Chapter 1

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 as the building block of next generation advance electronic devices. There exists a widespread attraction for TMOs within industries due to their several technological applications primarily useful for resolving issues related to cutting edge research. It is well-known that in TMOs, electrons occupy the *s*-shells of metal cations whereas *d*-shells are partially filled containing unpaired electrons which essentially evoke intriguing physical and chemical properties. In contrast to bulk, nanostructured TMOs are capable of offering superior structural, optical, magnetic, electronic and electrical properties.[1-4] Different TMOs like TiO_2, VO_2, MnO_2, Fe_2O_3, NiO, ZnO,WO_3, ZrO_2 and HfO_2 having diverse morphology and dimension are now being explored for their implementation in a range of industrial fields. A consistent research and development of TMOs has laid down promising applications in water desalination/purification, transparent semiconductor devices, spintronics, gas sensing, scintillation, UV detectors, photocatalysis, optoelectronics, energy storage, memory devices, fuel cells, optical coatings, insulation and abrasive materials etc. Apart from aforementioned potential applications, non-hazardous lead-free TMOs have also been investigated for biological applications as antibacterial agents including for biosensing, biotransportation, radiosensitisation, drug discovery and delivery etc. [2, 5-10]

In general, nanostructured materials are classified as the structures with variable dimensions between 1-100 nm. Depending on the shape and size, nanostructures are categorized into following:

- 0D (Zero dimensional) e.g. nanoparticles and nanodots

- 1D (One dimensional) e.g. nanotube and nanowires

- 2D (Two dimensional) e.g. nanosheets

- 3D (Three dimensional) e.g. nanocubes

When the size is reduced to nanometer range, most of the physical and chemical properties are modified constructively.[11, 12] A direct consequence of size reduction is evidenced in case of Fe_2O_3 nanoparticles. It is well-known that Fe_2O_3 shows antiferromagnetic ordering which transforms to superparamagnetic behavior if the nanoparticles attain a certain size of ~3 nm.[6, 13-15] In particular, the reduced particle size having very large surface to volume ratio results into unusual properties of TMOs. A variety of TMOs nanostructures including specific exposed facet and hierarchical structures such as nanotubes, nanoplates, nanobelts, nanoforests, nanorod arrays, nanobrush and tube-in-tube nanostructures can be achieved by employing different synthesis techniques like hydrothermal, solvothermal, sol-gel, liquid phase, vapor phase methods, thermal decomposition and so on. Interestingly, the different morphology of these nanostructured TMOs is easily obtained by controlling and tuning various synthesis parameters e.g. temperature, pressure, reactive and inert gas flow environment, solvent and surfactant etc.[16-26]

Another example of TMOs nanostructuring includes the size effect in modifying the structural properties of TiO_2 nanoparticles. TiO_2 exhibits three different crystal structures such as the anatase, rutile and brookite phase. Many researchers have systematically

studied the phase transformation in nanocrystalline TiO_2 and establish that the anatase phase becomes relatively more stable than that of rutile one once the particle size is reduced below ~14 nm. Above this critical particle size, the rutile phase of TiO_2 can be reversibly stabilized under ambient conditions.[27-30] Thus, the direct nanoarchitecturing of TMOs can facilitate better control of structure, optical, magnetic, electrical and other physical along with chemical properties.

Among all TMOs, Hafnium oxide (HfO_2) is of special scientific interest due to its excellent thermodynamic stability and ability to cope with existing hurdles within silicon based industry.[31] HfO_2 is an electrical insulator having a wide bandgap of ~5.7 eV and appropriate dielectric constant (k) value which has been successfully utilized to serve effectual solutions of the major issues in present complementary metal oxide semiconductor (CMOS) technology.[3, 32] In CMOS, the prominent concern of higher leakage current due to direct tunneling of electrons arises with down scaling of gate dielectric thickness below ~3 nm. In order to resolve this issue, a new type of material so called "high-k material" like HfO_2 is sought after to achieve CMOS devices with high performance.[33, 34] Recently, in the year 2007, HfO_2 is being used into Intel's 45 nm technology replacing conventional SiO_2 which reduced the leakage current density by an order of magnitude. This mitigated the heat dissipation issue in 45 nm technology node to a great extent.[35] Apart from its high-k value, HfO_2 possesses intriguing physical properties e.g. high density of ~9.8 g/cm^3, very high melting point of 2600 ^{o}C and refractive index of ~2 rendering promising applications in optical coating, anti-reflective coating, refractory, X-ray phosphors, spintronics and non-volatile memory including resistance random access memory (RRAM) and ferroelectric, FeRAM devices etc (**figure 1.1**).[36-41]
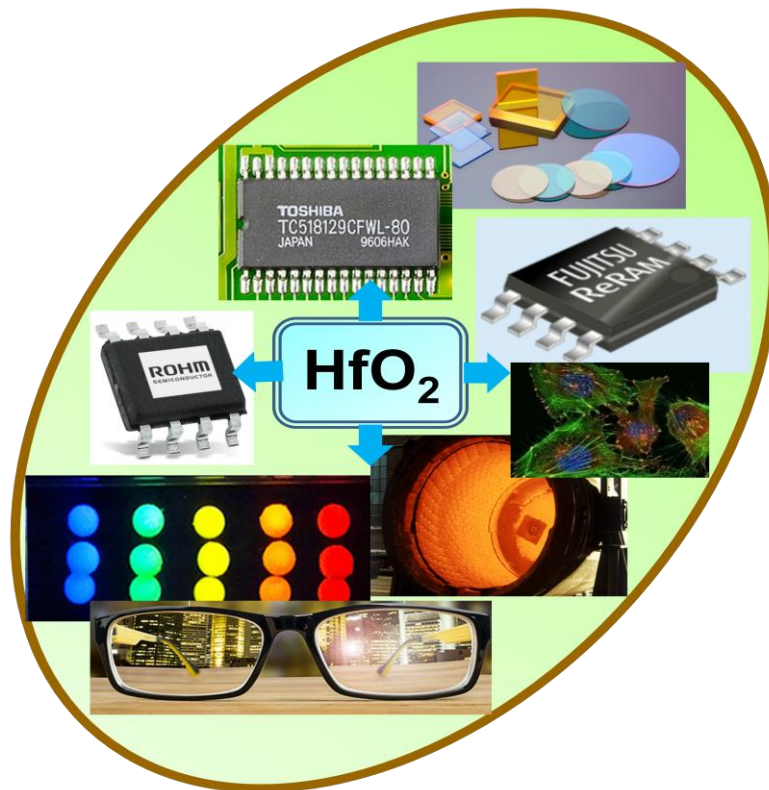
Figure 1.1 *Examples of potential applications of HfO$_2$ in various industries.*

1.1   Structure of HfO$_2$

HfO$_2$ is commonly referred as hafnia. Prior to the deployment of HfO$_2$ as a prospective electronic material in CMOS industry, its conventional use was primarily focused as a refractory ceramic material in reactors and thermocouple devices owing to its high melting temperature. It is known that HfO$_2$ is very much similar to ZrO$_2$ with almost identical physical and chemical properties. Since the discovery of transformation toughening in crystalline ZrO$_2$, a wide group of researchers has devoted systematic and consistent research to understand the crystallographic properties of crystalline HfO$_2$. The crystallography of HfO$_2$ shows significant impact on its different physical properties such as structural, electronic, magnetic, optical and so on.

1.1.1   Phases of HfO$_2$ at Ambient Pressure

In bulk, HfO$_2$ possesses polymorphism such as monoclinic (*m*), *P2$_1$/c*, tetragonal (*t*), *P4$_2$/nmc* and cubic (*c*), $Fm\overline{3}m$ phases. These three different structures of HfO$_2$ can exist at various temperature under normal pressure shown in **figure 1.2**. In contrast to chemically similar system, ZrO$_2$, the phase transformation among three phases of HfO$_2$ usually occurs at relatively higher temperature. According to thermodynamic studies of ZrO$_2$ and HfO$_2$, the phase transformation from monoclinic to tetragonal and eventually to cubic one is highly dependent on internal energy and entropy.[42] Therefore, the Gibbs free energy (*ΔG = ΔU + pΔV - TΔS*) related to such phase transformation in HfO$_2$ is very crucial for a clear understanding of its different crystalline phases. *ΔG*, *ΔU*, *ΔV*, *ΔS* is change in Gibbs free energy, internal energy, volume and entropy, respectively whereas *p* is pressure and *T* is the phase transformation temperature. The high temperature tetragonal and cubic phases of HfO$_2$ exhibit high symmetry which are more stable as per the entropy is concerned. Under minimum energy condition, *ΔG* must be zero at phase transition point i.e. *ΔG = ΔU + pΔV - TΔS = 0*. The first order phase transitions are referred to discontinuity in first derivatives of *G* which are entropy and volume. However, second order transitions have continuous first derivatives indicating no change in *S* or *V*.

Discontinuous first derivatives of *G (T, p)*:   *(δG/δT)p = S*, *(δG/δp)T = V*

In bulk HfO$_2$, the monoclinic phase remains stable at room temperature and transforms to tetragonal phase at ~2052 K which ultimately undergoes phase transition to cubic one at 2803 K.[43] The temperature of phase transformation in HfO$_2$ depends on several factors such as particle size, impurities, stress and so on. In monoclinic phase of HfO$_2$, the coordination number of Hf^{4+} is 7, whereas it increases to 8 in the high

temperature tetragonal or cubic phase.[44] According to the thermodynamic equations discussed above, the monoclinic ↔ tetragonal phase transformation is of first order due to substantial modification of the local bonding within structural configuration. Such phase transformation also reduces the lattice volume notably producing large strain in the crystal. On the other hand, a second order phase transition governs the tetragonal to cubic phase transformation since no significant change in volume is evidenced.[45]
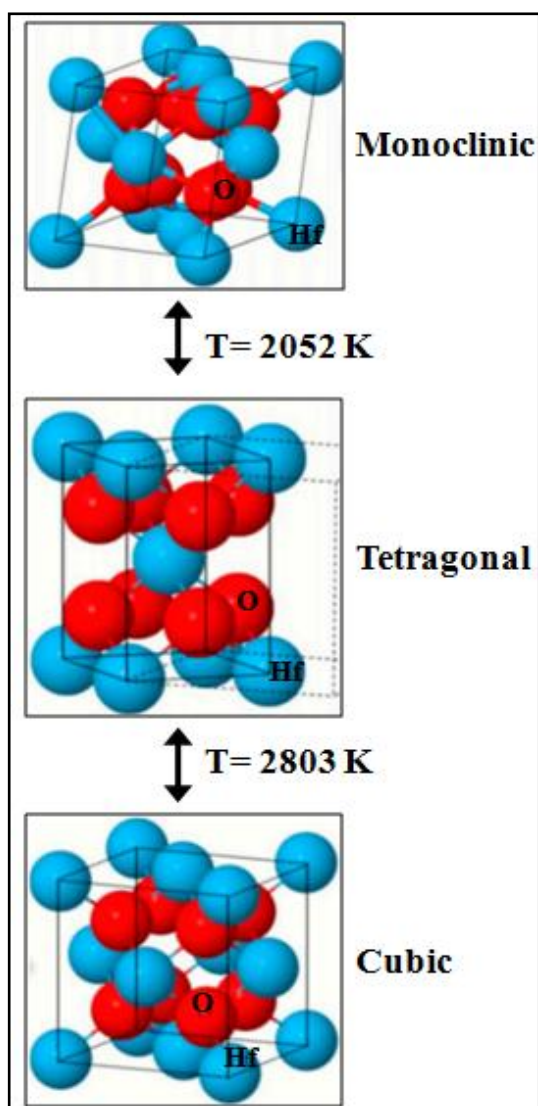
Figure 1.2 *Different phases of HfO$_2$ as a function of temperature under normal pressure condition.*

1.1.2 High Pressure Driven Phases of HfO$_2$

Apart from the phase transformation with increasing temperature, the crystalline monoclinic phase of HfO$_2$ becomes relatively unstable under an applied external pressure. Following the temperature-pressure (*T-P*) phase diagram depicted in **figure 1.3**, HfO$_2$ supposes to adopt an orthorhombic symmetry revealing two distinct polymorphs known as OrthoI (OI) and OrthoII (OII). High pressure induced OI and OII phases in HfO$_2$ are stable from 4 to 25 GPa and almost independent of temperature up to 1400 ^{o}C.[46] Based on the neutron diffraction study, it is established that OI stabilizes with space group, *Pbca* whereas OII acquires an orthorhombic cotunnite (PbCl$_2$)-type structure having space group, *Pmnb*.
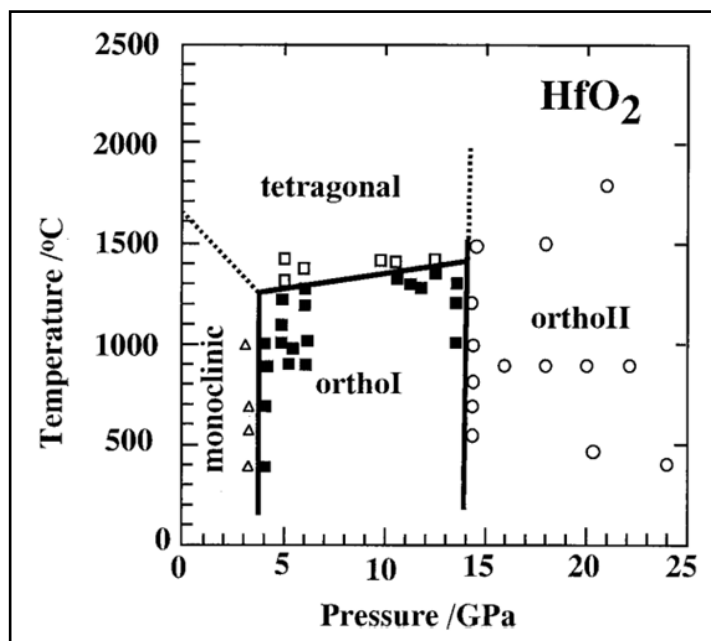
Figure 1.3 *Temperature-Pressure (T-P) phase diagram of HfO$_2$. (adapted from [46])*

Hf^{4+} ions form 7 and 9-fold coordination with oxygen in OI and OII phase, respectively.[47, 48] A reduction in volume is observed when the monoclinic phase of

HfO$_2$ transforms to OI phase. The pressure at which OI-to-OII phase transition occurs is not related to the thermodynamic equilibrium conditions due to reconstructive nature of this transition. According to first principle calculation and appropriate experiments, the high pressure OII phase of HfO$_2$ is considered for ultrahard materials because of its excellent bulk modulus property.

1.1.3 Stabilization of the High Temperature Tetragonal/Cubic Phase of HfO$_2$ at Room Temperature

In general, the phase stabilization in TMOs is understood in terms of the stability of a specific crystalline phase at ambient conditions which is usually observed at high temperature and pressure. Under normal temperature and pressure, the stability of specific phase in TMOs is achieved by alloying appropriate dopant or optimizing synthesis parameters such as temperature, grain size, solvent and oxygen partial pressure etc. There is an utmost requirement of a suitable method to achieve the high temperature tetragonal or cubic phase of HfO$_2$ at RT or moderate temperature that possesses distinct physical properties which are not exclusively realized in the monoclinic one. As far as the CMOS device applications are concerned, an amorphous phase of HfO$_2$ is used up to the growth temperature of ~300 $^{\circ}$C which does not exhibit any superior physical properties compared to the crystalline, monoclinic phase. First principle calculation predicts that the high temperature tetragonal or cubic phase of HfO$_2$ are technologically more important than that of the monoclinic one. While the monoclinic phase possesses a low *k* value of ~15, HfO$_2$, in its tetragonal or cubic phase shows the higher *k* value above ~30.[49] It is therefore more advantageous to employ HfO$_2$ crystallized in the high symmetrical phases of tetragonal or cubic for developing future CMOS with improved device performance and reliability.

1.1.3.1 Effect of Synthesis Conditions

The technologically relevant cubic phase of HfO_2 has been shown to be stabilized at room temperature without any dopant. The metastable cubic phase can be obtained in HfO_2 films annealed at 500 ^{o}C in vacuum. The allotropic modification from amorphous to cubic phase is varied between 30-1500 ^{o}C. The cubic phase remains stable upto 600 ^{o}C and partially transforms to the monoclinic one with increasing temperature upto 1400 ^{o}C. Such phase transformation becomes more prominent when HfO_2 films are annealed in air.[44] Sharath *et al*. demonstrate that the other high temperature tetragonal phase can be achieved in HfO_2 film deposited onto $TiN/SiO_2/Si(001)$ at substrate temperature of 320 ^{o}C depicted in **figure 1.4**.
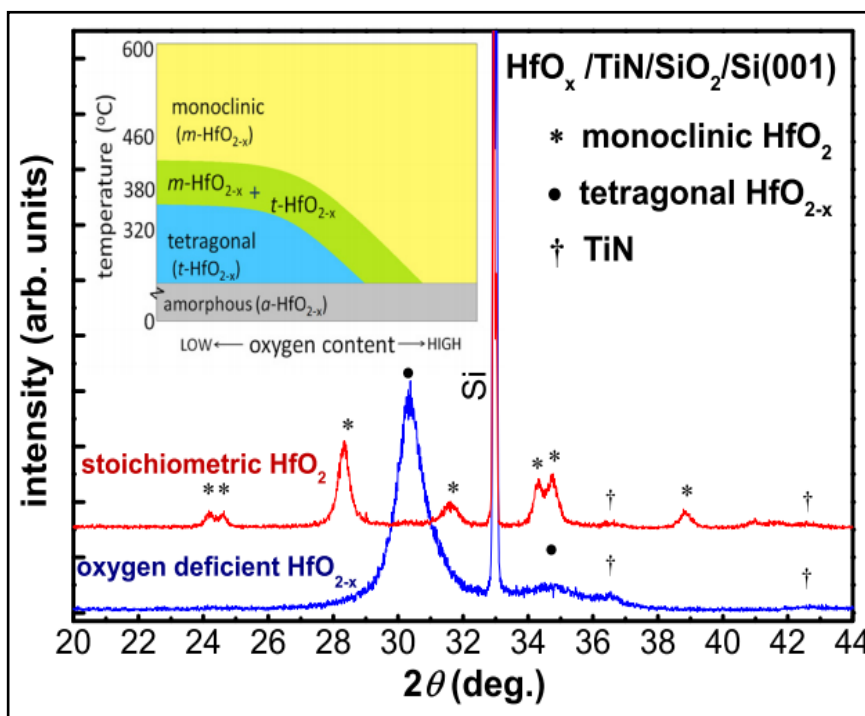
Figure 1.4 *XRD patterns demonstrating stabilization of the monoclinic and tetragonal phase in stoichiometric and oxygen deficient HfO_2 films. (adapted from [50])*

It is evident that while the stoichiometric HfO_2 crystallizes in monoclinic phase, oxygen deficient HfO_2 exhibits the tetragonal phase.[50] The stabilization of high temperature tetragonal or cubic phases in HfO_2 films are essentially governed by relative concentration of oxygen atoms and vacancies along with postdeposition annealing temperature and environment conditions. These phases become relatively more stable after engineering and optimizing the oxygen content present in film. The other crucial parameters like grain size and grain boundary energy also play a key role in such phase transformation processes.[44]

Besides the stabilization of tetragonal or cubic phase at room temperature in HfO_2 films, a similar cubic phase can also be stabilized in nanoparticles of HfO_2. **Figure 1.5** shows a direct precipitation of the monoclinic and cubic phase of HfO_2 obtained by utilizing an appropriate solvent without adding any surfactant and performing other post-synthesis treatments such as heating process. It has been suggested that the cubic phase of HfO_2 is achieved using a relatively more reductive solvent. After optimizing various synthesis parameters, the suitable preparation techniques have been proposed to produce
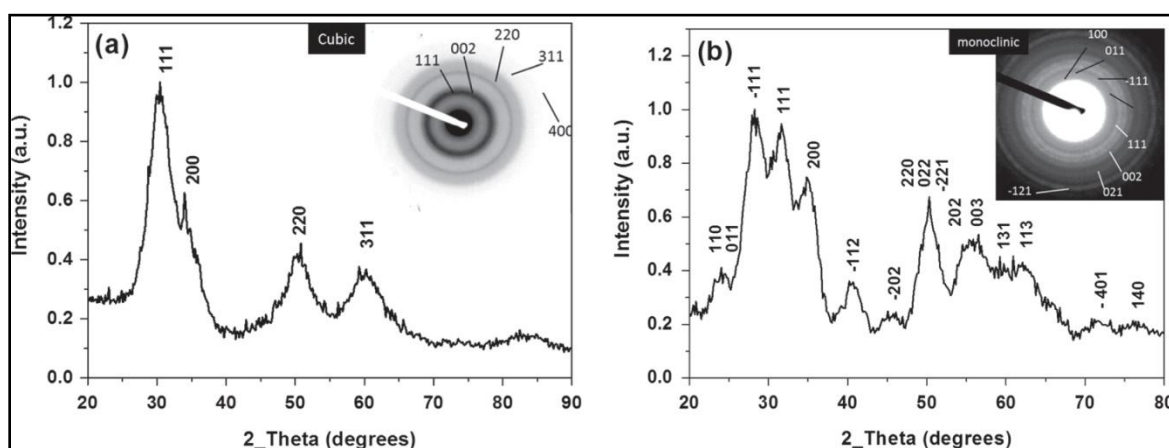
Figure 1.5 *XRD patterns of (**a**) cubic and (**b**) monoclinic HfO₂ nanoparticles. The insets show respective selected area electron diffraction (SAED) patterns. (adapted from [51])*

high-quality cubic HfO_2 nanoparticles which remain stable under ambient conditions.[51] Therefore, without any dopant, one can stabilize the high temperature cubic or tetragonal phase at room temperature by controlling and tuning of the stoichiometry of nanostructured HfO_2. However, the cubic or tetragonal HfO_2 stabilized in such a way is easily transformed to the undesirable low symmetry monoclinic phase after a slight modification of temperature in particular.

1.1.3.2   Effect of Dopants

i) Trivalent Ion

The phase control in HfO_2 by incorporating dopant is one of the peculiar method to stabilize the high temperature and pressure HfO_2 phases at ambient conditions. The notion of doping trivalent ion into HfO_2 lattice is very much effective for phase transformation due to difference in the oxidation states of dopant and Hf cation. In HfO_2 lattice, when a trivalent ion replaces Hf^{4+}, an electron is produced which disturbs the charge equilibrium. In order to compensate these electrons, oxygen vacancies are generated in the lattice.[52] The mechanism for the stabilization of tetragonal or cubic HfO_2 depends predominantly upon the difference between ionic radii of dopant and Hf cations. If the trivalent ion having lower ionic radius than that of Hf substitutes in the lattice, relative energy of tetragonal phase with respect to monoclinic one decreases significantly which prefer to stabilize the tetragonal HfO_2. In this case, the nearest oxygen atoms move in direction of the dopant sites displacing other oxygen atoms outwards due to structural relaxation. On the other side, the replacement of Hf atoms with oversized dopants stretch the bond length between dopant and oxygen atoms. Here, the lattice strain originating because of dissimilar ionic

radii is relatively lower compared to tetragonal HfO_2 thereby stabilizing the cubic phase of HfO_2 at room temperature.[53]

It is known that while the monoclinic phase of HfO_2 contains two different kinds of oxygen atom configurations namely three fold and four fold coordinated with Hf, for high temperature tetragonal and cubic phase, the local surrounding of all oxygen atoms is identical in the lattice. The generated oxygen vacancies prefer to reside at four fold coordinated Hf site. In tetragonal or cubic HfO_2, the presence of oxygen vacancies reduces coordination number of Hf to 7 and also decreases the concentration of nearby oxygen atoms. The shifting of oxygen atom in such a way is strongly directed nearing to dopants rather than Hf atoms. This rearrangement of oxygen atoms necessarily forms eight fold coordination with dopant inducing more and more 7 fold coordinated Hf atoms in the lattice. In this regard, first principle calculation predicts the stability of tetragonal and cubic phases of HfO_2 by incorporating undersized dopants e.g. Al, P and oversized dopants e.g. Y, Gd and Sc, respectively.[53] This theoretical assumption has been supported by a few experimental reports showing the stabilization of cubic phase at room temperature utilizing trivalent rare earth (RE) Lu and Eu ions having higher ionic radius than Hf.[54] However, these reports do not present a thorough discussion on the stabilization of high temperature phase of HfO_2.

ii) Tetravalent Ion

On the basis of ionic radius of tetravalent ion, a similar stabilization of tetragonal and cubic phase can be perceived in nanostructured HfO_2. This is experimentally evidenced in case of Ce doped HfO_2. Since the ionic radius of Ce is more than that of Hf, it is capable of stabilizing the cubic phase of HfO_2 at room temperature.[55] The tetragonal phase

stability of HfO_2 after incorporating tetravalent dopants of smaller ionic radius is not very reliable and captivating. In this context, recently, after doping undersized tetravalent Si, an unusual orthorhombic (*O*) phase is discovered in HfO_2 films. It is noteworthy that this orthorhombic phase is of non-centrosymmetric nature instead of centrosymmetric orthorhombic one observed under high pressure condition discussed earlier in section 1.1.2. The existence of polar *O* phase in HfO_2 films essentially evokes promising ferroelectric properties.[56] Previously, the formation of such a polar *O* phase is also reported for chemically analogous ZrO_2 after doping Mg.[57] The non-centrosymmetric orthorhombic phase in HfO_2 films has been extensively researched by doping various divalent, RE trivalent and tetravalent ions having different ionic radii including Mg, Ba, Sr, Y, La, Nd, Sm, Er, Al, Ga, In, Co, Ni, Ge and Zr etc.[58] Specifically, the stabilization of polar orthorhombic phase in HfO_2 by Zr doping is more appealing and advantageous inducing excellent ferroelectric properties since it can be formed at lower crystallization temperature compared to Si doped HfO_2 films. In addition, there exists relatively a wide composition range for Zr doped HfO_2 in contrast to any other dopant. Different deposition techniques like atomic layer deposition (ALD), sputtering and pulse laser deposition etc can be utilized to achieve this orthorhombic phase in doped HfO_2.

In view of the emergence of non-polar orthorhombic phase in bulk HfO_2 with increasing pressure, the explanation for existence of polar orthorhombic phase in nanostructured HfO_2 appears quite different than the bulk. Following the comprehensive first principle calculation, it is believed that the substantial reduction in grain size inducing prominent surface energy effects could control the stability of this orthorhombic phase. The estimated surface energy corresponding to *O* phase is found to be in between the tetragonal

and monoclinic HfO$_2$.[59] However, the surface free energy calculated using such computational model considers only a definite size of grain in the film. It is well known that the polycrystalline oxides exhibit a specific grain size distribution. Now, the origin and phase evolution of the polar *O* phase in Zr doped HfO$_2$ is understood after taking into account such grain size distributions. The presence of this *O* phase is also influenced by other factors like film thickness, asymmetric stress, top capping electrode, dopant and annealing temperature etc.[41] More importantly, such *O* phase can be obtained in film thickness of ~10 nm or even less onto Si substrates. Owing to outstanding compatibility and stability of HfO$_2$ with Si, a new class of non-volatile memory termed as FeRAM is now being implemented for practical applications. A systematic retention tests of HfO$_2$ based FeRAM show promising features due to appropriate relative permittivity and coercive field compared to standard perovskite based ferroelectrics.

1.2 Magnetic Properties of HfO$_2$

Earlier, most of the study on crystalline HfO$_2$ primarily deals with the exploration of structural properties. Bulk HfO$_2$ shows strong diamagnetic nature since its *d*-shell is completely occupied with no unpaired electrons. When the size is reduced to nanometer range, an unconventional and intriguing magnetic properties can appear in nanostructured HfO$_2$ which are entirely different from the bulk counterpart. In HfO$_2$ films, an unusual ferromagnetism at room temperature or higher temperature was first reported in the year, *2004*.[60] This room temperature ferromagnetism (RTFM) is extremely compelling as both Hf^{4+} and O^{2-} are non-magnetic ions with d^0 cation closed shell configuration. For this completely unexpected behavior in thin films of HfO$_2$, a new term is coined called as d^0-magnetism. Following RTFM in HfO$_2$, a similar phenomenon is also investigated in other

TMOs like ZnO, NiO, TiO$_2$, SnO$_2$, ZrO$_2$ and so on.[61-65] Besides, RTFM is also reported for various nanostructured HfO$_2$ like nanoparticles, nanoclusters and nanorods.[66, 67] Since the discovery of RTFM in HfO$_2$ films, the origin of long range ferromagnetic ordering present in non-magnetic TMOs has been the subject of consistent and progressive research. It is widely believed that such RTFM phenomenon in TMOs is exclusively related to lattice point defects such as cation and anion vacancies. As TMOs are more prone to oxygen vacancies, the oxygen related electronic defects can be easily formed in the host lattice.

In case of nanostructured HfO$_2$, oxygen vacancies (V_o) are inherent in nature during synthesis and deposition process which dominate other lattice defects such as metal vacancy (V_M), oxygen interstitial (O_i), metal interstitial (M_i), oxygen antisite (O_M), and metal antisite (M_O) forming under different oxygen chemical potentials.[52] The high oxygen chemical potential minimizing the binding energy of oxygen molecules can facilitate the formation of Hf metal vacancy (V_{Hf}). On the other side, at low oxygen chemical potential, different neutral and charged oxygen vacancies are produced in the lattice.[68] The energy required to form V_{Hf} is relatively higher than that of V_o. In addition, the formation of V_{Hf} is also difficult due to its higher oxidation state. Moreover, these oxygen related vacancies can essentially tend to form a defect or impurity band below conduction band of HfO$_2$.[69] A simple model based on molecular mechanics method suggests that these oxygen vacancies usually reside onto the surface rather than the bulk due to significant difference in surface energies.[70] According to first principle calculation, in monoclinic HfO$_2$, there may exist various oxygen vacancies after charge trapping including V_o^{--}, V_o^-, V_o, V_o^+ and V_o^{++} which are further distinguished by their

respective three or four fold coordinated atomic configurations.[71] In HfO_2 lattice, the donor electrons which are localized by correlations and local potential fluctuations can couple with spins in defect bands forming the molecular orbitals around an oxygen vacancy in HfO_2. In this way, two donor electrons trapped in an oxygen vacancy can produce so called F^o centers due to their specific spin arrangement which mainly induce an antiferromagnetic ordering. A singly occupied vacancies known as F^+ centers particularly develop the long range ferromagnetic ordering whereas an empty oxygen vacancies (F^{++} centers) do not take part in establishing the ferromagnetism at room temperature in nanostructured HfO_2. It can be understood that the generated oxygen vacancies are capable of mediating long range RTFM in HfO_2 through F^+ centre exchange mechanism.[72, 73] Contrary to above reports on RTFM in nanostructured HfO_2, a few first principle investigations claim a radically different origin of such ferromagnetic ordering at room temperature. A possibility for short range ferromagnetic ordering due to isolated cation vacancy giving rise to high-spin defect state is anticipated in low symmetry monoclinic phase of HfO_2.[74] Some other reports even show the absence of RTFM in nanostructured HfO_2 and further suggest the origin of such RTFM due to external parasitic factors present in environment.[75, 76]

In general, the character of exchange between the defect states evoking RTFM is discussed in terms of impurity band formation. Explicitly, the super-exchange model does not fit in here since this can only gives rise to short-ranged antiferromagnetic ordering at concentrations of magnetic cations $x < x_p$ (x_p is the cation percolation threshold). Such an existence of RTFM can also not be explained on the basis of the double-exchange mechanism dealing with ferromagnetic ordering facilitating observation of large magnetic

moments which is not the case in HfO_2. In addition, this mechanism can only occur within the mixed cation valence showing ferromagnetic interactions. In view of impurity band formation, the presence of defects in the lattice generates energy states within the band gap of HfO_2. An abundance of such defect related energy states tend to produce an impurity band near conduction band minimum. For ferromagnetic ordering, these materials have propensity to form shallow donors like charged V_o. Such donors can possibly form bound magnetic polarons when couple with cations in the $3d$ bands within their orbits. The interaction between donor electrons and the cations in the vicinity of molecular orbital induce the ferromagnetic ordering.[72] Such defect induced formation of the impurity bands effectively propagate ferromagnetic exchange if distance between the defects is higher than that of localization length. It is known that the spontaneous spin splitting of impurity band occurs when $3d$ density of states is larger satisfying the Stoner criterion. The spin split impurity band can also arise in the presence of magnetic defects. At appropriate defect concentration, such impurity bands tend to extend and mix with empty $3d$ states at the Fermi level. This can exchange electron from the impurity band to unoccupied $3d$ states resulting in spin-polarization of the impurity band. It further promotes and favors the long range ferromagnetic ordering at room temperature or even high Curie temperatures.[77]

RTFM observed in nanostructured HfO_2 is weak in nature since it is defect induced ferromagnetic ordering. This weak ferromagnetism can be significantly enhanced by oxygen engineering or incorporating a low concentration of transition metal ions/impurities. The ferromagnetic properties of HfO_2 has been shown to be affected in the presence of Y, Ni, Co, Fe and Al. Especially, the large magnetization is observed in HfO_2 nanoparticles after doping Ni which is mostly mediated by oxygen vacancies.

Consequently, different methods have been used to incorporate Ni metal ion into HfO_2 lattice to improve the ferromagnetism behavior.[78] On the other hand, Chang *et al*. demonstrate that the magnetization decreases with increasing concentration of cluster-free Co.[79] In Fe doped HfO_2, no obvious effect of Fe doping on RTFM is observed as the ferromagnetism arises because of oxygen related defects only.[80] For Y doped HfO_2 nanoparaticles, the ferromagnetic ordering improves upto a certain concentration of Y which further weakens at larger Y concentrations.[66] RTFM in nanostructured HfO_2 is controlled by oxygen vacancies content existing in the lattice whereas metal ion doping in most of the cases suppresses the ferromagnetic ordering by forming clusters or unwanted defect complexes highly unfavorable for RTFM. Wang et al. report the magnetic properties of RE (Gd) ion doped HfO_2 films. The study indicates very weak ferromagnetism in pure HfO_2 and no significant improvement of the ferromagnetic ordering is observed.[81] Surprisingly, the literature lacks of a systematic and thorough research study on the effect of rare earth dopants in modifying RTFM of nanostructured HfO_2.

1.3   Optical Properties of HfO_2

Owing to wide optical band gap and high refractive index of HfO_2, it is known to be completely transparent over a broad range of the electromagnetic spectrum encompassing visible region, in particular. The luminescence behavior of nanostructured TMOs reflects the characteristic of structural modifications and can be used as an efficient probe for investigating the local surrounding of host cation. A systematic analysis of the luminescence properties of HfO_2 can lead to exploration of various defect states in the host lattice, if present. Similar to parameters such as temperature and pressure including material composition changing the crystal structure of HfO_2, the resulting luminescence

properties can also evolve accordingly with structural modifications. The nanostructured HfO_2 exhibits intriguing intrinsic luminescence features in visible region useful for potential optoelectronic applications. As discussed, the nanostructured HfO_2 contains different lattice defects related to oxygen vacancies originating during synthesis and heat treatment processes. Such oxygen vacancy induced defects are likely to form intermediate energy levels within the bandgap of HfO_2. These defect states acting as electron traps are optically active in nature called as 'luminescent centers'.[82] Under UV light irradiation, HfO_2 predominantly shows a broadband emission spectrum producing blue light. The primary emission peaks in monoclinic HfO_2 are observed at ~2.1, 2.5, 2.9 and 3.6 eV distinctive to the defects states lying in bandgap.[83] Among the defect levels revealed from luminescence spectroscopy of HfO_2, the correct origin and nature of atomic defects providing the most intense emission peak at ~2.5 eV has been extensively studied by various research workers. Following the literature, on one side, it can be expected that the strong emission centered at ~2.5 eV in nanostructued HfO_2 arises due to oxygen vacancies.[51] On the other side, in chemically similar ZrO_2 system, an almost similar emission band is attributed to extrinsic metal impurities e.g. Hf, Fe and Ti present in the precursor having extremely low concentrations.[84] It is known that the optically active Ti^{3+} $(3d^1)$ ion is capable of producing 2.5 eV emission band via $3d^1(e_g \rightarrow t_{2g})$ electronic transition which is of radiative nature.[85] Later, a careful and closer inspection using other appropriate spectroscopic measurements and theoretical calculations establish the origin of 2.5 eV blue emission band in HfO_2 to be only defect related mainly comprised of charged oxygen vacancies formed after trapping of electrons.

The luminescence properties are greatly influenced by the crystal symmetry of the host. In particular, the hosts like HfO_2 having low symmetry monoclinic phase is investigated for its strong blue luminescence behavior. **Figure 1.6** shows the luminescence behavior of monoclinic phase HfO_2 revealing prominent emission peaks at ~2.2, 2.5 and 2.8 eV distinctly dominated by 2.5 eV emission band. However, in case of the high symmetry cubic HfO_2, along with these emission peaks, a characteristic peak is found to be located at ~3.1 eV.[86] The emission band at ~2.5 eV dominates the PL emission behavior of nanostructured HfO_2 irrespective of crystalline phase present in the host lattice. Also, the luminescence yield for the monoclinic HfO_2 is relatively much higher than that of the cubic HfO_2 nanoparticles.
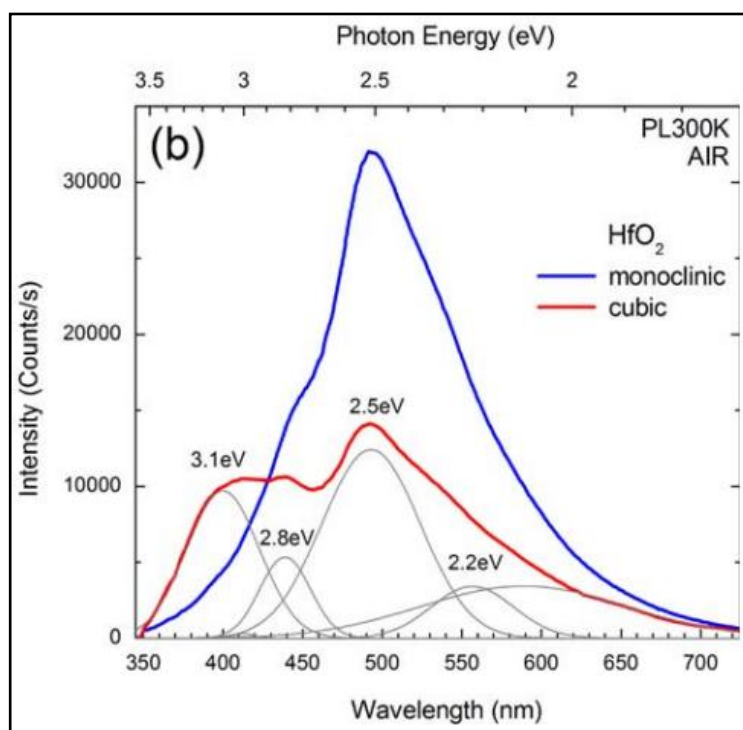
Figure 1.6 *The emission spectra of HfO₂ nanoparticles crystallized in the monoclinic (blue line) and cubic (red line) phase under ambient conditions. The deconvoluted peaks are grey in color (adapted from [86]).*

Apparently, the luminescence of monoclinic HfO_2 is associated only with different oxygen defects which lie deep in the impurity band. It is suggested that the characteristic emission peak at ~3.1 eV for cubic HfO_2 in no way can occur from the organic residues due to their large absorption threshold, usually greater than 4 eV. The other origin of same may be connected to Hf^{3+} defect states and/or some extrinsic radiative recombination taking place near defect centers which appear to be of significantly different nature in case of cubic HfO_2.[51]

The luminescence response of HfO_2 can be varied considerably by changing temperature, defect concentration, size and shape of particles etc.[83] If the particle size is reduced to few nanometers, the luminescence behavior is drastically modified due to very large surface-to volume ratio leading to wide discrepancy in concentration of defects. The difference in particle shape can produce dissimilar efficiency for adsorption of impurities rendering various kinds of optically active defects.[86] In fact, a highly tunable luminescence features are obtained after varying only the annealing temperature and consequently the particle size. Under optimized synthesis conditions, even white light emission can be perceived in nanostructured HfO_2 for potential application in ultra-violet white light emitting diodes (UV-WLEDs).

The monoclinic HfO_2 is proven to be a promising host for most of the RE elements due to better compliance with optoelectronic applications. When a tiny amount of RE ion is incorporated into HfO_2 lattice, it can induce remarkable characteristic emissions related to RE ion due to the presence of high crystal field energy. As a host, HfO_2 is capable of enhancing the luminescence behavior of RE activator ions. Such notable improvement in RE emission properties of HfO_2 is achieved by energy transfer (ET) process taking place

between specific energy levels of the host and RE activator ion. In the presence of RE ions

like Eu, Er, Tb and Ce etc, HfO_2 can produce a range of colors in the visible region.[54, 87-

89] Different emissions in RE activator ions occur primarily because of the distinct intra-

configurational *f-f* band transitions which can be dominated by electric or magnetic dipole

transitions. In most of the RE ions, the electric dipole transition governs the emission

behavior.[90] In contrast to singly RE ion doped HfO_2, incorporating double RE ions

simultaneously in the host constructively modifies the luminescence properties leading to

excellent control of RE ion emission behavior. In case of Eu doped HfO_2, after codoping

Li, Ta, Nb, and V, only Nb provides an enhanced and strong luminescence properties.

These codopants, however, serve as the charge compensating ions when Hf^{4+} is replaced by

Eu^{3+} in the host lattice.[91] Similarly, the emission behavior of Eu and Tb codoped HfO_2

can dramatically evolve with varying dopant concentrations.[92] The existence of two

different RE activator ions may produce the whole gamut of colors manifested by the

significant exchange of energetic electrons within various *f-f* transition levels. For such RE

codoped HfO_2, one of the two activator ions acts as the donor and can effectively sensitize

the luminescence behavior of the other ion called as the acceptor. In this context, the

transfer of energetic electrons from the donor to acceptor ion is understood on the basis of

Förster and Dexter energy transfer mechanisms also termed as multipolar and exchange

type interaction process, respectively. Either of the energy transfer mechanisms can be

dominated depending upon the distance between donor and acceptor active ion. The

exchange type interaction mechanism prevails when the critical distant between two active

ions is less than that of ~6 Å. Above this critical distance, the multipolar interaction

process controls the energy transfer between donor-acceptor ions.[93, 94] This energy

transfer of electrons within different levels of RE ions is essentially of nonradiative nature. The luminescence yield, thus can be improved considerably in RE codoped HfO_2

Looking at promising luminescent features and non-hazardous nature of RE doped HfO_2, it is being implemented in various biological imaging applications. The other luminescent materials such as quantum dots, dye-doped silica particles and metallic clusters have not been much revolutionized due to their poor photostability. On the other side, RE doped inorganic and biocompatible materials like HfO_2 are peculiarly used for cellular imaging, multiplexed histology, flow-cytometry, drug delivery, photodynamic therapy, *in vivo* whole animal and clinical imaging (e.g., angiography), tissue mapping and demarcation, real-time detection of intracellular events, signaling and bio-sensing, tracking cell migration, sensitive point-of-care detection including environment and bio-defense control.[95, 96] The inorganic based nanophosphors offer relatively much better photostability under severe conditions and do not degrade rapidly at the same time.

1.4   Resistive Random Access Memory Application of HfO_2

Since the first experimental report in year, *1967* on resistive switching in $Al/SiO_x/Au$ stratified structure, a number of metal oxide insulators have been substantially explored for resistive random access memory (RRAM) application. Among other emerging non-volatile memories like magneto resistive random access memory (MRAM), phase-change random access memory (PCRAM) and also FeRAM, RRAM can be integrated more easily due to its simple structure and great compatibility with current processing and scalability.[97] Basically, RRAM consists of a metal oxide insulator layer sandwiched between top and bottom metal electrodes. Such nonvolatile memory devices store and read information (i.e. 0 and 1) by rapidly switching between a low and high resistance states

(LRS/ON and HRS/OFF) under an applied bias voltage. In order to trigger the resistive switching, usually a certain initial bias voltage is required known as forming voltage (V_F) which is understood as the soft dielectric breakdown. In case of RRAM, the voltage at which the current in HRS increases abruptly to LRS is termed as SET voltage (V_{SET}). The voltage needed to switch from LRS to HRS state referring to RESET voltage (V_{RESET}) may occur in either positive or negative bias region.[98] Based on this observation, **figure 1.7** depicts two types of resistive switching modes possible in RRAM such as (i) unipolar and (ii) bipolar. For unipolar switching mode, both V_{SET} and V_{RESET} appear in either positive or negative bias region i.e. irrespective of electrical polarity. In the latter mode, V_{SET} and V_{RESET} are observed in positive and negative bias region, respectively or *vice-versa*.[97] In contrast to bipolar mode, the unipolar operation requires higher current to complete reset process which is due to the fact that the thermal effects govern the reset process corresponding to unipolar mode.[97]
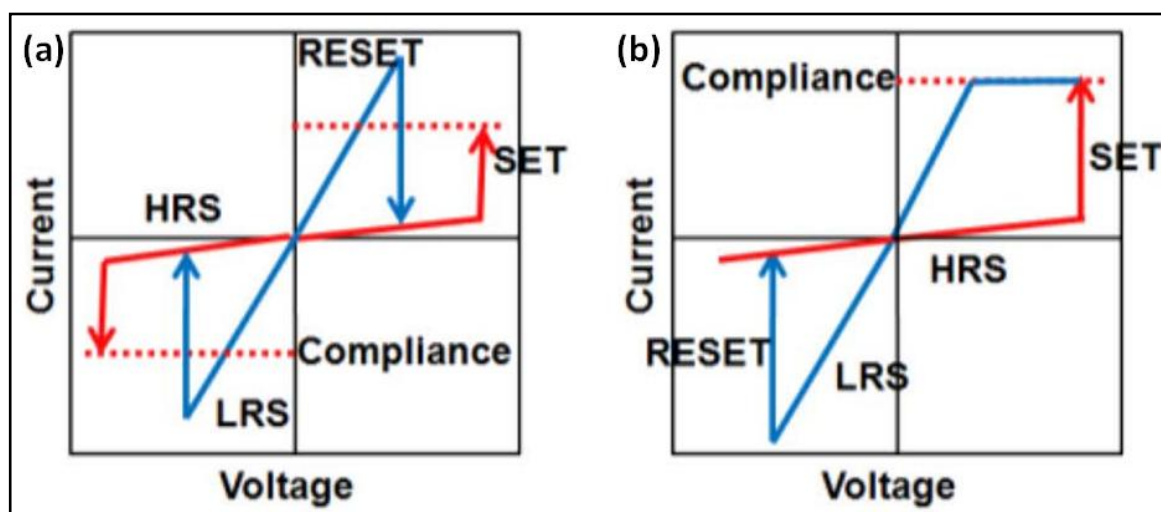
Figure 1.7 *Typical current-voltage (I-V) curves of RRAM in (**a**) unipolar and (**b**) bipolar resistive switching modes.*

The dominant current conduction mechanisms in SET and RESET processes are realized using different conduction models such as Schottky emission, Poole-Frenkel emission, Ohmic conduction and Fowler-Nordheim tunneling and space charge limited current in LRS and HRS states. In most of the cases, LRS state is governed by linear current-voltage behavior i.e. the Ohmic model whereas the current conduction in HRS is explained through non-linear current-voltage behaviors like Schottky emission ($\log(I)$ α $\sqrt{V}$), Poole-Frenkel (P-F) emission ($\log(I/V)$ α $\sqrt{V}$) and Fowler-Nordheim (F-N) tunneling (I/V^2 α V^{-1}) and space charge limited current (SCLC) (I α V^2).[97, 98] The resistive switching behavior in RRAMs is discussed in terms of the formation of conductive filaments (CFs), migration of oxygen vacancies/ions, Schottky barrier, cation migration and trapped charged carriers present at the interface or distributed randomly within metal oxide insulator film.[99] Different binary inorganic transition metal oxides like TiO_2, CuO, ZnO, NiO, CoO, ZrO_2, HfO_2, Ta_2O_5 and Gd_2O_3 etc have been systematically investigated for potential RRAM device applications.[98, 100] Among the binary metal oxides, HfO_2 is widely studied and preferred exhibiting enhanced resistive switching properties owing to its superior compatibility and thermal stability with CMOS processing and integration. HfO_2 based RRAM exhibits the stable, uniform and reproducible bipolar resistive switching behavior. It is broadly believed that the resistive switching characteristic in HfO_2 based RRAM is caused by the formation of several tiny localized conductive filaments (CFs) containing mobile metallic ions or charged oxygen vacancies generating conduction electrons. The switching between the HRS and LRS is described in terms of destruction and formation of such CFs, respectively occurring within the metal oxide layer. The rupture of CFs occurs due to local Joule heating effect. Under no bias condition, these

localized nanosize CFs show random motion within the metal oxide film. When a certain bias voltage is applied, these tiny CFs rearrange themselves and segregate to form the stronger and more conductive CFs.[98]

The oxygen vacancies driven resistive switching in HfO_2 based RRAM is necessarily controlled by modulating the concentration of oxygen content in the film. In some cases, even forming free resistive switching phenomenon is observed by precise tuning of the oxygen vacancies. Apart from the key role of oxygen content in switching behavior, other factors such as temperature, thickness of the film, top electrode material and dopant can significantly affect the performance of HfO_2 based RRAM. Thickness dependent switching behavior in oxygen deficient HfO_2 films reveals that the forming voltage can be suppressed considerably by optimizing thickness of the film.[50] In general, the bipolar resistive switching behavior is obtained using top electrode materials like TiN/Ti, Ti, Ta, Al and Pt.[98] However, if one utilizes top electrode material of Cu or Ni, the resistive switching behavior in HfO_2 is found to be of nonpolar nature.[101] The controlled resistive switching properties have been demonstrated in Al doped HfO_2 which occur because of the guided growth process of CFs.[102] After doping Ni into HfO_2 lattice, a large concentration of oxygen vacancies suggests the forming free resistive switching properties.[103] Moreover, RE ion, Gd doped HfO_2 shows much encouraging enhancement in RRAM device performance with better uniformity of different switching parameters. The promising RRAM feature is accomplished by minimizing the random motion of oxygen vacancy filaments formation which suppresses the oxygen ion migration barrier.[104] In fact, Gd doping can easily produce oxygen vacancies by reducing the V_o formation energy attained due dipole formation between V_o and Gd dopants. Gd^{3+} ions

substituting Hf^{4+} sites in the lattice drift the oxygen vacancies near Hf cation sites which eventually facilitate the controlled switching behavior in HfO_2.[105] Surprisingly, there exists meager reports dealing with RE ion doped HfO_2 based RRAM devices.

1.5 Objectives

The continuous downscaling of conventional gate dielectric i.e. SiO_2 has stimulated a progressive research to find a novel high-*k* dielectric material enabling us to overcome the major issues like high leakage current density, usually encountered in the current CMOS industry. For this reason, particularly, HfO_2 has been consistently studied for its deployment as an alternate to SiO_2 in CMOS technology due to its appropriate wide bandgap along with high-*k* value and outstanding thermal stability with silicon. HfO_2 possessing the monoclinic phase shows *k* value of ~15 which is four times higher than that of SiO_2 (~3.9). Based on above literature, the high temperature tetragonal and cubic phase of HfO_2 are technologically more important since they exhibit relatively larger *k* value such as ~70 and 30, respectively. Surprisingly, a few reports discuss the methodology to develop HfO_2 having high-*k* phases of either tetragonal or cubic by suitable dopants or controlling synthesis conditions. In this context, the optimization, comprehension and stabilization of the tetragonal or cubic phase of HfO_2 at room temperature is of utmost importance for its practical applications. Herein, the present work primarily aims to stabilize the high temperature cubic phase at room temperature after incorporating RE elements into nanostructured HfO_2 with optimized concentration along with processing temperature. Although the main objective of the thesis is inspired from a specific state-of-the-art problem, the outcomes of present work on nanostructured RE doped HfO_2 are of broader context and can be successfully implemented in various potential applications such as

imaging and memory devices etc. In addition to the systematic and concise literature review given in this chapter, the thesis offers a comprehensive discussion on the structure, magnetic, optical and electrical properties of nanostructured RE doped HfO_2 incorporated as following chapters:

Chapter 2 outlines the synthesis technique for preparation of pure and Dy and/or Sm doped HfO_2. The deposition of pristine and Sm or Dy doped HfO_2 thin films through electron beam evaporation technique is discussed briefly. A concise overview of the different instruments utilized in the thesis is provided. For example, the structural and microstructural characterizations of nanostructured HfO_2 have been carried out through X-ray diffraction (XRD), grazing incidence XRD, X-ray reflectivity, transmission electron microscopy and high resolution scanning electron microscopy. While X-ray photoelectron spectroscopy and electron probe micro analysis are used for elemental analysis, the optical properties have been explored by means of photoluminescence (PL) spectroscopy. Magnetic properties have been studied using magnetic property measurement system (MPMS), whereas the electrical properties are systematically investigated using semiconductor parameter analyzer for RRAM characterization.

Chapter 3 demonstrates structural transformation from monoclinic phase to high temperature cubic phase at room temperature after incorporating 11 at% of Dy. In contrast to diamagnetic behavior in bulk, HfO_2 nanoparticles show hysteresis loop indicating unusual ferromagnetism at room temperature. Surprisingly, RTFM in HfO_2 nanoparticles quenches after incorporating even 1 at% of Dy. On the other hand, 1 at% of Dy doped HfO_2 nanoparticles reveal excellent blue and yellow emissions producing cool white light. We propose an energy band diagram showing different transitions occurring in $Hf_{1-x}Dy_xO_2$.

In chapter 4, we show the stabilization of high temperature cubic phase of HfO_2 at room temperature by doping 12 at% of Sm. The phase transformation from the monoclinic to cubic phase is accompanied with a dramatic enhancement of lattice strain and reduction in particle size. Interestingly, HfO_2 nanoparticles reveal cool white emission without doping Sm. After incorporating 1 at% of Sm, HfO_2 produces strong emissions in near green and red regions. At higher Sm concentration, the PL behavior of HfO_2 diminishes significantly. Combining different excitation and emission processes, a schematic energy band diagram has been proposed.

Chapter 5 introduces a new concept of stabilizing the cubic phase of HfO_2 after codoping Dy and Sm. It has been established that after codoping Dy and Sm upto the total concentration of 13 at%, the stabilization of high temperature cubic phase of HfO_2 at room temperature is achieved. Dy and Sm codoped HfO_2 shows prominent emission peaks in blue, yellow and near red spectral regions producing purplish color light. We reveal the existence of an energy transfer from Dy^{3+} to Sm^{3+} ions inducing strong characteristic emissions. The rich PL emission behavior of the robust luminescent Dy and Sm codoped HfO_2 nanoparticles are considered as a prospective dusting powder for latent fingerprints (LFPs) imaging for promising application in forensic science. LFPs developed on several surfaces including aluminum foil, float glass, black colored glass, wine and red colored plastic sheets and stainless steel exhibit third-level details, good background contrast, selectivity and acceptable resolution.

Chapter 6 has been dedicated to exploration of pure and Dy or Sm doped HfO_2 films. The most important observation in this chapter is the stabilization of cubic phase at room temperature by doping at most half of Sm or Dy concentration compared to the

nanoparticles. These films exhibit the bipolar switching behavior which is of forming-free nature distinctive to RRAM device. After analyzing the switching behavior, it has been recognized that an abundance of oxygen vacancies forming 8-fold oxygen coordination to dopant ion play a crucial role in the stabilization of cubic phase at RT and also governs the forming-free switching behavior in HfO_2 based RRAM devices.

Chapter 7 outlines the main findings of the present work. We present the scopes of this work to be done in near future.