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Conclusions and Future Scope of Work

9.1 CONCLUSIONS

In this dissertation, a systematic study of the radiation effects by high energy radiation namely gamma and neutron were investigated on structural, surface chemical states and dielectric properties of two perovskite ferroelectric material systems i.e. Lead Zirconate Titanate ($PbZr_{0.52}Ti_{0.48}O_3$) and barium Strantium Titanate ($Ba_{0.5}Sr_{0.5}TiO_3$). The main findings of the investigations are as follow:

RF sputtering technique was used to grow $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin film and growth parameters were optimised including optimum substrate temperature and Ar flow rate. The crystal structure of the film was characterised using X-Ray diffraction technique and the BST phase was confirmed. Dielectric properties on as grown Ni/BST/Si configuration were measured and characteristic bell shaped C-V behavior along with small leakage current was observed. Further, BST thin films were investigated as a function of gamma irradiation doses and high energy gamma irradiation was performed on BST using ^{60}Co source. Gamma radiation induced structural and surface morphological changes were observed in comparison with pristine sample. An increasing FWHM of diffraction peak was observed with higher gamma dose and surface roughness was also increased due to gamma radiation induced surface modification. The surface chemical states were investigated using X-ray photoelectron spectroscopy and it was demonstrated that gamma ray treated BST surface layer exhibits shift of surface core-level features of Sr, Ba and Ti atoms towards higher binding energy. The XPS analysis indicated a shift in the core levels associated to a shift in Fermi level position which also signifies donor-like character of gamma treated BST. These variations of electronic structure are responsible for the increase of leakage current and accordingly decrease in dielectric capacitance in the gamma irradiated BST thin film. The decrease in optical band gap was observed with increasing gamma dose due to the change in localized states near to the band edges. The increase in binding energy shift is not because of a compound but could be a relaxed BST surface, gamma induced oxygen vacancies and residual defects.

The gamma radiation effects were investigated on electrical properties of interdigitated capacitor (IDC) patterned $Ba_{0.5}Sr_{0.5}TiO_3$ (BST) thin films, fabricated using photolithography technique. Gamma irradiation induced changes of the BST based IDC capacitor have been investigated under various doses from 0 kGy to 600 kGy. The capacitance of the BST varactors was measured at different frequencies from 200 kHz to 1 MHz. A decrease in capacitance for low doses ($\leq$ 50 kGy) and a noticeable increment above 50 kGy doses was observed. This indicates the presence of the different type of defects for different cumulative dose. Also increasing leakage current characteristics confirmed the current serving path provided by grain boundaries along with increased number of radiation induced defects. The changes in the electrical properties may be attributed by the radiation induced damage introduced to the device, causes to structural changes which have been revealed from XRD and AFM. A presence of space charge polarization is mainly responsible to increase the capacitance, caused due to structural changes by high gamma irradiation. The well-known bell shaped C-V characteristics did not distorted upto 600 kGy which suggest possible application of BST based tunable devices for radiation environment. The tunability (~25%) was observed of the un-irradiated device which remained nearly constant after gamma irradiation doses.

Further, neutron induced effects on BST based IDC patterned tunable varactors were also investigated. ^{252}Cf neutron source was used to irradiate the BST samples up to neutron fluence of $7.5x10^{11}$ n/cm^2. X-ray diffraction and atomic force microscopy characterisation were performed on neutron irradiated samples for their structural and morphological changes respectively. AFM results confirmed increasing roughness of the surface and degraded the surface quality with increasing neutron irradiation. The capacitance was found to decrease for lower neutron fluence and a significant rise in capacitance value towards pristine device at higher neutron fluences of $5x10^{11}$ n/cm^2 and $7.5x10^{11}$ n/cm^2, indicates the presence of the different type of defects in the BST film. The changes in the electrical properties by irradiation to the device could be attributed by induces defects, displacement damage, causes to structural changes which have been revealed from XRD. The increased number of defects due to neutron irradiation also confirmed by increasing leakage current characteristics. Also the presence of space charge polarization caused due to structural changes may be associated to the increase in capacitance value after certain neutron fluence.

Epitaxial heterostructure of ferroelectric PZT (001)/$SrRuO_3$(SRO) were grown on single crystal $SrTiO_3$ (001) substrates by pulsed laser deposition technique. Effects of high energy gamma radiation induced changes were studied in structural, surface morphology and surface chemical states of the PZT thin film. The FWHM of (001) diffraction peak was observed to increase with increasing gamma dose which reflects decrease in the crystallinity of PZT film, linked to radiation induced defects. AFM characterisation showed that the gamma exposed thin films has higher surface roughness with the increase of the gamma radiation dose and the formation of large sized clusters with voids takes place in the films at higher radiation doses. As expected, an increase of surface roughness with the increasing gamma dose in turn decreases the crystallinity. The dependence of the chemical states of the constituent elements of the PZT thin film on the gamma irradiation doses were investigated using XPS. There were two different binding energies of the Pb lines were observed correspond to both Pb (2+) and metallic Pb (0). The high BE shift of the Pb core level for initial gamma dose followed by shifting towards lower BE for higher gamma dose were demonstrated. The shifting towards higher and lower binding energy at the surface layer was attributed to the surface relaxation and reduction mechanism of Pb respectively. The Ti2*p* and Zr4*f* line in the PZT film could have been associated with surface relaxation only and reflected towards higher BE shift with increasing irradiation dose.

The epitaxial Pt/PZT/SRO tunable varactor devices were fabricated on single crystalline STO (001) substrates and platinum (Pt) electrode was deposited on top of PZT film in order to study the effect of radiation on the dielectric properties of the epitaxial film. Ferroelectric capacitance voltage (C-V) curves were acquired for discrete frequencies from 100 kHz to 500 kHz with small ac signal amplitude of 30 mV. The epitaxial pristine devices demonstrated higher dielectric tunability (55%) in comparison to the polycrystalline films and lower loss. The impact of ionizing radiation on electrical properties of the varactor devices was measured as a function of gamma-ray irradiation dose. Significant degradation of dielectric properties was reflected with the increasing radiation dose by measurement of C-V curve as well as loss tangent of PZT varactor. The C-V curves exhibited substantial changes in terms of negative voltage shift along with distortion in the curve shape after gamma-irradiation. The tunability were studied as a function of gamma-radiation dose and found to decreases linearly with increasing radiation dose. This degradation in the electrical properties can be attributed mainly by pinning of the domain walls, caused by radiation-induced defects accumulated at the domain boundaries with increasing dose on PZT varactor. The roles of radiation generated defects, charge carriers leads to significant enhancement of the leakage current with increasing radiation dose. The NDR behaviour in pristine PZT was found to disappear at higher 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. Synthesis of defect free epitaxial thin film enabled us to investigate the changes in intrinsic properties of the PZT based varactor.

This study shows that high energy radiation induced defects play important role to the electrical properties of the devices and the BST based devices are observed highly resistant to gamma and neutron radiation, which reflects possible use in space and nuclear applications. The results achieved would be highly valuable in order to prepare the maintenance schedules for the varactor devices functioning in a radiation environment and also to predict the operating life-time of such devices with integrated ferroelectric films.

9.2 FUTURE SCOPE OF WORK

With the assumption that defect and defect clusters play a key role in the loss of domain switching and domain wall mobility and these can also be evidenced by other experimental techniques. Further experimental work could be done to identify the concentrations and types of defects which are being generated from high energy radiations. A list of measurement techniques may include Rutherford backscattering spectrometry, Photoluminescence spectroscopy, Electron paramagnetic resonance spectroscopy (EPR) and Transmission electron microscopy (TEM) which have been used in other materials to characterize particular clusters such as di-vacancies/interstitials and complexes. These measurements will be applicable for detecting spectral features associated with the defects. There is a small amount of work can be undertaken in terms of modelling the radiation damage event, damage growth, and the relationship between defects and ferroelectric properties. The input can be generated with the help of local density approximation density functional theory (DFT) along with Molecular Dynamics (MD) to achieve most accurate damage cascade simulations. The information obtained through DFT and MD simulations are necessary ingredients in succeeding kinetic Monte Carlo (MC) calculations.