Chapter 5

Pulsed laser deposition of BST thin films

Ferroelectric thin films such as BST, PZT and PLZT are extensively being studied for the fabrication of DRAMS due to their high dielectric constant. The large and reversible remnant polarization of these materials make it attractive for nonvolatile ferroelectric RAM application. In this chapter we discuss the characterization of $\text{Ba}_{0.7}\text{Sr}_{0.3}\text{TiO}_3$ (BST) thin films grown by pulsed laser ablation on different substrates. The structural and electrical properties of the fabricated devices were studied. Growth of crystalline BST films was observed on $\text{La}_{0.5}\text{Sr}_{0.5}\text{CoO}_3$ (LSCO) and $\text{La}_{0.5}\text{Sr}_{0.5}\text{Co}_{1-x}\text{Ni}_x\text{O}_3$ (LSCNO) thin film electrodes at low substrate temperature. PtSi/LSCO/BST/LSCO and PtSi/LSCNO/BST/LSCNO heterostructures were fabricated and the structural and electrical characterizations of these were also carried out. The leakage current and charge storage density is found to be suitable for 64 and 256 Mb DRAM applications.
5.1 Introduction

Ferroelectric oxide thin films with perovskite structure are currently of great technological interest due to their excellent properties for the application in dynamic random access memories (DRAMS) [143]. For tunable device applications, such as varactors, filters, oscillators, and phase shifters, ferroelectric materials, whose working principle is based on the nonlinearity of the internal electrical polarization steerable by an external electric field, have attracted considerable attention. Compared to currently popular tuning elements such as p-i-n diodes, GaAs Schottky diodes or ferromagnetics, ferroelectric components offer the advantages of continuous, quick, low power tunability up to the highest gigahertz frequencies, and easy integration [144, 145].

Barium strontium titanate \( \text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3 \)(BST) an environment friendly lead-free material is an attractive candidate for microelectronic devices. BST can be integrated to semiconductor technology such as next generation of giga byte dynamic random access memories because of high dielectric permittivity and low dielectric loss [146–148]. BST is the solid solution between barium titanate (BaTiO\(_3\)) and strontium titanate (SrTiO\(_3\)) over the entire range of concentration. The dielectric and ferroelectric properties of \( \text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3 \) depend on Sr content. At room temperature \( \text{Ba}_x\text{Sr}_{(1-x)}\text{TiO}_3 \) is ferroelectric, when \( x \) is in the range of 0.7-1 and is paraelectric when \( x \) is in the range 0-0.7 [36]. As a result the electrical and optical properties of BST can be tailored over a broad range for various electronic applications [26].

Ferroelectric thin films have been successfully deposited by rf sputtering [121, 149], metal organic chemical vapor deposition [149], sol gel [146, 149]
and pulsed laser deposition [143, 149–152]. Among these process the laser ablation process is most superior since it posses the advantages viz., lower synthesis temperature, easier in controlling the stoichiometry of thin films, possibility in depositing oxide films of high melting point and the materials of metastable phase [149].

Leakage current characteristics of BST films are also highly influenced by the electrode and film electrode interface characteristics. Deposition conditions, composition and electrode structure play most significant role in leakage current characteristics. Understanding the current transport mechanism is crucial and most of the knowledge is based on the transport across the interfacial potential barrier at the cathode when thermionic field emission or a combination of this is dominant. For all the mechanisms the leakage current density $J$ increases with increasing temperature leading to the increased probability for the electrons to overcome or to tunnel the barrier either at the interface or in the bulk due to higher thermal energy [153].

It is widely accepted that oxygen vacancies play an important role in perovskite ferroelectrics. Though the oxygen ambient is used to prevent the formation of oxygen vacancies in the deposited film, it has been shown that oxide films grown using PLD at high oxygen ambient pressure are still oxygen deficient [151, 152, 154, 155]. The lattice of an $O_2$ deficient BST film expands beyond the size reported for corresponding bulk ceramics [152, 154, 155]. One of the main technological challenges is to find a suitable electrode material with low electrical resistivity good thermal stability, high resistance to oxidation and good adhesion both to substrate and the ferroelectric film. The interfacial defect layers may originate from accumulation of oxygen vacancies. Under the electric field oxygen vacancies
migrate towards the electrode and aggregate near the electrode interface. The perovskite structured titanate could not afford a large population of point defects [156]. In the case of conducting oxide electrodes or aqueous solution electrodes, oxygen vacancies in the perovskite film in the region near the film electrode interface can be compensated by oxygen from the electrodes. Thus the use of this kind of electrodes inhibits the accumulation of oxygen vacancies at the interface. As a result no interfacial defect layer forms at ferroelectric oxide or ferroelectric aqueous interfaces [156].

Perovskite conducting oxide La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) is obtained from ABO$_3$ perovskite LaCoO$_3$ by partial substitution of La$^{3+}$ by Sr$^{2+}$ [36, 157]. The crystal structure of LSCO is same as that of the perovskite ferroelectrics which makes it a potential candidate as electrode for ferroelectric memory devices. The LSCO which is a conductive oxide electrode act as oxygen vacancy sink for the BST capacitors thereby reducing the fatigue problem usually encountered while using conventional Pt electrode [109, 158–160]. The similar crystal structure of LSCO and perovskite ferroelectrics facilitates the easy growth of ferroelectrics over textured or epitaxially grown LSCO layer [161, 162].

Some problems of porosity and poor adhesion are often reported in BST films and very high temperature thermal treatment is generally required to achieve well-crystallized BST thick films. Such a high temperature process could limit drastically the application potential of these BST films in integrated circuits [26, 144]. Low temperature deposition was achieved for BST thin films with deposition techniques like ion beam sputtering without any oxide buffer layer. But the dielectric constant of these films were low [144]. A low processing temperature is crucial for application of these thin film materials in integrated electronic devices. With oxide buffer layer the
deposition temperature has been reduced and crystallinity was observed without any post deposition treatment at relatively low temperature.

In this chapter the detail study on the growth of ferroelectric Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST) films deposited on PtSi substrates are presented. The electrical characterization of PtSi/BST/Au is discussed. The conduction mechanism and the band structure is studied. BST thin films were deposited on oxide electrode material like La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) and La$_{0.5}$Sr$_{0.5}$Co$_{1-x}$Ni$_x$O$_3$ (LSCNO). This LSCO and LSCNO will serve as an electrode as well as a template for the ferroelectric BST. The films were deposited using both the third harmonics (355nm) as well as the fourth harmonics (266nm) of Nd:YAG laser.

Commercial Si/SiO$_2$/TiO$_2$/Pt (PtSi) wafers were used as the substrate for deposition. The structure of discrete capacitors is shown in figure 1.1. Both the top and bottom LSCO electrodes were deposited by rf magnetron sputtering. The sputtering power was kept at 100W with an argon gas pressure of 0.003mbar at 600$^\circ$C. The films were crystalline and has a thickness of about 400nm. The resistivity of all the samples were of the order 10$^{-5}$Ω cm. The detailed growth and characterization of LSCO thin films grown in the laboratory has been reported elsewhere [163].

### 5.2 Experimental Details

BST thin films were ablated using the third (355nm) and fourth harmonics of Nd:YAG laser (266nm). The repitation frequency was 10Hz with a pulse width of 8-9ns. The laser fluence was kept at 2J/cm$^2$.

The target for PLD was prepared by solid state reaction of Barium titanate (BaTiO$_3$) and strontium titanate (SrTiO$_3$). The mixture was
pressed and sintered at a temperature of 1450°C for 5hrs to obtain Ba$_{0.7}$Sr$_{0.3}$TiO$_3$ (BST). The target was fixed at an angle 45° to the direction of laser beam and it was rotated at a constant rpm during the laser deposition, so that pitting of the target surface by the laser beam will be uniform. The focused high-energy laser beam ionises the target material and the 'plume” produced spreads out in the forward direction towards the substrates and it is slightly divergent. The substrate was placed at a distance 4cm to the target surface. The gas (oxygen) was bled into the vacuum chamber continuously at a fixed flow rate, while the chamber was simultaneously pumped to maintain a constant background pressure during deposition. The flow of oxygen ambient gas was controlled by a mass flow controller. The substrate temperature ($T_s$) was varied from 300°C - 600°C. The oxygen partial pressure in the chamber is 0.15mbar.

The crystallinity of thin films was determined by X ray diffractometry (XRD) excited with CuK$_\alpha$ radiation ($\lambda = 1.541\text{"A} )$ and surface morphology by AFM and SEM. Thickness of the samples were measured using Dektak 6M stylus profiler. Electrical characterization was carried out using Keithley SMU unit. The dielectric constant was calculated from the capacitance measured at 1kHz using LCR meter and polarization by Sawyer Tower circuit.
5.3 Growth of thin films ablated using 355nm and 266nm

5.3.1 Growth on quartz substrates

To study the optical properties BST thin film are deposited on quartz substrates using third and fourth harmonics of Nd:YAG laser. The crystallinity of these films were compared.

Figure 5.1: XRD pattern of BST thin films grown on quartz substrates at various deposition temperature and post annealed at 600°C in O₂ atmosphere using 355nm

As deposited films were amorphous on all the films deposited on quartz irrespective of the ablation wavelength used. Hence these films were annealed in oxygen ambience to induce crystallinity. The films were annealed in excess oxygen flow for 1hr at 600°C. All the films showed perovskite crys-
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talline nature on annealing irrespective of the wavelength used for ablation.
The thickness of the films were about 800nm.

The XRD pattern of thin films deposited using 355nm of Nd:YAG laser is shown below (figure 5.1). A laser fluence of $2\text{J/cm}^2$ was used for ablation. The films were deposited at 0.1mbar oxygen pressure at $300^\circ\text{C}$ and annealed at $600^\circ\text{C}$ in oxygen ambience. The (100) oriented growth trend is ascribed to the fact (100) plane is a closely packed $\text{O}_2$ plane which has the lowest surface energy in perovskite structure [134].

The XRD pattern (as in figure 5.2) of BST thin film deposited using 266nm also show a similar pattern. In this case also the laser fluence was maintained at $2\text{J/cm}^2$. All the films deposited were amorphous and required post deposition treatment. When compared with 355nm the films deposited using 266nm were smooth and better crystalline under the same condition.
The oxygen rich phase in perovskite (001) is seen in the films deposited at lower temperature irrespective of the wavelength used for ablation. The grain size of the films were calculated using Debye Scherrer’s formula. The films deposited using 266nm show larger grain size than films deposited using 355nm. The variation of grain size with substrate temperature for films deposited using 355nm and 266nm is shown in figure 5.3.
5.3.2 Growth on Si substrates

Thin films were grown at various temperatures on Si substrates (100) at 0.1 mbar oxygen pressure. All the as deposited films on Si were found to be amorphous. This may be due to the low oxygen pressure in the chamber during deposition. These films were annealed in oxygen atmosphere at 600°C for 1hr. The post annealed films were found to be crystalline. Figure 5.4 shows the XRD pattern of BST thin film grown at different temperatures. It can be seen that the crystallinity is better for thin films grown at lower temperature. The preferred orientation of BST thin films at each substrate temperature are determined from the thermodynamical
equilibrium between various depositions variables, including stress occurred on the thin films. The (100) oriented growth trend is ascribed to the fact (100) plane is a closely packed O₂ plane which has the lowest surface energy in perovskite structure.

**Figure 5.4:** XRD pattern of BST thin films grown by ablation using 355nm on Si substrates at various substrate temperatures and then post annealed at 600°C in O₂ atmosphere.

The thin film BST deposited using 266nm also showed perovskite structure similar to that of figure 5.4. Here also the films deposited at lower substrate temperature on annealing shows better crystallinity.
5.3.3 Growth of BST thin films on Pt Si substrates

PtSi act as a good substrate for the deposition of perovskite oxides. XRD pattern given in figure 5.5 shows the growth of perovskite BST thin films. The films were deposited at a substrate temperature of 600°C at 0.1mabr. The PLD films were always found to be oxygen deficient which hinders the crystallinity. Hence they need post deposition annealing in oxygen presence. In the present study the as deposited BST films were found to be crystalline even without oxygen annealing. The (100) oriented growth trend is ascribed to the fact that (100) plane is a closely packed O₂ plane which has the lowest surface energy in perovskite structure.

![Figure 5.5: XRD pattern of PLD grown BST thin films on PtSi substrates at 600°C: (a) using 355nm of Nd:YAG laser (b) using 266nm of Nd:YAG laser](image)

The films were deposited using 266nm of Nd:YAG laser as well. The XRD pattern of thin films show perovskite structure. The films show better crystallinity compared to films grown by 355nm laser wavelength all the other conditions being the same.
5.3.4 Growth of BST thin films on oxide electrodes

Figure 5.6: The XRD pattern of Si/LSCO/BST and Si/LSCNO/BST grown at 500°C at 0.1 mbar using 266nm of Nd:YAG laser

BST thin films were deposited on oxide electrodes LSCO and LSCNO using both 266nm and 355nm of Nd:YAG laser. LSCO and LSCNO were deposited using rf magnetron sputtering. The conditions for the growth and the XRD pattern of LSCO and LSCNO is discussed in chapter 3.

BST thin films were grown by PLD at 500°C at 0.1 mbar oxygen pressure on La$_{0.5}$Sr$_{0.5}$CoO$_3$ (LSCO) and on LSCNO electrodes. LSCO was grown on Si (100) substrates using rf magnetron sputtering. The LSCO crystallizes in the perovskite structure. It was found that there is better growth of BST thin films on LSCO and LSCNO electrode. The as deposited films were found to be crystalline without post annealing. A typical XRD pattern of the layers Si/LSCO/BST is shown in figure 5.6.

The BST perovskite film were grown at a lower substrate temperature on the LSCO and LSCNO electrodes. These oxide electrodes act both as a
template and as electrode for BST thin films. The perovskite BST thin film has a lattice constant of 3.95 Å. The LSCO materials also have perovskite structure with lattice parameter $a = 3.805$ Å. Crystalline growth of BST on LSCO thin films is due to the close match among the crystal structure, lattice parameter and atomic arrangements between LSCO layer and BST material [164].

5.4 Surface morphology and composition analysis

![Figure 5.7: SEM image of films (a) ablated using 355nm (b) ablated using 266nm of Nd:YAG laser (c) cross sectional SEM image of Si/SiO$_2$/LSCO/BST and (d) cross sectional SEM image of PtSi/BST](image)
Figure 5.8: AFM image of BST thin films deposited using (a) third harmonics and (b) fourth harmonics of Nd:YAG laser on Si substrates.
Surface morphology of thin films were studied using SEM and AFM images. The cross sectional SEM images were used to study the electrode-film interface. The compositional analysis were carried out using EDX measurements. SEM image of BST thin films shows that the films are smooth. The SEM images of BST thin films deposited using 355nm and 266nm of Nd:YAG laser is shown below (figure 5.7).

![AFM image of BST thin films grown on LSCO oxide electrode using fourth harmonics of Nd:YAG laser on PtSi substrates.](image)

**Figure 5.9:** AFM image of BST thin films grown on LSCO oxide electrode using fourth harmonics of Nd:YAG laser on PtSi substrates.

The AFM image of BST thin film deposited on Si substrates is shown in figure 5.8. The average roughness of BST thin film deposited using 355nm of Nd:YAG laser on Si substrates is about 29nm and that using 266nm is 22nm. The AFM image of BST thin films deposited on oxide electrode LSCO is shown in figure 5.9. The average roughness was found to be 19nm.

The compositional analysis of thin films shows that the films with per-
optical characterization

Ovskite phase has Ba+Sr/Ti ratio approximately 1 irrespective of the substrate used.

5.5 Optical characterization

Optical studies was carried out on BST thin films grown on quartz substrate using UV Vis NIR spectroscopy. The as deposited films do not show good transmission as the films were milky in appearance.

Figure 5.10: Transmission spectra of BST thin films grown by PLD using 266nm on quartz substrates at substrate temperature 300°C and then annealed at 600°C in O₂ atmosphere for 266nm

The films deposited on quartz substrates using 355nm of Nd:YAG laser after post deposition annealing show transmission less than 70% in the
visible region. But the films deposited using 266nm and annealed in oxygen ambience showed transmission greater than 85%. The transmission spectra of BST thin films deposited using 266nm is shown in figure 5.10.

The band gap of BST thin films is calculated using Tauc plot. The absorption coefficient $\alpha$ is related to the photon energy $h\nu$ as given by equation (5.1)

$$(\alpha h\nu) = A(h\nu - E_g)^n$$

where $E_g$ is the energy band gap and $n = 1/2$ for direct allowed transitions between valance and conduction band. Inset of figure 5.7 shows the plot of $(\alpha h\nu)^2$ vs $h\nu$. Band gap of BST thin films is found to be 3.51eV.

Refractive index ($n$) of the thin film was derived by the envelope method using the equation 5.2 and 5.3 [80].

$$n = \left((N' + (N'^2 - n'^2)^{1/2})^{1/2}\right)$$

$$N' = 1/2(1 + n_s)^{1/2} + \frac{2n_s(T_{max} - T_{min})}{T_{max}T_{min}}$$

where $T_{max}$ and $T_{min}$ are the corresponding transmittance maximum and minimum at a particular wavelength $\lambda$ and $n_s$ is the refractive index of fused quartz. The refractive index of the thin film was calculated to be about 2.

5.6 Electrical Characterization

5.6.1 Leakage current density

The leakage current of the samples were found from the current – voltage (I-V) curve, where the current is measured at a specified voltage. The leakage
current is an important characteristic of thin film ferroelectric capacitors, it directly limits the charge retention and it influences the ferroelectric hysteresis loop. The leakage current is also a sensitive electrical probe of the material quality of heterostructure as it is strongly dependent on material aspects of the ferroelectric film and of electrode-ferroelectric interfaces [165]. Capacitor with low leakage current is ideal for microelectronic device application.

Devices are fabricated in the structure PtSi/BST/Au and PtSi/LSCO/BST/LSCO/Au structures for the electrical characterization. The top Au electrode is deposited using a shadow mask by rf magnetron sputtering. The leakage current mechanism in the two device structures are different.

PtSi/BST/Au

The true I – V characteristics was performed by first analyzing the I – t characteristics. As it can be seen from figure 5.11, the current value after 100 seconds can be taken to be a near approximation of the true leakage current.

The leakage current of the device PtSi/BST/Au with applied dc voltage is shown in the figure 5.12. The measurement was carried out at room temperature with top electrode negatively biased. The method of obtaining the I – V characteristics was repeated over several electrode dots on the same sample and also samples from different batches to ensure reliability of the obtained data. An analysis of the slope at different regions of the I – V plot in a log – log plot gives an idea of the conduction processes involved under the influence of varying electric fields.
To ensure the universality of the obtained data, the current and voltage values were converted into current density and electric fields $J - E$ and are plotted in figure 5.13. Initially, the leakage current shows an ohmic behavior for low fields. At slightly higher electric fields, there is an onset of non-linearity, the cause of which can be said to be the onset of the space charge limited conduction (SCLC) mechanism.
Figure 5.12: The room temperature leakage current with applied dc voltage for the device PtSi/BST/Au

The space charge limited current follows the law

\[ I = \frac{V(l+1)}{d(2l+1)} \quad (5.4) \]

\[ l = \frac{T_t}{T} \quad (5.5) \]

where, \( d \) = thickness and \( T_t \) is the temperature parameter characterizing the trap distribution and \( T \) is the absolute temperature, for a distributed-trap space-charge limited conduction [36]. The type of trap present can be judged by the behavior of the \( I - V \) characteristics of the sample. The presence of grain boundaries usually contribute to the trap distribution, through structural and chemical defects. The verification of this particular process lies in the film thickness dependence characteristics.
Since the film is composed of ultra-fine grains, the space charge mechanism is governed by the size of the grain and not the film thickness. It was already shown that the value of d corresponds to the grain size and not the film thickness [157].

Region (I) corresponds to the low field region, region (II) and (III) corresponds to the intermediate field region and very high field region is not considered here. The corresponding slopes in the different regions are indicated by ohmic in nature, i.e. an enrichment space charge contact. Waser [158], reported that the ultra-fine-grained films are fully depleted of charge carriers and the conduction mechanism is completely electrode controlled. Though, the electrode plays an important role in the leakage current value, yet the presence of grain boundaries and their properties can

**Figure 5.13:** The log J versus log E plot of the device PtSi/BST/Au device
Electrical Characterization

variably change the value of the leakage current by orders of magnitude. Further, the conduction mechanism varies for films with different thickness ranges. Films with lower thickness (< 0.1µm) repeatedly show electrode limited conduction process, while films with higher thickness tends to be dominated by bulk properties. This can be attributed to the fact that complete depletion [158] of the film takes place if the film thickness is less, while for thicker films, the film is not completely depleted.

The current equation, governing the Schottky mechanism is given by [158].

\[ J = A^{**}T^2 \exp(\alpha E^{1/2} - W_b)/k_b T) \] (5.6)

\[ \alpha = \sqrt{\frac{q^3}{4\pi \epsilon_r \epsilon_0}} \] (5.7)

\[ W_b = W_m - q\chi \] (5.8)

where, \( A^{**} \) is the effective Richardson constant which incorporates carrier mobility, \( T \) is the absolute temperature, \( E \) is the applied electric field, \( W_b \) is the zero field barrier height, \( k_b \) is the Boltzmann constant, \( q \) is the electronic charge, \( \epsilon_0 \) is the permittivity of free space and \( \epsilon_r \) is the relative dielectric constant. \( W_m \) is the work function of the metal electrode and \( \chi \) is the electron affinity of the insulator.

For SrTiO\(_3\) and BaTiO\(_3\), the reported value of the electron affinity are \( q\chi_{SrTiO_3} = 4.1 \text{ eV} \) [159] and \( q\chi_{BaTiO_3} = 2.45 \text{ eV} \) [160], respectively. Assuming the electron affinity of the BST film to be very nearly equal to SrTiO\(_3\), the barrier height is around 1 eV for the Au contact. The value of the barrier height justifies the presence of a Schottky or blocking contact at
the metal insulator interface. A charge depletion region is thus formed near the interface to account for the difference in the Fermi level of the insulator and the metal. Since the film is composed of numerous grains along the thickness each grain boundary contribute to the effective potential barrier for the conducting electron. Thus the behavior can be effectively viewed as the combined effect of the grain, grain boundary interfaces as well as the electrode interface.

In polycrystalline sample the deposited films can be thought of a series of grains, grain boundaries, and electrode interfaces. The field dependence of conductivity, or the \( J - E \) characteristics, of the films is a combined response of these three parts. Variations in the influences of different parts give rise to variation in \( J - E \) characteristics.

In the low field region (i) in the figure 5.13 the film shows ohmic nature. At room temperature, it can be assumed that enough charge carriers are present within the film, so as to contribute to the conduction process and hence a linear field dependence of conductivity can be observed.

The onset of the non-linear character for both types of contacts lie within region(ii) in the figure 5.13, where a prominent role of the electrode is revealed. The onset of non-linearity is a combined effect of the Schottky emission through the contact interface and the SCLC mechanism within the bulk. The leakage current in the films is dominated by space charge limited current (SCLC) mechanism which can be expressed in the following form [109].

\[
J = \frac{9\mu \varepsilon_0 \varepsilon_\tau E^2}{8d}
\]  (5.9)

where \( J \) is the leakage current density, \( \mu \) is the charge carrier mobility,
\( \epsilon_0 \) is the permittivity of free space, \( \epsilon_r \) is the dielectric constant of the film and \( d \) is the film thickness.

**Band Structure**

In terms of the energy-band picture, the function of the insulator is to raise a potential barrier between the electrodes, extending from the electrode Fermi level to the bottom of the conduction band of the insulator. This barrier impedes the flow of electrons from one electrode to the other, which would normally flow virtually unimpeded in the absence of an insulator (i.e. metal–metal contact). Then the height of the potential barrier is an important parameter in conductivity studies in metal-insulator systems. The shape of the potential barrier just within the surface of the insulator depends on whether or not the insulator is intrinsic or extrinsic, and on the relative magnitudes of the work functions of the metal and insulator. The mechanism of blocking or Schottky contact arises when the work function of the metal is higher than that of the insulator, which results in an outflow of electrons from the insulator to the metal contact to establish thermal-equilibrium conditions. A space-charge region of positive charge, the depletion region is thus created in the insulator and an equal negative charge resides at the metal electrode. If the insulator is thick enough, or the doping density is high, the depletion region at the interface effectively screens the interior of the insulator. Under these conditions, the interior of the insulator is field-free, and the bottom of the conduction band attains its equilibrium position above the Fermi level within the interior [36].
Figure 5.14 shows the band structure of the metal-insulator-metal contact as proposed by Saha et al [36]. Considering the band structure as shown in figure where the depletion region is very thin and the bulk resistance is quite high due to the presence of traps, it is possible to observe electrode to bulk-limited transition in the conduction process [161]. For initial voltage bias in the low to intermediate field region, the conduction process will be electrode-limited because of the high cathode-insulator barrier. The electrode-limited conduction process is by simultaneous thermal excitation of electrons from the cathode over the interfacial barrier with the barrier lowering effect due to the electric field. In that condition, the conduction process is purely a Schottky type and the J–E characteristics (as shown in Figure 5.13) are revealed which shows the effect of the blocking contact. At higher fields one of the two process can occur. If the barrier at the Fermi level becomes thin enough, field emission of electrons from the cathode to the conduction band of the insulator can take place or impact ionization can take place in the depletion region when the voltage
bias exceeds $3E_g/2$, where $E_g$ is the band gap of the insulator. Both these processes are characterized by a rapid increase in current with applied voltage, i.e. the contact resistance decreases extremely rapidly with increasing field. The electrode-limited process does not continue indefinitely, since the bulk resistance decreases much more slowly with increasing field than does the contact. Thus at some field, there will be a transition from the electrode limited process to the bulk-limited process, where the contact resistance falls to the value equal to that of the bulk and the voltage across the sample is equally shared between the contact and the bulk. Thereafter, all the voltage in excess of the transition voltage falls across the bulk and the remaining across the barrier, just sufficient to ensure current continuity throughout the system [36].

**PtSi/LSCO/BST/LSCO**

The current density versus electric field characteristics of the BST capacitor for the structure PtSi/LSCO/BST/LSCO is shown in figure 5.15. The leakage current density of BST thin film capacitor with LSCO electrode is found to be 200nA/cm$^2$ at a bias voltage of 2V for 800nm thick BST film. The low leakage current density of the capacitor with LSCO electrode makes it a potential candidate for gigabit density memory [166].
Figure 5.15: The room temperature leakage current density with applied field for the device PtSi/LSCO/BST/LSCO

The applied voltage can be divided into two regions based on the increase of Log J with V viz a low voltage region and a high voltage region. Here Log J increases with V in the low voltage region at a small rate as well as in the high voltage region.

Log J vs Log V plots of the capacitor shown in the figure 5.16 describes the leakage current mechanism in the low voltage region. In the low voltage regime the graph is linear with a slope of 1.31eV. The contact LSCO/BST can be considered to be ohmic like under low field strength. At high voltage the distribution of electrons between LSCO and BST can be disturbed and the leakage current deviates from ohmic behavior. In the high voltage region the conduction mechanism is dominated by Pool Frenkel mechanism.
To ensure the Pool Frenkel conduction mechanism, the data in the figure 5.16 is replotted as Log(J/E) vs $\sqrt{V}$ as shown in figure 5.17. The log(J/E) curve show small increase with $\sqrt{V}$ in the low voltage region. At high voltage the values increases linearly with $\sqrt{V}$. The variation of Log J with measurement voltage as a function of temperature is shown in figure 5.18. The variation of Log(J/E) with 1/T for various voltages is plotted. All the films showed good linearities with negative slopes suggesting thermally activated leakage current mechanism are operative. A typical plot of Log(J/E) with 1000/T at 50kV/cm is shown in figure 5.19. The activation energy is calculated from the slope of the this plot. The activation energy is about 1.21eV for a voltage of 50kV/cm.
Figure 5.17: Variation of Log J/E as a function of $\sqrt{V}$ for the device PtSi/LSCO/BST/LSCO

Figure 5.18: Variation of Log J as a function of voltage with temperature for the device PtSi/LSCO/BST/LSCO/Au
The activation energies at each voltage are calculated from the slopes of each plot. The activation energy as a function of $\sqrt{V}$ is plotted in figure 5.20. This figure shows the two different leakage current mechanism operating in the high and low voltage regions. In the high voltage region the activation energies decrease in a linear fashion with $\sqrt{V}$ with larger absolute values than those in the low voltage regions. Mean square linear fitting for the high voltage region when extrapolated to $V=0$ gives the activation energy at $V=0$ as 1.3eV.

In the low voltage region the linear decrease in activation energy with square root of the applied voltage suggests that the conduction is not purely ohmic but rather a type of field enhanced thermally activated process may be involved.
Figure 5.20: Variation of the activation energy for the device PtSi/LSCO/BST/LSCO/Au as a function of $\sqrt{V}$

This may be the reason for the slope being larger than 1 in the log J log V plot (figure 5.16). At high voltage region the leakage current deviates from ohmic or ohmic like behavior. The activation energy in the high voltage region decreases linearly with $\sqrt{V}$ suggesting that a field enhanced thermally activated process is responsible for electrical conduction in this region. The slopes of the plot log J-log V and that obtained by extrapolation of activation energy to V =0 are the same. At high voltages the electrical conduction mechanism can be attributed to Pool Frenkel emission mechanism.
A band structure based on the conduction mechanism is proposed in the present study. The ohmic nature of LSCO/BST implies that the surface states of the BST in contact with LSCO is different from metal electrode. The main difference is in the chemical bonding nature of the BST with oxide electrode. The oxygen ions in the LSCO strongly interact with oxygen and cations in the BST thus forming chemical bonds. In the case of metal/BST the chemical states of the surface dangling bonds can be preserved after contact formation but on LSCO/BST most of the dangling bonds disappear due to the interaction of oxide electrode with BST [167]. The contact between BST and LSCO is ohmic as observed in figure5.16. The oxygen vacancy concentration is reduced and the Fermi level is located closer to the center of the energy band. The LSCO can release oxygen to the oxygen deficient BST during the film formation. Figure5.21 shows the schematic energy bands for PtSi/LSCO/BST/LSCO devices.
5.6.2 Dielectric constant

In order to measure the capacitance several heterojunctions were fabricated viz PtSi/BST/Au, PtSi/LSCO/BST/LSCO were fabricated. The dielectric constant estimated using the relation

\[ C = \frac{A\varepsilon\varepsilon_r}{d} \]  

(5.10)

Where C is the measured capacitance in Farads, ε the free space dielectric constant (8.85x10^{-12} Fm), A the area of the capacitor (m^2) and d (m) the thickness of the ferroelectric thin film.

PtSi/BST/Au

The variation of dielectric constant with frequency for PtSi/BST/Au device is shown in figure 5.22. The dielectric constant is low for PtSi/BST/Au capacitors.

The dielectric constant of the crystallized BST films were found to be around 1436 at a frequency of 100kHz. As compared to sintered pellets of BST, the dielectric constant was found to be low, which is a consequence of the small grain size of the grown films. The dielectric constant showed dispersion with frequency which is due to the presence of internal interfacial barriers [162]. It can be seen from the figure that there is a tendency of decrease in the dielectric constant with increase in frequency, which suggests that at higher frequency the contribution from a possible dc conduction contribution decreases.
Figure 5.22: The capacitance-frequency variation of BST thin films deposited on PtSi/BST/Au devices

**PtSi/LSCO/BST/LSCO**

PtSi/LSCO/BST/LSCO structure showed appreciable capacitance with minimum loss. The variation of dielectric constant measured with PtSi/LSCO/BST/LSCO capacitor configuration with the BST film grown by PLD is shown figure5.23.

The dielectric constant of the crystallized films were found to be around 628 and the dissipation factor around 0.04 at a frequency of 100kHz. As compared to bulk values the dielectric constant was found to be low, which is a consequence of the small grain size of the grown films. The dielectric constant and the loss tangent do not have noticeable dispersion with frequency, indicating good quality of the present film and the absence of
internal interfacial barriers. However it can be seen from the figure that there is a tendency of decrease in the dielectric constant with increase in frequency, which suggests that at higher frequency the contribution from a possible dc conduction contribution decreases.

![Figure 5.23: The variation of dielectric constant and loss with frequency for BST films deposited on oxide electrode](image)

From the figure it can be seen that the dielectric constant is better for films grown on oxide electrodes. It was found that the loss is minimum for the capacitor fabricated with LSCO electrodes. This may be due to the better growth of BST thin films over LSCO electrodes. Several devices were fabricated on Si as well as on quartz substrates. Figure 5.24 shows the variation of dielectric loss with frequency for the BST capacitors fabricated on various substrates.
Figure 5.24: The variation of dielectric constant and loss with frequency for films deposited on oxide electrode on quartz and Si substrates.

The dielectric loss is found to be minimum for Quartz/LSCO/BST/Au heterojunction. It can be seen that the films deposited on quartz show lower loss but its dielectric constant is also lower compared to PtSi/LSCO/BST/LSCO.

The ferroelectric property of the BST thin films on oxide films in the configuration PtSi/LSCO/BST/LSCO has been studied.

Figure 5.25 shows the room temperature dielectric constant $\epsilon$ and dissipation factor $\tan \delta$ as a function of the applied dc electric field where the relative dielectric constant $\epsilon_r$ was calculated from the capacitance data using the classical formula of parallel-plate capacitors. The capacitance - voltage characteristics of the BST films were measured at a frequency of 1kHz. Hysteresis was observed in the films showing the ferroelectric phase.
Pulsed laser deposition of BST thin films at room temperature. The dielectric properties BST thin films are highly tunable through the application dc bias field.

The tunability is defined as the

\[
\text{tunability} = \frac{\epsilon(0) - \epsilon(E)}{\epsilon(0)} \times 100\%
\]

where \(\epsilon(0)\) and \(\epsilon(E)\) are the dielectric constant at zero field and at an applied field \(E\) respectively. The variation of tunability and figure of merit with the dc field is shown in figure 5.26.
The films show high tunability and figure of merit with oxide electrode. High value of tunability can be attributed to the better growth of BST thin films on oxide electrode.

5.6.3 Polarisation

PtSi/BST/Au

The ferroelectric property of the BST thin film was examined in metal ferroelectric metal MFM configuration. Figure 5.27 gives the room temperature P - E characteristic of the BST film. A saturated P-E hysteresis loop is obtained with a remnant polarization of 1\(\mu\)C/cm\(^2\) and coercive field
Figure 5.27: P-E hysteresis loop of the PtSi/BST/Au structure

The P-E curve shows that the polarisation is very low with a small coercive field. The remnant polarization of $1\mu\text{C/cm}^2$ and coercive field of $45\text{kV/cm}$. The saturation polarisation is about $1.8\mu\text{C/cm}^2$. The low value of the PtSi/BST/Au devices can be attributed to the smaller grain size (12nm) of thin films on PtSi substrates.

**PtSi/LSCO/BST/LSCO/Au**

The ferroelectric property of the BST thin films on oxide films in the configuration PtSi/LSCO/BST/LSCO/Au is studied. The P-E characteristics (figure 5.28) of the films shows hysteresis behavior with a remnant polarization of $4.8\mu\text{C/cm}^2$ and coercive field of $48\text{kV/cm}$. The saturation
polarisation is about $7.8 \mu C/cm^2$.

**Figure 5.28:** P-E hysteresis loop of the PtSi/LSCO/BST/LSCO/Au structure

The ferroelectric properties of PtSi/LSCNO/BST/LSCNO/Au is also studied using RT ferroelectric tester. The hysteresis behaviour of the device is shown in figure 5.29. The remnant polarization of $8 \mu C/cm^2$ and coercive field of $35kV/cm$ is obtained for films deposited on LSCNO. The saturation polarisation is about $10 \mu C/cm^2$.

The improved remnant polarization on LSCNO electrode can be attributed to the crystalline growth of BST thin films. The grain size of BST thin films on LSCNO electrode is $42nm$ where as that on LSCO is $35nm$. Hence the lower polarization of PtSi/LSCO/BST/LSCO/Au capacitors.
The grain size of BST films on oxide electrode is larger than PtSi/BST/Au structure. Hence both the oxide devices showed better ferroelectric property than PtSi/BST/Au devices.

5.7 Conclusion

Ferroelectric BST thin films were grown on different substrates by pulsed laser ablation. The films were deposited using both the third harmonics and fourth harmonics of Nd:YAG laser. The films deposited by laser ablation using 266nm were found to show better properties than those grown by ablating with 355nm. The films were deposited on Si and PtSi substrates to form capacitors with Au electrodes. The electrical characterization of
the device PtSi/BST/Au is studied and the conduction mechanism shows SCLC nature at intermediate fields. The polarization versus electric field plot shows ferroelectric nature. BST thin films deposited on LSCO and LSCNO, oxide perovskite electrodes, were found to be crystalline without any post deposition heat treatment. Thus LSCO and LSCNO serve as a template as well as bottom electrode for the BST thin film capacitors. The interface between the oxide electrode and the BST layer is sharp and free from defects. The dielectric constant of BST is studied as a function of frequency. The devices showed little dispersion with frequency. The loss was found to be minimum for BST capacitors with oxide electrodes. The leakage current shows that the BST films are insulating. The films showed Pool Frenkel emission at high fields. The P-E characteristics traces hysteresis loop with a good polarization and low coercive field.
Pulsed laser deposition of BST thin films