5.1 Introduction:

This chapter deals with the deposition as well as structural, microstructural and optical properties of crystalline BST5 (c-BST5) thin films. In contrast to the previous chapter, all BST5 films described in this chapter are deposited in situ at high temperatures. As mentioned in chapter 1, most of the studies on BST thin films for tunable microwave applications have been on single crystal substrates. In the previous chapter it was shown that crystallizing BST5 thin films on amorphous fused silica substrates is indeed possible. However, post deposition or ex situ annealing treatment failed to yield desired properties in terms of good surface morphology with suitable optical and electrical properties. The poor quality of ex situ crystallized BST5 film is mainly due to the difference in thermal expansion coefficient and the thermal shock encountered by the film and the substrate during the post deposition annealing process. As crystallization and densification takes place during the in situ growth process, BST5 films deposited this way are expected to give better optical and electrical properties.
5.2 Deposition of c-BST thin films:

BST5 thin films were deposited using the procedure mentioned in chapter 2. Two series of films were deposited as part of this study.

In order to investigate the effect of deposition temperature $T_d$, on the crystallinity, BST5 thin films were deposited at substrate temperatures from 400°C to 800°C in steps of 100°C (temperature series) at a constant OMP of 50%. In the second case, deposition temperature was fixed at 800°C and the OMP was varied from 0% to 100% in steps of 25% (OMP series) to determine the influence of OMP on the deposited BST5 thin films.

Initially, the sputtering chamber was evacuated to a base pressure of $2 \times 10^{-6}$ Torr after loading the cleaned substrates on to the substrate holder placed inside the vacuum chamber. All the films were deposited at a fixed power density of 3.0 Wcm$^{-2}$. A working pressure of 20 mTorr was constantly maintained using a mixture of high pure (99.99%) argon and oxygen. The Ar:O$_2$ ratio i.e. OMP was varied from 0 to 100% in steps of 25% (OMP series) while maintaining the $T_d$ at 800°C. The target to substrate distance was fixed at 5 cms. To vary the degree of crystallinity, the deposition temperature ($T_d$) was varied from room temperature to 800°C at intervals of 100°C (temperature series) with a fixed OMP of 50%. It was observed that without any heating, the un-cooled substrate temperature increased to about 120-130°C during the deposition, presumably due to ion bombardment. The thickness of thin films was around 500-600 nm. Prior to every deposition, the substrates were stabilized at the respective $T_d$ for an hour and rate of increase in temperature was about 10°C/min. After the deposition of BST5 films, the argon flow in to the chamber was cutoff and the film coated substrates were cooled down to $\frac{1}{4} T_d$ in oxygen atmosphere. The oxygen flow was cutoff when the temperature reached $\frac{1}{4} T_d$. This procedure was adopted to ensure that the substrates and films do not undergo thermal shock during the ramp up and down process and ensure oxidation of the deposited films.

As mentioned in chapter 1, the main aim of this thesis is to deposit and characterize crystalline BST5 on amorphous fused silica substrates. Hence, the primary substrate used was fused silica. For comparison c-BST5 films were deposited on LaAlO$_3$ (LAO), c-plane Al$_2$O$_3$ (AlO) and MgO single crystal substrates. For electrical
characterization, where a MIM structure is required, BST5 films were deposited on Pt/Si substrates under identical conditions.

Following the deposition of BST5 thin films, a series of characterization techniques probing the structural, microstructural and optical properties of the films were performed. The stoichiometry of the films was established by Rutherford Backscattering Spectrometry (RBS) analysis as described in chapter 2. The crystal structure of c-BST5 films deposited on fused silica substrates as a function of deposition temperatures and OMP were characterized using X-ray diffraction (XRD) technique. Following the XRD measurements, Dynamic Force Microscope (DFM) was employed to measure the surface morphology of the films, which provided high resolution images. The root mean square roughness (rms roughness) was also determined using DFM.

Optical constants such as refractive index and optical band-gap of BST5 films deposited on fused silica substrates were determined from the spectral transmittance data obtained from UV-Vis-NIR spectrophotometer. A correlation between the structural, microstructural and optical properties of BST5 films is discussed.

5.3 Structural characterization - Temperature series:

In this section, the structural properties of c-BST5 thin films deposited on various substrates as a function of T_d is discussed.

5.3.1 Structural characterization of c-BST5 films deposited on fused silica substrates:

The crystal structure of BST5 thin films grown at different deposition temperatures, T_d on fused silica substrates were analyzed by XRD θ–2θ scans using Co Kα radiation (λ=1.7889Å) and are shown in figure 5.1. The onset of crystallization for the BST5 films deposited on fused silica substrates was found to be 600°C. Cubic perovskite structure of polycrystalline BST5 films was observed for the films deposited at T_d ≥ 600°C. Films deposited at 500°C and below were found to be X-ray amorphous. The lattice constant calculated assuming a cubic crystal symmetry was about 3.954 ±0.01 Å for all the films deposited at various T_d. Crystallinity and crystallite size of the films were found to be strongly dependent on T_d. On comparing the intensity and the full width at half maximum (FWHM) of the major (110) peaks, it can be deduced that the crystallinity and crystallite size of the films increase with increase in T_d.
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Another point derived from the XRD patterns in the present case is that there is little or no tendency of preferential orientation in BST5 films deposited on fused silica substrates. The crystallite size, \( t \), as shown in figure 5.2 was estimated from the Full Width at Half Maximum (FWHM, \( \beta \)) of the XRD peak by Scherrer’s formula,

\[
t = \frac{0.9\lambda}{\beta \cos \theta}
\]

(5.1)

where, \( \lambda \) is the wavelength of the X-ray used and \( \theta \) is the diffraction angle.

Figure 5.1: X-ray diffraction pattern of BST5 thin films deposited on fused silica substrates at different deposition temperatures, \( T_d \).
The above figure 5.2 shows increase in crystallite size with increase in $T_d$. This variation can be attributed to the increase in grain growth due to sintering at higher substrate temperatures\(^1\),\(^2\). High quality films with good crystallinity were achieved on depositing BST5 at 800°C.

### 5.3.2 Structural characterization of c-BST5 films deposited on Pt/Si substrates:

Figure 5.3 shows the $T_d$ dependent $\theta$–$2\theta$ diffraction patterns of the BST5 films deposited on (111) oriented Pt/Si substrates, analyzed by X-ray diffraction technique using Cu K\(\alpha\) radiation ($\lambda=1.54056\text{Å}$). The films deposited at 500°C and below were x-ray amorphous and the onset of crystallization was found to be 600°C. All the crystalline films show hetero-epitaxial growth along [111] direction. Apart from the orientation of the Pt underlayer, the orientation of the deposited films depends on the thin film processing conditions such as rate of deposition, working pressure during sputtering and $T_d$. Where, $T_d$ not only facilitates crystallization of the film but also influences the orientation of the growing film. Improvement in the degree of crystallinity with increase in $T_d$ is evident from figure 5.3.
Figure 5.3: XRD pattern of BST5 deposited on a Pt/Si substrates at different temperatures showing (111) orientation

Apart from improvement in degree of crystallinity, a shift in the BST5 peak positions toward higher two-theta values can also be observed with increase in $T_d$ indicating a decrease in the lattice parameters. The lattice constant calculated assuming cubic crystal symmetry of the BST5 films deposited at 600, 700 and 800°C are 3.991, 3.973 and 3.950 Å, respectively. The reported lattice constant of the BST5 bulk is 3.947 Å. The higher lattice constant for the films might be due to strain. The misfit strain $u_m$, was calculated using the formula$^{3,4}$,

$$u_m = \frac{a_s - a_f}{a_s} \quad (5.2)$$
where, $a_b$ is the substrate lattice parameter or that of the lower lying layer (Pt, 3.923 Å) and $a_f$ is the lattice parameter of the deposited film. Misfit strain is generally calculated for epitaxial films.

The misfit strain calculated for the films deposited at 600°C is -1.75%. The misfit strain reduces with increase in $T_d$ to -1.27 % and -0.68% for the films deposited at 700°C and 800°C respectively.

The residual strain, $u_b$ is given as,

$$u_b = \frac{d_b - d_f}{d_b}$$  \hspace{1cm} (5.3)

where, $d_b$ is the inter-planar spacing of the bulk BST5 ($d_{b(111)}=2.279$ Å) and $d_f$ is that of the film. The strain calculated with respect to the bulk for the films deposited at 600°C is -1.09%. The residual strain reduces with increase in $T_d$, to -0.62 % and -0.04% for the films deposited at 700°C and 800°C respectively. Thus, the films deposited at 800°C are strain relieved when compared to the films deposited at lower substrate temperatures. This could be explained by considering that, in physical vapor deposition technique such as sputtering, the surface mobility of the adsorbed particles varies with the surface temperature (or deposition temperature, $T_d$) and the films grow in such a way that the total energy i.e., surface energy of the films, film–substrate interface energy and the strain energy in the films is minimized. At low $T_d$ the adsorbed particles have low surface mobility and so the diffusion length becomes very small causing the vapor molecules to freeze on impact, resulting in a highly stressed film. As $T_d$ increases the surface diffusion increases and so the atoms acquire sufficient energy to crystallize in such a way that the total energy is minimized. Thus, the films deposited at higher $T_d$ are generally stress relieved.

5.3.3 Structural characterization of c-BST5 films deposited on single crystal substrates:

Figure 5.4 shows the X-ray diffraction pattern of BST5 films deposited at 50% OMP and 800°C on various single crystal substrates such as Magnesium oxide (MgO), c-plane sapphire (AlO) and Lanthanum Aluminate (LAO). The XRD pattern of BST5 film deposited on fused silica substrate is shown for comparison.
The Au peak in diffraction pattern of BST5 film deposited on c-plane sapphire originates from the device structure patterned on them.

The diffraction pattern shows that BST5 films deposited on single crystal substrates have only pure perovskite phase. The BST5 films deposited on LAO do not show any sign of preferred orientation apart from the (110) prominent peak. The diffraction pattern is similar to that of BST5 films deposited on fused silica substrates. On the other hand, the BST5 films deposited on MgO and AlO show preferential orientation along (200). The orientation of the BST5 epilayer is considered to be associated with the surface free energy of the substrate used. Even if there exists a large lattice mismatch, the [200] orientation is strongly developed at high T_d.

The inter-planar spacing, d_{ikl} of the BST5 film deposited on various single crystal substrates were calculated from the diffraction angle of the prominent peak. The inter-planar spacing of BST5 film deposited on LAO and fused silica substrates were calculated from the diffraction angle of the (110) peak where as the diffraction angle of
the (200) peak was used for determining the inter-planar spacing of BST5 films deposited on MgO and AlO substrates. The measured $d_{110}$ values were 2.772 Å and 2.797 Å for BST5 films deposited on LAO and fused silica substrates respectively. The measured $d_{200}$ values of BST5 films deposited on MgO and AlO were 1.979 Å and 1.983 Å respectively. For bulk BST5, the $d_{110}$ value is 2.7918 Å and that of $d_{200}$ is 1.973 Å\(^9\). The difference in inter-planar spacing could be due to residual strain developed in the film either due to lattice mismatch\(^10\) or due to difference in thermal expansion coefficients\(^11\). The residual strain, $u_b$, calculated using the formula as discussed in the previous section for the films deposited on various substrates are given in table 5.1.

<table>
<thead>
<tr>
<th>Substrate material</th>
<th>Residual strain $u_b$ (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>MgO</td>
<td>-0.3</td>
</tr>
<tr>
<td>AlO</td>
<td>-0.5</td>
</tr>
<tr>
<td>LAO</td>
<td>0.7</td>
</tr>
<tr>
<td>Fused silica</td>
<td>-0.2</td>
</tr>
</tbody>
</table>

Table 5.1: Table showing the residual strain values of BST5 deposited on different substrates.

It could be inferred from the above table that the lattice constant of BST5 films deposited on LAO substrates are lower than the lattice constant of bulk BST5, inducing an in-plane compressive residual strain with respect to the bulk. On the other hand, BST5 film deposited on MgO and AlO substrates have a higher lattice constant than bulk BST5, inducing an in-plane tensile residual strain with respect to the bulk. A lowest residual strain value of -0.2% was obtained for the films deposited on fused silica substrates which are amorphous in nature. Unlike BST deposited on Pt/Si substrates, no noticeable variation in the strain value was observed for BST5 films deposited on fused silica substrates as a function of $T_d$. BST5 films were deposited on AlO substrates at 600, 700 and 800°C, in order to study the influence of $T_d$ on the strain in BST films deposited on single crystal substrates. The XRD pattern of BST5 films deposited on AlO substrates as a function of $T_d$ is shown in figure 5.5.
No noticeable change in the value of strain was observed on BST5 films deposited as a function of $T_d$ on AlO substrates. However, the peaks become intense and narrow with increase in $T_d$, which indicates that the crystallinity improves with increase in $T_d$. Interestingly, it was observed that the deposition temperature influences the direction of preferred orientation of BST5 films on AlO substrates. The films deposited at 600°C and 800°C had a preferred orientation along the [200] direction whereas the films deposited at 700°C were oriented along [110] direction.

The evolution of preferred orientation in polycrystalline thin films can be analyzed from the viewpoint of energy minimization. The total energy in any film deposited on a substrate is the sum of three components: (1) the surface energy of the film, (2) the film–substrate interface energy, and (3) the strain energy in the film. Films grow in such a way that the total energy is minimized. In the case of polycrystalline films grown on single crystal substrates, interface energy minimization can lead to the dominance of epitaxial orientations. In most other cases, the film generally grows along the plane with the lowest surface energy parallel to the surface of the substrate, thus minimizing the surface free energy of the film.
In a simple metal system, a plane with the smallest surface energy is the one with the highest packing density, such as the [111] planes in face-centered metals. However, it is not easy to calculate the surface free energies of ceramic systems with unit cells containing metal cations and anions, the determination of the surface free energy must take into consideration the surface packing densities and the thermal energy rendered by the substrate to the approaching species. It is known that the surface mobility of the approaching species is proportional to deposition temperature.

During crystallization in ceramic thin films, the nuclei will be preferentially oriented parallel to the thermodynamically stable planes such as the (110) and (111) planes, due to their high packing densities in the ABO$_3$ perovskite structure\textsuperscript{14}. In the present case, films deposited at 700°C favor crystallization along the (110) and (111) which are thermodynamically stable.

The interface energy minimization is favored for the films deposited at 600°C and 800°C, which lead to (200) orientation.

**5.4 Structural characterization of c-BST5 films deposited on fused silica substrates–OMP series:**

Figure 5.6 shows the XRD patterns of BST5 thin films deposited at 800°C on fused silica substrates as a function of OMP of 0, 25, 50, 75 and 100%. All the BST5 films show cubic perovskite structure with no secondary phase formation. Films deposited at 50% OMP show good crystalline quality. The inter-planar spacing of (110) peak was obtained from the peak positions according to the following Bragg formula: 

\[ d_{110} = \frac{\lambda}{2 \sin \theta} \]

where $\lambda$ is 1.7889 Å, the wavelength of X-rays for Co K$_\alpha$ radiation and $\theta$ is the position of the (110) diffraction peak. The values are plotted in figure 5.7 as a function of OMP.
Figure 5.6: X-ray diffraction pattern of BST5 thin films deposited on fused silica substrates at different OMP.

Figure 5.7: Variation in inter-planar spacing \((d_{110})\) in BST5 thin films deposited on fused silica substrates as function of OMP.

The slight increase in inter-planar distances at lower OMP is the result of lattice strain due to defects in the form of oxygen vacancies\(^{15}\). Oxygen vacancies affect the nearest neighbor distance by reducing the Coulomb attractive force between cations and anions, resulting in an increased lattice parameter\(^{16}\). The intensity of the diffraction peak
and crystallite size increases with increase in OMP from 0 to 50%, which indicates improved crystalline quality. Whereas, the films deposited at higher OMPs show deteriorating crystalline quality. The films deposited at 0% and 25% OMP have excess Ti as confirmed by RBS analysis. The excess Ti passivates the film’s grain boundaries, which prohibits grain growth in BST5 films. A possible explanation for the observed deteriorating crystalline quality for the films deposited at 75% and 100% OMP is the low rates of deposition. Films deposited at low rates have been shown to have smaller grains with low peak intensity than those deposited at higher rates. However, the nucleation and growth kinetics for BST5 films deposited in pure oxygen atmosphere is not well understood and further studies have to be carried out to understand the sputtering process in pure oxygen atmosphere (high OMP).

The variation in crystallite size with OMP is shown in figure 5.8.

The variation in crystallite size with OMP is shown in figure 5.8.

![Figure 5.8](image-url)  
**Figure 5.8**: Graph showing the variation in crystallite size in BST5 thin films deposited on fused silica substrates as function of OMP.

5.5 Microstructural characterization – Temperature series:

In this section, the microstructural properties of c-BST5 thin films deposited on various substrates as a function of Tₐ has been discussed.

5.5.1 Microstructural characterization of c-BST5 films deposited on fused silica substrates:

We studied the surface morphology of the BST5 films using DFM. Figure 5.9 shows the two dimensional and corresponding three-dimensional DFM images of the
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BST5 thin films deposited at different temperatures. The DFM micrographs indicate that the BST5 thin films are in general crack-free and relatively smooth. The evolution of the surface structures and grain growth are clearly visible through these images.

Figure 5.9: 1μm x 1μm DFM images of BST5 films deposited at different temperatures on fused silica substrates.

It is noted that the increase in substrate temperature leads to increase in surface roughness in these thin films. As seen in figure 5.10, an increase in substrate temperature
Deposition from 600 to 800°C, the root-mean-square (rms) value of surface roughness of BST5 thin films increases from 3.17 to 7.52 nm. In addition, the crystallite size and hence the grain size of the films increases with increase in substrate temperature due to sintering.\textsuperscript{19,20}

![Graph showing the variation in rms roughness in BST5 thin films deposited on fused silica substrates as a function of T_d.](image)

**Figure 5.10**: Graph showing the variation in rms roughness in BST5 thin films deposited on fused silica substrates as a function of T_d.

Although the surface roughness of BST5 films is found to increase with increase in substrate temperature, it is also accompanied by enhanced grain growth and improvement in crystallinity. These can influence the dielectric properties of BST5 films to a great extent.\textsuperscript{21,22} This is confirmed by the dielectric property measurements discussed in chapter 6.

### 5.5.2 Microstructural characterization of c-BST5 films deposited on Pt/Si substrates:

The two dimensional and its corresponding three-dimensional, DFM image of BST5 films deposited on Pt/Si substrates at different T_d in figure 5.11 shows that the surfaces of the BST5 thin films are smooth. The grains are densely and regularly packed without cracks.
Figure 5.11: 2 μm x 2 μm DFM image of BST5 films deposited at different temperatures on Pt/Si substrates.
It is also observed that the films deposited at higher T_d have larger grains because of sintering. In figure 5.12, the closed circles represent the variation in rms roughness of BST5 films measured over a 2μm² area. We see that the rms roughness decreases up to a T_d of 500°C, peaks at 600°C and decreases on further increase in T_d. The observed behavior of the films is in good agreement with that predicted by Yang et al.²³ i.e., increase in T_d generally reduces the roughness because thermal diffusion promotes surface reconstruction that flattens a rough surface and eliminates voided columnar structure.

Figure 5.12: rms roughness of (●) BST5 film and (○) Pt under-layer. The inset shows the dependence of rms roughness on the misfit strain of BST5 films.

It can be seen from the inset of figure 5.12 for crystalline films, that the magnitude of misfit strain has a good influence on the rms roughness of the films. We can see that the value of rms roughness decreases with decrease in misfit strain. So, by appropriately controlling the deposition parameters such as T_d, the magnitude of \( u_m \) can be controlled which in turn influences the surface morphology of the deposited films.
The effect of $T_d$ on the surface morphology of the Pt layer was also investigated and is shown in figure 5.13. The open circles in figure 5.12 indicate the variation in rms roughness of Pt layer with $T_d$. In this case also, we find that the trend is almost similar to that of the rms roughness of BST5 layer. The films deposited at 700 and 800°C show lower surface roughness than that of the Pt underlayer. This might be because $T_d$ value of 700 and 800°C corresponds to $T_d/T_m$ value of 0.47 and 0.52 respectively (which is half the value of the melting temperature, $T_m$ of both BST5 ($T_m$ ~ 2073K) and Pt ($T_m$ − 2045K)).
Figure 5.13: 2 μm x 2 μm DFM image of the Pt layer on Si substrates.
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Thus the surface morphology of the BST5 layer is not only controlled by the processing conditions but also by the variation in morphology of the Pt underlayer. It can therefore be inferred that Pt acts as the seed layer, which influences the surface morphology of BST5 films deposited over it. The experimental evidence clearly suggests that the temperature at which the BST5 film is deposited can considerably change the surface morphology of the Pt layer and that these variations should be taken into account while optimizing processing conditions for the BST overlayers.

5.5.3 Microstructural characterization of c-BST5 films deposited on single crystal substrates:

Figure 5.14 show the 1 μm×1 μm DFM micrographs of BST5 films deposited at 800°C and 50 % OMP on single crystal substrates of AIO, MgO and LAO. It is obvious from the DFM images, that the surface morphology of BST5 thin films deposited on one type of substrate is different from that deposited on the other. In general, the crystal structure, lattice constant and thermal expansion coefficient of the substrate and the thin film as well as the processing conditions have a marked influence on the film nucleation and the relevant film structure.

In the present case, it is observed that the BST5 films deposited on MgO and AIO substrates, which indicated a preferred (200) orientation have very large grains with smaller sub-grains. Whereas BST5 films deposited on LAO substrates with no preferred orientation show a dense surface morphology with smaller grains. Therefore, surface morphology and roughness of BST5 thin films is influenced by the film texture/orientation which results from the nature of the substrate used.
Figure 5.14: 1 μm x 1 μm DFM image of BST5 films deposited on various single crystal substrates.
It has been suggested that small grain size, which leads to larger grain boundary area and the associated interfacial capacitance is a major contributing factor to the lower value of dielectric permittivity observed in BST thin films relative to their bulk counterpart\textsuperscript{24}. The dielectric properties of these films are discussed in chapter 6.

5.6 Microstructural characterization of c-BST5 films deposited on fused silica substrates– OMP series:

The microstructure of the BST5 films deposited on fused silica substrates as a function of OMP is shown in figure 5.15.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure_5.15.png}
\caption{1 \(\mu\)m x 1 \(\mu\)m DFM image of BST5 films deposited on fused silica substrates at different OMP.}
\end{figure}
Figure 5.15: (continued) 1 μm x 1 μm DFM image of BST5 films deposited on fused silica substrates at different OMP.
It can be observed from figure 5.16 that the surface roughness increases marginally with increase in OMP up to 50% OMP. It is generally expected that films deposited with low OMP have a rough surface due to high rates of deposition. But in the present case, we found that films deposited in 100% Ar atmosphere have a smooth morphology when compared to the films deposited at 50% OMP. This is because, films deposited at low (0 and 25%) OMP have a Ti-rich phase, the excess Ti passivates the film’s grain boundaries and hence the films deposited at low OMP have a smooth surface. On the other hand films deposited at high (75 and 100%) OMP have the lowest surface roughness as expected due to low rates of deposition. The results obtained here compliment the XRD observations.

Figure 5.16: Graph showing the variation in rms roughness in BST5 thin films deposited on fused silica substrates as function of OMP.
5.7 Optical properties:

The optical constants of BST5 thin films are highly influenced by the structure, composition and fabrication techniques. A typical transmittance spectrum of c-BST5 film deposited on amorphous fused silica substrate is shown in figure 5.17 below.

![Transmittance Spectrum](image)

**Figure 5.17**: A typical spectral transmittance spectra of crystalline BST5 film deposited on fused silica substrates compared with that of the uncoated substrate.

As discussed in chapter 3, the spectrum can be divided into four regions: a transparent oscillating region, weak absorption, medium absorption and a region of strong absorption, where the transmittance decreases drastically.

The refractive index $n_f(\lambda)$ as a function of wavelength have been determined from the transmittance spectrum following the methods of Manifacier\textsuperscript{25} and Swanepoel\textsuperscript{26}. Here, $\lambda$ indicates the wavelength. If two envelopes are drawn through the maxima $T_M(\lambda)$ and minima $T_m(\lambda)$ of the oscillating transmittance, the refractive index is given as:

$$n_f(\lambda) = \left[ N + \left( N^2 - n_s(\lambda)^2 \right)^{1/2} \right]^{1/2}$$  \hspace{1cm} (5.4)
where,

\[
N = 2n_s(\lambda) \frac{T_M - T_m}{T_M T_m} + \frac{n_s(\lambda)^2 + 1}{2}
\] (5.5)

and \(n_s\) is the refractive index of the thick bare fused silica substrate. The refractive index of the bare substrate is given by the famous expression,

\[
n_s(\lambda) = \frac{1}{T_s(\lambda)} + \left( \frac{1}{T_s(\lambda)^2} - 1 \right)^{\frac{1}{2}}
\] (5.6)

where, \(T_s(\lambda)\) is the transmission of the thick bare fused silica substrate as shown in figure 5.17. The calculated \(n_s(\lambda)\) is shown in figure 5.18 along with the refractive index calculated for c-BST5 film deposited on fused silica substrate, for comparison.

**Figure 5.18:** Graph showing the variation in refractive index as a function of wavelength for c-BST5 film and bare fused silica substrate.
5.7.1 Optical characterization of c-BST5 films deposited on fused silica substrates-

Temperature series:

Figure 5.19: Spectral transmittance of c-BST5 films deposited on fused silica substrates at different $T_d$.

The spectral transmittance of c-BST5 films deposited at different temperatures is shown in figure 5.19. The transparency of the films exhibits a sharp decrease near the UV region. The films in general are highly transparent for wavelengths longer than 340 nm. The transmission drops rapidly at 340 nm, and the cutoff wavelength occurs at about 320 nm. This decrease is due to the fundamental absorption edge of the material at this wavelength. A close look at the transmittance spectra reveals that the c-BST5 films deposited at 600°C are comparatively more transparent than the films deposited at higher substrate temperatures. In other words, with increase in deposition temperature, the transmittivity decreases. This is attributed to increase in grain size and/or roughening$^{27}$. This complements the DFM results, which show an increase in grain size and rms roughness with increase in $T_d$.

The variation in refractive index as a function of wavelength for the films grown at different deposition temperatures is shown in figure 5.20. The inset in figure 5.20
shows the value of refractive index at $\lambda = 550\text{nm}$ as a function of deposition temperature. It is observed that the refractive index value increases with increase in $T_d$.

![Graph showing variation in refractive index with wavelength and deposition temperature](image)

**Figure 5.20**: Variation in refractive index as a function of wavelength for BST5 films deposited on fused silica substrates. The inset shows the variation in refractive index ($@\lambda=550\text{nm}$) for BST5 thin films as a function of $T_d$.

It is well known that the refractive index of a transparent thin film is directly proportional to its electronic polarization and the electronic polarization is in turn inversely proportional to the inter-atomic separation$^{28}$. It can also be directly correlated to the film packing density, microstructure and crystallinity. Higher deposition temperature $T_d$ increases the mobility of adsorbed atoms on the substrate surface, which leads to enhanced crystallinity and densification. The XRD studies showed that the films deposited at $800\,^\circ\text{C}$ had sharper and more intense peaks than the films deposited at $600$ and $700\,^\circ\text{C}$, suggesting better crystallinity in the films deposited at $800\,^\circ\text{C}$.

The band-gap of the films deposited at different temperatures was determined using the Tauc plot as explained in chapter 3. An optical band-gap value to $3.7 \pm 0.1\text{eV}$ was obtained for all the films.
5.7.2 Optical characterization of c-BST5 films deposited on fused silica substrates-
OMP series:

The variation in refractive index as a function of wavelength for the c-BST5 films
deposited on fused silica substrates is shown in figure 5.21. It is found that the index of
refraction is strongly dependent on OMP.

![Dispersion in refractive index of c-BST5 thin films deposited at different OMP.](image)

**Figure 5.21:** Dispersion in refractive index of c-BST5 thin films deposited at different OMP.

![Graph showing the variation in refractive index as a function of OMP.](image)

**Figure 5.22:** Graph showing the variation in refractive index as a function of OMP.
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The refractive index measured at 550 nm as a function of OMP is shown in figure 5.22. Highest value of refractive index of about 2.33 was obtained for the films deposited at 50% OMP. Films deposited at 0 and 25% OMP show lower value of refractive index and the films deposited at 75% and 100% OMP show refractive index values similar to the BST5 films deposited at 50% OMP within the error limits of the measurement technique.

The lower value of refractive index for the films deposited at 0 and 25% OMP might be attributed to the variation of the packing density, as shown in table 5.2. The refractive index data are indicative of the film packing density\textsuperscript{29,30}. The relation between refractive index \( n_f \) and packing density \( P_d \) is given in chapter 4. The oxygen partial pressure (i.e., OMP) can influence the incorporation and stoichiometry of oxygen in the deposited films, which in turn can influence the packing density. Oxygen vacancies are easily formed when OMP is low, and adequate oxygen can eliminate oxygen vacancies\textsuperscript{31}. The films deposited at 0 and 25% OMP have oxygen vacancies (as confirmed by RBS) and have low packing density which causes the decrease in refractive index. The films deposited at higher OMP have good oxygen stoichiometry and high packing density and so the refractive index value approaches the bulk value.

<table>
<thead>
<tr>
<th>OMP (%)</th>
<th>Packing Density (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0</td>
<td>91</td>
</tr>
<tr>
<td>25</td>
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\textbf{Table 5.2:} Packing density of c-BST5 thin films deposited at different OMP.

The band-gap of c-BST5 is also found to be dependent on OMP, as seen in the transmission edge in figure 5.23.
The absorption at low wavelengths for BST5 films deposited on fused silica substrates is related to the fundamental absorption which refers to the band-to-band transition, i.e., to the excitation of an electron from the valence band to the conduction band. The energy gap, $E_g$, of BST5 can be obtained from the following equation:

$$\alpha h\nu = \text{const} \times \left( \frac{h\nu}{E_g} - 1 \right)^2$$  \hspace{1cm} (5.7)

where, $h\nu$ is the photon energy. The absorption coefficient, $\alpha$ is given as:

$$\alpha = \frac{\ln(1/T)}{d}$$  \hspace{1cm} (5.8)

in which $T$ is the transmittance at a wavelength, $\lambda$ and $d$ is the film thickness. More details of this technique are provided in chapter 3.
Chapter V

The $(\alpha h \nu)^2$ vs. $h \nu$ plot for the c-BST5 films on fused silica substrates as represented by equation 5.7 shows good linearity above 3.7 eV. The representative plot of $(\alpha h \nu)^2$ vs. $h \nu$ is shown in figure 5.24 for c-BST5 films deposited at 0% and 100% OMP.

Figure 5.24: Plot of $(\alpha h \nu)^2$ versus $h \nu$ for the c-BST5 films deposited on fused silica substrates at 0 and 100% OMP.

The band-gap, $E_g$ of c-BST5 films deposited as a function of OMP was determined by extrapolating the linear portion of the plot to $(\alpha h \nu)^2=0$, thus supporting the model of direct allowed electronic transition for deposited thin films. Electronic transition between the valence and conduction bands in the crystal starts at the absorption edge, which corresponds to the minimum energy difference $E_g$ between the lowest energy state of the conduction band and the highest energy state of the valence band. The optical band-gap of the c-BST5 films as a function of OMP is shown in figure 5.25.
Figure 5.25: Graph showing the variation in optical band-gap as a function of OMP.

It is observed that the films deposited at 0 and 25% OMP have higher band-gap than those deposited at higher OMP. The band-gap of BST films depends on annealing / deposition temperature, crystallinity, grain size and defects. In the present case, the most probable reason for higher value of band-gap for the c-BST5 films deposited at lower OMPs are defects in the form of oxygen vacancies. It was confirmed from the RBS analysis that BST5 films deposited at low OMP have oxygen vacancies. The increase in $E_g$ can be explained by the Burstein–Moss effect\textsuperscript{33,34} as discussed in chapter 4.
Chapter V

5.8 Summary:

In summary, BST5 thin films were deposited in situ at elevated substrate temperatures. Two series of films were grown and they were (i) OMP series and (ii) temperature series. In the case of OMP series, BST5 thin films were deposited on fused silica substrates at fixed deposition temperature of 800°C while varying the OMP from 0% to 100% in steps of 25%. In the case of temperature series, the OMP was fixed at 50% and the films were deposited on fused silica, Pt/Si, MgO, LAO and AlO substrates at different temperatures from 600°C to 800°C in steps of 100°C. The XRD results on BST5 films deposited on fused silica substrates indicated an increase in degree of crystallinity with increase in substrate temperature without change in lattice parameter, while BST5 films deposited at 0% and 25% OMP showed an increase in lattice constant. The increase in lattice constant was attributed to strain due to defects in the form of oxygen vacancies. Films deposited on Pt/Si substrates show epitaxial growth along (111) plane whereas films deposited on MgO and AlO show polycrystalline behavior with preferred orientation along (200) direction. The misfit strain calculated for the BST5 films deposited at 600°C on Pt/Si substrates was -1.75%. The misfit strain reduces with increase in deposition temperature to -1.27% and -0.68% for the films deposited at 700°C and 800°C respectively.

In the case of BST5 films deposited on fused silica substrates, the surface roughness of the films increased from 2.17 to 7.52 nm with increase in deposition temperature from 600 to 800°C while the rms roughness showed decreasing trend for the films deposited above 50% OMP. The decrease in rms roughness is attributed to lower rates of deposition. The optical band gap was 3.7 eV±0.1 eV for all the BST5 films, irrespective of their deposition temperature while refractive index increased from 2.28 to 2.33 with increase in deposition temperature from 600 to 800°C. The increase in refractive index is attributed to increase in packing density due to sintering. The band gap of the films deposited at low (0 and 25%) OMP show higher values than that deposited at OMPs ≥ 50%. The higher value of $E_g$ can be explained using the Burstein–Moss effect.
Deposition of c-BST thin films and its structural, microstructural and optical properties

References:

5 JCPDS card No. 04-0802 for Pt (a=3.923 Å).
9 JCPDS card No. 39-1395 for bulk Ba$_{0.5}$Sr$_{0.5}$TiO$_3$.


