PREFACE

Hafnium oxide (HfO_2) has been consistently researched as a prospective material mainly as an alternate to silicon for semiconductor industry. Because of its appropriate high-*k* value and the high thermal stability against silicon, HfO_2 is proven as a potential candidate for gate dielectric material in metal oxide field effect transistors (MOSFETs). In the year 2007, HfO_2 is being used as the gate dielectric in Intel's 45 nm quad core processor replacing SiO_2. Additionally, HfO_2 finds promising applications in anti-reflection coatings, X-ray phosphors, cellular imaging, ferroelectric and resistive random access memories (FeRAM and RRAM) and so on. Bulk HfO_2 crystallizes in monoclinic phase at room temperature which transforms to the tetragonal and cubic phase at 1700 and 2600 ^{o}C, respectively. According to the reported literatures, the technologically relevant high temperature tetragonal and cubic phase of HfO_2 exhibit the high dielectric constant, *k*, ~70 and 25, respectively. First principle calculation suggests that the high temperature tetragonal and cubic phase of HfO_2 can be stabilized at room temperature by an appropriate dopant of lower valency. In this context, a few authors discuss the diverse effect of trivalent element doping having different ionic radii than Hf on the stability of tetragonal and cubic phase of HfO_2. It has been established that while the undersized dopants such as Si, Ge, Sn, P, Al or Ti stabilize the tetragonal phase, the dopants with oversize ionic radii like Y, Gd or Sc than Hf favour the stabilization of the cubic phase at room temperature.

Besides, the stabilization of the high temperature cubic phase of HfO_2, it is shown to possess rich magnetic and optical properties when size is reduced to nanometer range. Being HfO_2 a non-magnetic transition metal oxide with d^0 cations, the recent discovery of unusual room temperature ferromagnetism (RTFM) in HfO_2 thin film is fascinating and compelling for materials research communities. A wide group of researchers believes that required defects such as oxygen vacancies (V_o) can be held responsible for such type of ferromagnetic ordering present in diamagnetic oxides at room temperature. In this regard, Coey *et al.* report observation of RTFM in the monoclinic HfO_2 thin films originating due to unpaired electrons in extended molecular orbital of the defects. N. H. Hong reports RTFM with a large magnetic moment in HfO_2 thin films. Apart from RTFM observed in thin films, ferromagnetic behavior has also been observed in HfO_2 nanoparticles, nanoclusters and nanorods synthesized via various chemical routes at room temperature. Liu *et al.* have shown this behavior in nanorods and Dohčević-Mitrović *et al.* report the same in nanopowders. Besides, RTFM has also been demonstrated in yttrium (Y) and nickel (Ni) doped HfO_2 nanoparticles. Further, HfO_2 has been emerged as an outstanding host showing excellent photoluminescence properties. As a host, HfO_2 shows remarkable photoluminescence properties originating due to defect centers created within the band gap of HfO_2. It is known that Hf and O vacancies are most likely to be produced during the synthesis of HfO_2 and heat treatments. The different uncharged and charged oxygen vacancies by electron trap such as V_o, V_o^+ and V_o^{++} etc exist in HfO_2 lattice which act as the luminescence centers. In this regard, most recently, Villa *et al.* show that the luminescence in HfO_2 nanocrystals is modified tremendously by annealing at different temperatures. Upon incorporation of a rare earth ion in the host HfO_2, the host can also sensitize the luminescence of activator ion and improves the optical performance. Due to wide band gap, ~5.9 eV of HfO_2, it provides a better compliance for the most of RE ions including Eu, Nb and Tb etc producing excellent emissions in visible region. Wiatrowska *et al*. demonstrate modeling of photoluminescence behavior of Eu doped HfO_2 by codoping

Li, Ta, Nb and V used as charge compensating ions for Eu^{3+} substituted at Hf^{4+} in lattice. Only HfO_2:Eu,Nb powders reveal an enhanced and intense photoluminescence properties. Lauria *et al.* have established that the photoluminescence properties of HfO_2:Eu/Tb nanoparticles are drastically modified depending on the monoclinic and cubic phase stabilized by a nonradiative Lu^{3+} ion. Such potential luminescent materials are also actively used in latent fingerprint imaging in forensic sciences. The development of latent fingerprints (LFPs) detected at the site of crime is considered as an imperative physical evidence in forensic investigations. In this regard, Wang *et al*. have shown that luminescent YVO_4:Eu red-emitting nanocrystals of ~40 nm and $LaPO_4$:Ce,Tb green-emitting nanobelts with an average diameter of ~19 nm and length ~340 nm develop LFPs with exceptional contrast and selectivity having very less background intervention under 254 nm UV irradiation. However, use of deep UV radiations for LFPs development ultimately increase the overall processing cost. Therefore, one needs to develop luminescent nanosized powders excitable at higher wavelengths which is certainly advantageous for developing LFPs at relatively cheaper processing cost.

Along with the rich physical properties, HfO_2 has also been attracted significant attention for RRAM application in next generation data storage devices. RRAM nonvolatile memory devices store and read information by switching between a low and high resistive states under an applied bias voltage. In this regard, the stable, uniform and reproducible bipolar resistive switching in HfO_2 based RRAM device has been reported by Jančovič *et al*. and Hua *et al*. Looking at the rich evolution of structure with temperature in HfO_2, our objective is to stabilize the high temperature tetragonal or cubic phase at room temperature by either reducing dimension and/or incorporating rare earth (RE) dopants.

Not only structure, rare earth dopants in HfO_2 nanoparticles demonstrate excellent optical properties which can be potentially explored for latent fingerprint imaging useful in forensic investigations. The robustness of luminescent RE doped HfO_2 can also be perceived for various optoelectronic device applications. Further, we also intend to stabilize the cubic phase in rare earth doped HfO_2 thin films along with systematic investigation on the electrical properties important for RRAM memory applications. The effect of different synthesis conditions such as temperature, oxygen partial pressure, film thickness, top electrode material and dopant on the resistive switching behavior of HfO_2 is to be studied. Our thorough investigations on multifunctional nanostructured rare earth doped HfO_2 reveal several key findings which have not been reported earlier.

In this context, we unveil that high temperature cubic phase which is observed at 2600 ^oC, can be stabilized at room temperature after doping optimum concentration of Dy or Sm. In contrast to diamagnetic behavior in bulk, HfO_2 nanoparticles show unusual ferromagnetism at room temperature. Further, 1 at% of Dy or Sm doped HfO_2 demonstrates excellent emissions in visible region producing cool white light.

Further, we introduce the concept of stabilizing the cubic phase of HfO_2 even after codoping Dy and Sm with an optimum concentration. Dy and Sm codoped HfO_2 shows prominent emission peaks in blue, yellow and near red spectral regions producing purplish colored light. Owing to outstanding luminescence properties of RE doped HfO_2 nanophosphors, for the first time, we examine their perspective as dusting powder for LFPs imaging. LFPs developed onto several surfaces exhibit third-level details, good background contrast, selectivity and acceptable resolution.

Not only in RE doped HfO_2 nanoparticles, but also we demonstrate that the cubic phase is even stabilized at room temperature in thin films after doping with half of the Sm or Dy concentration. These films exhibit the bipolar switching behavior which is of forming-free nature distinctive to RRAM device.

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