PREFACE

Nanostructured binary transition metal oxides (TMOs) are technologically important class of smart materials that possess high interest because of their great chemical stability, simple structure and low-cost production. These functional materials are considered to be the building blocks of next-generation advanced electronic devices. Different TMOs such as TiO_2, VO_2, MnO_2, Fe_2O_3, NiO, ZnO, WO_3, ZrO_2 and HfO_2, having diverse morphology and dimensions, are now being explored for their implementation in a wide range of applications such as photocatalysis, transparent semiconductor devices, spintronics, sensing of toxic compounds, scintillation, optoelectronics, energy storage, fuel cells, memory devices etc. Among all TMOs, hafnium oxide (HfO_2) has been consistently researched as a prospective material, mainly as an alternative to silicon for the semiconductor industry. Because of its appropriate high-*k* value and high thermal stability against silicon, HfO_2 is proven to be a potential candidate for gate dielectric material in metal oxide field effect transistors (MOSFETs). Since 2007, HfO_2 has been used as the gate dielectric in Intel's 45 nm quad-core processor, replacing SiO_2. Moreover, HfO_2 finds promising applications in anti-reflection coatings, X-ray phosphors, gas/liquid sensing, latent fingerprint imaging, cellular imaging, ferroelectric and resistive switching memory devices, etc. At room temperature, bulk HfO_2 crystallizes into a monoclinic phase, transforming to tetragonal and cubic phases at 1700 °C and 2600 °C, respectively. Reported literature indicates that the high temperature tetragonal and cubic phases of HfO_2 exhibit high dielectric constant (*k)* of approximately 70 and 25, respectively. First principle calculations suggest that these high temperature phases can be stabilized at room temperature by doping with elements of lower valency. Various authors have explored the impact of trivalent element doping, with ionic radii different from that of Hf, on the stability of the tetragonal and cubic phases of HfO_2. It has been found that dopants with smaller ionic radii, such as Si, Ge, Sn, P, Al or Ti stabilize the tetragonal phase, while those with larger ionic radii, such as Y, Gd, Sc, Dy or Sm stabilize the cubic phase at room temperature.

HfO_2 nanostructures are usually insulators with an ionic conduction where oxygen ions are the primary mobile species. However, impurities, crystallographic defects and especially oxygen vacancies created during synthesis can introduce intermediate states in the band gap region, turning it into an n-type semiconductor suitable for various technological applications. There are limited reports available in the literature on the sensing activity of HfO_2 nanostructures. Capone *et al. and* Durrani *et al.* analyzed the CO gas sensing properties of the HfO_2 thin films. HfO_2 based nanostructures are also investigated for their sensitivity toward hydrogen, propane and humidity. Besides, HfO_2 has garnered significant attention for its potential applications in next-generation data storage devices. Resistive switching based memory devices operate by switching between low and high resistive states under an applied bias voltage. In this context, stable, uniform and reproducible bipolar resistive switching in HfO_2 based memory devices has been reported by Jančovič *et al.*, Hua *et al.* and Kumar *et al.*

The synthesis of HfO_2 plays a crucial role in optimizing the performance of nanostructured devices by desirably tuning the required parameters. Nowadays, green synthesis is gaining popularity over conventional synthesis methods as it is environment-friendly and cost-effective for large-scale production. Advanced thin film deposition techniques, such as atomic layer deposition (ALD), pulsed laser deposition (PLD), ion beam sputtering (IBS) and molecular beam epitaxy (MBE), are used to have firm control over HfO_2 film thickness, density, surface roughness, etc., which play a pivotal role in determining the performance, stability and endurance of the device.

In this work, we aim to provide a comprehensive exploration of nanostructured HfO_2, focusing on both structural characteristics and multifunctional attributes. The study is motivated by the potential applications of HfO_2 in advanced sensing technologies and resistive switching devices, making it particularly relevant in the context of emerging electronics and memory technologies. The primary objectives of this study include investigating the morphological intricacies of HfO_2 nanoparticles and thin films, examining their crystalline structure and evaluating their multifunctional properties, particularly in the realms of sensing applications and resistive switching performance.

Organization of Thesis

The thesis is organized into **Seven Chapters** as follows.

Chapter 1 provides a concise overview of the structural, microstructural, physical and chemical properties of HfO_2 nanostructures, along with a brief literature survey on the green synthesis methods. Our investigation extends to various applications of HfO_2 nanoparticles and thin films, such as optical devices, toxic compound sensors and resistive switching memory devices. This chapter shows the noteworthy outcomes of the research, summarizing the key contributions in this field. Based on the literature survey, the objective of the thesis is outlined and accordingly, the results, discussions and important findings are presented in four different chapters.

In **Chapter 2**, we present a summary of the methodologies utilized for the synthesis of HfO_2 nanoparticles, such as sol-gel and green synthesis methods, along with the fabrication of HfO_2 thin films using ion beam sputtering and molecular beam epitaxy. The chapter also addresses characterization techniques that are used for data collection and calibration. The structural and microstructural analysis is carried out using X-ray diffractometer, X-ray reflectometer, Raman spectrometer, FTIR spectrometer, TEM

AFM, XPS and AES. Absorbance spectra and optical band gap are examined using UV-visible spectrophotometer. Sensing performance is evaluated through a potentiostat through electrochemical impedance spectroscopy. A ferroelectric loop tracer is used for *P-V* hysteresis measurements. For electrical measurements, such as *I-V* cycles, retention and endurance measurements, etc., a semiconductor parameter analyzer is utilized.

Chapter 3 discusses the stabilization of the high-temperature cubic phase of HfO_2 at room temperature by doping Pr up to 15 at%. While the monoclinic phase remains stable below 7 at%, the coexistence of monoclinic and cubic phases is observed between 7 and 13 at% of Pr. With doping, the average particle size is reduced from 35 to 10 nm, accompanied by enhanced strain estimated from Williamson-Hall plots. The optical bandgap decreases from 5.42 eV in pure HfO_2 to 5.06 eV in 15 at% Pr doped HfO_2 due to non-stoichiometry and formation of sub-bands near the conduction band. Such exciting results are discussed on the basis of enhanced oxygen vacancies inducing 8-fold oxygen coordinated Pr^{3+} ions in the lattice that stabilize the cubic phase of HfO_2.

In **Chapter 4**, we have synthesized HfO_2 nanoparticles via green route using orange peel extracts (1, 2 and 4 wt%). HfO_2 nanoparticles synthesized with 4 wt% orange peel extract and calcined at 900 ^{0}C for 1 h (HO-4-OPE) show well dispersed nanoparticles of size 34 nm with maximum yield. A sensing framework to detect liquid NH_3 is developed using HfO_2 nanoparticle coated electrode and electrochemical impedance spectroscopy. We have successfully detected liquid NH_3 of concentrations 50 to 500 ppm with charge transfer resistance as the sensing parameter. An exponential relation between charge transfer resistance and NH_3 concentration is observed. Here, for the first time, we have used the green synthesis technique to synthesize HfO_2 nanoparticles for the liquid NH_3 sensing application.

In **Chapter 5**, we demonstrate the performance of RRAM devices using HfO_2 thin films deposited using the ion beam sputtering technique on p^{++}-Si (100) substrate by varying thickness from 10 to 30 nm with density in the range of 9.1-8.6 g/cm^3. A drastic change in the average grain size from ~ 90 to ~ 2000 nm is noticed along with a structural transformation from orthorhombic to dominant monoclinic phase when the thickness is increased from 20 to 30 nm. The phase transformation is accompanied by a significant increase in the average grain size along with a decrease in the oxygen vacancy. Further, a red shift in the absorption peak and a reduced band gap of HfO_2 film having 30 nm thickness well corroborates with the above fact. Among all films, the film of 20 nm thickness shows better switching behavior with an ON/OFF ratio of ~ 7, attributed to the appropriate grain size, enhanced crystallization, and oxygen vacancies. The ON/OFF ratio observed here is higher than that of monoclinic (~ 3), tetragonal (~ 5) and cubic (~ 3) phases, reported earlier. The endurance and retention measurements show the excellent reliability of the 20 nm thick device. Schematically, the switching mechanism has been discussed based on the Ohmic and Poole-Frenkel conduction models, which is attributed to the formation and rupture of conductive filaments consisting of oxygen vacancies.

Chapter 6 describes the structure, morphology and resistive switching aspects of molecular beam epitaxy grown HfO_2 thin films fabricated on p^{++}-Si (100) substrate at substrate temperature of 300 and 500 °C. The crystalline nature and monoclinic phase ($P2_1/c$) of the HfO_2 films are confirmed by the GIXRD patterns. The density of the HfO_2 layer is found to be 9.1 and 9.2 g/cm^3, whereas the root mean square roughness is found to be 1.34 and 2.40 nm with average grain size of 140 nm in the films with substrate temperature of 300 and 500 °C, respectively. Both films demonstrate forming free volatile resistive switching behavior with SET voltage of -3.1 and -3.6 V, along with the ON/OFF ratio of ~ 2 and ~ 4 for the films with substrate temperature of 300 and 500 °C, respectively. Memory device based on HfO_2 film with higher substrate temperature exhibits a better ON/OFF ratio due to higher crystallinity and availability of more oxygen vacancies. A comprehensive mechanism of resistive switching is also discussed in this chapter, considering the transport of Ag ions and oxygen vacancies.

In Chapter 7, we have summarized the important findings of this thesis work, along with a discussion of the future prospects. We have been working on the structure and multifunctional properties of nanostructured HfO_2 for sensing and resistive switching applications. We would like to extend our work into application-oriented domains such as optoelectronic devices using HfO_2 nanoparticles. Resistive switching performance of HfO_2 based memory devices could be optimized and explored for neuromorphic computing applications.

A list of journals and books used to bind up the thesis has been given at the end as references.