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Introduction

Advances in nanotechnology have created new ideas and directions for the research and development of novel futuristic electronic devices. The physical properties of materials change by downsizing from bulk to thin film leading to the development of miniaturized electronic devices with improved performances. These thin films and nanostructures are utilized in numerous applications, i.e. photonics, electronics, and energy harvesting (Yu et al., 2016)(Fortunato et al., 2012). In today's world, electronic devices have become an important part of our day to day life. Electronic devices are used in simple gadgets such as watches, phone, and music players to complex supercomputers. These electronic devices are designed for different requirements and are integrated into memory, sensors, display, and several other applications (Chang et al., 2015). This demand has led to investigating the materials which can be used in multiple devices' applications.

1.1 Multifunctional Materials and Devices

Nowadays, the emphasis is given by the research community of material science on the synthesis of new materials and structures which can be efficiently used for sensing, memory applications, optoelectronics and photonics, energy harvesting, healthcare, transportation, and many more applications by exploiting its different properties (Lendlein and Trask, 2018). These materials have specific electronic, optical, magnetic, thermal, and other properties which can be tailored to suit a specific requirement for different applications. Materials having more than one such properties existing together are termed as multifunctional, in contrast to monofunctional counterparts (Ferreira et al., 2016). These materials can perform the structural function, a combination of structural and non-structural function or both, enabling its wide range of capabilities. Multifunctional materials are found in either pristine state or engineered to acquire multifunctional properties by several techniques. The materials are advantageous over others owing to its efficient and versatile properties, smaller size, low cost, light-weight, less complex and low power consumption capabilities (Lendlein and Trask, 2018)(Ferreira et al., 2016)(Salonitis et al., 2010). A schematic of application of multifunctional materials are shown in figure 1.1.

Several multifunctional materials are offered by nature and observed on a daily basis, i.e. biomaterials such as skin which has several layers and performs multiple functions in conjunction with guarding our flesh (Christodoulou and Venables, 2003). Several materials such as metal oxide semiconductors (MOS), composites, hybrids, or heterostructure are designed and investigated for their multifunctionality, which can be harnessed in several applications. Binary and ternary metal oxides are such materials which have more than one properties existing together and hence have been used in a plethora of applications. These materials in thin film and nanostructures have shown better carrier mobility, transparency, uniformity over a large area, and environmental stability (Meng et al., 2018). Few of these oxides are intrinsically multifunctional, and few are doped to tailor the properties to induce multifunctionality.

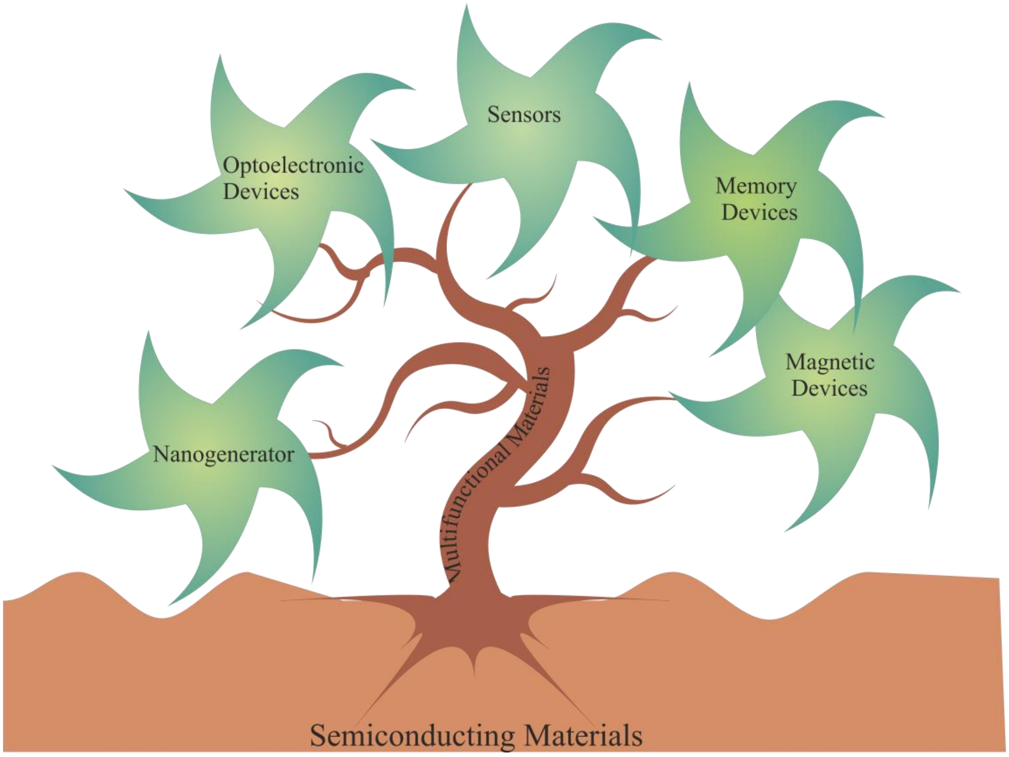

Figure 1.1: Schematic of applications of multifunctional materials

1.2 Multifunctional Binary Metal Oxide

Binary oxide materials are found abundant in nature and cover the range from insulator to metal to semiconductor. However, binary metal oxide semiconductors are more explored materials by the research community because of its different and versatile functionalities as compared to elemental semiconductors. These materials have different electronic structure, defect states, synthesis techniques, optical and electronic properties, and charge transport mechanism in comparison to elemental counterparts (Yu et al., 2016). These properties allow them to acquire conventional as well as new functionalities. Some of the most explored binary oxide materials are ZnO, SnO_2, TiO_2, HfO_2, CuO, and NiO. These semiconductors are explored for numerous applications such as gas sensing, memory cells, optoelectronic devices, solar cells, photocatalysis, transistors, biosensors and diluted magnetic materials with several other applications. Recently, remarkable advances for electronics applications of these materials are achieved in terms of new transparent conducting oxides, synthesis of p-type semiconductors for homojunction transistors, advancement in printing electronics based on metal oxide semiconductors, and also commercialization flat displays based on amorphous oxide which is of great importance(Yu et al., 2016). Among various binary metal oxides, ZnO is one of the most explored oxide semiconductors. It is of great importance in the semiconductor industry because of its availability in nature, low processing cost and low-temperature requirement, availability as single crystal, synthesis of various nanostructures by simple methods, easy fabrication of devices and non-toxicity.

Optoelectronic devices have gained prominent recognition due to its wide applications. These devices are used in displays, LEDs, as photodetectors, traffic signals, optical recording media, high-resolution printers, video games, and automobiles (Dupuis and Krames, 2008). Recently, researchers are focusing on developing high-quality optoelectronic devices by optimizing the materials as well as modulating the electronic properties which suit the need of the applications. Materials such as silicon carbide (SiC), III-V compound semiconductor, organic semiconductors, carbon nanotubes (CNTs), graphene, II-VI chalcogenides and II-VI metal oxides have been widely investigated for optoelectronic device applications (Carter and Edmond, 1993; Haase et al., 1991; Minami, 2005; Nakamura et al., 1991; Yu et al., 2016). For many years, gallium nitride is considered as one of the most suitable materials because of its high mobility and realization of p-type GaN by doping (Dupuis and Krames, 2008). In recent years, attention of research community is shifted on MOS for optoelectronic devices owing to its high mobility, optical transparency, easy fabrication techniques, large area electrical uniformity, high robustness, mechanical flexibility and thermal stability (Yu et al., 2016). These MOSs have band gap near to 3 eV which makes them transparent in the visible spectrum. The strong interaction between *2p* orbitals of the oxygen atoms and *ns* electrons of metal led to having high electron mobility, low effective mass, large band gap and small density of states on valance band (VB). However, these materials suffer from lack of realization of p-type MOSs because of hole compensation by different point defects and hindrance provided by localized 2p oxygen atoms in the movement of holes (Yu et al., 2016). ZnO is one such MOS which is widely investigated for different optoelectronic devices.

Zinc oxide is a wide band gap MOS and has room temperature direct band gap of 3.37 eV (Wang, 2004a). It exists in the cubic and hexagonal wurtzite crystal structure. The most stable crystal structure of ZnO is hexagonal wurtzite structure, and here, a zinc atom is tetragonally connected to four oxygen atoms and vice versa (Klingshirn, 2007). This tetrahedral coordination in ZnO results in asymmetry and is responsible for piezoelectric and pyroelectric functional properties (Klingshirn, 2007). It is an intrinsic n-type conductor because of the several intrinsic and extrinsic defects present in the material (Janotti and Van de Walle, 2009). The p-type ZnO is required to synthesize homojunction based devices, and hence, investigations are focused on realizing p-type ZnO by doping other elements(Fan et al., 2013). It has a large room temperature exciton binding energy of 60 meV (Klingshirn, 2007). The wide band gap in conjunction with high exciton binding energy of ZnO makes one of the important materials for optoelectronic devices, such as photodetectors and LEDs. The availability of ZnO in single crystal form is also a reason for its wide popularity over GaN for optoelectronic applications (Janotti and Van de Walle, 2009). Less lattice mismatch between ZnO and GaN has provided an advantage to use ZnO as a substrate for GaN-based devices. Responsiveness of ZnO to wet chemical etching makes it advantageous over other semiconductors in device fabrication. The alteration of ZnO band gap is achieved by alloying it with MgO and CdO to increase and decrease the band gap, respectively (Janotti and Van de Walle, 2009). The conductivity of ZnO is controlled by doping with different elements. Transparency of ZnO in visible light makes it a promising candidate as TCO in solar cells. The band gap of ZnO falls in the range of ultraviolet (UV) radiations, and thus, a suitable candidate for UV detectors/sensors (Janotti and Van de Walle, 2009). Apart from that, it shows hardness to thermal radiations, indicating its importance in many applications. ZnO is investigated for several other applications such as gas sensors, thin film transistors, memory devices, nanogenerators, biosensors and dilute magnetic semiconductors (Djurišić et al., 2012)(Ü. Özgür et al., 2005)(Özgür et al., 2010a). Different deposition techniques are used to fabricate ZnO, which results in different defect density and hence affects the properties (Schmidt-Mende and MacManus-Driscoll, 2007a)(Djurišić et al., 2010a). ZnO is synthesized in bulk, thin films and nanostructures demonstrating different physical properties. One dimensional (1-D) nanostructures of ZnO is investigated extensively for numerous applications owing to its large surface to volume ratio. Several morphologies of 1-D nanostructures of zinc oxide such as nanorods, nanotubes, nanowires, nanoparticles, nanopods, flowers, brooms, and helix are reported, and various properties are understood to further use it in different applications (Schmidt-mende and Macmanus-driscoll, 2007)(Wang, 2004a).

1.3 Multifunctional Ternary Metal Oxides

The most explored ternary oxides belong to the class of ferroelectric, ferromagnetic, and multiferroic materials. Ferroelectric material shows spontaneous polarization and its reversal under the presence of the electric field, ferromagnetic material shows spontaneous magnetic polarization and its reversal under the application of a magnetic field. Multiferroic materials have both ferroelectric and ferromagnetic properties existing together. In these materials, applied magnetic fields may induce change in electric polarization and magnetic polarization can be induced by applying the electric field. This effect is known as magnetoelectric coupling, and it provides an additional degree of freedom in these devices to be used in novel applications (Sando et al., 2014). There are several multiferroic ternary oxides such as $BaTiO_3$, $BiMnO_3$, $TbMnO_3$, $PbZr_{1-x}Ti_xO_3$ (PZT) and $BiFeO_3$ (BFO) which are used in multiple applications such as magnetic recording read head, FeRAM, photovoltaics, thermal energy harvesting devices and other electronic devices (Rao et al., 2012; Sando et al., 2014; Vopson, 2015). Several memory devices are realized from these materials by exploiting their magnetic and ferroelectric properties.

The demand for high speed, low power, high density, and non-volatile memory is increasing in today's advanced information technological world. The widely used flash memories or silicon-based static random access memory (SRAM) and dynamic random access memory (DRAM) are suffering from the limited scaling issues, high power consumption, and low operating speed (Ielmini, 2016a). Several memory devices such as phase change random access memory (PCRRAM)(Wuttig and Yamada, 2007), magnetic random access memory (MRAM)(Zhu et al., 2000), ferroelectric random access memory (FeRRAM) (Ishiwara, 2012) and resistive random access memory (RRAM) (Kumari et al., 2018b) are investigated by the researcher to replace or complement the existing memory devices. Among these explored memory devices, RRAM is believed to be a promising candidate owing to its high speed, low power consumption, simple structure, high endurance, and good scaling properties (Ielmini, 2016b). RRAMs are a simple metal-insulator–metal (MIM) structure. Embedded RRAM shows lower power consumption and high speed, which is advantageous over flash memories. The crossbar RRAM has high density in comparison to DRAM and has better speed than flash memories with non-volatile behaviour and 3D integration capability (Ielmini, 2016b). Hence, RRAMs are showing ideal characteristics which may fill the gap of generally used flash and DRAM memory devices. Several materials such as organic materials (Stewart et al., 2004), carbon materials(Li et al., 2008), binary(M. Liu et al., 2009) and ternary oxides (Kumari et al., 2018b) are explored for RRAM applications. Out of these, only a few multiferroic ternary oxides have been explored widely for RRAM applications. These ternary oxides provide manipulation of RRAM characteristic in the presence of magnetic and electric field owing to their ferroic properties. BFO is one of the most explored multiferroic oxides, which has room temperature ferroelectric and antiferromagnetic behaviour (Wang, 2003). This material is investigated for RRAM applications in various configurations.

BFO is a perovskite material with chemical formula ABO_3 where A and B are cations of different vacancy and O is anion. It has R3C space group and possesses a rhombohedral structure in which two perovskite unit cells are connected along the body diagonal (Wang, 2003). It is a direct band gap material with band values fall in 2.3-3.0 eV energy window (Sando et al., 2018a)(Sando et al., 2014). This band gap range falls near the absorption edge of visible light. The attention on BFO materials started in 2003 after demonstrating large electric polarization (~60 $\mu C/cm^2$) in high-quality pulsed laser deposition (PLD) grown epitaxial BFO thin films by Ramesh and his group (Wang, 2003). Curie temperature of BFO is ~1100 K. Bulk BFO exhibits G-type antiferromagnetism below Neal temperature T_N=643 K. Coexistence of ferroelectric, magnetic and optical properties enables BFO to be used in multifunctional devices for several applications such as spintronic, electronics and photonics (Sando et al., 2014). It has been used as gas sensors (Das et al., 2015), solar cells (Feng, 2015), four stage memory devices

(Liu et al., 2014), and RRAM (Kumari et al., 2018b). BFO has been widely investigated in RRAM device applications showing both unipolar and bipolar switching behaviour (Katiyar et al., 2015a)(Shuai et al., 2011). This material has been investigated for RRAM devices with the different electrodes such as gold, aluminium, platinum, silver, and copper (M. Li et al., 2010) and several mechanisms are reported to explain the switching behaviours in these devices (Lin et al., 2014).

1.4 Motivation

The multifunctional MOS based few devices have been commercialized but still there is need of extensive research work to provide stable, high performance and reliable characteristics of these devices. Hence, in order for successful implementation of these multifunctional electronic devices, understanding of material physics and chemistry along with devices' processing issues and device physics are required.

ZnO is explored for numerous applications but still one of the challenging aspects is to improve the performance of ZnO based devices. Extrinsic and intrinsic defects significantly affects the physical properties of ZnO (Janotti and Van de Walle, 2009). Hence, understanding the defect chemistry is required in order to comprehend its influence on the properties to further use it in suitable applications. Also, synthesizing p-type ZnO is required in order to use it in homojunctions based optoelectronics devices (Janotti and Van de Walle, 2009). Nanostructures are preferred over thin film because it offers high surface to volume ratio and thus, more interacting and reactive surfaces. Hence, synthesizing n-type and p-type ZnO nanostructures will provide enhanced performance for different devices (Janotti and Van de Walle, 2009). ZnO based heterojunction are explored and still there is a lot to explore about the performance of these devices with different nanostructures and with different p-type materials.

$BiFeO_3$ (BFO) is also an interesting multifunctional system and is explored various applications including RRAMs in different electrode configurations(M. Li et al., 2010). Most of the BFO thin films are deposited using vacuum base PLD and radio frequency (RF) sputtering techniques, which are relatively cumbersome and costly techniques. Depositing good quality BFO thin film is still a challenging process using solution process as it leads to presence of secondary phases(Zhang et al., 2016). Both unipolar and bipolar RRAM characteristics are reported in BFO, depending on device configurations together with electrode materials. The type of electrodes severally affects switching mechanism and hence, understanding the effect of these electrodes is required in order to understand the device physics.

1.5 Objective

The primary focus of this dissertation is to explore multifunction materials for device applications by impregnating it with external dopant or in pristine state. The objective of this thesis is summarized in the following points:

1) Synthesizing zinc rich ZnO by doping it with additional zinc atoms to understand its effect on the physical properties of ZnO using thermal CVD method,
2) Realization and characterization of solution processed n and p-type ZnO nanorods to developing homojunction and heterojunction devices,
3) Synthesis and characterization of solution processed BFO thin films for their RRAM application, and
4) Fabrication of Ag/BFO/FTO and Al/BFO/FTO RRAM device and investigating the effect of electrodes towards understanding switching mechanism of these devices.

1.6 Thesis Layout

This thesis is structured into nine chapters. **Chapter 1** provides a general introduction about multifunctional materials focusing on ZnO and BFO based electronic devices. It also discusses about the motivation and objective of this thesis. **Chapter 2** of this thesis discusses about ZnO material properties, deposition techniques, doping, nanostructures and ZnO based optoelectronic devices. It also provides an insight into BFO properties, deposition techniques, structures and devices. **Chapter 3** describes about the research gaps i.e. issues present in ZnO and BFO and possible strategies to bridge the gaps. **Chapter 4** discusses about the impact of excess zinc on ZnO thin film synthesized using CVD. It also explained about the structural, microstructural, optical and electrical characterization of synthesized thin films and its possible applications. **Chapter 5** presents synthesis of solution derived p-type ZnO nanorods and ZnO based homojunctions along with structural, microstructural, optical and electrical characterization. **Chapter 6** provides insight about ZnO nanorods based heterojunctions and its characterizations. **Chapter 7** reports solution processed BFO synthesis and its structural, microstructural and optical characterization substantiating its phase purity. It also discusses about RRAM characteristics and its switching mechanism using electrical characterization. **Chapter 8** discusses the effect of aluminium electrode on RRAM characteristics of solution derived BFO thin films. Finally, **Chapter 9** includes conclusion of this thesis and probable future aspects towards the extension of this work.