CHAPTER 6
Ferroelectric Capacitors
Ferroelectric capacitors were fabricated using LSCO and LSCNO as the electrodes. BST and PZT were used as the ferroelectric material. The structural, electrical and polarization properties of the capacitors were analyzed and were compared with a capacitor fabricated using conventional electrode, ITO. LSCNO emerges as new electrode material for ferroelectric applications.
6.1 Introduction

Ferroelectric thin films have potential applications in nonvolatile ferroelectric random access memory and microelectromechanical systems [1-5]. The wide applications of these materials make them an important topic of research in the recent years. Non volatile ferroelectric random access memory (FeRAM) can be realized using a ferroelectric capacitor. The spontaneous polarization of the ferroelectric material is used in the realization of ferroelectric memory device. The two directions of the spontaneous polarization can be used to represent the two binary logic states “0” and “1” of the memory device [2, 6-7].

Low leakage current, good resistance to breakdown, large polarization, low coercive field, negligible fatigue, minimal imprint are the important prerequisite for the use of ferroelectric capacitors in commercial memory device [6-8]. The reliability of the ferroelectric capacitor depends immensely on the choice of bottom electrode. The electrode material has direct influence on the nucleation, microstructure and electrical properties of the ferroelectric material [2, 9-11]. The electrode must have low resistance, better adhesion to the ferroelectric and layer under the electrode and should provide chemically stable environment for the growth of ferroelectric material and the operation of the device [9,12].

The major degradation factors of the ferroelectric capacitors are fatigue, imprint and logic state retention loss [2, 7, 13]. Fatigue is the loss of switchable polarization when subjected to repeated read/write cycles. The main reason for fatigue is the entrapment of oxygen vacancies, which are the main ionic defects in the ferroelectric-electrode interface. These defects will develop space charge at the interface. This causes the pinning of the domain thereby reducing the switchable polarization with increasing polarization reversal [14, 15]. Imprint is the preference of a certain polarization state over the other. The asymmetric distribution of the charge defects or the oxygen vacancies is the possible cause for imprint [16, 17]. Logic state retention loss is the failure when the capacitor
and the corresponding memory element are unable to maintain a polarization state and clearly discriminate it from the opposite state for almost indefinitely. The asymmetry in the configuration of top and bottom electrode can cause the retention loss [6, 13].

The most commonly used electrode for ferroelectric memory devices is platinum (Pt) [18, 19]. The major drawback of using Pt electrode is fatigue due to the formation of oxygen depletion layer at the Pt-ferroelectric interface [15, 20]. The switchable polarization of the ferroelectric capacitor using Pt electrode is reported to reduce to 50% of its initial value after $10^6$ cycles [21]. Another metallic electrode is Al. PZT crystallizes in a cubic non ferroelectric phase over Al leading to poor ferroelectric properties [22]. The fatigue and imprint can be effectively reduced by the use of oxide electrodes due to their capability to absorb oxygen vacancies and/or their role as effective diffusion barrier [6, 11, 13]. There are two categories for the oxide electrodes: one is the common metal oxide such as RuO$_2$, and IrO$_2$; the other group is conductive perovskite oxides, such as LaNiO$_3$, La$_{0.5}$Sr$_{0.5}$CoO$_3$ and SrRuO$_3$.

The fatigue of the PZT capacitor is found to be reduced when using RuO$_2$, and IrO$_2$ as electrodes [23-26]. But the capacitors fabricated using RuO$_2$ had high leakage current due to the formation of Pb$_2$RuO$_7$, whereas that prepared using IrO$_2$ suffered from the inter diffusion of Ir with PZT [27, 28]. Conductive oxide electrode ITO has been utilized as the electrode for PZT capacitor. Even though PZT crystallizes readily on ITO, the electrode has high sheet resistivity which further increases when the heterostructure is annealed in oxygen [29, 30]. Cuprate superconductors are also used as electrodes for ferroelectric devices due to its fatigue resistance. But the anisotropic conductivity and thermal and chemical instability of the cuprate superconductors constraints its processing and usage [31].
Conductive perovskite oxide $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO), $\text{LaNiO}_3$ (LNO), and $\text{SrRuO}_3$ has similar crystal structure as that of ferroelectric and has good chemical stability [12, 32, 33]. Therefore they can serve as electrodes as well as growth template layers and protective barriers during device fabrication [33, 34]. These electrodes being conductive oxides reduce the accumulation of oxygen vacancies at the ferroelectric-electrode interface thereby effectively reducing fatigue and imprint [11, 15]. The perovskite oxide electrode enables the growth of ferroelectric layer along preferred orientation. Thus the leakage current behavior is reduced and the ferroelectric properties are enhanced [34, 35]. Also the better surface morphology of the perovskite electrodes gives good texture characteristics which gives better performance for the device [11, 36].

Ferroelectric capacitors using LSCO electrodes are reported to give superior device performance compared to capacitors using other electrodes. One reason for this phenomenon is the low lattice mismatch between LSCO and Pb-based ferroelectrics which promote the epitaxial growth of the ferroelectric layer over LSCO [33, 37]. LSCO is also the most conductive oxide among the conductive perovskite oxides with a room temperature bulk resistivity of 90-120 $\mu \Omega \text{cm}$ [38]. The large oxygen non stoichiometry in LSCO gives it high oxide ion diffusivity [39]. Therefore the LSCO electrodes effectively suppresses the polarization fatigue as it act as a sink of oxygen vacancies [14, 20]. This property of LSCO also reduces effectively the imprint behavior of ferroelectric capacitor [20]. LSCO can be grown at the similar growth conditions of the ferroelectric layer, ie at lower substrate temperature compared to other perovskite electrodes [9, 37]. This property is particularly interesting considering the device integration. LSCO can promote perovskite phase formation not only of Pb-based ferroelectrics, but also of other ferroelectric materials such as $\text{Ba}_{1-x}\text{Sr}_x\text{TiO}_3$ [9, 40].
Among the various ferroelectric materials perovskites and layered perovskites are widely investigated for ferroelectric memory applications. The lead based perovskite (PZT) is one of the promising candidates among the perovskite oxide due to its large remanent polarization and low coercive field [2, 7]. The lower crystallization temperature and duration for crystallization makes PZT a more attractive candidate for integration into complementary metal oxide semiconductor (CMOS) technology [8, 33]. The natural fatigue resistant behavior makes SrBi$_2$Ta$_2$O$_6$ (SBT) a promising candidate among layered perovskite. But the high crystallization temperature and lower dielectric constant makes the integration of SBT capacitors difficult [41]. A fairly new candidate among the perovskite oxides is Ba$_{1-x}$Sr$_x$TiO$_3$. Its large dielectric constant and fatigue free nature makes it another interesting candidate for ferroelectric memory device fabrication [42, 43].

In this chapter we discuss the preparation and characterization of ferroelectric capacitors using La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) and La$_{0.5}$Sr$_{0.5}$Co$_{0.5}$Ni$_{0.5}$O$_3$ (LSCNO) as electrodes. The devices were fabricated on p-type Si $<100>$ and Pt/TiO$_2$/SiO$_2$/Si substrates. Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) and PbZr$_{0.52}$Ti$_{0.48}$O$_3$ (PZT) was used as the ferroelectric materials for the fabrication of the device. Structural, electrical and ferroelectric characteristic of the fabricated device were investigated. The properties of the device are compared with the device fabricated using conventional electrode ITO.

6.2 Experimental Details

Ferroelectric capacitors were fabricated with BST and PZT as the ferroelectric material using LSCO and LSCNO as the electrode materials. Figure 6.1 shows the schematic diagram of the ferroelectric capacitor fabricated.
The ferroelectric capacitors fabricated using BST had the structure Si/LSCO/BST/LSCO and Pt/TiO₂/SiO₂/Si/LSCNO/BST/LSCNO. The top and bottom electrodes of LSCO and LSCNO were fabricated using rf magnetron sputtering. The electrodes were deposited at an rf power of 150 W at a target to substrate distance of 4 cm. The effect of crystallinity of the bottom electrode on the ferroelectric properties of the capacitors was compared by depositing the LSCO bottom electrode both at room temperature and at a substrate temperature of 600 °C. The LSCNO bottom electrodes for the capacitors were fabricated at a substrate temperature of 600 °C. The top electrodes for both the capacitors using LSCO and LSCNO were fabricated at room temperature. BST thin films were deposited by pulsed laser deposition using third harmonics (355 nm) of Q-switched pulsed Nd:YAG laser. Repetition frequency was 10 Hz with a pulse width of 6 -7 ns. Laser fluence was kept at 20 mJ. The deposition was carried out under an oxygen partial pressure of 0.1 mbar and substrate temperature during deposition was kept at 500 °C. An amorphous thin layer of BST (60 Å) was deposited at room temperature prior to the deposition of BST thin film at substrate temperature of 500 °C. This amorphous BST layer forms a buffer layer
for the growth of crystalline BST. The ferroelectric capacitors were also fabricated using PZT and they have the following structure: Pt/TiO$_2$/SiO$_2$/Si/LSCO/PZT/LSCO and Pt/TiO$_2$/SiO$_2$/Si/LSCNO/PZT/LSCNO. The LSCO and LSCNO electrodes were fabricated using rf magnetron sputtering. The bottom electrodes were deposited at substrate temperature of 600°C and the top electrodes were deposited at room temperature. The PZT layer was deposited by pulsed laser deposition. The deposition was carried out under an oxygen partial pressure of 0.1 mbar and the substrate temperature during deposition was kept at 300 °C.

The structural characterizations of the heterostructure were carried out using a Rigaku X-ray diffractometer with Cu K$_\alpha$ radiation ($\lambda=1.5418$ Å). The electrical properties of the device were studied using a Keithly Source Measure Unit (SMU 236). The Polarization-Electric field (P-E) measurements were obtained using RT66A ferroelectric tester.

6.3. Results and Discussion

6.3.1. Structural Properties

The X-Ray Diffraction (XRD) pattern of the Si/LSCO/BST heterostructure is as given in figure 6.2. The BST thin film was found to be polycrystalline in nature with no preferred orientation. Similar XRD pattern was also observed for the BST film grown on LSCNO as the bottom electrode. The perovskite phase of LSCO or LSCNO forms a better growth surface for the growth of perovskite BST [34]. In most processing conditions the ferroelectric layer develop the similar structure of the perovskite electrode layer below it [44].
Figure 6.2. The XRD pattern of the Si/LSCO/BST heterostructure. The indexed patterns correspond to that of BST.

LSCO bottom electrode layer is reported to induce the growth of PZT with certain texture because of the small mismatch between LSCO and PZT crystal lattice [45]. But the structural analysis of the Pt/TiO$_2$/SiO$_2$/Si/LSCO/PZT and Pt/TiO$_2$/SiO$_2$/Si/LSCNO/PZT revealed that only pyrochlore phase of PZT could be grown on LSCO and LSCNO bottom electrodes. The formed pyrochlore phase could not be transformed into perovskite PZT with post deposition annealing. The pyrochlore phase is a non-stoichiometric phase compared to perovskite phase and cannot completely transmit into perovskite phase even when annealed in high crystallization temperatures, if oxygen is insufficient for forming the perovskite phase [46]. The Pb deficiency may also lead to the growth of pyrochlore phase. Further optimization of composition and deposition parameters is necessary to grow perovskite PZT film.
6.3.2 Electrical Properties

The leakage current is an important characteristic of thin film capacitor. It influences the hysteresis loop and directly limits the charge retention. The leakage current is also a sensitive probe of the material quality of the metal-ferroelectric-metal surface, and it strongly dependant on the material aspect of the ferroelectric film and the electrode ferroelectric interfaces [47].

![Figure 6.3](image)

Figure 6.3. Current density ($J$) vs. electric field characteristics of BST capacitor (a) with LSCO electrode and (b) with ITO electrode

High leakage conduction in capacitors is a severe problem which can prevent their practical use for FeRAM. Recently there were reports on the reduced leakage current for PZT capacitors using nonconductive oxide electrodes [48]. Capacitor with low leakage current is ideal for microelectronic device application. The current density ($J$) versus electric field characteristics of the BST capacitor, one with LSCO and another with ITO as electrode are given in
The leakage current of the BST capacitor using LSCO electrode is about four orders of magnitude less than that using ITO electrode. The low leakage current density of the capacitor with LSCO electrode makes it a potential candidate for FeRAM device fabrication.

6.3.3 Polarization Properties

The polarization properties of the ferroelectric capacitor are analyzed using the P-E hysteresis loop. The polarization properties may be broadly classified into two categories: (1) using BST as the ferroelectric and (2) using PZT as the ferroelectric. The hysteresis loop measurements of the capacitors were made for various applied voltages.

i) BST Capacitor

![Polarization hysteresis of BST capacitor fabricated using ITO electrodes](image)

Figure 6.4. Polarization hysteresis of BST capacitor fabricated using ITO electrodes

BST capacitors were fabricated with both LSCO and LSCNO as the electrodes. The polarization properties of these capacitors were compared with that
fabricated using conventional ITO electrode. Figure 6.4 gives the P-E hysteresis loop of a BST capacitor fabricated using ITO as the top and bottom electrodes. The hysteresis loop is like that of a typical lossy dielectric and it does not show any saturation polarization. The lossy behavior of the device is due to the large leakage current associated with the capacitor [27].

The LSCO bottom electrodes were fabricated under two different growth conditions. The influence of the crystallinity of the bottom electrode on the ferroelectric properties of the capacitor was thus compared.

![Figure 6.5. P-E hysteresis loop of a BST capacitor with the LSCO as the top and bottom electrode with the bottom electrode deposited at room temperature](image)

**Figure 6.5.** P-E hysteresis loop of a BST capacitor with the LSCO as the top and bottom electrode with the bottom electrode deposited at room temperature

Figure 6.5 gives the P-E hysteresis loops of the BST capacitor fabricated using LSCO bottom electrode deposited at room temperature. In this case also the hysteresis loop was like a lossy dielectric with the lossy behavior increasing with the increase in applied voltage. The lossy behavior of the capacitor may be due to large leakage current of the device. The bottom electrode in this case was fabricated at room temperature at a sputtering gas pressure of 0.003 mbar with
Ar:O₂ ratio 80:20. The crystallinity of the bottom electrode was poor with a smaller grain size (8 nm). The electrode material directly influences the nucleation, microstructure and electrical properties of the ferroelectric layer [49]. The reduced crystallinity of the bottom electrode is reported to increase the leakage current of the ferroelectric capacitor [27]. During hysteresis loop measurement, the RT66A tester measures the charge collected on an integrating capacitor and converts it to polarization. The charge due to leakage also collects on the integrating capacitor and is therefore included in calculating the polarization. Thus leaky capacitors give false exaggerated polarization values.

![P-E hysteresis loop](image)

**Figure 6.6.** P-E hysteresis loop of a BST capacitor with the LSCO as the top and bottom electrode. The bottom electrode deposited at a substrate temperature of 600 °C.

The P-E hysteresis loop of the BST capacitor fabricated with the LSCO bottom electrode deposited at a substrate temperature of 600 °C is as shown in figure 6.6. The bottom electrode was fabricated at a sputtering gas pressure of 0.1 mbar with Ar:O₂ ratio 50:50. The top electrode of the capacitor was fabricated at room temperature at a sputtering gas pressure of 0.003 mbar with Ar:O₂ ratio 80:20.
The capacitor showed hysteresis behavior with the saturation and remanent polarization of 2 and 0.64 \( \mu \text{C/cm}^2 \) respectively, at room temperature with a coercive field of 25 kV/cm for an applied voltage of 4.4 V. The improved ferroelectric properties of the capacitor is due to the better crystallinity (grain size = 30 nm) and low resistivity (2x10\(^{-3}\) \( \Omega \text{cm} \)) of the bottom electrode. The improved crystallinity of the bottom electrode is found to improve the ferroelectric properties [50].

LSCNO was also used as the electrode for the fabrication BST capacitor. The LSCNO bottom electrode was deposited over Pt/TiO\(_2\)/SiO\(_2\)/Si substrate at a substrate temperature of 300 °C at a sputtering gas pressure of 0.1 mbar with Ar:O\(_2\) ratio of 50:50. The top electrode was fabricated at room temperature at a sputtering gas pressure of 0.003 mbar with Ar:O\(_2\) ratio of 20:80. Figure 6.7 gives the P-E hysteresis loop of the BST capacitor fabricated using LSCNO as the electrodes.

![Figure 6.7 P-E hysteresis loop of the BST capacitor fabricated using LSCNO as the electrodes](image)

**Figure 6.7** P-E hysteresis loop of the BST capacitor fabricated using LSCNO as the electrodes
The figure clearly indicates an improved ferroelectric behavior with large remanant polarization and low coercive field compared to the capacitors prepared using LSCO as the electrodes. The device had a remanent polarization of 6.7 μC/cm² and coercive field of 28.7 kV/cm for an applied voltage of 2.8 V. The better ferroelectric behavior of the device can be attributed to the better crystallinity (30 nm) and conductivity (ρ = 3.3x10⁻⁴ Ωcm) of the LSCNO electrodes. The improved conductivity of this LSCNO bottom electrode is due to the parallel conduction through the Pt layer beneath the LSCNO layer. The double electrode layer improves the ferroelectric properties with higher remanent polarization and low coercive field. The ferroelectric property of the Pb₀.₆Sr₀.₄TiO₃ layer deposited on the double electrode layer LSCO/Pt was better than that on single oxide layer such as LSCO [18]. The above result further substantiate that the conductivity and crystallinity of the bottom electrode are crucial in the properties of a ferroelectric capacitor.

The value of the coercive field E_c for the BST capacitor fabricated using both LSCO and LSCNO is larger than the reported values [51]. This is due to the small grain size of the BST thin film. Also the amorphous BST buffer layer act as a capacitive interface layer connected in series with the crystalline BST layer, thereby splitting the voltage that is applied to the multilayer films. This buffer layers reduces the dielectric constant of the device thereby increasing the coercive field [52].

ii) PZT Capacitor

Ferroelectric capacitors were also fabricated using PZT as the ferroelectric using LSCO and LSCNO as the electrodes. The ferroelectric properties of the PZT capacitor fabricated using LSCO as the electrode was compared with that prepared using LSCNO.
Figure 6.8 gives the P-E hysteresis loop of the PZT capacitor fabricated using LSCO as the electrodes. The LSCO bottom electrode in this case was fabricated at a substrate temperature of 500 °C on Pt/TiO$_2$/SiO$_2$/Si substrates. The sputtering gas pressure was 0.003 mbar with Ar:O$_2$ ratio 20:80. The top LSCO electrode was fabricated at room temperature at a sputtering gas pressure of 0.003 mbar with Ar:O$_2$ ratio 20:80. The device exhibited poor ferroelectric property with very low remanent polarization and high coercive field.

\begin{align*}
P_r &= 0.29 \mu C/cm^2 \\
P_t &= 0.24 \mu C/cm^2 \\
E_c &= 61.45 kV/cm
\end{align*}

![Figure 6.8](image_url)

**Figure 6.8** The P-E hysteresis loop of the PZT capacitor fabricated using LSCO as the electrodes

Figure 6.9 shows the P-E hysteresis loop of a PZT capacitor fabricated using LSCNO as the electrode. The bottom electrode was fabricated at a substrate temperature of 600 °C and the top electrode was fabricated at room temperature. The LSCNO electrode gave better ferroelectric properties to the PZT capacitor than that using LSCO electrode. The capacitor gave a remanent polarization of 2.9 \mu C/cm$^2$ with a coercive field of 58.4 kV/cm at an applied voltage of 7 V.
The better ferroelectric properties of the PZT using LSCNO electrode may be due to better crystallinity and conductivity of the LSCNO electrode compared to LSCO electrode. An improvement in the crystallinity of the bottom electrode is reported to enhance the remanent polarization of the capacitor [50].

\[
\begin{align*}
P_e &= 5.7 \mu C/cm^2 \\
P_r &= 2.9 \mu C/cm^2 \\
E_c &= 58.4 kV/cm
\end{align*}
\]

Figure 6.9 The P-E hysteresis loop of a PZT capacitor fabricated using LSCNO as the electrode

The hysteresis loop exhibited a discontinuity in polarization as the capacitor is switched from negative to positive voltage. The gap is more loss of retained charge during the period between setting the polarization state to negative \( P_r \) and starting the sweep of positive voltage. The loss of retained charge may be due to domain switching induced either by stress or space charge field [53]. The observed low saturation and remanent polarization of the capacitor is due to the pyrochlore phase of the PZT thin film [46]. Also the polarization is found to be less saturated in the capacitors. This is due to the applied voltage division
between the PZT and LSCNO layer. Therefore the voltage on the PZT layer is too low to make the polarization to saturate [54].

### 6.4 Conclusion

BST and PZT capacitors were fabricated using LSCO and LSCNO as the electrode materials. The structural, electrical and polarization behavior of the capacitors were studied and compared with ferroelectric capacitors fabricated using conventional ITO electrode. The LSCO electrode provides a low leakage current and better ferroelectric properties compared to conventional ITO electrode. The ferroelectric properties were found to depend on the crystallinity and conductivity of the bottom electrode. The capacitors fabricated using LSCNO as the electrode gave better ferroelectric properties than that using LSCO electrode. LSCNO opens up the possibility of a novel electrode material for ferroelectric devices.
References


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