3
Identified Issues/Gaps and Possible Solutions

3.1 Issues/Gaps in ZnO

Multifunctional MOS have interesting properties and are getting wider attention by the researchers of electronic industries due to their use in multiple applications. ZnO is one of the most important multifunctional MOS which has been investigated widely owing to its unique physical properties. The wider band gap of ZnO and it intrinsic n-type conductivity has made ZnO an interesting candidate for numerous applications such as light-emitting diodes, UV photodetector, gas sensors, transparent electronics, solar cells, and piezoelectric devices. There are several properties which are governed by controlling and manipulating the intrinsic/extrinsic defects in ZnO i.e. carrier density and room temperature magnetism. Hence, a detail investigation of defects present inside ZnO is needed in order to use its potential for various applications. Properties of ZnO such as luminescence efficiency, doping efficiency and minority carrier life time are directly or indirectly affected by defects present inside the system (Janotti and Van de Walle, 2007a). It also affects diffusion mechanisms associated with growth mechanism, processing, device performance, and degradation. Apart from that, migrations of these point defects inside the material also affect physical properties severely. The migration studies help us to investigate incorporation of these defects during growth and processing of material. Intrinsic point defects i.e. interstitial, vacancies, substitution, and antisites have drastic effects on intrinsic properties of a material.

ZnO has many intrinsic point defects present which are zinc and oxygen vacancies, substitution at zinc and oxygen sites, zinc and oxygen interstitials, antistes, and presence of foreign element like hydrogen as unintentional doping (Janotti and Van de Walle, 2009). Since, these defects plays a crucial role in changing the physical properties of ZnO hence, it is important to understand these defects and have a control over manipulation of these defects to achieve the desired physical properties. ZnO has intrinsic n-type conductivity and oxygen vacancies/zinc interstitials defects are often responsible for that. Additionally, the presence of unintentional hydrogen atoms has also been given credit for n-type conductivity of ZnO. DFT studies have shown that hydrogen in interstitial space develops a strong bond with oxygen and behaves as shallow donor (McCluskey and Jokela, 2009). However, this defect is mobile at higher temperatures and is not stable. Another report tells that hydrogen can substitute at oxygen atoms which also behave like a shallow donor and stability is more than interstitial form of hydrogen and hence is accountable for n-type behavior. Till now, there is no consensus of the type of defects responsible for n-type conductivity. However, majority of reports are emphasizing oxygen vacancies/zinc interstitials as the main source. Since oxygen atoms are incorporated from atmosphere for ZnO synthesis and depend on synthesis and annealing conditions, hence, are difficult to control. There are many studies conducted on oxygen vacancies effects on ZnO physical properties, both experimentally and theoretically (Sharon and Muthukumaran, 2018)(Can et al., 2012). However, there is a very little information available on the influence of zinc interstitials on the properties of zinc oxide (Sun and Wang, 2003)(Erhart

and Albe, 2006). Putting additional zinc atom in the ZnO system can either lead to interstitial formation or antiste formation when zinc will go to oxygen vacancies sites. The formation energy of antisite formation is higher than the formation energy of zinc interstitial (~ 4 eV) and since low energy processes are more favorable, zinc atoms should go to interstitial positions (McCluskey and Jokela, 2009). There are two interstitial positions available in ZnO where zinc atoms can reside and those are octahedral and tetrahedral voids. Radius of zinc is comparable to octahedral void and hence, zinc should probably occupy those interstitial spaces. Hence, detailed understanding of zinc interstitials defects are important in understanding their impact on physical and electronic properties to harness their potentials (Janotti and Van de Walle, 2007a).

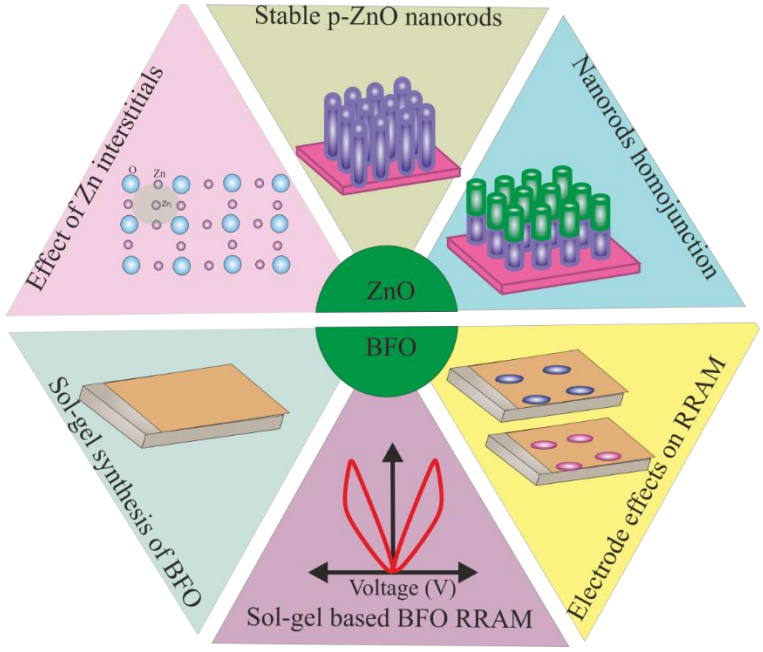

Figure 3.1 : Schematic of gaps present in ZnO and BFO

Native point defects in smaller concentration up to 0.01 ppm can exhibit significant changes in electrical and optical properties of ZnO (Janotti and Van de Walle, 2009). ZnO has been explored as potential candidate for dilute magnetic semiconductor by doping with different transition metals. Another important aspect of zinc oxide which needs to be addressed is synthesizing the stable p-type electrically conducting ZnO. The possibility of controlled p-type ZnO will lead to tremendous applications particularly in LEDs and lasers. The heterojunction based optoelectronic devices leads to lattice mismatch and several defects are present at the interface. These defects act as trapping sites and prevent the recombination process of excitons. Hence, the desired luminous efficiency is not achieved in heterojunction devices. To overcome such problem, homojunction based ZnO devices needs to be realized (Janotti and Van de Walle, 2009). The synthesis of p-type dopant in ZnO is challenging because it is compensated by donor defects intrinsically present in ZnO. There are several dopants which are used in ZnO at zinc and oxygen sites to achieve p-type conductivity. Further, p-type conductivity in ZnO is reported by doping with group IA element such as lithium, sodium, and potassium (Capper et al., 2011). These dopant atoms, however, act as either deep acceptors or migrate into interstitial spaces because of their smaller size and thus, acting as a donor compensating the effect of p-type conductivity.

Doping of group V element such as nitrogen, phosphorous, arsenic, and antimony are explored for p-type characteristics (Capper et al., 2011). Because of the high electronegativity of oxygen atoms, only nitrogen is a favorable candidate which acts as a shallow acceptor and others acts as deep acceptors. Other group V elements are reported to form a complex with two

zinc vacancies and hence results in p-type conductivity (Capper et al., 2011). However, high formation energy is reported for these complexes hence, its realization is not favorable. Further, low defect energy levels are resulted from group IA elements and can result in relatively better stable p-type conductivity in ZnO. Out of all dopants on group IA, lithium has the smallest ionic radii and is comparable with the ionic radii of zinc atoms. When Li is substituted at zinc site, it acts as a shallow acceptor however, due to smallest and comparable size of lithium to interstitial position; it may migrate to interstitial sites (Capper et al., 2011). These interstitial lithium atoms act as a donor and compensates the effect of acceptor produced from substituted lithium atoms. This results in unstable p-type conductivity of ZnO. There have been reports on increased resistivity of ZnO by several orders with lithium dopant which makes it an interesting topic to understand and realize stable p- ZnO by lithium and hydrogen co-doping (E Senthil Kumar et al., 2011). Techniques such as co-doping method is introduced in which lithium along with other element such as nitrogen, hydrogen, and nickel is doped together to realize stable p-type conductivity. The co-doping method is supposed to increase the acceptor solubility limit by bringing the acceptor energy levels near to shallow levels. Hydrogen is not a suitable co-dopant atom as it forms complexes such as Li_{Zn}-H and Li_i-Li_{Zn} which creates instability in the system (E Senthil Kumar et al., 2011). The smaller size of nitrogen atom also makes the co-doping method unsuitable for realization of p-ZnO because of the unstable nature. However, nickel co-doping with lithium is explored and resulted in lower resistivity with stable p- ZnO material. Thin film based homojunction using the same has been reported on ZnO (E Senthil Kumar et al., 2011). Also the same group has reported nickel doped low resistive ZnO and the reason is attributed to splitting of d-bands of nickel atoms.

Nanostructures of ZnO have attracted tremendous attention of the research community because of its wide uses in electronics and optoelectronics. 0 and 3 dimensional structures such as quantum dots and nanoparticles have aspect ratio nearly equal to one. One dimensional structure such as nanorods, nanowires, nanotubes, nanofibers and nanobelts etc have attracted significant attention of research community since it has large surface to volume ratio. These structures are important source to investigate the change in physical properties according to change in dimensionalities. Nanorods of ZnO have been investigated widely for different optoelectronic applications because of its large surface area. Hence, realization of p-type ZnO nanorods is important in order to synthesize one dimensional homojunction and heterojunction structures of ZnO for different optoelectronic devices such as solar cell, LEDs, photodetectors and lasers.

3.2 Issues/Gaps in BFO

RRAM has gained significant attention in past few years owing to its fast response, scalability up to 5 nm, high density structure and low power consumption. Many multiferroic materials have been explored for RRAM applications. BFO is one such multiferroic perovskite structure which exhibit ferroelectric and antiferromagnetic properties together in the same phase. It also exhibit room temperature weak ferromagnetism and hence, room temperature ME properties (Wu et al., 2016). This property provides advantage of controlling the electric properties by applying magnetic field and vice versa. Hence, BFO based RRAM can use this magneto-dielectric properties to produce changes in RRAM characteristics by applying additional electric or magnetic field. BFO tends to have oxygen vacancies present in the lattice which leads to high leakage current which further limits the ferroelectric properties of BFO. However, these oxygen vacancies can play a significant role in filamentary based resistive switching of BFO. The type of switching mechanism depends on the type of growth mechanism along with the electrodes deposited on BFO. The growth process also governs the presence of oxygen vacancies. Since the leakage current is high in BFO, hence even thicker films can be used for RRAM applications. Thin film of BFO are realized by using PLD, sputtering, CBD and spin

coating methods (Wu et al., 2016). BFO has been reported to exhibit unipolar as well as bipolar RRAM behaviour against the applied electric bias. The unipolar and bipolar characteristics depend on the growth mechanism and electrode used. The observed memory characteristics are attributed to large leakage current and ferroelectric properties. PLD and sputtering methods are generally used to synthesize BFO thin film for RRAM applications. The existence of unipolar/bipolar characteristics in BFO is still a matter of investigation and needs to be explored with different synthesis techniques and in electrode configurations. Sol-gel synthesis is a simple low cost effective technique which has attracted the research community widely because of its ability to provide control over precursors and large area synthesis of thin films and nanostructures (Zhang et al., 2016). Initially for sol-gel synthesis of BFO, metal alkoxides precursors in DI solvent were used for spin coating deposition. These metal alkoxide precursors are costly and also leads to carbon contamination of the film which restricts its use for high quality thin film deposition(Zhang et al., 2016).

Nowadays for sol-gel preparation, nitrate salts of bismuth and iron are used to synthesize BFO thin film. These salts are less costly, have smaller decomposition temperature, and have good solubility in water, alcohols and in other solvents. Ethylene glycol and 2-methoxyethanol are two solvents, widely used to prepare BFO sol-gel solution. Out of these, 2-methoxyethanol has a linear structure which helps to facilitate a better stable and highly dense solution and is more favourable over ethylene glycol. The highly stable and dense gel in 2-ME helps in better crystallization and facilitates an oriented growth of BFO thin films(Zhang et al., 2016). Apart from that, it has better solubility and viscosity which is necessary for spin coating process. Sometime, to adjust the viscosity, further a chelating agent is used. Apart from that a chelating agent is used to adjust the viscosity also. Despite of using right precursors and right solvent, the sol-gel deposited BFO suffers from secondary phase formation (Zhang et al., 2016). The factor which governs the secondary phase formation is iron valency in BFO and loss of bismuth which starts evaporating after certain temperature (Zhang et al., 2016). The pure phase BFO can be achieved by choosing the optimal post-annealing temperature for the films. To compensate the bismuth losses at higher annealing temperature which is necessary for better crystallization, additional amount of bismuth precursor is added in the solution. Hence, understanding the RRAM characteristics on sol-gel deposited pure phase BFO is required to explore its unipolar and bipolar switching behaviours. It has been reported that the type of switching mechanism is affected by the top and bottom electrode as well because the interface at metal-insulator junction plays crucial role in the switching phenomenon. Hence, understanding the electrode based RRAM characteristics is important. The gaps present in these two materials are summarized in figure 3.1.

3.3 Approach

Based on the literature review and mentioned issues/gaps, we address some of these adopting the following approaches:

a) Synthesizing excess zinc containing ZnO and understanding its properties with respect to pristine ZnO
b) Developing stable low cost p-ZnO nanorods and further use it to synthesize homojunctions for different applications
c) Realization of phase pure BFO through solution process
d) Understanding the RRAM characteristics of sol-gel derived pristine and doped BFO with respect to different electrodes