocrystalline films were directly grown by a template-free one-step electrochemical deposition process. The $\text{Au/In-CeO}_2/\text{FTO}$ capacitor exhibits stable bipolar resistive switching behavior. The resistive switching behavior may be related to the oxygen vacancies, giving rise to the formation of straight and extensible conducting filaments along the electric fields. Superior stability in resistive switching characteristics was also observed, indicating that CeO_2 is a potential material for next-generation nonvolatile memory applications. Various elements have been doped into CeO_2 for investigating doping effects on the resistive switching properties of CeO_2 .

The studies presented in this dissertation have demonstrated great potential to fabricate novel CeO_2 by radio frequency magnetron sputtering. Doping Indium or Gadolinium into ceria can enhance the performances of the resistive switching behaviour. This study provides a new research direction towards developing new approaches to fabricate novel nanoelectronics devices.

Chapter 1 Introduction

Conventional semiconductor based memory have been widely used in integrated circuit technologies in the past decades, especially portable mobile electronic devices in real life such as mobiles and laptops. Memory will play an important role in the next decade which can meet requirements of high speed, small size and low power consumption. Semiconductor memories have been classified in two types by their character which are Random Access Memories (RAMs) and Read-only Memories (ROMs) ^{1 2}. RAMs can be used for reading or writing information at the same time. However, the use of ROMS for read is more than writing information ^{3 4}.

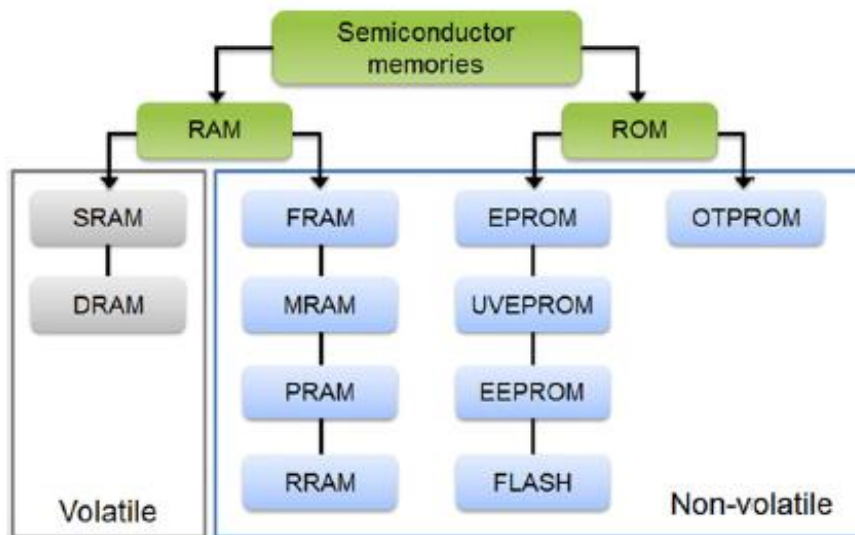


Figure 1-1: Categories of standard semiconductor memories ³

The existing categories of semiconductor memories are shown in figure1-1. Non-volatile memories (NVMs) can store information when the power is off. The information stored in volatile memorise is lost when power is cut. All ROMs and parts of RAMs are NVMs. Furthermore, volatile RAMs can be divided into static random access memories (SRAMs) and dynamic random access memories (DRAMs). DRAMs is based on the capacitor area, and the feature size of DRAMs cannot reach below 30nm

without solving problems such as serial resistance or current leakage issues ⁵. Hence, there emerge several different classes of memories such as; ferroelectric RAMs (FRAMs), magnetic RAMs (MRAMs), phase-change RAMs (PRAMs) and resistive RAMs (RRAMs) ^{6 7 9}. FRAMs and MRAMs had similar issues of reliability and scalability ⁹. Hence, the RRAMs class is one of the best candidates for next generation memories that have competitive advantages of high-density and low cost, fast speed, low power consumption, and high performance with endurance and retention ¹⁰, and good compatibility with CMOS processes ¹¹.

resistive random access memories (RRAM) have attracted a lot of interest as a promising candidate for next generation non-volatile memories ^{2 12 13}. So far, various materials including metal sulphides ¹⁴, organic compounds ¹⁵, metal oxides ¹⁶, non-metal oxides ¹⁷ and phase-change materials ¹⁸ have been used as resistive switching materials. For electrode materials, Au ¹⁹, Pt ¹⁹, W ²⁰, al. ²¹, Ni ²², Ag ²³, Ti ²⁴ and many other metals and alloys ^{25 26 27 28} were also used. Unfortunately, most of the reported materials have not been completely optimized yet for their commercial applications as a RRAM material. The possible reasons behind these limitations are the requirements for further improvements in their reliability issues (uniformity in switching parameters).

Although the physical explanations behind the RRAM operational mechanism is still not fully understood, according to some observations, the implementations of several specific physical or chemical conditions to the electrodes/resistive switching layers can predict the resistive switching behaviour. For instance, by utilizing highly reactive or inert metal electrodes with resistive switching materials having specific thermodynamic stabilities, band gap energies and therefore, different band-offsets to the metal electrodes, several different conduction mechanisms are expected²⁹. Furthermore,

implementing different current compliances³⁰ and regulating voltage sweep rates³¹ results in different responses because of different carrier conduction mechanisms.

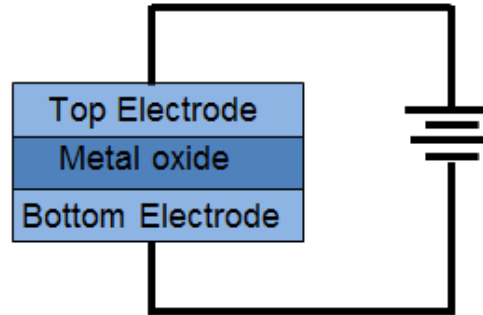


Figure 1-2: The Metal Insulator Metal (MIM) structure of RRAM

Younis et al. studied the observed switching phenomena¹⁰. The resistive switching phenomena are associated with (1) the band bending caused by the charge trapping, (2) the change in the oxidation state of the cations that redox reaction, (3) the motion of electrons and/or (4) oxygen vacancy defects that can be rapidly formed and eliminated. To meet the requirements of RRAMs, the switching materials should have moderate band gap and high dielectric constants³². Most metal oxides showed resistive switching effects such as NiO, TiO₂ and Cu₂O³². The resistive switching behaviour has also been observed in many other different materials, such as group IV and III-V semiconductors and organic compounds, but their resistive switching behaviour is threshold type (volatile)¹¹ which cannot overcome RAM's current problems of low size, high speed and low energy consumption.

Ceria is a well-known rare-earth metal oxide with a high dielectric constant (26), large bandgap (3.6 eV), and high refractive index (2.2–2.3). Moreover, it occupies multiple oxidation states (+3/+4) which indicates its great potential suitability for memories.

In this project, we utilize physical and chemical methods, radio frequency (RF) sputtering and electrochemical deposition, to fabricate ceria thin films. Sputtering, as a kind of Physical Vapour Deposition (PVD), is widely utilized in thin film industry. As to the deposition principle of PVD or sputter, thin film can be deposited through bombarding ions on a target made of deposited materials. Unlike most deposition methods, sputtering does not involve any chemical interactions during deposition³³. The energy used to promote film growth can be compensated by the bombardment of the target with ejected energetic ions. Thus, good quality thin films can be deposited by sputtering at moderate temperatures (<500°C)³³. Because of low deposition temperature, a wide variety of materials can be considered as a substrate by using sputtering various applications³³. In RF magnetron sputtering, the properties of the deposited thin films critically depend on the sputter conditions such as oxygen partial pressure, substrate temperature, and sputter power³⁴. Low deposition temperature, before/post deposition modification of substrate/ film surface by ions even on the nano level and easy to control further parameters are advantages of RF sputtering³⁵. An extra conductive layer may be patterned on the substrate. This project starts with cerium oxide thin film and then doping cerium is also tested to tune their RS properties. Finally, current-voltage (I-V) characteristics and microstructure of the RRAM device is measured for the main properties such as retention, endurance, and others.

Chapter 2 Literature review

This chapter starts with basic properties of Ceria. Then classification of resistive switching behaviour is followed by briefly reviewing two of the most common resistive switching mechanisms. The second section focuses on different methodologies to synthesize Ceria films.

2.1. Cerium Oxide

2.1.1 Electrical Properties

As the element of the second member in the lanthanide series, Ce has high stable features ³⁶. The three most weakly-bound 4f electrons results in cerium performing stable cerium oxide state in nature ³⁷. Cerium usually has two types of oxides in nature which are cerium dioxide (CeO_2) and cerium sesquioxide (Ce_2O_3). However, due to highest stability of CeO_2 , cerium dioxide is much more common.

2.1.2 Crystal Structure

The Cerium dioxide (CeO_2) fluorite structure (FCC) is shown in figure 2-1. The cube corners are occupied by oxygen atoms and cerium is at the centre.

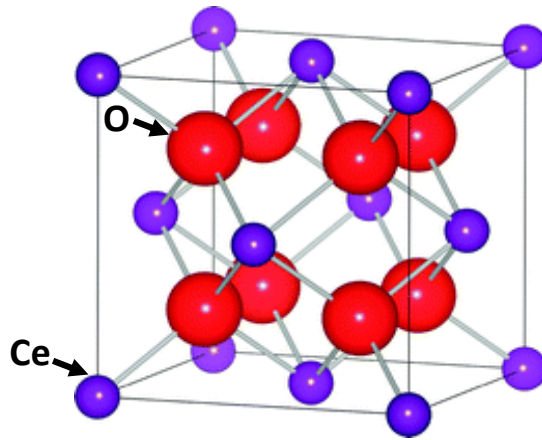


Figure 2-1: FCC structure for CeO_2 ³⁸

2.1.3 Microstructure:

Depending on various synthesis conditions, method and substrate morphology, CeO_2 film can form several different microstructures. Grains have a large effect on the electrical properties in thin films by forming depletion layers with low conductivity similar to Schottky barriers in metal-insulator junctions ³⁹.

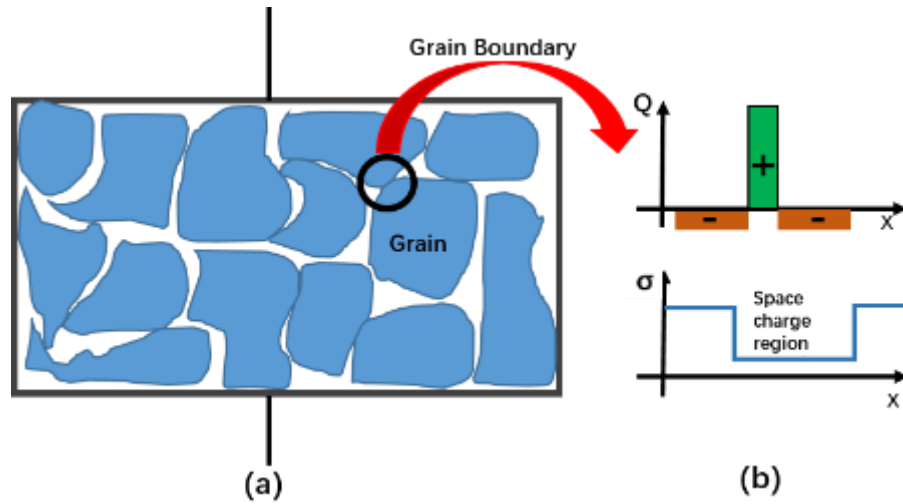


Figure 2-2 (a) Cross-section of CeO_2 thin film device (b) Space charge region and the consequent change of the conductivity

Figure 2-2(a) shows the cross-section of CeO_2 devices with the grain and grain boundary. The space charge region and the reduced conductivity are shown in figure 2-2(b). The space charge region can exceed the grain size which results in distributed conductivities far below the bulk conductivity of the material ⁴⁰.

2.2. Classification of resistive switching behaviour:

Based on I - V characteristics resistive switching behaviour can be classified as two types: unipolar and bipolar switching.

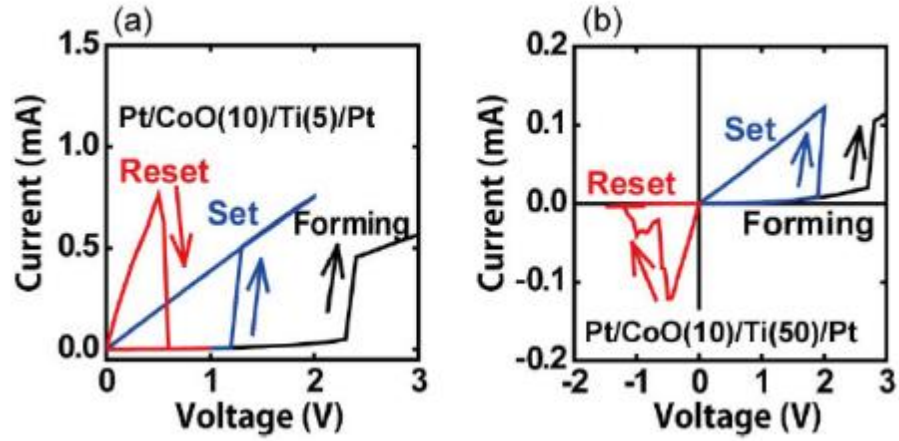


Figure 2-3: (a) Unipolar and (b) bipolar operations of CoO-based RRAM with the bottom electrode of Pt and the top electrode consisting of Ti/Pt ¹¹

In Figure 2-3, I - V characteristics of unipolar and bipolar have been showed. The difference between unipolar and bipolar is the switching direction depends on the amplitude of the applied voltage or the polarity³². In unipolar switching behaviour, the reset and set process depends on the applied voltage amplitude. Bipolar switching behaviour, unlike unipolar switching behaviour, performs with the change of voltage polarity. It depends on the polarity of applied voltage shown in Figure 2-3(b), and the types of switching behaviour are decided by the kinds of switching materials. The unipolar switching behaviour occurs with many highly insulating oxides³². For an RRAM device, there may be a requirement for forming process to apply a high voltage stress to trigger the device, but it varies from material to material and system to system.

2.3. Possible mechanisms

There are several different mechanisms discussed about different materials that address switching kinetics in switching materials. There are several review papers that discuss the possible mechanisms^{41 42 43 44 45}. Currently, there is no certain mechanism about

how the resistive switching behaviour occurs⁴⁶. However, several possible mechanisms have been categorized and most of them are based on the formation and rupture of filaments^{47 48 49 50 51}.

One of these mechanisms is filamentary mechanism, which is defined by the phenomenon that a filamentary conducting path can be built or destroyed during resistive switching processes^{52 53 54}. The basic mechanism of filaments is that one or multiple filaments (local conducting channel) are formed or ruptured in the insular layer as a result of external stimuli, such as an electric field². This thesis focuses on filament path, because compared with previous studies, the material (CeO_2) used in this project is based on filamentary mechanism.

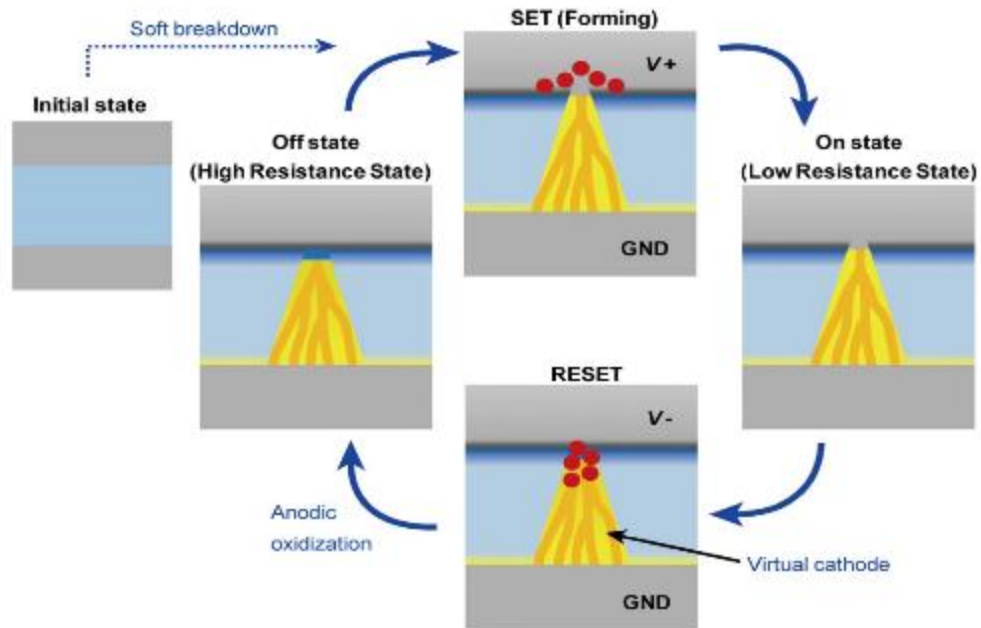


Figure 2-4: Schematics of the initial state (as-prepared sample) and (1) forming, (2) reset, and (3) set processes¹¹

Figure 2-4 is a schematic showing how filamentary mechanism conducting paths form and rupture. Some materials may need a forming process by applied high voltage, and

in this process, filamentary conducting paths can be formed as a soft breakdown in the dielectric material ³². The process from High Resistance State (HRS) to Low Resistance State (LRS) is a SET process, and from LRS to HRS is a RESET process. When applying a positive voltage on TE, a large number of carriers can be trapped by vacancies. The filamentary is formed and the device becomes LRS. When switching from positive voltage to negative voltage, the vacancies release many carriers. With the rupture of the filamentary conducting path, the device becomes in a High Resistance State ⁴⁸. Akinaga H. pointed out that the possible mechanism behind the formation and rupture of the filaments is thermal redox and anodization near the interface between the metal electrode and the oxide ¹¹. Normally, people consider the Joule heating caused by applied voltage as the main reason for rupture of a filamentary conducting path ⁴⁹. The typical mechanism of filaments is normally independent with the touching area between device electrodes ^{12 14}.

2.3.1. Electrochemical metallization cells

Resistive switching devices based on cation migrations are usually in terms as electrochemical metallization (ECM) cells ². Similar to other RRAMs, the basic structure of an ECM cells is metal-insulator-metal (MIM) style with an electrochemically active electrode such as Ag or Cu and an electrochemically inert electrode such as Pt or W ². The material used in the insulator layer in ECM cells can be a solid electrolyte material such as Ag doped Ge-Se or a dielectric material like SiO₂. Usually, the metallic cations come from electrode materials. Hence, an electrochemically active material should be a good candidate to the electrode material (anode), such as Cu ^{55 56 57}, Ag ⁵⁸, and Ni ⁵⁹. However, for the other electrode material

(cathode), relatively inert materials can be selected such as Pt^{55 60}, W⁵⁸, or active materials such as Ag⁶¹. There are plenty of materials including chalcogenides (Cu₂S⁶², Ge_xS_x⁶³, Zn_xCd_{1-x}S⁶⁴, GeTe⁶⁵), many oxides (Ta₂O₅⁶⁶, HfO₂⁶⁷, Al₂O₃⁶⁸, MoO_x⁶⁹, ZrO_x⁷⁰, SrTiO₃⁷¹, TiO₂⁷², CuO_x⁷³, ZnO⁷⁴), halides (AgI⁷⁵, RbAg₄I₅⁷⁶) as well as some organics frequently reported previously as the insulating or resistive switching materials sandwiched between cathode and anode. In resistive switching process, oxidized electrode materials lead to migrations of cations towards the inert electrode, and finally result in the formation and rupture of metal filaments in ECM cells; this process that causes resistive switching behaviour between HRS and LRS is reversible. Filaments are formed locally and only affected by local electrical and chemical conditions. Hence, for ECM cells, electrochemical redox reactions can be used to explain Ag or Cu conducting filaments.

2.3.2. Valency change memory:

Cation migration based metal filaments are not the only device that can show resistive switching behaviour. Another major resistive switching device such as binary transition oxides device is based on the migration of anions such as oxygen anions². Normally, oxygen anions are described as their charged positive part: oxygen vacancies². Different effects classified the anion migration based model as 2 types². One type path is an interface-type path that the resistive switching takes place at the interface between electrode and switching materials in Figure 2-5³². The Schottky barrier can be changed by the cumulated oxygen vacancies at the interface. This kind of switching behaviour shows the area dependence of the cell resistance.

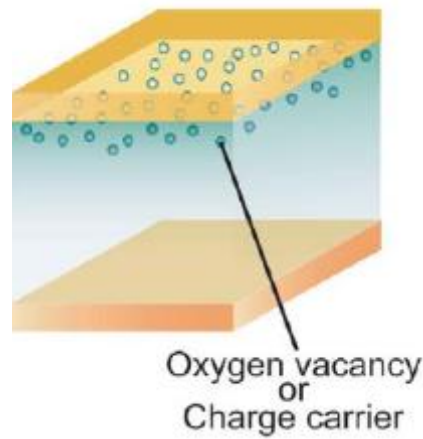


Figure 2-5: an interface-type conducting path ³²

Another type of model is based on filaments composed by a new phase with a different valence state of cations or oxygen vacancies. This kind of model also is named as valency change memory (VCM) and its shows bipolar switching behaviour ². During the valency change process, a new phase that conductive filaments can be formed and rupture caused by oxygen vacancies combining and disappears.

2.4. Cerium oxide based RRAM:

Owing to high dielectric constant value, moderate band gap ($\sim 3.6\text{eV}$) ¹ and by occupying various valence states (Ce^{3+} and Ce^{4+}), Cerium oxide has great advantages for the applications of RRAM. In the past, several different methodologies (including physical and chemical methods) have been implemented to fabricate cerium oxide based materials as RRAM cells ².

Younis et al. have reported the electrochemical synthesis of CeO_2 thin films al. ¹⁰. By increasing the local pH value in the vicinity of the electrode, nitrate ions and H_2O are electrochemically reduced at the surface of the working electrode. Then, at a suitable

temperature, the precipitation of cerium ions (cerium hydroxide) is induced by this increase in local PH. Furthermore, $\text{Ce}(\text{OH})_3$ can be transformed into CeO_2 and H_2 ¹⁰.

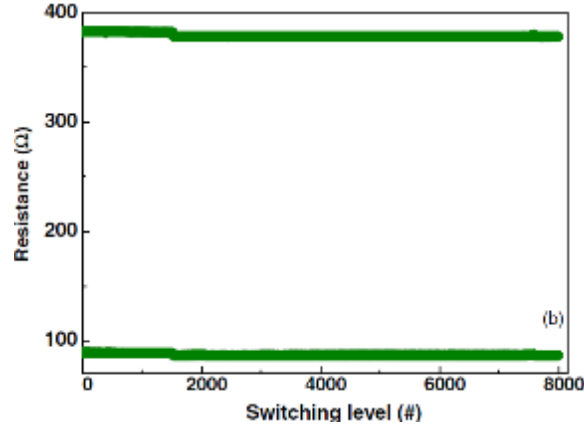


Figure 2-6: Endurance performances (for 60 s) of as-prepared CeO_2 film ¹⁰

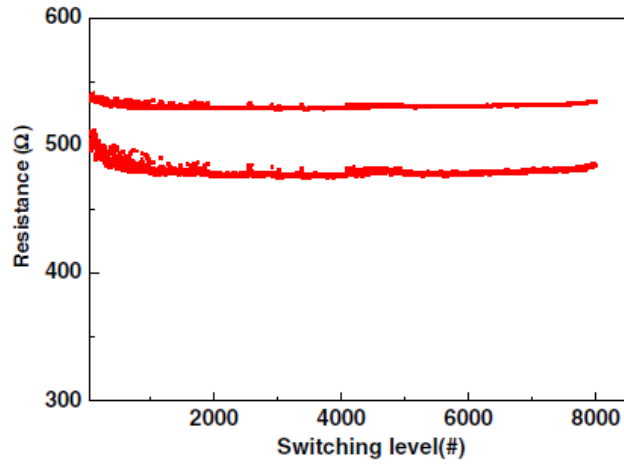


Figure 2-7: Endurance performances (for 60 s) of the annealed CeO_2 film ¹⁰

Oxygen vacancy level is the dominant resistive switching characteristics shown in cerium oxide thin films ¹⁰. Figures 2-6 and 2-7 show the endurance performances of as-prepared (before annealing) and annealed CeO_2 films. The window of annealed CeO_2 in figure 2-7 is much smaller than as-prepared film in figure 2-6. CeO_2 film annealed in air

which is an oxygen environment fills oxygen vacancies that caused the reduction in resistive switching behaviour.

Lin et al. used RF sputtering to fabricate CeO_2 thin films on SiO_2/Si substrates⁷⁷. During deposition, the substrate temperature was kept at 250 °C and the working pressure was maintained at 10mTorr by a mixture of Ar and O_2 with a flow rate ratio of 12 sccm: 6 sccm.

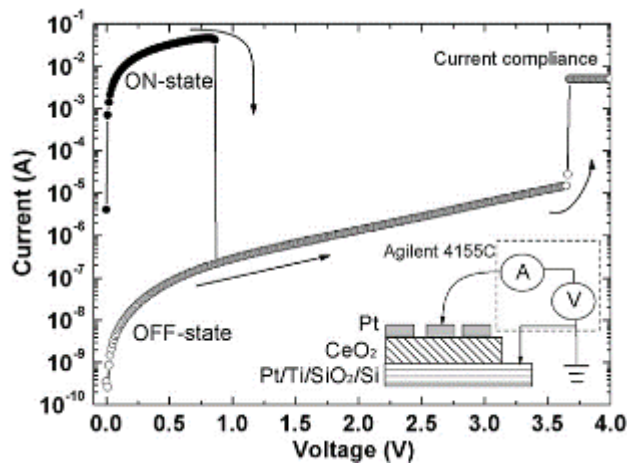


Figure 2-8: *I-V* characteristics of the Pt/ CeO_2 /Pt device in semi-logarithmic plot⁷⁷

The performance of RF sputtering made CeO_2 shown in figure 2-8, and the resistance ratio between OFF-state and ON-state can reach five orders of magnitude.

In Dou's work, they used electron beam evaporation to deposit a CeO_2 film on substrate⁷⁸. *I-V* characteristics of CeO_2 film made by electron beam evaporation have been showed as below figure 2-9.

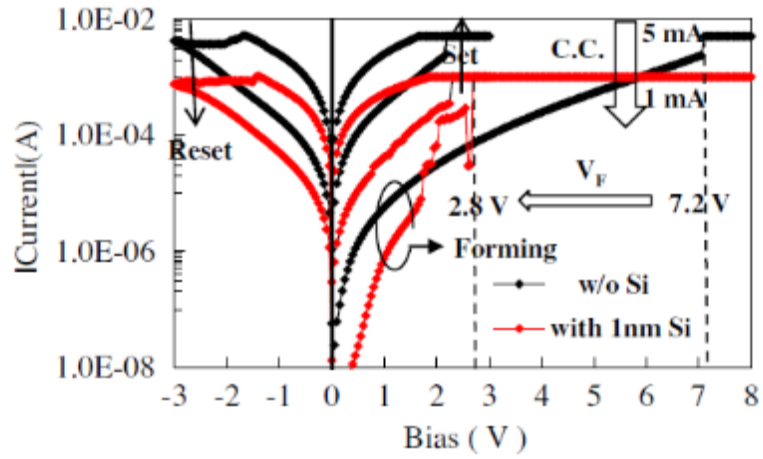


Figure 2-9: I - V characteristics of the W/CeO₂/Si/TiN and W/CeO₂/TiN device ⁷⁸

A Si layer between CeO₂ and BE has been added by Dou et al. The basic mechanism is that the oxygen vacancy level increases to promote the performance of a CeO₂ film. The formation of Ce-silicate introduced more oxygen vacancies at the interface and the possible mechanism is shown in figure 2-10.

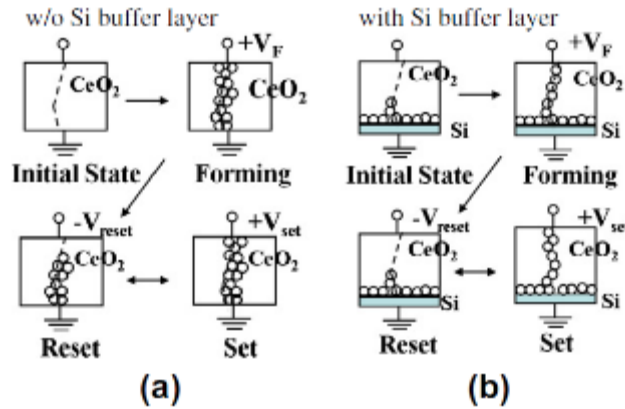


Figure 2-10 Schematic illustrations of RS behaviours of (a) the W/CeO₂/TiN device and (b) the W/CeO₂/Si/TiN device

Because Ce-silicate can be form at the CeO_x/Si interface at 400°C in N₂ ambient environments, for W/CeO₂/Si/TiN devices after 400°C annealing in N₂ ambient environments, the Ce-silicate layer also can be formed between CeO₂ and the Si-layer.

During the formation of silicate, the oxygen ions at the surface of CeO_2 were involved in the oxidation process of Si, and thus oxygen vacancies were left to the surface of CeO_2 . After the formation of Ce-silicate, the number of oxygen vacancies increased. Moreover, because oxygen vacancies in CeO_2 tend to rearrange into a line, if positive voltage was applied, the last part of filaments would be formation. Then, because only parts of the filaments were needed to form in the devices, the forming voltage could be reduced. Thus, the Si layer increased oxygen vacancies make the formation of conductive filaments became easier and the performance of devices improved.

Apparently, the role of interfaces among switching materials and electrodes materials is very critical. Younis et al.⁷⁹ introduced the concept of interface engineering to improve the resistive switching characteristics in CeO_2 nanocube based film. The schematics of the process are shown in figure 2-11.

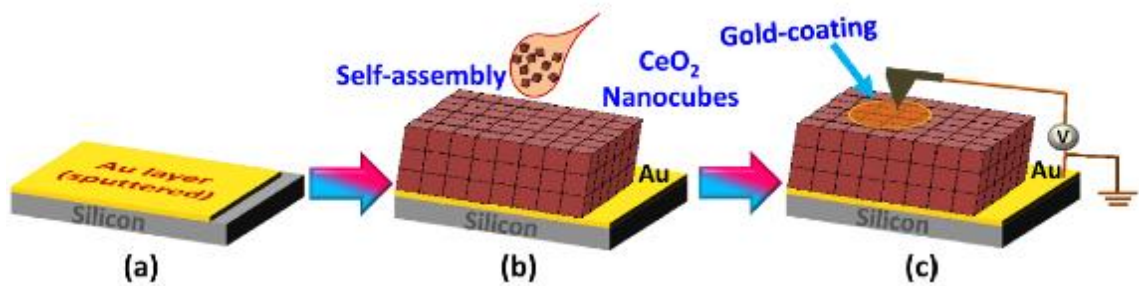


Figure 2-11: (a and b) Schematics for the self-assembly of CeO_2 nano-cubes to form a RS device (c) setup for I–V measurements⁷⁹

The cerium oxide nano-cubes were made by a chemical method. Heating and centrifuging cerium nitrate aqueous solution mixed with toluene, oleic and tert-butylamine obtained cerium oxide nano-cubes. The film was finally thermally annealed at 200°C for 2h under vacuum⁷⁹. This film exhibits high performance in resistive switching behaviour. The resistance ratio between HRS and LRS can reach four orders

of magnitude. The endurance of nano-cubes cerium oxide film is shown in Figure 2-12 (c).

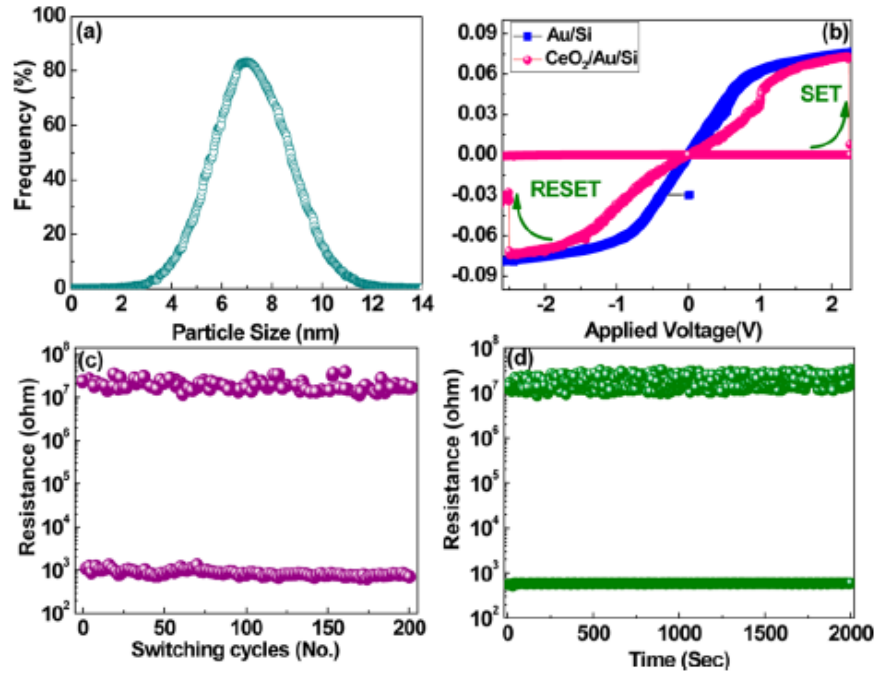


Figure 2-12: (a) Particle-size distributions of the CeO₂ nanocubes. (b) *I*–*V* characteristics (c) Endurance performance of the device for 200 switching cycles. (d) Data retention performance of the device for 2000s⁷⁹

The size distribution of the as-synthesized CeO₂ nanocubes is shown in figure 2-12(a). A bipolar resistive switching behaviour of nanocube-based CeO₂ film is plotted in figure 2-12(b). The window (ratio of resistance in HRS and LRS) of the as-fabricated device is four orders of magnitude in figure 2-12(c). In addition, this device exhibits high uniformity of the set and reset voltages with high/low resistances during 30 successive cycles. The result of retention test at room temperature for 2000s was plotted in figure 2-12(d).

2.5. Radio frequency (RF) Sputtering of CeO₂ nanostructures:

Various nanostructured ceria films were fabricated by RF sputtering for different applications.

Sundaram et al. deposited cerium dioxide on glass substrate by RF magnetron sputtering⁸⁰. The deposition rates as a function of molar fraction of oxygen with different input power levels were studied. The deposition conditions to get quality films for optical transmission have been optimized. The molar fraction of oxygen in system in resistive switching memory is also important.

They used 99.9% cerium dioxide as a target, and the distance between target and substrate was 3.2cm. Pre-sputtering before each deposition was necessary for removing contamination, and the substrate temperature was in range 80–140°C. The oxygen pressure and input power was changed in the experiments⁸⁰.

Power level (W)	Partial pressure of O ₂	Alpha step average deposition rate (nm h ⁻¹)	Bausch Lomb average deposition rate (nm h ⁻¹)
150	0.286	370.0	384.6
150	0.545	368.0	353.2
150	0.615	272.0	276.4

Table 2-1: Measured average deposition rate with oxygen pressure⁸⁰

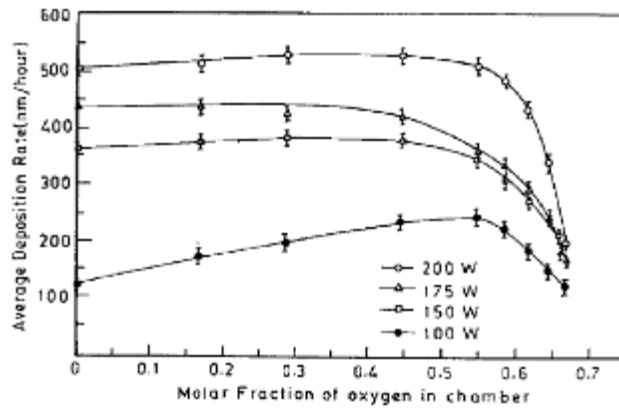


Figure 2-13: Deposition rate of CeO_2 film in different fraction of oxygen for various input power levels⁸⁰

Table 2-1 shows the deposition rates measured in 150w input power with different oxygen molar fractions. It shows that in same input power deposition rate is not increase with increasing of oxygen pressure⁸⁰. Figure 2-13 shows the deposition rates of cerium oxide films as a function of molar fraction of oxygen for different power levels that 100W, 150W, 175W and 200W. In figure 2-13, higher input powers caused higher deposition rates. Figure 2-13 shows the powers when the molar fraction of oxygen was around a deposition rate of 0.45.

Briand et al. studied the epitaxial growth of CeO_2 thin films as a function of deposition temperature (200–800 °C), RF magnetron power (25–125W) and target-substrate distance (2–6 cm)⁸¹.

The target used in this paper was sintered 99% purity CeO_2 powder. This CeO_2 target was sintered with oxygen flow. An n-type Si (111) wafer was used as substrate. In RRAM, Si or SiO_2 are always used as substrate with a conductive layer like TiO. The film deposited in argon environment and substrate temperature was between 200 and 800°C. The input power was between 25W and 125W. All the deposited thin films were characterized by XRD as shown in figures 2-14 and 2-15⁸¹.

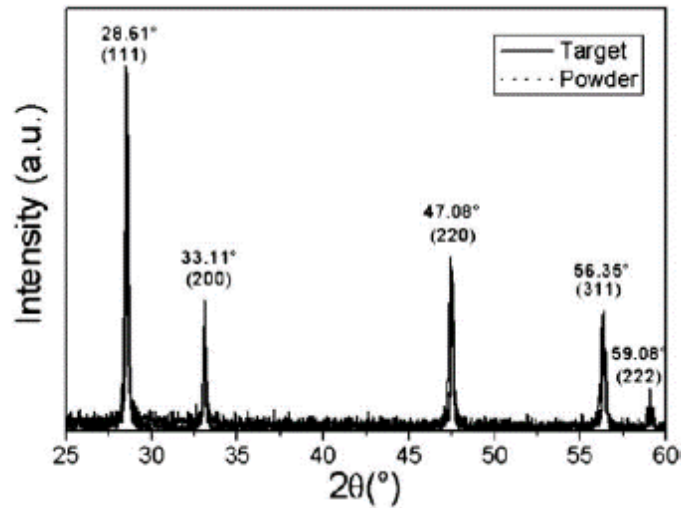


Figure 2-14: XRD patterns comparison between CeO₂ starting powder and sintered target⁸¹

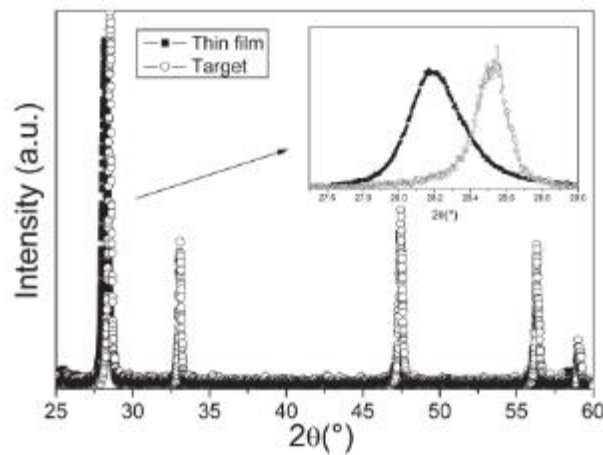


Figure 2-15: XRD patterns of CeO₂ target and CeO₂ thin film grown on Si(111) by RF magnetron sputtering⁸¹

The XRD patterns of CeO₂ starting powder and as-sintered target are shown in figure 2-14. They indicate a non-textured structure of the target⁸¹. Figure 2-15 presented the XRD patterns of the target and of as-deposited CeO₂ thin film with the 90W input power, distance between target and substrate at 2 cm, a pressure of 10 Pa, and a temperature of 600°C. Figure 2-14 showed a strong peak located at 28.2° for the film and near a pattern located at 28.6° for the target, which is attributed to a (111) plane⁸¹. In their study, the effects of different deposition parameters such as deposition

temperature, input power and target-substrate distance on the crystalline quality of CeO_2 thin films deposited by RF magnetron sputtering on Si (111) substrates were investigated by XRD. The target – substrate distance and input power influence the growth rate.

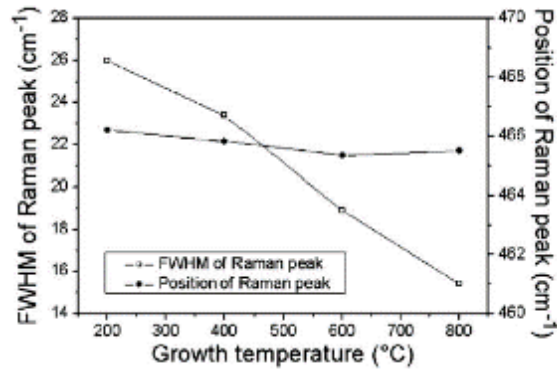


Figure 2-16: Evolutions of the FWHM of Raman peak for different growth temperatures⁸¹

The crystalline quality of the deposited layers is more dependent on the growth temperature. Figure 2-16 presents the evolutions of the FWHM of Raman peak for different growth temperatures included between 200 and 800°C. A strong reduce of the FWHM can be observed from 200°C to 800°C. With the increasing temperature, the quality of crystal in CeO_2 thin film can further improve⁸².

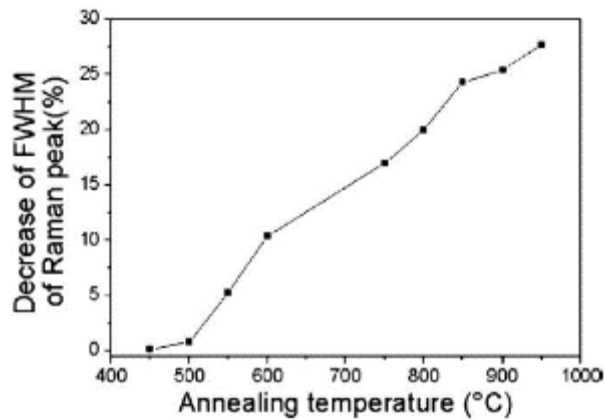


Figure 2-17: Reduction of the FWHM of CeO_2 Raman peak versus RTA temperature⁸²

Their results also showed that the crystalline quality of the films can be strongly improved by a post-rapid thermal annealing. In figure 2-17, a reduction of FWHM of Raman peak can be observed with increasing temperature.

2.6. Other sputtered RRAM materials:

Electrical properties of RF sputtered ZrO_2 thin films used in RRAM were studied by Lin et al. They also compared the influence of different TE and BE on switching performance⁸³.

In their experiment part, a structure SiO_2 had been used as substrate which was deposited a 20-nm thick Ti layer and an 80-nm thick Pt layer by electron beam evaporation at room temperature. The substrate temperature was kept at 250°C and the working pressure was maintained at 10mTorr by a mixture of Ar and O_2 at a mixing ratio of 2:1⁸³.

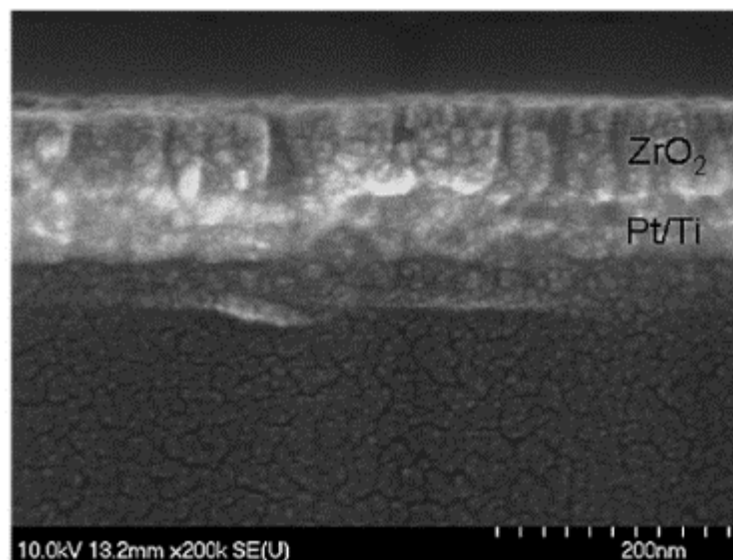


Figure 2-18: The cross-sectional SEM image of the $\text{ZrO}_2/\text{Pt}/\text{Ti}$ structure⁸³

Figure 2-18 shows the cross-sectional scanning electron microscope (SEM) Images. A columnar structure along the film thickness is observed. The crystal orientation of substrate plays an important role in the process of deposition ⁸³.

Effect of different top electrode materials such as Pt, Cu, Ni and Ag on resistive switching characteristics had been studied by Lin et al. as shown in figure 19(a).

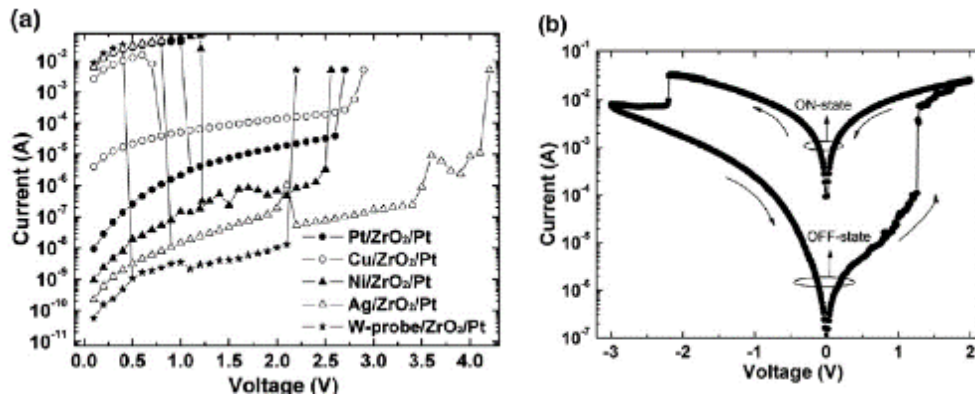


Figure 2-19: (a) $I - V$ curves of ZrO₂-based memory devices by using Pt, Cu, Ni, Ag, and W-probe as top electrodes (b) $I - V$ curve of the Ti/ZrO₂/Pt device ⁸³

And different TE and BE shows different switching properties ⁸³. For example, the bipolar and unipolar resistive switching behaviour in ZrO₂ film appears in Figures 2-19(a) and 2-19(b). The reason for that still unknown, but a hypothesis has been made by Lin. As the resistive switching characteristic can be influenced by the oxygen content and defects, the bipolar behaviour of the Ti/ZrO₂/Pt device is influenced by having Ti serving as an oxygen gettering material to reduce the oxygen vacancies at the Ti/ZrO₂ interface. That will change the oxygen vacancies distribution within the ZrO₂ bulk memory film further leading to asymmetric trap levels.

Yang et al. used single phase cuprous oxide (Cu_2O) as switching materials in RRAM. Single phase cuprous oxide thin films were deposited on TiN substrate with RF sputtering⁸⁴.

Cu_2O were used as a target in RF sputtering process⁸⁴. The working pressure was 9×10^{-1} Pa without oxygen to avoid the formation the formation of Cu_2O and CuO mixture. During deposition, RF sputtering power was at 50–200W and the substrate temperature was 200°C. After deposition, the thin film was annealed in N_2 environment for 1 min⁸⁴.

Figure 2-20 shows the scanning electron microscopy images of deposited Cu_2O thin film and figure 2-21 shows the switching properties of Cu_2O -based RRAM. The resistance ratio between HRS and LRS can only reach almost three orders of magnitude.

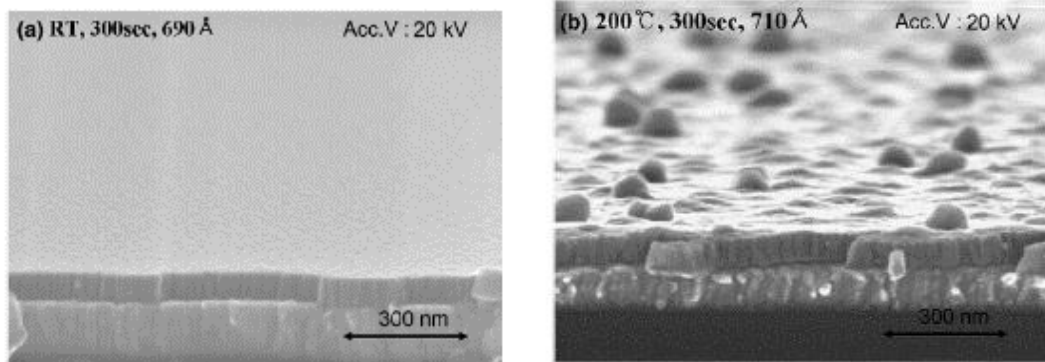


Figure 2-20: SEM images⁸⁴

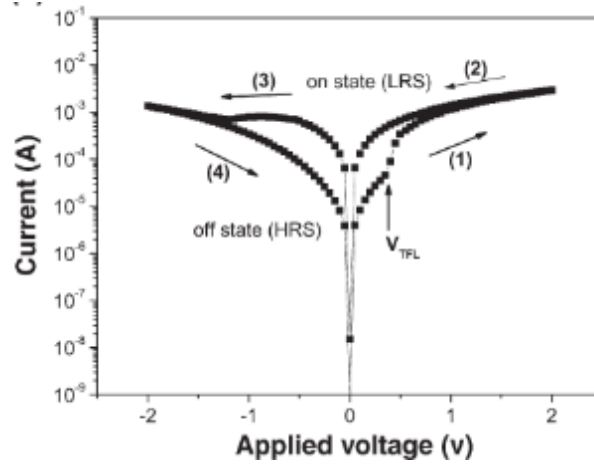


Figure 2-21: $I - V$ curves of Cu_2O -based memory devices ⁸⁴

Jung et al. investigated the reversible resistive switching behaviour of RF sputtered BaTiO_3 based RRAM ⁸⁵. BaTiO_3 thin films were deposited on a $\text{Pt}/\text{Ti}/\text{SiO}_2/\text{Si}$ substrate at 300°C . The working pressure for deposition was maintained at 6.7×10^{-1} Pa by a mixture of argon and oxygen ($\text{Ar} : \text{O}_2 = 3:1$). After the deposition, BaTiO_3 thin films were annealed at 700°C for 1 h in a tube furnace to enhance crystallization ⁸⁵.

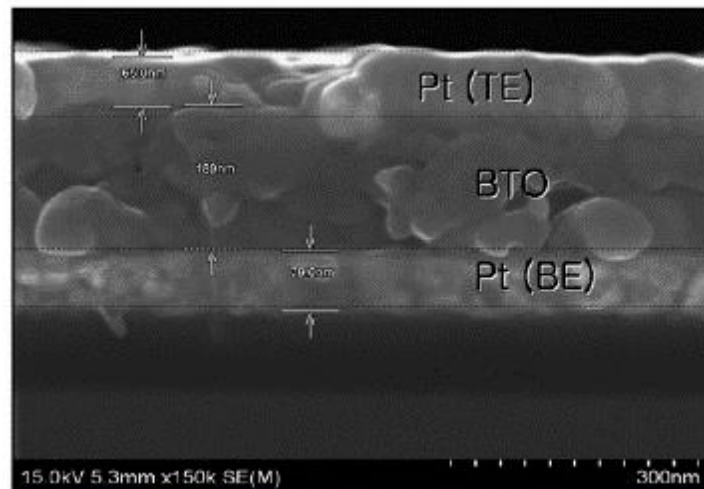


Figure 2-22: Cross-sectional SEM image of the $\text{Pt}/\text{BTO}/\text{Pt}$ device ⁸⁵

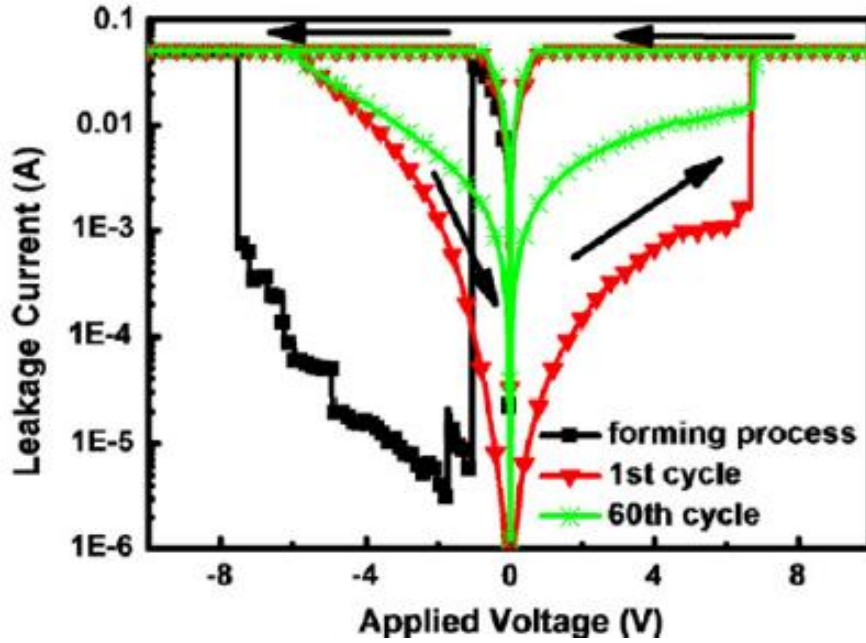


Figure 2-23: *I-V* characteristic curves of Pt/BaTiO₃/Pt device with the various cycle numbers ⁸⁵.

The cross-sectional SEM image is presented in Figure 2-22. Figure 2-23 shows the *I-V* characteristics for Pt/BTO/Pt RRAM device. A forming process has been shown in figure 2-23. Before resistance switching a negative biased-voltage on top electrode was applied and this process is called “forming process”. Before the device runs 50 cycles, the size of hysteretic window was broad. For cycle 60, the hysteresis loop becomes smaller pointing towards gradual decreasing performance of the device. As a result, a gradual transition from LRS to HRS was observed instead of a discrete step. The voltage for HRS to LRS transition (SET process) was around +6.5 V.

2.7. Fabrication of cerium oxide by chemical methods

Cerium oxide film have been recently deposited by some different methods, such as hydrolysis ⁸⁶, hydrothermal ⁸⁷, precipitation ^{88 89 90 91}, thermal deposition ⁹², flame-synthesis ⁹³, sol-gel ⁹⁴, solvothermal ^{87 95} and electrochemical ⁹⁶.

Figure 2-24 shows the morphology of self-assembled ceria. Both the shape and size of the cerium can be controlled by adjust the concentration of $\text{Ce}(\text{NO}_3)_3$. The grain of ceria shows a strong tendency to assemble into 2D arrays with a regular pattern with the increasing size of nanocubes.

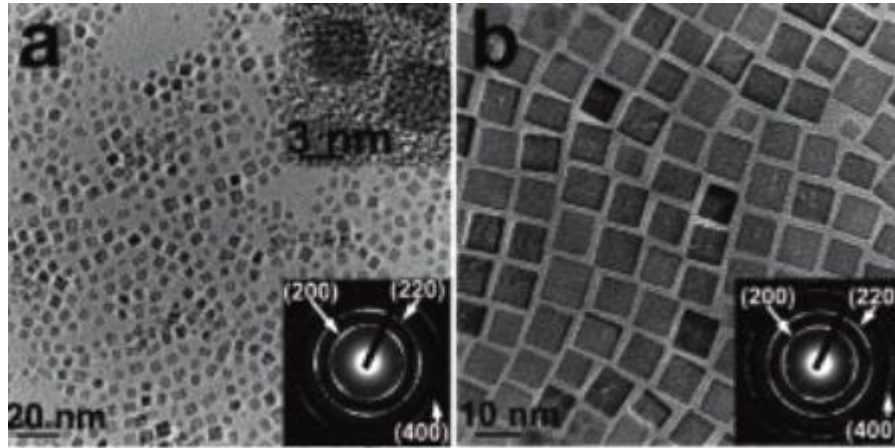


Figure 2-24: TEM images of ceria nanocubes with the average sizes

of (a) 4.43 nm, (b) 7.76 nm⁹⁷

Gd-doped ceria was synthesised via electrochemical deposition route by Tong's group⁹⁸. The SEM images of porous CeO_2 and Gd-doped were showed in Figure 2-25. Porous CeO_2 and Gd-doped CeO_2 showed excellent optical and magnetic performance.

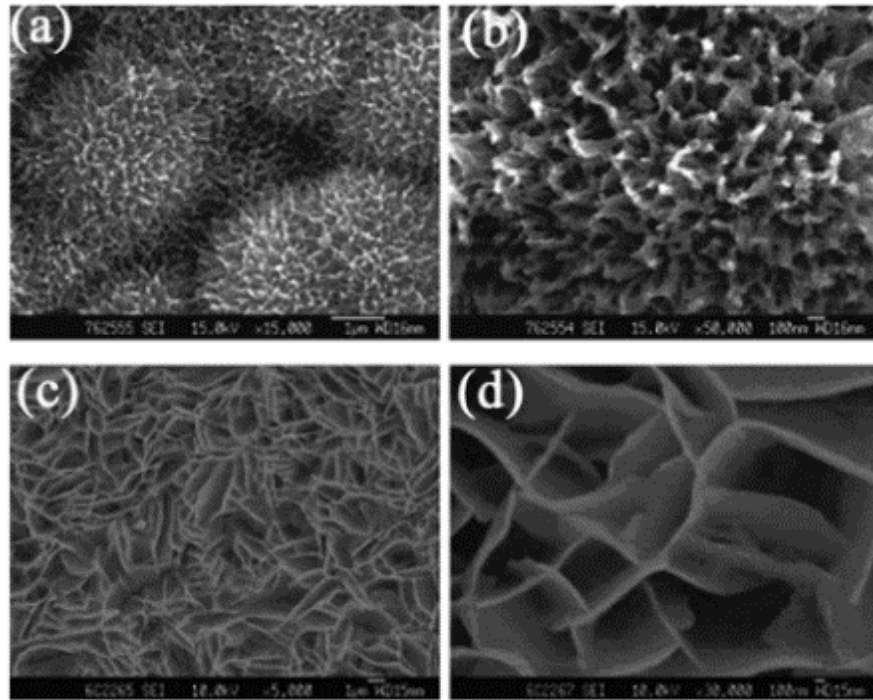


Figure 2-25: SEM images of porous CeO_2 (a) and (b) and Gd-doped CeO_2 (c) and (d) prepared by an electrochemical deposition route⁹⁸.

Switer's group used a low energy consumption route to deposit CeO_2 and sintered CeO_2 at high temperature⁹⁶. Figure 2-26(b) showed after CeO_2 sintered at 1300°C for 2 hours, the grain fractured. They showed that the relative density become higher with increasing sintering temperature.

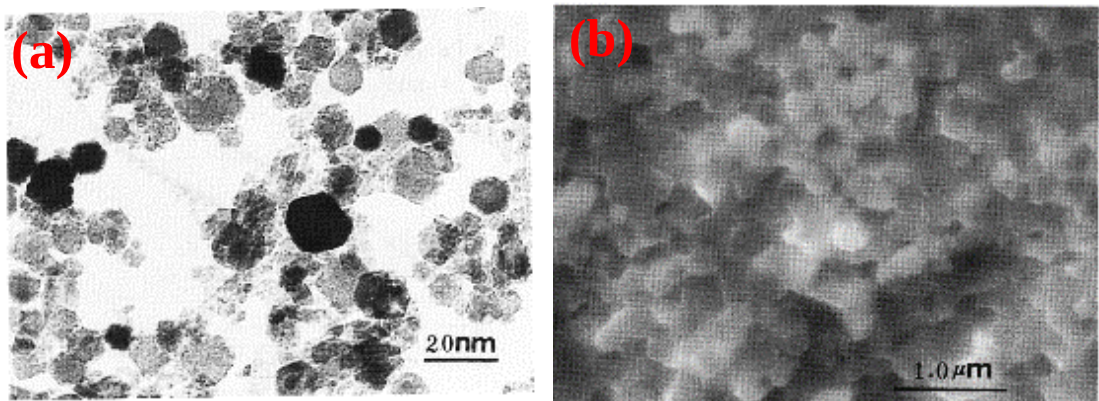


Figure 2-26: TEM images of CeO_2 before (a) and after sintering (b)⁹⁶

Chapter 3 Experiment Methods

This chapter describes deposition methods that are used in the later chapters of this dissertation. Fabrication conditions are presented here. Two different synthesis methods are used for deposit CeO_2 films: electrochemical deposition and RF sputtering. The characterization techniques are also included in this chapter.

3.1. Film synthesis

3.1.1. Radio frequency (RF) magnetron sputtering

Sputtering, as a kind of Physical Vapour Deposition (PVD), is widely utilized in the thin film industry. For deposition principle of PVD or sputter, thin films can be deposited though ejected ions landing on a target made of deposited materials.

The structure of sputter system is shown in figure 3-1. A 50-nm-thick gold bottom electrode (BE) was coated on a (111)-oriented Si substrate. The CeO_2 films were deposited on Au/Si at different temperatures with a gas mixture of 35sccm:15sccm Ar/O_2 by radio-frequency (RF) magnetron sputtering. A ceramic CeO_2 target was used to fabricate the films at different sputter temperatures and powers. Prior to RF sputtering at 10^{-6} mTorr pressure, the base pressure of the chamber was achieved at 20mTorr.

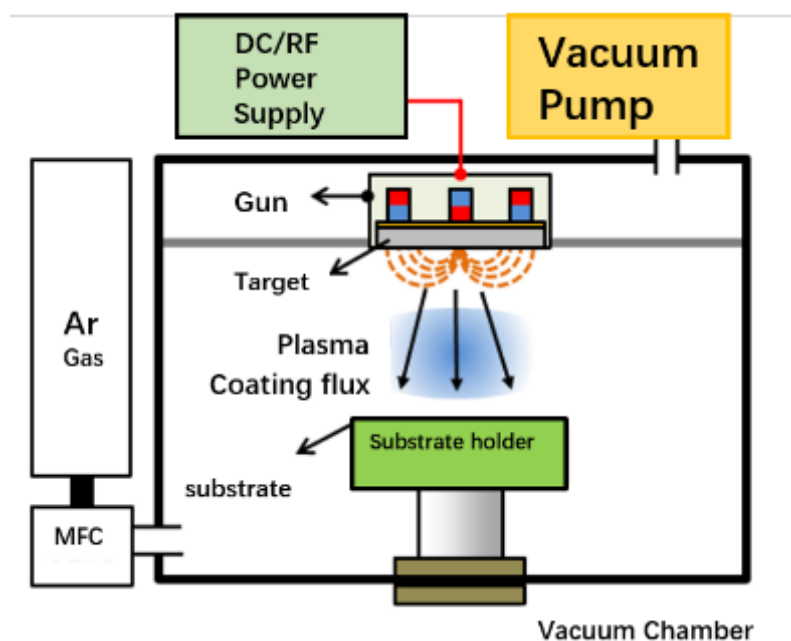


Figure 3-1: RF sputter system

3.1.2. Electrochemical Deposition

Electrochemical deposition is a chemical process which utilises electron/ion transfer between electrodes and the electrolyte to oxidized or reduced to synthesize specific materials. That reaction occurs at the surface of electrode. With extra power, electrons transfer between the electrode and the electrolyte. This electrochemical is discussed in this chapter.

For electrochemical synthesis, there are three different modes that (1) potentiostatic, (2) galvanostatic and (3) pulse period deposition. Current, potential and charge are the key parameters to control the quality of thin film deposited by electrochemical synthesis. This chapter focuses on galvanostatic interactions, which can be used to prepare uniform thin films.

In the galvanostatic deposition process, the applied current reaction rate remains constant. The traditional structure of electrochemical system is shown in figure 3-2. In

this work, the film is deposited on working electrode and counter reaction react at the counter electrode. Against the potential of the electrochemical cell, a constant current is applied. During the reaction electron transfer between electrodes, the process redox reaction grain grows on the interface of electrode and electrolyte to formation crystal. Hence, the grain grow rate was controlled by the current.

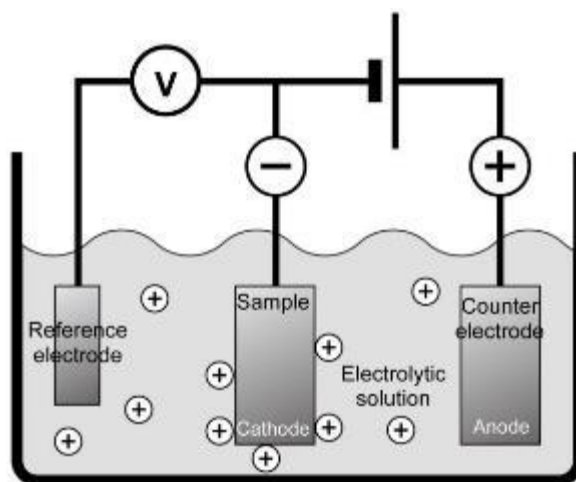


Figure 3-2: The schematic illustration of electrochemical synthesis setup ⁹⁹

3.2. Film Characterizations

3.2.1. X-ray Diffraction

X-ray diffraction (XRD) is normally used to determine the crystal material structure.

Monochromatic X-rays test a crystalline sample by X-ray diffraction. Each detected X-ray signal corresponds to a coherent reflection according to Bragg's Law. As shown in figure 3-3, between two planes of atoms the reflection of X-ray is $A = d \sin \theta$. For the planes of the crystal, the Bragg's law is satisfied ¹⁰⁰:

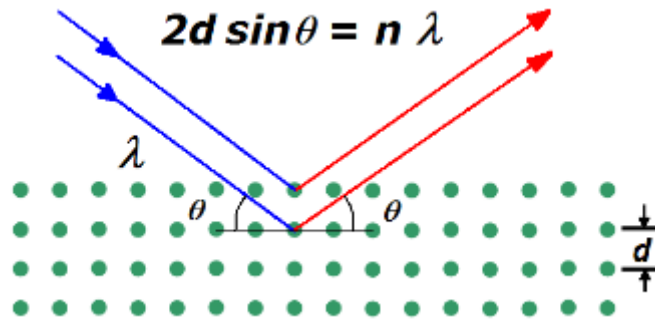


Figure 3-3: Schematic diagram of diffraction on a set of planes

3.2.2. Scanning Electron Microscope

Scanning electron microscope (SEM) is widely used for examine surface morphology of the samples. Lanthanum hexaboride (LaB_6) thermionic emitters emit electrons to visualise the samples surface. Thermionic emission occurs when the filament is heated up to temperatures between 2000 and 2700 K. The electrons generated and accelerate from the electron gun in the range 0.1 – 30 keV towards the sample¹⁰¹. A series of lenses focus the electron beam onto the sample. A schematic of the SEM structure is shown in figure 3-4.

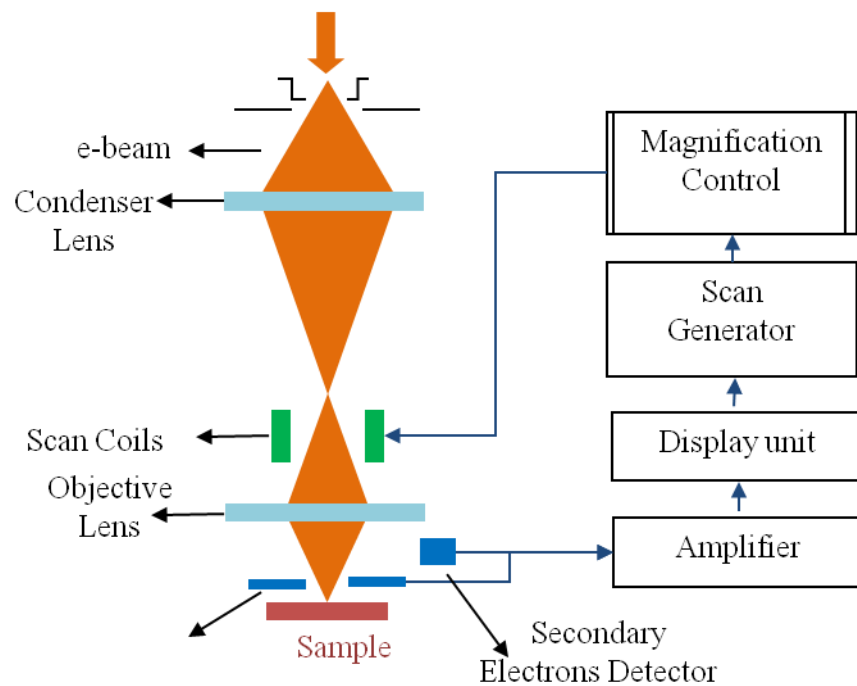


Figure 3-4: Diagram of the basic components of a SEM

3.2.3. Atomic Force Microscopy

Atomic Force Microscopy (AFM) or scanning-force microscopy is used to test the surface of the film. A nanoscale mechanical probe travels along the surface to get the surface information. Because AFM is based on atomic force, the resolution exceeds the optical diffraction limit. The accuracy of AFM depends on the sharpness of the needle or probe, and super sharp needles (even to an atom thickness) can get higher resolution and more detail images. The sketching of AFM structure is shown in figure 3-5.

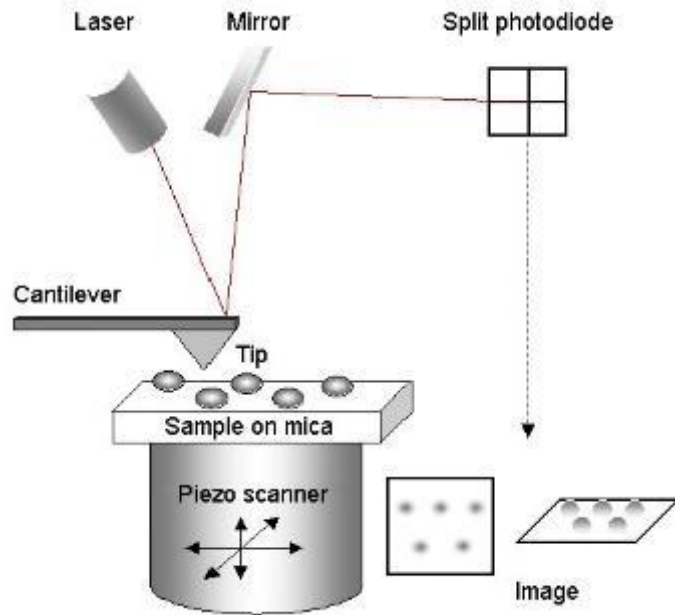


Figure 3-5: Diagram of the basic components of an AFM

3.2.4. Transmission Electron Microscopy

A transmission electron microscope (TEM) is an effective way to investigate the microstructure of the materials. Compared with SEM, TEM can get better quality and higher resolution images. The electron wavelength is determined by the transmission speed of electron and to get better quality images shorter wavelength is necessary. The small particles can be observed after electrons travel through the sample. A simple structure of transmission electron microscope is shown in figure 3-6.

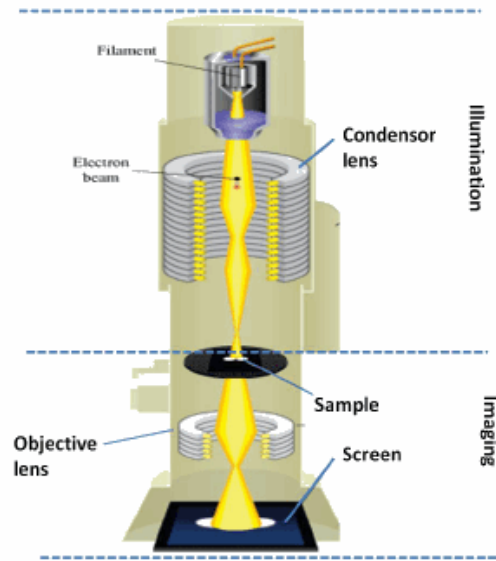


Figure 3-6: Diagram of the basic components of a TEM.

3.2.5. Electrical Measurements

A 50-nm-thick gold bottom electrode (BE) was coated on a (111)-oriented Si substrate as bottom electrode. An Autolab 302N electrochemical workstation controlled with Nova software was setup to examine the I-V curve. The voltage can sweep in a range of -5V to 5V by different sweeping steps. The schematics of the measurement setup is shown in figure 3-7.

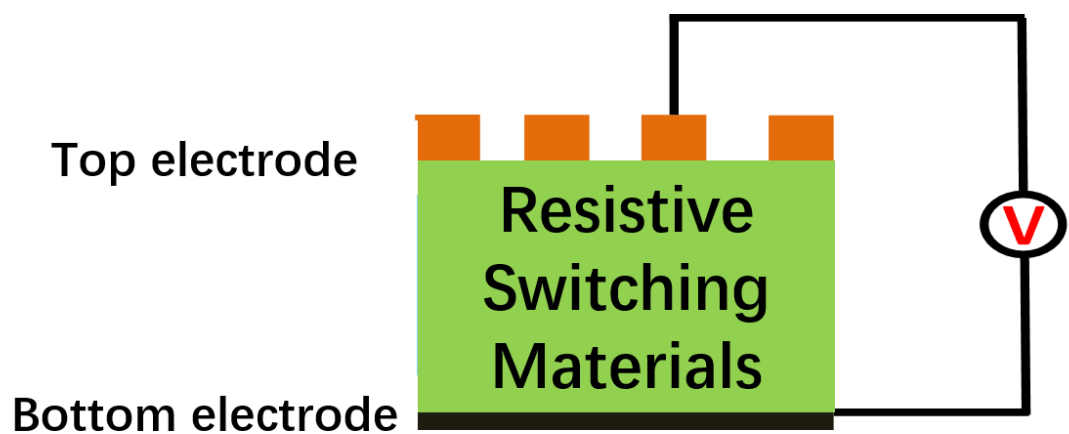


Figure 3-7: Schematic diagram of the I-V measurement setup.

Chapter 4 Results and discussion

4.1 Impact of Deposition Parameters Resistive Switching

4.1.1. Characteristics of CeO₂ based Memories XRD results

In Figure 4-1, the X-ray diffraction spectra of CeO₂ thin films deposited on gold coated silicon substrate (111) with 80W power at different synthesis parameters (temperature and power) are shown. All observed CeO₂ peaks matched well and were indexed by using JCPDS-No. 04-008-0316.

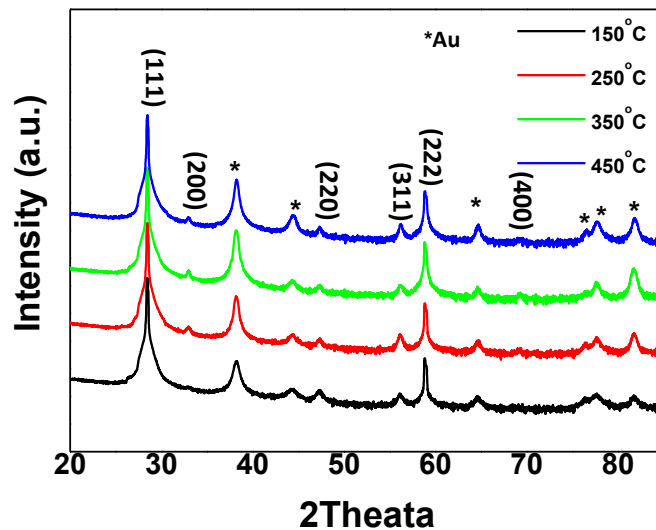


Figure 4-1: X-ray diffraction pattern of Ceria films deposited at various temperatures and at sputter powers of 80W

In Figure 4-2 (a), the X-ray diffraction spectra of CeO₂ thin films deposited on gold coated silicon substrate by 80W power at different synthesis parameters (temperature and power) are shown. All observed CeO₂ peaks matched well and were indexed by using JCPDS-No. 04-008-0316. The CeO₂ (111) peaks of both Silicon substrate and CeO₂ are differentiable at slow scan rates as depicted from figure 4-2 (b).

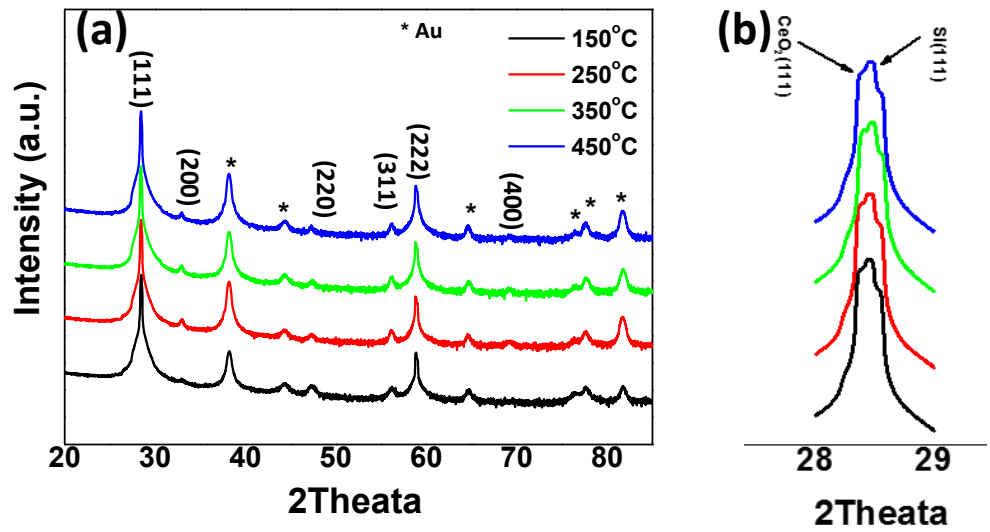


Figure 4-2: X-ray diffraction pattern of Ceria films deposited at various temperatures and at sputter powers of (a) 90W (b) The slow scan of (a) between 2-theta 28–29 degrees

For both Ceria films deposited at 80W and 90W power, by increasing synthesis temperature, the intensity of (111) peak decreased; however, the intensities of (200) and (400) peaks increased. This trend may indicate the formation of some textures (columnar or granular) within the film. Also, increased crystallinity was observed in samples prepared at high temperatures. Similar trends were observed for the samples prepared at a sputter power of 90W. However, high sputter power may increase crystal growth rate and hence, well defined grains were observed at relatively lower temperatures which is further verified by microscopy analysis. Our results also well coincides with previous reports in which substrates temperatures were adjusted to regulate the crystallinity of the resultant cerium oxide films¹⁰²

4.1.2. SEM results

The surface morphologies of CeO_2 film deposited at different temperatures and at different sputter 80W powers are shown from figures 4-3 to 4-6.

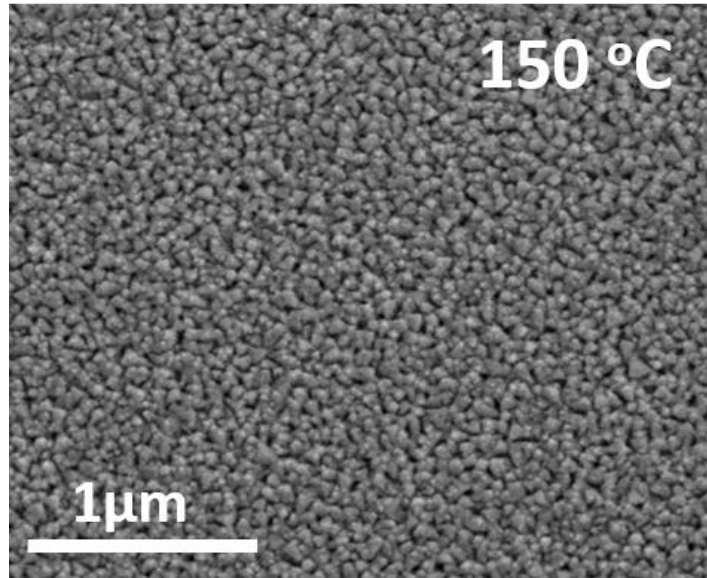


Figure 4-3: Scanning electron microscopy image of CeO_2 film deposited at 80W sputter power
at 150°C

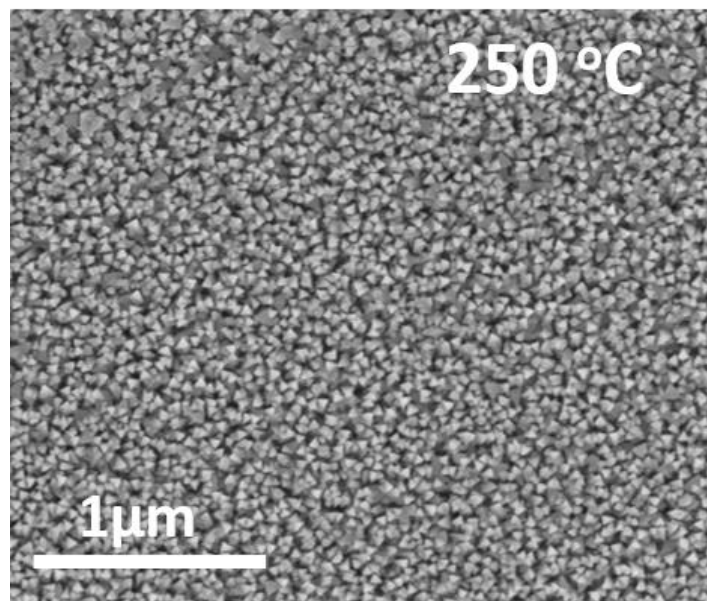


Figure 4-4: Scanning electron microscopy image of CeO_2 film deposited at 80W sputter power
at 250°C

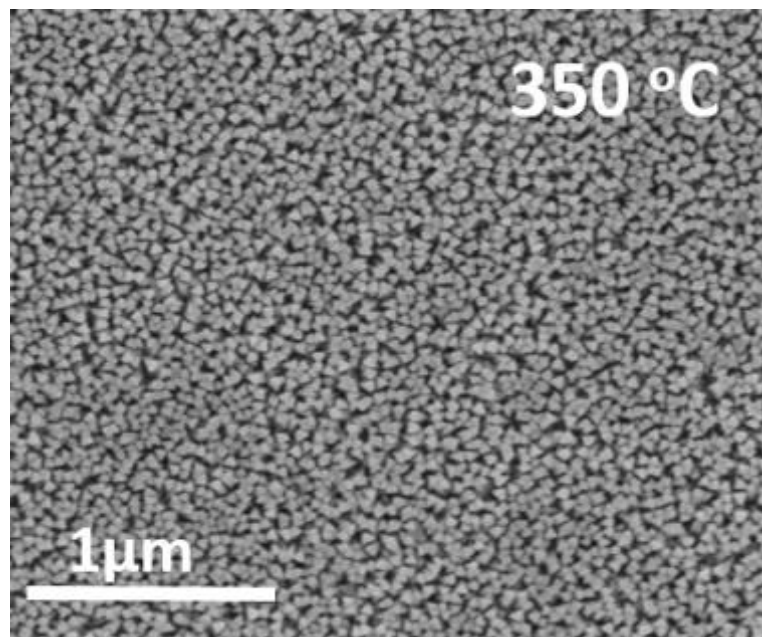


Figure 4-5: Scanning electron microscopy image of CeO₂ film deposited at 80W sputter power at 350°C

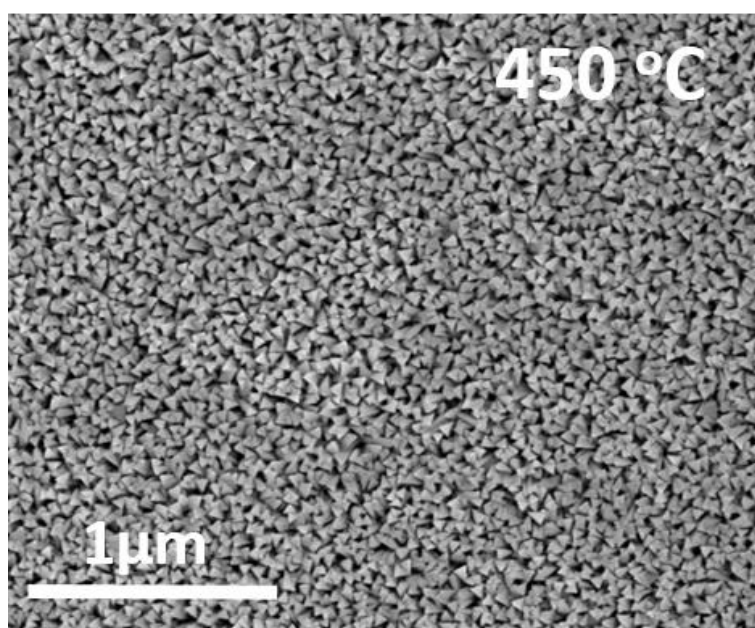


Figure 4-6: Scanning electron microscopy image of CeO₂ film deposited at 80W sputter power at 450°C

Figures 4-3 to 4-6 show that film crystallinity was greatly improved at high temperatures. The grains transformed from irregular shape to polyhedral shape by increasing synthesis temperature from 150°C to 450°C, which further authenticates our XRD results as shown in the SEM results. At low temperatures, the {111} facet has lower formation energy as compared to {100} and {110}, which facilitates the growth rate in the (111) direction that results in the of irregular grain shape formation ¹⁰³. At high deposition temperatures, the {100} facet acquires lower formation energy as compared to {111} and {110}, which restricts the grain growth in the (111) direction. Moreover, at high temperatures, the grain growth rate was much faster in (200) and (400) directions caused to form regular or polyhedral shaped grains as shown in figures 4-3 and 4-4. It is also noteworthy that the samples prepared at low temperatures acquired a loosely packed structure with minimal number of pores in it. While at high temperatures, due to the growth of regular shaped grains, the films become closely packed having obvious pores of size about 50 nm as shown in figure 4-6. In order to minimize surface energy at higher temperatures, particles tend to share common faces to maximize the packing that results in the formation of obvious pores.

The surface morphologies of CeO₂ film deposited at different temperatures and at different sputter 90W powers are shown from figures 4-7 to 4-10.

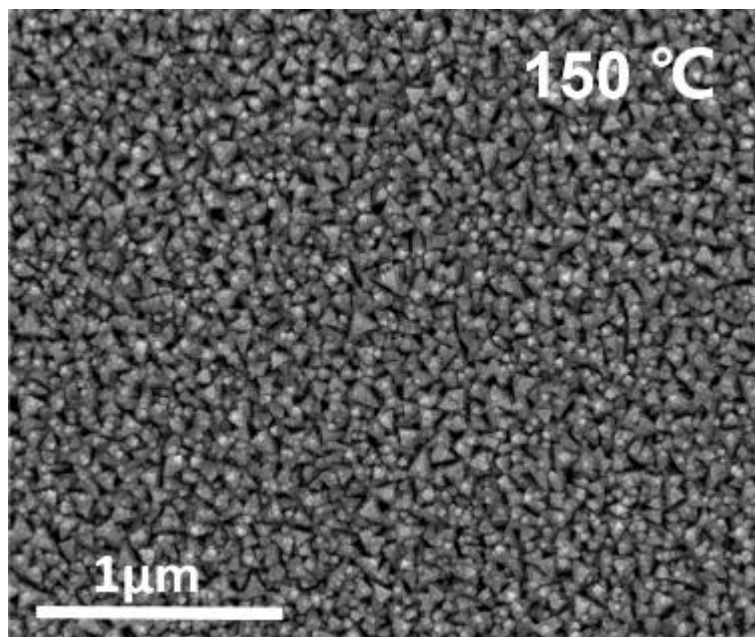


Figure 4-7: Scanning electron microscopy image of CeO_2 film deposited at 90W sputter power
at 150°C

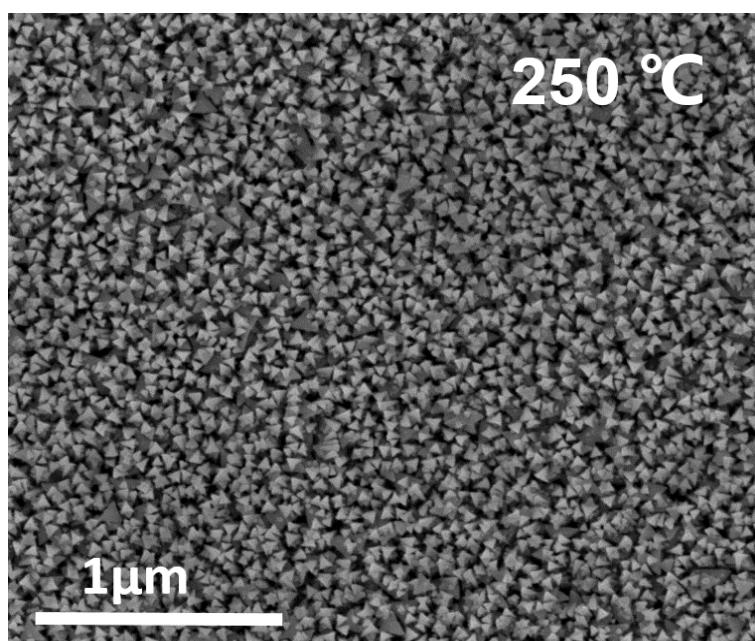


Figure 4-8: Scanning electron microscopy image of CeO_2 film deposited at 90W sputter power
at 250°C

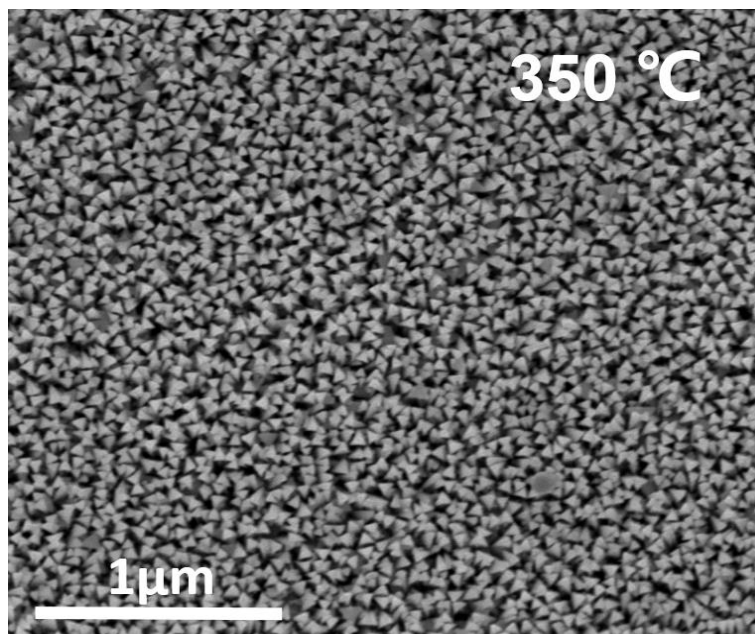


Figure 4-9: Scanning electron microscopy image of CeO₂ film deposited at 90W sputter power
at 350°C

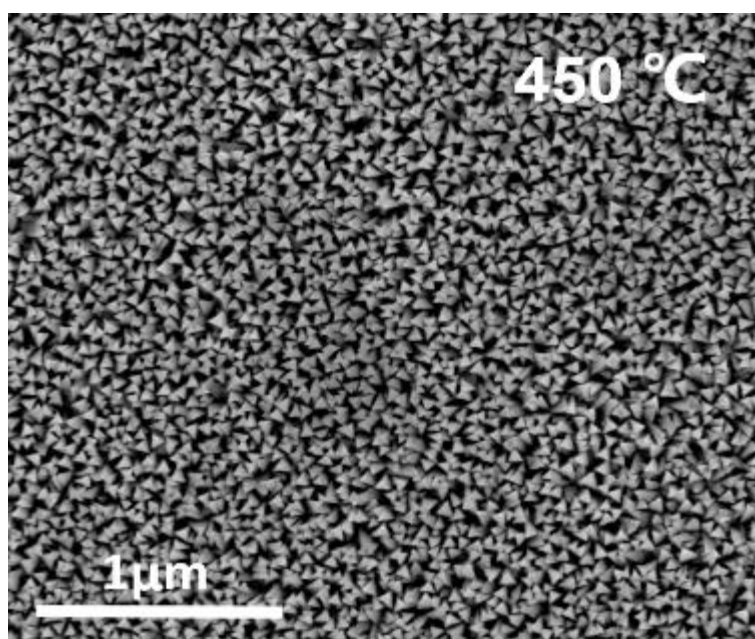


Figure 4-10: Scanning electron microscopy image of CeO₂ film deposited at 90W sputter power
at 450°C

The samples deposited at high sputter power have relatively fast crystal growth rates and therefore, well-defined polyhedral shaped grains were achieved at low deposition temperatures (350°C) as shown in figure 4-9. Many reports show that sputter power has a strong influence on crystal growth rate that results in improved crystallinity at lower temperatures.

4.1.3. AFM results

<i>Temperatures</i>	<i>Power(80W)</i>	<i>Power(90W)</i>
<i>150°C</i>	10.9nm	12.4nm
<i>250°C</i>	13.4nm	16.6nm
<i>350°C</i>	14.7nm	19.4nm
<i>450°C</i>	19.7nm	21.8nm

Table 4-1: Root-mean-square roughness (R_q) of CeO₂ film deposited at different power and temperature

The films surface roughness was also measured by conducting atomic force microscopy as shown from figures 4-11 to 4-17. The samples prepared at 150°C were found to be more flat (less rough) than samples prepared at high temperatures. It has been experimentally established that the roughness is proportional to the sputtering rate. If the sputter rate is high, there is a large probability to attain large surface roughness²⁰.

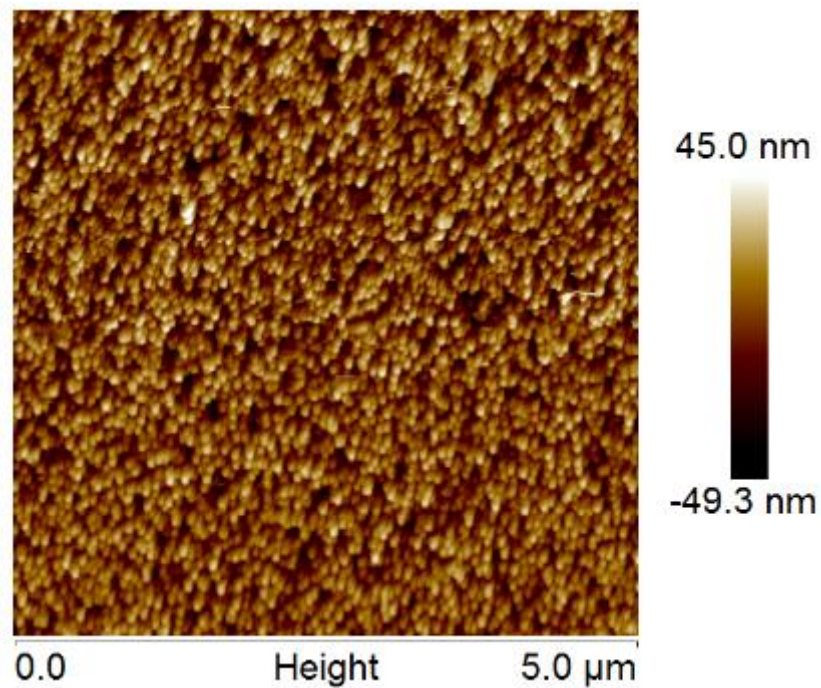


Figure 4-11: Atomic force microscopy (AFM) image of CeO_2 film deposited using 80W sputter power at 250°C

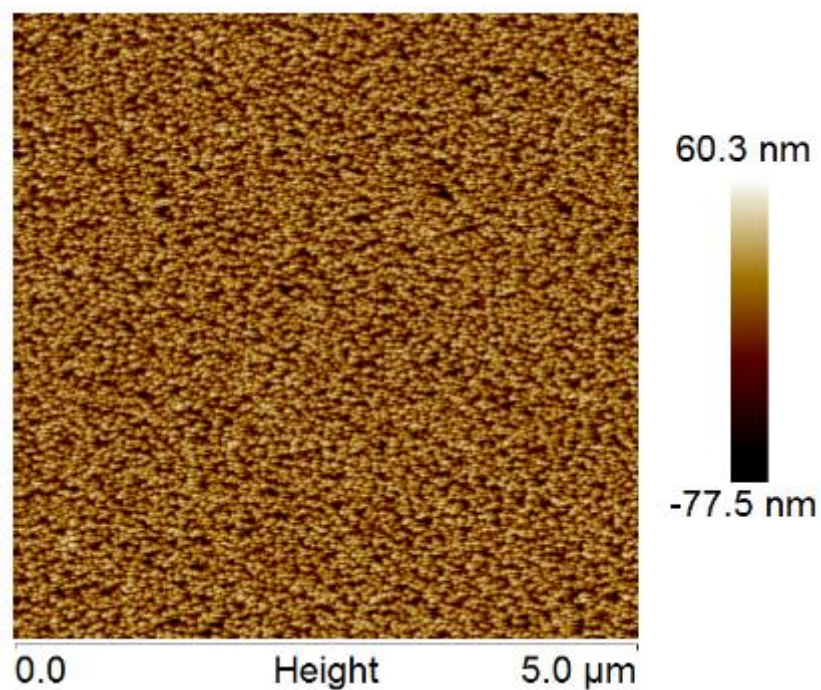


Figure 4-12: Atomic force microscopy (AFM) image of CeO_2 film deposited using 80W sputter power at 350°C

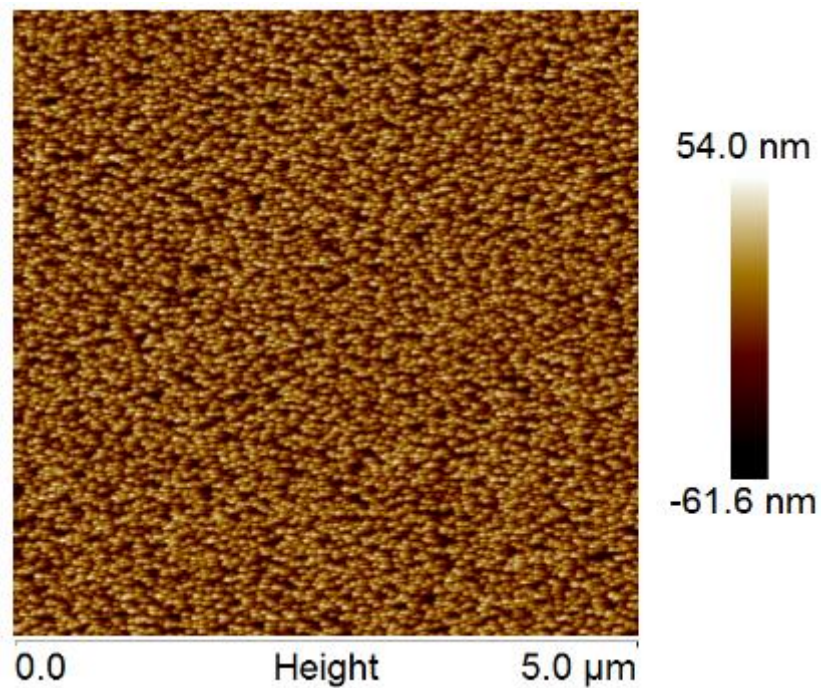


Figure 4-13: Atomic force microscopy (AFM) image of CeO_2 film deposited using 80W sputter power at 450°C

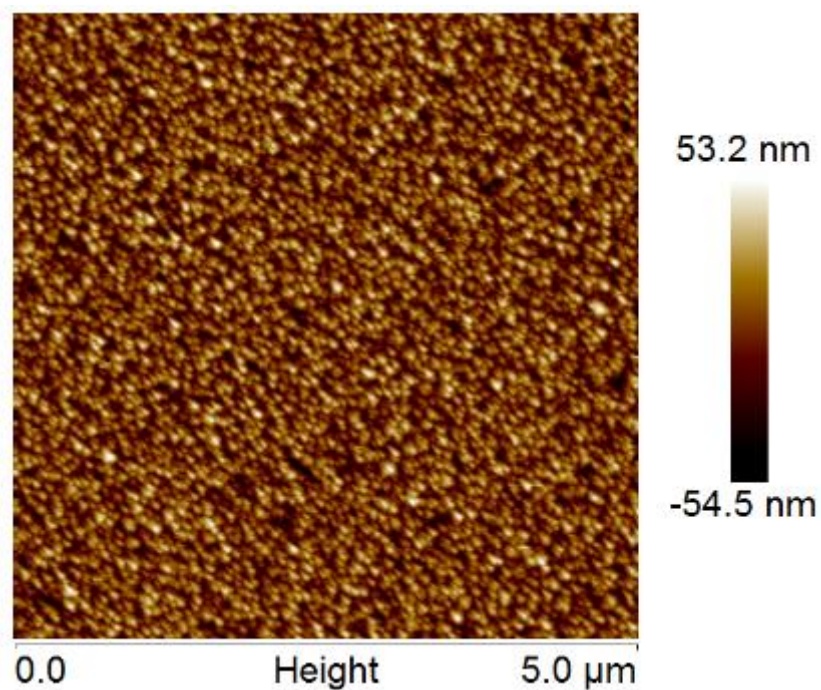


Figure 4-14: Atomic force microscopy (AFM) image of CeO_2 film deposited using 90W sputter power at 150°C

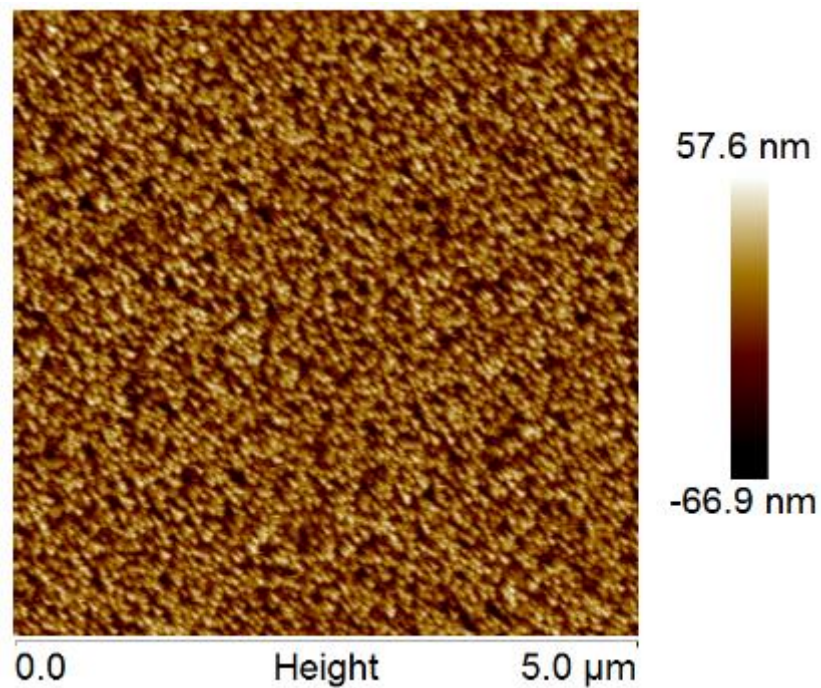


Figure 4-15: Atomic force microscopy (AFM) image of CeO_2 film deposited using 90W sputter power at 250°C

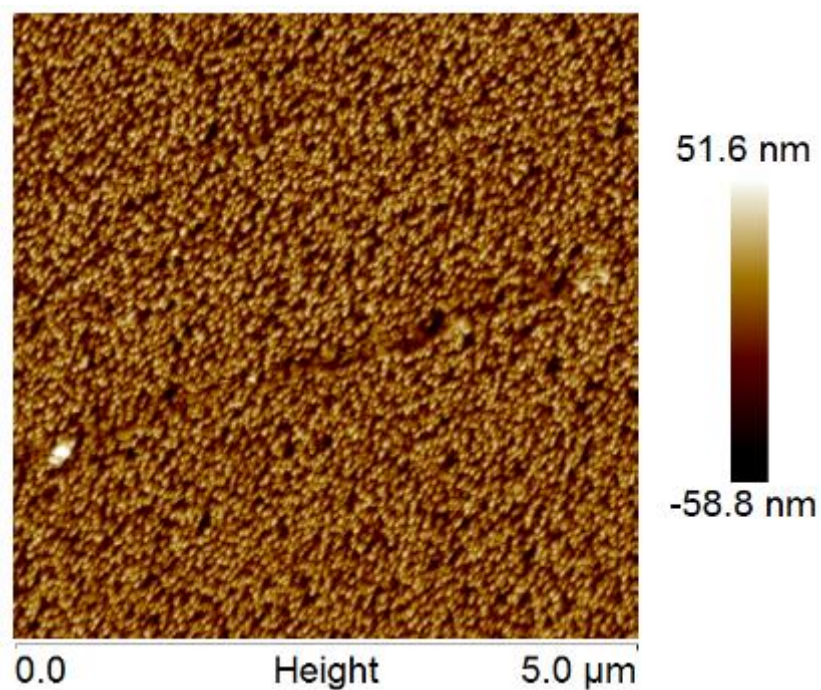


Figure 4-16: Atomic force microscopy (AFM) image of CeO_2 film deposited using 90W sputter power at 350°C

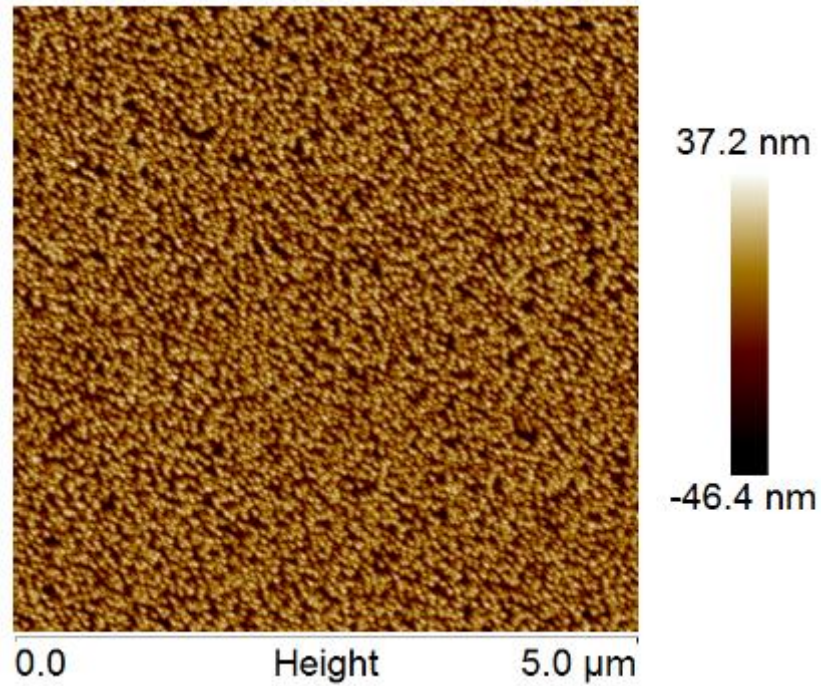


Figure 4-17: Atomic force microscopy (AFM) image of CeO_2 film deposited using 90W sputter power at 450°C

4.1.4. TEM results

To further investigate the influence of deposition parameters (power and temperature) on films growth, the cross-sectional transmission electron microscopy studies were conducted, as shown from figures 4-18 to 4-21. Our TEM results confirmed that the crystallinity of films increased with increasing temperature. As the $\{111\}$ facet occupy lowest formation energy than $\{100\}$ and $\{110\}$, the growth rate in (111) direction is facilitated and hence a less rough or flat surface was observed for films grown at 150°C as shown in figure 4-18. Also, it is generally known that with a low deposition rate, the depositing layer tends to follow the crystal orientation of the substrate²⁰ and as a result, irregular grain shapes were observed¹⁰³.

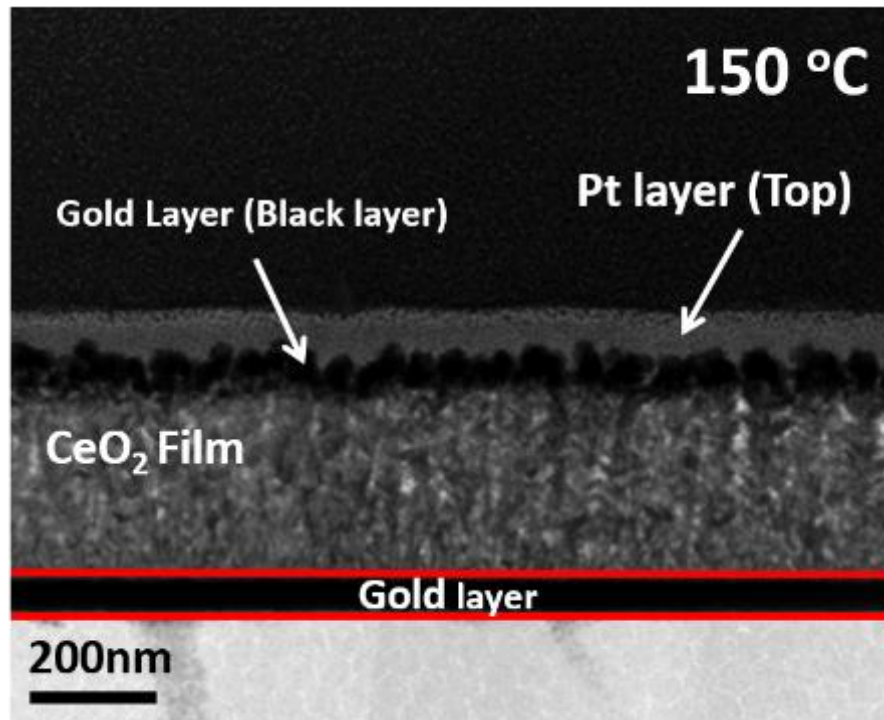


Figure 4-18: Transmission electron microscopy cross-sectional image of CeO₂ film deposited using 80W sputter power at 150°C

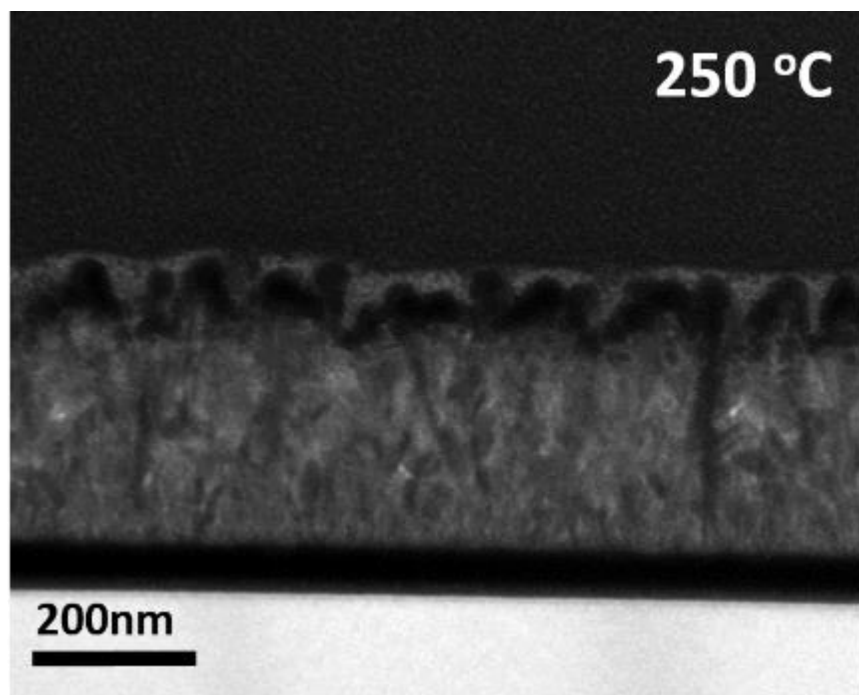


Figure 4-19: Transmission electron microscopy cross-sectional image of CeO₂ film deposited using 80W sputter power at 250°C

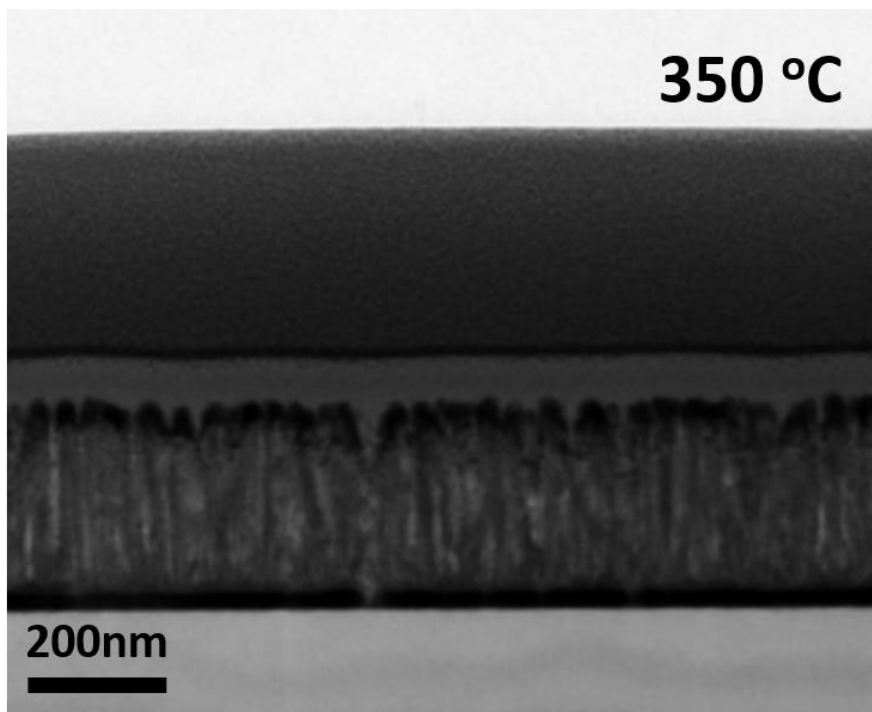


Figure 4-20: Transmission electron microscopy cross-sectional image of CeO₂ film deposited using 80W sputter power at 350°C

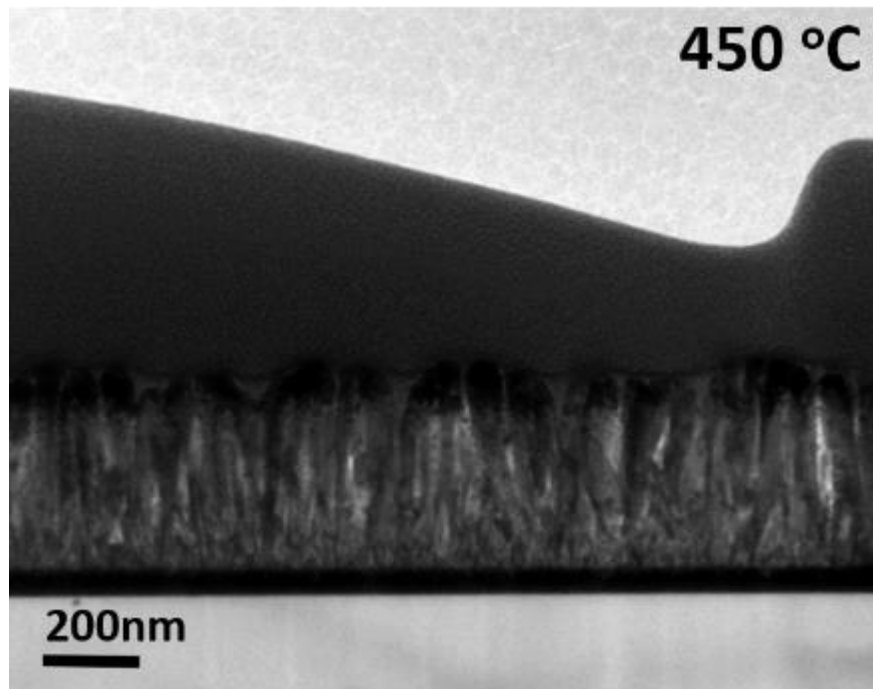


Figure 4-21: Transmission electron microscopy cross-sectional image of CeO₂ film deposited using 80W sputter power at 450°C

The films thicknesses were also found to increase from 250nm to 360nm by increasing deposition temperature as shown as above. High temperatures (more energy) tend to increase the growth rate of films. This affects the structure mainly when the arriving particles are still moving around along the growing film (or substrate) surface and subsequently, new particles come and bury them. Therefore, the deposition parameters may have strong influence on both the diffusion length/time and on the arrival rate of particles which definitely forms thicker film. Also, the sputter rate has great influence on surface roughness of the films.

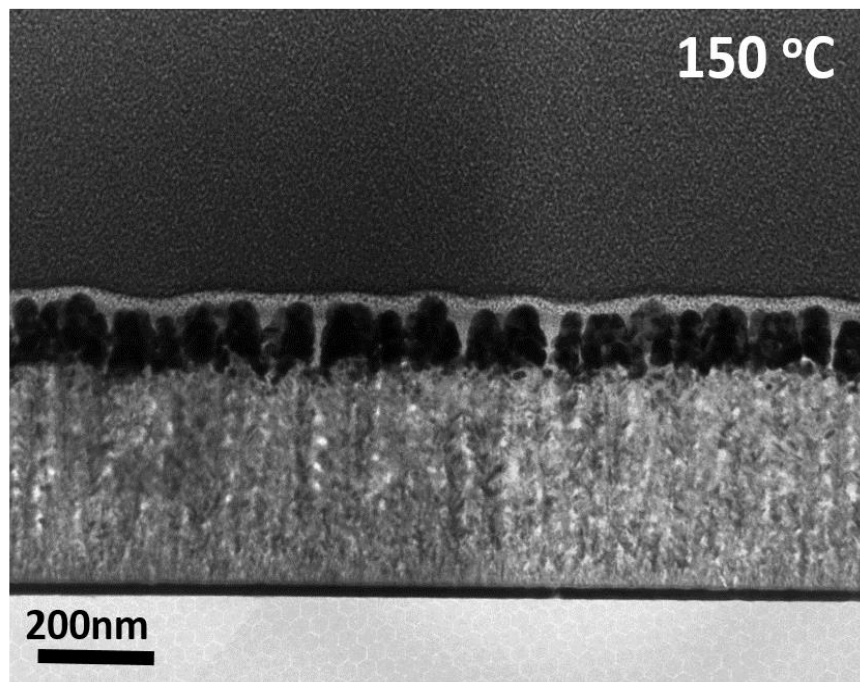


Figure 4-22: Transmission electron microscopy cross-sectional image of CeO₂ film deposited using 90W sputter power at 150°C

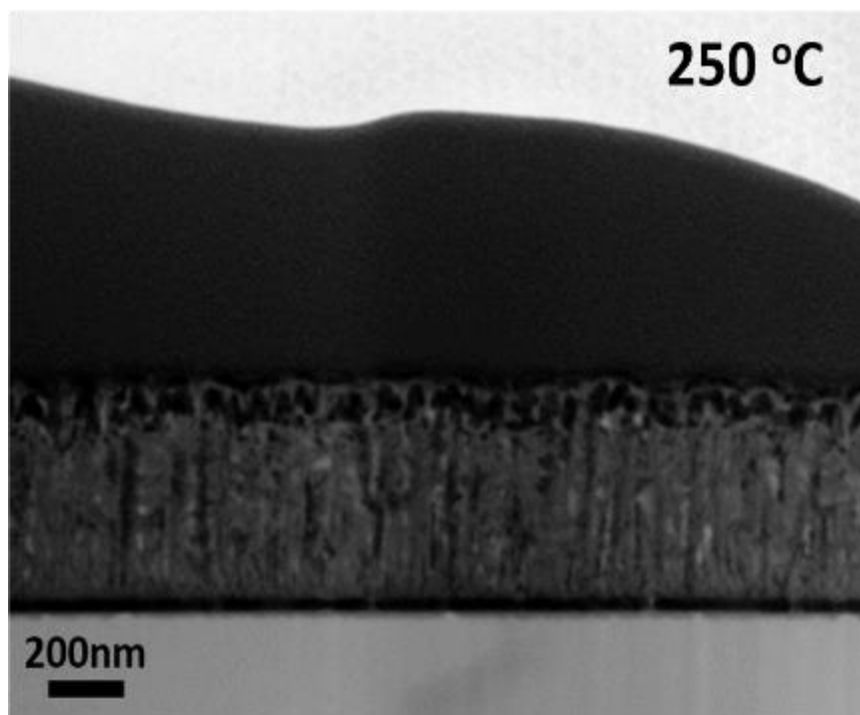


Figure 4-23: Transmission electron microscopy cross-sectional image of CeO₂ film deposited using 90 W sputter power at 250°C

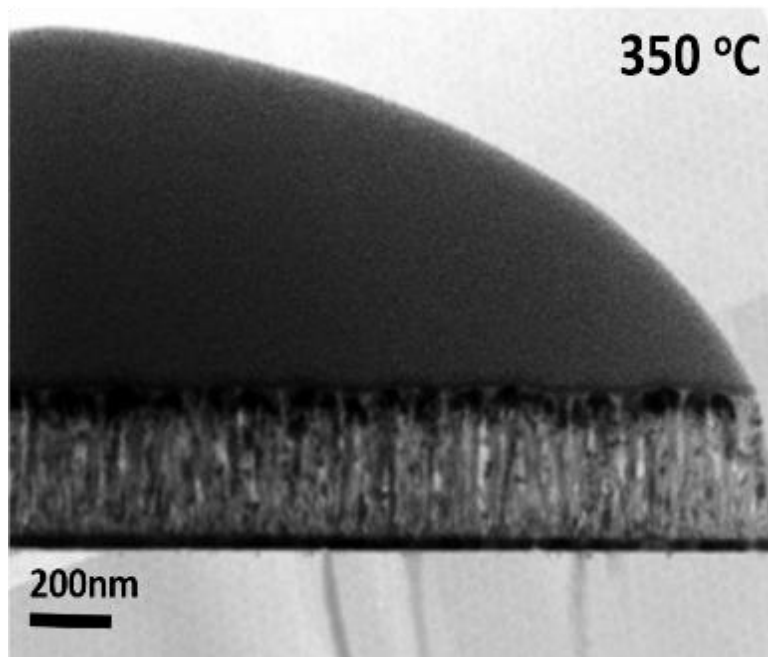


Figure 4-24: Transmission electron microscopy cross-sectional image of CeO_2 film deposited using 90 W sputter power at 350°C

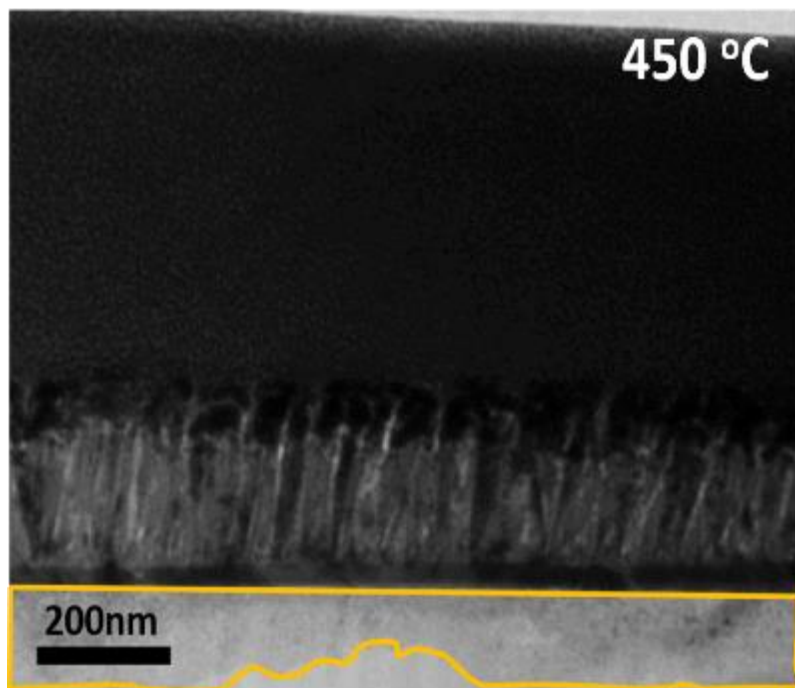


Figure 4-25: Transmission electron microscopy cross-sectional image of CeO_2 film deposited using 90W sputter power at 450°C

Another interesting observation was recorded for the samples deposited at high sputter power (90W). The films thickness was found to decrease by increasing deposition temperatures. The measured films thicknesses were dropped from 400nm to 240 nm by increasing temperature from 150°C to 450°C. As the sputtering power increased, the energy of particles arriving at the substrate increased, leaving more energy for surface diffusion resulting in enhanced grain size. However, high temperatures in conjunction with high power force the species to acquire a non-equilibrium position due to too large kinetic energies. Therefore, species (Ce) may diffuse into the substrate material which results in reduced film thickness as shown in figure 4-27(highlighted region around substrate).

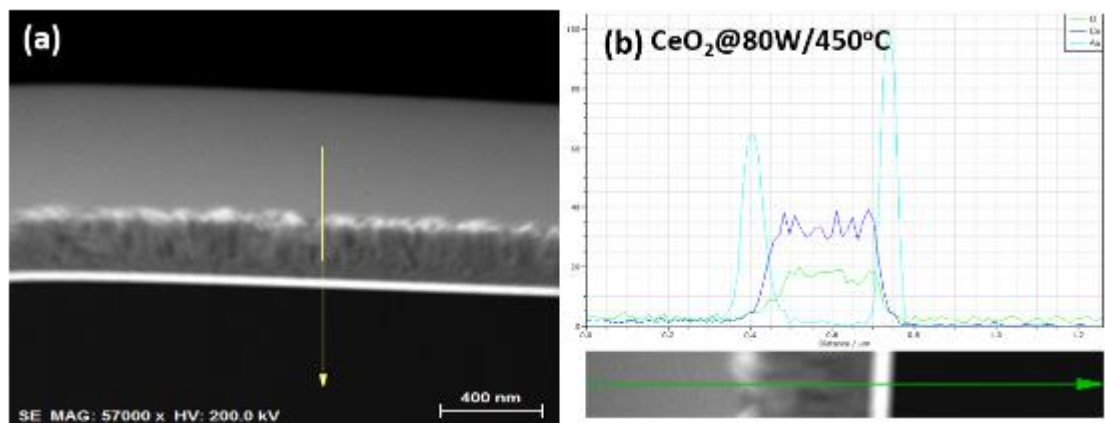


Figure 4-26: Energy dispersive spectroscopy images of CeO₂ film deposited using 80W sputter power at 450°C

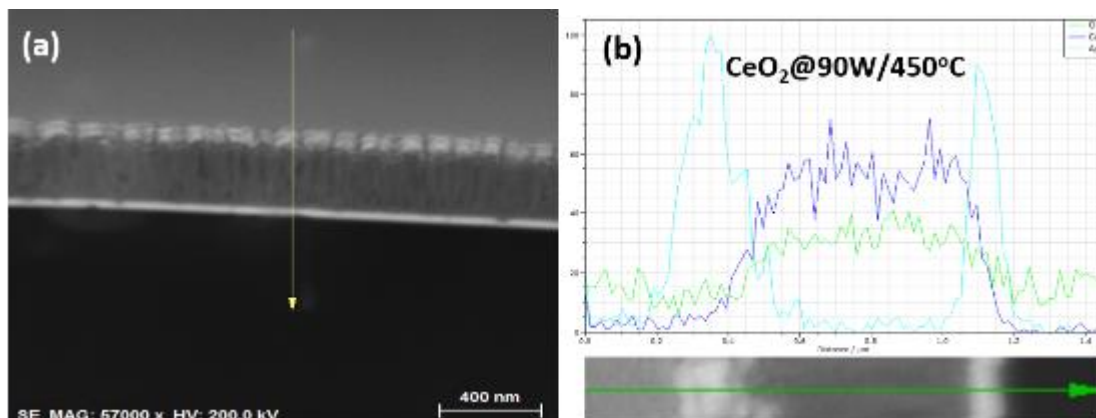


Figure 4-27: Energy dispersive spectroscopy images of CeO₂ film deposited using 90W sputter power at 450°C

To further investigate this effect, energy dispersive spectroscopy on the SEM cross-section image of the same sample was conducted and shown in figure 4-26 and 4-27 of supporting information. The cure of Ce³⁺ or Ce⁴⁺ atom and O²⁻ atom was found to be symmetrical from start to the end at the interface between gold layer and CeO₂ film. This indicates that there is no or very little diffusion of Ce species into substrate material for the sample with reduced growth rates (80W@450°C). However, for films deposited at 90W power, the elements distribution was not symmetrical and a portion of Ce³⁺ or Ce⁴⁺ specie peak resides into the peak of the gold layer. This is a clear evidence to support our postulation that at high growth rates there is a chance to have some diffusion effects of Ce species into substrate material which leads to the reduced films thickness. Furthermore, the surface roughness of the samples prepared at high power was found to follow the same trend as samples prepared at low sputter power. Therefore, it is expected that low surface roughness or flat samples are expected to demonstrate better electrical properties as compared to rough surface occupied samples.

4.1.5. Electrical Properties

For convenience, the samples prepared at 80W and 90W sputter powers and at temperatures (150°C, 250°C, 350°C and 450°C) were re-named S-80-01, S-80-02, S-80-03, S-80-04, S-90-01, S-90-02, S-90-03 and S-90-04, respectively.

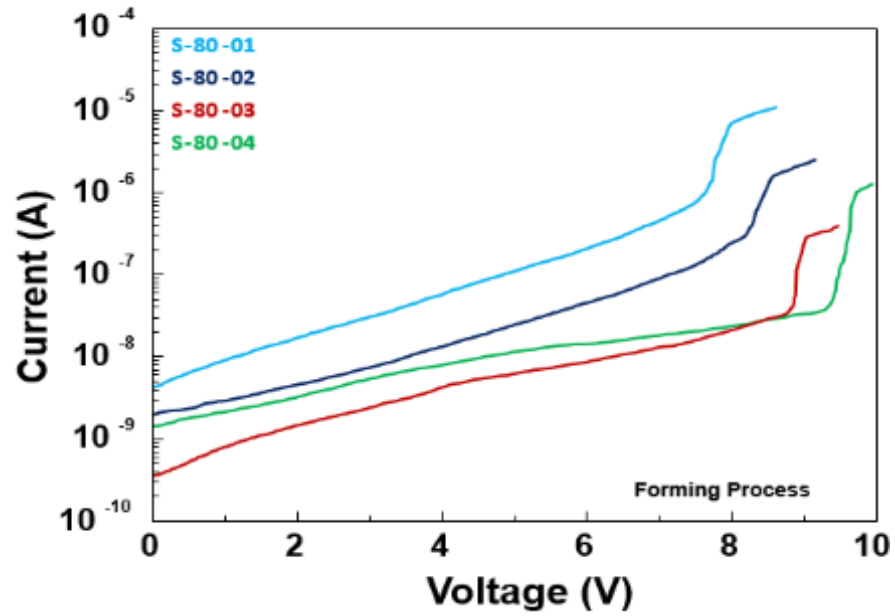


Figure 4-28: Typical electroforming processes of as-fabricated ceria devices prepared at sputter power of 80W

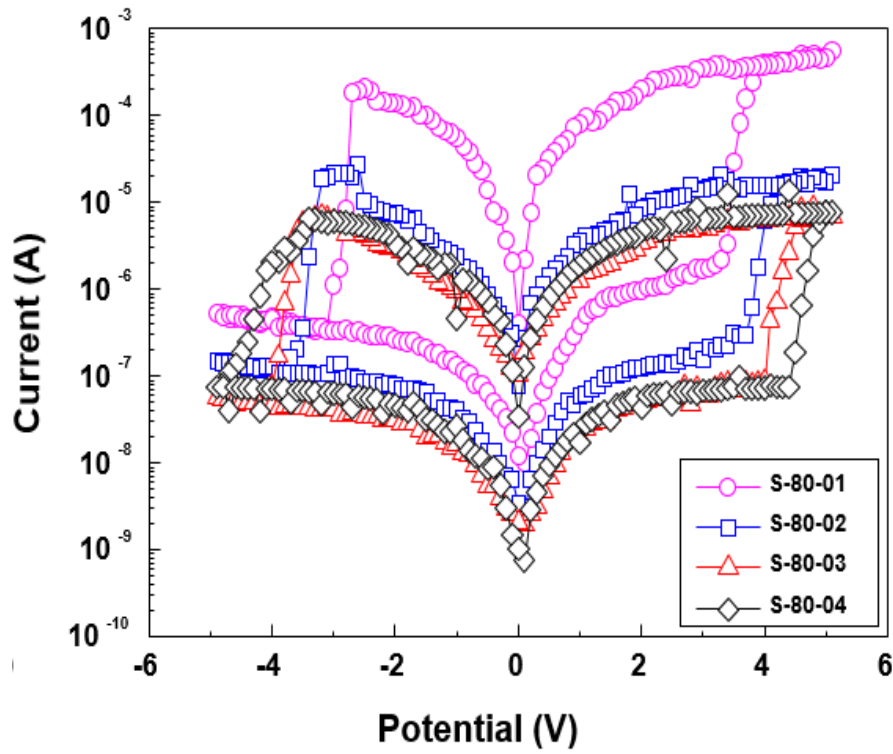


Figure 4-29: bipolar resistive switching behaviours of CeO₂ films obtained via classical CV measurements with a voltage sweep rate of 0.5Vs⁻¹

The current-voltage curves of as-fabricated S-80 samples are demonstrated in figure 4-28. The figure shows that electroforming process is essential to triggering the resistive switching processes in all devices. Interestingly, the device (S-80-01) requires less forming potential compared to other devices pointing towards its superior nature over other samples. After electroforming processes, successive bipolar resistive switching behaviours were achieved for all samples as shown in figure 4-29. The devices required comparatively much smaller potentials to demonstrate RS behaviour than their corresponding electroforming potentials and the set voltages of all devices were recorded as 3.2V, 3.8V, 4.1V and 4.5V. Similarly, the devices reset back from already achieved low resistance state (ON) to high resistance state at subsequent negative voltages. It is noteworthy to mention that our devices exhibit typical bipolar resistive

switching, that is, the cell can only be written with a positive bias and erased with a negative one which was verified by numerous measurements.

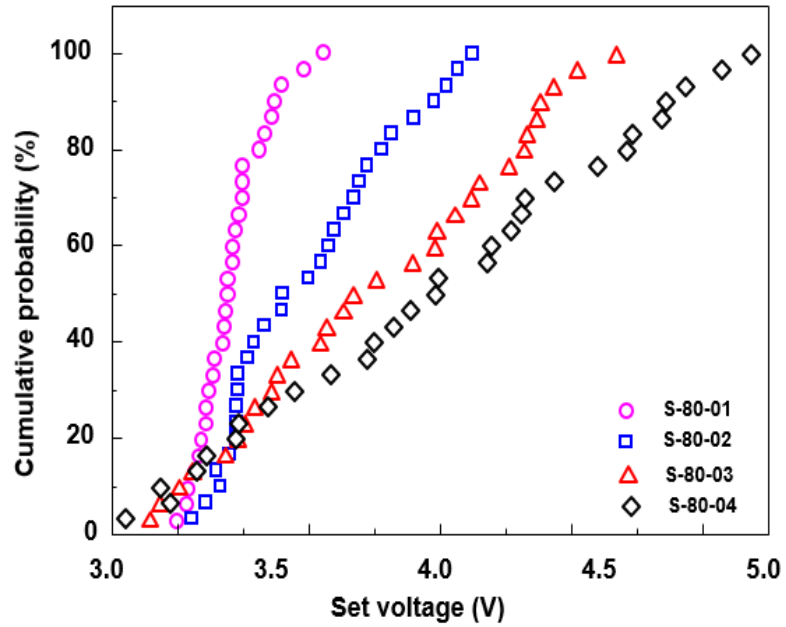


Figure 4-30: Statistical distribution of set potentials of S-80 samples for 30 consecutive switching cycles

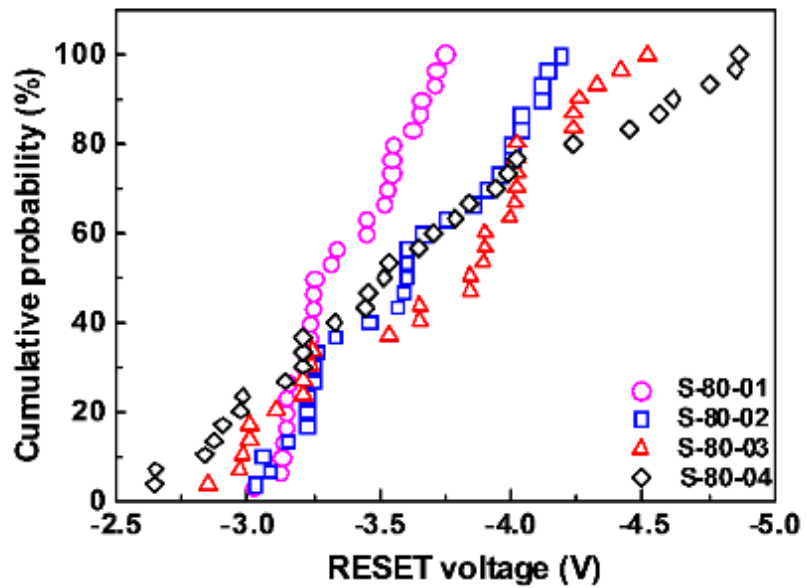


Figure 4-31: Cumulative probabilities of reset potentials of S-80 samples for 30 consecutive switching cycles.

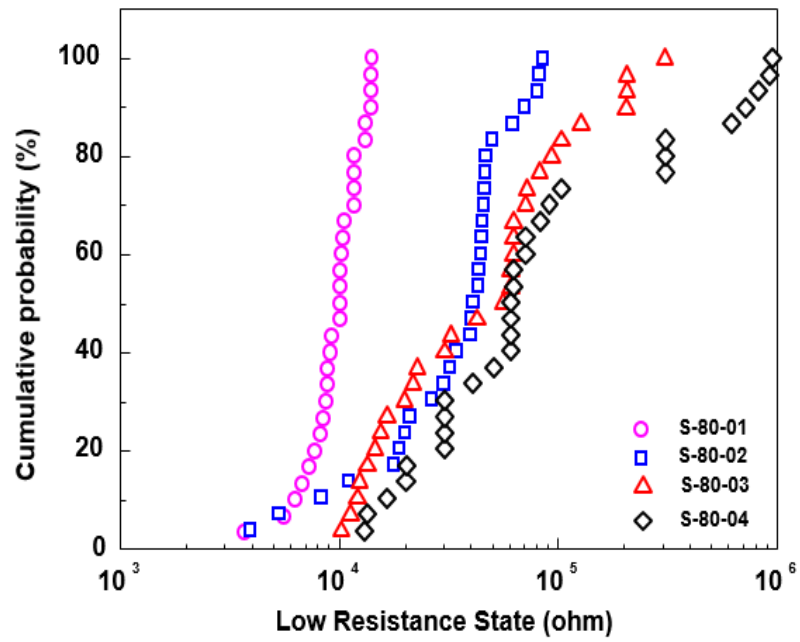


Figure 4-32: cumulative probabilities of low resistance state values of S-80 samples for 30 consecutive switching cycles.

Also, S-80-01 demonstrated superior RS behaviour in terms of low device set potential and achievable high on/off ratio. Furthermore, the distributions of RS parameters such as switching voltage (V_{SET}), resistance of low resistance state of all devices were plotted in figures 4-30 and 4-32, whereas the Au/CeO₂/Au/Si memory devices were repeatedly switched between ON and OFF states. Thirty (30) consecutive cycles were implemented to drag the statistical data of all devices. The distribution of V_{SET} for S-80-01 was spread to $\sim 0.4V$, which is much smaller than the voltage distribution recorded as 1V, 1.4V and 2V for S-80-02, S-80-03 and S-80-04, respectively. The similar trend was achieved for the low resistance state and reset potential values with minimum variation for S-80-01 was recorded as compared to the rest of devices as shown in figures 4-32. Sample S-80-01 possesses a less porous, dense structure with comparatively less rough surface over other samples may be the reasons to obtain pronounced RS behaviour of S-80-01.

The current-voltage characteristics of all samples prepared at sputtering power of 90W were also recorded and the average values of five different sets of readings in terms of switching parameters are depicted in figures 4-33 to 4-36. The sample S-90-01 (according to SEM and TEM investigations) express dense and less porous structure, and demonstrated enhanced RS performance as compared to samples prepared at 90W and at high temperatures (250°C, 350°C and 450°C).

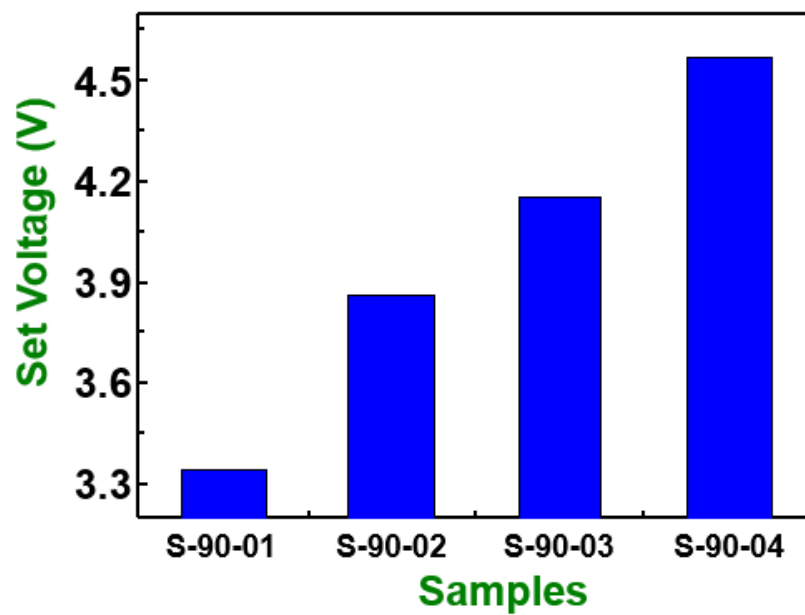


Figure 4-33: The average values of five different sets of readings for S-90 samples set potential

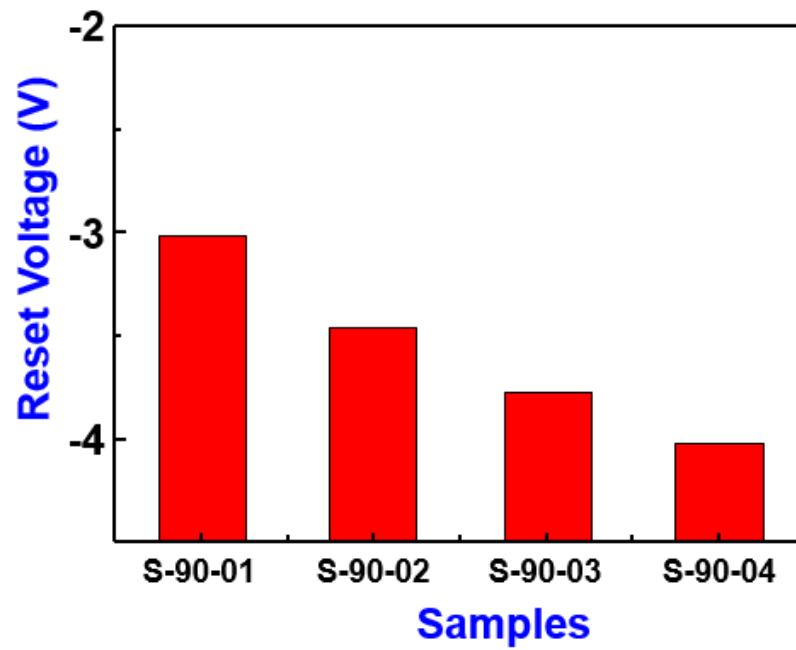


Figure 4-34: The average values of five different sets of readings for S-90 samples reset potentials

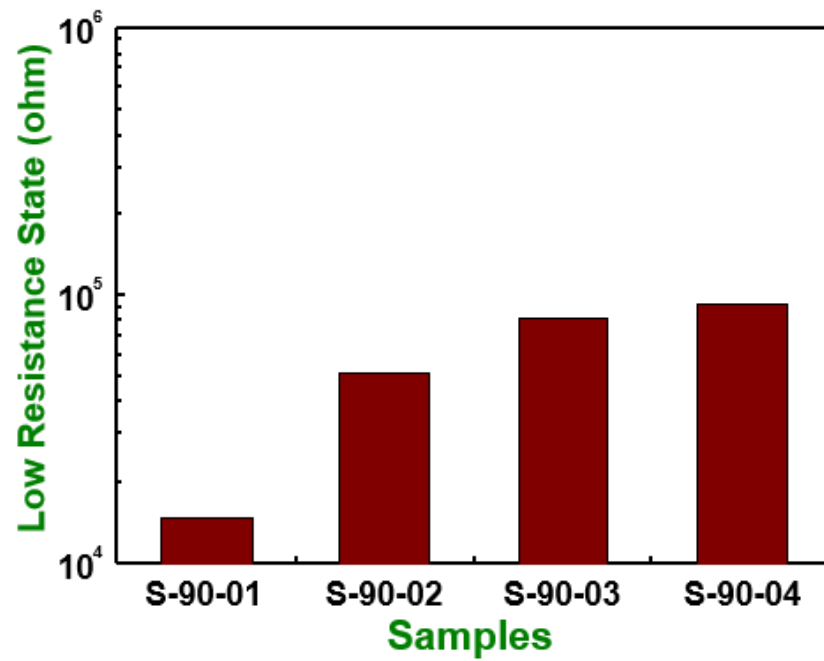


Figure 4-35: The average values of five different sets of readings for S-90 samples low resistance states values

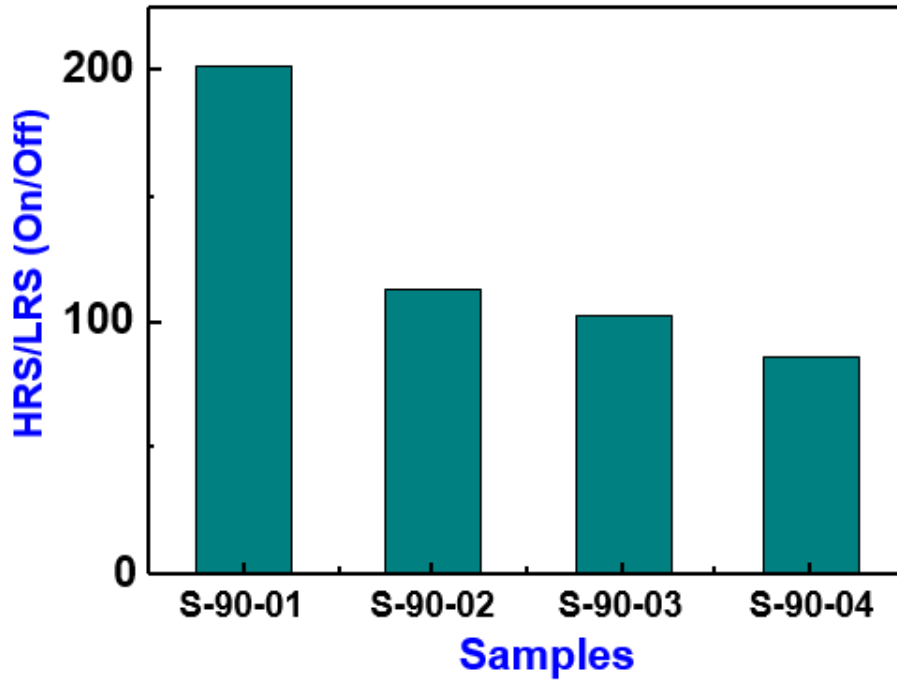


Figure 4-36: The average values of five different sets of readings for S-90 samples HRS/LRS ratios

The average resistance for S-90 samples at low resistance state in five different reading cycles have been shown in Figure 4-35. The sample S-90-1 shows the lowest resistance at low resistance state. The average resistance is not changed a lot when deposition temperature increases from 250°C, 350°C and 450°C. In figure 4-36, the average ratio between high resistance state and low resistance state in five different reading sets have been shown. It shows similar results with Figure 4-35 that the sample S-90-01 showed the best performance in all the samples.

To estimate the programming and erasing times of all fabricated devices, we implemented the pulse characteristics. To define the program and erase (*P/E*) conditions, the typical programming and erasing characteristics under ac pulse biases

were measured over pulse widths ranging from 100 ns to 100 ms with pulse heights of +4 V and -4V as shown in figures 4-37 and 4-38.

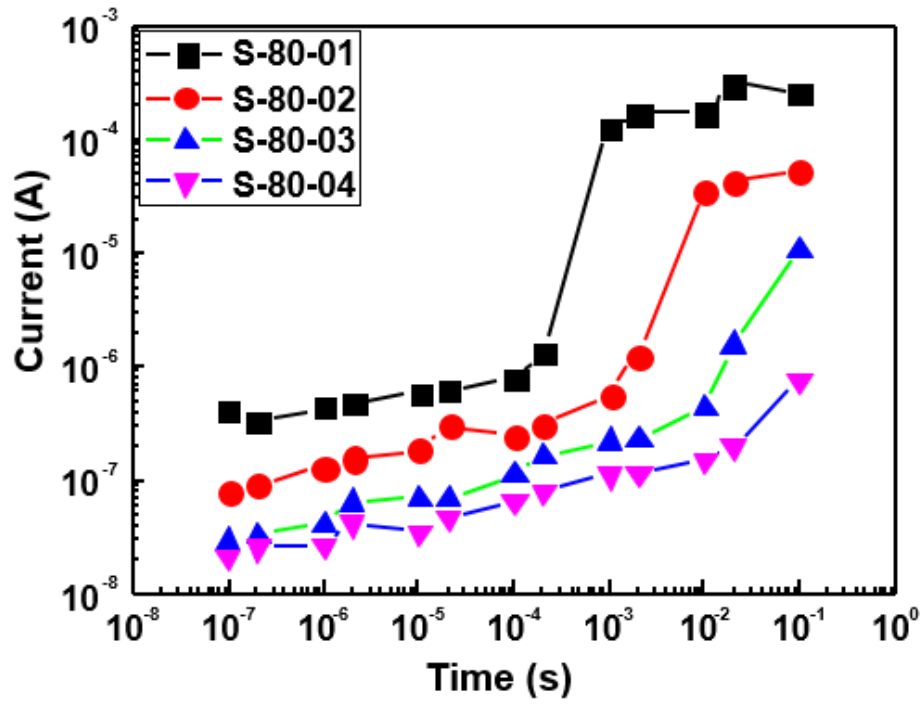


Figure 4-37: Programming time estimation for S-80 samples.

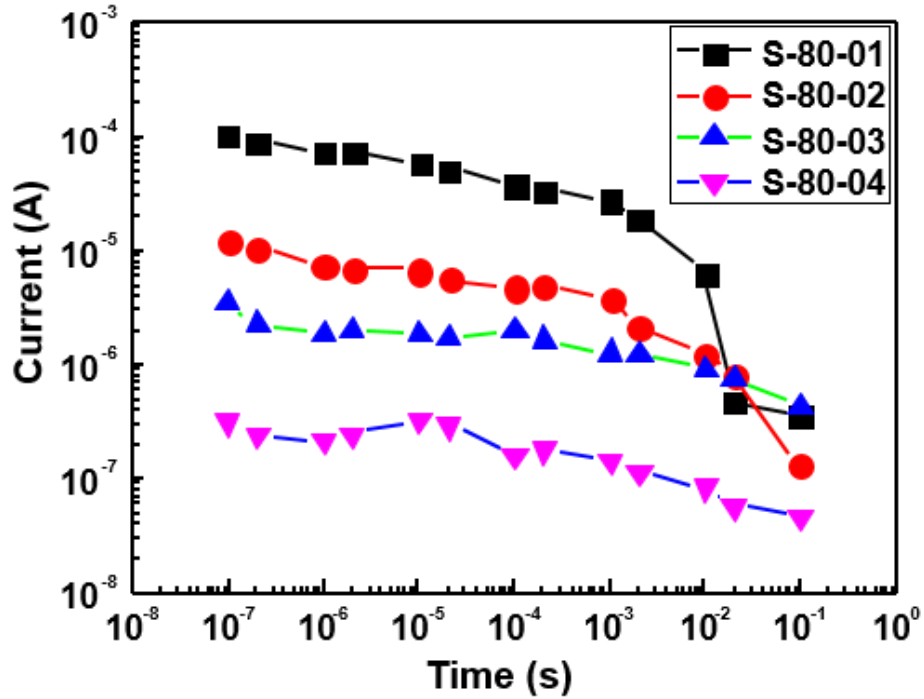


Figure 4-38: Erasing response time estimation for S-80 samples.

To record the current level of the device, a comparatively less potential (DC= 0.7V) was implemented as a read voltage. In the program test, the device S-80-01 switched from a high to low resistance state at +4V/0.1ms, about an order of magnitude faster than S-80-02 (+4V/5ms). Although the samples S-80-03 and S-80-04 switched from HRS to LRS in pulse potentiation at 50 and 100ms, their programming response was not as efficient as S-80-01 as shown in figure 4-41. Moreover, the devices S-80-01 and S-80-02 completely swapped their states from low to high resistance at -4V/1ms, -4V/50ms. However, S-80-03 and S-80-04 did not demonstrate any distinct transition from HRS to LRS states by pulse potentiation as shown in figure 4-42. The implementation of -4V may not be a suitable choice to observe a back transition in their conductance states. However, imposing -5V pulse amplitudes (results not shown here) on these devices showed a discrete jump in their current levels from low to high at about 50 and 100ms, respectively. Therefore, it can be inferred that the S-80-01 device is far superior to other

devices by demonstrating excellent response times in data programming and erasing conditions.

To investigate the conduction and switching mechanisms of the memory devices, we replotted the current-voltage characteristics of S-80-01 in log-log scale. Figures 4-39 and 4-40 show the logarithmic plots of the positive voltage sweep region in the high and low resistance states, respectively. Additionally, the similar trend appeared for the negative voltage sweep region. The current-voltage histogram in LRS shows an Ohmic behaviour, which might be due to the formation of conductive filaments in the device during the SET process (figure 4-1-40).

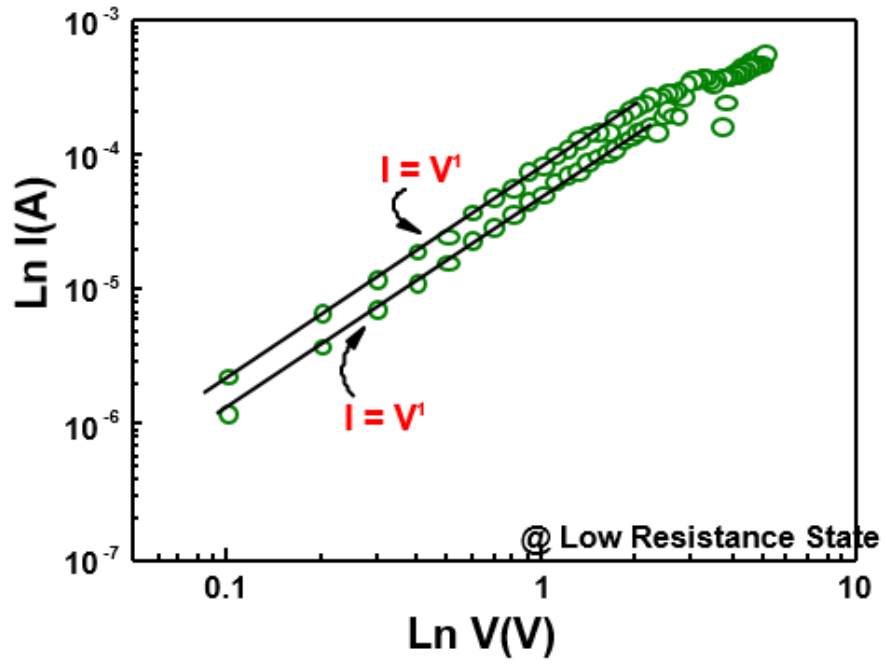


Figure 4-39: Log-log plot of the I - V curves of the S-80-01 RRAM cell at the low resistance state

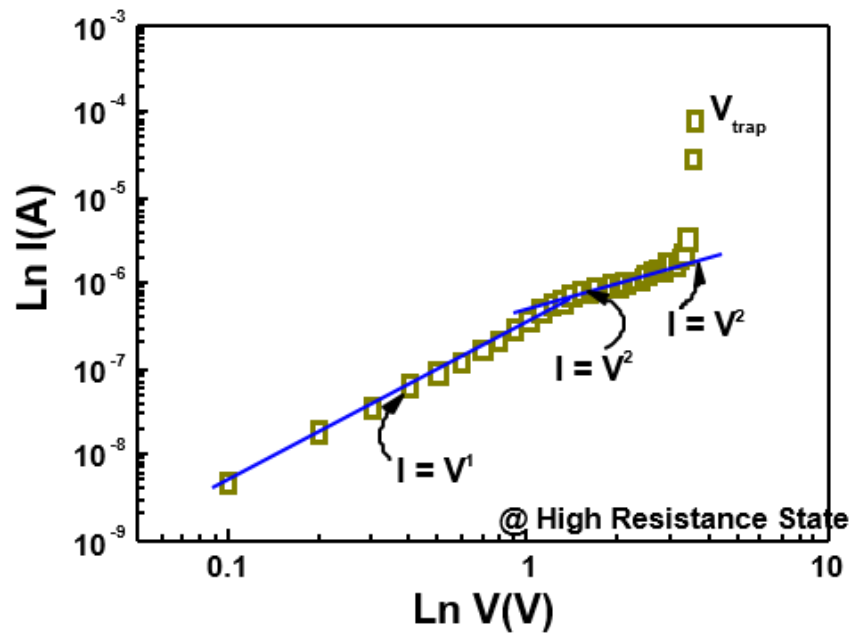


Figure 4-40: Log-log plot of the I - V curves of the S-80-01 RRAM cell at the high resistive state

On the other hand, the conduction mechanism in high resistive state seems more complicated. At the HRS, the slopes are divided into three regions (as shown in figure 4-39). In the low-voltage region, the slope corresponds to the ohm's law ($I \propto V$). In the medium-voltage region, the HRS follows the Child's law ($I \propto V^2$) and at high potentials, a steep current increase region was found that corresponds to a trap-filled limited voltage approximation, in which the HRS current increases rapidly corresponding to an abrupt increase in voltage. The charge transportation in HRS is in agreement to the classical trap-controlled space charge limited conduction (SCLC) which has been reported in many reports¹⁰. The entirely deviating conduction response of the device in two regions also suggests that the high conductivity in the ON-state device should have a confined, filamentary effect rather than a homogeneously distributed effect. Thus, the active medium of the device is much smaller than actual device size, which is highly desirable to overcome the scaling limits for next generation non-volatile memories.

The superior RS performance of S-80-01 may also be attributed to its dense structure, better homogeneity and especially lower surface roughness than other samples. Surface roughness may influence the Hall mobility of semiconductors. Therefore, the Hall mobility of all samples was measured and found to follow the above postulate. The Hall mobilities were recorded as 9.08 cm²/V-s, 7.57 cm²/V-s, 5.24 cm²/V-s and 4.85 cm²/V-s for S-80-01, S-80-02, S-80-03 and S-80-04, respectively. As RS phenomenon is regarded as a confined process, the degree of roughness irregularity at short lateral length scales may have significant influence on the conductivity of metallic/semiconducting thin films^{104,105}. This may be a possible reason to observe the distinct variations in RS behaviours of all samples.

In summary, we investigate the influence of sputter deposition conditions on the crystal structure, grains growth and surface morphologies of ceria. The samples prepared at low temperatures were found to have low crystallinity, but loosely packed structure with less porosity. However, by increasing sputter power and temperature, the crystallinity of samples was improved and well defined polyhedral shaped grains were achieved. Moreover, the resistive switching characteristics were also investigated for all fabricated samples. The samples with less porosity, dense structure and relatively flat surfaces demonstrated superior resistive switching performance. The results reported here imply that by decreasing surface roughness of active switching layer in RRAM cells may offer an effective way to improve RS characteristics.

4.2. Effect of In doping by using RF sputtering method to improve the RS characteristics of CeO₂

Doping is an efficient way to enhance the electrical properties of semiconductor materials. Hence, In-doped CeO₂ was deposited by sputter to investigate the influence on switching behaviour. Also, effects of deposition conditions on switching behaviour are discussed in this chapter.

As before mentioned, because Ceria has a large bandgap (~3.6eV), the temperature influence on the formation of electron-hole pair can be ignored. A local charge imbalance can produce the extrinsic oxygen vacancies by doping.

4.2.1 Temperature effect

To investigate synthesis temperature, the CeO₂ films were deposited on Au/Si at different temperatures with a gas mixture of 35sccm:15sccm Ar/O₂ by radio-frequency (RF) magnetron sputtering. Prior to RF sputtering at 10⁻⁶ mTorr pressure, the base pressure of the chamber was achieved at 20mTorr.

4.2.1.1 XRD results

In Figure 4-41, the X-ray diffraction spectra of In-doped CeO₂ thin films deposited on gold coated silicon substrate (111) by 80W power at different synthesis parameters (temperature and power) are shown. All observed peaks were matched well and indexed by using JCPDS-No. 04-008-0316.

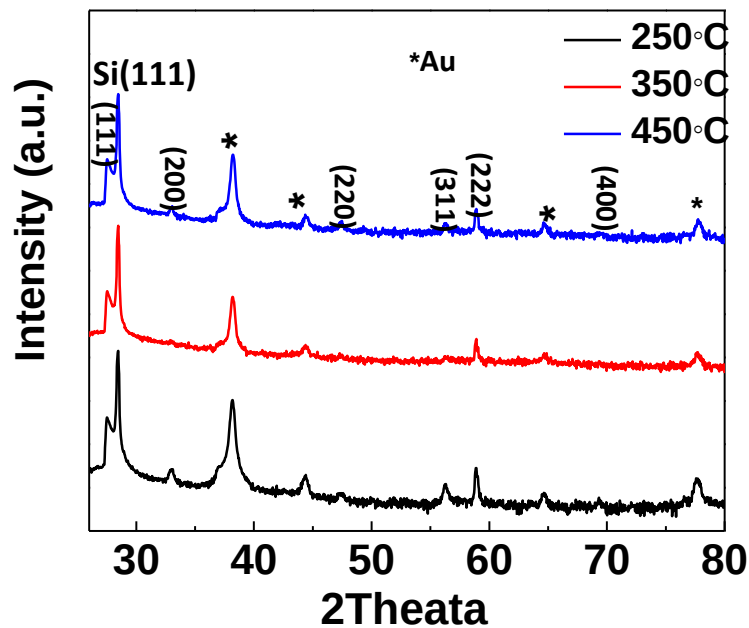


Figure 4-41: X-ray diffraction pattern of In-doped Ceria films deposited at various temperatures and at sputter powers of 90W

By increasing synthesis temperature, the intensity of (111) peak and (400) peaks become lower; however, the intensities of (200) almost disappeared for films deposited at 350°C. As same as pure CeO₂ film, there are some textures (columnar or granular) within the film. Increased crystallinity was also observed in samples prepared at high temperatures. However, high sputter power may increase crystal growth rate and hence, well defined grains were observed at relatively lower temperatures, which will be further verified by microscopy analysis.

Films deposited at 250°C have a broader FWHM than other deposition temperatures. It indicates that the grain size of the film which deposited in 250°C is the smallest which may produce more oxygen vacancies in all different deposition temperature.

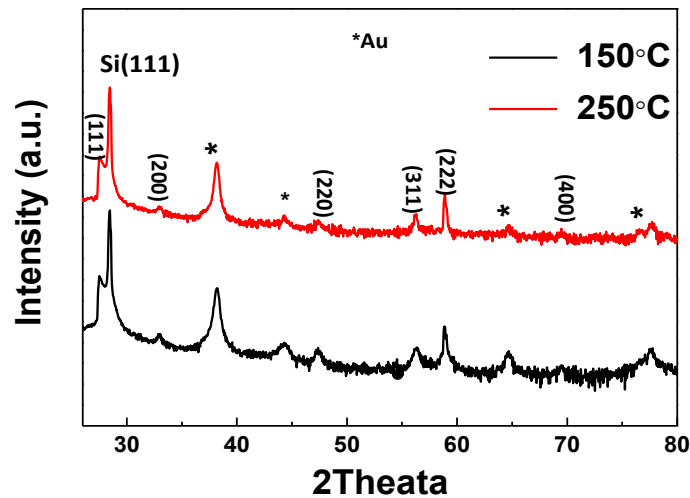


Figure 4-42: X-ray diffraction pattern of In-doped Ceria films deposited at various temperatures and at sputter powers of 100W

For the films deposited by 100W power, peak width goes broader with temperature decrease. The different between films deposited by 90W is (400) plane. Other planes have same trend, (111) and (222) plane did not change with temperature decrease.

4.2.1.2 SEM results

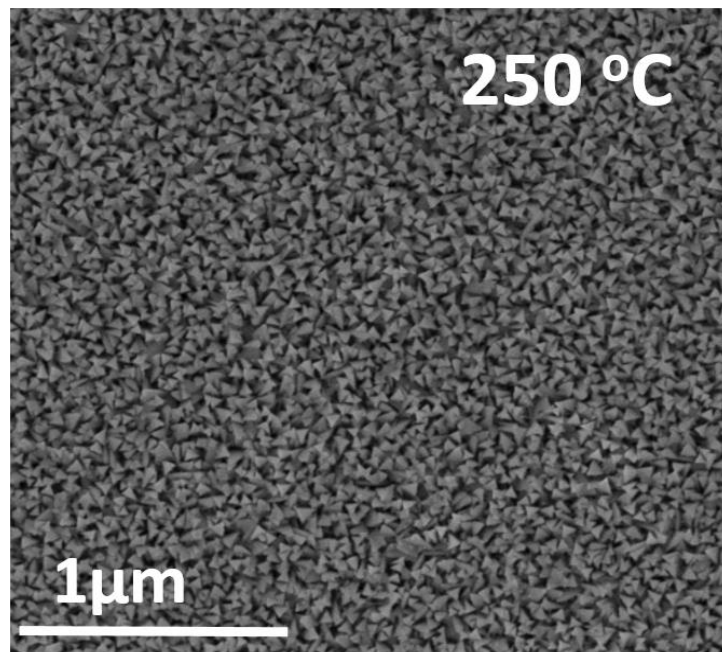


Figure 4-43: Scanning electron microscopy image of In-doped CeO₂ film deposited at 90W sputter power at 250°C

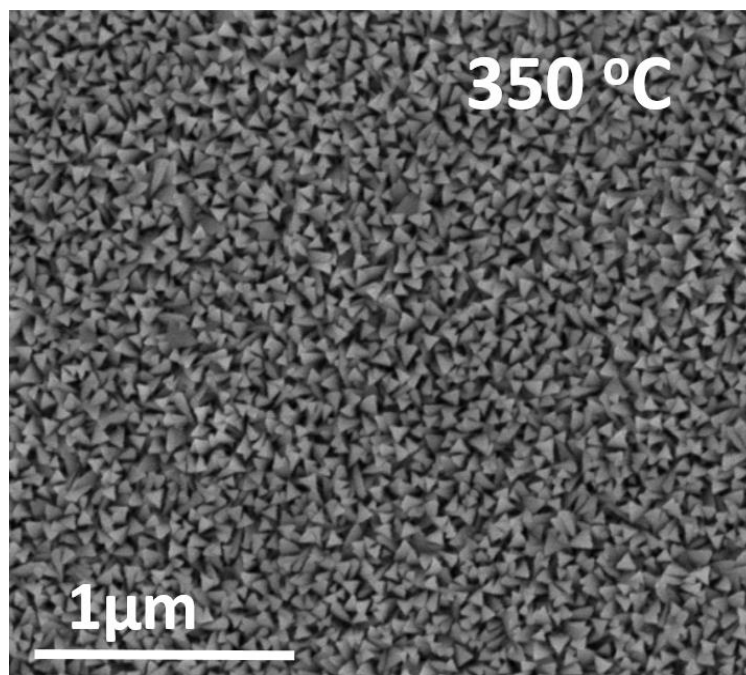


Figure 4-44: Scanning electron microscopy image of In-doped CeO₂ film deposited at 90W sputter power at 350°C

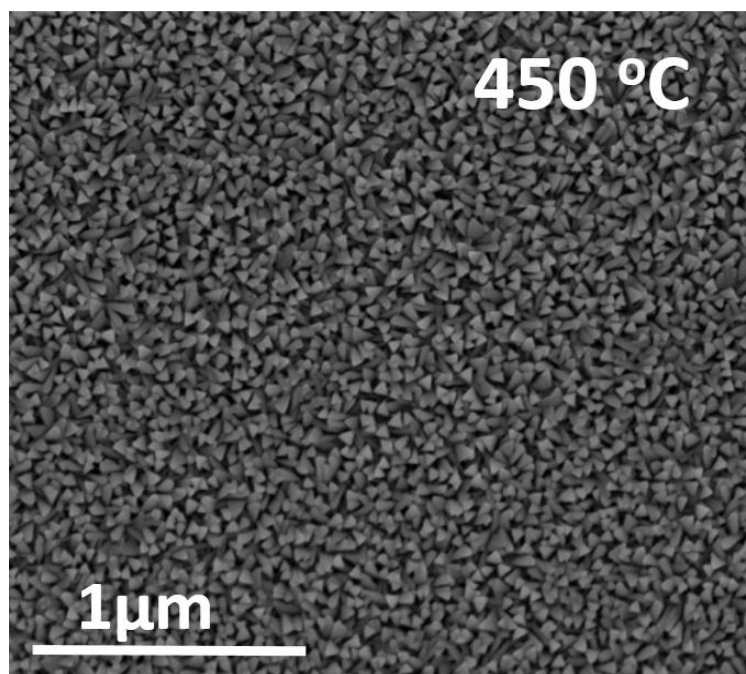


Figure 4-45: Scanning electron microscopy image of In-doped CeO₂ film deposited at 90W sputter power at 450°C

The deposition temperature effects on morphology will be investigated by SEM. The results have been shown in figures 4-43 to 4-45. The figures show that film crystallinity was greatly improved at high temperatures. The results of SEM show same trend as XRD. The grain size of films decreased with the drop of deposit temperature. But with the increase, the shape of grain did not change a lot. In-doped CeO_2 films became more uniform when deposited temperature increases.

4.2.1.3 Electrical Properties

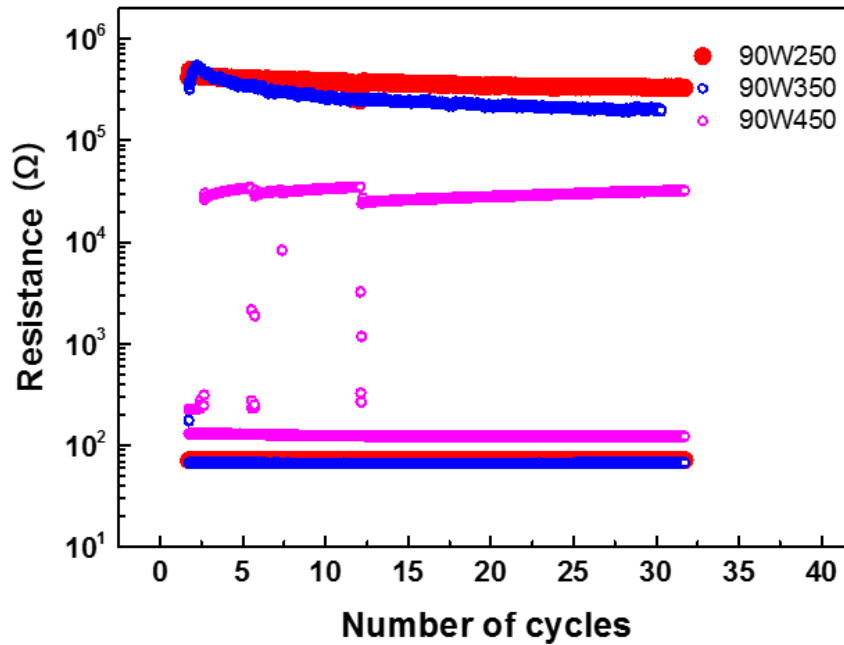


Figure 4-46: On-off ratio of In-doped CeO_2 deposited by 90W power and various temperatures

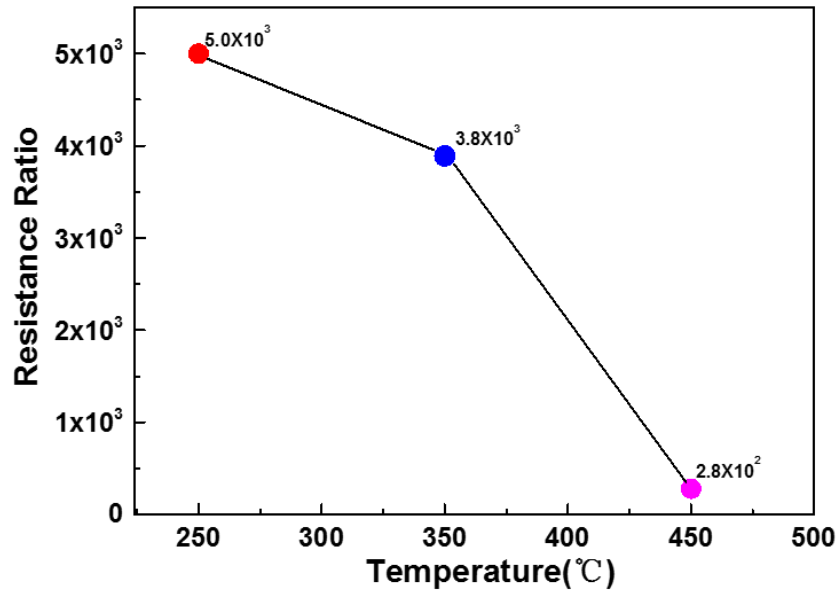


Figure 4-47: Temperature effect of On-off ratio of In-doped CeO₂ deposited by 90W power and various temperatures

Figures 4-46 and 4-47 show the effect of deposit temperature on film electrical properties. For In-doped CeO₂ films, films deposited at a relative lower temperature have higher electrical properties. Combine with SEM results, at lower temperature, the interface between top electrode and film is more flat, which plays a key role in switching behaviour.

4.2.2 Pressure effect

To investigate synthesis pressure, the CeO₂ films were deposited on Au/Si at different pressure, but with a certain gas mixture of 35sccm:15sccm Ar/O₂ by radio-frequency (RF) magnetron sputtering. Prior to RF sputtering at 10^{-6} mTorr pressure, the base pressure of the chamber was achieved at 10 mTorr and 20 mTorr. Deposition temperature is 150°C.

4.2.2.1 XRD results

In Figure 4-48, the X-ray diffraction spectra of CeO₂ thin films deposited on gold coated silicon substrate (111) by 80W power at different synthesis parameters (temperature and power) are shown. All observed CeO₂ peaks were matched well and indexed by using JCPDS-No. 04-008-0316.

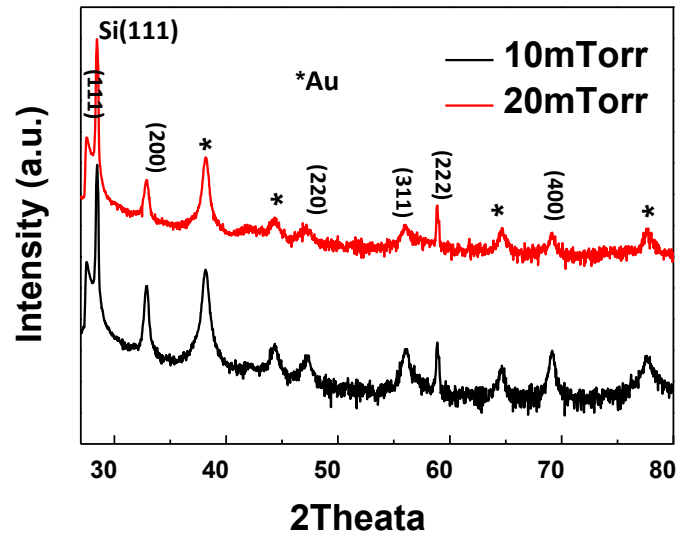


Figure 4-48: X-ray diffraction pattern of In-doped Ceria films deposited at various pressures and at a sputtering power of 90W

By increasing synthesis pressure, the intensity of (200) peak and (400) peak become lower; however, the intensities of (111) peak is higher at 20 mTorr. It indicates that to get higher crystallinity higher pressure is a necessary way.

4.2.2.2 SEM results

To further investigate the pressure effect on film morphology, the scanning electron microscope was used to examine Ceria film. The surface morphologies of In-doped CeO_2 film deposited at different pressure and at different sputter 80W powers are shown from figures 4-49 and 4-50.

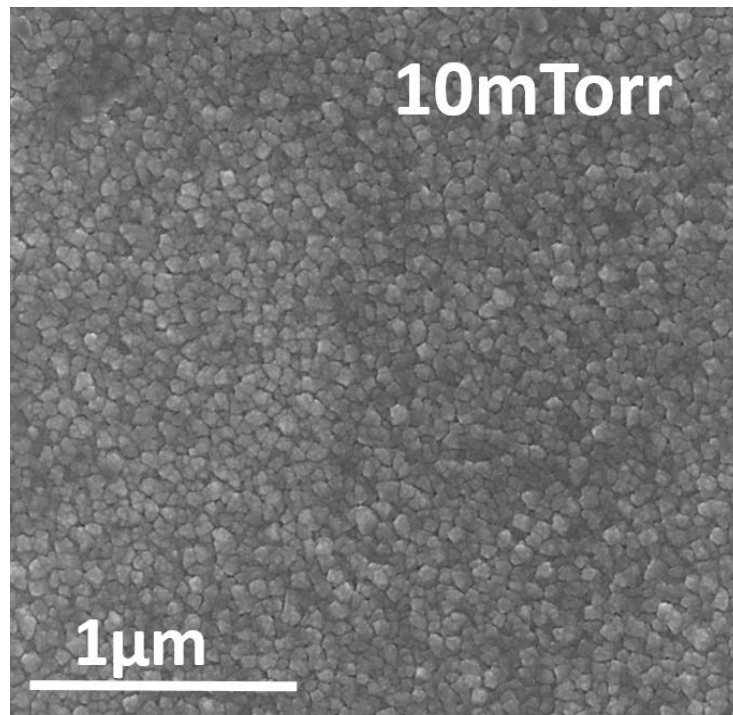


Figure 4-49: Scanning electron microscopy image of In-doped CeO_2 film deposited using 90W and sputter pressure at 10mTorr

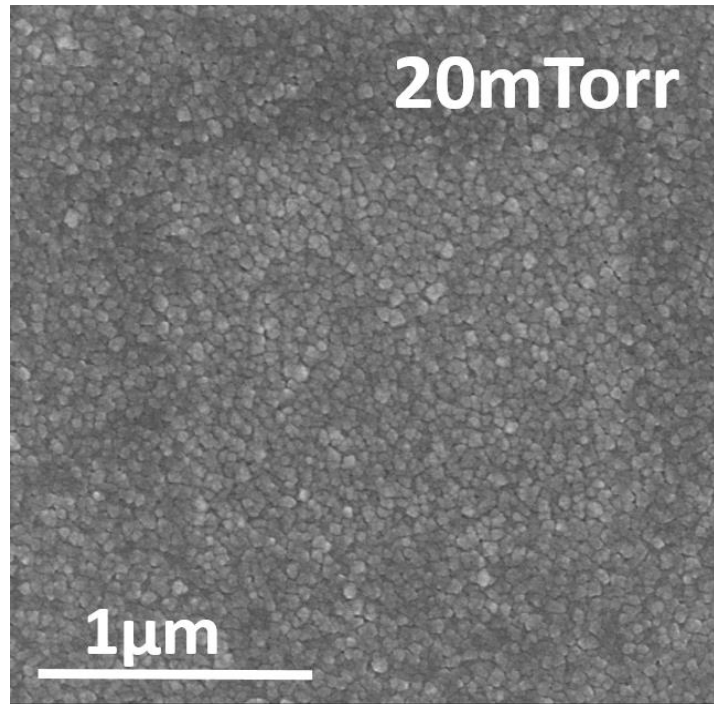


Figure 4-50: Scanning electron microscopy image of In-doped CeO₂ film deposited using 90W and sputter pressure at 20mTorr

In figure 4-49, the grain size decreased when pressure increased. However, the grain shape more uniform when is synthesising pressure is 20 mTorr. Combining with results mentioned at chapter 3, it can be explained by that the cohesion progress of grain happened. The grain shape tries to transfer from irregular shape to regular shape or polyhedral as mentioned previously.

4.3 Electrodeposition of In-doped CeO₂ on Transparent Substrates and Their Resistive Switching Characteristics

In doped CeO₂ nanocrystalline thin films were directly grown on FTO substrate and their resistive switching characteristics were investigated. The doping of In in CeO₂ nanocrystalline films leads to an excellent non-volatile behaviour with a narrow

dispersion of on/off ratio, and this study investigated the potential of In doped CeO₂ nanocrystalline films in next-generation memory devices.

The growth of CeO₂ nanocrystalline films on FTO was carried out using an electrodeposition process. Electrodeposition was carried out using an aqueous solution containing Ce(NO₃)₃ (99% purity, Sigma) by current deposition (-0.8V) at 75°C using an Autolab 302N Potentiostat. A standard three-electrode setup in an undivided cell was used. Tin-doped indium oxide (FTO, 9.3~9.7 Ω, Asahi Glass Corporation, Japan, 1.1 mm×26 mm×30 mm) was used as the working electrode while platinum foil (0.2mm×mm10 mm×20 mm) was used as the counter electrode. The distance between the two electrodes was 30 mm. The reference electrode was an Ag/AgCl electrode in 4 M KCl solution, against which all the potentials reported herein were measured. The morphologies of the samples were observed by field emission scanning electron microscopy (FEI Nova Nano SEM 230 FESEM) and transmission electron microscopy (TEM, Philips CM200). To measure the electrical property of the films, Au top electrodes (250 micrometer in diameter) were patterned and deposited by sputtering using a metal shadow mask. Voltage-current curves of the films were measured using an Autolab 302N electrochemical workstation controlled with Nova software. During measurement, the working electrode and sensor electrode were connected to the top Au electrode, and the reference and counter electrode were connected to the FTO substrate.

4.3.1 XRD Results

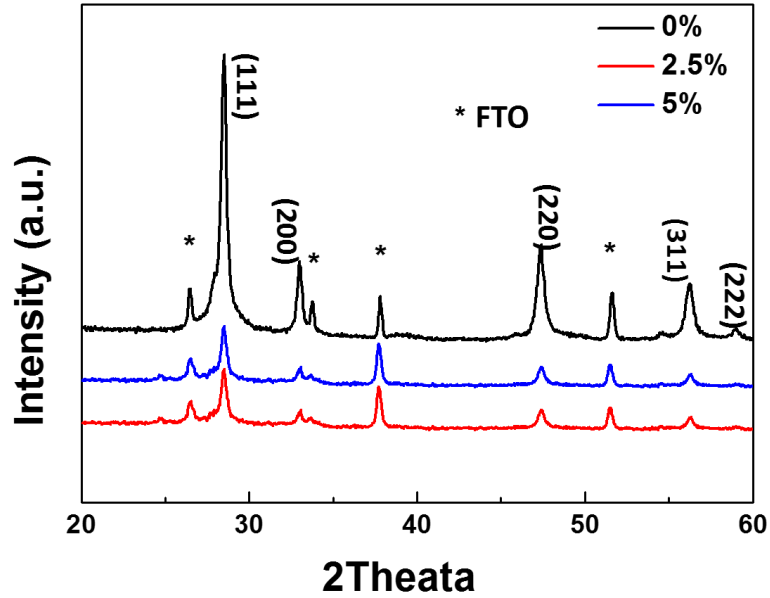


Figure 4-51: X-ray diffraction pattern of different In-doping concentrations Ceria films

Figure 4-51 shows XRD patterns of electrodeposited CeO_2 nanocrystalline thin films with different doping concentrations. The figure shows that all the visible peaks belong to CeO_2 phase (JCPDF-No. 04-008-0316) and no impurity peaks are found. In addition, with the increasing of indium doping concentration, the peaks shift to lower 2θ angle. Hence, by applying Bragg's law, there is a trend that higher In-doping concentration and d-spacing is increasing. The intensity of pure Ceria film is much stronger than doped CeO_2 . That means pure CeO_2 has better crystallinity than others. The CeO_2 (111) peak of 2.5% In-doped CeO_2 film is broader than the 5% doped Ceria peak, which indicates that the grain decreased when the doping level is increasing. Some further SEM and TEM evidence is needed to confirm these results.

4.3.2 SEM Results

The surface morphologies of CeO_2 film doped at various Indium concentrations are shown from figures 4-52 and 4-53. For 2.5% doped Ceria film, grain size is smaller but more uniform than high concentration doping. The surface morphology changed a lot by increasing doping concentration. Besides, a dense layer with small nanoparticles on the surface of the substrate can be found, which indicates that the CeO_2 were grown from this dense layer. In figures 4-52 and 4-53, the doped Ceria grain shape shows a long strip shape. This long strip is more clear at higher doping concentration levels.

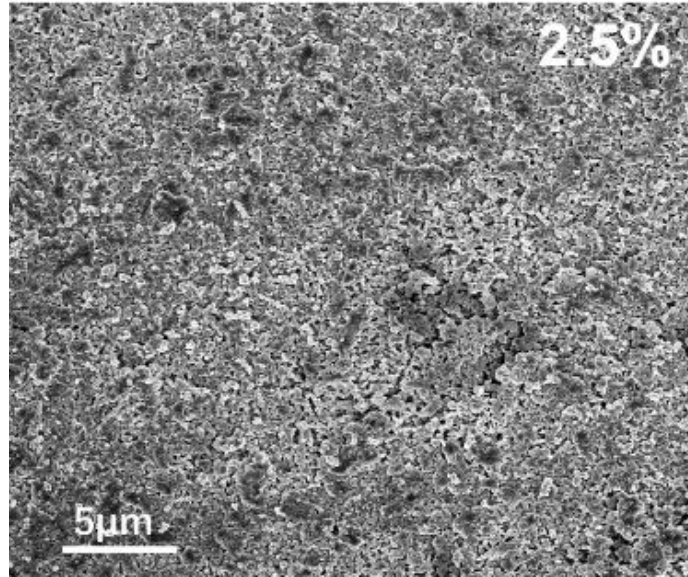


Figure 4-52: Scanning electron microscopy image of 2.5%(Wt.%) In-doping concentrations
Ceria films

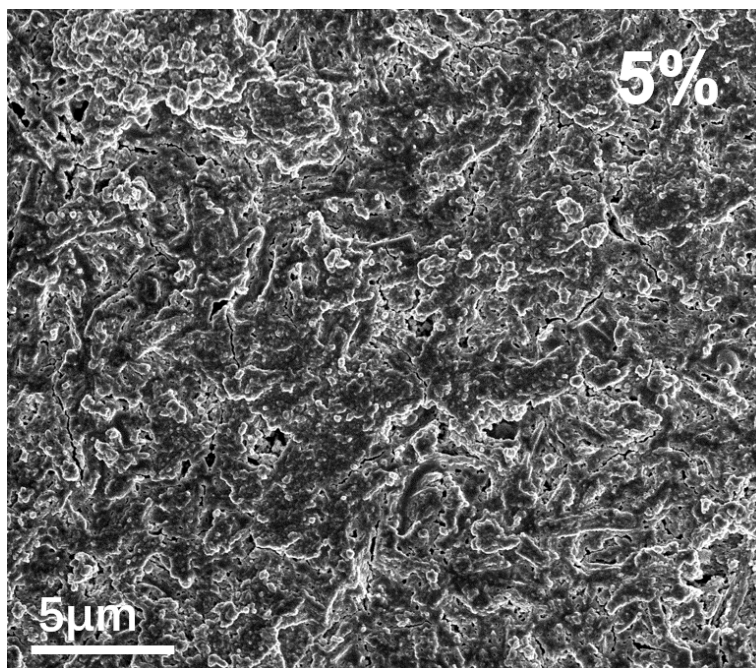


Figure 4-53: Scanning electron microscopy image of 5%(Wt.%) In-doping concentrations Ceria films

4.3.3 TEM Results

To further investigate the influence of doping concentration on films growth, the high-resolution transmission electron (HRTEM) microscopy studies were conducted as shown from figure 4-54 to 4-55.

In figure 4-54, the HRTEM images showed well-resolved lattice fringes and inter-planar spacing 0.314 nm corresponds to (111) plane. These value matches well with the XRD results 0.311nm for the (111) plane.

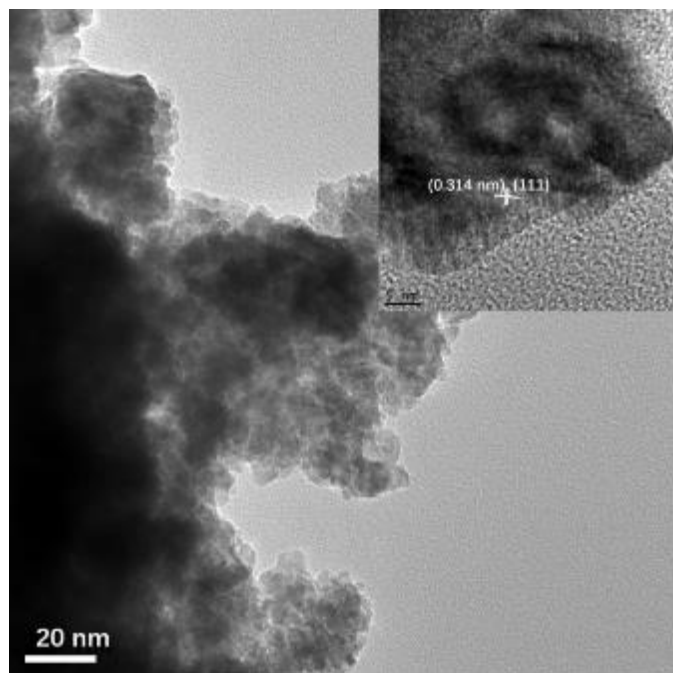


Figure 4-54: Transmission electron microscopy image of 2.5%(Wt.%) In-doping CeO₂ film

HRTEM images in Figure 4-55 further confirm the crystal structure of In-doped CeO₂ film with a measured lattice spacing of 0.32 nm, assigned to be the (111) plane of the anatase phase that matched with XRD results.

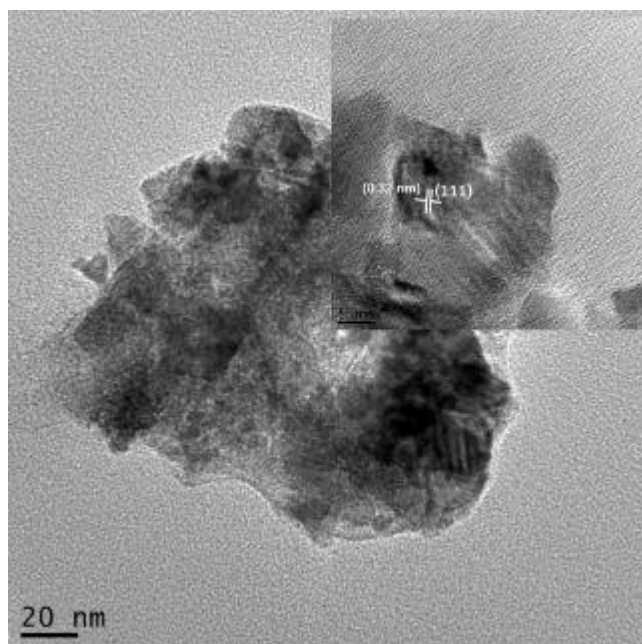


Figure 4-55: Transmission electron microscopy image of 5%(Wt.%) In-doping CeO₂ film

4.3.4 Electrical properties

Figures 4-56 and 4-57 show the typical I-V characteristics of Au/In-CeO₂/FTO capacitor, measured by sweeping voltage, at a speed of 1V/s, in the sequence of 0→5→0→ -5→0 V. During the measurements, the bias voltages were applied on the TE with BE grounded, and neither a forming process nor a current compliance was necessary for activating the memory effort.

In figure 4-56, when a sweep voltage from zero to positive was applied on I-V characteristics of Au/2.5%In-CeO₂/FTO device, a sudden resistance from high resistance status (HRS) to low resistance status (LRS) was observed at about 4 V. As the applied voltage swept from positive to zero, the LRS was maintained. Sweeping from negative to zero, an increase of resistance was observed at about -2 V. The improved endurance properties of the devices were investigated by applying electrical pulses. During the switching process, a 0.2 ms voltage pulse of 4V switches the device to the on-state (LRS), while a 0.2 ms voltage pulse of -4V is used to turn the device state back to the off-state (HRS). The evolution of resistance of the two well-resolved states in 100 cycles is shown in Figure 4-58. Under the pulse condition, both the HRS and LRS states are stable and the resistance fluctuations are very small within the range of experimental error. The resistance ratios of HRS to LRS are about 11 times, without degradation up to 100 cycles.

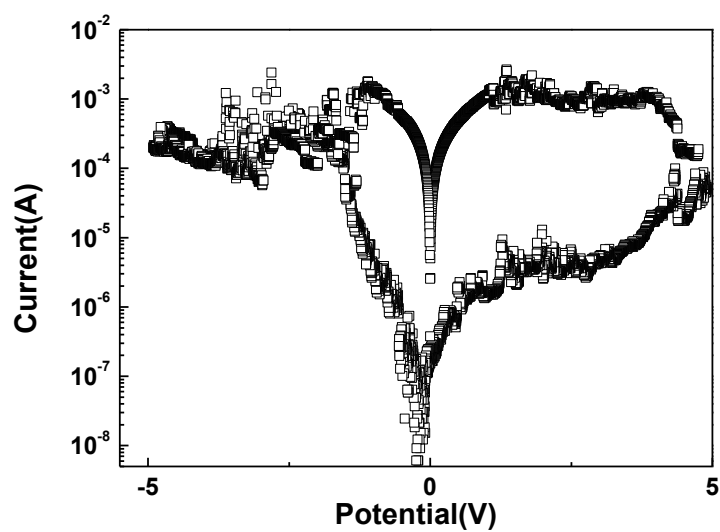


Figure 4-56: Current-voltage characteristics of the Au/2.5(Wt.%)In-doped CeO_2 /FTO device.

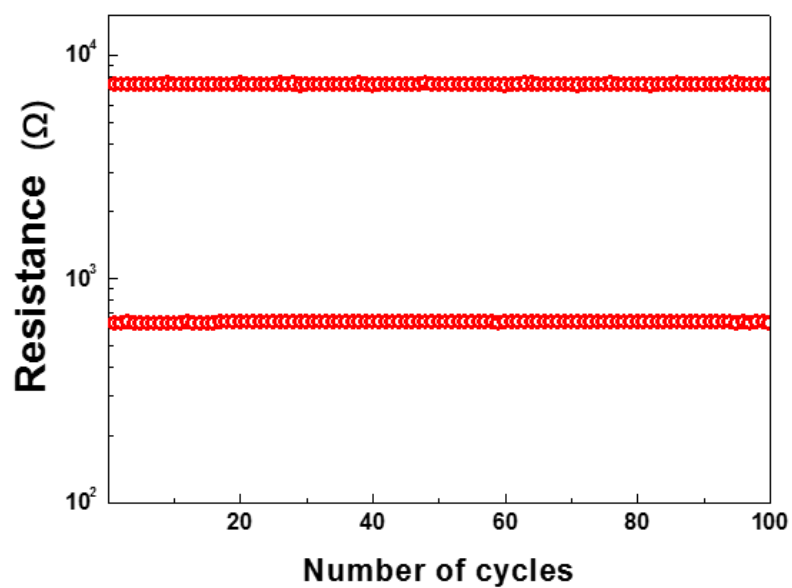


Figure 4-57: Electric pulse-induced resistance switching of the Au/2.5%(Wt.%) In- CeO_2 /FTO device.

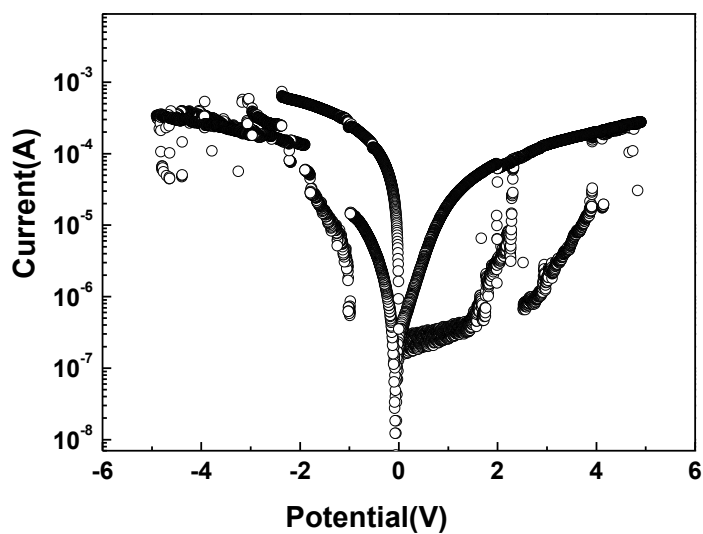


Figure 4-58: Current-voltage characteristics of the Au/5(Wt.%) In-doped CeO₂/FTO device.

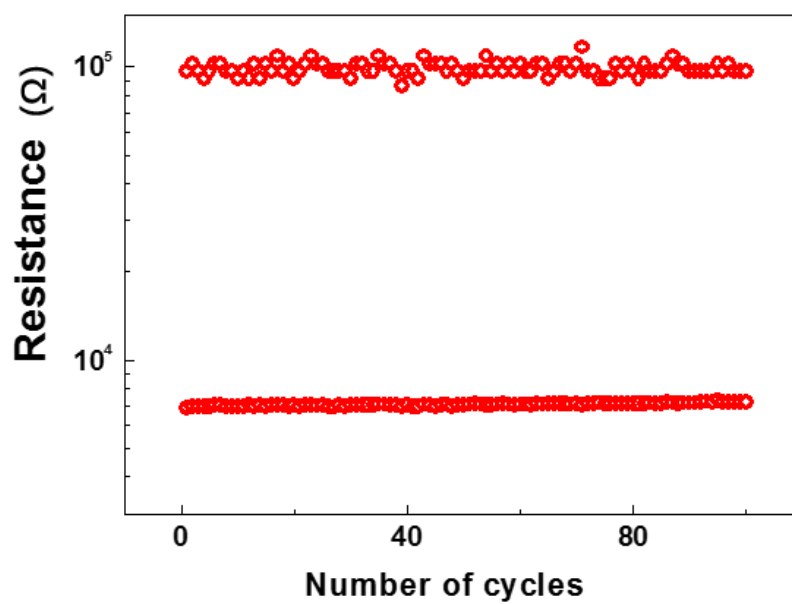


Figure 4-59 Electric pulse-induced resistance switching of the Au/5%(Wt.%) In-CeO₂/FTO device.

Comparing different doping concentrations, better switching behaviour appeared at higher doping concentrations. The mechanisms of resistive switching in In-CeO₂ are interesting but still controversial. The filamentary mechanism has been reported to

explain the resistive switching behavior in CeO_2 films. According to filament theory, resistive switching effect originates from the formation and the rupture of conductive filaments, which may be realized by the electrical migration and thermal diffusion of defects, such as oxygen vacancies. It is well known that the doping of In will introduce more oxygen vacancies in CeO_2 . Therefore, conducting filaments in CeO_2 might be created by the alignment of the oxygen vacancies under an applied electric field. As the mobility of defects at the surfaces is much higher than that in the crystal, oxygen vacancies can easily condense to form tiny filaments on the surface of the CeO_2 . The gathering of these tiny filaments gives rise to the formation of straight and extensible conducting filaments along the direction of electric field. As current conduction in doped CeO_2 , which has more oxygen vacancies, is more stable than that in branched thin films, a superior stability in the resistive switching behavior can be achieved in In doped CeO_2 .

4.4 Electro-deposition of Gd-doped CeO₂ on Transparent Substrates and Their Resistive Switching Characteristics

4.4.1 XRD Results

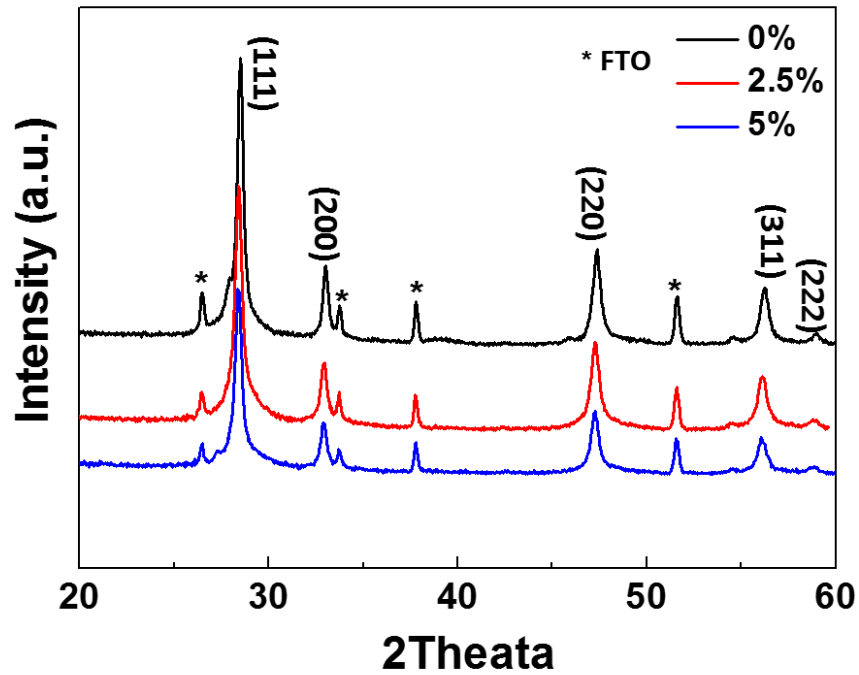


Figure 4-60: X-ray diffraction pattern of different Gd-doping concentrations Ceria films

Figure 4-60 shows XRD patterns of electrodeposited CeO₂ nanocrystalline thin films with different doping concentrations. Figure 4-62 shows that all the visible peaks belong to the CeO₂ phase (JCPDF-No. 04-008-0316) and no impurity peaks are found. In addition, with the increasing of indium doping concentration, the peaks shift to lower 2Theta angle. Hence, by applying the Bragg's law, there is a trend that higher In-doping concentration increases d-spacing. The intensity of pure Ceria film is much stronger than doped CeO₂. That means pure CeO₂ is more crystalline than others. The CeO₂ (111) peak of 5% Gd-doped CeO₂ film is boarder than 2.5% doped Ceria indicating that the grain size decreased when the doping level is increasing. With the increasing of

doping concentration, intensity of (111) peak decreases, which indicates some texture trend when doping concentration increases. Some further SEM and TEM experiments are needed to confirm.

4.4.2 SEM Results

The surface morphologies of CeO_2 film doped at various Indium concentrations are shown from figures 4-61 and 4-62. For 5% doped Ceria film, grain size is smaller and more uniform than high concentration doping. The surface morphology is changed a lot by increasing doping concentration. Besides, a dense layer with small nanoparticles on the surface of the substrate can be found, which indicates that the CeO_2 were grown from this dense layer. In figures 4-61 and 4-63, the doped Ceria grain shape show a long strip shape. This long strip is more clear at higher doping concentration levels. This shows same trend with XRD results that 5% Gd-doped Ceria showed with texture.

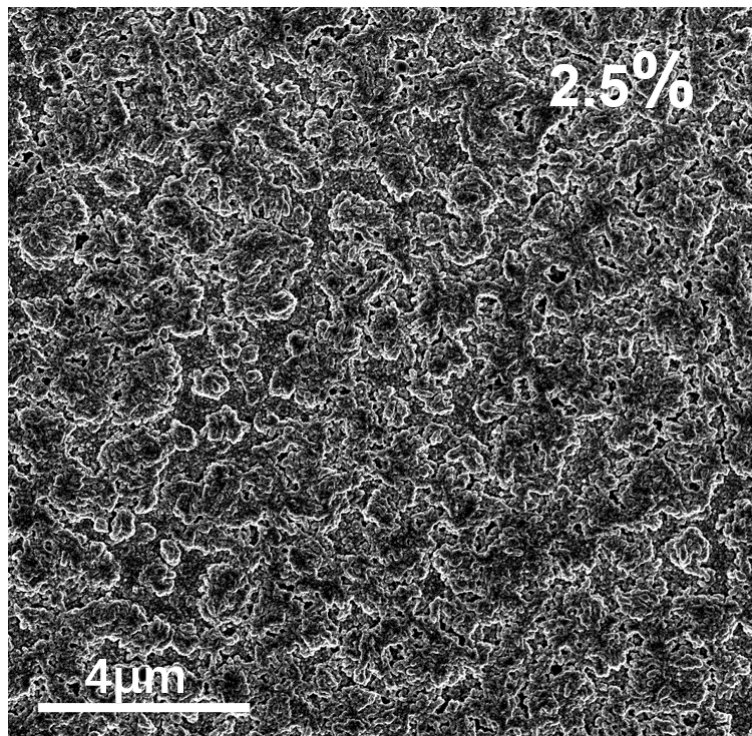


Figure 4-61: Scanning electron microscopy image of 2.5%(Wt.%) Gd-doped Ceria film

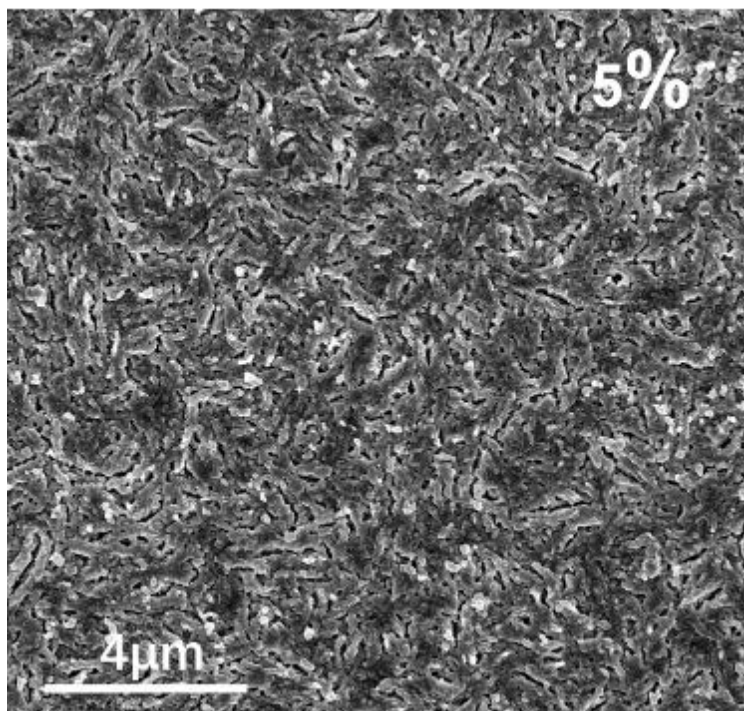


Figure 4-62: Scanning electron microscopy image of 5%(Wt.%) Gd-doped Ceria film

4.4.3 TEM Results

To further investigate the influence of doping concentration on films growth, the high-resolution transmission electron (HRTEM) microscopy studies were conducted as shown from figure 4-63 to 4-64.

In figure 4-63, the HRTEM images showed well-resolved lattice fringes and inter-planar spacing 0.314nm corresponds to (111) plane. These value matches well with the XRD results 0.311nm for (111) plane.

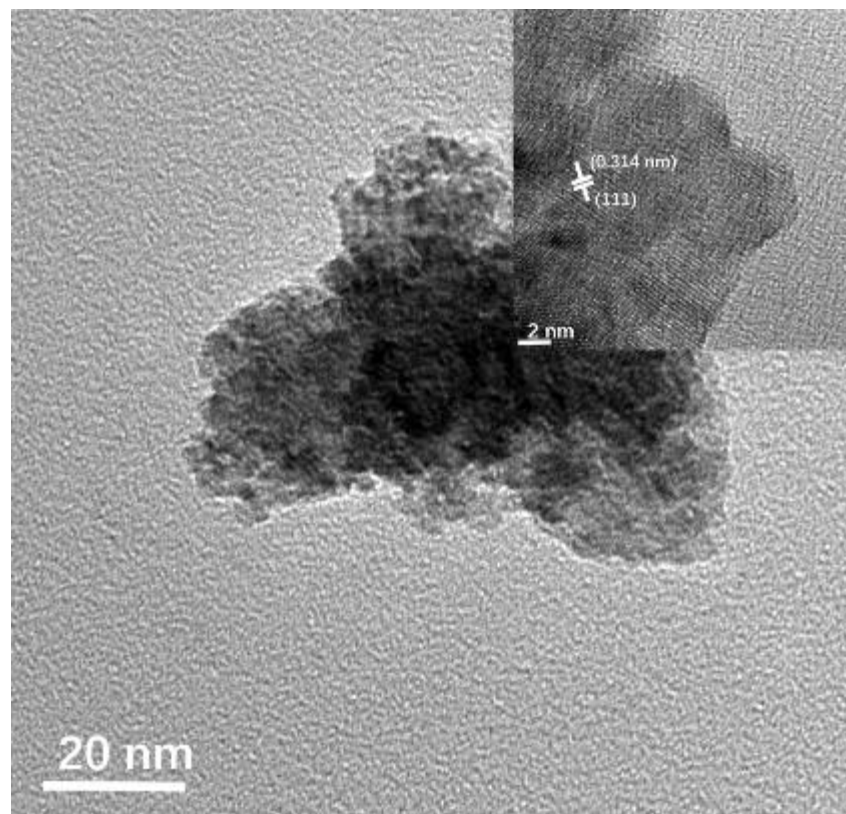


Figure 4-63: Transmission electron microscopy images of 2.5%(Wt.%) Gd-doped CeO₂ film

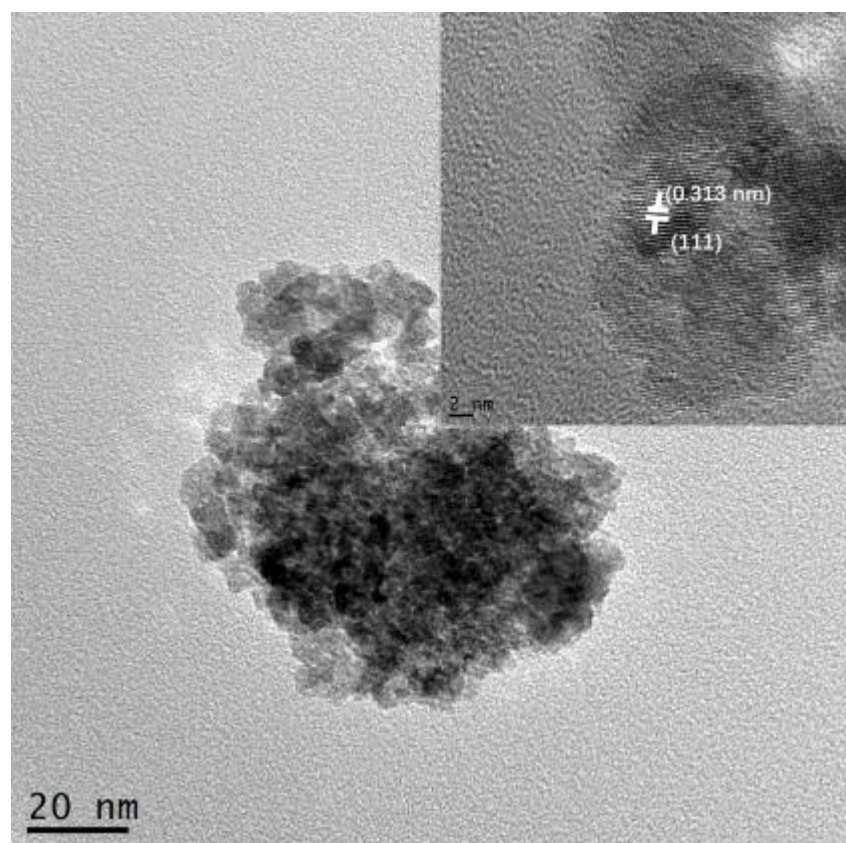


Figure 4-64: Transmission electron microscopy images of 5%(Wt.%) Gd-doped CeO₂ film

HRTEM images in Figure 4-64 further confirms the crystal structure of Gd-doped CeO_2 film with a measured lattice spacing of 0.313nm, assigned to be the (111) plane of the anatase phase that matched with XRD results.

4.4.4 Electrical properties

Figures 4-65 to 4-68 show the typical I-V characteristics of Au/Gd- CeO_2 /FTO capacitor, measured by sweeping voltage, at a speed of 1V/s, in the sequence of $0 \rightarrow 5 \rightarrow 0 \rightarrow -5 \rightarrow 0$ V. During the measurements, the bias voltages were applied on the TE with BE grounded, and neither a forming process nor a current compliance was necessary for activating the memory effort.

In figure 4-65, the resistance changes from HRS to LRS occurred at 5V in the Au/2.5%Gd- CeO_2 /FTO device. A reversed voltage applied on the device an increase of resistance was observed about -5 V. The improved endurance properties of the devices were investigated by applying electrical pulses. During the switching process, a 0.2 ms voltage pulse of 4V switches the device to the on-state (LRS), while a 0.2 ms voltage pulse of -4V is used to turn the device state back to the off-state (HRS). The evolution of resistance of the two well-resolved states in 100 cycles is shown in Figure 4-65. Under the pulse condition, both the HRS and LRS states are stable and the resistance fluctuations are very small within the range of experimental error. The resistance ratios of HRS to LRS are about 11 times, without degradation up to 100 cycles.

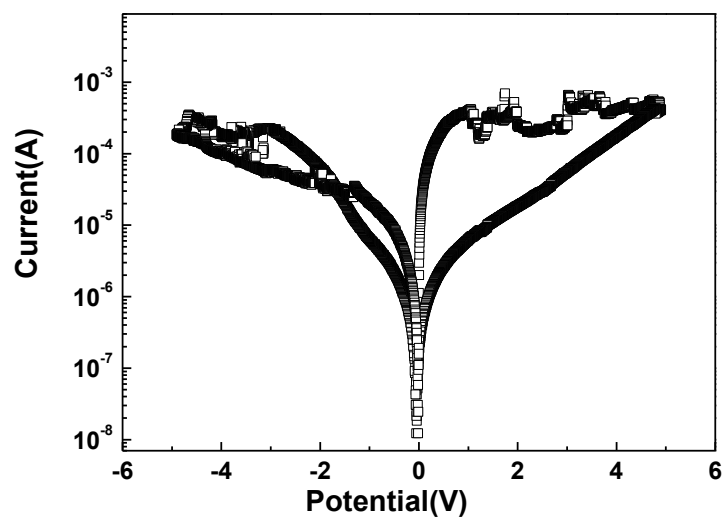


Figure 4-65: Current-voltage characteristics of the Au/2.5(Wt.%)Gd-doped CeO_2/FTO device.

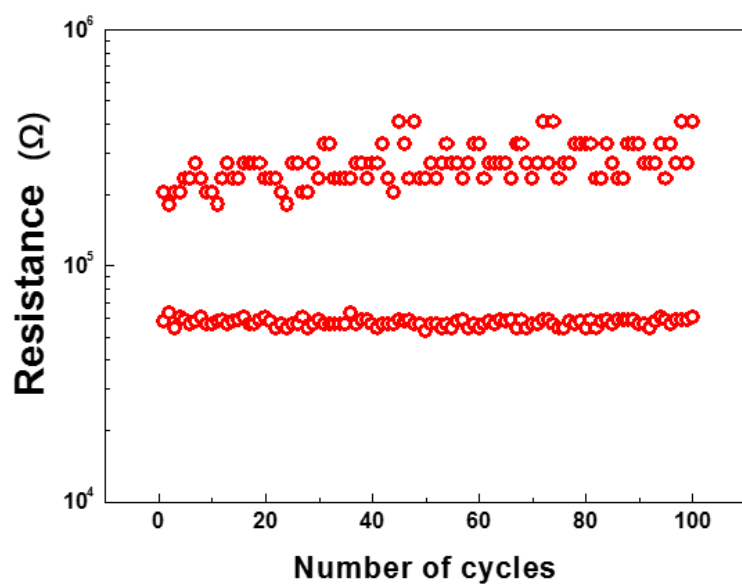


Figure 4-66: Electric pulse-induced resistance switching of the Au/2.5(Wt.%)Gd- CeO_2/FTO device.

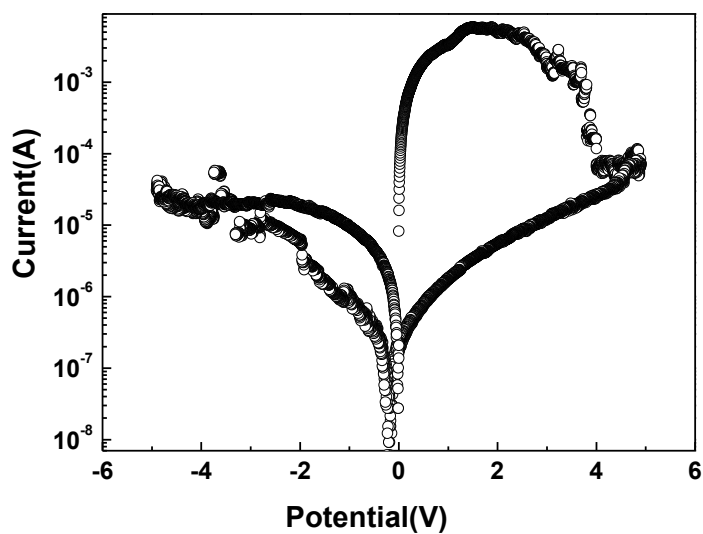


Figure 4-67: Current-voltage characteristics of the Au/5(Wt.%)Gd-doped CeO₂/FTO device.

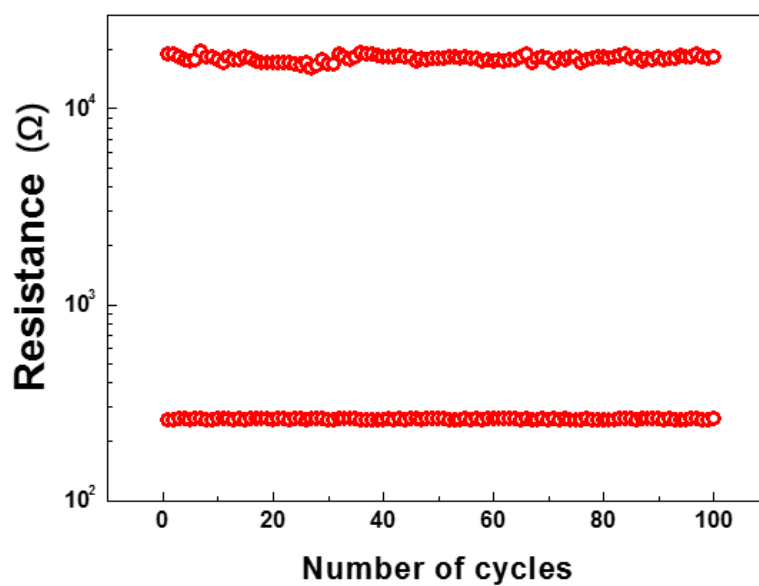


Figure 4-68: Electric pulse-induced resistance switching of the Au/5%(Wt.%)Gd-CeO₂/FTO device.

In figure 4-68, Au/5%-Gd-CeO₂/FTO device showed better switching properties. Higher doping concentration produced more oxygen vacancies which played a key role in the switching behaviour mechanism.

In summary, Gd-doped CeO₂ were successfully fabricated on FTO substrates and their bipolar resistive switching characteristics were observed. The formation of more oxygen vacancies leads to the formation of straight and extensible conducting filaments along CeO₂ nanocrystalline thin films, resulting in stable resistive switching behaviour with narrow dispersion in the resistance state. The present work demonstrates that Gadolinium doped ceria prepared by this method have the potential for next generation non-volatile memory applications.

Chapter 5 Conclusions

In this study, CeO₂ thin films with excellent resistive switching properties were prepared. The results show that CeO₂ is a good candidate for next-generation non-volatile memory applications. In detail, two different approaches including RF sputtering and electrochemical deposition were used to prepare CeO₂ thin films. Also, doping was used to enhance the device performance.

(1) Fabricating CeO₂ film by radio frequency sputtering

The influence of sputter deposition conditions on the crystal structure, grains growth and surface morphologies of ceria was investigated. The samples prepared at low temperatures were found to have low crystallinity, but loosely packed structure with less porosity. Thin films deposited at high temperature showed more uniform morphology. By increasing sputter power and temperature, the crystallinity of samples was improved and well defined polyhedral shaped grains were obtained. Moreover, the resistive switching characteristics were also investigated for all samples. The samples with less porosity, dense structure and relatively flat surfaces demonstrated superior resistive switching performance. The results imply that by decreasing surface roughness of active

switching layer in RRAM cells may offer an effective way to improve RS characteristics.

For indium doped CeO_2 deposited by sputtering, films deposited at a relative lower deposition temperature perform high RS behaviour. In-doped CeO_2 showed better performance than pure CeO_2 film. Pressure influence on the morphology was also investigated.

(2) Fabricating doped CeO_2 film by electrochemical deposition

Gd and In doped CeO_2 were successfully fabricated on FTO substrates and their bipolar resistive switching characteristics were observed. The formation of more oxygen vacancies leads to the formation of straight and extensible conducting filaments along CeO_2 nanocrystalline thin films, resulting in stable resistive switching behaviour with narrow dispersion in the resistance state. The present work demonstrates that doped ceria prepared by this method have the potential for next generation non-volatile memory applications.

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