Chapter 7 ***Summary and Future Scope***

7.1 Summary

A thorough exploration of the structural, microstructural, optical, electrochemical and electrical characteristics of multifunctional nanostructured HfO_2 have been provided in the present thesis. The high temperature tetragonal and cubic phases of HfO_2 hold significant promise for industrial applications, particularly in enhancing the performance of complementary metal oxide semiconductor devices due to their favorable high *k* value. Here, we have focused on stabilizing the cubic phase of HfO_2 at room temperature by introducing praseodymium (Pr) into its lattice. A comprehensive investigation of green synthesis and fabrication of nanostructured HfO_2 for potential applications in advanced sensing technologies and resistive switching devices is outlined, making it particularly relevant in the context of emerging electronic and next generation memory technologies. The key findings of the thesis are presented below.

We discussed 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 remained stable below 7 at%, the coexistence of monoclinic and cubic phases was observed between 7 and 13 at% of Pr. With doping, the average particle size was reduced from 35 to 10 nm, accompanied by enhanced strain estimated from Williamson-Hall plots. The optical bandgap decreased from 5.42 eV in pure HfO_2 to 5.06 eV after doping 15 at% of Pr due to non-stoichiometry and the formation of sub-bands near the conduction band. Such exciting results were discussed on the basis of enhanced oxygen vacancies inducing 8-fold oxygen coordinated Pr^{3+} ions in the lattice that stabilized the cubic phase of HfO_2.

Due to the environmental impact of conventional synthesis methods, green synthesis routes have recently attracted significant attention. We synthesized HfO_2 nanoparticles via green route using orange peel extracts (1, 2 and 4 wt%) and studied their sensing properties. HfO_2 nanoparticles synthesized with 4 wt% orange peel extract and calcined at 900 ^{0}C for 1 h (HO-4-OPE) demonstrated well dispersed nanoparticles of size 34 nm with maximum yield. A sensing framework to detect liquid NH_3 was developed using HfO_2 nanoparticle coated electrode and electrochemical impedance spectroscopy. We successfully detected liquid NH_3 of concentrations 50 to 500 ppm with charge transfer resistance as the sensing parameter. The prediction model based on charge transfer resistance showed an R^2 value of 0.95 to predict liquid NH_3 concentration.

We demonstrated the performance of non-volatile 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 was noticed along with a structural transformation from orthorhombic to dominant monoclinic phase as the thickness increased from 20 to 30 nm. The phase transformation was 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 corroborated with the above fact. Among all films, the film of 20 nm thickness exhibited 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 was higher than that of monoclinic (~ 3), tetragonal (~ 5) and cubic (~ 3) phases, reported earlier. The endurance and retention measurements displayed the excellent reliability in case of the 20 nm thick film. The switching mechanism was discussed based on the Ohmic and Poole-Frenkel conduction models, which was attributed to the formation and rupture of conductive filaments consisting of oxygen vacancies.

We observed the volatile resistive switching behavior in case 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 were confirmed by the GIXRD patterns. The density of the HfO_2 layer was found to be 9.1 and 9.2 g/cm^3, whereas the root mean square roughness was found to be 1.34 and 2.40 nm with average grain size of 143 and 137 nm in the films with substrate temperature of 300 and 500 °C, respectively. Both films demonstrated 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 exhibited a better ON/OFF ratio due to higher crystallinity and availability of more oxygen vacancies. Considering the transport of Ag ions and oxygen vacancies, a comprehensive mechanism of volatile resistive switching was also discussed.

7.2 Future Scope

This thesis delved into the synthesis and in-depth characterizations of HfO_2 nanostructures along with detailed analyses of their structural, microstructural, optical, electrochemical and resistive switching properties. Based on the above findings and potential applications of HfO_2, several directions for future research are proposed.

- Considering the sustainability and environmental impact, greener methods could be adopted for the synthesis of HfO_2 nanostructures. For a better understanding of the correlation of local structure and physical properties of HfO_2, sophisticated characterization methods such as extended X-ray absorption fine structure (EXAFS) can be employed.

- Swift heavy ion (SHI) irradiations on HfO_2 films could be used for nanopatterning and material modification to obtain desirable properties for optoelectronic device applications.

- Given the significant potential of HfO_2 based memory devices, future research can focus on improving resistive switching behavior by optimizing fabrication parameters and selecting appropriate dopants. HfO_2 based memory devices could be utilized in advanced neuromorphic computing devices.