EFFECTS OF STRAIN ON DIELECTRIC PROPERTIES OF FERROELECTRIC Ba0.5Sr0.5TiO3 FILMS

Hongrui Liu
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EFFECTS OF STRAIN ON DIELECTRIC PROPERTIES OF
FERROELECTRIC $Ba_{0.5}Sr_{0.5}TiO_3$ FILMS

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EFFECTS OF STRAIN ON DIELECTRIC PROPERTIES OF
FERROELECTRIC $Ba_{0.5}Sr_{0.5}TiO_3$ FILMS

A research dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University

by

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Abstract

EFFECTS OF STRAIN ON DIELECTRIC PROPERTIES OF FERROELECTRIC Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ FILMS

By Hongrui Liu

A research dissertation submitted in partial fulfillment of the requirements for the degree of Doctor of Philosophy at Virginia Commonwealth University

Virginia Commonwealth University, 2012.

Major Director: Hadis Morkoç, Professor, Dept. Electrical and Computer Engineering

Owing to the large electric-field-dependent permittivity, ferroelectric thin films have attracted a great deal of attention on applications in miniature tunable microwave components with high performance and cost reduction, such as phase shifters, tunable oscillators, delay lines, and antennas. These tunable devices require large change in the dielectric constant with applied field and a low loss at microwave frequencies. As one of the promising ferroelectric materials, barium strontium titanate thin film, especially Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) films, have raises great research interests due to its high dielectric constant, which is tunable in an external electric field, combined with relative low loss at
microwave frequencies. Tunable microwave components, such as phase shifter, based on the BST films have been widely investigated.

Since the polarization, the significant characterization of ferroelectrics, is very sensitive to distortion in crystal structure of ferroelectrics, strain can be effectively utilized to tailor the dielectric properties of BST films. Due to the lattice-mismatch from the substrate and various deposition conditions, epitaxial BST thin film usually contains residual strain generated during film growth. Strain control by improved deposition technique and implementing thermal treatment as well as choosing suitable substrate has attracted intensive attentions in ferroelectric film fabrication. Theory predicts that high dielectric properties can be achieved when free strain or slightly tensile strain left in the BST thin film at room temperature. Microwave application, such as phase shifter, also expects the enhanced tunability by an applied electric field.

In this dissertation, single crystalline BST thin films deposited by radio frequency magnetron sputtering on SrTiO$_3$ and DyScO$_3$ substrates were studied. The crystal structure characteristics, including lattice parameters and film strain, were determined using X-ray diffraction. A new growth technique, three-step technique, was introduced and implemented into BST thin film deposition. The application of this new technique in deposition dramatically reduced the compressive strain in the films. We use microwave measurements on coplanar waveguides to evidence the improvement on dielectric properties achieved by tailoring the film strain. Additionally, we studied the BST film
deposited by pulsed laser deposition (PLD) with introducing a sputtered seed layer of BST thin film. Compared with the BST film directly deposited on the substrate by PLD deposition, the films with a seed layer showed a large enhancement on the dielectric constant and tunability. The discussion on the change in film strain and dielectric performance of the PLD deposited films further proved the influence of film strain on dielectric properties.

We discussed the design, fabrication, and measurement of coplanar waveguide transmission lines as phase shifters fabricated BST films. The thin BST films (~700 nm) on DyScO$_3$ substrates deposited by sputtering demonstrated that the three-step deposition technique improved differential phase shift and microwave figure of merit to a great extent. The introduction of the sputtered seed layer into the PLD deposition of a thicker BST film (~2.15 μm) showed a dramatically enhancement on differential phase shift and microwave figure of merit. The enhanced performance on different series of BST films in microwave frequencies is consistent with the improvement on crystal structure, especially with the change in film strain.
Chapter 1 Introduction

Ferroelectric materials have been studied for many decades as potential candidates for non-volatile random access memory devices, non linear optics, motion and heat sensors, and wide range voltage controlled capacitors \[1-3\]. In the recent two decades, ferroelectric thin films have raised a great research interests due to the high sensitivity of the permittivity to the applied electric field, relatively low loss, fast switching speeds, and good power handling capability. In consideration of the commercial needs, the utilization of ferroelectric thin films in the microwave components are more attractive due to the reduced cost and miniaturized device comparing with that of bulk material. A great deal of studies has concentrated on the various aspects of tunable ferroelectric devices, including material science and device designs \[4-6\]. The optimal balance of the strong electric-field-dependent dielectric permittivity and the relative low dielectric loss at microwave frequencies always excites interest on improving the fabrication technique of ferroelectric films.
1.1 Ferroelectricity

The name of ferroelectric is firstly given by an analogy with ferromagnetic properties. Before the term ferroelectric was used, ferromagnetism was already known, defined by a material possesses permanent magnetic moment. The prefix “ferro”, meaning iron, was actually a misnomer in its first usage in ferroelectric because most ferroelectric materials do not have iron in their lattice [7]. For some ferroelectrics, iron contaminants even degrade the electric performance [8]. Ferroelectricity was firstly found in 1920, in potassium sodium tartrate, namely Rochelle salt by Valasek [9], which was then used to make pyroelectric sensors raised a great interest till the new ferroelectric materials BaTiO$_3$ with high permittivity emerged and led a new epoch of ferroelectrics.

As a starting point, it is helpful to give a clear introduction of ferroelectric material. The fact that ferroelectric materials attract so many attentions could be attributed to its special crystal structure characteristics and its typical reversible spontaneous electric polarization (electric dipoles). Ferroelectrics are a special group of compounds that have noncentrosymmetric crystal structure, which produces electric dipoles. These dipoles can switch their directions under the influence of an externally applied electric field or an internal electric field from the adjacent unit cells. The amount of the dipole moment per unit volume is described as spontaneous polarization. This physical property due to the existence of spontaneous polarization even in the absence of external electric field is called ferroelectricity [10]. It is worth to clarify that the ferroelectrics and ferromagnetics
are different. Even though both ferroelectrics and ferromagnetics have spontaneous polarization, domain structure, hysteresis loop, and Curie temperature, their fundamentals are different. On Curie point, ferroelectrics changes from ferroelectric to paraelectric states and even changes its crystal symmetry to centrosymmetric, while ferromagnetics changes from spontaneously magnetized to magnetically disordered state but not change its crystal structure. Above the Curie temperature, the electric dipoles in the ferroelectrics disappear, while individual magnetic moments or unpaired electron spins in ferromagnetics still exist but cancel each other yielding zero in the total net amount then.

1.1.1 Perovskite structure

Ferroelectrics have attracted a great deal of attention for over half a century [11-13] since the first ceramic ferroelectric compound, BaTiO$_3$, was founded in 1940s [14]. To investigate the properties and application of ferroelectrics, we should begin from its special crystal structure. Most ferroelectric materials are in perovskite structure, which named after a specific mineral know as perovskite (CaTiO$_3$). The mineral perovskite, which was first described in 1830’s by the geologist Gustav Rose, was named after a famous Russian mineralogist Count Lev Perovskii. Perovskite generally describes an ABO$_3$ type of crystal structure with a prototypal centrosymmetric cubic cell. As an ideal example, we firstly use BaTiO$_3$ to discuss perovskite structure and typical ferroelectric
behavior. Barium titanate, BaTiO$_3$, has a typical perovskite structure as shown in Figure 1.1. Barium ions, which are the largest size among these three type of ions (~158 pm), occupy the corners of the Cubic cell, oxygen ions are featured on the face centers and build up a oxygen octahedra, and the smallest titanium ions (~60 pm) is sitting at the center of the cubes where is also the center of the oxygen octahedra.

![Figure 1.1 Unit cell and crystal structure of perovskite material BaTiO$_3$.](image)

Actually, the structure is temperature dependent. As shown in Figure 1.2, when the temperature is below the Curie point, where ferroelectrics transfers from ferroelectric to paraelectric state, the titanium ion moves in a specific direction away from the symmetrical center of the oxygen octahedra, such as moving upward or downward. Then the center of positive charges in the unit cell does not coincide with the center of negative charges, and thus the structure is not centrosymmetrical anymore. The electric dipole moment along the up/down direction is consequently formed. This is spontaneous polarization, which is the typical characteristic of the ferroelectric phase. Ferroelectrics
only possess the spontaneous polarization in a certain temperature range. Above the Curie temperature, the titanium ion goes back to the symmetrical center position in the Figure 1.2 Crystal structure of BaTiO$_3$ changes from centrosymmetrical structure in the paraelectric (PE) phase to non-centrosymmetrical structural in ferroelectric (FE) phases with the presence of upward or downward polarization at Curie temperature.

oxygen octahedra. Consequently, the spontaneous polarization disappears due to the crystal structure changing from noncentrosymmetric to centrosymmetric. Then the ferroelectrics are in paraelectric. It is worth to mention that the spontaneous polarization of BaTiO$_3$ drops abruptly to zero at $T_c$ as the red curve shown in Figure1.2. The
discontinuous phase transition is called first-order phase transition, which will be discussed again in the section 1.1.3 and Chapter 6.

### 1.1.2 Hysteresis loop

Another important characteristic of ferroelectrics is ferroelectric hysteresis loop in the field versus polarization curve, which is actually a process of spontaneous polarization reorientation. The permanent electric dipoles in the ferroelectric materials tend to spontaneously align with other electric dipoles in adjacent unit cells and subsequently form a domain, in which many unit cells have the same polarization direction. However, the polarization domains have different polarization direction and can cancel each other in a system level. Therefore, the net polarization is zero when the ferroelectrics have not affected by the external electric field. Figure 1.3 shows how polarization changes with the application of external electric field. When a small magnitude of electric filed in positive direction begins to apply on the ferroelectric materials, there is only a near linear relationship between polarization $P$ and electric filed $E$ since few domains are switched, as the OA part of the PE curve shown in Figure 1.3. There is only a little polarization induced and reversible as the paraelectric behavior. As the electric field gradually increases in the positive direction, the domains, which were not in the same direction as
Figure 1.3 Typical ferroelectric hysteresis loop and spontaneous polarization

the externally applied electric field, begin to be switched toward the direction along the field. Consequently, the polarization starts to increases abruptly in the positive direction, as shown on the curve AB. After most domains are aligned in the same direction as the external electric field, the increase of the polarization will slow down as the electric field rises further (BC curve). At point C, the polarization reaches to its saturation state $P_s$, in which the crystal possesses only one polarization direction along the external electric field and the whole crystal looks like a single domain with a positive polarization direction. When the electric field decreases its strength to zero, the polarization decreases
gradually but still keeps a positive remanent polarization $P_r$ at point D, since not all domains have enough energy to switch back. The remanent polarization $P_r$ cannot be removed until the applied field in the negative direction increases to a certain value (point E in Figure 1.3). At point E, the external applied electric field reducing the polarization to zero is called coercive electric field of the material. As the electric field keeps increasing in the negative direction, the domains begin to be switched and then reach to the saturation state in the negative direction at point F. After that, the decreasing electric field in the negative direction causes negative polarization decreases. When the strength of the electric field decreases to zero in the negative direction, the polarization reaches its remanent polarization in the negative direction (point G). If the external electric field is applied gradually again in the positive direction, the remanent polarization in the negative direction will be reduced and completely removed at the coercive field in the positive direction. Further increasing of the applied electric field in the positive direction will cause the domains switch their polarization direction in response to the electric field. With the increasing of positive polarization, the hysteresis loop will complete when the polarization reach its saturation in the positive direction again (point C). The relationship between $P$ and $E$ along the route of CDEFGC in Figure 1.3, which is repeatable, is called hysteresis loop.
1.1.3 Phase transition

The PE hysteresis loop is a typical and unique behavior of ferroelectric materials in ferroelectric state. However, it only exists in a certain temperature range. When the temperature is above the Curie temperature, there is no remanent polarization due to the disappearance of the spontaneous polarization. The polarization only exists under an applied electric field. When the electric field is removed or changed direction, the polarization will return to zero or reverse immediately in response to the external applied electric field as shown in Figure 1.4.

Figure 1.4 The relationship between polarization and applied electric field in ferroelectric and paraelectric states

Figure 1.5 shows the diagram of free energy against polarization and the atomic displacement in a ferroelectric material at a temperature higher than, equal to, and lower
than the Curie temperature. Below the Curie temperature, the free energy, the red curve in Figure 1.5, looks like a double well with two equal energy minima for the system corresponding to the spontaneous polarization in two directions in absence of an applied electric field. The cation in the center of the oxygen octahedra, such as the titanium ion in BST or BTO, has to move away from the symmetric center position to a position owing to the minimum energy principle. Under the ferroelectric phase, the lowest energy of the titanium ion is not at the symmetrical center in the oxygen octahedra but at the up/down positions in the figure where are energetically more stable than a non-polar configuration.

Figure 1.5 Free energy as a function of polarization and the atomic displacement of ferroelectric materials at temperature higher than, equal to, and lower than the Curie point
with $P=0$. Thus the electric dipole and the spontaneous polarization are produced. To switch the spontaneous polarization from one direction to the other under the applied external electric field, such as from up direction to down direction in the figure, an activation is required to shift the titanium ion from one lowest energy position to the other lowest energy position by crossing an energy barrier. Therefore, the titanium ion possesses more energy at the symmetric center under ferroelectric phase, which must be offered from outside. Above the Curie temperature, the titanium ion has the lowest energy only at the symmetrical center in the oxygen octahedra and consequently goes back to the center position as shown the blue curve in Figure 1.5. Therefore, there is no electric dipole or spontaneous polarization in the structure. Energy is required to shift the titanium away from the center position. At the Curie point, the energy curve (grey curve in Figure 1.5) shows a flat segment near zero polarization because the titanium ion has the lowest energy at the center position and easily shifts back and forth away from the center position as well. There is no energy barrier or the activation energy required to shift the titanium ion away from the center position at the Curie point. Consequently, the dielectric constant reaches its peak value at or around the Curie point for the ferroelectric materials. However, the high dielectric constants of ferroelectrics at Curie point are of little practical application due to its temperature sensitivity [10]. In consideration of both the requirement of high dielectric constant and the avoidance of temperature sensitivity, the application of ferroelectric materials is usually set at 50 degree higher than the Curie
temperature. It is worth to notice that the energy diagram of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ is not exactly as the one shown in Figure 1.5. With the temperature rise up toward the Curie point, the spontaneous polarization decreases. If the spontaneous polarization decreases continuously towards zero as $T$ approaches to $T_c$, it is called second-order phase transition; while if the spontaneous polarization drops abruptly to zero at $T_c$, the discontinuous phase transition is called first-order phase transition. The phase transition shown in Figure 1.5 is second-order phase transition. The phase transition of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ generally is first-order phase transition. In figure 1.2, the polarization curve drops abruptly to zero at $T_c$ well describe the first-order phase transition of Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ material. More discussions are detailed in Chapter 6.
1.2 Barium strontium titanate

Barium strontium titanate (Ba$_x$Sr$_{1-x}$TiO$_3$) thin film is one of the promising ferroelectric thin films for the fabrication of tunable varactors owing to its high tunability and relatively low loss [15, 16]. From a material viewpoint, barium strontium titanate (Ba$_x$Sr$_{1-x}$TiO$_3$) can be categorized as a solid solution of barium titanate (BaTiO$_3$) and Strontium titanate (SrTiO$_3$) and expressed as (BaTiO$_3$)$_x$(SrTiO$_3$)$_{1-x}$ (Figure 1.6). The solid solution could have any composition ratio (with varied x) because Ba$^{2+}$ and Sr$^{2+}$ have the same perovskite crystal structure type and comparable ion radii. BaTiO$_3$ is a ferroelectric material with the Curie temperature of 120ºC, while SrTiO$_3$ is a paraelectric material with no ferroelectric phase transition. The composition of the BaTiO$_3$ and SrTiO$_3$ determines
the micro-structure and the dielectric properties as well as Curie temperature of the film. Ferroelectrics with Curie temperature below the operating temperature are desired, since ferroelectric materials has no hysteresis in paraelectric phase. In the series of Ba$_x$Sr$_{1-x}$TiO$_3$ with the value of $x$ varing from 0 to 1, the Curie temperature, at which Ba$_x$Sr$_{1-x}$TiO$_3$ undergoes a phase transition between the ferroelectric and the paraelectric, varies from 42 K for the pure SrTiO$_3$ to about 400 K for BaTiO$_3$ [17, 18]. As shown in Figure 1.7, low-Ba-composition in the specimen is not suitable for room temperature application due to their low Curie temperature, such as Ba$_{0.1}$Sr$_{0.9}$TiO$_3$ usually used to build devices operating at liquid nitrogen temperature associated with high temperature superconductors, while high-Ba compound has high loss problem.

Among the series of Ba$_x$Sr$_{1-x}$TiO$_3$, the 50/50 composition, Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST), has attracts a particular interest due to its Curie temperature theoretically around room temperature which promises a high tunability (ferroelectric usually displays its highest tunability around Curie temperature) and low loss at microwave frequencies as well as appropriate practical operating temperature. On the other hand, BST ($x=0.5$) films have in general shown little to no hysteresis in the dielectric constant with DC bias at room temperature [19-22]. Due to its multiple advantages, such as small size, light weight, fast switching speed, good reliability, high tunability, low power consumption, low cost, and relative low loss [23], BST thin film received ample attention on the applications of microwave components in both military and commercial radar and communication systems, such as phase shifters, varactors, tunable filters, and antenna. As a result, BST
thin films have been widely investigated in the recent two decades intending to increase tunability and limit the dielectric loss simultaneously [24-26].

Figure 1.7 Dielectric constant (up figure) and Loss tangent at 10 GHz (down figure) of Ba$_x$Sr$_{1-x}$TiO$_3$ single crystal as a function of temperature [17]
1.3 Organization of the dissertation

This dissertation is concerned with the deposition technique, crystal structure, and dielectric properties of barium strontium titanate (BST) films for the tunable microwave applications. The core objectives are to enhance the film’s dielectric constant and tunability and keep the loss in a relative low level to achieve a better performance in microwave frequencies.

In this work, we studied a series of BST film deposited by radio frequency magnetron sputtering and pulsed laser deposition on SrTiO$_3$ and DyScO$_3$ substrates. Crystal structure and dielectric properties as well as simple microwave applications have been exploited on different series BST films.

Chapter 1 introduces ferroelectricity and typical perovskite structure as well as the ferroelectric barium strontium titanate thin film. The introduction of typical characteristics of ferroelectrics, hysteresis and phase transition, in the viewpoint of ion displacement and free energy change is helpful for the discussion of the dielectric performance improvement in the following chapters.

In Chapter 2, the epitaxial film growth of BST thin film is introduced. Generally, deposition technique and growth conditions as well as substrate of choice can significantly affect the crystalline and structure quality of the thin film deposition. Firstly, this chapter describes the mechanism of radio frequency magnetron sputtering system and the deposition conditions used in this work. After the substrate selection section,
most important, the three-step deposition method, a new deposition technique, and post-deposition thermal treatment are introduced. Last, we raise the film strain discussion to assess the distortion in the films, is discussed.

Chapter 3 and Chapter 4 focus on the BST thin films deposited by sputtering using the three-step deposition technique on SrTiO$_3$ and DyScO$_3$ substrate, respectively. Epitaxial relationship and lattice parameters are characterized by X-ray diffraction. The dramatically reduced film strain implies the advantage of the implementation of the three-step technique as well as post-deposition thermal treatment. Before the electric measurement, the design, fabrication, and equipments used in the measurement are introduced. The electric-field-dependent capacitance measurement employed on the interdigital capacitors at low frequency (1 MHz) demonstrates the improvement on electric properties of the films due to the reduced film strain. Microwave measurements employed on the coplanar waveguide further reveal the high dielectric constant and tunability companied with low loss achieved on the BST thin films in this work. The relationship between the film strain and the dielectric properties is established.

Chapter 5 shifts the focus on improving the dielectric properties of the thicker BST films (~2 μm) deposited by pulsed laser deposition (PLD). A sputtered seed layer of BST thin film was sandwiched between the PLD deposited BST thick film and the STO substrate. The effect of introducing the seed layer on the crystal structure and its dielectric properties is presented.
As a simple microwave application, coplanar waveguide phase shifter based on BST films is discussed in Chapter 6. The detailed measurement process is described, followed by the microwave measurement results exhibition of the coplanar phase shifters fabricated on the sputtered BST thin films on DyScO\textsubscript{3} substrates and the PLD deposited BST films on STO substrates. These results suggest that the BST thin film deposited by sputtering using three-step technique produced a large differential phase shift and optimal microwave figure of merit. The coplanar phase shifters on PLD deposited films with seed layer also show a dramatic improvement on both differential phase shift and figure of merit. The good performance of coplanar phase shifter based on the BST films shows the potential of BST film applied on microwave components in practical application. Chapter 7 provides a summary of the results achieved in this thesis.
Chapter 2 Sputtering deposition and structure quality of BST thin films

Many efforts have been made on the ferroelectric thin film, especially BST thin film, by various processing techniques, such as sputtering, pulsed laser ablation deposition (PLD), molecular beam epitaxy (MBE), screen printing, sol-gel, metal-organic chemical vapor deposition (MOCVD), liquid injection or mist CVD, chemical solution deposition, and hybrid and modified deposition processes [27-33]. A process for high quality ferroelectric thin film deposition is better to satisfy the following requirements: (1) relative low processing temperature so as not to damage substrate composition or crystal structure of surface layer; (2) produce film with good quality and reproducibility; (3) relative simple operation; (4) low environment contamination; (5) low cost. Among the above techniques, sputter deposition is a very popular deposition technique in ferroelectric thin film growth and has been extensively studied in the last two decades owing to its relatively simple operation, good composition control, and low cost. The limitation of sputtering system is the control of stoichiometric composition in co-sputtering process, the thickness uniformity, and the conformal coverage of the films. However, the above limitation does not affect too much on this work because the studied samples have limited surface area (1 cm$^2$) and only a single target involved into the sputtering process. Pulsed laser ablation deposition, also called pulsed laser deposition (PLD), is another popular physical vapor deposition technique that has been widely investigated in the ferroelectric film deposition,
including BST film deposition. Using multiple targets and rotating the substrate holder, uniform coverage and good quality of ferroelectric films can be obtained. The limitation is still on the uniform coating of large area and conformal step coverage. Due to the limited size and experienced deposition, the above limitation does not affect in this work either. In this dissertation, the depositions of BST thin films on various substrates were all implemented using a radio frequency (RF) magnetron sputtering system, except for the samples with PLD deposited BST thicker top layers in Chapter 5.

2.1 RF magnetron sputtering system

Sputtering deposition is a physical vapor deposition process for depositing thin films, which ejects the atoms from the surface of the target to the substrate by bombarding the target with an incoming flux of highly energetic particles. The substrate is placed in a vacuum chamber that is pumped down to a prescribed process pressure. Sputtering starts with a creation of a plasma or glow discharge in an inert gas environment. The source target is attached to the sputtering gun coupled as the cathode; while the substrate holder is connected with the anode. An electric field with sufficient strength is applied between the anode and cathode to accelerate the positive charged inert gas ions generated in the plasma region moving to the negative biased target plate at a very high speed. This
collision creates a momentum transfer and ejects atomic size high energetic incident particles from the target, which lately deposit as a thin film into the surface of the substrate.

As shown in Figure 2.1, this multisource sputtering system operates in two modes, DC and RF modes, with three sources available for co-deposition. DC sputtering is applied to conducting materials. If the target is non-conducting material, the positive charge will build up on the material and consequently stop sputtering. RF sputtering can be applied to both conducting and non-conducting materials. An alternating electric field was applied at a typical radio frequency of 13.56 MHz for generating plasma. Gas mixture used in the system includes the oxygen and the inert gas Argon. Oxygen is used to ensure a stoichiometric composition of the deposited film. As shown in Figure 2.2, Argon is ionized to Ar$^+$ ions and is accelerated by the electric field. The Argon ions fly to the
target at a very high speed and transfer their kinetic energy to the target, which ejects the atoms in or near the surface of the target. The ejected particles move to the heated surface of the substrate and form films. A magnet array is placed underneath the target to increase the percentage of electrons taking part in ionization, increase the possibility of electrons striking the Argon atoms, increase the length of the electron path, and thereby increase the ionization efficiency significantly. The magnet array also confines those ions in a torus-shaped region to further increase the ionization probability near the surface of the target. Using the magnet array is also help to lower the voltage need to strike the plasma, control uniformity of deposited films, reduce wafer heating from electron bombardment, and increase deposition rate.

Figure 2.2 Schematic diagram of the off-axis RF magnetron sputtering mechanism
In this work, the off-axis radio frequency (RF) magnetron sputtering system was used to deposit Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) thin films. In the growth chamber, the substrate is held below the heater and faces down toward the sources. The off-axis angle between the substrate and the source is about 20º to protect the source from contaminating by the particles falling down. The deposition condition is discussed as below.

Ferroelectric thin film deposition by sputtering system is sensitive to any influence in the deposition process. Any change of the deposition condition could possibly affect the nucleation and the film epitaxy, thus seriously influence the structure quality of the thin film. The deposition temperature, pressure, the composition of the gas environment, and the RF power supply are all substantial crucial parameters that can determine the structure quality of the deposited films. A great many of studies have focused on the effect of those parameters on epitaxial ferroelectric films [34-36]. In this work, the sputtering was carried on at 120 W RF power at a pressure of 2 mTorr with a 6:1 Ar/O$_2$ gas mixture during the whole growth process. The deposition temperature, which seriously affects the crystal quality and growth rate as well as the crystal structure, is the most critical parameter for the complex oxide growth, especially for the BST thin film growth. In this work, the three-step technique effectively utilizes the deposition temperature influence to improve the structure quality of the BST thin film.
2.2 Substrate selection for ferroelectric film epitaxial growth

Unlike bulk material, the ferroelectric thin film can be affected by another factor that is the relationship with the substrate. The requirements of substrate materials for ferroelectric thin film deposition should be considered from two viewpoints, which are the possibility of high quality film epitaxial and the dielectric properties of the substrate itself.

The importance of a suitable substrate with high quality crystalline surface, on which an epitaxial film is grown, cannot be overemphasized. For oxide ferroelectric film with perovskite structure, such as BST, chemically and structurally compatible perovskite substrate materials and quality of the substrate surface significantly affect the epitaxial growth of the thin film, especial the nucleation process [37]. First of all, this presumes a close match of the lattice parameters between the substrate and the deposited film as shown in Figure 2.3. A small mismatch possibly introduces large distortion to the thin film. Subsequently, the affected structure quality of the thin film has a strong impact on the function of the ferroelectric thin films. To achieve structure perfection, substrates should have similar crystal structure type and close lattice parameters in the crystal plane facing to the deposited film in order to offer an accommodative foundation to the nucleation. High quality (smooth and isotropic) of the surface and similar thermal expansion constant to the epitaxial film should be taken into account as well in the pursuit of high quality thin film epitaxies. On the other hand, substrates preferably have
low dielectric constant and low dielectric loss as well as temperature independent dielectric properties in the consideration of microwave devices applications [38].

**Figure 2.3 The epitaxial relationship of the BST thin film and the substrate**

In our work, the substrate of SrTiO$_3$ and DyScO$_3$ with the square surface area of 1 cm$^2$ and the thickness of 0.5 mm were used for the deposition of the BST thin films using RF sputtering system. The reason of choosing those substrates will be explained in the following chapters.
2.3 Epitaxial growth and three-step technique

To improve the perfection of the crystal structure and subsequently enhance the properties of the BST thin film, we proposed and implemented a new deposition technique into the sputtering deposition of BST thin film, namely the three-step deposition method. This deposition method still keeps the same optimized radio-frequency power of 120 W and atmosphere (at a pressure of 2 mTorr with a 6:1 Ar/O₂ gas mixture), but change the procedure of the deposition by the following steps.

Figure 2.4 shows the schematic of the film structure of the three-step deposition. First, a 70-nm-thick BST nucleation layer was deposited on the substrate at a high temperature $T_1 = 1,068 \, \text{K}$. The substrate temperature was then decreased to $T_2$ within 30 min and a low-temperature BST interlayer 180 nm in thickness was deposited. Structures with different deposition temperature for interlayer ($T_2$ from 573 to 873 K) were investigated.
in order to find the best suitable $T_2$. During the third step, the substrate temperature was increased back to 1,068 K within 30 min and a 450-nm-thick BST film was deposited as the top layer. Control films with the thickness of 700 nm were grown at $T_1 = 1,068$ K only. The BST films deposited by the three-step deposition have the same total thickness as the control film does. It is worth noting that the best deposition temperature for the interlayers varies depending on the substrate material.
2.4 Crystal structure characterization and film strain

The crystal structure and orientation of the as-grown and annealed BST thin films were examined through the $2\theta$-$\omega$ and $\omega$-rocking curve scans by high resolution X-ray diffraction (HRXRD) using Cu Kα radiation. The $2\theta$-$\omega$ scan was operated in the $2\theta$ scan range of $42^\circ$ - $69^\circ$ with a step size of $0.002^\circ$ and 0.5 s counting time per data point at 45 kV and 40 mA, while the $\omega$-rocking curve scan used a step size of $0.005^\circ$ with a 0.2 s counting time per data point. The single-crystal BST (002) reflection and (022) reflection were observed in the symmetric and skew-symmetric $2\theta$-$\omega$ scan, respectively, on the as-grown and annealed epitaxial BST thin films. The reflections of the substrate were used as a calibration in the lattice-parameter calculation. According to the international diffraction data, the $2\theta$ peaks position should be at 46.471º and 67.824º for the (002) and (022) reflection of the STO substrate. The out-of-plane lattice parameter $c$ was obtained directly by using the peak position of the symmetric-scan of the film, while the in-plane lattice parameter $a$ was determined by the combination of both the symmetric and skew-symmetric scans.
To evaluate the crystal structure quality of the BST thin films, we calculate the residual strain in the films. The equilibrium (strain-free) lattice parameters $a_0$, which is different from the BST bulk lattice parameter, was used in the film strain calculation [39]. The presence of oxygen vacancies in the film and the interaction between the film and substrate make the equilibrium (strain-free) lattice parameter of BST thin film different from the ideal bulk one. Thus, the ideal bulk lattice parameter (3.947 Å) should not be used in the film strain calculation [40]. The equilibrium lattice parameter is a function of the measured in-plane lattice parameter $a$ and out-of-plane lattice parameter $c$ as well as the elastic constants as

$$a_0 = \frac{c+2\left(\frac{c_{12}}{c_{11}}\right)a}{1+2\left(\frac{c_{12}}{c_{11}}\right)}$$

Eq. 2-1
where $c_{ij}$ are the average elastic constants of bulk SrTiO$_3$ and BaTiO$_3$ single crystals, $c_{11} = 3.11645 \times 10^{11}$ N/m$^2$ and $c_{12} = 1.39805 \times 10^{11}$ N/m$^2$ [40]. Then the in-plane residual strain in the film is given by

$$x_{1,2} = \frac{a-a_0}{a_0}$$

Eq. 2-1

The residual strain in the film has a dramatic effect on the dielectric characteristics of the ferroelectric thin films. The in-plane compressive strain, corresponding to the negative value for $x_{1,2}$, generally decreases the dielectric constant and tunability [41-43]. The residual strain in the film arises from several contributions, including deposition technique, post-deposition thermal treatment, lattice mismatch from the substrate, difference in thermal expansion coefficient between the film and the substrate, and the thickness of the film [44]. Therefore, with the aim of enhancing dielectric properties, one of the best methods is optimizing the deposition technique and choosing the suitable substrate.
In our previous work [45], we found that the thickness of the film effect the film strain. As shown in Figure 2.6, the thicker the film is, the less the film strain shows (bottom figure). The out-of-plane lattice parameter $c$ decrease remarkably with the increasing of
the thickness, while the in-plane lattice parameter $a$ has only a relatively small change in value possibly due to the clamping from the substrate.

### 2.5 Post-deposition thermal treatment

To improve the crystal quality of the as-grown sputtered ferroelectric thin films, post-deposition thermal treatment is one of the effective methods and has been wildly used in practice [46, 47]. Annealing process improves the crystal structure by reducing the residual stain in the BST thin film and further impact the dielectric properties [48, 49].

In order to investigate the effect of post-deposition thermal treatments on the structure perfection of the sputtered BST thin films, we tested three samples using X-ray diffraction, including one piece of as-grown sample, one piece annealed at 1223 K, and the other one annealed at 1273 K. The three samples were all partials of the same BST thin film grown on STO substrate. The annealing was implemented in a tube furnace inside which O$_2$ atmosphere was employed with the oxygen mass-flow rate of 20 sccm to prevent losing oxygen from the BST films during thermal treatment. Thermal treatment takes 8 hours at the set temperature, which was favorable to relax the distortion in the films to a great extent, and subsequently was verified to enhance dielectric properties. The rocking curves of the three samples were displayed in Figure 2.7. The full width of half maximum (FWHM) of the $\omega$-rocking curve of the (002) BST reflection of the as-
grown, 1223 K-annealed, and 1273 K-annealed film are 37.8 arc min, 33.8 arc min, and 27.0 arc min, respectively. Therefore thermal treatment can obviously narrower the peak and enhance the intensity for the rocking curve. The improvement of the crystal quality by annealing depends on the thermal treatment condition. For the BST thin film sputtered on STO substrate in our work, the optimized annealing condition is at 1223 K for 8 hours with oxygen mass-flow rate of 20 sccm.

Figure 2.7 The ω-rocking curve of the (002) BST reflection of the as-grown, 1223 K-annealed, and 1273 K-annealed BST films on STO substrate.
SrTiO$_3$ (STO) is a suitable substrate for the epitaxial growth of BST thin film. Firstly, STO and BST have similar chemical composition and crystal structure. From the view of crystal structure, BaTiO$_3$ (BTO) and SrTiO$_3$ (STO) both are in perovskite structure, which has the Ba$^{2+}$ ions or the Sr$^{2+}$ ions are taken as the corners of the cube, oxygen ions on the center of each face to build up oxygen octahedra, and titanium ion possess the center position in the cubic cell (Figure 1.1). Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ (BST) could be considered as some of Ba$^{2+}$ ions substituted by Sr$^{2+}$ ion in the structure of BaTiO$_3$. Due to the comparable ion radii, 0.135 nm for Ba$^{2+}$ ion and 0.127 nm for Sr$^{2+}$ ion [50], the substitution of Ba$^{2+}$ ion by Sr$^{2+}$ ion to compositing the Ba$_{0.5}$Sr$_{0.5}$TiO$_3$ structure does not change too much lattice parameter from the original BaTiO$_3$ structure. Actually, the lattice parameters are 3.905 Å for bulk STO single crystal and 3.947 Å for bulk BST single crystal [51]. Therefore, the similar composition and close lattice parameter is one of the guaranty for the successful film epitaxial. On the other hand, the thermal expansion coefficients of BST and STO are similar, $\alpha_{\text{BST}}$=10.5 *10$^{-6}$ K$^{-1}$ [44], $\alpha_{\text{STO}}$=8.8 *10$^{-6}$ K$^{-1}$ [52]. The dielectric constant of STO is 300 at room temperature. And its dielectric tangent loss is as low as ~0.0098 according to our previous research [2]. Its Curie temperature as low as 42 K gives a promise that STO substrate is very stable and has little to no change on dielectric properties within the temperature range of the
measurements. Even though its dielectric constant (~300) is not as low as we expected for a microwave device, the similar composition and close lattice parameter also make STO a good substrate choice to study the BST thin film growth.

### 3.1 The effect of three-step deposition on crystal structure of BST thin film

BST thin films were deposited on STO substrate by off-axis radio frequency (RF) magnetron sputtering using a 3-inch-diameter \( \text{Ba}_{0.5}\text{Sr}_{0.5}\text{TiO}_3 \) stoichiometric target. The deposition was carried on at 120 W RF power under a gas mixture of 6:1 Ar/O\(_2\) with the pressure of 2 mTorr during the whole growth process. To control the strain in BST structures, we employed the three-step growth technique as introduced in Chapter 2. First, a 70-nm-thick BST nucleation layer was deposited on the STO substrate at a high temperature \( T_1 = 1,068 \) K. The substrate temperature was then decreased to \( T_2 \) within 30 min and a low-temperature BST interlayer 180 nm in thickness was deposited. The substrate temperature \( T_2 \) was varied, and the structures with \( T_2 = 773, 673 \) and 573 K were grown (denoted as Films A, B and C, respectively). During the third step, the substrate temperature was heat up back to 1,068 K within 30 min and a 450-nm-thick BST film was deposited as the top layer. A control film (Film D) with the thickness of 700 nm was grown at a single deposition temperature of \( T_1 = 1,068 \) K. To improve the
crystal quality of the BST layer and its dielectric properties, a part of every film was annealed at 1,273 K for 8 hours after the deposition in a tube furnace. The O$_2$ atmosphere (O$_2$ mass-flow rate of 20 sccm) was employed to prevent losing oxygen from the BST films during post-deposition thermal treatment, which procedure was verified to relieve strain and enhance the dielectric properties [53]. The structure perfection and lattice

![Graphs showing HRXRD 2θ-ω symmetric (002) and skew-symmetric (022) reflections for as-grown and annealed BST thin films deposited on STO substrate by the three-step technique (Film C) and the control film D.](image)

Figure 3.1 The HRXRD 2θ-ω symmetric (002) (figure a for Film C and figure c for Film D) and skew-symmetric (022) (figure b for Film C and figure d for Film D) reflections of as-grown (black curve) and annealed (red curve) BST thin film deposited on STO substrate by the three-step technique (Film C) and the control film D, respectively.
parameters of the as-grown and annealed BST films were assessed by high-resolution X-ray diffraction (HRXRD) using $2\theta$-$\omega$ and $\omega$-rocking curve scans.

Figure 3.1 compares the XRD $2\theta$-$\omega$ scan of the symmetric (002) and skew-symmetric (022) reflections of the as-grown and annealed BST film grown by the three-step method with $T_2 = 573$ K and the reference film. As shown in Figure 3.1-a, the double-peak $2\theta$-$\omega$ pattern for the (002) reflection of as-grown film grown by the three-step technique (red curve) suggests that those layers in Film C have different lattice parameters due to their different deposition temperatures. The double-peak feature is also seen, albeit less pronounced, in the (022) reflection (Figure 3.1-b) from the skew-symmetric scan. Generally, the thicker the layer is, the higher the reflection intensity is in XRD scan. Therefore, we presume that the more intense peak at lower $2\theta$ is from the top BST layer with the thickness of deposited at high temperature $T_1$, while the reflection at higher $2\theta$ is from the 180-nm-thick interlayer deposited at lower temperature $T_2$. The position of the reflection at lower $2\theta$ is also similar to that from the control film grown at the same temperature of 1,068 K in Figure 3.1-c. It is consistent with our previous assumption that the peak with lower $2\theta$ is contributed by the top layer of Film C. The nucleation layer most likely cannot be resolved on the HRXRD scans because of its thinness (70 nm). Thermal treatment at 1273 K for 8 hours dramatically decreases the difference in lattice parameters between the different layers grown at temperatures $T_1$ and $T_2$, respectively, in the tri-layer structures and subsequently merged the peaks into a single BST peak which is shown as the black curves in Figure 3.1-a and 3.1-b. The reflections from the control
layer also become narrower and more symmetric upon annealing as shown in Figure 3.1-c and 3.1-d, in which the red curves represent the scan on the annealed control film and the black curve displays the scan on the as-grown one. A shoulder at higher angles on the HRXRD pattern from the as-grown control film is indicative of non-uniform strain due to the off-axis sputtering, which is relaxed and less obvious after the thermal treatment (Figure 3.1-c). The HRXRD patterns of the films grown with $T_2 = 673$ and $773$ K (Film B and Film C) are similar to those shown in Figure 3.1-a and 3.1-b. Upon annealing, full width of half maximum (FWHM) of the $\omega$-rocking curve of the (002) BST reflections decreased dramatically for all films. For instance, the FWHM was decreased from 37.8 to

<table>
<thead>
<tr>
<th>BST/STO</th>
<th>status</th>
<th>$c$ (Å)</th>
<th>$a$ (Å)</th>
<th>Strain $x_{1,2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film A</td>
<td>As-grown</td>
<td>4.098/3.990</td>
<td>3.987/3.983</td>
<td>-0.014/-0.001</td>
</tr>
<tr>
<td>BST/STO with $T_2 = 773$ K</td>
<td>Annealed</td>
<td>3.975</td>
<td>3.968</td>
<td>-0.001</td>
</tr>
<tr>
<td>Film B</td>
<td>As-grown</td>
<td>4.092/4.013</td>
<td>3.980/3.984</td>
<td>-0.015/-0.004</td>
</tr>
<tr>
<td>BST/STO with $T_2 = 673$ K</td>
<td>Annealed</td>
<td>3.984</td>
<td>3.959</td>
<td>-0.003</td>
</tr>
<tr>
<td>Film C</td>
<td>As-grown</td>
<td>4.088/4.002</td>
<td>3.975/3.956</td>
<td>-0.015/-0.006</td>
</tr>
<tr>
<td>BST/STO with $T_2 = 573$ K</td>
<td>Annealed</td>
<td>3.984</td>
<td>3.954</td>
<td>-0.004</td>
</tr>
<tr>
<td>Film D</td>
<td>As-grown</td>
<td>4.113</td>
<td>3.987</td>
<td>-0.016</td>
</tr>
<tr>
<td>BST/STO Control film</td>
<td>Annealed</td>
<td>3.998</td>
<td>3.958</td>
<td>-0.005</td>
</tr>
</tbody>
</table>

Table 3.1 The lattice parameters and film strain of the control layer and the structures grown by the three-step method with different interlayer-growth-temperatures. Two values of lattice parameter represent the two BST peaks in the same reflection in the HRXRD scans. BST films on STO substrate.
27.0 arc min for the BST (002) reflection on Film A. The out-of-plane lattice parameter $c$ and in-plane lattice parameter $a$ were derived from the HRXRD symmetric and skew-symmetric scans as discussed in Chapter 2. The film strains of all the three-step deposited films and the control film were calculated using the in-plane and out-of-plane lattice parameters as well as the equilibrium lattice parameters. The lattice parameters and film strains of Film A-D are summarized in Table 3.1.

The lattice parameters related to the double-peak feature of HRXRD scans for the as-grown films are listed in Table 3.1. As discussed above, the larger lattice parameter corresponding to the low $2\theta$ peak in the HRXRD scans is assigned to the top layer while the smaller one to the low-temperature-grown interlayer for Film A, B, and C. The film strain with the negative values in Table 3.1 represents the compressive residual strain in the films. In the as-grown tri-layer structures, the top layers of every sample have similar film strain, while the interlayers grown at different temperatures show different film strain. The compressive residual strain in the as-grown control film is similar to the one top layers of the as-grown Film A-C, which were deposited at the same temperature as the control film did. It implies that the deposition temperature seriously influences the lattice distortion in each layer. As the experimental results shown, the interlayer deposition temperature of 773 K is believed to yield the least strained interlayer in the as-grown three-step deposited films.
After thermal treatment, the double peaks of the three-step deposited films all merged into a single peak in the HRXRD pattern, which subsequently led to a single lattice parameter for each film. As shown in Table 3.1, the post-deposition thermal treatment dramatically contracts both the out-of-plane and in-plane lattice parameters due to the
film relaxation. One of the main reasons is that oxygen vacancies were filled by annealing the samples in flowing oxygen atmosphere. The fact that the as-grown BST thin films contain significant amount of oxygen vacancies can be estimated by the much larger cell volume for the lattice structure of the as-grown films compared with that of annealed films. The decrease on the amount of the oxygen vacancies due to the re-fill in the thermal treatment subsequently causes a lattice compression in all BST films after annealing. The lattice parameters and the film strain of the annealed films were compared in the following figure.

As shown in Figure 3.2, all the annealed films deposited by the three-step position method show less compressive residual strain than the control film. The different deposition temperature for the interlayer in the three-step deposition significantly affects the degradation of the compressive residual strain upon annealing. Film A displays the smallest out-of-plane lattice parameter and the largest in-plane lattice parameter. The similar lattice parameters in both directions yield the less distortion in the film that results in a less compressive residual strain. There is only -0.001 residual strain left in the annealed Film A, which is a large degradation compared to the residual strain of -0.005 in the control film. As aforementioned discussion about the difference of the as-grown interlayer, the least film strain in the interlayer showed in the as-grown Film A. We believe the least compressive film strain upon annealing is attributed to the optimized interlayer deposition temperature. Therefore, it is verified that the three-step deposition technique with the optimized deposition temperature of 773 K for the interlayer
effectively relaxes the BST thin films deposited on STO substrates upon annealing and reduces the compressive residual strain to a very great extent.

### 3.2 Electrical tunability at low frequency

Ferroelectric thin films generally have a high dielectric permittivity that can be controlled by the application of small DC bias voltages [54], which makes them a promising candidate for the application of miniature effective tunable devices with high speed. Therefore, the high tunability of the BST thin film is one of the great interests and been widely investigated [55, 56]. Interdigital capacitor (IDC) structure is small in size, which allows fabricating many devices on the same sample with limited surface area. It is easy to be fabricated and measured, which is attribute to the simple symmetric design. Therefore, IDC was chosen to preliminarily test the electrical quality of the BST thin films in our work. Using IDCs, we can simply measure the capacitance as a function of the applied electric field to estimate the tunability and dissipation loss of the BST thin films and further find the optimized deposition technique.
Figure 3.3 Schematic of the interdigital capacitor used in this work

As shown in Figure 3.3, the interdigital capacitors used in this work have designed with 12 fingers. The fingers have the width of 5μm and the length of 80 μm with the separation of 5 μm between fingers. The IDCs were fabricated with a 50-nm-thick Cr layer deposited by e-beam evaporation and a protective thin layer of Au deposited by thermal evaporation on the top of the BST films through the normal lift-off procedure. The metal contactor of Cr was selected due to its good adhesion. To preliminarily test the tunability of the BST thin films, we measured the capacitance of IDCs of each film using a Hewlett-Packard 4284 Precision LCR meter at 1 MHz.
Figure 3.4 Capacitance vs. DC bias at room temperature at 1 MHz for IDC devices on as-grown and annealed Film A (figure A) and Film D (figure B). (BST/STO)
The capacitance-voltage measurement of IDCs was employed on all BST thin films deposited on STO substrates. Figure 3.4 demonstrates the capacitance changes with the applied DC bias in ±40 V on the IDCs fabricated on the three-step deposited Film A and the control film D. The double curves of each sample represent the measurement under both voltage sweep directions.

As-grown films (see the two inset figures in Figure 3.4) show C-V curves with a large separation between the voltages corresponding to the maxima of capacitance under both directions of the voltage sweep (butterfly shape). However, the separation of the as-grown film A (Figure 3.4-A) was slightly smaller than the as-grown control film (Figure 3.4-B). It is worth noting that the separation between the curves when sweeping from positive to negative bias and vice versa is attributed to the internal polarization caused by the electric field in the layers, arising from the ferroelectric nature of BST. Since the Curie temperature of bulk BST material is around 250 K, BST should be in paraelectric phase at room temperature. However, the compressive residual strain in the film increases the Curie temperature and makes the BST thin films show ferroelectric phase at room temperature. The butterfly shape of C-V characteristics correlates with the presence of a large strain in the as-grown films and implies that the as-grown films are all in the ferroelectric state. Upon annealing, the separation between the capacitance maxima drastically reduces. Annealed film A has nearly no separation, while annealed Film B, C, and D have similar separations in various degrees, which correlates with larger residual
strains in these three structures. The reducing of the separation is consistent with the increasing of the capacitance tunability.

As shown in Figure 3.4, thermal treatment increases the capacitance value and tunability dramatically on both three-step deposited Film A and the control film D. Film A shows the significant increase of the tuning of capacitance from 1.5% to 27.6% upon annealing at 1273 K for 8 hours. Special emphasis is that the dramatic increase in overall capacitance upon annealing is attributed to an increase in the dielectric constant of the film. The control film D also exhibits the large but substantially lower improvement of the capacitance tuning from 1.0% to 15.4% upon annealing (See Figure 3.4-B). However, the existence of the pronounced separation between the capacitance maxima for two opposite sweep directions suggests that the annealed Film D is still in ferroelectric phase.

Table 3.2 The film strain, capacitance tunability, and dissipation of the three-step deposited BST films A, B, and C as well as the control film D.

<table>
<thead>
<tr>
<th>Films</th>
<th>Growth technique</th>
<th>Strain $x_{1,2}$</th>
<th>Tuning (%) of capacitance</th>
<th>Dissipation at 1MHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film A</td>
<td>Three-step with $T_2=773$ K</td>
<td>-0.001</td>
<td>27.6</td>
<td>0.020</td>
</tr>
<tr>
<td>Film B</td>
<td>Three-step with $T_2=673$ K</td>
<td>-0.003</td>
<td>17.6</td>
<td>0.019</td>
</tr>
<tr>
<td>Film C</td>
<td>Three-step with $T_2=573$ K</td>
<td>-0.004</td>
<td>14.5</td>
<td>0.018</td>
</tr>
<tr>
<td>Film D</td>
<td>Control film deposited at $T=1068$ K</td>
<td>-0.005</td>
<td>15.4</td>
<td>0.015</td>
</tr>
</tbody>
</table>
In this work, the capacitance tunability was calculated as \( \frac{C_{\text{max}} - C_{\text{min}}}{C_{\text{max}}} \) in the applied voltage range from -40V to +40V at 1 MHz. Large tunability enables the miniaturization of microwave component. The tunability and the dissipation of each film were summarized in Table 3.2. The improvement of the capacitance tunability is in a good agreement with the degradation of the film strain. Film A with the least film strain shows the largest tuning of capacitance at 1 MHz. It is predictable that the dissipation increases as the tunability increasing. However, the dissipation of Film A of only 0.020 is still acceptable.

3.3 Dielectric property of BST thin film on STO substrate at microwave frequencies

The practice application of the BST thin film is aim at the operation under microwave frequencies. To reveal the dielectric performance of the BST films at microwave frequencies, we used network analysis techniques to measure the complex impedance of the devices fabricated on the BST thin film deposited on STO substrate.
3.3.1 Coplanar waveguide transmission line for determination of dielectric properties of BST thin film

![Figure 3.5 Schematic of CPW fabricated on a double-layer dielectric substrate](image)

In this work, coplanar waveguide lines were used to determine the dielectric properties of the BST thin film as well as act as simple phase shifters. As shown in Figure 3.5, the coplanar waveguide (CPW) were fabricated by depositing a thick metal layer (~2 μm) on the BST thin films grown on dielectric substrates. The conductors have a center single strip separated by a narrow gap from two ground planes on either side. In this work, the thickness of BST film is $h_2$ (700 nm) and the thickness of the substrate is $h_1$ (0.5 mm). The total capacitance $C_{CPW}$ is the sum of the partial capacitance $C_1$, $C_2$, and $C_{air}$,

$$C_{CPW} = C_1 + C_2 + C_{air}$$ Eq. 3.1
where $C_{\text{air}}$, $C_1$, and $C_2$ are the partial capacitance from air, the lower substrate layer and the upper BST thin film, respectively, and are given by

$$C_{\text{air}} = 4\varepsilon_0 \frac{K(k_0)}{K(k_0')},$$  \hspace{1cm} \text{Eq. 3.2}$$

$$C_1 = 2\varepsilon_0 (\epsilon_{r1} - 1) \frac{K(k_1)}{K(k_1')},$$  \hspace{1cm} \text{Eq. 3.3}$$

$$C_2 = 2\varepsilon_0 (\epsilon_{r2} - \epsilon_{r1}) \frac{K(k_2)}{K(k_2')}.$$  \hspace{1cm} \text{Eq. 3.4}$$

where $\varepsilon_0$, $\epsilon_{r1}$, and $\epsilon_{r2}$ are the vacuum permittivity, the relative dielectric constant of the substrate, and the relative dielectric constant of the BST thin film, respectively. The complete elliptic integrals $K(k_i)$ and $K(k_i')$ have

$$k_0 = \frac{s}{s+2w},$$  \hspace{1cm} \text{Eq. 3.5}$$

$$k_1 = \frac{\sinh (\pi s/4h_1)}{\sinh ([\pi (S+2W)]/4h_1)},$$  \hspace{1cm} \text{Eq. 3.6}$$

$$k_2 = \frac{\sinh (\pi s/4h_2)}{\sinh ([\pi (S+2W)]/4h_2)},$$  \hspace{1cm} \text{Eq. 3.7}$$

$$k_i' = \sqrt{1 - k_i^2} \hspace{1cm} (i = 0, 1, 2).$$  \hspace{1cm} \text{Eq. 3.8}$$

where $h_1$ and $h_2$ are the thickness of the substrate and the BST film, $S$ and $W$ are the width of the signal line and the separation between the signal line and the ground plane, respectively, as shown in Figure 3.5. In our work, the values of $S$ and $W$ are 60 $\mu$m and 5 $\mu$m.

Substituting Eqs 3.2-3.4 into Eq 3.1, the total capacitance is given as

$$C_{CPW} = 4\varepsilon_0 \frac{K(k_0)}{K(k_0')} + 2\varepsilon_0 (\epsilon_{r1} - 1) \frac{K(k_1)}{K(k_1')} + 2\varepsilon_0 (\epsilon_{r2} - \epsilon_{r1}) \frac{K(k_2)}{K(k_2')}.$$  \hspace{1cm} \text{Eq. 3.9}$$
Using quasi-static approximation, the effective dielectric constant is defined as

$$\varepsilon_{\text{eff}} = \frac{\varepsilon_{\text{CPW}}}{\varepsilon_{\text{air}}}$$

Eq. 3.10

Substituting Eqs. 3.2 and 3.9 into Eq. 3.10 gives

$$\varepsilon_{\text{eff}} = 1 + q_1 (\varepsilon_{r1} - 1) + q_2 (\varepsilon_{r2} - \varepsilon_{r1})$$

Eq. 3.11

where the filling factors $q_1$ and $q_2$ are defined as

$$q_1 = \frac{1}{2} \frac{K(k_1') K(k_0')} {K(k_1') K(k_0)}$$

Eq. 3.12

$$q_2 = \frac{1}{2} \frac{K(k_2') K(k_0')} {K(k_2') K(k_0)}$$

Eq. 3.13

According to Eq. 3.11, the contribution of the thin film to the total effective dielectric constant is directly proportional to the filling factor $q_2$. Therefore, the filling factors demonstrate the proportionality of electromagnetic energy inside each dielectric layer.

The characteristic impedance of the CPW, $Z_0$, is given as

$$Z_0 = \frac{1}{c \varepsilon_{\text{air}} \sqrt{\varepsilon_{\text{eff}}}} = \frac{30\pi}{\sqrt{\varepsilon_{\text{eff}}}} \frac{K(k_0')}{K(k_0)}$$

Eq. 3.14

The characteristic impedance of CPW will be used to analysis the conductor loss in the next section. The optimized characteristic impedance is 50 $\Omega$, and also be used to design the value of S and W to minimize the impedance mismatch in order to reducing the loss.

As soon as we get the effective dielectric constant from the experiment, using the above method, we can get the relative dielectric constant of the BST film by calculation.

Using the conformal mapping method, we could estimate the dielectric loss on the BST films. Coplanar waveguides have three types of losses: dielectric, ohmic, and
radiation/surface wave. In our work, since the line width is much shorter than the electromagnetic wavelength, the radiation loss can be neglected. Therefore, we assume that the loss of the CPW is mainly due to conductor loss and dielectric loss. The total attenuation $\alpha$ is given by

$$\alpha = \alpha_c + \alpha_d$$  \hspace{1cm} \text{Eq. 3.15}

where $\alpha_c$ is the attenuation constant due to conductor loss in CPW device and $\alpha_d$ is the attenuation constant due to the dielectric loss came from both the BST film and the substrate. First, let’s look at the conductor loss part. In order to minimize the conductor loss, the thickness of the metal conductor should be much greater than the skin depth $\delta$ in the metal. In our case, the thickness of conductor, $t$, is around 2 $\mu$m which is much larger than the skin depth. The attenuation constant $\alpha_c$ (unit in Nepers/meter) is given by

$$\alpha_c = \frac{R_c + R_g}{2Z_0}$$  \hspace{1cm} \text{Eq. 3.16}

where $R_c$ is the series resistance of the center strip (in $\Omega/m$) and is given by

$$R_c = \frac{R_s}{4S(1-k_0^2)K^2(k_0)} \left[ \pi + \ln \left( \frac{4\pi S}{t} \right) - k_0 \ln \left( \frac{1+k_0}{1-k_0} \right) \right]$$  \hspace{1cm} \text{Eq. 3.17}

$R_g$ is the series resistance of the ground planes (in $\Omega/m$) and is given by

$$R_g = \frac{k_0 R_s}{4S(1-k_0^2)K^2(k_0)} \left[ \pi + \ln \left( \frac{4\pi(S+2w)}{t} \right) - \frac{1}{k_0} \ln \left( \frac{1+k_0}{1-k_0} \right) \right]$$  \hspace{1cm} \text{Eq. 3.18}

and $Z_0$ is the characteristic impedance of the CPW device which was given in Eq. 3.14.

The term $R_s$ is the resistance due to the skin effect and given by

$$R_s = \frac{1}{\delta \sigma}$$  \hspace{1cm} \text{Eq. 3.19}
where $\sigma$ is the conductivity of the metal conductor and is $6.173 \times 10^7$ S/m for the Ag stacks conductor in our work. The skin depth $\delta$ in meter is given by

$$\delta = \sqrt{\frac{2}{\omega \mu \sigma}}$$

Eq. 3.20

where $\omega = 2\pi f$ with the measurement frequency $f$ in Hz and $\mu = \mu_0 \mu_r$ with the permeability constant $\mu_0 = 4\pi \times 10^{-7}$ Henry/meter and relative permeability of 1 for silver. Therefore, we could rewrite Eq. 3.20 and 3.19 as

$$\delta = \frac{1}{\sqrt{24.7 \pi^2 f}}$$

Eq. 3.21

$$R_s = 2.53 \times 10^{-7} f^{1/2}$$

Eq. 3.22

As described in Eq. 3.16, another important contribution to the total loss is due to the dielectric loss. The effective loss tangent $\tan\delta_{\text{eff}}$ is contributed from both the BST film and the substrate and given by

$$\varepsilon_{\text{eff}} \tan\delta_{\text{eff}} = q_1 \varepsilon_{r1} \tan\delta_1 + q_2 \varepsilon_{r2} \tan\delta_2$$

Eq. 3.23

where $\tan\delta_1$ and $\tan\delta_2$ are the loss tangent from the substrate and the BST film, respectively. The effective loss tangent can be obtained from the dielectric attenuation constant as [57]

$$\alpha_d = 0.91 \sqrt{\varepsilon_{\text{eff}} f \tan\delta_{\text{eff}}}$$

Eq. 3.24

In Eq. 3.24, the unit of the dielectric attenuation constant is dB/cm and the unit of the frequency is in GHz.
Substituting the loss of CPW device in measurement into Eq. 3.15-3.23, we could calculate the dielectric loss tangent of the BST film, \( \tan \delta_2 \). It indicates that due to the inevitable error of TRL calibration near zero frequency, the measurement and calculation results at low frequency could be not accurate. Many experiments proofed this assumption [57]. In addition, the industry application is more interested in high frequency. Our measurements were employed in the frequency range of 2-20 GHz.

### 3.3.2 Fabrication technique and measurement setting

![Figure 3.6 Schematic of the top view of CPW and the cross-section view of the metal stacks in CPW fabrication](image)

As shown in Figure 3.6, the coplanar waveguide used in this work has a signal line with the width of 60 \( \mu \)m in the center and a separation of 5\( \mu \)m between the edge of the signal
line and the ground planes on both sides. The length of the CPW transmission lines varied from 0.2 mm to 1.5 mm. For the evaluation of dielectric properties of the prepared structures, coplanar waveguides were photolithographically fabricated on the top of BST films using a four-layer Cr/Ti/Ag/Au (50/25/2000/50 nm) metal stacks (Figure 3.6). The chromium layer has a good adhesion to the BST film, the silver was chosen as the main part of the electrode due to its good conductivity of $6.173 \times 10^7$ S/meter, and the protective gold layer covers the surface of the silver contactor due to its hard oxidation and good conductivity. To avoid high loss contributed from the metal at high frequency, the thickness of the metal stack was designed to be large than four times of the skin depth of the silver contactor. For the fabrication of the thick-metal electrodes, a tri-layer liftoff procedure using a PMMA/chromium/photoresist stack was performed and thick metal films were deposited by electron-beam evaporation.

Microwave measurement was performed using an Alessi probe station with the ground-signal-ground probes connected to a Hewlett-Packard 8510C vector network analyzer. Hewlett-Packard 83651B series synthesized sweeper was used in the microwave measurement within the frequency range of 2-20 GHz. Hewlett-Packard E3632A DC power supply was used to apply bias voltages of 0 V to ±30 V between the signal line and the ground planes, corresponding to the applied electric field between 0 to 60 kV/cm on the CPW. Calibration to the probe tips was carried out using the thru-reflect-line (TRL) calibration method. Two-port scattering parameters (S Parameters) measurements were employed using Hewlett-Packard 8517B S parameter test set. HTBasic-9.5 software
was used to extract the effective dielectric constant and the effective dielectric loss from the raw data in the measurements.

The complex propagation constant \( \gamma = \alpha + i\beta \) calculated from the S parameters was used to describe the microwave propagation on the CPWs [58]. \( \alpha \) is the attenuation constant and \( \beta \) is the phase constant. The attenuation constant \( \alpha \) contains two parts, the dielectric loss \( \alpha_d \) and the conductor loss \( \alpha_c \). The effective permittivity of the coplanar waveguide transmission line, can be obtained by

\[
\varepsilon_{\text{eff}} = -\left(\frac{c_0 \gamma}{2\pi f}\right)^2
\]

Eq. 3.25

where \( c_0 \) is the speed of light in a vacuum and \( f \) is the measurement frequency. As the propagation constant \( \gamma \) is complex quantity, so is the calculated effective permittivity.

Then real part of the above effective permittivity, namely the effective dielectric constant, could also be obtained at the same time. The effective loss tangent is given using the above effective permittivity by the following expression

\[
\tan \delta_{\text{eff}} = \frac{\varepsilon''_{\text{eff}}}{\varepsilon'_{\text{eff}}}
\]

where \( \varepsilon''_{\text{eff}} \) and \( \varepsilon'_{\text{eff}} \) are the real and imaginary parts of the effective permittivity, respectively.

In fact, the MultiCal program has been used in our work to set up the conjunction with HP 8510C vector network analyzer. Using this program, the effective dielectric constant and the effective loss of the CPW transmission lines were easily obtained from the
measurement raw data. Microwave measurements were performed on the CPW devices. Based on the theoretical analysis in the section 3.3.1, the relative dielectric constant and the dielectric loss tangent of the BST thin film can be calculated using the effective dielectric constant and effective loss.

### 3.3.3 Dielectric property of BST thin film on STO substrate

**Table 3.3 The dielectric properties summary of the three-step deposited BST films A, B, and C as well as the control film D.**

<table>
<thead>
<tr>
<th>Films</th>
<th>Growth technique</th>
<th>Strain $x_{1,2}$</th>
<th>Dielectric constant $\varepsilon_r$</th>
<th>Tunability (%) in 60 kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film A</td>
<td>Three-step with $T_2=773$ K</td>
<td>-0.001</td>
<td>1631</td>
<td>36.7</td>
</tr>
<tr>
<td>Film B</td>
<td>Three-step with $T_2=673$ K</td>
<td>-0.003</td>
<td>1181</td>
<td>24.8</td>
</tr>
<tr>
<td>Film C</td>
<td>Three-step with $T_2=573$ K</td>
<td>-0.004</td>
<td>1111</td>
<td>26.8</td>
</tr>
<tr>
<td>Film D</td>
<td>Control film deposited at $T=1068$ K</td>
<td>-0.005</td>
<td>1024</td>
<td>33.3</td>
</tr>
</tbody>
</table>

The dielectric constant of the BST structures extracted from the measured results using Conformal Mapping on CPW transmission lines with various lengths are summarized in Table 3.3. Assuming that all of the loss in the system is due to either conductor loss or dielectric loss, i.e. no radiation or surface wave losses, the dielectric loss (tan δ) of the BST layers can also be extracted as the aforementioned calculation method. In this work,
the dielectric tunability was calculated as \( \frac{\varepsilon_{\text{max}} - \varepsilon_{\text{min}}}{\varepsilon_{\text{max}}} \) in the applied voltage range. As shown in Table 3.3, the relative dielectric constant of Film A deposited under the optimum conditions is as high as 1631 and exhibits high tunability of 36.7% at 10 GHz in the range of DC bias voltages from 0 to 30 V comparing with 15.4% tuning for the control film exhibiting much lower \( \varepsilon_r \) of 1024. To the best of our knowledge, the value of relative dielectric constant in Film A is higher than values reported in the literature for BST films thinner than 1 \( \mu \text{m} \).
Chapter 4 Film strain and Dielectric properties of BST thin film on DyScO$_3$ substrate

4.1 Dysprosium scandate substrate

As the aforementioned discussion, in order to achieve BST thin films of high structural quality, selection of optimum substrates and optimizing the film deposition process are critical. Strontium titanate (STO) has been widely investigated as a substrate material for BST film epitaxial for years. The three-step deposition technique was verified to effectively improve the structure quality and the dielectric properties of the BST thin films on the STO substrates in Chapter 3. However, in the consideration of microwave applications, STO is not the best choice due to its high dielectric constant (~300). The substrates with low relative dielectric constant and commercially availability are needed. Recently, many rare earth scandates have attracted a rising interest as substrate materials for ferroelectric thin film deposition. The crystal structure of rare earth scandates is orthorhombic in space group No. 62 $Pnma$ with typical pseudocubic structure with the lattice parameters of 3.9-4.05 Å in (110) plane [59, 60]. The cubic/pseudocubic lattice parameters of the substrates under consideration for BST film deposition are summarized in Figure 4.1.
DyScO$_3$ is the scandate substrate used in this work for the deposition of the BST thin films. DyScO$_3$ has orthorhombic lattice structure with the lattice parameters of $a=5.720$ Å, $b=7.890$ Å, and $c=5.442$ Å [59, 60]. Its pseudocubic unit cell can be obtained by rotating the orthorhombic cell in $45^\circ$ as shown in Figure 4.2. The lattice parameter of the pseudocubic lattice can be obtained by the following calculation.

\[
a_{pc} = \frac{\sqrt{a^2+c^2}}{2} = 3.947 \text{ Å}; \quad b_{pc} = \frac{b}{2} = 3.945 \text{ Å}
\]

Eq. 4.1

The pseudocubic lattice structure of DyScO$_3$ has the in-plane lattice parameter 3.947 Å and the out-of-plane lattice parameter of 3.945 Å at room temperature, which are very close to 3.947 Å of bulk Ba$_{0.5}$Sr$_{0.5}$TiO$_3$. In the [110] direction, DyScO$_3$ has a similar
AO/BO$_2$ stacking to STO and BST, which makes the DyScO$_3$ substrate accommodate to the epitaxial deposition of BST thin film.

![Diagram of DyScO$_3$ unit cell with pseudocubic lattice structure]

Figure 4.2 Unit cell of DyScO$_3$ with the pseudocubic lattice structure

As aforementioned, to enhance structural quality of the epitaxial films, substrates of choice must have small lattice mismatch and similar thermal expansion as well as having both low dielectric constant and low dielectric loss for microwave applications. DyScO$_3$ has the similar thermal expansion coefficients ($\alpha_{\text{DyScO}_3}=8.4 \times 10^{-6}$ K$^{-1}$ and $\alpha_{\text{BST}}=10.5 \times 10^{-6}$ K$^{-1}$), absence of phase transitions from 25 to 1273 K, no dielectric anomaly form 100 to
423 K, and low relative dielectric constant ~20. With the help of the three-step deposition technique, the BST thin film deposited on DyScO₃ substrate could have more practical application at microwave frequencies. In this chapter, our work focuses on the microstructure characteristics and dielectric properties of the BST thin films deposited on the DyScO₃ substrate by the three-step technique.

4.2 Deposition and crystal structure of the BST thin film on DyScO₃ substrate

The BST thin films epitaxially deposited on DyScO₃ substrates by Radio Frequency magnetron sputtering were investigated at microwave frequencies. To improve the structural perfection of the films, we implemented the aforementioned three-step
deposition method. To improve the temperature uniformity of substrate during the BST film deposition, a thin layer of metal, including a 300-nm-thick titanium layer and a protect 30-nm-thick platinum layer, were deposited on the back of the substrate by e-beam evaporation as shown in Figure 4.3. The deposition was carried on at 120 W RF power and a pressure of 2 mTorr in a 6:1 Ar/O₂ gas mixture during the deposition process. In the three-step deposition procedure, a 70-nm-thick BST nucleation layer was firstly deposited on the STO substrate at a high temperature T₁ = 1,068 K. The substrate temperature was then decreased to T₂ within 30 min and a low-temperature BST interlayer 180 nm in thickness was deposited. On the third step, the substrate temperature was increased back to 1,068 K within 30 min and a 450-nm-thick BST film was deposited as the top layer. During the interlayer deposition, the substrate temperature T₂ of 873, 773, and 673 K (denoted as films E, F, and G, respectively) were used to vary the films’ crystallinity and resulting microwave properties. A control film (Film H) with the thickness of 700 nm was grown in one-step at T₁ = 1,068 K. To improve the crystal quality of the BST layer and its dielectric properties, we employed a post-deposition thermal treatment on a part of every film (Film E-H) at 1298 K for 8 hours in a tube furnace, which is a different annealing temperature from the one applied on Film A-D in Chapter 3. The O₂ atmosphere (O₂ mass-flow rate of 20 sccm) was employed to prevent losing oxygen from the BST films during thermal treatment. This procedure was proved in the previous chapters to relieve strain and enhance the dielectric properties.
The crystalline properties of the as-grown and annealed BST films were characterized by high resolution X-ray diffraction (HRXRD) using 2θ-ω and ω-rocking curve scans. The out-of-plane and in-plane epitaxial relationships deduced from HRXRD measurements are (001) BST//(101) DyScO₃ and (100) BST//(010) DyScO₃, respectively, in agreement with findings by M. D. Diegalski et al. [61] for the growth of SrTiO₃ on DyScO₃. Figure 4.4 shows the XRD 2θ-ω scan of the symmetric (002) reflection from the three-step Film E (Figure 4.4-a) and the control Film H (Figure 4.4-b). Unlike the control layer featuring only a single (002) reflection, the as-grown three-step film shows two peaks (Figure 4.4-a), suggesting that the BST layers grown at different temperatures have different lattice parameters. Generally, the thicker the layer is the higher the reflection intensity is in HRXRD scan when the layers have comparable structural quality. We presume that the relatively more intense peak at 2θ ≈ 43.95° is from the top 450-nm BST layer grown at T₁=1068 K, while the broader and weaker reflection is from the 180-nm-thick BST interlayer grown at T₂=873 K. The HRXRD pattern from the control film grown at the same temperature of 1068 K as that of the top layer in the three-step Film E exhibits a single peak centered at 43.9° (Figure 4.4b), close to that from the more intense peak for Film E in Figure 4.4-a. The seed layer most likely cannot be resolved on HRXRD scans due to its thinness (70 nm) /quality. Upon the thermal treatment at 1273 K for 8 hours in flowing oxygen, two peaks observed for the as-grown films merge into a single, asymmetric peak showing a small-angle tail (Figure 4.4-a). The asymmetric shape of the
Figure 4.4 HRXRD 20-ω scan of (002) reflection from as-deposited and annealed (a) three-step grown Film E and (b) control Film H.
reflection suggests the presence of a lattice-parameter gradient along the growth direction in the sample grown by the three-step method.

The out-of-plane, \( c \), and in-plane, \( a \), lattice parameters of the BST films were deduced from the symmetric (002) and skew-symmetric (022) reflections. To improve the accuracy in determination of the lattice parameters, diffraction (202) and (242) reflections from the DyScO\(_3\) substrate were used as an internal standard in case of symmetric and skew-symmetric scans, respectively. The lattice parameters of the annealed films so deduced are listed in Table 4.1. Note that the lattice parameters of the films grown by the three-step method represent the top-most layer of the structure in accord with the abovementioned simulations of the asymmetric reflection curves. All the films showed a larger out-of-plane lattice parameter than their in-plane ones \((c>a)\), indicative of compressive in-plane deformation. The presence of oxygen vacancies in the film and the lattice mismatch between the deposited layer and the substrate make the equilibrium (strain-free) lattice parameter of BST thin film different from the ideal bulk one. Similar to the lattice parameter calculation of the BST thin film on STO substrate on the previous chapter, we use the equilibrium lattice parameter, \( a_0 = \left[ c + 2 \left( \frac{c_{12}}{c_{11}} \right) a \right] / \left[ 1 + 2 \left( \frac{c_{12}}{c_{11}} \right) \right] \), in the calculation. The in-plane residual strain in the film is then given by \( x_{1,2} = (a - a_0) / a_0 \). All the films were found to exhibit compressive in-plane lattice distortion (film strain \( x_{1,2} < 0 \)). Film E and F have larger in-plane and smaller out-of-plane lattice parameters due to relatively small distortion \((x_{1,2} = -0.002)\) as compared to the control one.
(\(x_{1,2}=-0.006\) for Film H). This is attributed to generation of high concentration of point defects during the low temperature growth of the BST interlayer in the three-step deposition process, which facilitate the formation and propagation of dislocations, thus promoting strain relaxation [62]. With larger lattice parameters than the substrate, the interlayer partially compensates for the compressive strain in the top BST layer and reduces the mismatch between the top layer and the substrate. This mechanism is similar to the compliance effect: a thin freestanding substrate that shares the mismatch strain during the heteroepitaxy [63]. Upon post-deposition annealing, the point defects in the interlayer, especially the oxygen vacancies, were gradually reduced. The contracted lattice structure of the interlayer helps to relax the BST top layer. However, for the relatively low growth temperature of the interlayer (such as Film G), point defects generated in abundance may facilitate formation of stacking faults during the deposition, thus hardening the material [62]. Therefore, the choice of temperature used for the

### Table 4.1 The lattice parameters and film strain of Film E, F, G, and H.

<table>
<thead>
<tr>
<th>Films</th>
<th>Growth technique</th>
<th>c (Å)</th>
<th>a (Å)</th>
<th>Film strain (x_{1,2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>Three-step, (T_2=873) K</td>
<td>3.989</td>
<td>3.971</td>
<td>-0.002</td>
</tr>
<tr>
<td>F</td>
<td>Three-step, (T_2=773) K</td>
<td>3.987</td>
<td>3.972</td>
<td>-0.002</td>
</tr>
<tr>
<td>G</td>
<td>Three-step, (T_2=673) K</td>
<td>4.007</td>
<td>3.970</td>
<td>-0.005</td>
</tr>
<tr>
<td>H</td>
<td>Control film</td>
<td>4.004</td>
<td>3.955</td>
<td>-0.006</td>
</tr>
</tbody>
</table>
interlayer growth is important for high quality BST film deposition. However, further studies are warranted before the theoretical elucidation can be found for the interlayer effect on the BST film deposition.

4.2 Strain affected tunability at low frequency

Interdigital capacitors (IDCs) were fabricated on Film E, F, G, and H with a 50-nm-thick layer of Cr and a 30-nm-thick Au layer, which were deposited by e-beam evaporation. The capacitance tuning of the IDC devices was measured in the voltage range of 0-40 V at a frequency of 1 MHz using a Hewlett-Packard 4284 LCR meter.

![Figure 4.5](image.png)

**Figure 4.5** The dependence of the tuning of the capacitance on the film strain of Film E, F, G, and H.
After the post-deposition thermal treatment with proper annealing condition, all films show a large tunability of capacitance in the bias range of 40 V. Since the separation between fingers is 5 μm in the IDC design, the corresponding applied electric field is ±80 kV/cm in the measurement. The tunability of the IDCs on all films, which was calculated as \( \frac{C_{\text{max}}-C_{\text{min}}}{C_{\text{max}}} \), was summarized in Figure 4.5. All three-step deposited films (Film E, F, and G) have larger tuning than the control film does. The large tunability of ~50% was achieved on Film E and F in the applied bias of 80 kV/cm at 1 MHz. As shown in Figure 4.5, the improvement of the capacitance tuning is consistent with the reduction of the film strain. The tuning of capacitance increases substantially from 22.2% on Film H to 48.9% on Film E when the compressive residual strain decreased from -0.006 on Film H to -0.002 on Film E, respectively. It indicates that the three-step deposition with a proper interlayer growth temperature (typically 773-873 K for the BST films deposited on DyScO\(_3\) substrates) could improve the structural perfection of BST films and enhance electric properties, especially the tunability, to a great extent.
4.3 Dielectric property of BST thin film on DyScO$_3$ substrate at microwave frequencies

To study the dielectric properties of the three-step deposited BST thin films on DyScO$_3$ substrates, microwave measurements were performed on the coplanar waveguides (CPWs) fabricated with a four-layer Cr/Ti/Ag/Au (50/25/2000/50 nm) metal stacks deposited by electron-beam evaporation. A PMMA/chromium/photoresist stack and a tri-layer lift-off procedure were used in the lithography process of the thick metal device fabrication. The CPWs have a signal line with the width of 60 μm in the center and a separation of 5μm between the edge of the signal line and the ground planes on both sides. The length of the CPW transmission lines varied from 0.2 mm to 1.4 mm.

The thru-reflect-line (TRL) calibration method was employed to assess the dielectric constants, tunability, and dielectric loss of the BST films through the measurement carried out by an HP 8510C vector network analyzer in the frequency range from 2 to 20 GHz. A DC bias of up to 30 V was applied between the signal and ground lines to tailor the electric field and thus to control the dielectric constant of the BST layers.

Figure 4.6 shows the effective dielectric constant measured the CPWs with various length fabricated on Film E, which was deposited by the three-step technique with the interlayer deposition temperature at $T_2=873$ K. The measurement was employed on CPWs with a -30 to 30 V DC bias, equal to a maximum applied electric field of $\pm 60$ kV/cm owing to the 5-μm-width gap between the signal line and the ground plane in the design of CPW.
Figure 4.6 displays the dependence of effective dielectric constant on the applied electric field. The effective dielectric constant decreases when the applied electric field increases. It shows complete symmetrical on both directions of the electric field due to the symmetrical design of the CPWs. It is observed that the effective dielectric constant is frequency-dependent. When the frequency increases, the effective dielectric constant decreases.

![Graph showing the dependence of effective dielectric constant on the applied electric field. The graph displays multiple curves for different applied electric fields ranging from -60 kV/cm to 60 kV/cm, with frequency ranging from 2 GHz to 20 GHz. The effective dielectric constant decreases as the frequency increases and as the applied electric field increases. The graph highlights the symmetrical nature of the curves in both directions of the electric field.]
Conformal Mapping is a fast tool for determining the impedance and effective dielectric permittivity in a coplanar waveguide. The effective dielectric permittivity ($\varepsilon_{\text{eff}}$) of the CPW structure shown in Figure 4.6 can be expressed as Eq. 4.11.

$$\varepsilon_{\text{eff}} = 1 + q_1(\varepsilon_{r1} - 1) + q_2(\varepsilon_{r2} - \varepsilon_{r1})$$

with the filling factors (Eq. 4.12 and 4.13).

$$q_1 = \frac{1}{2} \frac{\kappa(k_1) \kappa'(k_0)}{\kappa(k_1) \kappa'(k_0)}; \quad q_2 = \frac{1}{2} \frac{\kappa(k_2) \kappa'(k_0)}{\kappa(k_2) \kappa'(k_0)}$$

Using the conformal Mapping method, we obtained the relative dielectric constant of each film.

![Graph showing insertion loss in unit length on CPWs fabricated on Film E.](image)

**Figure 4.7** The insertion loss in unit length on CPWs fabricated on Film E.
One of the disadvantages in using ferroelectric materials for tunable microwave devices is the relatively high dielectric loss tangent that leads to microwave dissipation. Many studies have been done on the minimization of the dielectric loss on the ferroelectric thin films by improving thin film fabrication method and material enhancement, such as doping [64-68] or multilayering the ferroelectric thin film [69, 70]. The dielectric loss in the BST thin films E-H was also studied. The insertion loss in unit length calculated using the s-parameter $S_{21}$ in the measurement employed on Film E was displayed in Figure 4.7.

As shown in Figure 4.7, the insertion loss increases with the frequencies as well as the applied electric fields. Assuming that all of the loss in the system is due to either conductor loss or dielectric loss, i.e. no radiation or surface wave losses, the tan $\delta$ of the BST layers can also be extracted using Eq. 4.23 and 4.24.

$$\varepsilon_{eff} \tan \delta_{eff} = q_1 \varepsilon_{r1} \tan \delta_1 + q_2 \varepsilon_{r2} \tan \delta_2$$  \hspace{1cm} \text{Eq. 4.23}

$$\alpha_d = 0.91 \sqrt{\varepsilon_{eff} f \tan \delta_{eff}}$$  \hspace{1cm} \text{Eq. 4.24}

Using the effective dielectric constant and the insertion loss obtained from the measurement at microwave frequency, we got the relative dielectric constant and the dielectric loss of the BST thin film through calculation.

Figure 4.8 shows the relative dielectric constant and dielectric loss of Film E measured in the applied electric field from -60 kV/cm to 60 kV/cm at 10 GHz. The relative dielectric constant of the BST thin film achieved 1018 at zero bias, which is an appreciable value
for the BST thin film with the thickness of 700 nm. The electric field dependent tuning of
the dielectric constant, defined by \( \frac{\varepsilon_r(0) - \varepsilon_r(V)}{\varepsilon_r(0)} \), is 39.2\% in the applied electric

![Graph](image)

**Figure 4.8** The relative dielectric constant and tangent loss of Film E measured in
the applied electric field of \( \pm 60 \text{ kV/cm} \) at 10 GHz

field of 60 kV/cm at the frequency of 10 GHz. The dielectric loss tangent also decreases
with the electric field applied on the device. On zero bias, the loss tan δ reached its
maximum of 0.021, which is relatively low in the consideration of the high dielectric
constant of 1018. It is worth noting that, the post-deposition thermal treatment did not
increase the dielectric loss, even though the crystal quality and tunability of the dielectric
constant improved dramatically upon annealing.
In order to describe the performance on the devices fabricated on the BST thin films, the intrinsic figure of merit, which is defined as the tunability of the relative dielectric constant (in percent) divided by the value of the dielectric loss tangent, is used in this work. Owing to the high tunability and relative low dielectric loss, the intrinsic figure of merit of Film E achieved 1867 on the applied voltage of 30 V at 10 GHz. The intrinsic figure of merit is frequency-dependent due the frequency-dependent dielectric constant.

![Figure 4.9 Dielectric constant and tuning of film F and H in the range of the electric field of 60 kV/cm at 5, 10, 15 GHz, respectively](image-url)
Figure 4.9 shows the comparison of the dielectric tunability of the three-step technique deposited Film F and the control Film H at different frequencies. The dielectric constant $\varepsilon_r$ decreases when the operation frequency increases at low bias, especially zero bias. While, at high applied electric field, the dependence of the dielectric constant on frequencies is not as sensitive as it does at low electric field. Therefore, the dielectric tunability decreases with the frequency. As shown in Figure 4.9, the three-step deposited film F displays the relative dielectric constants of 1198, 1099, 1048 and high dielectric-constant tuning of 50.7%, 47.9%, 45.8% at the electric field of 60 kV/cm at 5, 10, and 15 GHz, respectively, comparing to the control film H with the relative dielectric constant of 1035, 956, 910 and dielectric-constant tuning of only 21.3%, 20.2%, 19.2% at 5, 10, and 15 GHz, respectively. Film F produced a much better tunability, which was over two-fold of the control one did. The intrinsic figure of merit of Film F achieved as high as $\sim$2300 at microwave frequencies. The large improvement on both the tunability and intrinsic figure of merit is conformable with the increasing crystal quality by reducing the residual strain in the films. The large enhancement on dielectric tunability as well as the low loss promises the thin BST films have more applications in practice.
4.4 Comparison of BST thin films deposited on STO and DyScO$_3$ substrate on crystal structure and dielectric tunability

In our work, the epitaxial BST thin films deposited on STO substrates and DyScO$_3$ substrates, respectively, using the three-step deposition technique, both demonstrated dramatic effects on alleviating the residual strain and enhancing the dielectric properties. After the post-deposition thermal treatment, the BST thin films grown using sputtering at a single temperature (1068 K) exhibited compressive strain of -0.005 in the BST film on STO substrate (Film D) and -0.006 in the BST film on DyScO$_3$ substrate (Film H). Using the three-step deposition technique, the residual compressive strain in the annealed BST film dramatically reduced to -0.001 in the BST film on STO substrate (Film A) and -0.002 in the BST film on DyScO$_3$ substrate (Film F). The improvement on crystal structure by introducing the three-step technique is consistent within these two series of BST films on different substrates. The improvement on dielectric properties also further proved the advantage of utilization of this new technique. The electric field dependent tuning of relative dielectric constant achieved 47.9% on Film F, three-step deposited BST film on DyScO$_3$ substrate, in the applied electric field of 60 kV/cm at the frequency of 10 GHz, which was higher than the best tuning of 36.7% obtained on BST films deposited on STO substrates using three-step method. The improvement on dielectric properties is well agreement with reduction of the film strain in each series of the BST films.
Table 4.2 The comparison of lattice structure and dielectric properties between the annealed BST films (Film A and E) deposited on STO and DyScO$_3$ substrates, respectively, using three-step technique.

<table>
<thead>
<tr>
<th>Films</th>
<th>substrate</th>
<th>Lattice parameter</th>
<th>Cell Volume (Å$^2$)</th>
<th>Strain $x_{1,2}$</th>
<th>Dielectric tunability (%) in 60 kV/cm at 10 GHz</th>
</tr>
</thead>
<tbody>
<tr>
<td>Film A</td>
<td>STO</td>
<td>$c$ (Å)</td>
<td>$a$ (Å)</td>
<td>62.59</td>
<td>-0.001</td>
</tr>
<tr>
<td>Film F</td>
<td>DyScO$_3$</td>
<td>3.975</td>
<td>3.968</td>
<td>62.90</td>
<td>-0.002</td>
</tr>
</tbody>
</table>

Comparing the two best films with the least strain on each substrate, Film A and Film F, we found that Film F had a slight larger compressive strain but exhibits a higher dielectric tuning at microwave frequency. Within the calculation error as shown in Figure 3.2, we consider that Films F and A possess similar compressive strain.

Part of the reason of the improved dielectric tunability is possibly attributed to the larger unit cell volume and number of oxygen vacancies. Actually, the number of oxygen vacancies and the unit cell volume plays a significant role in determining the dielectric properties of the film [71]. The increased oxygen vacancies bring more defect dipoles, which results to an increased polarizability. The larger unit cell volume also enhances the ionic polarizability. As shown in Table 4.2, Film F has a large unit cell volume in the crystal structure due to the larger lattice parameter in both directions, which implies more oxygen vacancies possessed in the structure as well. The enhanced dielectric tunability is consistent with the observed difference in unit cell volume between Films A and F. The
difference in lattice parameters is highly possibility caused by the different lattice mismatch from the substrate. As we discussed in the beginning of this chapter, the lattice-match between the substrate and the deposited film significantly affects the epitaxial deposition, especially the epitaxy of the first nucleation layer. DyScO$_3$ has a larger in-plane lattice parameter (3.945 Å) in its pseudocubic structure than the lattice parameter of STO (3.905 Å). The large in-plane lattice parameter has higher possibility to cause larger in-plane lattice parameter to the nucleation layer. The following epitaxial growth was closely dependents on the below layer structure. Therefore, the structure with a large cell volume is built up on the substrate with a larger lattice parameter. Based on the above discussion, the observation of the larger lattice parameter and cell volume associated with larger dielectric tunability agrees well with other reported research works [71].

The other possible reason for different tuning achieved on these two series can be attributed to the different dielectric constant of the substrate. The STO substrate has the dielectric constant of ~300, while the DSO substrate has dielectric constant of only ~20. The large dielectric constant of the STO substrate makes the substrate occupy a certain amount of the applied voltages in the measurement. This make the real applied electric field on the BST layer or CPWs in Film A is not as strong as we expect in the calculation. The lower applied electric field consequently yields out less dielectric tunability. On the other hand, Film F has nearly no this kind of problem. The dielectric constant of the measurement object layer (BST layer) is more than 1000, while the dielectric constant of the DSO substrate is only ~20. It means that the DSO substrate hardly affects the amount
of the electric field applied on the CPWs built on BST layer. Therefore, nearly full amount of the applied electric field was applied on the CPWs and consequently yield out the high dielectric tunability in the measurement. This fact further verifies that low dielectric constant is one of the requirements for choosing the substrate for BST thin film deposition, especially in the consideration of microwave applications.

With the larger dielectric tunability in the deposited BST film and the low dielectric constant in the substrate, the BST film deposited on DyScO$_3$ exhibits a good potential in the application of microwave components.
Chapter 5 Enhanced dielectric property on PLD deposited BST film by introducing a thin BST seed layer

5.1 Introducing of the sputtered BST seed layer into PLD deposition

The three-step technique is aimed to tailor the residual film train by introducing an interlayer, which is deposited at different growth condition, to reduce the misfit between the deposited film and the substrate. This idea of using interlayer could be also used in the ferroelectric film deposition by other technique. Due to the slow deposition rate of the sputtering system, films with the thickness of several microns usually could hardly be obtained by sputtering deposition. Pulsed laser deposition (PLD) is another popular deposition technique for the ferroelectric film, such as BST film. In this chapter, we reported that the reduced film strain and enhanced dielectric properties on PLD deposited BST films on STO substrates by introducing a thin BST seed layer deposited by sputtering system.

As shown in Figure 5.1, on the first step of the film P1 deposition, BST film of thickness 400 nm were deposited as a seed layer on STO substrates by off-axis RF magnetron sputtering system. The deposition was carried on at 120 W RF power under a gas mixture of 6:1 Ar/O₂ with the pressure of 2 mTorr during the whole growth process. The substrate
temperature was at 1023 K during the deposition. After the seed layer deposition, a 2.15-μm-thick BST film was deposited at 1023 K by PLD in a 100 mTorr oxygen atmosphere. The energy fluence and repetition rate for the 248 nm KrF laser were 1.7 J/cm² and 25 Hz, respectively. The deposition was done for about 1 hour and the target-substrate distance was 7.5 cm. The thickness of the film was measured by cross sectional SEM imaging. The reference film P2, which had no seed layer, was directly deposited on STO substrate in the same growth condition as described above. To improve the crystal quality, we employed a post-deposition thermal treatment on both the films P1 and P2 at 1298 K for 8 hours in a tube furnace. The O₂ atmosphere (O₂ mass-flow rate of 20 sccm) was employed to prevent losing oxygen from the BST films during thermal treatment. It was the same annealing condition implemented on Films E-H in Chapter 4 to effectively relieve strain and enhance the dielectric properties. The as-grown and annealed films
were characterized by HRXRD to obtain the crystal structure. The lattice parameters and residual strain were summarized in Table 5.1.

**Table 5.1 The lattice parameters and film strain of the PLD deposited BST films with (Film P1) or without (Film P2) the sputtered seed layer on the STO substrate.**

<table>
<thead>
<tr>
<th>Films</th>
<th>seed layer</th>
<th>c (Å)</th>
<th>a (Å)</th>
<th>Film strain (x_{1,2})</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>with</td>
<td>3.955±0.003</td>
<td>3.959±0.008</td>
<td>0.0004±0.0020</td>
</tr>
<tr>
<td>P2</td>
<td>without</td>
<td>3.953±0.002</td>
<td>3.965±0.007</td>
<td>0.0016±0.0018</td>
</tr>
</tbody>
</table>

After thermal treatment, the crystal structure of both films P1 and P2 became tensile strained, on which the in-plane lattice parameter \(a\) is smaller than the out-of-plane lattice parameter \(c\). However, the introducing of the thin sputtered seed layer made Film P1 more relaxed and result in a less tensile strain of only 0.0004, which was very close to free strain. The slightly smaller volume of the unit lattice cell implies the less oxygen vacancies in Film P1 than those in Film P2. The sputtered BST thin film D (the control film grown at a single temperature of 1068 K) in Table 3.1 has lattice parameter of \(c=3.998\) Å and \(a=3.958\) Å. Film P1 has similar in-plane lattice parameters \(a=3.959\) Å while much smaller out-of-plane lattice parameter \(c=3.955\) Å compared with Film D. The similar in-plane lattice parameters of Films D and P1 are close to the cubic lattice parameter 3.947 Å of bulk BST, while the one of Film P2 is 3.965 Å that is larger P1.
This decreasing in the in-plane lattice parameter implies that the seed layer is helpful to relax the film by reducing the misfit between the BST film and the STO substrate (the lattice parameter of bulk STO is 3.905 Å). The large difference of out-of-plane lattice parameters between the PLD deposited films and the sputtered film (Film D) could be partially explained by the reducing of oxygen vacancies generated during deposition. Oxygen vacancies affect the nearest neighbor distance by reducing the Coulomb attractive force between cation and anion atoms, resulting in an increased lattice parameter and unit cell volume [71]. Since the expansion of the unit cell in in-plane direction is limited at some extent by the clamping of the layer below the film (substrate or seed layer in this work); the out-of-plane lattice parameter is preferentially affected much seriously by the oxygen vacancies. The much larger out-of-plane lattice parameter as well as large cell volume in Film D implies that there were much more oxygen vacancies in the thin film deposited by sputtering system. As a very high energy technique, the pulsed laser deposition with a proper oxygen atmosphere, 100 mTorr in this work, could reduce the oxygen vacancies during the deposition to a great extent. The oxygen pressure is an important parameter for high crystal quality film deposition by PLD and seriously affects the structure distortion as well as dielectric properties [72]. The post-deposition thermal treatment is another important process to film the oxygen vacancies in the films and subsequently cause the lattice contraction. On the other hand, the smaller out-of-plane lattice parameter of Film P1 than Film D could be also attributed to its much larger thickness. Generally, the thicker the deposited film is, the more relax
the structure lattice [45]. This conclusion was also been confirmed in Figure 2.6. The relaxation will reduce the difference between the in-plane and out-of-plane lattice parameters. The thickness of Film P1 is much larger than Film D, therefore the much less structure distortion is predictable on Film P1.

5.2 Dielectric property on BST films affected by adding seed layers

To investigate the effect of dielectric properties of the PLD deposited BST films on introducing the seed layer, microwave measurements were performed on the coplanar waveguides (CPWs) fabricated with a four-layer Cr/Ti/Ag/Au (50/25/2000/50 nm) metal stacks by a tri-layer lift-off procedure. The CPWs have a signal line with the width of 60 μm in the center and a separation of 5μm between the edge of the signal line and the ground planes on both sides. The length of the CPW transmission lines has been varied from 0.2 mm to 1.4 mm. The thru-reflect-line (TRL) calibration method was employed to assess the dielectric constants, tunability, and dielectric loss of the BST films through the measurement carried out by an HP 8510C vector network analyzer in the frequency range from 2 to 20 GHz. A DC bias of up to 30 V was applied to test the dielectric tunability of the BST layers.
Figure 5.2 The effective dielectric constant and loss measured on (left figures) Film P1 and (right figures) Film P2, which are with or without seed layers, respectively, at an applied electric field of 0-60 kV/cm in 2-20 GHz.

Figure 5.2 shows the measured effective dielectric constant and loss on Films P1 and P2, respectively, at an applied electric field of 0-60 kV/cm at the frequency range of 2-20 GHz. Both films showed an electric-field-dependence of the effective dielectric constant and its symmetry on both electric-field directions. When the applied electric field increases, both the effective dielectric constant and the loss decrease gradually. It is worth noting that the value of the electric field was simply estimated by dividing the bias...
voltage by the separation between the signal line and the ground plane of the CPW device. Therefore the actual field was overestimated within the BST layer since the field decreases with depth within the films. The only difference between Film P1 and P2 in the BST film fabrication was with or without adding the seed layers. It is observed that Film P1 with the sputtered seed layer displays a dramatically high effective dielectric constant as well as high loss than that of Film P2.

![Graph](image)

**Figure 5.3** The relative dielectric constant and loss tangent of Film P1 measured at an applied electric field of 0-60 kV/cm at 10 GHz

Using the effective dielectric constant and the loss shown in Figure 5.2, we can obtain the relative dielectric constant and the loss tangent of the BST film. As shown in Figure 5.3,
the relative dielectric constant of the BST is strongly dependent on the applied electric field. The dielectric loss does not change too much with the electric field and keeps on a relatively low value of 0.016-0.025 at 10 GHz. The comparison of the dielectric properties between Films P1 and P2 measured at 10 GHz was summarized in Table 5.2. We found that Film P1 achieved the relative dielectric constant as high as 1440 at zero bias, which was a doubled value of that of Film P2, and kept its dielectric loss still at a relative low value 0.025, which was almost the same as Film P2 did. In the applied electric field of 60 kV/cm, Film P1 had the dielectric tunability, defined by \([\varepsilon_r(0) - \varepsilon_r(V)]/\varepsilon_r(0)\), as high as 63.0%, which is even higher than the value reported in our previous work [2]. The tunability of the PLD deposited BST film with the sputtered seed layer achieved 59% in 60 kV/cm at 10 GHz. However, the thickness of the BST film in the previous work was 3 μm, which is nearly one and half fold of the thickness of Film P1. It is a dramatic improvement that Film P1 with a smaller thickness achieved a even higher dielectric tunability of 63.0% than the 3-μm BST film reported in the previous work. The thinner in the thickness and the higher in the tunability in the film is a promising for low cost as well as the high performance in the practice application. The improvement is mainly attributed to the different post-deposition thermal treatment conditions. The one we used in previous work was at 1223 K, while the current annealing temperature is at 1298 K. The higher temperature during annealing probably made more oxygen vacancies filled and subsequently relieve the distortion in the film structure. The lattice parameters were \(c=3.955\) Å and \(a=3.959\) Å for Film P1 while \(c=3.950\) Å and
$a=3.963$ Å for the 3-μm BST film in the previous work. The improvement of the dielectric properties by the less distortion of the film will be further discussed in the following section.

**Table 5.2 The comparison of dielectric properties between Films P1 and P2 measured at 10 GHz**

<table>
<thead>
<tr>
<th>Films</th>
<th>Seed layer</th>
<th>Dielectric constant</th>
<th>Loss tanδ</th>
<th>Dielectric tunability in 60 kV/cm</th>
<th>Dielectric tunability in 20 kV/cm</th>
<th>Intrinsic figure of merit in 60 kV/cm</th>
<th>Intrinsic figure of merit in 20 kV/cm</th>
</tr>
</thead>
<tbody>
<tr>
<td>P1</td>
<td>w.</td>
<td>1440</td>
<td>0.025</td>
<td>63.0%</td>
<td>35.9%</td>
<td>2520</td>
<td>1436</td>
</tr>
<tr>
<td>P2</td>
<td>w/o</td>
<td>712</td>
<td>0.024</td>
<td>46.2%</td>
<td>18.7%</td>
<td>1925</td>
<td>778</td>
</tr>
</tbody>
</table>

As shown in Table 5.2, with the help of the seed layer, Film P1 showed a much high tunability (63.0% vs. 46.2%) compared with Film P2. In the consideration of the similar low dielectric loss and much different tunability, the intrinsic figure of merit of Film P1, defined as the tunability of the relative dielectric constant (in percent) divided by the value of the dielectric loss tangent, achieved much higher than Film P2 without seed layer. The intrinsic figure of merit achieved 1925 on Film P2 in 60 kV/cm at 10 GHz and was increased to as high as 2520 with the help of seed layer on Film P1. We found that the dependence of the tunability on the electric field is not linear in the applied electric
field range of 0-60 kV/cm. Half of the tunability (35.9/63.0) was accomplished on Film P1 in 0-20 kV/cm. Compared with Film P2, both dielectric tunability and intrinsic figure of merit show two-fold values on Film P1. The large improvement on the sensitivity of dielectric properties in low electric field demonstrates the application possibility of low-power consumption tuning elements.

![Dielectric constant of Films P1 and P2](image)

**Figure 5.4** Dielectric constant of Films P1 and P2 in the applied electric field of 60 kV/cm at 5, 10, 15, and 20 GHz, respectively.

As shown in Figure 5.4, the relative dielectric constant as well as the tuning upon electric field of both Films P1 and P2 showed higher values at lower frequencies. The relative
dielectric constant at zero bias were 841, 712, 665, and 600 on Film P2 at 5, 10, 15, 20 GHz, respectively, while the dielectric constant increased to 1690, 1440, 1299, and 1288 at 5, 10, 15, 20 GHz, respectively, on Film P1 by adding the seed layer before the PLD deposition. Figure 5.4 showed the dramatic improvement on the dielectric tuning by the introduction of the seed layer as well. The tuning in 60 kV/cm (applied bias of 30 V) was 39.8-47.1% at 5-20 GHz on Film P2 and was improved to 59.9-65.3% at 5-20 GHz on Film P1 with a sputtered seed layer. This improvement in the value of dielectric constant and its tuning is expectable with the consideration of the alleviation of the residual tensile strain in the film by the introduction of the seed layer as evidenced by the HRXRD measurements.

![Figure 5.5 Theoretical analysis of the strain-dielectric constant dependence for BST at room temperature [40]](image-url)
The residual strain is a very significant factor affecting the dielectric properties. The distortion of the lattice structure affects the ionic positions and vibrations and subsequently influences the polarization in the ferroelectric films. According to the phenomenological theory developed by Devonshire [73], the ferroelectric behavior could be explained by Gibbs free energy (G). W. Chang et al. theoretically estimated the dielectric constant variation with the strain for BST at room temperature and plotted the following figure.

As discussed in the previous section, the compressive strain limits the dielectric constant and tunability of the BST films. The film with a slight tensile strain shows the highest dielectric constant in Figure 5.5. The slight tensile strain, which means the magnitude of the lattice parameter is larger on in-plane direction than on out-of-plane direction, increases the space for ionic motion in in-plane direction in unit cell. Consequently, the in-plane ionic polarization is more convenient to form and develop with the in-plane applied electric field when the film is under a slight tensile strain. On the other hand, when the magnitude of tensile strain exceeds a certain value (0.0012), the large tensile strain decreases the dielectric property of the BST film at room temperature. When the in-plane lattice parameter is much larger than the out-of-plane lattice parameter, spontaneous polarization caused by the displacement of Ti$^{3+}$ cation away from the symmetrical center in the unit cell is greatly enhanced along the in-plane direction, which is parallel to the direction of the applied electric field. This confines additional field-
induced dielectric polarization because the ionic polarization can be easily saturated with the preexisting in-plane permanent dipoles, resulting in a reduced in-plane dielectric constant and tunability [72].

As shown in Table 5.1, both Films P1 and P2 had tensile residual strain and showed larger in-plane lattice parameters than the out-of-plane ones. The strain was 0.0004 in Film P1 and 0.0016 in Film P2. The nearly free strain film P1 also showed much higher dielectric constant than Film P2 with a larger tensile strain. This observation is consistent with the theoretical analysis in Figure 5.5. As shown in Table 5.2, the dielectric constant of 1440 for Film P1 with the tensile strain of 0.0004 and the dielectric constant of 712 for Film P2 with the tensile strain of 0.0016 are also consistent with the estimated value in Figure 5.5. The introduction of the sputtered seed layer reduced the structure distortion in the film and consequently enhanced the dielectric properties of the PLD deposited BST film.
Chapter 6 Microwave application of BST films

Owing to the sensitive electric field dependent permittivity, ferroelectrics have been widely investigated for microwave applications in this two decades. Applications, such as ferroelectric film based phase shifters, have been intensively studied [58, 74]. The large tunability and relatively low dielectric loss of BST thin film raises the possibility of achieving a large phase shift associated with relatively low loss on a miniature tunable microwave devices.

![Coplanar Waveguide](image)

Figure 6.1 The coplanar phase shifter used in the microwave frequencies measurement.

In addition to using the CPW transmission line to determine the dielectric properties of the BST films, we also use it as a simple phase shifter to further discuss the microwave properties of the films. With the electric field applied between the signal line and the ground plane, coplanar waveguide could polarize the BST film to some extent and
subsequently tuning the dielectric constant. In the tuning process, the phase velocity of
the propagating microwave radiation, \( \frac{1}{\sqrt{\mu_{\text{eff}}\varepsilon_{\text{eff}}}} \), was changed. The phase between input
and output ports was also changed as a function of the applied field. We investigated the
phase shift along the coplanar waveguide transmission lines in applied electric field at
microwave frequencies.

To examine the phase shift ability at microwave frequencies, the coplanar waveguides
with the length of 0.14 cm were used as phase shifters. The complex propagation constant
(\( \gamma = \alpha + i\beta \)) defining microwave propagation on the coplanar transmission lines was
obtained from the two-port scattering parameters (S parameters), where \( \alpha \) is the
attenuation constant, which contains both the dielectric loss (\( \alpha_d \)) and the conductor loss
(\( \alpha_c \)), and \( \beta \) is the phase constant. The effective permittivity of the coplanar waveguide,
which was used to calculate the relative dielectric constant of the BST thin film in the
previous two chapters, was obtained by the complex propagation constant. The phase
shift can be obtained from the \( S_{12} \) parameter measured at different bias voltage. The
insertion loss (IL) is the dB expression of the transmission coefficient \( |S_{21}| \) [75]. It is
given by

\[
\text{IL} = -20 \log_{10}|S_{21}| \text{ (dB)} \quad \text{Eq. 6.1}
\]

It is the extra loss produced by the intrinsic loss in the device or impedance mismatch.

Input return loss \( (\text{RL}_{\text{in}}) \) is a quantity description of how close the actual input impedance
of the net work is to the nominal system impedance value and is given by
It is noted that the value of the return loss is negative. The linear part \(|S_{11}|\) is equivalent to the reflected voltage magnitude divided by the incident voltage magnitude. The output return loss (\(RL_{\text{out}}\)) has a similar definition to the input return loss but applies to the output port (port 2 in the two-port system) instead of the input port. It is given by

\[
RL_{\text{out}} = 20 \log_{10}|S_{22}| \text{ (dB)} \quad \text{Eq. 6.3}
\]

The performance of phase shifters is quantified by the microwave figure of merit, which was defined by the ratio of the differential phase shift to the insertion loss

\[
\text{Microwave figure of merit} = \frac{\varphi(V) - \varphi(0)}{IL} \quad \text{Eq. 6.3}
\]

where \(\varphi(V)\) and \(\varphi(0)\) are the phase with the unit in degree at DC bias of V and zero bias, respectively. The microwave figure of merit of the phase shifter, with the unit of \(^\circ$/dB, is utilized to show the combined effects of both tunability and losses on the CPW transmission lines.

### 6.1 Coplanar phase shifter based on BST thin film on DyScO\(_3\) substrate

Typical scattering parameter data was obtained from the microwave measurements on the BST thin films deposited on the DyScO\(_3\) substrates, including the three-step deposited films (Films E, F, and G) and the control film (Film H). With the utilization of the three-
step technique, Film F achieved tunability as large as 47.9% at the applied electric field of 60 kV/cm at 10 GHz, while the control film H only had 21.3% tuning.

Here, Film F, deposited by the three-step technique with the interlayer growth temperature at 773 K, was used as an example to demonstrate the calculation of the differential phase shift and microwave figure of merit. The phase of CPW transmission line, obtained from the $S_{12}$ parameter, on Film F at the applied electrical bias of 0-60 kV/cm at the frequency range of 2-20 GHz is shown in Figure 6.2. With the applied electric field increasing between the single line and the ground plane, the phase of the $S_{12}$ parameter gradually shifts. The differential phase shift is shown in Figure 6.3.
The differential phase shift was strongly dependent on the applied electric field. When the applied field was increased to 60 kV/cm, the differential phase shift reaches to the highest value in the whole frequency range in the measurement. This improvement comes from the property of the electric-field-dependent dielectric tunability.

The insertion loss involving both conductor loss from the transmission line and the dielectric loss from the film itself obtained from the $S_{21}$ parameter was displayed in Figure 6.4.
As shown in Figure 6.4, the insertion loss of the CPWs is frequency dependent. The increasing of the dielectric loss with the frequency is derived from the damped oscillations of the dipoles in the dielectric thin films as well as the substrate aligning with the applied electric field. With the frequency increases, the rapid oscillations of the dipoles need to consume energy. This increasing energy consumption results in the increasing insertion loss. The conductor loss is also affected by the frequencies. As the discussion in Chapter 4, the conductor attenuation constant \( \alpha_c \) of CPW transmission lines is directly proportional to the skin effect surface resistance \( R_s \), which is a frequency dependent variable at microwave frequency. As the frequency increases, the
metal losses on conductor of the CPWs increase due to the increasing on the skin effect surface resistance. To minimize conductor loss, we increases the thickness of the conductor to ~2 μm, which is 3-4 times thicker than the skin depth. Even though the skin effect has been considered in the design of the CPWs, the conductor loss still is affected by the frequency and contributes to the increasing insertion loss of the CPWs aligning with the frequency. With the contributions from the conductor loss and dielectric loss, the insertion loss increases with the frequency. On the other hand, it is predictable that the insertion loss is electric field dependent, which is consistent with the applied electric field dependent dielectric loss shown in Figure 4.8. The conductor loss generally is not affected too much by the applied electric field. With the electric field increasing, the insertion loss decreases in the entire frequency range of 2-20 GHz as shown in Figure 6.5.

![Figure 6.5 The return loss per unit length of the CPW phase shifter on film F](image)
The return loss calculated through the $S_{11}$ parameter of the CPW transmission line on Film F measured at the applied electric field of 0, 30, and 60 kV/cm was shown in Figure 6.5. The wave trough of the return loss oscillation curve shifts towards the high frequencies when the electric field applied on the single line and ground planes. The shift of the return loss is consistent with the phase shift of the CPWs.

**Table 6.1** The differential phase shift and microwave figure of merit measured under the electric field of 60 kV/cm at 10 GHz as well as film strain of the three-step deposited films E, F, G and the control film H.

<table>
<thead>
<tr>
<th>Films</th>
<th>Film strain</th>
<th>Differential phase shift (º/cm)</th>
<th>Insertion loss (dB/cm)</th>
<th>Microwave figure of merit (º/dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td>E</td>
<td>-0.002</td>
<td>145.2</td>
<td>6.3</td>
<td>23.0</td>
</tr>
<tr>
<td>F</td>
<td>-0.002</td>
<td>145.7</td>
<td>6.7</td>
<td>21.5</td>
</tr>
<tr>
<td>G</td>
<td>-0.005</td>
<td>132.6</td>
<td>16.5</td>
<td>8.0</td>
</tr>
<tr>
<td>H</td>
<td>-0.006</td>
<td>77.5</td>
<td>10.0</td>
<td>7.7</td>
</tr>
</tbody>
</table>

We applied all the above calculation on all three-step deposited films (Film E, F, and G) and the control film (Film H). The films with different deposition processes produced different phase shift performance on the CPW transmission lines. The differential phase shift and microwave figure of merit of the CPW transmission lines on Film E-H
measured under the applied electric field of 60 kV/cm at 10 GHz are summarized in Table 6.1. For the convenience of discussion, the residual film strain is also put into the table. At an electric field of 60 kV/cm, the differential phase shifts were 145.7º/cm and 256.1º/cm at 10 and 20 GHz, respectively, which were substantially higher than the corresponding values of 77.5º/cm and 142.7º/cm obtained on the control Film H. With the consideration of loss, the performance of phase shifters can be described using the figure of merit given by \( \text{Figure of merit} = \frac{\phi(V) - \phi(0)}{IL} \), where \( \phi(V) \) and \( \phi(0) \) are the differential phase shift under DC bias field of \( E \) and 0 V/cm, respectively, and \( IL \) represents the insertion loss per unit length. In the conformal mapping method, the insertion loss, derived from the scattering parameter \( S_{21} \), is attributed to both the conductor loss from the transmission line and the dielectric loss from the film. Films E and F have relative low insertion loss of 6.3 and 6.7 dB/cm, respectively, while the control film showed a relative high insertion loss of 10.1 dB/cm. As shown in Table 6.1, the structures deposited via the three-step method (Films E, F, and G) showed improvement in both the differential phase shift and the figure of merit compared with the control film H. The best performance was achieved on Films E and F deposited with \( T_2 = 873 \text{ K} \) and 773 K, respectively, which showed a two-fold improvement over the control structure in terms of the differential phase shift (145 °/cm vs. 77.5°/cm) and a three times enhancement of the figure of merit (23.0°/dB vs. 7.7°/dB). This differential phase shift is higher than the value of 90°/cm achieved on the much thicker, annealed (3-
μm-thick) BST films using the same simple CPW geometry and applied field, while the figure of merit is only somewhat lower than that obtained in the latter case in our previous work (23.0%/dB vs. 35%/dB) [76].

The improvement of BST-film-based phase shifter at microwave frequencies is consistent with the reduced film strain in the films fabricated by the three-step deposition technique. Although the mechanism responsible for the reduced film clamping by a nearly lattice-matched substrate requires further microscopic investigations, the experimental results obtained so far indicate the effectiveness of the implemented deposition method in achieving BST thin films with high microwave tunability.

6.2 Coplanar phase shifter on PLD deposited BST films with sputtered seed layers

We also studied the coplanar phase shifter performance on the PLD deposited BST film on STO substrates with or without the introduction of the sputtered seed layers. With the assistant of introducing sputtered seed layer, the PLD deposited Film P1 is the most relaxed film in this work and produces the largest dielectric tunability (63.0% in 60 kV/cm at 10 GHz) promising for real phase shifter applications.

The CPW transmission lines with the same design as the ones fabricated on the BST thin film on DyScO$_3$ substrate were fabricated on Films P1 and P2, which were the BST films
deposited by pulsed laser deposition (PLD) on STO substrates with and without a sputtered BST seed layer, respectively. The thickness of the PLD deposited BST film is 2.15 μm in both Films P1 and P2, and the thickness of the sputtered seed layer of Film P1 is 400 nm. After post-deposition thermal treatment, Film P1 showed a slight tensile strain of 0.0004, while Film P2 showed a larger tensile strain of 0.0016. Consisting with its less crystal structure distortion, Film P1 showed a higher dielectric constant of 1440 at zero bias and a larger tunability of 63.0% in an applied electric field of 60 kV/cm at 10 GHz compared with the dielectric constant of 712 and tunability of 46.2% for Film P2. The detail of crystal characteristics and dielectric properties were analyzed in Chapter 5.

In addition to using the CPW lines as a means to determine the dielectric constant and insertion loss on Films P1 and P2, we also use the CPW transmission line as a simple phase shifter to further study the microwave properties of the films. The two-port s-parameters were measured on the coplanar phase shifter using the HP 8510C vector network analyzer in the frequency range from 2 to 20 GHz with an applied bias of 0-30 V corresponding to the maximum of the applied electric field of 60 kV/cm due to the 5-μm-width separation between the signal line and the ground plane in the CPWs.

The phase shift along the coplanar waveguide transmission lines under the applied electric field as well as corresponding insertion loss were measured on both Films P1 and P2 at microwave frequencies. The differential phase shift and the insertion loss were all normalized to unit length and shown in Figure 6.6. Both differential phase shift and insertion loss were electric field dependent. When the electric field became stronger, the
differential phase shift increased gradually on both films, while the insertion loss was decreased gradually on both films. We found that Film P1 with the sputtered seed layer showed much larger differential phase shift than Film P2, which has no sputtered seed layer in the film structure. The differential phase shift of the CPW on Film P2 at 60 kV/cm was even less than the one at 20 kV/cm on Film P1. The different dependence of phase shift on applied electric field on Films P1 and P2 is consistent with their different
dielectric tunability. As shown in Figure 6.6, near half of the phase shift under the applied electric field of 60 kV/cm was accomplished in 0-20 kV/cm, which was in good agreement with the dielectric tuning under applied electric field. The insertion loss mainly has two parts of contribution, the conductor loss from the transmission line and the dielectric loss from both the BST film and the substrate. The conductor loss generally does not affect too much upon electric field, while the dielectric loss decreases with the applied electric field increasing. Therefore, the insertion loss decreases when electric field applied on the CPW transmission lines.

Table 6.2 Differential phase shift and microwave figure of merit of Film P1 and P2 measured at an applied electric field of 60 kV/cm at 5, 10, 15, and 20 GHz.

<table>
<thead>
<tr>
<th>Films</th>
<th>Seed layer</th>
<th>Differential phase shift (%/cm)</th>
<th>Microwave figure of merit (%/dB)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>5 GHz</td>
<td>10 GHz</td>
</tr>
<tr>
<td>P1</td>
<td>w.</td>
<td>240</td>
<td>416</td>
</tr>
<tr>
<td>P2</td>
<td>w/o</td>
<td>96</td>
<td>177</td>
</tr>
</tbody>
</table>

The differential phase shift and microwave figure of merit measured on Films P1 and P2 under the applied electric field of 60 kV/cm at microwave frequencies were summarized in Table 6.2. With the introduction of the sputtered seed layer, CPWs achieved a differential phase shift of 204 %/cm, 416 %/cm, 582 %/cm, and 719 %/cm on Film P1 at 5, 10, 15, and 20 GHz, respectively, while a differential phase shift of only 96 %/cm, 177 %/cm,
240 °/cm, and 302 °/cm was observed on Film P2 at 5, 10, 15, and 20 GHz, respectively. Coplanar phase shifters produced 2.5 times larger phase shift on Film P1 than on Film P2. Using the measured insertion loss at zero bias, which was the highest loss in the electric field range, as a function of frequency and the differential phase shift, we calculated the microwave figure of merit of both films at microwave frequencies. The microwave figure of merit achieved 33.3 °/dB, 36.2 °/dB, 38.2 °/dB, and 41.3 °/dB on Film P1 at 5, 10, 15, and 20 GHz, respectively, while only 16.2 °/dB, 21.0 °/dB, 24.7 °/dB, and 20.6 °/dB on Film P2 at 5, 10, 15, and 20 GHz, respectively. Film P1 had near twice microwave figure of merit as that of Film P2. The improvement at differential phase shift and microwave figure of merit is consistent with the enhanced dielectric properties on Film P1 with introducing the sputtered seed layer in deposition.

6.3 Future work on two-degree tuning phase shifter based on BST film deposited on polycrystalline YIG substrate

In the previous two sections, the coplanar phase shifter based on BST films measured under applied electric field was discussed. However, when the electric field was applied on the CPW devices to tune the phase constant, the characteristic impedance was synchronously changed with the effective dielectric constant. The characteristic impedance is affected by both the effective permittivity and the effective permeability, as
described by $\eta_0 = \sqrt{\frac{\mu_{\text{eff}}}{\varepsilon_{\text{eff}}}}$. Therefore, if we can independently tune the permeability and permittivity respectively, the phase shift and the constant the impedance can be obtained simultaneously. Based on this idea, the ferroelectric/ferrite bilayer structure attracts considerable attention in the phase shifter application near ferromagnetic resonance frequency (FMR), because the permeability of a ferrite material could be control by the application of external magnetic field [77, 78]. We considered to combine ferrite material yttrium iron garnet (YIG) with our BST films. In our previous work, we built a coplanar waveguide on a PLD deposited 5-μm-thick BST layer on a liquid phase epitaxy (LPE) 5.3-μm-thick YIG layer on a gadolinium gallium garnet (GGG) substrate. The coplanar phase shifter based on the BST/YIG/GGG structure was measured in an applied electric field of 0-75 kV/cm and an external magnetic varied from 1600-1800 Oe. Under the two-degree-freedom-tuning, the coplanar phase shifter achieved a differential phase shift of 52 °/cm with a return loss of 24.9 dB [76].

Due to the inherent crystallographic incompatibility between these two materials, it is a challenge to deposited high quality BST film directly on bulk YIG substrate. Seldom work has been done by other research group. Jia et al. reported a PLD deposited BST film on polycrystalline YIG substrate with ion-beam assisted-deposition (IBAD) grown MgO and Si3N4 buffer layer. With the complicated structure, BST film was obtained and produced a 25% capacitance tuning at an electric field of 80 kV/cm.
In this work, we directly deposited BST film on polycrystalline YIG substrate without any buffer layer. BST thin film with the thickness of 700 nm was deposited on a 800-μm-thick polycrystalline YIG substrate. The YIG substrates were cut from a 3-mm-thick bulk polycrystalline YIG ceramic. In order to reduce the surface roughness produced during mechanical cutting, a multiple-step polishing process, including a mechanical polishing followed by chemical etching and thermal treatment, was employed on the surface of those substrates. Even though many efforts had been done to alleviate the roughness, the surface was not as smooth as the commercial single crystal substrate. Before deposition, YIG substrates were cleaned by a routine cleaning procedure, in which the substrate was dipped and sonic vibrated in acetone and then in methanol followed by DI water rinsing, and finally dried by blowing nitrogen. BST thin films were deposited by off-axis RF magnetron sputtering system within a gas mixture of Argon and Oxygen. The deposition atmosphere is at 2 mTorr pressure with the Ar-to-O2 ratio of 6:1. During deposition, the substrate temperature was maintained at 1068 K. The RF power was carried out at 120 W. After deposition, the film was annealed at 1273 K for 8 hours in flowing oxygen atmosphere to improve the crystal quality as well as enhance dielectric properties.
Figure 6.7 X-ray diffraction 2θ scan for the BST thin film deposited on polycrystalline YIG substrate.

X-ray diffraction 2θ scan on a BST film showed a subtle (00l) reflection of BST on the polycrystalline YIG substrate as shown in Figure 6.7. The intensity of both the peaks from BST film and the peaks from YIG substrate are very low and not clear. It implies the poor crystal structure quality of the film, which mainly is attributed to the low quality polycrystalline of the substrate. I have to admit that, due to the faint refraction peak with low intensity, the accuracy of corresponding epitaxial orientation of the deposited film is questionable. Even though the BST film had low structure quality, microwave measurement still showed the good performance on dielectric properties. CPW lines with the length of 0.2-1.4 mm fabricated on the BST/YIG structure were used to determine the
dielectric constant and lately were employed as coplanar phase shifter in microwave measurements.

As shown in Figure 6.8, the annealed films had the relative dielectric constant of 783 and 857 at zero bias at the frequency of 5 and 10 GHz, respectively. The dielectric tuning was quite stable on ~18.8% in the applied electric field of 60 kV/cm at the whole frequency range of 5-10 GHz. The large dielectric constant and tunability are comparable to those reported for BST films deposited on a single-crystal YIG substrate [77].
Figure 6.9 (a) Square of the effective phase constant of BST/YIG structure under different applied magnetic fields; (b) Tuning of the phase constant at different electric fields under a magnetic field of 1500 Oe.

From the results of TRL calibration, the square of the normalized effective phase constant, which is the imaginary part of the propagation constant, $\gamma$, normalized by $c/\omega$, were shown in Figure 6.9. The square of the normalized effective phase constant can be described the effective permittivity and effective permeability by $\beta_{\text{eff}}^2 = e_{\text{eff}} \mu_{\text{eff}}$ [错误！未定义书签。]. Ferromagnetic resonances (FMR) with peak frequencies ranging from 5-6.5 GHz are clearly seen due to the ferrite YIG substrate. The FMR frequency shifts to
higher value when the magnetic field is increased. Figure 6.9-b shows the square of the effective propagation constants at different applied dc electric fields for a magnetic field of 1500 Oe, where the FMR peak position does not change with varying applied electric field [79].

Figure 6. 10 (a) Demonstration of alleviation of the impedance-mismatch, revealed as the return loss approaching the impedance-match value, by applying a magnetic field; (b) Differential phase shift achieved after applying a 60 kV/cm electric field under different magnetic fields. The reference condition is at a magnetic field of 1400 Oe and no electric field.
An example of reducing the impedance mismatch via magnetic field tuning is shown in Figure 6.10-a. With no electric field, the initial impedance-matched condition is at a magnetic field of 1600 Oe. When a 60 kV/cm electric field was applied to induce a phase shift, the return loss decreased from around 47 dB to 27 dB. The mismatch of the impedance is alleviated when magnetic field is increased, and accordingly the return loss improves to 32 dB at a magnetic field of 1900 Oe. The return loss is expected to increase further towards the initial impedance-match condition if a larger magnetic field is applied. As demonstrated in Figure 6.10-b, the differential phase shift increases from ~29 º/cm to ~77 º/cm at 5 GHz after increasing the magnetic field from 1400 Oe to 1900 Oe. Although even higher differential phase shifts can be achieved if the operation frequency is closer to the FMR frequency, the high loss due to the absorption of electromagnetic power caused by FMR will make the phase shifter not useful.

In sum, the sputtered BST thin film was deposited on polycrystalline YIG substrate without utilizing any buffer layer. Even though the film show a low crystal quality with a uncertain crystal epitaxial orientation, the dielectric properties still showed high dielectric constant and tunability. Preliminary microwave measurements under the control of both external electric field and magnetic field demonstrated the two-degree-freedom tuning and effectively alleviated impedance-mismatch on the coplanar phase shifter. However, this work has not been completed due to the unsatisfied crystal structure of the BST film. More explorations on deposition technique and optimized growth conditions are needed to produce high quality and well orientated BST thin film on polycrystalline
YIG substrate. With the improvement on crystal structure, the BST films would have higher possibility to yield better dielectric properties and phase shift abilities associated lower power consumption.
Chapter 7 Summary

This dissertation has investigated BST films on crystal structure, dielectric properties, and simple microwave applications – coplanar phase shifters. The motivation of this study was to produce BST films with better dielectric performance for tunable microwave component applications and discuss the effect of film strain on dielectric properties. The large dielectric tunability combined with relative low loss exhibits the BST films a potential in microwave applications to achieve better performance associated with the miniaturized device and reduced produce cost.

The epitaxial growth and microwave application of BST thin films have been widely studied in these two decades. The growth of thin films on substrates with similar crystal structure makes the possibility to enhance the electric performance of the BST thin films using the film strain introduced by the epitaxial growth, which is partially attributed to the lattice mismatch between the film and the substrate. Much of the existing work put attentions on using MgO and LaAlO$_3$ as substrates to the BST film deposition. Considering the similar composition, close lattice structure, and similar thermal expansion coefficients, SrTiO$_3$ has more advantages to be substrate for yielding BST film with better crystal structure quality. DyScO$_3$ substrate is also very attractive due to its quite close lattice parameters to BST, which is a desirable prerequisite for successful thin film epitaxial growth. Its low dielectric constant and low loss gives another benefit as a
substrate for the microwave device application. On the other hand, the effect of deposition conditions on tailoring film strain have attracts a great deal of attentions since the film strain significantly affects the electric properties of the BST film. Steps have never stopped on the way to pursue the better tunability and higher dielectric constant as well as low loss on the BST film.

In this thesis, BST thin films deposited on STO substrates and DyScO₃ substrates have both been investigated. X-ray diffraction techniques have been used as the main tool to characterize the crystal structure of the deposited films. Using the Bragg peaks detected by XRD technique, both in-plane and out-of-plane lattice parameters can be obtained and subsequently residual strain can be estimated quantitatively for each BST film. Although the as-grown films have relatively high in-plane compressive strain, a post-deposition thermal treatment at 1273-1298 K for 8 hours in oxygen dramatically reduced the compressive strain left in the films. The BST thin film deposited on both STO and DyScO₃ substrates still showed compressive strain even after thermal treatment. In order to reduce the film strain and enhance the structure quality, we propose to a new technique to improve the sputtering deposition, namely the three-step deposition technique. In the new method, a high-temperature growth of BST nucleation layer at 1068 K followed by a relatively low-temperature deposition of BST interlayer (temperature of 573-873 K were employed in this work), and a high-temperature deposition again at 1068 K of the top layer. Post-deposition anneals were used to further reduce the film strain as well as density of structural defects and thus to improve the dielectric properties. XRD
measurements revealed the substantial improvement of structural quality of the films fabricated via the three-step method as compared to the reference films grown at a single temperature of 1068 K. Microwave measurement on coplanar waveguides based on BST thin films were employed to exploit the dielectric properties of the BST thin films on both STO and DyScO$_3$ substrates.

On STO substrates, the BST thin films deposited by sputtering system dramatically reduced the compressive strain from -0.005 to -0.001 by using the three-step deposition method with the interlayer deposited 773 K. Associated with the improvement on crystal structure, the dielectric properties were also enhanced on the films deposited the three-step technique. The dielectric constant achieved as high as 1631 at 10 GHz and the large microwave dielectric constant tuning of 36.7% were obtained for electric field varied from 0 to 60 kV/cm. On the other hand, the three-step technique also works well on the BST films deposited on DyScO$_3$ substrates. The utilization of three-step technique for growing BST thin film deposited on DyScO$_3$ substrates by sputtering system also brought a degradation on residual compressive strain and a improvement on dielectric properties. After the post-deposition thermal treatment at 1298 K for 8 hours, the higher relative dielectric constant of ~1100 and a larger tunability of 47.9% were achieved on the three-step deposited film under the applied electric field 60 kV/cm at 10 GHz. The impressive large dielectric tunability was attributed to the reduced compressive strain in the crystal structure.
Generally, the thicker the epitaxial film is, the more relaxation the crystal structure shows. Due to the limited growth rate, the BST film with the thickness more than 1 micrometer is not convenient to be carried out by sputtering system. In such a case, the pulsed laser deposition is more attractive to fulfill the deposition. In this work, in order to improve the crystal structure and dielectric properties of the thicker BST films (~ 2 μm) deposited by pulsed laser deposition, we implemented a seed layer of BST thin film (400 nm) deposited by sputtering system before the PLD deposition. With the assistance of thermal treatment at 1298 K for 8 hours, the introduction of the seed layer made the BST film more relaxed and resulted in a slight tensile stain of 0.0004 in the lattice structure. Microwave measurement further evidenced the dramatic improvement on dielectric properties. Addition the seed layer, the annealed BST film showed a much higher tunability (63.0% vs. 46.2%) and exhibited a two-fold value on the relative dielectric constant. With the similar low loss found on both films with and without seed layer, the intrinsic figure of merit, which is defined as the tunability of the relative dielectric constant in percent divided by loss tangent, increases from 1925 to 2520 by introducing of the sputtered seed layer. The improvement of dielectric properties is consistent with the theoretical analysis of the relationship between the strain and the dielectric constant. Our attention was later tended to the microwave application of the BST films. A ferroelectric tunable coplanar phase shifters based on BST films were measured in microwave frequencies on both the thin BST films deposited by sputtering system using three-step technique and the thick BST film deposited by PLD with the introducing of
sputtered seed layers. The large differential phase shift and high phase shift figure of merit further confirmed the advantage of improving the deposition technique. Differential phase shift of 145 °/cm and Microwave figure of merit of 23 °/dB were achieved in applied electric field of 60 kV/cm at 10 GHz on the sputtering BST thin film with the thickness of 700 nm deposited on DyScO$_3$ substrate using the three-step technique. For the film deposited on STO substrate by PLD, the measurement on coplanar phase shifters showed that the introducing of the sputtered seed layer increased the differential phase shift from 177 to 416 °/cm and also enhance the microwave figure of merit from 21.0 to 36.2 °/dB in 60 kV/cm at 10 GHz.

The electric and magnetic field two-degree-freedom tuned coplanar phase shifter based on BST thin film deposited on polycrystalline YIG substrate has been preliminary investigated. The electric field was used to tuning the permittivity while the magnetic field was used to tuning the permeability. The magnetic field tuned permeability could effectively reduce the impedance changing due to the applied electric field. The return loss was decreased from 47 dB to 27 dB, however, with the application of the magnetic field, the return loss was increased to 32 dB. These preliminary measurement results light the way to design impedance matching phase shifter. However, due to the polycrystalline structure and low quality surface of the YIG substrate, we have not obtained high quality and well crystal oriented BST film. More deposition technique and growth conditions need to exploit to improve the epitaxial growth of BST film on polycrystalline YIG substrate.
In conclusion, the crystal structure of epitaxial BST films deposited by either sputtering or PLD technique were all optimized by reducing strain using new deposition methods. Three step method effectively reduces the compressive strain in the sputtered film and consequently improved the dielectric properties. The introduction of the sputtered seed layer was proved dramatically enhance the dielectric tunability achieved by reduce the tensile residual strain in the PLD deposited film. This work implies that, using proper deposition and thermal treatment, we can produce high quality BST films with enhanced dielectric performance by control the residual strain in the film. These results demonstrate the potential of BST films in tunable microwave components applications.
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