Chapter 7

This thesis provided a comprehensive investigation on the structure, magnetic, optical and electrical properties of multifunctional nanostructured pure, Dy and/or Sm doped HfO_2. The present work dealt with two different forms i.e. nanoparticles and thin films of HfO_2. The high temperature tetragonal and cubic phases of HfO_2 are promising from industrial point of view due to their appropriate high-*k* value which facilitate the fabrication of CMOS devices with improved performance. In this context, we particularly examined the stabilization of cubic phase at room temperature after incorporating Dy and/or Sm into HfO_2 lattice. In addition to intriguing structural transformation, the systematic studies on the effect of Dy and/or Sm dopants in modifying magnetic, optical and electrical properties produced captivating results which could be implemented for practical applications like LFPs imaging for the first time and as non-volatile data storage in RRAM devices. The key findings of the thesis are outlined below.

7.1 Stabilization of the High Temperature Cubic Phase at Room Temperature

HfO_2 nanoparticles synthesized via a Pechini type sol–gel technique crystallized with monoclinic phase, $P2_1/c$, at room temperature. By incorporating 11 at% of Dy into the HfO_2 lattice, the monoclinic phase transformed completely to the cubic phase, $Fm\bar{3}m$, followed by a mixed phase of monoclinic and cubic at intermediate concentrations (5–9 at%) of Dy. In case of Sm doped HfO_2, although the monoclinic structure was retained at 1 at% of Sm, the monoclinic to cubic phase transformation at room temperature was achieved by incorporating Sm^{3+} ions upto 12 at% followed by the coexistence of

monoclinic and cubic phase at intermediate Sm concentration (5-11 at%). Selected area electron diffraction patterns established the monoclinic and the cubic phase as observed from XRD patterns. Not only the particle size obtained from TEM matched well with the size calculated from W-H plot, the lattice spacing estimated from high resolution TEM also confirmed the monoclinic phase in HfO_2 and cubic phase in $Hf_{0.89}Sm_{0.11}O_2$ and $Hf_{0.88}Sm_{0.12}O_2$ nanoparticles. A mechanism for stabilization of the high temperature cubic phase in Dy or Sm doped HfO_2 was analyzed based on the substitution of Dy^{3+} or Sm^{3+} for Hf^{4+} ions and the formation of oxygen vacancies. The significant difference in ionic radii of Dy^{3+}, Sm^{3+} and Hf^{4+} ion induced considerably large strain in the lattice examined from W-H analysis. XPS investigation revealed that a lower valency of Dy or Sm accompanied with oxygen vacancies leading to 8-fold coordination with dopant ion and stabilized the high temperature cubic phase at room temperature. Further, we introduced the concept for stabilizing high temperature cubic phase of HfO_2 after codoping Dy and Sm. At low Dy and Sm concentration i.e. 0 to 2 at%, while the monoclinic phase was found to be preserved with crystallite size ranging from ~10-25 nm, Le-Bail profile refinement of XRD patterns revealed an exponential increase in lattice volume evidenced due to negative pressure effect. However, after codoping Dy and Sm upto the total concentration of 13 at%, we successfully demonstrated the stabilization of high temperature cubic phase of HfO_2 at room temperature. Therefore, the stabilization of cubic phase of HfO_2 at room temperature was accomplished with concentration of rare earth dopants attaining ~13 at% irrespective of the nature of dopant.

7.2 Room Temperature Ferromagnetism and its Origin

HfO_2 nanoparticles exhibited considerable hysteresis loop indicating the ferromagnetic ordering at room temperature. However, RTFM in HfO_2 nanoparticles was quenched after incorporating even 1 at% of Dy. Although the maximum magnetization enhanced linearly, the coercivity of ~25±5 Oe remained constant with increasing Dy concentration upto 11 at%. RTFM in HfO_2 was attributed to oxygen vacancies mediating long range ferromagnetic ordering via F^+ center exchange mechanism. The dramatic suppression of room temperature ferromagnetic ordering in Dy doped HfO_2 could be ascribed to the formation of unwanted defect complexes like Dy^{3+}–V_o–Dy^{3+}. Such defect complexes essentially produced F^{++} centers which hindered the long range ferromagnetic ordering in HfO_2 lattice. The suppression of ferromagnetic ordering in Dy doped HfO_2 discouraged to perform magnetic study in either Sm doped HfO_2 or Dy and Sm codoped HfO_2 nanoparticles. RTFM observed in diamagnetic HfO_2 nanoparticles thus confirmed the crucial role of nanoparticles and optimum concentration of oxygen vacancies. Increasing oxygen vacancies with increasing dopant concentration quenched the ferromagnetic behavior in rare earth doped HfO_2 nanoparticles.

7.3 Excellent Luminescence Properties

After incorporating 1 at% of Dy, the systematic photoluminescence investigations demonstrated excellent emissions in blue and yellow region producing cool white light under the excitation with UV light of wavelength 352 nm. The intensity of blue and yellow emission peaks reduced with increasing Dy concentration upto 11 at% due to the concentration quenching effect. The characteristic emissions corresponding to Dy^{3+} ion were induced by the non-radiative weak energy transfer occurring between charge transfer

band of the host and distinct energy levels of Dy^{3+} activator ion. We proposed a tentative energy band diagram to show the energetic processes taking place in Dy doped HfO_2 nanoparticles. For Sm doped HfO_2, the strong emission peaks near green and red regions were revealed in $Hf_{0.99}Sm_{0.01}O_2$ nanoparticles which diminished substantially at higher Sm concentration. The proposed schematic energy band diagram illustrated that the emissions related to Sm^{3+} active ion were partially accompanied by the charge transfer from optically active defect states present in HfO_2 to Sm^{3+} energy levels having comparable energy. Further, exciting Dy and Sm codoped HfO_2 with 393 nm, the prominent emissions in blue, yellow and near red regions yielded purplish light emerging primarily due to the energy transfer from Dy^{3+} (donor) to Sm^{3+} (acceptor) ions through multipolar interaction suggested by time resolved decay spectra. Combining excitation and emission spectra, we proposed a schematic energy band diagram for rare earth doped and codoped HfO_2 nanoparticles.

7.4 Latent Fingerprint Imaging for Forensic Science

Considering the rich luminescence behavior, for the first time, Dy and Sm codoped HfO_2 nanophosphors were explored for their robustness in the development of LFPs useful for collecting physical evidences in forensic investigations. Herein, these HfO_2 based nanophosphors offered a rapid and cost-effective approach for LFPs imaging under irradiation of light having wavelength of 395 nm. Dy and Sm codoped HfO_2 could develop LFPs with good selectivity and resolution over multivariate surfaces like float glass, black colored glass, purplish, wine and red colored plastic sheets, stainless steel and aluminum foil etc. Owing to nanosized nature of particles, all the developed LFPs exhibited low background interference facilitating the extraction of crucial third-level details such as enclosure, double bifurcation and termination-bifurcation etc.

7.5 Stabilization of Cubic Phase at Room Temperature and RRAM Device Application

We systematically examined the structural evolution and resistive switching behavior of pristine and Sm or Dy doped HfO_2 films of ~60 nm deposited on p^{++}-Si (100) substrates through electron beam evaporation technique. Although we reported that 12 at% of Sm or 11 at% of Dy doped in HfO_2 nanoparticles stabilized the cubic phase at RT, here the stabilization of cubic phase was achieved after doping at most half of these dopant concentration. Further, these films demonstrated the bipolar switching behavior distinctive to RRAM device. The resistive switching characteristics were found to be of forming-free nature. The switching behavior was discussed after employing different conduction models such as the Ohmic and Poole-Frenkel emission. We concluded that the monoclinic to cubic phase transformation and resistive switching phenomenon was governed by the abundant formation of oxygen vacancies producing 8-fold oxygen coordination to Sm^{3+} or Dy^{3+} ion evidenced from XPS spectra. The resistive switching mechanism was illustrated through the formation of conducting filaments pictorially in HfO_2 based RRAM which could be further investigated to fabricate data storage devices.

7.6 Future Outlook

The thesis discussed the preparation and detailed material characterizations along with appropriate analysis of structure, magnetic, optical and electrical properties of nanostructured pristine, Dy and/or Sm doped HfO_2. In view of above findings and potential applications, we suggest a few possible research scopes that can be extended in near future.

- **Local probe analysis:** In the present work, we demonstrated oxygen vacancy induced stabilization of the high temperature cubic phase in Dy and/or Sm doped HfO_2 which can be further investigated through sophisticated technique like extended X-ray absorption fine structure (EXAFS) to obtain a more detailed insight.
- **Biological applications:** In addition to LFPs imaging using Dy and Sm codoped HfO_2 nanophosphors, one can also develop luminescent HfO_2 as efficient probes for potential bio-imaging .
- **Improvement of RRAM device:** Since HfO_2 based RRAM is one of the interesting next generation data storage device, we further intend to study thickness and composition dependent resistive switching behavior to fabricate RRAM device with better performance.