1
Introduction

Communication technologies demands compact electronic circuitry with more extended functionality. There has been considerable demand to reduce the size of device and execute inexpensive tunable microwave and RF components to meet with the rapid growth of communication systems in current years. Electric field dependent permittivity, low loss and small size are the necessary features for the next generation microwave applications. By designing state of the art system and development of innovative electronic components, these requirements can be achieved. Tunable capacitor is the crucial component in tunable microwave and RF devices which is used for electrically tuning of the radio frequency. These capacitors are required to be developed in military and commercial systems i.e. tunable band-select filters for wireless communications, tunable radiating structures for frequency hopping and phase shifters for electronic scanning antennas. The tuning of the resonance frequency on a different channel can be explained by turning the knob mechanically of a classic radio. Modern multipurpose cellular phones maintain a large number of principles and frequency bands [ETSI, 2008]. Multiple switches are used to select multiple non-tunable circuits for multi-band operation. Single tunable circuit can replace some of the circuits which save valuable components and space on a device panel. The size of devices has also decreased for the past several years and significant improvement in the performance was achieved due to size scaling, linked with "Moore's Law". The reconfigurability of the circuit help to reduce the dimensions of tunable circuits. Devices with scaling oxides dimensions are operated at slightly large electric fields since the device operating voltage cannot be scaled more assertively than the device dimensions. The devices with thinner oxides exhibit large leakage currents since carriers can easily tunnel directly between the substrate and gate electrode [Felix *et al*, 2003] which is a big concern for ground-based mobile and satellite systems electronics where power conservation is important.

Therefore, IC manufacturers are considering several high-κ gate dielectrics to replace SiO_2 to reconcile the need for reduced leakage currents in highly scaled devices [Wilk *et al*, 2001]. The major benefit of alternative high-k dielectrics is higher dielectric constants. The high dielectric constant is responsible to fabricate a gate stack which is thinner than SiO_2, but maintains similar presentation. However, a reconfigurable low-voltage RF circuit considers electrically tunable components which are usually metal-insulator-metal (MIM) tunable capacitors for several reasons, especially electrical field dependent permittivity, size and low dielectric losses [Bahl, 2003]. These requirements enforce considerable challenges on existing technologies and generate a necessity for new technologies and materials. The recent competing technologies are semiconductor varactor diodes, MEMS and ferroelectric devices for tunable circuits. Tunable microwave devices have paid more attention because of their wide applications in commercial, defence and space based communications. The microwave devices can be tuned in principle, by either magnetic or electric field. An electromagnetic wave propagates in the medium with magnetic susceptibility of 'μ' and dielectric constant of ε. The device tunability can be changed by applying an external electric or magnetic field, if either ε or μ of the materials is used to fabricate the device; the device would be tunable correspondingly.

Perovskite ferroelectrics are extraordinary materials which have high dielectric value and spontaneous polarization which can be switched reversibly by an applied electric field. Ferroelectrics have been developed for electrically tunable applications, such as phase shifters, tunable oscillators and varactors [Zhang *et al*, 2009; Subramanyam *et al*, 2000]. Ferrites are magnetically tunable materials and can be tuned by external applied magnetic field. Furthermore, microwave devices based on ferroelectric material was found to have much better performance over ferrite-based devices.

Ferroelectric technologies have received widespread attention because of their ability to achieve desirable characteristics for tunable microwave applications, having high-k and electrical field dependent dielectric permittivity [Tombak *et al*, 2003; Kim *et al*, 2002]. This considers them as potential candidates for tunable devices, which is of great interest in microwave engineering. Changing phase velocity with the change in dielectric constant by the applied field of the ferroelectric films, allows tuning of the films. The critical parameters needed are high tunability and low dielectric loss for optimum performance at microwave frequencies. Some materials which have shown a variable permittivity with electric field are $SrTiO_3$, (Ba, Sr)TiO_3, (Pb, Zr)TiO_3, (Pb, Ca)TiO_3, Ba(Ti, Sn)O_3, and Ba (Ti, Zr)O_3. In particular, Barium Strontium Titanate (BST) and Lead Zirconate (PZT) have been found as the most suitable perovskite ferroelectric materials because of the higher dielectric constant, high tenability, high power handling and low dielectric loss at room temperature [Acikel *et al*, 2002; Park *et al*, 2002; Lingxia *et al*, 2015]. Its high capacitance density allows the fabrication of high value capacitors in a very small area. The parameters that have been identified to affect the dielectric properties of perovskite oxide films are film composition, microstructure and surface morphology. Applications of ferroelectric thin films in microwave devices have been investigated by several group [Bao *et al*, 2008; Xi *et al*, 2000] for use in frequency-agile devices. Theoretical considerations for description and analysis of ferroelectrics has been summarised by Tagantsev *et al* [Tagantsev *et al*, 2003] and reviewed thoroughly the progress in the development of electrically tunable dielectric materials. It is worth mentioning that perovskite diectric are suitable for tunable application with high dielectric constatnt, low losses and tunable behaviour with effect from an applied electric field.

1.1 MOTIVATION AND OBJECTIVES

For devices used in space systems, nuclear installation and military applications, radiation exposure is an additional reliability concern. Electronics are exposed to various forms of radiation, such as charged and uncharged high energy radiation including gamma and neutron. Total ionizing dose irradiation causes the buildup of oxide vacancy and interface trap charges in the film. Si and SiO_2 thin film based devices have been fundamentally investigated for past several years and found to be sensitive to ionizing radiations. Device deterioration and increased power consumption reduces operation life time of electronic components in space systems. Many researchers have investigated radiation induced defects in semiconductor device [Yas, 2012; Trefilova *et al* 2001] and reported that irradiation of metal oxide devices with high level of ionizing radiation results in generation of point defects, defect clusters and dislocation center [Srour and Palko, 2013; Arshak and Korostynska, 2001]. The most crucial part of MIM devices are oxide layer where electron hole pairs are generated along with point defects due to irradiation and leads to changes in device properties [Miao *et al*, 2009]. Charge distribution in the devices is significantly influenced by the radiation induced phenomenon which can distort local field near interfaces and defects.

A lot of work has been done in the radiation effects community to investigate changes in MOS threshold voltage shifts after irradiation. However, not much work has been devoted to studying the effects of irradiation on the degradation and long-term reliability of perovskite oxide based tunable devices. These effects are addressed in this dissertation. An important area of research has looked at the behaviour of ferroelectric tunable devices within extreme environments. In such environments the material is prone to degradation or radiation induced changes. Several niche applications expose the material to substantial doses of ionizing radiation, be it from gamma rays, neutrons, space radiation, etc. Recently, the interest in these ferroelectric perovskite oxide thin films has been received attention and electronic properties were investigated for the irradiation hardness of the devices. It was revealed that role of the microstructure and phase-purity of the films is important on the radiation induced changes [Bastani *et al*, 2013]. Ionizing effects and atom displacement effects are the two main factors for the radiation-induced degradation in the ferroelectric properties. Point defects play a fundamental role in determining the physical and dielectric properties of perovskite materials and oxygen vacancies are present in the form of shottky or frenkel defects. These defects can produce pinning of the domain walls by easily accumulating along the domain walls and grain boundaries. Local field opposite to the direction of external field due to trapped charges might be originated by large amounts of the electron–hole pairs, generated by ionizing radiation. Therefore new materials and devices are required to be investigated for their reliability under gamma radiation exposure to study radiation induced changes in the device properties. Although much has been learned about radiation effects in conventional electronics in the past, relatively little is known about radiation effects on perovskite ferroelectric materials. Therefore, any attempt to contribute to the understanding of radiation damage in perovskite oxides is helpful in contributing to the general knowledge of radiation effects in the oxide films.

Typical experimental approaches to study ferroelectric thin film properties are usually based on electrical characterizations, e.g. capacitance-voltage and current-voltage characteristics. The device performance and the physical properties such as polarization, dielectric behavior and their dc leakage current are closely related to the microstructure and the interfaces between thin film layers. However, such macroscopic methods are rather limited to identify the microstructural, surface and interface properties due to the interdependence of parameters. Radiation induced changes in macroscopic device performance are caused by electrically active microscopic defects. In addition, the microscopic properties cannot be directly accessed from such experimental approach. Therefore study shall be based on the understanding the relation between defects and macroscopic properties. One of our objectives is to make use of x-ray diffraction (XRD) and X-ray photoemission spectroscopy (XPS) to investigate the structural and electronic chemical states properties of ferroelectrics thin films. XPS has been widely used for many years to study semiconductor interface formation and is applied in the present work on perovskite-structure materials. Such XPS investigations of ferroelectric films were rarely performed and no systematic study of the influence of gamma irradiation is available in literature. XPS spectroscopy is an important analytical technique to study the near surface chemistry of materials [Baniecki *et al*, 2006]. The main work of present thesis is dedicated to radiation induced changes in thin film perovskite based capacitors. These devices are also called dielectric varactors or tunable capacitors and the perovskite oxide thin films are used as dielectric layers in these capacitors. The advantages of employing the technology of such devices are a passive integration, the relatively high permittivity of thin ferroelectric films and continuous (low voltage) tuning (typically <40Vdc), [Klee *et al*, 2001] with no hermetic packaging, and no moving parts.

1.2 ORGANISATION OF THESIS

This thesis is concerned with the deposition and integration of perovskite oxides; BST and PZT thin films for voltage tunable microwave circuits. The core objectives are to realise perovskite thin films with radiation induced effects on dielectric tunability and losses and to demonstrate these films in a microwave integrated circuit. Therefore, this thesis is somewhat multidisciplinary; the two major areas of investigation are in the fields of materials science and microwave engineering. The present work has been focused on the realization of fabrication of novel ferroelectric tunable oxide thin films and their characterization for various physical properties viz. structural, surface, photoemission spectroscopy and electrical properties for its use in high energy radiation environments. Thin film structures based on BST and PZT were fabricated and characterized. A specific concern is to investigate the irradiation effects on surface and structure of the films for dielectric layer and finally radiation response on macroscopic capacitance-voltage (C-V) and Current-voltage (I-V)/leakage current characteristics. The contents of each chapter are described briefly below:

Chapter 2 describes basic theory of dielectrics and ferroelectricity. The need for microwave tunable devices was briefed. Various frequency-agile technologies were discussed and importance of the Barium Strontium Titanate (BST) and Lead Zirconate Titanate (PZT) thin films for microwave tunable applications has been described. MIM and IDC configurations were discussed. Effects of radiation and its response on microstructural and dielectric properties of perovskite oxides were also discussed.

Chapter 3 describes various experimental techniques which have been used in this research work. It gives the details of the various thin film deposition set up and the basic principles of structural, physical and electrical characterizations of the thin film. A brief on sample irradiation under high energy gamma and neutron radiation were discussed.

Chapter 4 addresses the growth, structural and microstructural studies of $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films grown by RF sputtering technique. The deposition parameters were optimized to obtain good quality film by varying Ar flow rate and substrate temperature. After realization desired structural properties and electrical performance, gamma irradiation effects were studied and compared the structural properties of irradiated BST thin films with respect to pristine. The surface chemical states of gamma-ray irradiated BST thin films were also investigated by XPS. Microwave variable capacitors or varactors, are formed by depositing metal electrode using thermal evaporation on the surface of the BST films.

Chapter 5 deals with dielectric behavior and leakage current of BST thin films as a function of gamma dose on gold plated IDC structure. Varactors of interdigitated capacitor (IDC) structure were fabricated using photolithography on BST films, deposited on sapphire substrates. The radiation induced electrical properties of BST thin films varactor are discussed. The C-V and I-V characteristics and tunable properties were measured of BST thin films using IDC structure before and after sample irradiation at different cumulative doses.

Chapter 6 addresses neutron radiation induced response on C-V and I-V characteristics of BST thin films on IDC structure to investigate the conduction properties as a function of neutron fluence. The neutron induced structural and surface morphologies of BST thin films were also discussed.

Chapter 7 describes the growth and characterization of epitaxial PZT thin film, deposited by pulsed laser deposition on SRO substrate. A novel material composition $PbZr_{0.52}Ti_{0.48}O_3$ (PZT) with a much higher dielectric constant was chosen for high tunability application. The study on structural and chemical states of epitaxial grown PZT thin films were carried out at different gamma doses. In addition, surface roughness and leakage current characteristics of PZT thin films were measured as a function of gamma doses. Moreover, XPS is used to account for the possible change in surface chemical states in PZT films.

Chapter 8 deals with impact of gamma radiation on electrical properties of the PZT based varactor devices as a function of gamma-ray irradiation dose. The ferroelectric properties were studied by C-V measurements on various Pt electrode areas, deposited by lift off technique on PZT thin films. The C-V measurements were carried out as a function of gamma irradiation doses and the observed behaviour has been attributed to the radiation induced point defects, ionized oxygen vacancies and the trap controlled space charge current. The device tunability was calculated from C-V measurement and showed the role of irradiation on tunability. DC leakage conduction studies were also performed and analyzed to confirm the presence of defects in these thin films varactor.

Chapter 9 gives the summary and conclusions of the present study and future work was discussed that will give more insight into the understanding of radiation induced properties. Throughout this thesis, we have successfully observed the role of structure and oxygen vacancy defects on the dielectric properties of thin film complex oxides, allowing a greater understanding of radiation induced changes in macroscopic properties of voltage tunable ferroelectric devices.

1.3 LIST OF PUBLICATIONS

1.3.1 Peer Reviewed Journas Publications

The findings of present thesis work have been recognised by various renowned peer reviewed journals. A list of publications is as follows:

1. **S. S. Barala**, V. S. Bhati and M. Kumar, "High energy photon induced Fermi-level shift of $Ba_{0.5}Sr_{0.5}TiO_3$ thin films", *Thin Solid Films,* Vol. 639, pp. 107-112, 2017.

2. **S. S. Barala**, B. Raul, N. Banerjee, and M. Kumar, "Modulation of Pb chemical state of epitaxial PZT thin films under high energy irradiation", *Journal of Applied Physics*, Vol. 120, pp. 115305, 2016.

3. **S. S. Barala**, J. Singh, Mohit Kumar and M. Kumar, "High Tolerance of BST Thin Film based Varactor under Neutron Irradiation", *IEEE Transactions on Electron Devices,* Vol. 63, pp. 3677-3682, 2016.

4. **S. S. Barala**, N. Banerjee and M. Kumar, "Effect of Gamma Ray Irradiation on Epitaxial $Pb(Zr,Ti)O_3$ /$SrRuO_3$ Tunable Varactor Devices", *Journal of Electronic Materials*, Vol. 45, pp. 4122-4128, 2016.

5. S. Ranwa, **S. S. Barala**, M. Fanetti and M. Kumar, "Effect of gamma irradiation on Schottky-contacted vertically aligned ZnO nanorodbased hydrogen sensor", *Nanotechnology,* Vol. 27, No. 34, pp. 345502, 2016.

6. **S. S. Barala**, J. Singh, S. Ranwa and M. Kumar, "Radiation Induced Response of $Ba_{0.5}Sr_{0.5}TiO_3$ based Tunable Capacitors under Gamma Irradiation", *IEEE Transactions Nuclear Science,* Vol. 62, pp. 1873-1878, 2015.

1.3.2 Conference Paper

1. **S. S Barala,** S. Ranwa and M. Kumar, "Gamma Radiation Effects on Electrical and Structural Properties of $Ba_{0.5}Sr_{0.5}TiO_3$ based Capacitor", *18th International Workshop on Physics of Semiconductor Devices (18th IWPSD),* IISc, Bangalore, India, December 7-10, 2015.