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Gamma Radiation Induced Structural and Surfcae Chemical Changes in $PbZrTiO_3$ Thin Film

7.1 INTRODUCTION

Perovskite oxides have a particularly wide range of applications with their ferroelectric and piezoelectric properties and have been explored in sensors, transducers and electronics components. Lead zirconate ($PbZr_{1-x}Ti_xO_3$) based devices has several commercially applications including voltage tunable capacitors, infrared detectors, microactuators and non-volatile ferroelectric random-access memory (Fe-RAM). $PbZr_{1-x}Ti_xO_3$ (PZT) thin films have emerged as leading candidates among the various tunable ferroelectric materials, for such applications due to their highly nonlinear dielectric response to an applied electric field [Kingon, and Srinivasan, 2005]. Among various approaches, ferroelectric/dielectric layered composite is proved to be a flexible and efficient way [Tagantsev *et* al, 2003; Cole *et* al, 2003]. Significant efforts have also been invested to maintain high dielectric tunability while decreased dielectric losses through epitaxial growth of the PZT film. This can also be achieved by constructing a variety of composite structures consisting of multi layer ferroelectric materials and oxides with smaller losses and leakage current [Kong *et al*, 2010; Dimos *et al*, 1998]. Its chemical formula is expressed as $PbZr_xTi_{1-x}O_3$ where x is the fraction of Lead zirconate. PZT exhibits both piezoelectric and ferroelectric properties meaning that it can retain a spontaneous electric polarization and the strength of the polarization is coupled to the strain field in the crystal. Epitaxial template structure is considered as a promising method [Lu *et al*, 2003] to improve devices properties for its high tunability and low loss tangent. Epitaxial strain engineering on ferroelectric thin film can significantly enhance their properties and provide opportunity to many new applications and novel functionalities [Zhang *et al,* 2005]. Variety of heterostructures and multilayers have been included for many promising ferroelectric based devices, such as tunable varactors and memory capacitors. The demonstration of the devices with their ferroelectric properties such as leakage current, polarization, imprint and fatigue are governed by the interfaces between the constituent layers and finally the whole microstructure of the films. However in such heterostructure, it is desirable to have each layer with epitaxially nature and smooth surface to reduce the density of defects to minimize any degradation at the interfaces. Jeon *et al* focused on film texturing to improve the dielectric properties interms of increased tunability and lower dielectric loss of BST thin films [Jeon *et al*, 2002]. Y. Lin *et al* and Nakayama *et al* have reported electrical properties and the fatigue characteristics of the PZT films with effect of the crystal orientation [Y. Lin *et al,* 1998; Nakayama *et al*, 2004]. It is observed that (100) structure of PZT thin films in both Ti-rich and Zr-rich compositions revealed a better fatigue characteristic in comparison of (111) oriented PZT films [Chen *et al*, 2001]. Hence, electrical properties are also governed by the orientation of the PZT films.

However, large lattice mismatch and severe interface diffusion on bare silicon restrict deposition of epitaxial ferroelectric films on bare silicon substrates. Therefore, high-quality epitaxial or high oriented ferroelectric films were achieved by using different structural templates and buffer layers to overcome these issues to grow on the silicon substrates which included layers such as $LaNiO_3$, $LaSrCoO_3$, MgO, $SrTiO_3$ (STO). Metallic perovskite type oxides were frequently used among the buffer layers as an epitaxial template for growth of ferroelectric films as well as bottom electrode. Similarly $LaSrCoO_3$, $SrRuO_3$ (SRO) and $LaNiO_3$ have also been realized as a potential template material [Chae *et al*, 2002].

PZT based device might be used in the future in radiation environments such as space and nuclear reactor. Potential satellite and spacecraft applications of PZT include microwave communication devices and Fe-RAM. Radiation effects comprise the variety of changes in the microscopic and macroscopic properties upon exposure to ionizing radiation. There is a wide range of radiation damage phenomena, however, are unique to a particular thin films and depend on its structure, composition, physical dimensions etc. Radiation effects are mainly displacement and ionization effects. Displacement effects pertain to those properties tied to the arrangement of atoms within a structure, while ionization effects relate to the re-distribution of electrons within the thin film materials. Gamma irradiations produce change primarily through ionizations and isolated Frenkel pairs. A large amount of electron-hole pairs are generated by the ionizing radiation. These mobile charge carriers are separated by applied electric fields within the material. Strong localized fields occurring near structural discontinuities such as the grain boundaries and ferroelectric-electrode interfaces. Oxygen vacancies in the form of Shottky or Frenkel defects are naturally present in oxides and concentration of such vacancies can be reduced or increased by numerous ways. Physical and chemical properties of inorganic materials are principally governed by the point defetcs. The changes in the material properties hold good for both bulk as well as surface of oxides, where large number of point defects exist and demonstrate a complex and rich chemistry. The nature of oxygen vacancies changes abruptly which is associated to the electronic structure of the material and ultimately gives rise to significant changes in macroscopic properties of the devices.

In this chapter, we report the preparation and characterization of $PbZr_{0.52}Ti_{0.48}O_3$(PZT) epitaxial structured thin films deposited by pulsed laser deposition for high tunability application at low operating voltage. The PZT films were irradiated with ^{60}Co gamma radiation source for different gamma dose. Also structural and chemical states of epitaxially grown PZT thin films were investigated at different gamma doses. In addition, surface roughness and leakage current characteristics of PZT thin films as a function of gamma dose was measured. Moreover, XPS is used to account for the possible change in electronic structure of BST. The thin film growth procedure and their structural and microstructural characterization are discussed in next sections.

7.2 PLD GROWN EPITAXIAL PZT THIN FILM

Pulsed laser deposition (PLD) process involves ejected atoms form a highly directional plume immediately after ablation, with the axis projected out from the target. Thin films are formed on a substrate from the vapour phase by the nucleation and growth of individual islands (or clusters) as discussed in Chapter 2. The atoms get adsorbed on the surface of the substrate. Subsequently adsorbed atoms, which strongly depend on temperature of the substrate surface can diffuse on the substrate surface with own diffusion coefficient. Thereafter depending on the material's vapour pressure and bonding of the atoms to the substrate, these atoms can either re-evaporate or form clusters. The free energy of the cluster, relatively to an assembly of individual atoms is a governing factor to make balance between growth and dissolution process for a given cluster.

PZT thin films are made using PLD where a high intensity KrF excimer laser is used to ablate material within a vacuum chamber. A plasma is formed which expands and collected on a single crystal $SrTiO_3$(STO) substrate. The substrate temperature is controlled along with other deposition parameters; target-substrate distance, laser fluence, substrate temperature and background gas mixture. Single crystal substrates of $SrTiO_3$ (001), with a typical size of 5 mm x 5 mm x 0.5mm was used. Prior to annealing, the substrates were cleaned using acetone and ethanol under ultra-sonic agitation. $SrRuO_3$ (SRO) layer was grown on STO substrate. A PLD system from Faculty of Science and Technology and MESA+ Institute for Nanotechnology, University of Twente, The Netherlands was used for the PZT film deposition. The deposition was carried out by Dr Mahesh Kumar during his visit to the University of Twente. KrF 248 nm excimer laser with pulse duration of 25 ns was used to ablate material from sintered power or

single crystal targets. A rectangular mask was used to create a well-defined and homogeneous laser profile on the target. The laser fluence was controlled using a variable beam attenuator. The background gas pressure was in the range of 0.15−0.08 mbar. The resistive heater allowed for accurate temperature control up to 850 ^{0}C in this setup. The infrared laser was aligned on the backside of the sample plate prior to every deposition. $SrRuO_3$ growth by PLD was done at an energy density of 2.5 J/cm^2, a laser repetition rate of 4 Hz and a spotsize of 2.5 mm^2. $SrRuO_3$ was ablated from a compressed powder pellet with a target-substrate distance of 50 mm. The background pressure was set to 0.13 mbar with a gas mixture consisting of equal parts of oxygen and argon. The substrate temperature was set between 600 ^{0}C. Samples were post-annealed during cool-down at a rate of 25^0/min in 100 mbar of oxygen. PZT films were grown using a laser fluence of 3.5 J/cm^2, a spot size of 1.8 mm^2, laser repetition rate of 10 Hz, substrate temperature of 600 ◦C, target substrate distance of 5 cm and a pressure of 0.10 mbar oxygen. The samples were cooled down at a rate of 10^0/min in the growth pressure. Epitaxial $PbZr_{0.52}Ti_{0.48}O_3$ (200nm) layers using $SrRuO_3$(100nm) bottom electrode were grown on $SrTiO_3$(STO) substrate by PLD.

Table 7.1: PZT Deposition parameter

Parameters	PZT	SRO
Pressure	0.10 mbar (O_2)	0.13 mbar (O_2)
Energy Density	3.5 J/cm^2	2.5 J/cm^2
Deposition Temp.	600 ^{0}C	600 ^{0}C
Laser Pulse Frequency	10 Hz	4 Hz
Target to substrate distance	60 mm	50 mm
Deposition rate	.042 nm/pulse	.022 nm/pulse

7.2.1 Gamma Irradiation of PZT thin film

The PZT samples were then irradiated with gamma radiation using ^{60}Co radiation source at dose rate of 3 kGy/h upto 200 kGy. The structural characterizations were performed before and after gamma irradiation.

7.3 STURUCTURAL ANALYSIS OF PZT/SRO/STO THIN FILM

X-ray diffraction (XRD) 2θ-ω scans were carried out using Cu Kα radiation to determine the crystalline orientation and phase of PZT film. XRD patterns of the thin film heterostructure are shown in Figure 7.1. The appearance of the (*00l*) Bragg peaks, commensurating with the single crystalline STO (001) substrate proves the epitaxial growth and no additional peaks emphasizes the phase purity of the complex oxide heterostructure. According to intensity ratio of (00*l*) peaks, it was confirmed that highly (001) oriented PZT thin film were grown. In order to study the effect of gamma radiation, we have evaluated the structural properties of PZT films as a function of gamma doses. XRD spectra are shown in Figure 7.2 and changes in FWHM of the 2θ peak for different gamma dose are observed. The FWHM of (001) diffraction peak varied gradually from 0.148 to 0.168 with increased gamma dose from 0 kGy to 200 kGy respectively, reflects decrease in the crystallinity of PZT film which is related to defects. It is likely that irradiation allows generation of oxygen vacancies resulting in the increase of FWHM. The result suggests that gamma irradiation put a remarkable effect on the structure of the film which favors an increase in oxygen vacancies, hence give rise to surface relaxation in the gamma irradiated film.

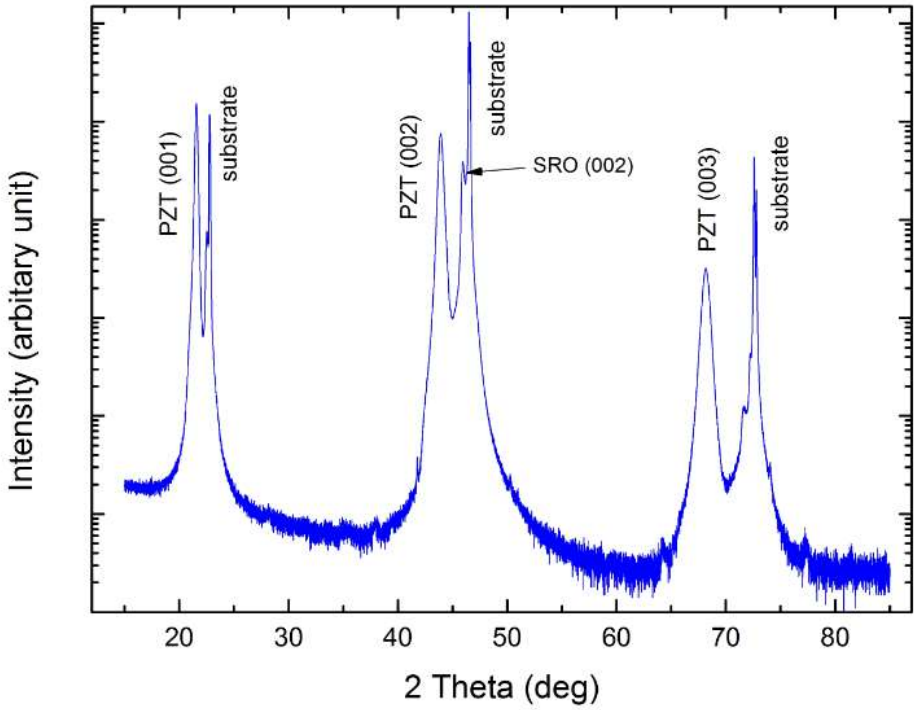

Figure 7.1: XRD 2θ-ω scan of pristine PZT epitaxial film

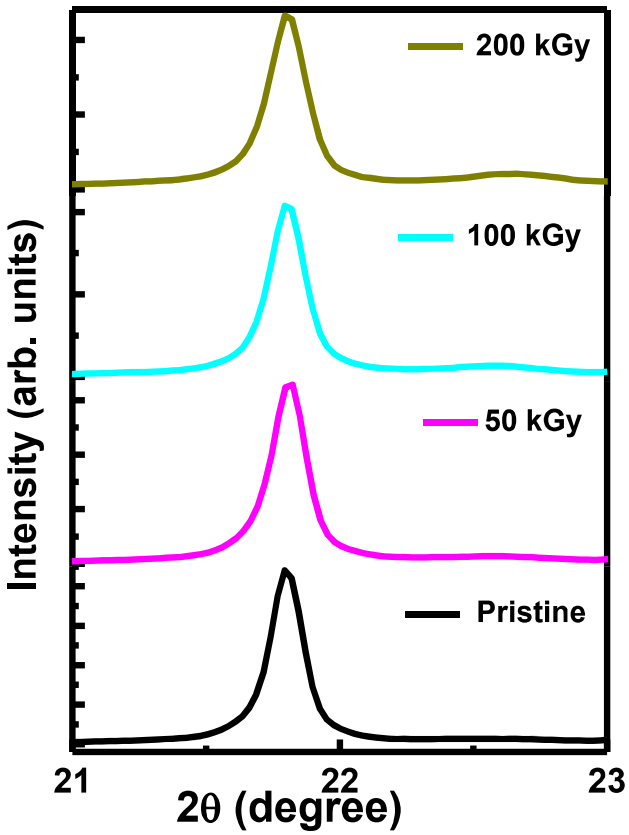

Figure 7.2: XRD scan PZT epitaxial film (001) diffraction peak at different gamma radiation doses.

7.4 SURFACE MORPHOLOGICAL STUDY

The surface morphologies observations were investigated by using an atomic force microscope (AFM). The AFM images recorded for the PZT thin films, exposed to different levels of the gamma radiation dose and shown in Figure 7.3. These images clearly show that the as-deposited thin film is smoother as compared to gamma irradiated films. The exposed thin films become more and more rough with the increase of the gamma radiation dose showing partial contribution of radiation induced defects and the formation of large sized clusters with voids takes place in the films exposed to higher radiation doses. It can be seen from AFM images that film tends to become rougher with increasing gamma dose due to radiation induced defects on the film surface and showed an increased root mean square (RMS) roughness from around 5.2 nm for pristine to 7.8 nm for 200 kGy sample. The interaction of gamma radiation to the film induces defects on the film which leads to disturbance on the film surface.

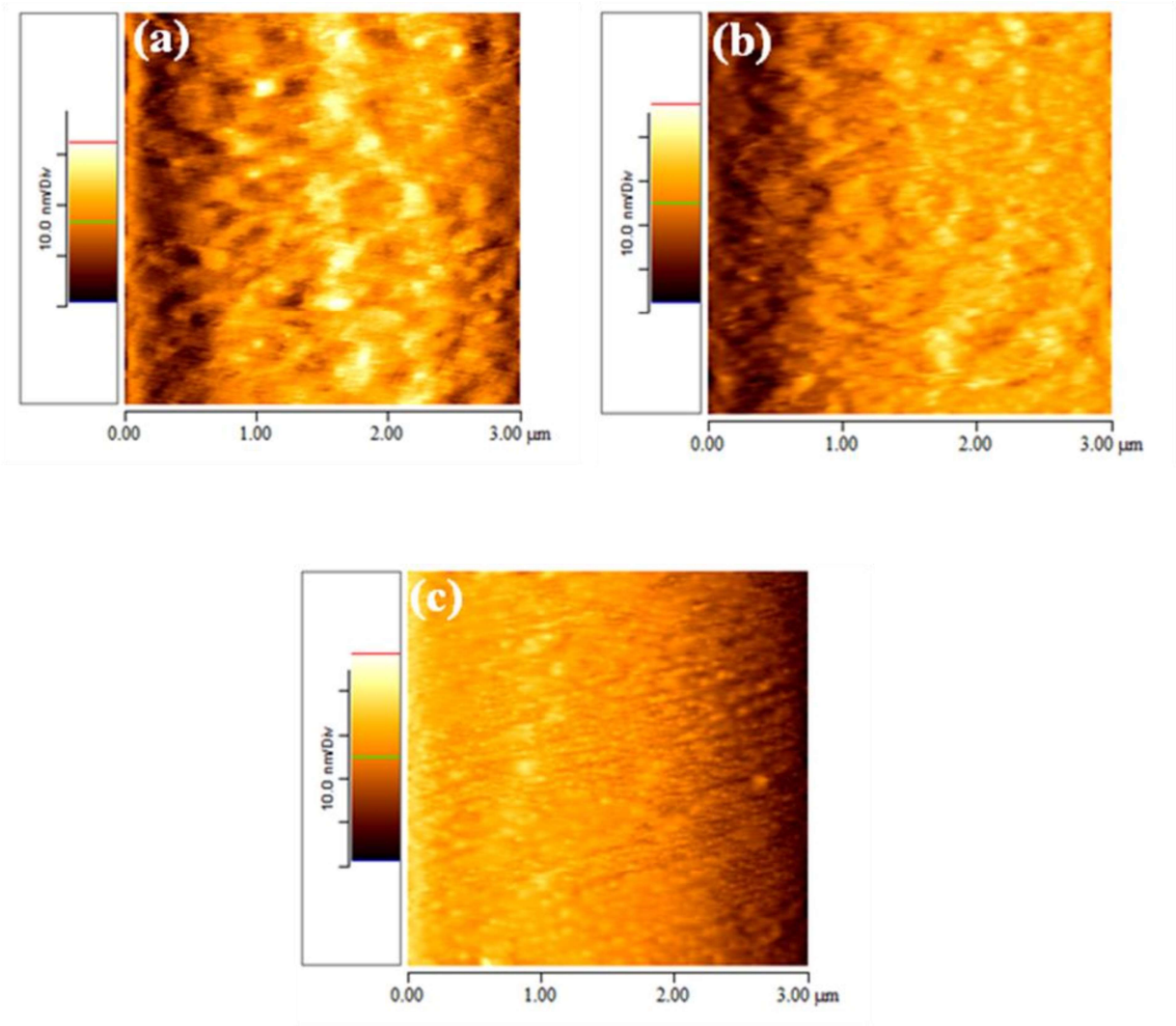

Figure 7.3: AFM images of the PZT films (a) Pristine, (b) 50 KGy and (c) 200 KGy.

7.5 X-RAY PHOTOELECTRON SPECTROSCOPIC ON PZT

At present electronic properties of the electronic oxides are found crucial to functional applications whereas better understanding of surface behavior would be of significant interest. Piezoelectric properties of thin films are greatly influenced by atomic concentration of the elements in the film and their positions in the ABO_3 internal structure [Sugyiama *et al*, 1997]. The distribution of valance electrons produces measurable shift in core level spectra. The atomic composition with high surface sensitivity can be measured by XPS. The distinct advantage of XPS is to cause relatively little irradiation induced damage to easily reducible materials such as

ions containing Pb^{2+} and considered non destructive technique. Significant progress have been carried out to understand the physics of core-level photoemission from surface of PZT however the surface electronic properties and even the core level spectra of such complex oxide is still uncertain in different aspects. Fujisaki *et al* has studied chemical states of degraded layer on PZT surface and investigated the role of surface layer in the macroscopic properties [Fujisaki *et al*, 1997]. Effects of chemical etching have been studied from the XPS surface analysis and the intensity variations of the Pb-O and Ti-O peaks were analyzed [Kang *et al*, 2002]. Ar-ion etching is being used for surface cleaning and depth profiling and the ions had an apparent effect on chemical compositions and lattice atom displacement in PZT thin films [Chang and He, 2004; Kim *et al*, 2003]. Metallic Pb (Pb^0) and PbO (Pb^{2+}) in PZT were resolved using Ar-ion bombardment by Chang *et al* and Kim *et al*. XPS depth profiling shows evidences of oxygen deficiency associated with the reduction of Pb^{2+} to Pb^0 and attributed to preferential sputtering of oxygen at the surface of PZT thin films [Watts *et al*, 2005].

The X-ray Photoelectron Spectroscopy (XPS) measurements described in this section were performed at Indian Institute of Science (IISC), Bangalore using Al K_α radiation(1486.6 eV) and a takeoff angle of $\theta=45^0$. The pressure was kept 10^{-9} Torr in the analysis chamber during the scans. For PZT samples which are highly insulating, a positive charge zone will be developed on the surface as the photoelectrons are emitted out of the sample surface. This would result in a shift in the XPS peak position due to positive potential which can vary from few volts to tens of volts. Binding energy of adventitious carbon, C 1s peak with a characteristic binding energy is used as the reference for calibration in such a case. The core electron of an element has a specific binding energy and governed by the chemical environment of the element. The core electron of the same atom can exhibit a binding energy change if bonded to different chemical species. This variation in the binding energy will result in the shift of the corresponding XPS peak.

It has been studied that high energy X-ray and gamma ray irradiations may result in polarization loss and possible retention failure in ferroelectric thin films, as reported previously in $Pb(Zr,Ti)O_3$ and $PbTiO_3$ thin-film devices [Schwank *et al*, 1990; Gruverman *et al,* 2002]. Ferroelectric properties dependes on the nature of defects and compositions [Mukhopadhyay and Chen, 1993]. The irradiation induced deterioration may be more severe in military and space applications due to the higher possibility to be exposed to high energy irradiations for ferroelectric thin films. High energy gamma-ray irradiation can displace large number of atoms from their own site to the other sites, which lead to change in chemical environment of the atom and in turn may affect the chemical state of the atom. Recently many of reported studies were focused on gamma ray irradiation on PZT thin films and high radiation hardness was observed than semiconductor materials [Gao *et* al, 1998; Yang *et al*, 2014]. Scott *et al* reported radiation hardness of the PZT thin film above 50 kGy of total doses [Scott *et al*, 1989]. High energy radiation induced structural changes in device material, by changing in the atomic concentration due to the bond breaking and its possible reorganization after irradiation [Rai *et al*, 2010]. The ferroelectric properties are important to most of the devices but have not been explored in much detail with respect to the effect of the surface chemistry in radiation environment. Previous XPS studies for perovskite oxides have shown different chemical states of constituent atoms in the PZT and BST thin films and surface core-level shifts have been revealed by various mechanisms including oxygen vacancies, under-coordinated atoms reduction [Rajopadhye *et al*, 1987] and interface relaxation of surface [Cracium and Singh, 2000; Baniecki *et al,* 2006]. Properties of oxides materials are directly or indirectly correlated to the existence of defects, oxygen vacancies. These defects determine the optical, transport and electronic properties of the material and also lead the chemistry of film surface. To the best of our knowledge, there is yet no report on the effects of gamma irradiation on surface chemical states of epitaxial PZT thin films however the irradiation resistance is important to the device reliability. Consequently, it is important to investigate and understand the effects of high energy irradiation on the chemical states of epitaxial ferroelectric films for their potential use in such environment. The object of this work is to investigate the changes in chemical states of epitaxially grown PZT thin films.

The PZT films have three components (e.g. TiO_2, PbO, and ZrO_2,) in a PZT solid solution. The surface chemical states of gamma irradiated PZT films were investigated with XPS analysis. The XPS analysis for the elements of Pb, Zr and Ti was performed to estimate peak energies more accurately and the peak energies were extracted by curve-fitting on the XPS spectra. The curve fitting results were obtained by the subtraction of a Shirley background, followed by Voigt function. All the spectra of Pb, Zr and Ti consist of two peaks corresponding to their angular moments of the electrons. The photoemission core level spectra of Pb4$f_{7/2}$ and Pb4$f_{5/2}$ spin-orbit-spin doublets are shown in Figure 7.4 for pristine and gamma irradiated samples. The Pb4*f* core level spectra of pristine thin film, as shown in Figure 7.4(a) are fitted with singlet at binding energy (BE) of 137.8 eV and 142.7 eV for $4f_{7/2}$ and $4f_{5/2}$ chemical states respectively [Chang *et al*, 2004]. From Figure 7.4(b) and (c), It is noted that there is a demonstration of irregular shift with increasing radiation doses. It was observed from this analysis that higher binding energy shift was observed with respect to the pristine at initial increasing dose of gamma-ray irradiation, similar to HfO_2, reported by Cheng *et al* [Cheng *et al*,2013]. The chemical states are shifted towards higher B.E and found at 138.1 eV ($4f_{7/2}$) and 142.9 eV ($4f_{5/2}$) at 50 kGy gamma dose as reflected from Figure 7.4(b). This higher chemical shift of lead could be attributed by radiation induced surface relaxation or defect state of the PZT layer by gamma radiation induced defects [Cracium and Singh, 2000; Li *et al*, 2005].

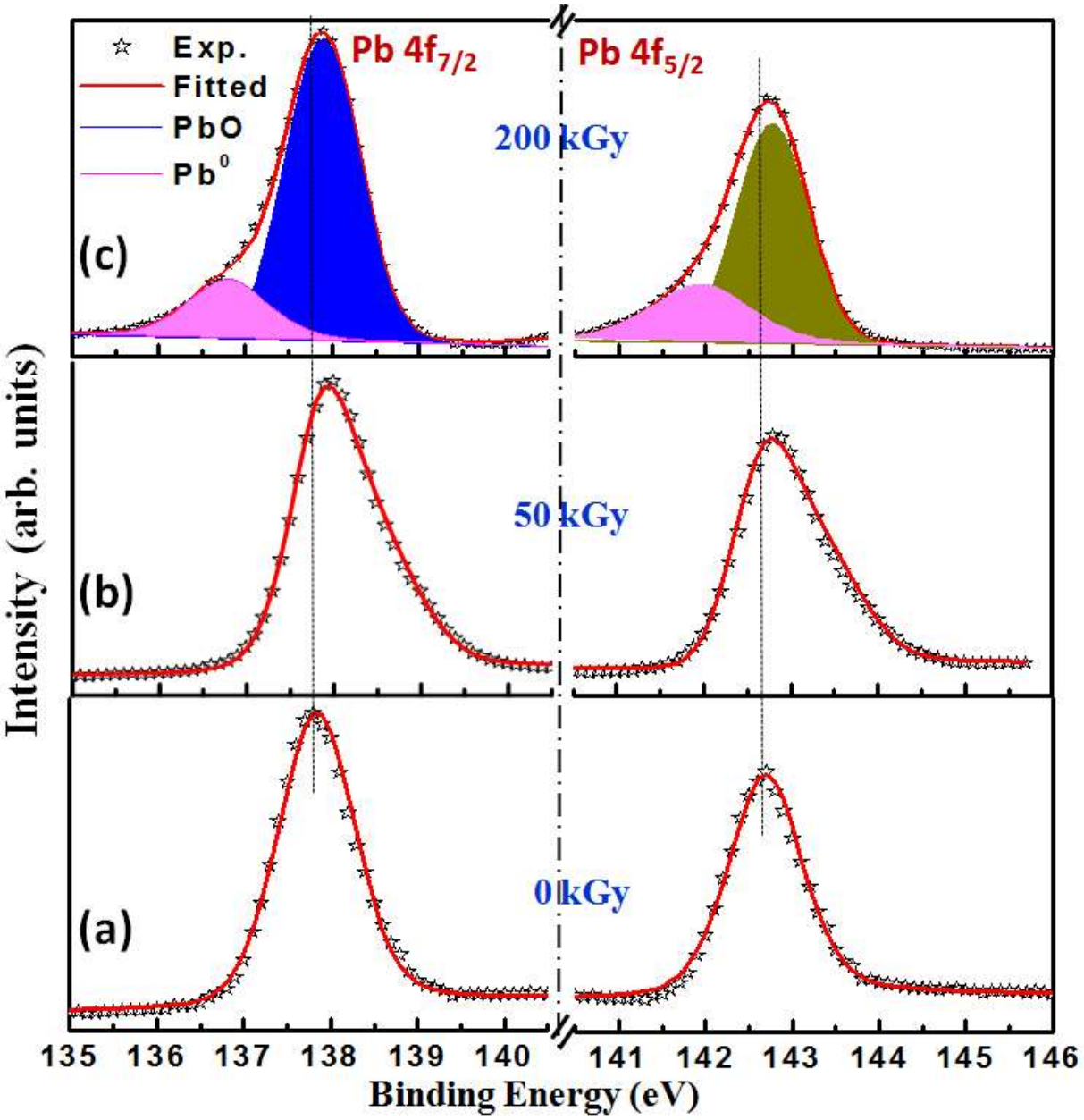

Figure 7.4: XPS core level spectra of Pb 4f ($4f_{7/2}$ and $4f_{5/2}$) (a) Pristine, (b) 50 kGy, and (c) 200 kGy.

The fitting for Pb4*f* core level for gamma dose of 200 kGy could not be derived by singlet and curve fitting was performed with doublets in both $4f_{5/2}$ and $4f_{7/2}$ states. Moreover second components of Pb 4f core level spectra at higher gamma dose of 200 kGy shifted towards lower BE and lies at 136.8 eV ($4f_{7/2}$) and 141.9 eV ($4f_{5/2}$) because of reduction in metallic Pb from PbO in PZT. At the dose of 200 kGy the corresponding Pb 4f levels were located about ~1eV lower BE than pristine, assigned as metallic Pb peak. The emergence of metallic Pb can be explained due to preferential sputtering of oxygen ions and reduction of Pb^{2+} ions to metallic Pb^0 [Kim *et* al, 2003]. As revealed by Figure 7.4(c), the lead atoms within the XPS investigation were found to be partially reduced to Pb^0 after radiation exposure as similarly reported for many oxides on Ar ion bombardment [Rajopadhye *et al*, 1987; Kim *et al*, 1976]. The PZT surface undergoes surface depletion of lead along with chemical reduction of Pb^{2+} to its metallic state [Mukhopadhyay *et al*, 1993]. Possibly gamma radiation bombardment breaks the chemical Pb-O bond to metallic Pb and oxygen, as a result of bond breaking and its reorganization in the film after gamma-irradiation.

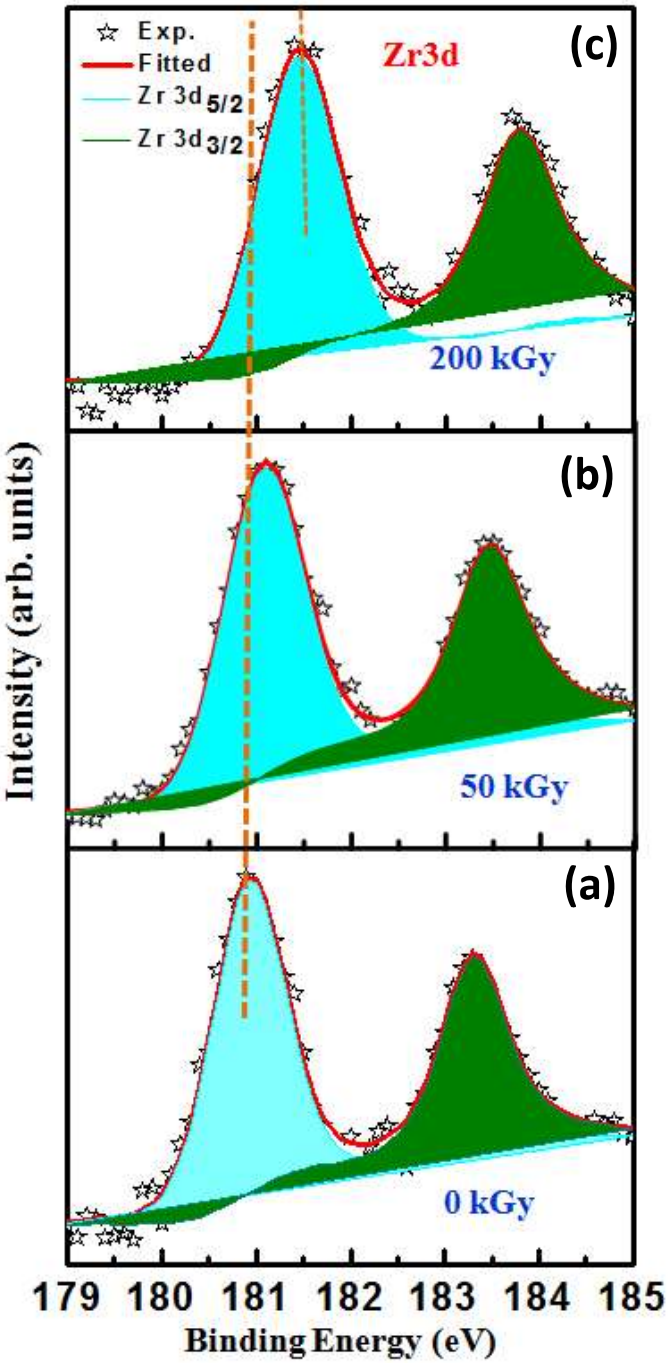

Figure 7.5: XPS core level spectra of Zr 3d ($3d_{5/2}$ and $3d_{3/2}$) (a) Pristine, (b) 50 kGy, and (c) 200 kGy

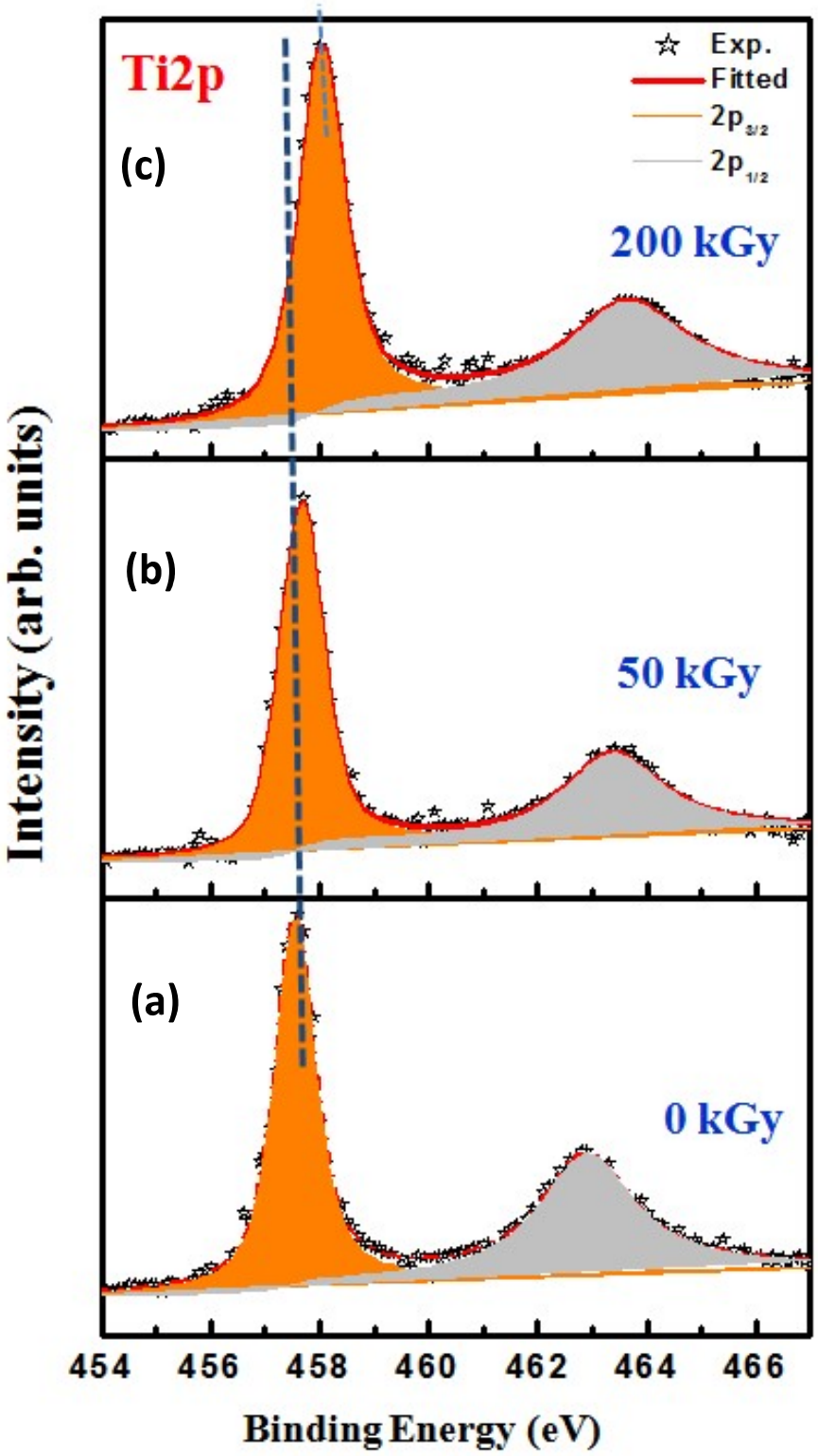

Figure 7.6: XPS core level spectra of Ti 2p ($2p_{3/2}$ and $2p_{1/2}$) (a) Pristine, (b) 50 kGy, and (c) 200 kGy

The Zr3*d* photoemission core level spectra are shown in Figure 7.5 for gamma-irradiated and peaks are observed at binding energies of 180.9 eV and 183.3 eV, respectively for pristine film. The Ti2*p* photoemission core level spectra are shown in Figure 7.6 for gamma-irradiated doses of 0 kGy (pristine), 50 kGy and 200 kGy. From the Ti2*p* XPS spectra of pristine Ti2$p_{3/2}$ and Ti2$p_{1/2}$ peaks are observed at binding energies of 457.5 eV and 462.8 eV, respectively. The Zr3*d* and Ti2*p* line shape at all the doses can be described by chemical shift towards higher BE. The higher binding energy shift were attributed to Zr and Ti atoms in relaxed surface[Li *et* al, 2005; Cracium and Singh, 2000] as similar to Pb atoms. The Zr3*d* and Ti2*p* spectra do not exhibit any noticeable change towards lower binding energy.

7.5 LEAKAGE CURRENT ANALYSIS

For electrical characteristics measurements, Pt electrodes were patterned by photolithography technique onto PZT films. Metal-ferroelectric-metal (MFM) structure was employed for measuring the leakage current (I-V) behaviour by SCS Keithley 4200 system. Figure 7.7 displays the dependence of the leakage current of the capacitor as a function of applied bias at different gamma dose up to 200 kGy. The dip in the current of pristine device has been described as negative differential resistivity (NDR) by Scott *et al* [Scott *et al*, 1994], caused as a result of double injection of both electrons and holes into PZT from electrode and trap filling process[Zhu *et al*, 2013; Chen *et al*, 1997]. The increase in the leakage current after gamma irradiation, in turn barrier reduction may be expected to be caused by the migration of oxygen from the surface as well as loss from the bulk [Rajopadhye *et al*, 1987]. Dih *et al* have reported the role of oxygen in increasing the conductivity [Dih and Fulrath, 1978]. The increasing leakage current may be attributed to the gamma radiation induced defects on the PZT film. The reduced Pb^{2+} in PZT contains some missing oxygen ions, where each missing O^{2-} ions require two additional electrons to maintain the electrical neutrality. The valency of the metal ion should reduce in such reduced metal oxides so that the free electrons might be available, contribute in increasing current [Lazarusand and Sham, 1982]. The increase in the leakage current and disappearance of NDR were associated with metallic Pb produced by gamma irradiation.

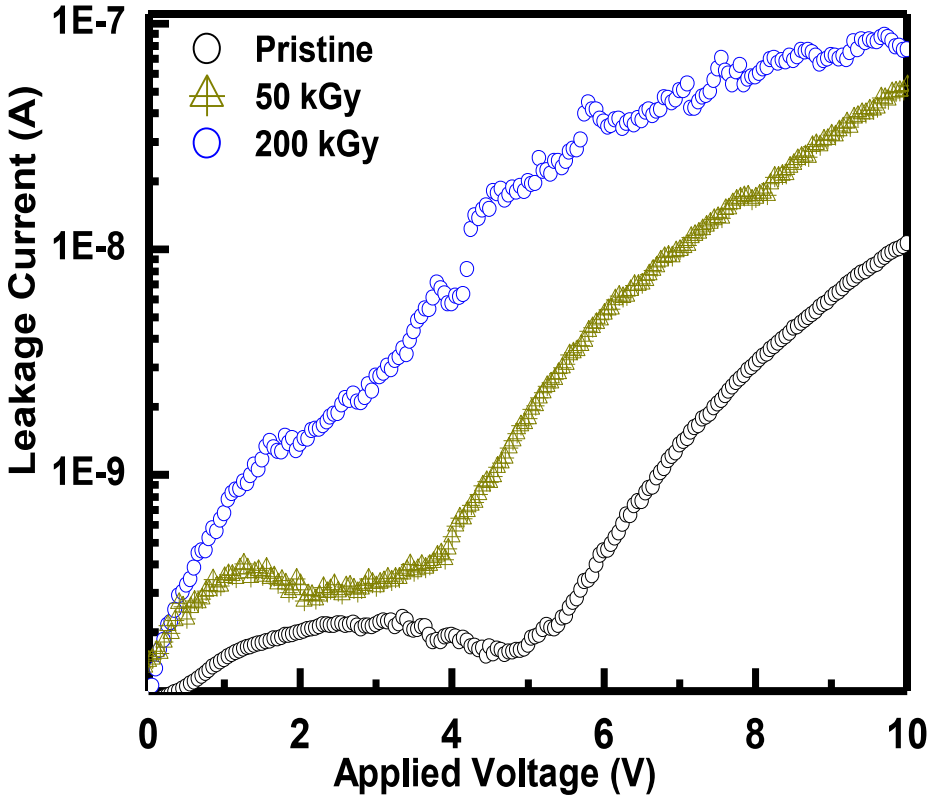

Figure 7.7: Leakage current characteristics of Pt/PZT capacitor as a function of gamma dose.

7.6 CONCLUSIONS

In this chapter, epitaxial heterostructure of ferroelectric PZT(001)/$SrRuO_3$(SRO) were grown on single crystal $SrTiO_3$ (001) substrates by pulsed laser deposition technique and platinum (Pt) electrode was deposited on top of PZT film. Gamma radiation induced changes

were observed in structural and morphology of the PZT thin film. The FWHM of (001) diffraction peak increased gradually with increased gamma dose and shows decrease in the crystallinity of PZT film which is related to defects. The dependence of the chemical states of the constituent elements of the PZT thin film on the gamma irradiation doses were investigated using XPS. The different binding energies of the Pb lines correspond to both Pb (2+) and metallic Pb (0) were observed. The high BE shift of the Pb lines for initial gamma dose followed by shifting towards lower BE at the surface layer were attributable to the surface relaxation and reduction mechanism of Pb respectively. The Ti2*p* and Zr*4f* line in the PZT film could have been associated with surface relaxation only and reflected towards higher BE shift with increasing irradiation dose. This study has shown the effects of the gamma radiation induced defects on the structure and dielectric properties. As expected, an increase of surface roughness with the increasing gamma dose in turn decreases the crystallinity. The NDR behaviour in pristine PZT was found to disappear at gamma dose of 200 kGy, in turn favour the presence of metallic Pb in the PZT film. These results corroborate the increase of the leakage current of Pt/PZT capacitor as a function of gamma dose.