LOW TEMPERATURE GROWTH, CHARACTERIZATION AND APPLICATIONS OF RF-SPUTTERED SrTiO₃ AND BaSrTiO₃ THIN FILMS

A THESIS SUBMITTED TO

THE GRADUATE SCHOOL OF ENGINEERING AND SCIENCE OF BILKENT UNIVERSITY

IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR

THE DEGREE OF

MASTER OF SCIENCE

IN

MATERIALS SCIENCE AND NANOTECHNOLOGY

By Türkan Bayrak March 2016 LOW TEMPERATURE GROWTH, CHARACTERIZATION AND APPLICATIONS OF RF-SPUTTERED $\rm SrTiO_3$ and $\rm BaSrTiO_3$ THIN FILMS By Türkan Bayrak March 2016

We certify that we have read this thesis and that in our opinion it is fully adequate, in scope and in quality, as a thesis for the degree of Master of Science.

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ABSTRACT

LOW TEMPERATURE GROWTH, CHARACTERIZATION AND APPLICATIONS OF RF-SPUTTERED SrTiO₃ AND BaSrTiO₃ THIN FILMS

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Among the several perovskite ferroelectric oxides, $SrTiO_3$ (STO) and $BaSrTiO_3$ (BST) thin films have attracted significant attention due to their potential applications in oxide-based electronics. However, reliability and performance of STO and BST thin films depend usually on the precise knowledge of microstructure, as well as optical and electrical properties.

STO and BST thin films were deposited at room-temperature on Si (100), UVgrade fused silica, quartz substrates and TiO₂ nanofibers by radio frequency (RF) magnetron sputtering using different plasma power, oxygen mixing ratios (OMRs) and deposition pressure levels. As-deposited thin films showed amorphous-like nanocrystalline microstructure almost independent of the deposition conditions. Influence of post-deposition annealing at various temperatures of RF sputtered STO thin films were also investigated. All films were found to be highly transparent (>75%) in the visible region, and both STO and BST films exhibited well defined main absorption edges: the calculated indirect and direct band gaps for STO films were in the range of 2.32 to 4.55 eV. The refractive index of the STO films increased with OMR and post-deposition annealing for 3 mTorr deposition for STO, BST and STO annealing study. However, there is no correlation for 5 mTorr deposition. The refractive indices of BST films were in the range of 1.90-2.07 at 550 nm depending on their deposition conditions. The optical band gap of the BST films were calculated the ranging in 3.60 to 4.30 eV.

Electrical dielectric constant values of the STO thin films were extracted from frequency or voltage dependent capacitance measurements using micro-fabricated Ag/STO/p-Si device structures. High dielectric constant values reaching up to 100 were obtained. All STO samples exhibited more than 2.5 μ C/cm² charge storage capacity and low dielectric loss (less than 0.07 at 100 kHz). Post-deposition annealing at 800°C for 1 h resulted in polycrystalline BST thin films with increased refractive indices and dielectric constants, along with reduced optical transmission values. Frequency dependent dielectric constants were found to be in the range of 46-72, and the observed leakage current was very small,less than 1μ A. Our experimental results show that these low temperature grown STO and BST films have the potential for various electrical applications.

Keywords: Strontium titanate thin film, Barium strontium titanate thin film, nanocrystalline, polycrystalline, annealing, sputter deposition, room temperature deposition, butterfly curve, ferroelectric, dielectric constant, photocatalytic activity.

ÖZET

SrTiO₃ VE BaSrTiO₃ İNCE FİLMLERİN DÜŞÜK SICAKLIKTA DEPOLANMASI, KARAKTERİZASYONU VE UYGULAMALARI

Türkan Bayrak Malzeme Bilimi ve Nanoteknoloji, Yüksek Lisans Tez Danışmanı: Necmi Bıyıklı March 2016

Perovskit tipi ferroelektirik oksit malzemeler arasından $SrTiO_3$ (STO) ve $BaSrTiO_3$ (BST) ince filmler potansiyel oksit tabanlı elektronik uygulamalar açsından ilgi uyandırıcı hale gelmiştir. Fakat STO ve BST ince filmlerin güvenirlilikleri ve verimlilikleri mikroyapılarına olduğu gibi optik ve elektriksel sabitlerine de ekseriyetle bağlıdır.

STO ve BST ince filmler oda scaklığında Si(100), UV sınıfı kaynaşmalı silika, quartz alttaş üzerine ve TiO₂ nanofiberler üzerine saçtırma metodunun radyo frekansı ile alıan magnetronu ile farklı plazma güçü, farklı oksijen karıştırma oranı (OKO) ve farklı depolama basıncı kullanılarak depolanmıştır. Tavlama işleminden geçmeyen örnekler depolama koşullarından bağımsız olarak amorf yapıda nanokristal mikro yapı göstermiştır. Ayrıca tavlama çalışmasında beş farklı tavlama sıcaklığının etkisi amorf büyüyen stokiyometrik RF-saçtırma yöntemi ile büyütülmüş STO filmler üzerinde incelenmiştir.

Bütün filmler görünür bölgede yüksek geçirgenliğe sahiptir ve STO and BST filmler belirgin soğurma bölgesi sergiledikleri görülmüştür: Direk ve indirek olan band aralı ğihesaplamaları STO filmlerin band aralığının 2.32 ile 4.55 eV aralıında olduğunu göstermiştir. 3 mTorr basışda depolanan STO filmlerin, BST ve tavlama çalşmasında kırılma indisinin ise OKO ve tavlama ile arttğıgözlemlenmiştir. Fakat 5 mTorr da depolanan filmler için bir bağlant bulunamamştır. BST filmlerin kırılma indilslerinin 550 nm deki değerlerinin 1.90 ile 2.07 arasında depolama koşuluna bağlı olarak değiştiği gözlemlenmiştir. BST filmlerin band aralıklarının 3.60 ile 4.30 eV aralığında olduğu hesaplanmıştır.

STO filmlerin dielektrik sabitleri Ag/STO/p-Si yapısından frekans ya da voltaj

bağımlı kapasitans ölçümünden alınan kapasitans değerinden hesaplanmıştır. Dielektrik sabiti en yüksek 100 olarak bulunmuştur. Tüm STO örneklerin yük depolama kapasitelerinin 2.5 μ C/cm² dan fazla olduşu ve dielektirik kaypların düşük olduu not edilmiştir (100 kHz için 0.07 den düşük). 800°C de 1 saatlık tavlamanın etkisiyle polikristal BST filmler elde edilmiş ve kırılma indisinin ve dielektirik sabitinin arttışınot edilmiştir. Fakat optik geçirgenliği azalmştır. Frekansa bağlı dielektirik sabiti değeri 46 ile 72 arasındadır ve 1 μ A değerinde düşük kaçak akım gözlemlenmiştir.

Sonuçlar düşük scaklıkta depolanan STO ve BST filmlerin çeşitli aygıt uygulamarında potansiyeli olduğunu göstermektedir.

Anahtar sözcükler: Strontium titanat ince film, Barium strontium titanat ince film, nanokristalite, polikristalite, tavlama, saştırma ile depolama, oda scaklığında depolama, kelebek eğrisi, ferroelektirik, yalıtkanlık sabiti, fotokatalitik aktivite.

Acknowledgement

First of all, I would like to thank Assist. Prof. Dr. Necmi Bıyıklı for his guidelines, advice and support with an utmost kindness throughout this research. I also would like to thank to my thesis committee Assist. Prof. Dr. Ali Kemal Okyay and Assist. Prof. Dr. Bilge İmer.

I would like to thank Dr. Eda Goldenberg for her patience and sharing her knowledge with willingness whenever I needed.

I sincerely thankful our collaborators Assoc. Prof. Dr. Tamer Uyar and Dr. Ash Çelebioğlu for electrospinning TiO₂ nanofibers to produce a novel material $SrTiO_3/TiO_2$ and measurement of its photocatalytic performance. Gratitude extends to Assist. Prof. Dr. Aykutlu Dana and Dr. İkram Orak for their efforts in the fabrication and characterization of thin film transistors and memristors using RF sputtered $SrTiO_3$. I also would like to thank Assoc. Prof. Dr. Halit Altuntaş from Çankırı Karatekin University for sharing his extensive knowledge about electrical characterizations. I would like to thank Assist. Prof. Dr. Çağlar Elbüken, who lended me 23.6 inch computer monitor, which helped me a lot after 14 inc laptop screen.

Mustafa Güler is gratefully acknowledged for his help during FIB and TEM sample preparation and imaging. I would like to thank Dr. Gökçe Çelik and Neşe Güngör for their generous support on optical measurements. I would like to thank Dr. Mustafa Tahsin Güler from Kırıkkale University for sharing his knowledge on LabVieW. Additionally, I would like to thank Dr. Murat Güneş from EneRIns Energy Co. for sharing their expertise.

I debt of gratitude former and current members of the Bıyıklı Research Group Dr. Mehmet Yılmaz, Dr. Çağla Özgıt-Akgün, Dr. Petro Deminskyi, Seda Kizir, Ali Haider, Shahid Ali Leghari, Talha Masood Khan and Murat Serhatlıoğlu as well as student Office 310, 116 and Z-07, Yıldız Gözde Sağlam, Şeyma Canik Arslan, Ahmet Emin Topal, Alper Devrim Özkan, Canan Kurşungöz, Türkan Gamze Ulusoy, Sami Bolat, Amir Ghobadi, Amin Nazirzadeh, Merve Marçalı, Burak Tekcan, and Fatih Bilge Atar. I would like to extend my thanks to Elif Uzcengiz Şimşek, Bartu Şimşek and Meryem Hatip.

I would not believe to make good friendship after the age of 24 but they showed me that there is still hope to be a good friendship, many thanks to Seda Kizir, Aygül Zengin and Latif Önen, for the moral support and encourage.

Finally, I would like to thank to my parents and lovely sister for their love and support. I am especially thankful to my friends, Hacer Akça Acar, Çiğdem Bakkaloğlu, Fehmiye Keleş, Aslıhan Saçlıoğlu, and Şeyma Özcan for their deepest friendships. To Orhun and Kaan

Their father had not just given me a strong background in electromagnetism and the experiments of fundamental quantum physics in my undergraduate studies at Ankara University, who had thought me the knowledge is more important than power, wealth, and even happiness. Their father as a scientist and a person is candle on my walk.

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Chapter 1

Introduction

The potential for substantial down-sizing of electronic ingredients and integration with microelectronics due to the rapid development of ferroelectronic technology is the main driving force for ferroelectric materials research. In excess of 300 ferroelectric materials have been distinguished until now [1]. Among them, SrTiO₃ (STO) and BaSrTiO₃ (BST) are the most important ferroelectric perovskite materials.

STO is an attractive material due to the chemical stability, compatibility with high temperature processes, and decent electrical and opto-electronic properties, featuring a significant promise for micro/nano-electronic applications [4]. Moreover, BST thin films recently received great attention and they are key elements for the development of high performance electronic devices. Additionally, it provides room temperature operation. The field-dependent permittivity and temperature-dependent polarity proves to be useful for microelectronic applications. Excellent reviews by Tagantsev *et al.* [5] and Ahmed *et al.* [1] provide in-depth insight in the use of ferroelectric materials for microwave applications. Furthermore, room-temperature (RT) grown amorphous STO thin films were investigated for CMOS-compatible memristor device and tunability applications [6]. Amorphous STO exhibits nonvolatile bipolar resistive switching mechanism with 10^3-10^4 switching ratios and over repeated 10^5 s long READ cycles [6].

Understanding of its fundamental materials properties characterization through compositional, structural, optical, and electrical characterization is crucial for the device compatibility analysis of ferroelectric oxide films. In addition, high deposition temperatures used conventionally form an obstacle to the commercialization of these devices and low-temperature STO and BST synthesis is therefore, of significant interest [7]. STO and BST thin films have been studied on variety of substrates, however integration of STO and BST with Si substrates is highly desirable for CMOS-applications [8,9]. For instance, in fieldeffect transistor based on metal-oxide semiconductor (MOSFET) technology the power-horse of microelectronics, gate oxide thickness continues to decrease and alternative high-k dielectric materials are needed [10]. In the recent years, STO and BST thin films have been extensively studied, however most of the studies mainly focused on the correlation between film microstructure and optical properties including photo luminescence mechanism, optical constants, or only on their electrical characteristics [11–16]. Moreover, to the best of our knowledge only limited number of experimental work were reported on room temperature grown STO and BST thin films (< 200nm - thick) with the dependence of deposition parameters [17]. A thorough understanding of the material properties requires a systematic study; therefore, it is essential to correlate the film characteristics with deposition parameters. In the present thesis, STO and BST have been sputtered directly on Si(100), quartz and UV-grade fused silica (UVFS) substrates by radio frequency (RF)-magnetron sputtering at room temperature due to the investigation of the influence of oxygen mixing ratio (OMR), plasma power, and post-deposition annealing on the film structural, surface, optical, and electrical characteristics.

This thesis is organized as follows. After introduction, basic background information about perovskite structure, ferroelectric and its relation with the tunability and high k dielectric properties is provided in Chapter 2. Additionally, basic principles of the sputtering method including its opportunities and challenges, deposition of ferroelectric thin films oxides are discussed here. Finally, brief literature review about STO and BST, deposited with alternative method, were provided here too. Experimental procedure i.e., optimization recipes for sputter deposition, substrate preparation and characterization methods is presented Chapter 3. In Chapter 4, structural, morphological, optical and electrical characterization results are discussed. This chapter is divided in four group. First group includes STO and BST thin film characterization. Second group is about optimization recipes for the high deposition rate and understanding of the new magnetron unit. Characterization of STO as a function of post deposition annealing temperature is showed as third group. And finally, STO deposited on TiO_2 nano-fibers and its photocatalytic properties are presented in the last section. In Chapter 5, conclusion and future research directions are presented. Chapter 2

Theoretical Background of Perovskite Ferroelectrics

Understanding the principles of ferroelectricity, properties of ferroelectric materials are important for potential applications micro-nano electronics. Basic theoretical background about perovskite ferroelectric tunable material is given in this chapter.

2.1 Basic Concepts of Ferroelectrics

Ferroelectricity was discovered in 1920 in with the following material $KNaC_4H_4O_6.4H_2O$ also known as Rochelle Salt. A ferroelectric crystal is dielectric which has two or more orientational states of different nonzero electric polarization in applied zero electric field. This is referred as a "spontaneous" polarization. Electrical polarization at zero electric field is different in these orientational states.

2.2 Origin of the Dielectric Response and Tunability of Ferroelectric Materials

Ferroelectrics are well-known materials due to their high dielectric constant and high tunability. The origin of the high dielectric permittivity and high degree of tunability will be discussed here.

<u>Dielectric response of the ferroelectrics</u>: Ideal ferroelectric materials possess phase transitions. This makes the relative permittivity of the material is temperature dependent and pass through a phase transition when the temperature is increased. The crystal is polar phase and has a spontaneous polarization when the electric field is removed below the phase transition temperature as named Curie temperature (T_c) due to the reason of it Ti ion in the oxygen cage is not shifting from the center and thus, it is not creating the induced dipole. Above T_c , crystal is in non-polar phase, where the spontaneous polarization is nearly lost. The nature of the high dielectric permittivity of the ferroelectric material is explained of the compensation of microscopic forces that maintains the material in non-polar phase at zero electric field. Restoring force acting in opposition to the poling action of the applied field is weak due to the recompense of the microscopic forces. This is the reason of the high dielectric permittivity of ferroelectric materials. In Figure 2.1 temperature dependent phase transition from polar phase to non polar phase and additionally, polarization dependent dielectric constant for a ferroelectric material can be seen. The "Landau theory" explains



Figure 2.1: Temperature dependent dielectric constant and polarization of a ferroelectric material [1].

the dielectric response based on "Helmholtz free energy" \mathbf{F} of the crystal as a function of polarization \mathbf{P} :

$$F = \frac{1}{2}\alpha P^2 + \frac{1}{4}\beta P^4$$
 (2.1)

where α and β are both coefficients. The derivative of **F** with a function of the **P** gives the electric field **E**:

$$E = \alpha P + \beta P^3 \tag{2.2}$$

The equation below shows the relative dielectric permittivity of the ferroelectrics:

$$E = \frac{\delta P}{\varepsilon_0 \delta E} = \frac{1}{\varepsilon_0 (\alpha + 3P^2)} = \varepsilon(0) \frac{1}{1 + 3P^2 \varepsilon_0 \varepsilon(0)\beta}$$
(2.3)

Where $\varepsilon(0) = \frac{1}{\varepsilon_0 \alpha}$ and $\varepsilon_0 = 8.85 \times 10^{-12} F/m$. This equation exhibits the dielectric permittivity in zero electric field and non zero electric field. In the case of P = 0 then the equation is that:

$$\varepsilon = \varepsilon(0) = \frac{1}{\varepsilon_0 \alpha} \tag{2.4}$$

The coefficient α can be calculated as a linear function of temperature [18].

<u>Tunability of the Ferroelectrics</u>: Tunability in ferroelectric film can be achieved via different ways;

- Electrical tunability of the permittivity
- Electrical tunability of the permeability
- Magnetic tunability of the permittivity
- Magnetic tunability of the permeability
- Simultaneous tunability of permittivity and permeability

Permeability is the material response to an applied magnetic field, which shows the level of magnetization. Similar to permittivity, permeability can be defined as $\mu = \mu_{\rm r}\mu_0$, where, $\mu_{\rm r}$ is the relative permeability and $\mu_0 (= 4\pi x 10^{-7} H/m)$ is the permeability of free space. In this work I will discuss on electrical tuning of the permittivity since ferroelectric based tunable materials are mostly used in field tunable applications. Nonlinear relation between P and E curves in Fig. 2.1 indicates electrically tunable dielectric function.

Tunability, n, can be represented by the following equation:

$$n = \frac{\varepsilon(0)}{\varepsilon(E_0)} \tag{2.5}$$

where $\varepsilon(0)$ and $\varepsilon(E_0)$, are the permittivity of the material at zero field and nonzero electric field, respectively. Relative tunability can be defined as;

$$n_{\rm r} = \frac{\varepsilon(0) - \varepsilon(E_0)}{\varepsilon(E_0)} = \frac{n-1}{n}$$
(2.6)

The trend here is: The higher zero field permittivity $\varepsilon(0)$, the higher the tunability can be achieved.

2.2.1 Dielectric Loss in Ferroelectrics

The dielectric loss mechanism is important for tunable ferroelectric device applications, notably in microwave frequencies.

In electromagnetic theory, an electromagnetic wave travels with a velocity of phase $v_{\rm p} = \frac{1}{\sqrt{\varepsilon\mu}}$ in a dielectric medium, where ε and μ are the dielectric constant and magnetic permeability, respectively. The impedance of the dielectric medium is $z = \sqrt{\frac{\mu}{\varepsilon}}$, where the imaginary part of ε is related to conductivity and therefore to the dielectric loss mechanism.

The performance of the ferroelectric tunable devices are evaluated generally using a "figure of merit" (FOM), $k = n_r / \tan(\delta)$. The "loss tangent", $\tan(\delta)$, is a dissipation factor of the electromagnetic energy as the wave propagates within the medium.

The FOM of tunable devices are getting higher if the dielectric loss is reduced.

The loss in the ferroelectric material are divided into two mechanism: (i) intrinsic and (ii) extrinsic loss.

(i)Intrinsic loss

The origin of loss mechanism comes from the interaction of the applied AC field and phonon within the crystal lattice of the material. The theory of the loss mechanism is related to the energy of photon as known as "Planck-Einstein relation" $h\nu$, where ν is the frequency of AC field [19], is absorbed during thermal phonon collisions, which occupy higher energies. In literature three main fundamental loss mechanism were noted: (1) three quantum [5, 20, 21], (2) four quantum [22], and (3) quasi-Debye [5, 20].

(ii)Extrinsic Loss

Extrinsic loss mechanism in ferroelectric materials originate from the movement of the defects of the charges caused by the AC electric field resulting in a generation of acoustic waves at the frequency of the applied electric field. This is an additional loss mechanism proposed by Schlöman [23].

Another extrinsic loss mechanism is especially for microwave frequency range [24]. In this frequency range, charge at the crystallite boundaries [24] or its creeping to the border of the depletion layer of the electrode mainly responsible for this loss mechanism [25].

The last extrinsic loss mechanism which is noted in literature is that quasi-Debye contribution induced by random field defects. It originate from local polar regions because of the defects and structural imperfections within the tunable ferroelectric materials. [26]

Ferroelectric material can be doped with oxides, for instance MgO, Al₂O₃, and ZrO₂ [27, 28]. For SrTiO₃ and BaSrTiO₃, typical dopant ions are Mn^{+2} , Mn^{+3} , Ni⁺², Mg⁺², Al⁺², In⁺², and Cr⁺³. These dopant ions act as electron acceptors with less charge than 4+, replacing Ti⁺⁴, thus preventing the reduction of Ti⁺⁴ to Ti⁺³. One of the extrinsic loss mechanism which is called quasi-Debye might be explained by the dielectric loss originating from the electron transver to Ti atoms from oxygen vacancies. Therefore, the optimized amount of acceptor dopant level can reduce the dielectric loss in ferroelectric materials.

2.2.2 Tunability as a Function of Permittivity

Ferroelectric materials are being used in various applications. Depending on the application, higher tunability with high or low dielectric constant or vise versa might be desirable. Tunability and dielectric constant dependence of the applications may help tailoring the properties of these materials. Tunability can be increased by the dielectric constant of the material in both ferroelectric and paraelectric phases. However higher tunability implies higher dielectric loss as well.

2.3 Perovskite Structure in Crystallinity and Relation to the Ferroelectric Oxides

Perovskite structure is one of the four groups in ferroelectric material family. Other three are the pyrochlore $(Cd_2Nb_2O_7)$, tungsten-bronze $(PbNb_2O_9)$ and bismuth layer $(PbBi_2Nb_2O_4)$ structures. If the crystal has polar space group, crystal produces the spontaneous polarization under nonzero electric field. Multiple symmetry-related states are signature of the ferroelectricity. On the other hand, paraelectric phase posses just a single state.

Perovskite oxide family with ABO₃ composition is the most widely studied ferroelectric oxide. A and B each represents a cation element and belongs to the space group of Pm3m. In perovskite crystal structure oxygen occupies the face centers, B cation is metal ion with small radius surrounded by the octahedral cage of the oxygen ions and A cation(s) is at the corner. Cohen *et al.* [29] has investigated the nature of ferroelectricity on two perovsike oxides; BaTiO₃ and PbTiO₃ demonstrated that hybridization between the titanium 3d states and the oxygen 2p states is responsible for ferroelectricity. Crystal structure of ferroelectrics can be experimentally observed with X-Ray and neutron-diffraction methods. X-Ray diffraction with pair-density correlation function (PDF) analysis [30] and X-ray absorbtion fine structure spectroscopy (EXAFS) methods are important to verify ferrolectric properties of the materials under investigation.

2.4 Perovskite Oxide Ferroelectric Thin Films

Ferroelectric oxide thin films (with thickness less than a few hundred nanometers) are very attractive for microelectronic applications including integrated devices [31], ultrathin high-k gate dielectrics [32], capacitors [33], light emitters [34], dynamic random access memories [35], microwave tunable devices [5], and electroluminescence elements [36–38] due to their high dielectric constants, low leakage currents, and decent optical properties. Beginning of the 1980s, ferroelectric

based thin film devices have gained a considerable interest for further miniaturization. Additionally, ferroelectric thin film based semiconductor integrated circuits might take advantage of reducing the manufacturing costs.

Ferroelectric thin films have been studied on different substrates in literature, especially MgO, single crystal sapphire, and LaAlO₃ due to the good lattice match. These substrate have similar lattice parameters with ferroelectrics such as $SrTiO_3$ and BaSrTiO₃, significantly improving the quality of the deposited ferroelectric films. Si substrates are conventionally not suitable for deposition of oxide ferroelectric thin films due to the large lattice mismatched. However, Si wafer as a substrate is 100% compatible for integrated circuit technology. Therefore, research efforts for improving the quality of ferroelectric thin films on Si substrate are necessary. Thickness [2], crystallinity, growth temperature [2,39,40], deposition method, composition, annealing, and processing conditions, all have influence on the structural, morphological, optical, and electrical properties of the ferroelectric thin films.

2.4.1 Sputter Deposition of Perovskite Oxide Ferroelectric Thin Films

Sputtering is a thin film deposition method by utilizing energetic Ar plasma to eject atoms from the solid target surface. This descriptive overview of the operational principles of sputtering for the deposition of ferroelectric oxide.

Conventional sputter deposition systems have two types of magnetrons; dc and rf. In dc sputtering, plasma is accelerated by an electric field through to the cathode. Electric field between the electrodes causes the ionization of the neutral Ar gas to Ar^+ ions. The accelerated Ar^+ ions hit the target and transfer their kinetic energy to the sputtering target. As a result, target atoms are removed from the surface and they are gathered onto the substrate. However, ferroelectric oxides are insulators and dc sputtering does not work for deposition because the charge forms at surface of the insulating target and electric field is neutralized causing the plasma to vanish. This problem can be handled by applying an ac electric field instead of dc electric field. Moreover, this ac field should be excited at higher frequencies otherwise resputtering occurs and the film growth rate reduces significantly [41].

Using rf frequencies is one of the solution to overcome this problem due to the fact that heavy Ar^+ ions can not respond to an rf electric field. Thus, deposition of non-conducting materials via sputtering becomes possible [42]. RF electric field generates the plasma but only the electrons with low effective mass respond to the lower energies. Ar^+ ions are accelerated by the target self bias voltage and sputtering deposition starts with ejected atoms from the target surface. Total gas pressure, deposition pressure, rf power, substrate, and temperature are the main control parameters that can be adjusted for rf sputtering deposition. High gas pressure causes increased thermalization of removing target atoms resulting in good uniformity performance [43]. On the other hand, introduction of oxygen to the sputtering chamber results in O⁻ ions and negative oxygen ions tend to move to the formation of non-stoichiometric films [41]. Additionally, increased deposition pressure results in reduction of the growth rate [44] due to the increasing gas collision. A typicall basic rf sputtering set up is shown schematically in Fig. 2.2.

2.4.2 SrTiO₃

STO is one of the most important ferroelectric perovskite materials due to its chemical stability, compatibility with high temperature processes, and attractive electrical and opto-electronic properties, featuring a significant promise for micro/nano-electronic applications. SrTiO₃ is a perovskite-type oxide that follows the general formula of ABO₃. In SrTiO₃ crystals, Ti⁺⁴ ions are located in the middle of the octahedral cage formed by O²⁻ ions, while each Sr⁺² ion is surrounded by four TiO₆ octahedra. Thus, each Sr⁺² ion is coordinated by a total of 12 O²⁻ ions. The hybridization of Ti 3d and O 2p states facilitates the formation of covalent bonds between these elements, and is responsible for the



Figure 2.2: RF sputtering set up.

ferroelectric behavior of SrTiO₃. The noted lattice parameter of STO is about 0.39 nm (Fig. 2.3). In addition, ionic bonds also exist between Sr^{+2} and O^{-2} ions, and the material exhibits both physical and chemical bonding properties. SrTiO₃ has three different crystal structure as a function of the temperature, tetragonal (110 K-65 K), orthorhombic (55 K-35 K) and rhombohedral (< 10K).

In literature, the band gap of STO is reported in the range of 3.22 [45]- 4.7 [46] eV. Thus, STO behaves like a semiconductor material with direct band gap. Also, STO is known as a good insulator with indirect band gap. In the band structure, oxygen 2s and 2p orbital which correspond to the highest occupied molecular orbital (HOMO) and empty d orbitals which correspond to the lowest unoccupied molecular orbital (LUMO). The corresponding gap between HOMO and the LUMO states are enough to STO as an insulator. The thin film STO shows different properties on different substrates which affect crystalline regions

in the film.



Figure 2.3: Cubic SrTiO₃ at RT. (taken from the website of Technische Universitat Braunschweig, Institut für Elektrische Messtechnik und Grundlagen der Electrotechnik.)

Furthermore crystal structure of STO depends strongly on deposition methods. Pervoskite [47], single crystalline [48], polycrystalline [49, 50], crystalline nano particles [50] structures for STO thin films were noted in literature. Ion beam sputter [51], atomic layer deposition [52], pulsed laser deposition [53, 54], verneuil method [55], polymeric precursor method [56], microwave assisted [9], hydrothermal method, molecular beam epitaxy [57], metal organic chemical vapor deposition, [5] and RF sputtering [31, 32, 47, 50, 58] had been noted as deposition methods to obtain STO thin films. It has been reported that sputtered deposition STO thin films under non-oxidizing Ar atmosphere produces oxygen vacancies in the films [59], thus film stoichiometry and other material properties can be tuned via changing the O_2/Ar ratio.

Photoluminescence spectroscopy of STO thin films is used to determine electronic and optical properties. There are many studies in the literature to study photo carrier recombination dynamics of amorphous [56], undoped [51], Ar⁺ irradiated, electron doped [60], Nb doped [53], La doped [61], and highly photo-excited [62] STO crystals. A theoretical study of PL on STO, structural order-disorder and PL behavior are closely related, which was confirmed with presence of electronic exited states [61].

Deposition	Crystallinity	Thickness	Dielectric Constant	$Tan\delta$	Ref.
RF Sputter	Polycrystalline	387 nm	60 @ 100 kHz	0.35 @ 100 kHz	[46]
Bulk	Single Crystal	0.07-1.00 cm	224-330 @ 1MHz	NA	[66]
Pulse Laser Deposition	NA	NA	> 950	< 0.01	[67]
Polymeric Precursor	Polycrytalline	$\sim 600 nm$	475 @ 1kHz	0.050 @ 1kHz	[68]
Solgel	NA	600 nm	200 @ 100 kHz	0.04 @ 100 kHz	[69]
MOCVD	NA	800 nm	225 @ 100 kHz	0.008 @ 100 kHz	[70]
Solgel	NA	800 nm	130 @ 100 kHz	0.022 @ 100 kHz	[71]
Laser Ablation Perovskite	NA	1000 nm	239 @ 100 kHz	NA	[72]
RF Sputter	NA	20 nm	12-18	NA	[73]
MBE	NA	100-150 A	175	NA	[74]

Table 2.1: The effect of deposition methods on crystallinity and dielectric constant of STO films.

Dielectric constant is another important phenomena for STO thin films. It depends on various factors such as, growth temperature, annealing temperature, crystallite size, thickness, substrate and composition. Thickness dependent dielectric properties as a function of temperature on SrRuO₃/LaAlO₃ substrate by pulsed laser deposition were noted by Li et al. and Kingon et al. [63–65]. According to their studies, dielectric constant increased with annealing. Moeckly et al. observed the dielectric loss of the STO on $LaAlO_3$ substrate at 2 GHz and 10 kHz [75]. The data shows that higher permittivity, higher loss tangent as a function of temperature. Literature review of the dielectric constants of STO are shown in Table 2.1.In another study, room-temperature (RT) grown amorphous STO was investigated for CMOS-compatible memristor device and tunability applications [6,7]. They noted that oxygen deficient amorphous STO memristors exhibit nonvolatile bipolar resistive switching mechanism with 10^3 - 10^4 switching ratios [6]. Room-temperature RF-sputtered archetypical perovskite oxide STO is an important form of STO and understanding of its functional properties through compositional and structural engineering might be crucial for the development of nano-scale resistive switching devices.

In addition, high deposition temperatures form an obstacle to the commercialization of these devices and low-temperature STO synthesis is therefore, of significant interest [7]. STO thin films have been deposited on variety of substrates, however integration of STO with Si substrates is highly desirable for CMOS-investigation [8, 9]. For instance, in metal-oxide semiconductor fieldeffect transistor (MOSFET) technologythe power-horse of microelectronicsgate oxide thickness continues to decrease and alternative high-k dielectric materials are needed [10]. Table 2.1 shows the effect of deposition tecniques on crystallinity and dielectric constant of these films.

The refractive index of bulk $SrTiO_3$ is in the range of 2.31 to 2.38. Refractive indices of the thin film STO were noted by Baumert *et al.* [76] and it is in the range of 2.14 to 2.33 at 632 nm. Moreover, Panomsuvan *et al.* [51] calculated both envelope method from transmission and ellipsometry measurements they found the refractive indices are between 1.88 to 2.01 for amorphous and 2.09 for polycrystalline STO at 620 nm. Benthem *et al.* [77] reported (both theoretical and experimental) on the variation of optical band gap values of Fe-doped STO thin films, and stated that STO films have well determined indirect (3.25 eV) and direct (3.75 eV) band gap energies. Moreover, Frye *et al.* [62] studied the effect of oxidation state on single crystalline STO films using ellipsometry, and found that STO band gap energies range from 3.58 to 3.90 eV for direct, and from 3.00 to 3.77 eV for indirect transitions as a function of oxidation/reduction. They further concluded that the reduction in band gap energies might be due to the variation in oxidation state of the film and stoichiometric variation. PL spectroscopy was used to determine optical properties of deposited STO films.

There are many studies reporting on the photo-carrier recombination dynamics of amorphous, un-doped and doped STO thin films [50, 60, 78–80]. Yamada *et al.* reported on PL behavior of STO bulk crystals and nanoparticles under weak continuous wave and strong pulse laser excitations. They observed a 2.9 eV blue emission band for bulk STO crystals, and 2.4 and 2.9 eV emission bands for STO nanoparticles under strong pulse excitation. However, at weak excitation they observed emission from 1.7, 2.4, 2.9 and 3.3 eV bands. In their work, 1.7 and 2.4 eV emission peaks are attributed to the defect or impurity related mechanisms while 2.9 eV emission peak is related to the intrinsic carrier recombination. They reported that Auger recombination process is significant in nanoparticles, and the increased final state density and reduced dielectric constant can be related to the enhancement of Auger recombination.
2.4.3 BaSrTiO₃

BST is an attractive material for room-temperature tunable electrical device applications. The Curie temperature of BaTiO₃ is 116°C and it can be reduced further to room temperature by alloying with SrTiO₃, which has a Curie temperature of -243°C. Increasing Sr concentration, Curie temperature linearly decreases from RT to cryogenic temperatures. In literature, variation of x, Sr mole fraction, as a function of Curie temperature of the general expression of BST, $Ba_{1-x}Sr_xTiO_3$, is noted [81]. It can be seen from this study that RT operation is provided by x < 0.4. Another study also shows the adjustable Curie Temperature of BST with the formula of $Ba_xSr_{1-x}TiO_3$. The composition of x must be in the



Figure 2.4: Structure of BST a) polar and b) non-polar phase [1].



range of 0.63 to 0.5 for room temperature operations [82]. The importance of

Figure 2.5: Thickness dependence of the capacitance density (A/C) of the BST thin film with different Ti concentrations and different temperatures [2].

the Curie temperature is that if materials operate at near Curie temperature, it shows considerably large permittivity and electrically tunability. This is why it is important to tune the Curie temperature near RT for microelectronic applications. BST thin films received great attention due to their potential for high performance electronic devices [83] due to the superior tunability, low loss, RT operation, and additionally being lead—free tunable perovskite. Figure 2.4 explains the tunability mechanism in BST crystal structure [1]. Polar phase and non-polar phase can be seen along with the Curie temperature, respectively.

As mostly perovskite-oxide crystal structure, oxygen occupies the face centers, small titanium ion is in the octahedral cage of oxygen ions, whereas barium and strontium ions are at the corner in both polar and non-polar phase. In Fig. 2.4 (a) Ti ion has shifted from its centre resulting in non-zero polarization and by applying electric field, tunable properties arise due to displacement of the titanium ions and creation induced dipoles. There are many factors which influences the quality of BST thin films, including, processing methods, substrate material, substrate and annealing temperature, film composition, crystalline structure, microstructure, surface morphology, film thickness, and electrode material. Various substrates were used for BST deposition crystal sapphire, MgO, and LaAlO₃ are the most widely used for BST deposition due to the similar lattice parameters with BST, minimizing losses due to the lattice mismatch.

The excellent literature review about dielectric constant of BST film with different composition, capacitor structure, and deposition methods is presented by the Ezhilvalavan *et al.* [84] Additionally, Tagantsev *et al.* mentions in their review report dielectric constant and $\tan(\delta)$ values of as-deposited and annealed BST on MgO and LaAlO₃ substrate [5]. Dielectric properties of the BST is thickness dependent and also more than a order of magnitude lower than its bulk form. In Fig. 2.5 (a) and (b) thickness dependence of the capacitance density (A/C) of the BST thin film with different Ti concentrations and capacitance density of the Ba_{0.7}Sr_{0.3}TiO₃ at different temperatures were given based on parallel plate capacitor model [2]. Frequency dependent dielectric constants of 400 nm spin coated Ba_xSr_{1-x}TiO₃ for two different x concentration (0.8,0.4) were noted by Pontes *et al.* [85]. Dielectric constant and leakage current were also noted as a function of OMR by Tsai *et al.* [86]. Dielectric constant reached the maximum value at 50% OMR. Therefore, dielectric constant of the BST films are influenced by oxygen stoichiometry as well as composition, grain size, and crystallinity.

Perovskite type of ferroelectric oxide has a large dielectric constant due to the polarization of the electric dipole. Increased oxygen content might increase for the polarization of the electric dipole. The electrical properties bulk and thin film BST with different compositions are reported in the literature. Though less, optical and structural properties of BST were also mentioned in the literature. XRD spectrum analysis of BST films deposited on fused quartz substrate by using rf sputtering with different substrate temperature is noted by Li *et al.* [87]. They noted pseudocubic structure with (100), (110), (111), (200) and (210) diffraction peaks within the 2θ range from 20° to 67° . Noh *et al.* reported amorphous 55 nm $Ba_xSr_{1-x}TiO_3$ deposited on single crystal MgO (001) substrate by rf sputtering [3]. Thielsch *et al.* presented XRD scans of BST on MgO (001) substrate deposited by using off-axis laser deposition. Only (001) and (002) reflections of the film are visible and film growth was oriented in c axis [88]. The synchrotron X-ray scattering showed that nucleation started around 500-600°C and perovskite phase was observed around 700°C. XRD patterns of BST deposited on Pt/SiO₂/Si by using rf sputtering with three different substrate temperature (500°C, 600°C and 650° C) were reported Lee at al. [89] They noted that crystallinity increased with the deposition temperature and films deposited at 600°C and 650°C have different textures with [110] and [100] cubic perovskite structure, respectively [17]. BST exhibits different growth characteristics on different substrates.

In general, BST shows grainy growth characteristic. However, AFM investigation of BST on Pt/SiO₂/Si and MgO substrates show island growth and layer by layer growth characteristics, respectively [3,89]. Additionally, different phases of BST as a function of annealing temperature is noted by Noh *et al.* and shown in Fig. 2.6. The transmission spectrum of BST thin film on fused quartz substrate shows well-defined band gap at 320 nm, while transmission reached above 75% for the wavelengths longer than 460 nm [87]. The refractive index was calculated by using envelope method of Manifacier *et al.* from the transmission spectrum [90].



Figure 2.6: Temperature dependent crystallinity of BST films [3].

Refractive indices of BST thin film, are reported in the literature as a function of wavelength, substrate temperature, sputtering pressure, oxygen to Ar ratio (O_2/Ar) , annealing temperature, packing density (p) and stoichiometry [88,91]. Direct band gap of the Ba_xSr_{1-x}TiO₃ films with various composition and bulk values were reported by Thielsch *et al.* [88]. Optical band gap energies of the composite BST thin films could not be found in the literature. However, direct band gap energies of SrTiO₃ and BaTiO₃ are 3.2 eV and 3.6 eV, respectively. Direct band gap of amorphous BaTiO₃ is reported to be in the range of 4.3 to 4.6 eV [92–94].

BST is suitable material for memory applications in the "Gbit era" for instance, DRAM capacitors due to the its attractive properties such as low leakage current, high dielectric constant, and room temperature operation. Literature review on dielectric properties of BST are given Table 2.2.

Deposition	Thickness	Dielectric Constant	$Tan\delta$	Ref.
Polymeric Precursor	400 nm	680 @ 100 kHz	0.01 @ 100 kHz	[85]
Sputtering	80 nm	548-219 @ 100 kHz	0.083-0.014 @ 100 kHz	[95]
Sputtering	500 nm	180-320	NA	[96]
Pulse Laser Deposition	300 nm	160-360 @ 100 kHz	0.0032-0.0306 @ 100kHz	[97]
Sputtering	400 nm	280 at 100kHz	>0.01 at 100kHz	[98]
Sputtering	60-120 nm	239-638 @ 100 kHz	0.0072-0.015 @ 100 kHz	[76]
Review Paper	20-300 nm	200-600 @ 100 kHz	NA	[99]

Table 2.2: Dielectric constant of BST films, as a literature review.

2.5 Photocatalytic Activity of SrTiO₃

2.5.1 Theoretical Background and Literature Survey

TiO₂ has been remarked since 90s due to its superior properties in many applications i.e., photocatalysis, water and air purification, self cleaning surfaces, antibacterial power, dye sensitized solar cells etc. As a typical $A^{2+}B^{4+}O^{3-}$ type perovskite, STO has been known with the capability of decomposing H₂O into H₂ and O₂ as a photocatalyst. The enhanced photocatalytic performance of STO/TiO₂ heterojunction was offered by many studies. The main mechanism for the enhanced photocatalytic activity of the STO/TiO₂ composite can be described as following: When STO and TiO₂ are under UV light excitation, electrons in STO immigrates to the conduction band (CB) of TiO₂ and holes in TiO₂ are transported to the valance band (VB) of STO. The electron-hole transfer is thermodynamiclly preferable due to the lower CB and VB of STO with respect to TiO₂. At the same time, excited conduction band electron converts the dissolved oxygen molecules to the superoxide radical anions,O₂⁻, protonation of the hydroperoxy radicals, producing hydroxyl radical OH as follows (Fig. 2.7):



Figure 2.7: Schematic diagram showing the energy band structure and separation of electron-hole pair in the $STO/TiO_2/STO$ heterostructure.

 $(\text{STO/TiO}_2) + h\nu \rightarrow (\text{STO/TiO}_2)(e_{\text{CB}} + h_{\text{VB}})$ $h^+ + \text{OH} \rightarrow \text{OH}$ $e^- + \text{O}_2 \rightarrow \text{O}_2$ $\text{O}_2 + \text{H}_2 \text{O} \rightarrow \text{HO}_2 + \text{OH}$ $\text{HO}_2 + \text{H}_2 \text{O} \rightarrow \text{HO}_2 + \text{OH}$ $\text{HO}_2 + \text{H}_2 \text{O} \rightarrow \text{H}_2 \text{O}_2 + \text{OH}$ $\text{H}_2 \text{O}_2 \rightarrow 2\text{OH}$ $\text{OH} + \text{MB} \rightarrow \text{CO}_2 + \text{H}_2 \text{O}$

In literature, Cr [100], Ag [101], Pb [101], Ni/La [102], Mn, Ir, Rh, [103] Ru and Sb doped STO [104], STO nanoparticle on TiO₂ [105], STO/TiO₂ nanotube formation and STO modification by ion bombardmant are used for catalytic templetes. Therefore, sputtered STO onto TiO₂ nanofibers forming STO/TiO₂ core—shell nano heterostructures can be promising for enhanced photocatalytic activation. Chapter 3

Experimental Details

3.1 Preparation of Substrates

3.1.1 Planar Substrates

Si (100), UV-grade fused silica, and quartz substrates were cleaned by sequential ultrasonic agitation in acetone, isopropanol, deionized (DI) water for 2 min and dried with N_2 , followed by a de-hydration bake at 110°C for 5 min. Afterwards, substrates were put in the deposition chamber, immediately.

3.1.2 Nanofiber Templates Prepared by Electrospinning

Electrospun TiO₂ nanofiber templates were prepared by Poly(vinylpyrrolidone) (PVP, Mw 1.3×10^6 , Sigma-Aldrich), titaniumisopropoxide (TTIP, 97%, Sigma-Aldrich), ethanol ($\geq 99.8\%$ Sigma-Aldrich), glacial acetic acid (100%, Merck) and N,N-dimethylformamide (DMF,Pestanal, Riedel). PVP-TTIP solution was used as a precursor. For PVP-TTIP solution, TTIP (2.88 mL) was stirred in a glacial acetic acid (2mL)/ethanol (2mL) solvent system for 15 min. PVP (0.6 g) solution in ethanol (3mL) was added to the above. The yellowish PVP-TTIP solution was obtained after 2 h stirred of resulting mixture. Electrospinning of the prepared solutions was carried out by 15 kV (Spellman, SL Series) voltage bias difference to the metallic needle (~0.6 mm of inner diameter) and stationary metal collector covered with a piece of clean aluminum foil. The tip and collector distance was adjusted between 10 and 12 cm. The electrospinning setup was enclesed chamber at 25°C and 10% relative humidity. Fiber diameters were investigated by scanning electron microscopy which is mentioned in section 3.7 with details.

3.2 SrTiO₃ and BaSrTiO₃ Deposition Using RF Magnetron Sputtering

3.2.1 SrTiO₃ Deposition

STO thin films were deposited using an off-plane axis VAKSIS NanoD 4S RFmagnetron sputtering system. The experiments are divided in to two groups due to the reason of RF-magnetron modification during my studies. The first and second groups are referred to be before magnetron change and after magnetron change, respectively.

The first group: STO thin films were deposited under three different $O_2/(Ar+O_2)$ (OMR) environment, 0% 0/(0+30), 10% 3/(3+27), 20% 6/(6+24), under 75 and 100 W RF power on p-type Si and UV-FS substrates with different deposition time (between 10 min to 30 min) at RT. Additionally, two deposition pressures were studied, 3 mTorr (0.40 Pa) and 5 mTorr (0.67 Pa) with a target-to-substrate distance of 50 mm by using substrate extension in front of the RF-Magnetron. VAKSIS NanoD 4S RF-magnetron sputtering system with additional substrate holder (extension) is shown in Fig. 3.1.

	Deposition Power (W)	Deposition Pressure (mTorr)	$\mathrm{O_2/(O_2+Ar)}$	Time (min)
1 st Group ¹	75	3	0/(0+30)	15
-	75	3	3/(3+27)	25
	75	3	6/(6+24)	25
	75	5	0/(0+30)	10
	75	5	3/(3+27)	30
	75	5	6/(6+24)	30
	100	5	3/(3+27)	25
	100	5	6/(6+24)	25
2 nd Group	100	1	0/(0+30)	30
	150	3	0/(0+100)	120
	100	3	0/(0+50)	20
	100	3	0/(0+50)	100
	100	5	0/(0+50)	100
	100	7	0/(0+50)	100
	100	10	0/(0+50)	100
	100	15	0/(0+50)	100
	120	3	0/(0+50)	100
	120	5	0/(0+50)	100
	120	7	0/(0+50)	100
	120	10	0/(0+50)	100
	120	15	0/(0+50)	100
Fiber-STO	75	3	0/(0+30)	3
	75	3	0/(0+30)	5
	120	10	0/(0+50)	240

Table 3.1: Recipe development of RF-sputtered SrTiO₃

The second group: To understand the behaviour of the changed magnetron unit and also the rotational substrate holder to improve uniformity, STO thin films were deposited under 100, 120 and 150 W RF-power with different Ar flow (30 and 50 sccm) while the O_2 flow to the chamber was kept constant at 0 sccm (No O_2 flow). Six different deposition pressure (1, 3, 5, 7, 10, 15 mTorr) were studied for 40 min and 100 min deposition at RT with a target-to-substrate distance of 11 cm by using rotation with extension (Fig. 3.2). STO was also deposited on electrospun TiO₂ nanofibers for the investigation of the photocatalytic activity. STO was deposited at 75 and 120 W, 3 and 10 mTorr deposition pressure under pure argon environment (30 and 50 sccm Ar) for 3, 5 and 240 min with rotational substrate holder.

¹This group of deposition was repeated at least three times.



Figure 3.1: View of the sputter chamber: RF magnetron, DC magnetron, and substrate extension along with rotational substrate holder.

For annealing study, STO films were deposited at 0% OMR (30 sccm Ar, 0 sccm O_2) under 100 W RF power, 7 mTorr (0.93 Pa) for 20 min at RT on p-type Si (100) and UV-FS substrate with a target-to-substrate distance of 50 mm by using substrate extension in front of the RF-Magnetron. All depositions were performed using a stoichiometric SrTiO₃ ceramic target (50 mm diameter, purity 99.9%). Deposition was not started before the base pressure (PB) of the chamber reached < 6.510^{-6} Torr (0.9 mPa). All details for deposition conditions for both groups are given Table 3.1.



Figure 3.2: Sputter chamber RF magnetron, DC magnetron (covered with Al foil) and rotational substrate holder with extension (width:4 mm).

3.2.2 BaSrTiO₃ Deposition

BST thin films were deposited on Si (100) and UVFS at RT using off-plane axis VAKSIS NanoD 4S rf magnetron sputtering system. Ar and O₂ were introduced into the system using separate lines. During the film deposition, O₂ flow to total gas flow ratio was kept constant at 3.3%. The depositions were performed using BaTiO₃/SrTiO₃ ceramic targets (50 mm) with a constant target-to-substrate distance of 50 mm.The chamber base pressure was < 6.510⁻⁶ Torr. The effect of deposition pressure, (three different deposition pressures, 5 (0.67 Pa), 7 (0.93 Pa), 10 (1.33 Pa) mTorr) was studied, for films deposited at a constant RF power of 75 W. The deposition conditions are summarized in Table 3.2.

Base Pressure (Torr)	$<\!\!6.5 \mathrm{x} 10^{-6}$
Deposition Pressure $(P_D)(mTorr)$	5 (0.67 Pa), 7 (0.93 Pa) and 10 (1.33 Pa)
$O_2/(O_2+Ar)$	3.3%
RF Power (W)	$75 \mathrm{W}$
Target Size (mm)	50
Target Substrate Holder Distance (mm)	50
Deposition Time (min)	15-20
Annealing Temperature (°C) and time (h)	800° C and 1 h in O ₂ flow

Table 3.2: The deposition conditions of RF sputtered $BaSrTiO_3$.

3.3 Characterization Methods

3.3.1 Structural Characterication

3.3.1.1 Grazing-Incidence X-Ray Diffraction and Line Profile Analysis

Grazing-incidence X-ray diffraction (GIXRD) measurements were carried out in a PANalyticalX'Pert PRO materials research diffractometer (MRD) system using Cu K alfa ($\lambda = 1.5406 \text{\AA}$) radiation with an angle of incidence (w), which was optimized for each individual sample at 0.3°. The GIXRD patterns were recorded within the 2Theta range of 20°-80° with a step size and counting time of 0.1° and 10 s, respectively. Peak positions and the corresponding interplanar spacing values were obtained by fitting the data from GIXRD by using PANalytical X'Pert HighScore Plus Software. Line profile analysis (LPA) was applied to each recorded GIXRD pattern by using the same software. The interplanar spacing (d_{hkl}) was also calculated for the most intense peak using Bragg's law:

$$d_{\rm hkl} = \frac{n\lambda}{2\sin\theta} \tag{3.1}$$

Where n is an integer representing the order of diffraction, λ is the wavelength of incident monochromatic X-ray beam, θ is the diffraction angle and *hkl* represent the miller indices of diffracting planes [106]. Lattice parameter was roughly calculated by substituting d₀₁₁ for STO and d₀₀₂ for BST values in Eqn. (2), which relates the interplanar spacing (d_{hkl}), miller indices (hkl), and lattice parameter (a) for cubic crystals. Grain sizes of the annealed films were estimated from the (011)diffraction for STO, (002) for BST reflection using Eqn. (3), the well-known Scherrer formula by neglecting the instrumental broadening and assuming that the observed broadening is only related to the size effect;

$$d = \frac{a}{\sqrt{h_2 + k_2 + l_2}}$$
(3.2)

Grain sizes of the annealed films were estimated from the (011) for STO, (002) for BST reflection using Eqn. (3), the well-known Scherrer formula by neglecting the instrumental broadening and assuming that the observed broadening is only related to the size effect;

$$D = \frac{0.9\lambda}{B\cos\Theta} \tag{3.3}$$

where λ , B and ϕ are the wavelength of the radiation used ($CuK = 1.5418 \text{\AA}$), broadening (FWHM) and Bragg diffraction angle of the selected reflection, respectively [106, 107].

3.3.2 X-Ray Photoelectron Spectroscopy

Surface and bulk film chemical compositions were measured by X-ray photoelectron spectroscopy (XPS; Thermo Scientific 20 K-Alpha spectrometer) with a monochromatized Al $K\alpha$ with 1486.6 eV X-ray source. Pass energy, step size, and spot size were 30 eV, 0.1 eV, and 400 μ m, respectively. To reach the bulk film, etching of the thin film samples were carried out insitu for 30 s and 60s for just annealing study, ion milling process was applied with an Ar beam having an acceleration voltage of 1 kV. High resolution XPS data were corrected for charging by shifting peaks with respect to the adventitious C peak located at 284.8 eV by using Avantage Software, without applying any restrictions to spectral location and FWHM values.

3.3.3 Scanning Electron Microscopy

Surface morphologies of the deposited films were investigated using scanning electron microscopy (SEM, FEI Nova NanoSEM 430). Samples were coated 5 nm Au/Pd alloy before the putting inside SEM chamber by using Gatan Model 682 precision etching coating system due to in order to presentelectron of the charging.

Surface morphologies of the deposited films were investigated also by FEI Nova 600i Nanolab focused ion beam (FIB)-SEM system for high resolution surface imaging resolving the grain structure of the film surface.

3.3.4 Atomic Force Microscopy

Asylum Research MFP-3D and Park Systems XE-100 atomic force microscope (AFM) operating in tapping mode using a triangular tip was used for surface characterization of STO and BST thin films with the scanning rate of 1.2 Hz. Film surface roughnesses of the as-deposited and annealed films were measured from a 1x1 m scanned areas.

3.3.5 Transmission Electron Microscopy and Selected Area Electron Diffraction

FEI Tecnai G2 F30 transmission electron microscope (TEM) system operating at a voltage under 300 kV was used for HR-TEM analysis of crystal structure. For preperation of the thin film sample for TEM, samples were prepared using FIB at an acceleration voltage of 30 kV, using different beam currents in the range of 50 pÅ to 6.5 nÅ. Damaged layers form between at the film and substrate interfaces, which were removed by FIB milling at reduced beam voltages of 5 kV. For obtaining selected area diffraction patterns (SAED), 40μ M size aperture was used.

3.3.2 Optical Characterization

3.4.1 Spectroscopic Ellipsometry

A variable angle spectroscopic ellipsometer (V-VASE, J.A. Woollam Co. Inc.) with rotating analyzer and xenon light source for wavelengths ranging from 250 to 1200 nm was used for the ellipsometric analysis. The ellipsometric angles $(\psi \text{ and } \Delta)$ were fixed at three angles of incidence (i.e., 65°, 70° and 75°). The optical properties were modeled using the homogeneous TaucLorentz (TL) and Gaussian functions for a three-layer model including the substrate, film, and

surface roughness, while simple grading model was added into the calculations for annealed films in order to improve the fitting quality. Best fit data were used for the determination of optical constants, film thickness t, and the film surface roughness. If not stated otherwise, all n and k values in this thesis correspond to a wavelength of 550 nm. The absorption coefficient, $\alpha(\lambda) = 4\pi k(\lambda)/\lambda$, was calculated from the $k(\lambda)$ values. The optical band gap energy, E_g , was evaluated using the absorption coefficient, which is associated with direct transition photon absorption:

$$\alpha(E) = B \frac{(E - E_g)^m}{E}$$
(3.4)

Where m is a power factor generally being $\frac{1}{2}$ for direct bandgap materials. Assuming that $m = \frac{1}{2}$, the optical energy bandgap is determined by extrapolation of the linear part of the absorption spectrum to $(\alpha E)^2 = 0$ [77].

3.4.2 Ultraviolet-Visible-Near Infrared Spectrophotometry

Two different spectrophometries were used for the transmission measurements of deposited samples on transparent substrates. The first one was Ocean Optics HR4000CG-UV-NIR single beam spectrophometer in the wavelength range of 2501000 nm relative to air and the second one was Carry 5000 UV-VIS-NIR single beam spectrophotometer in the wavelength range of 2002000 nm relative to air.

3.4.3 Photoluminescence Measurement

Thin film photoluminescence (PL) measurements were carried out by two different photoluminescence measurement systems. The first one is a timeresolved fluorescence spectrophotometer (JobinYvon, model FL-1057 TCSPC) in the wavelength range of 300580 nm and the second one is Carry, Eclipse model fluorescence spectrophotometer in the wavelength range from 320 nm to 605 nm with 10 nm slit width, where the excitation wavelength was chosen between the range 270 to 310 nm.

3.3.3 Electrical Characterization

Metal-insulator-semiconductor (MIS) capacitor structures with STO and BST thin films as the insulator layer were fabricated on highly doped p-Si substrates using class 100 and 1000 cleanroom facilities (UNAM Cleanroom Facility-UCF). Fabrication steps are listed below: (1) Cleaning samples with acetone (2 min with sonification), isopropanol (2 min with sonification), De-ionised (DI) water, De-hydration bake : 110°C, 5 min. (2) Formation of top contacts

- 80 nm Ag by using VAKSIS PVD Vapor 3S Thermal evaporation. system or VAKSIS Midas e-beam evaporator.

- Patterning of the Ag top contacts by photolithography:
- (a) Spin Coating of HMDS by using Laurell spinner system: 5000 rpm, 40s.
- (b) Spin Coating AZ 5214 E photoresist: 4000 rpm, 50s.
- (c) Pre-exposure: 110° C, 50 s.
- (d) Exposure UV radiation using EVG620 mask aligner, 60 mJ.
- (e) Development: 1 volume AZ 400K developer and 4 volumes DI-water.
- (d) Rinsing with DI water, drying with N_2 .

(3) Photoresist Stripping: acetone (2 min with sonification), isopropanol (2 min with sonification), DI water, Dry N_2 . Figure 3.3 shows the cross section of the prepared samples for electrical measurements.

Current-voltage (I-V) and capacitance-voltage (C-V) characteristics of the test structures were measured using a semiconductor parameter analyzer (Keithley 4200-SCS), which is connected to a DC/RF probe station (Cascade Microtech PM-5). I-V measurements were carried out in order to estimate the dielectric



Figure 3.3: Cross section of the Si/STO/Ag MIS capacitor structure fabricated for the electrical characterization.

breakdown voltage (V_{bd}), dielectric breakdown field (E_{bd}) and charge storage capacity ($CSC = \epsilon_o \epsilon_r E_{bd}$) [46] of the BST and STO films. With the breakdown correction, for C-V characterization, voltage was applied to the test structure to the determine the accumulation capacitance. Dielectric properties were directly calculated from the accumulation capacitance and corresponding voltage in accumulation region for the frequency dependent dielectric properties of the fabricated test structures, measurement within the 200 Hz⁻¹ to 2 MHz frequency range at room temperature using Agilent E4980A Precision LCR meter were carried out. Dielectric constants (ϵ) of the films were calculated from $C = \epsilon_o \epsilon_r t/A$, where C, t, ϵ_o , ϵ_r , and A are the accumulation capacitance, film thickness, permittivity of free space, permittivity of dielectric, and the area of electrode, respectively. Dielectric loss function is calculated via the formula of tan $\delta = G/C\omega$ [46]. The electric field-induced tunability describes the ability of a material to change its permittivity by the electric field and is defined as:

$$n_{\rm r} = \frac{\epsilon(0) - \epsilon(E)}{\epsilon(0)} \tag{3.5}$$

Where $\epsilon(0)$ and $\epsilon(E)$ are the permittivities in the absence and presence of field, respectively [29]. 0.5 V dc bias was applied to characterize the tunable properties of the BST films. The frequency dependent figure of merit, $FOM = n_r / \tan(\delta)$ [29], of the BST films are also determined.

Table 3.3: The deposition conditions of RF Sputtered $SrTiO_3$ for annealing study.

Base Pressure (mPa)	< 0.87
Deposition Pressure $(P_D)(Pa)$	0.93
$O_2/(O_2+Ar)$	$0(0{+}30)\%$
RF Power (W)	100 W
Target Size (mm)	50
Target Substrate Holder Distance (mm)	61
Deposition Time (min)	20
Annealing Temperature (°C) and Time (h)	300, 600, 700, 800, and 900°C and 1 h in O_2 flow
Annealing Time (min) for $700^{\rm o}{\rm C}$	$15, 30, 45$ in O_2 flow

3.4 Post Deposition Annealing

Samples were annealed using an ATV-Unitherm (RTA SRO-704) rapid thermal annealing system. In order to investigate the effect of annealing on physical properties, STO samples were annealed at 700°C and BST films were annealed at 800° C for 1 h in O₂ (200 sccm) ambient. For the investigation of post-deposition annealing temperature effect on physical, optical, and electrical properties, films were annealed at five different temperatures: 300°C, 600°C, 700°C, 800°C and 900° C for 1 h in O₂ ambient (200 sccm). The annealing temperature is increased until the observation of polycrystalline phases which were seen at 700°C, then time-dependent annealing procedure was investigated to see when crystallization started exactly, 15 min, 30 min and 45 min annealing at 700°C was carried out. The temperature was increased to the target temperature in 1 h, and the samples were taken out from the annealing chamber after the system was cooled down below 80°C. As-deposited and annealed samples at 300°C, 600°C, 700°C, 800°C, 900°C for an hour and 15 min, 30 min, 45 min at 700°C are labeled as STO-RT, STO-300, STO-600, STO-700, STO-800, STO-900 and STO-700/15, STO-700/30, STO-700/45, respectively. The summary of the deposition and annealed conditions are summarized in Table 3.3.

3.5 Characterization of $SrTiO_3$ Deposited Nanofibers

STO coated nanofibers were characterized by using SEM, energy dispersive X-ray analysis (EDX), TEM, XRD, and photocatalytic activity measurements. SEM study was carried out using Quanta 200 FEG SEM (FEI) equipment. Samples were coated with 5 nm Au/Pd alloy. TEM and EDX analyses were perfomed using a Tecnai G2 F30 transmission electron microscope (FEI). TEM samples were prepared by putting a small piece of STO coated TiO₂ nanofibers into the ethanol solvent followed by sonification about 15 min to obtain individual STO coated TiO₂ nanofibers dispersed in the solvent. STO coated TiO₂ nanofibers containing solvent was drop-casted onto a copper grid and allowed to dry. Chemical composition of STO coated nanofibers were investigated by EDX anayses. Crystal structure and phases were determined by the XRD PANalyticalX'Pert PRO materials research diffractometer (MRD) diffractometer using Cu K alfa radiation.

The photocatalytic activity of the STO nanofibers was analyzed through photo induced degradation of methylene blue (MB) in aqueous medium (15.6 M). The nanofibrous mats (weight: 5 mg) were immersed in quartz cuvettes containing the MB solution. The cuvettes were exposed to UV light (300 W, Osram, Ultra-Vitalux, sunlight simulation) placed at a distance of 15 cm. Dye concentrations in the cuvettes were measured using a UV–Vis–NIR spectrophotometer (Varian Cary 100). The nanofibrous mats were pushed to the bottom of the cuvettes during the UVVis spectroscopy. The degradation rate of MB were calculated by using the absorption peak points and defined as C/C₀ where C₀ and C represent the initial concentration of MB before UV irradiation and after a specific time of UV irradiation, respectively.

Chapter 4

Results and Discussion

The work described in this chapter was published and submitted in part as:

¹⁻ E. Goldenberg, T. Bayrak, C. Ozgit-Akgun, A. Haider, S. A. Leghari, M. Kumar, and N. Biyikli. (2015) "Effect of O_2/Ar flow ratio and post-deposition annealing on the structural, optical and electrical characteristics of SrTiO₃ thin films deposited by RF sputtering at room temperature." Thin Solid Films, 590, 193-199.

²⁻ E. Goldenberg, T. Bayrak, C. Ozgit-Akgun, A. Haider, S. A. Leghari and N. Biyikli.(2015) "Structural, Optical and Electrical Characteristics of Low Temperature Grown BaSrTiO_x Thin Films." Submitted to Journal of American Ceramic Society. –revised

³⁻ T. Bayrak, S. A. Leghari, C. Ozgit-Akgun, S. Kizir, N. Biyikli and E. Goldenberg.(2016) "Structural, optical, and electrical evolution of room-temperature RF-sputtered SrTiO_x thin films: Influence of RF power, Ar/O_2 flow ratio, and post-deposition annealing." Submitted to Journal of Applied Physics A. –revised

The first group STO results are divided into three subgroups deposited at 3 mTorr, 5mTorr, and annealing study: The first set of results are related to $SrTiO_3$ which are deposited at 3 mTorr deposition pressure at 75 W with 0%, 10% and 20% OMR. For ease of discussion, films deposited using 0%, 10%, and 20% OMR are referred as STO^0 , STO^{10} , and STO^{20} , respectively.

The second group of samples are deposited at 5 mTorr with 75 and 100 W and 0%, 10% and 20% OMR.

BST results were also presented in this section. These BST samples were also deposited before the RF magnetron was changed.

Results of the second group of STO and influence of post- deposition annealing, as well as STO coated TiO_2 nano fibers and their investigation of photocatalytic activity are presented.

Characterization results are presented for the second group of samples deposited after rf magnetron modification. The characterization results comprise deposition rate, transmission, and spectroscopic ellipsometry as a function of RF power, Ar flow, and deposition pressure. Detailed deposition parameters were given in section 3.

4.1 SrTiO₃

4.1.1 SrTiO₃ Sputtered under 3 mTorr Deposition Pressure

4.1.1.1 Film Morphology And Structural Characterization

Film crystallinity and the formation of crystalline phases are affected by the process parameters and the post-deposition annealing temperature. All RTgrown STO samples were amorphous in their as-deposited state, as determined by

GIXRD measurements. GIXRD patterns of as-deposited STO^{20} , annealed STO^{0} , STO^{10} and STO^{20} films are demonstrated in Fig. 4.1.



Figure 4.1: GIXRD patterns of annealed STO⁰, STO¹⁰, and STO²⁰ thin films deposited on Si (100) substrates. Annealing was carried out at 700°C for 1h in O_2 environment.

Upon annealing at 700°C for 1h in O_2 atmosphere, STO²⁰ became polycrystalline, whereas films deposited at low O_2 flow rates remained amorphous or turned into nano-crystalline form. Nano-crystallite formation was ascribed to the observed relatively broad diffraction peaks observed between 25° and 35°, compare to as-deposited sample. For the polycrystalline film, the major phase was identified to be cubic STO (ICSD code: 98-018-1652) with (001), (011), (111), (002), (012), (112), (022), and (013) reflections appearing at 22.3°, 32.3°, 39.7°, 46.4°, 52.3°, 57.7°, 67.8° and 77.0° 2Theta positions, respectively. On the other hand, the remaining reflection at 27.8° was related to the formation of rutile TiO_2 phase (ICSD code: 98-008-5494). The interplanar spacing for (011); i.e., d_{110} , was calculated from the corresponding 2Theta position using Bragg law as described in the experimental methodology chapter and found to be 2.7681 Å. Furthermore, the lattice constant of the cubic STO unit cell and the average crystallite size were estimated to be 3.9147 Å and 5.2 nm, respectively. Although our results, in general, are in good agreement with the literature, the estimated crystallite size of annealed STO²⁰ thin film was smaller than the reported values

OMR	Condition	Power (W)	Sr at.%	Ti at.%	O at.%	Ar at.%	Sr/Ti
0%	As-deposited	75	9.59	11.86	75.34	3.21	0.81
	Annealed		8.81	11.03	76.58	3.58	0.80
10%	As-deposited	75	10.91	25.03	61.17	2.89	0.44
	Annealed		17.65	16.75	64.06	1.54	1.05
20%	As-deposited	75	11.51	25.03	60.66	2.80	0.46
	Annealed		17.43	17.78	61.27	2.52	0.93

Table 4.1: Bulk elemental compositions of as-deposited and annealed STO thin films with different (O_2/O_2+Ar) as determined by XPS survey scans. Data were collected after 30 s of in-situ Ar etching.

of 20 nm, which were acquired for films deposited at high substrate temperature and/or annealed after their deposition at similar temperatures (>400°C) [51,59]. The calculated lattice parameter a, was slightly higher than that given in the ICSD reference (i.e., 3.9110 Å) which possibly indicates the presence of a compressive residual stress.

Mainly two parameters are responsible from the formation of strain in thin films: (1) lattice mismatch, and (2) difference between the material's and substrate's thermal expansion coefficients [56]. These results indicate that STO should ideally be deposited on heated substrates and/or annealed at high temperatures after its deposition in order to obtain films with improved crystal properties.

XPS survey scans of as-deposited and annealed STO films were performed as a function of oxygen concentration in the chamber, and the evaluation of the chemical state of the film elements were done. The data showed the presence of Sr, Ti, O, and Ar species in the film. In Table 4.1, the elemental composition of the STO films after 30 s in-situ Ar etching is presented. We observed 1.54 to 3.58 at.% Ar incorporation in the films which might be due to Ar ion etching. As can be seen from the table, Sr/Ti concentration ratio was 0.80, 0.44 and 0.46 for films deposited at 0%, 10% and 20% O₂ concentrations, respectively. Annealing



Figure 4.2: SEM images of annealed STO thin films deposited using (a) $10\% O_2$ and (b) $20\% O_2$ flow ratios.

has an apparent impact on films deposited at oxygen rich environment. This might be due to diffusion of Sr and Ti atoms with annealing. High resolution XPS analysis indicated Ti and O-rich STO films. Excess Ti and O might favor sub-oxide phase formation, hence lower film dielectric responses. In our XRD analysis, we observed TiO_2 sub-oxide phase formation which is consistent with the XPS analysis. Surface morphologies of STO films were examined by SEM and AFM. As revealed by SEM images, as-deposited thin films were found to possess a smooth surface, whereas annealed films had a grainy surface morphology as can be seen Fig 4.2.

AFM surface scans of annealed STO^{10} and STO^{20} thin films are presented in Fig. 4.3. Root mean square (rms) roughnesses of the as-deposited films were determined as <0.2 nm (0.12 and 0.16 nm) independent of the deposition parameters. After post-deposition annealing, rms roughness values of the films increased significantly up to 2.7 nm. Polycrystalline film exhibited a slightly higher roughness value as a result of the formation of larger grains. These results were confirmed with spectroscopic ellipsometry analysis as well.



Figure 4.3: AFM surface morphologies of annealed STO thin films deposited using (a) 10% O₂, and (b) 20% O₂ flow ratios.

4.1.1.2 Optical Properties

Figure 4.4 presents the optical transmission vs. wavelength plots of as-deposited and annealed STO thin films. It is seen that the film transmittance is approximately ~ 60% in the VIS and NIR spectral regions for the film deposited using 0% O_2 ; whereas, for films deposited in O_2 rich environment it reaches to ~ 70%. After post-deposition annealing, average transmission values increased up to ~ 80% in the same spectrum. All as-deposited and annealed thin films showed well-defined absorption edges in the UV spectrum. Absorption edges of the films shifted to lower wavelengths with the introduction of O_2 during sputtering. On the other



Figure 4.4: Spectral optical transmission plots of as-deposited and annealed STO thin films deposited on UVFS substrates. Annealing was carried out at 700° C for 1h in O₂ environment.

hand, there was no significant difference between the absorption edges of films deposited with 10% and 20% O₂ concentrations.

The optical band gap (E_g) values were calculated using the $k(\lambda)$ spectra, which were obtained from ellipsometry measurements as described in Section 3.4.1 In order to determine the indirect and direct band gap energies for STO⁰ thin films, $(\alpha h\nu)^{1/2}$ and $(\alpha h\nu)^2$ vs. E graphs were plotted, which are presented in Fig. 4.5(a) and (b), respectively.

Estimated direct and indirect band gap energies and summary of the measured refractive index (n) and extinction coefficient (k) data of as-deposited and annealed STO thin films is presented in Table 4.2. Indirect E_g values were found to be ~ 2.50, 3.15, and 3.25 eV for STO⁰, STO¹⁰, and STO²⁰ thin films, respectively. After annealing at 700°C for 1 h, E_g value increased to 2.80 eV for STO⁰ films, whereas it remained unchanged for STO¹⁰ and STO²⁰ films. Direct band gap energy values were higher as compared to indirect bang gap energies, and they were found to be 3.00 eV for STO⁰, and 4.27 eV for STO¹⁰ and STO²⁰ thin films. As clearly observed from Table 4.2, optical band gap energies increase with oxygen concentration.

In the present study, indirect band gap energies are found to be within the

Table 4.2: Refractive index (n), extinction coefficient (k), and energy band gap (E_g) values of as-deposited and annealed STO thin films.

As-deposited					Annealed			
$\mathrm{O_2/(O_2+Ar)}$	n (@550 nm)	k (@550 nm)	$\rm E_g(eV) indirect$	${\rm E_g(eV)}$ direct	n (@550 nm)	k (@550 nm)	$E_g(eV) indirect \\$	${\rm E}_{\rm g}({\rm eV})$ direct
0/0+30	2.06	0.04	2.50	3.00	2.10	0.01	2.80	3.10
3/3+27	2.09	0.00	3.15	4.27	2.11	0.00	3.15	4.25
6/6+24	2.05	0.00	3.25	4.27	2.12	0.00	3.25	4.25

range of data already reported in literature; however, the larger direct band gap energies, which were observed for all STO thin films, might be attributed to strain-induced defects and/or to the presence of small nano-crystallites in the microstructure. Film refractive indices (n) were found to be between 2.05 and 2.09 for as-deposited films, which slightly increased after post deposition annealing, indicating film densification.



Figure 4.5: Energy bang gap values of as-deposited and annealed STO⁰ thin films corresponding to (a) indirect $(\lambda E)^{1/2}$ and (b) direct $(\lambda E)^2$ as a function of E.

The effect of post deposition annealing treatment on n values is presented



Figure 4.6: Spectral refractive index plots of as-deposited and annealed STO thin films.



Figure 4.7: Photoluminescence spectra of as-deposited and annealed thin films deposited on Si substrates.

in Fig. 4.6. No significant changes were observed in the VIS spectrum of asdeposited STO films sputtered using 0% and 20% O₂ flows. Upon post-deposition annealing, refractive indices increased for both thin film samples. Furthermore, the change in n values, however, was more pronounced for the films deposited using higher O₂ flow rates. Although we obtained some stoichiometric variations in as-deposited and annealed films, we attribute the changes in optical properties to improved film microstructure and film densification.

STO film thicknesses and growth rates were also extracted from the ellipsometric data, and found to be 16.4, 3.4, and 3.5 nm/min for STO⁰, STO¹⁰, and STO²⁰ films, respectively. As can be seen, the deposition rate first decreased with increasing O_2 flow rate, but the change was not significant with further increase.

The PL emission data for un-doped amorphous STO thin films grown at low temperatures are quite limited in the literature. It is known that the optical properties of STO thin films strongly depend on the doped carrier density, temperature, and microstructure including its crystallite size. PL emission spectrum of as-deposited and annealed STO films on Si substrates is given in Fig. 4.7. A broad emission peak in the wavelength range of 350 nm (\sim 3.5 eV) to 450 nm $(\sim 2.75 \text{ eV})$ was observed for all STO films. STO thin films sputtered in oxygen deficient environment exhibited PL emission at a lower wavelength ($\sim 360 \text{ nm}$ for STO^{0}). With the introduction of oxygen into the sputtering chamber, PL characteristics of the deposited STO films changed and a secondary emission peak appeared as a shoulder at 385 nm for STO^{10} and STO^{20} samples. The observed 385 nm (3.22 eV) peak intensity increased with the O₂ flow rate. In the present study, red shift observed for the PL emission peak might be caused by the reorganization of defect levels and band gap shrinkage due to the re-normalization effect [41,42]. In our work we did not observe low energy PL emission bands, however we observed low dielectric constants compared to high temperature grown STO films. This might be due to carrier recombination. Moreover, PL emission peak intensity further increased after the post-deposition annealing. It is known that photoemission in STO thin films is due to the defect levels related to oxygen deficiency and doping. As reported by Kan *et al.* [36], irradiation with Ar^+ ions improves the PL emission of STO films as a direct function of the irradiation time. According to Kan *et al.*, Ar^+ ion treatment produces defect levels and the observed blue emission can be attributed to defects that are related with oxygen deficiency. In their study, they also studied the emission spectrum of oxygen deficient crystalline STO thin films deposited at 700°C, and observed that the films show a broad blue emission. In general, it is accepted that post-deposition annealing leads to an overall reduction in defect-related luminescence and improves crystalline quality.

4.1.1.3 Electrical Properties

Electrical properties of the as-deposited and annealed STO thin films were extracted from the C-V and I-V characteristics of Ag/STO/p-Si MIS capacitor structures. The C-V behavior of the STO²⁰ thin film at different frequencies is illustrated in Fig. 4.8(a), as an example. The three typical regions of a C-V curve, i.e., accumulation, depletion, and inversion, were clearly observed for all of the four plots given in Fig. 4.8. Dielectric constants were calculated from these plots, using the maximum capacitance values in the accumulation region, as a function of different oxygen concentrations and post-deposition annealing. In Fig. 4.8(b), dielectric constants of as-deposited and annealed STO⁰ and STO²⁰ films are presented as a function of frequency.



Figure 4.8: (a) C-V characteristics of $Ag/STO^{20}/p$ -Si MIS structure as a function of frequency, (b) STO thin film dielectric constants as a function of frequency, and (c) C-V hysteresis curve at 50 kHz for annealed STO¹⁰ thin film.

Lower ε_{STO} values were obtained for films deposited at high oxygen flow rates. Furthermore, ε_{STO} values of the film sputtered in pure Ar ambient were found to be more stable, compare to films deposited in oxygen rich environment, as a function of frequency. Dielectric constants (@100 kHz) were in the range of 38-66 for as-deposited films, which decreased to ~ 30 after post-deposition annealing irrespective of the deposition conditions.

This might be due to the interfacial states, which occur after annealing. Although greater dielectric constant values, in the range of 250 to 800, are reported for high temperature-grown STO thin films, the $\varepsilon_{\rm STO}$ values obtained in the present work are in good agreement with those previously reported for thin films deposited at low temperatures [31,108,109]. Low dielectric constant values might be caused by small crystallite sizes and the accommodation of interface layers, which is known to lower the polarization in perovskite lattice [110]. Sakabe *et al.* [111] studied the effects of grain size on dielectric properties of BaTiO₃ ceramics, and reported that the dielectric constant increases with crystallite size.

STO¹⁰ thin films, after post-deposition annealing process, exhibited C-V hysteresis behavior independent of the measurement frequency. Figure 4.8 (c) shows the dc voltage sweep from positive to negative bias at 50 kHz, and the following reverse sweep. Dawber *et al.* [112] defined this kind of a butterfly loop, where the capacitance is different for increasing or decreasing voltages, as one of the unique ferroelectric material characteristics. However, in the literature, the butterfly loop was mostly attributed to charge injection, and carrier trapping and/or space charge redistribution under the electrode area, or net positive charges which cause a positive shift during the voltage sweep [73, 112]. Furthermore, it might also be explained by switching of ferroelectric domains [112]. Interesting enough to note, this phenomenon was not detected in as-deposited films.

I-V measurements were carried out in order to estimate the dielectric breakdown voltage (V_{bd}), dielectric breakdown field (E_{bd}), and CSC of the STO films. Typical I-V characteristics of the Ag/STO/p-Si MIS capacitor structure measured with in the range of +10 to 10 V are depicted in Fig. 4.9. The calculated V_{bd} values were 3.4 and 4.8 V for as-deposited, and 3.3 and 5.8 V for annealed STO⁰ and STO²⁰ thin films, respectively. For films sputtered using 10% O_2 , a lower



Figure 4.9: I-V characteristics at 50 kHz for as-deposited and annealed STO thin films.

 V_{bd} value of 1.9 V was obtained; however, we did not observe any breakdown for the annealed STO¹⁰ thin film up to 30 V. The E_{bd} and corresponding CSC values were calculated to be 0.14, 0.22, and 0.55 MV cm⁻¹, and 0.75, 0.85, and 2.23 μ C cm⁻² for as-deposited STO⁰, STO¹⁰, and STO²⁰ thin films, respectively. CSC of the annealed films was found to be 0.32 μ C cm⁻² for STO⁰, and 2.5 C cm⁻² for STO²⁰ thin films using the corresponding E _{bd} values. As can be seen from CSC values as deposited and annealed STO thin films deposited at high oxygen flow (e.g., 20% O₂) show promising charge storage performance particularly for DRAM applications.

4.1.2 SrTiO₃ Sputtered at 5 mTorr Deposition Pressure

4.1.2.1 Film Microstructure, Composition and Surface Morphology

Figure 4.10 shows GIXRD scans of the as-deposited and annealed STO films deposited by utilizing 10% OMR with 100 W RF plasma power at 5 mTorr constant pressure. All films showed amorphous-like nanocrystalline phase before and after annealing treatment. It has been reported that STO thin films exhibit crystallinity at relatively high substrate temperatures due to the high energy barrier between the perovskite phase and intermediate phase [84]. However, elevated



Figure 4.10: GIXRD patterns of as-deposited and annealed STO thin films deposited 100 W with 10% OMR ratio on Si (100) substrates. Annealing was carried out at 700°C for 1h in O_2 environment.

substrate temperatures might lead to the formation of inter layers which could result in high leakage current and low dielectric constant values. In addition, it is reported that crystallinity of sputtered films is improved with applied plasma power due to the energy of electrons and ions in plasma [113]. Thus, kinetic energy of the positive ions collided with the target, which enhances the energy of the sputtered atoms arriving to the substrate surface, assisting further improvement in crystallization [114]. However, in our study, we were not able

OMR	Condition	Power (W)	Sr at.%	Ti at.%	O at.%	Ar at.%	$\mathrm{Sr/Ti}$
0%	As-deposited	75	9.95 12.21	12.35	75.34	3.37	0.74
10%	As-deposited	75	12.31 15.06 12.31	12.77 24.39	70.62	$\frac{2.55}{1.55}$	0.50 1.18 0.50
10%	As-deposited	100	12.51 17.57 15.09	24.39 11.63 17.41	69.33 65.10	$\frac{2.35}{1.47}$	1.51
20%	As-deposited	75	11.42	25.35	60.44	2.39 2.39 2.80	0.87
20%	As-deposited Annealed	100	13.79 15.80	25.21 21.36	$58.36 \\ 60.13$	$2.64 \\ 2.71$	$0.55 \\ 0.74$

Table 4.3: Bulk elemental compositions of as-deposited and annealed STO thin films as determined by XPS survey scans. Data were collected after 30 s of in—situ Ar etching.

to observe a considerable difference between crystallinity of 75 and 100 W samples. Aforementioned power effect is not pronounced for our RT deposited STO films towards improvement of film crystallinity, RT deposition was followed by a high-temperature (700°C, 1h) annealing process. However, our GIXRD results indicated no considerable improvement of the structural properties with annealing.

Survey and high-resolution XPS scans of as-deposited and annealed STO films were recorded as a function of RF plasma power and OMR. The data revealed the presence of Sr, Ti, O, and Ar elements in the films. Elemental compositions of the STO films are presented in Table 4.3. The Sr/Ti elemental ratio was found to vary between 0.45 and 1.51. 10% OMR with both deposition powers results in relatively high Sr/Ti ratio. Post-deposition annealing affected the Sr/Ti ratio being reduced for 10% OMR, while increased for 20% OMR. XPS analyses indicated O-rich STO films. Vink *et al.* noted that excess oxygen might originate from the presence of physically trapped oxygen [115]. Sputtering of highly oxygenated targets such as $BaTiO_3$, $LiNbO_3$, and $SrTiO_3$ may suffer from negative ion effects [116]. For films deposited at RT, excess oxygen might result from
physically trapped and chemically bonded oxygen in the form of hydroxyl groups originating from water vapor impurity at the vacuum reactor, similar results were obtained by Noda *et al.* [117]

Figure 4.11 shows the SEM image of annealed STO which deposited at 0% OMR at 75 W film surface. Some flakes can be easily seen on the surface. These results indicate that annealing at 700°C increases the local density of the film, resulting in flake formations. In contrast, the as-deposited and annealed films with other deposition conditions show a relatively smooth surface. Point-like formations appeared after Pd/Au coating for SEM characterization.



Figure 4.11: SEM surface morphologies of annealed STO thin films, some flakes on the surface were seen at 75W deposition power in pure argon environment deposition at 5 mtorr deposition pressure.

Material characteristics of thin films can be affected by surface morphology. A good example for this is the correlation between optical transmittance and surface roughness of the film. In Fig. 4.12 (a) and (b) AFM images are presented for the films deposited with 75 W plasma power at 0% (annealed), 10% (annealed) OMR. The cluster-like nano-grains are distributed uniformly with a root-mean-square roughness of 8.28 nm, which is in good agreement with SEM images. As-deposited STO films again show a relatively smooth surface, with a root-mean-square roughness of 0.23 nm, which also agrees with our SEM observations.



Figure 4.12: AFM surafce morphologies of (a) 0% (b) 10% annealed STO thin films.

In general, the surface roughness increased with OMR and annealing. This can be explained by the shorter mean free path and increased number of collisions between sputtered atoms under higher oxygen flow, which reduces the diffusion energy of sputtered atoms and results in a higher surface roughness. The different behavior at higher power levels indicate that RF power has an influence on surface morphology of the sputtered thin films. Higher energy of the sputtered ions might cause might lead to surface damage which increases surface roughness.

4.1.2.2 Optical Properties

Optical transmittance spectra of as-deposited and annealed STO films shows a strong absorption zone near-UV region and a transparent zone in visible to near-IR regions. Films deposited at a power of 75 and 100 W with 10% and 20% OMR values showed $\sim 80\%$ average transmittance in visible region, independent of the deposition conditions. After annealing at 700°C, 1h, higher transparency with respect to as-deposited films was observed; This might be due to improved film microstructure. All STO films exhibited well-defined optical band-edge in the UV spectrum. The main absorption edge slightly shifted towards to higher energies except for films deposited with 75 W plasma power at 20% OMR. The



Figure 4.13: Spectral optical transmission plots of (a) as-deposited and (b) annealed STO thin films deposited on UVFS substrates.

as-deposited and annealed STO film deposited at 0% OMR showed 70% transparency in the visible region, while this value increased to 77% following annealing. After post-deposition annealing, transparency increased to 77% in visible region. This might be attributed to the light scattering loss for its higher surface roughness. Optical constants of STO films were obtained by using Tauc-Lorentz oscillator model, as presented in Experimental Methodology section. In Fig. 4.13 (a) and (b), refractive indices and extinction coefficients are presented for films deposited with 75 W and 100 W plasma power for 10% and 20% OMR values.

Figure 4.14 (a) and (b) shows the refractive indices and extinction coefficient of as-deposited and annealed STO film deposited in pure argon environment, respectively. The summary of the acquired data are presented in Table 4.4. Film refractive indices (n) were found to be between 1.83 and 2.36 at 550 nm for asdeposited and annealed films. The change in n values is more pronounced for the films deposited using higher OMR values.

By using the $k(\lambda)$ spectra, which were obtained from ellipsometry measurements, the indirect and direct band gap energies for the films are determined. The extracted indirect E_g and direct E_g values of STO films are presented in Table 4.4. Indirect E_g values did not change for 75 and 100 W with 10% and 20% OMR (found to be ~ 3.60 and ~ 3.40eV, respectively). After annealing at 700°C for 1h, indirect E_g value increased to 3.78 eV for 75 W samples. However, E_g values did



Figure 4.14: Refractive index and extinction coefficient of STO thin films on Si substrates (a) as-deposited and (b) annealed.

Table 4.4: Refractive index (n), extinction coefficient (k), and energy band gap (E_g) values of as-deposited and annealed STO thin films deposited at 5 mTorr pressure.

	As-deposited			Annealed					
$\mathrm{O_2/(O_2+Ar)}$	Deposition Power (W)	n	k	$E_g(eV)$ indirect	$E_g(eV)$ direct	n	k	$E_g(eV)$ indirect	$E_g(eV)$ direct
0/0+30	75	2.36	0.07	2.25	2.95	2.32	0.05	2.45	2.95
3/3+27	75	1.89	0.00	3.60	4.15	1.83	0.00	3.78	4.20
,	100	1.90	0.01	3.40	4.00	1.99	0.01	3.78	4.30
6/6+24	75	2.06	0.01	3.60	4.25	2.13	0.01	3.60	4.20
	100	2.05	0.01	3.40	4.20	2.04	0.01	3.40	4.20

not change for 100 W samples. Direct E_g 's were higher as compared to indirect E_g 's, and they were extracted as 4.15 and 4.20 eV for 75 W, and 4.00 and 4.20 eV for 100 W, 10% and 20% OMR, respectively. For 0% OMR, direct E_g values were found to be ~2.96 eV and ~2.95 eV also, indirect E_g values were found to be 2.25 eV and 2.45 eV for as-deposited and annealed films, respectively.

Summary of the measured refractive index (n) and extinction coefficient (k), data of as-deposited and annealed STO thin films are presented in Table 4.4 as well. Film thicknesses were also extracted from the ellipsometric data, and the corresponding deposition rates were calculated as 3.6 and 3.4 nm/min for as-deposited, and 3.5 and 3.1 nm/min for annealed films deposited at 75 W with 10% and 20% OMR, respectively. Additionally, deposition rate of STO thin films was observed to increase with RF power (Table 4.5).

Figure 4.15 (a) and (b) show the RT-PL spectra of as-deposited and annealed STO films on Si substrates. The excitation wavelength was chosen as 310 nm, slit width 2.5 μ m. PL spectra of all samples consisted of three broad luminescence peaks about 3.44, 3.26, and 2.93 eV for as-deposited, and 3.42, 3.26, and 2.95 eV for annealed films deposited at 75 W. However, the peaks of the films deposited at 100 W shifted towards lower energies. The first peak of as-deposited film at 100 W was detected around 3.17 eV for 10% and 3.21 eV for 20% OMR; the second and third peaks were identified at 2.95 and 2.70 eV for 10% and 20% OMR, respectively. After annealing, the first peak was around 3.16 eV for 10% and 20% OMR, respectively. The third peak was found at 2.70 eV for both samples.

OMR	Condition	Power (W)	Thickness (nm)	GPM (nm/min)	RMS (nm)
0%	As-deposited	75	125	12.5	0.23
	Annealed		129	12.9	8.28
10%	As-deposited	75	108	3.6	1.12
	Annealed		105	3.5	0.89
10%	As-deposited	100	127	5.0	1.30
	Annealed		115	4.6	1.35
20%	As-deposited	75	103	3.4	1.56
	Annealed		91	3.1	1.54
20%	As-deposited	100	128	5.1	1.49
	Annealed		125	5.0	1.54

Table 4.5: Thickness and growth rate of the as-deposited and annealed STO thin films extracted from spectroscopic ellipsometry analysis.

In addition, the peak intensities for 100 W samples were higher than the 75 W counterparts. The blue PL band is observed at 2.95, 2.93, 2.92 and relatively weak 2.70 eV in all samples which reflects an intrinsic carrier recombination process [70]. The intense peaks of the photoluminescence spectra reflected the main band-edge emission. The rather broad emissions are generally correlated with the disordered structure. Our experimental result is in good agreement with the above-mentioned observations indicating that the amorphous phase might be responsible for the observed broad emission peaks around 3.40 and 3.20 eV [118]

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Figure 4.15: Photoluminescence spectra of (a) as-deposited and (b) annealed thin films deposited on Si substrates.

4.1.2.3 Electrical Properties

Figure 4.16 (a) and (b) shows the dielectric constant and the dielectric loss of the MIS device structure for the annealed film as a function of frequency at zero bias voltage. It is well known that when MIS device is biased in accumulation region, whole capacitive response is due to the insulator characteristics [46]. Thus, for determination of the accumulation region of the MIS structure, C-V measurements were performed in the range of (+2, -2 V).

C-V measurement range was defined by taking into account the breakdown voltage values obtained from I-V measurements. After extracting the accumulation voltage, capacitance-frequency (C-f) of the films was measured and the dielectric constant was calculated using the equation which was given in the experimental methodology section.

The dielectric constant values (at 100 kHz) of the films deposited at 100 W and subsequently annealed, increased with OMR from 10 (10% OMR) to 28 (20% OMR) and 51 (10% OMR) to 100 (20% OMR), respectively. However, its value decreased with OMR for as-deposited (75 W) and annealed films from 60 to 58, and from 62 to 49, respectively. The increase of the dielectric constants of the films deposited at 100 W plasma power with increased OMR values might be due



Figure 4.16: (a) Dielectric constants and (b) dielectric loss values of annealed STO thin films (inset figures show as-deposited films) as a function of frequency.

to the higher oxygen incorporation in the films which possibly enhances the polarization in the STO films [73]. Furthermore, the reason of the 75 W films having lower dielectric constant than 100 W sample, might be attributed to the thicker interfacial layer, or smaller grain size of the nanocrystalline films. RT grown films might reveal higher density of defects as expected for an amorphous layer. Moreover, high temperature annealing and measurement temperature affects the dielectric constant [119]. The STO films exhibited relatively low dielectric losses, as shown in Fig. 4.16 (b), particularly at low frequencies. Dielectric loss might originate from ohmic losses and can be avoided via thicker contact metal alloys [120].

OMR	Condition	Power (W)	$\varepsilon_{ m r}$	$tan(\delta)$
0%	As-deposited	75	31.68	0.03
	Annealed		57.40	0.31
10%	As-deposited	75	56.66	0.00
	Annealed		61.73	0.03
10%	As-deposited	100	10.42	0.02
	Annealed		50.75	0.03
20%	As-deposited	75	57.79	0.02
	Annealed		48.90	0.07
20%	As-deposited	100	28.42	0.02
	Annealed		99.29	0.02

Table 4.6: Dielectric constant ($\varepsilon_{\rm r}$), dielectric loss ($tan(\delta)$) of as-deposited and annealed STO thin films at 100 kHz.

Charge storage capacity (CSC) of the devices was calculated from the breakdown values of the I-V measurements. In Table 4.6, V_{bd} , E_{bd} , ε_r , and dielectric loss (tan(δ)) are given for as-deposited and annealed films. Breakdown field (E_{bd}) was evaluated as 0.73 MV/cm (as-deposited) and 0.58 MV/cm (annealed) for films deposited at 20% OMR at 75 W.

The measured E_{bd} values correspond to 3.73 and 2.51 μ C/cm² CSC for asdeposited and annealed films, respectively. No breakdown voltages were observed for films deposited with 10% OMR at 75 W and with 10% and 20% OMR at 100 W up to 20 V bias.

The results for 0% OMR should be apart from the results mentioned above. C-V characterization of the films suggests that no breakdown occurs in the range of -10 to +10 V. C-V characteristics of the Ag/STO/p-Si structure were acquired at five different frequencies (50-100-300-600 and 900 kHz) for both films, and shows two distinct regimes of accumulation/inversion in the as-deposited sample. However, the annealed film exhibited C-V hysteresis behavior independent of the measurement frequency. Figure 4.17 shows the dc voltage sweeping for STO film grown in pure argon environment from positive to negative bias at 50, 100, 300, 600 and 900 kHz, and reverse sweep followed. Frequency dependent dielectric



Figure 4.17: C-V characterization of the annealed STO thin film deposited in pure argon environment with different frequencies.

constant and dielectric loss function of both films are given in Fig. 4.18. The dielectric constant decreases with increasing frequency for the annealed film, while the as-deposited film shows a stable dielectric constant value with increasing frequency. Dielectric losses, in contrast, are found to increase with frequency in both annealed and as-deposited films.

Representative dielectric constants and losses at 100 kHz are given for both films in Table 4.6. Dielectric constants appear to be lower in this study in comparison with other film preparation techniques in the literature. However, our method is nevertheless promising as a RT deposition technique which is capable of yielding nanocrystalline STO at relatively low thicknesses.



Figure 4.18: Dielectric constant and loss of the annealed STO thin film deposited in pure argon environment as a function of frequency.

4.2 $BaSrTiO_3$

4.2.1 Film Microstructure, Composition, and Surface Morphology

All as-deposited films were amorphous with some nanocrystallinity, while postdeposition annealing treatment at 800°C for 1 h resulted in polycrystalline thin films. Figure 4.19 shows the GIXRD patterns of BST thin films after annealing and it indicates a cubic crystal structure with stoichiometric variations for films deposited at different deposition pressures (5 (0.67 Pa), 7 (0.93 Pa), 10 (1.33 Pa) mTorr) (ICSD reference codes: 98-009-0006, 98-015-4403, 98-016-4371). (011), (111), (002), (112), and (022) reflections were observed for all annealed films. Additional reflections appeared that corresponding to (001) and (013) at high deposition pressures. The interplanar spacing (d_{hkl}) values were calculated as 0.1991, 0.1990, and 0.1971 nm from (002) planes. Lattice parameter (a) values were calculated to be 0.3983 for 5 mTorr, 0.3980 for 7 mTorr, and 0.3941 nm for 10 mTorr films. Lattice parameter values were in good agreement with those noted for bulk crystals (0.395 nm) [121]. Crystallite size values were also calculated from the (002) reflection using Scherrer formula and found to be 5.8, 6.3, and



Figure 4.19: GIXRD patterns of annealed BST thin films, which indicate a cubic crystal structure with stoichiometric variations for films deposited at different chamber pressures.

7.2 nm for 5, 7, 10 mTorr deposition pressure, respectively. It is clearly that crystallinity was improved for annealed films deposited at higher P_D ; this might be explained by the healing of oxygen vacancies. A similar material behavior for films deposited at a higher deposition temperature (i.e., 700°C) and oxygen pressures has also been reported by Alema *et al.* [122].

Survey and bulk scans of XPS for as-deposited and annealed BST films were also experimented. The data obtained confirmed the presence of Ba, Sr, Ti, and O elements in the films. Summary of the elemental compositions of the BST films are presented in Table 4.7. XPS analysis indicated Ti and O rich BST films. Excess Ti and O might form amorphous or crystalline TiO_x, which can lower the dielectric permittivity (section 4.2.3) at grain boundaries. However, there were no indications of crystalline TiO_x phase in the GIXRD patterns. Another explanation of the excess O inside the film might be sputtering from targets such as BaTiO₃, LiNbO₃, and SrTiO₃ may suffer from negative ion effects [116] also known as physically trapped oxygen [115]. For films deposited at RT, excess oxygen might result from physically trapped and chemically bonded oxygen in the form of hydroxyl groups originating from humidity within the vacuum reactor, which was reported by Noda *et al.* as well [117].

P_D (Pa)	Condition	Ba at.%	Sr at.%	Ti at.%	O at.%	Ar at.%
- m	A 1 1/1	T 00	0.00	1 7 40	69.49	1 50
5 m Iorr	As-deposited	7.69	9.80	17.49	63.43	1.59
	Annealed	7.73	9.87	17.53	63.56	1.31
$7 \mathrm{mTorr}$	As-deposited	5.36	8.33	25.20	58.53	2.48
	Annealed	5.39	8.37	25.30	57.94	3.00
$10 \mathrm{mTorr}$	As-deposited	5.71	8.58	24.47	58.61	2.63
	Annealed	6.55	9.00	24.30	58.82	1.33

Table 4.7: Elemental composition of BST films before and after annealing. XPS data were collected after 90 s of Ar ion etching.

Surface morphologies of the films were analysed by AFM and SEM. Figures 4.20 (a)-(c) show the AFM surface morphologies of as-deposited ($P_D=5$ and 7 mTorr) and annealed ($P_D=7$ mTorr) thin films. Rms roughnesses tend to be decreasing with P_D for as-deposited films, and were observed to be 2.13, 0.31, and 0.78 nm for films deposited at 5, 7, and 10 mTorr, respectively. Surface roughness increased considerably with the annealing, the roughness values were extracted 3.60, 2.14, and 7.05 nm for 5, 7, and 10 mTorr deposition pressures, respectively.

Plan-view SEM images in Fig. 4.21 show annealed BST films, which were deposited at 5 and 10 mTorr chamber pressures. The film deposited at 5 mTorr had a very rough surface morphology (8.34 nm). However, void formation was observed for the film deposited at 10 mTorr, which might be related to the film densification and/or stress formation. Surface roughness values for both as-deposited and annealed BST thin films were also confirmed by spectroscopic ellipsometry analysis. Results of ellipsometric calculation is in good agreement with those obtained from AFM and SEM studies.



Figure 4.20: AFM surface morphologies (a) as-deposited ($P_D=5$ (b) 7 mTorr (c) annealed ($P_D=7$ mTorr) BST thin films.

4.2.2 Optical Properties

In Figure 4.22 (a), spectral transmission of as-deposited BST thin films deposited on transparent substrates are presented for different deposition pressure values. Absorption-free films were obtained for as-deposited films (k < 10⁻⁴). Well defined main absorption edge was observed for all deposition pressures. However, annealing at 800°C, 1 h, lowered the optical transmission spectra indicating weak absorption ($k \ge 2x10^{-2}$) and/or light scattering (see Figure 4.22 (b)). Reduction in the optical transmission generally appeared with increasing grain size and surface roughness after annealing process. This result is also confirmed by XRD and ellipsometry measurements. Additionally, lower transmission with annealing was



Figure 4.21: (a) 5 mTorr and (b) 10 mTorr deposition pressure of annealed BST thin film surface morphology.

more pronounced for films deposited at high P_D (see inset of Figure 4.22 (b)). Decrease in film thickness with post-deposition annealing was also observed (as also indicated by a shift in the interference maxima). This reduction is associated with evaporation and/or densification of the films. Present transparencies of the as-deposited and annealed BST films are comparable to those reported in literature [123–125].



Figure 4.22: Transmission spectra of (a) as-deposited and (b) annealed BST films grown under different deposition pressures. Inset figure (c) shows the comparison of as-deposited and annealed films.

Optical constants of the films were determined by spectroscopic ellipsometry data. Figures 4.23 (a) and (b) show the measured, calculated, and fitted data of ellipsometric angles psi (ψ) and delta (Δ) at the incident angles of 70° and 75° for

	As-deposited			Annealed		
P_D (mTorr)	n	k	$E_{g}(eV)$	n	k	$E_{\rm g}({\rm eV})$
5 7 10	1.96 1.90 1.90	$0.00 \\ 0.00 \\ 0.00$	$ \begin{array}{r} 4.30 \\ 4.30 \\ 4.30 \end{array} $	2.00 1.98 2.07	$0.00 \\ 0.06 \\ 0.00$	$3.69 \\ 3.68 \\ 3.60$

Table 4.8: Refractive index (n), extinction coefficient (k), and energy band gap (E_g) values of as-deposited and annealed BST thin films.

the film deposited at 7 mTorr. The summary of all (n, k) values are given in Table 4.8. The MSE values were in the range of 2 to 9 for all BST films. Optically



Figure 4.23: Ellipsometeric fit parameters (a) ψ (b) Δ in degrees.

determined surface roughnesses of the films were 1.5 and up to 16 nm for asdeposited and annealed films, respectively. In Figure 4.24 show the refractive index (n) values for different P_D . As seen from this figure, the dispersion curves rise rapidly towards the shorter wavelengths.

The strong increase in n at shorter wavelengths in Fig. 4.24 (c) is associated with the fundamental band gap absorption (see Fig. 4.22 (a) and (b)). The refractive index decreased with P_D from 1.96 to 1.90 for as-deposited films. The effect of post-deposition annealing on n are presented in Figure 4.24 (a) for films deposited at different P_D . Refractive index values increased with annealing for the film deposited at 5 mTorr (1.96 to 2.00), and 7 mTorr (1.90 to 1.98), while a significant increase was observed (1.90 to 2.07) for 10 mTorr deposition pressure. Refractive index values of the oxide films were imposed by packing density and microstructure [125]. Amorphous films (as-deposited) exhibited lower refractive indices indicating less dense films; while denser films were obtained after post-deposition annealing, mainly due to crystallization. In Figure 4.24 (c), the distribution of n at $\lambda = 550$ nm for a graded film deposited at P_D=10 mTorr was shown. The total fitting was done by fitting the optical constants divided into 11 layers in depth, and calculations was performed in each individual layer. The value of n increases from 1.78 to 2.32, which might be related to the formation of an interface layer between SiO₂ and BST.

In Figure 4.24 (d), $(\alpha E)^2$ plot is presented as a function of energy for asdeposited BST films (P_D=10 mTorr). The optical band gap of the as-deposited film was found to be 4.30 eV. Post-deposition annealing decreased the optical band gap. The E_g value of the film deposited at P_D=10 mTorr (i.e., 3.60 eV) was found to be close to the bulk value [126], whereas films deposited at lower pressures showed slightly higher values. The flaws in polycrystalline thin films, i.e., the presence of mechanical stress due to lattice distortion in the grain boundaries, might have influenced the optical band gap.

PL spectra at RT of BST films deposited on Si and UVFS substrates and annealed at 800°C for 1h are presented in Fig. 4.25 (a) and (b), respectively. Excitation wavelength of 250 nm was used. In Figure 4.25 (a), the films exhibited broad emission spectra centered at 337 nm, related to the main band gap emission. Spectral PL emission plots are presented for annealed BST films in Fig. 4.25 (b).

The emission intensities decrease with annealing. Post-deposition annealing treatment leads to an overall reduction in the defect-related luminescence, and improves film crystal quality (which is also revealed by GIXRD, see Fig. 4.19). However, in the present case, the PL emission intensities decreased with annealing. Similar results were reported for ABO₃-type perovskites including SrTiO₃,



Figure 4.24: Optical properties of BST thin films (a),(b) refractive indices of films as a function of wavelength, (c) depth profile analysis of refractive index and (d) direct $(\lambda E)^2$ vs.E.

 $BaTiO_3$ [2] mainly due to the structural disorder. The localized electronic levels between the valance and conduction bands produce a disordered phase in structural symmetry [38].

4.2.3 Electrical Properties

Electrical characteristics of the BST films, including frequency-dependent dielectric constant (ε) and dielectric loss, dielectric breakdown voltage (V_{bd}), dielectric breakdown field (E_{bd}), and charge storage capacity (CSC) were estimated from the results of RT C-V and I-V measurements of Ag/BST/p-Si MIS capacitor structures. Frequency dependent ε , dielectric loss values and I-V characterization of as-deposited and annealed BST thin films are presented in Fig. 4.26 (a),



Figure 4.25: PL spectra of (a) as-deposited and (b) annealed BST films. Excitation wavelength: 270 nm.

(b) and (c), respectively. Average ε of the as-deposited films were found to range between 46 and 53 (up to 800 kHz), and slightly increased with increasing frequency (Fig. 4.26a). After the post-deposition annealing treatment, ε increased and reached up to 66, 79, and 62 for films deposited at 5, 7, and 10 mTorr chamber pressures, respectively.



Figure 4.26: (a) Dielectric constant of BST thin films deposited under different pressure as a function of a frequency (b) Dielectric loss values (c) J-V characteristics of as-deposited and annealed BST thin film.

Average dielectric loss value in the measurement range was 0.02 for all asdeposited films independent of the sputtering conditions; however, for annealed films, the dielectric loss values increased to 0.04 within the same frequency range (see Fig. 4.26b). It should be noted that the dielectric losses, which were relatively low (i.e., <0.05) up to 100 kHz, increased at high frequencies and reached to 0.25-0.30 for as-deposited films. I-V behavior of the as-deposited and annealed films ($P_D=7$ mTorr) are given in Fig. 4.26c. V_{bd} values were found to be in the range of 3.0 to 4.7 V for as-deposited, and 4.1 to 8.3 V for annealed films as a function of P_D . Furthermore, E_{bd} and corresponding CSC values were calculated to be 0.25, 0.30, and 0.27 MV cm⁻¹, and 1.1, 1.2, and 1.3 μ C cm⁻² for as-deposited, and 0.30, 0.36, and 0.72 MV cm⁻², and 1.1, 2.5, and 3.9 μ C cm⁻² for annealed BST films as a function of P_D (5, 7, and 10 mTorr), respectively.



Figure 4.27: Tunability values of as-deposited and annealed BST thin films as a function of deposition pressure.

BST films are widely studied for applications in DRAMs and microwave tunable devices. For tunable device applications, low dielectric loss factor $(\tan \delta)$ and high dielectric tunability of the films are of critical importance. The performance of a tunable dielectric material is generally evaluated using the figure of merit (FOM) which desired to be as high as possible. The FOM value indicates that the candidate material for a tunable microwave application cannot take full advantage of its high tunability if the loss tangent factor is not low enough. Figure 4.27 shows that the tunability vs. deposition pressure at 1 MHz and Fig. 4.28 shows the FOM as a function of frequency for all deposited BST films. The tunability at 1 MHz reached the highest value for the film deposited at 7 mTorr. It decreased for both 5 mTorr or 10 mTorr deposition pressures. Due to the experimental set up limitation we werenot able to measure the behavior of the BST films in microwave GHz regime. In addition, relatively small RMS (0.31 nm for deposited at 7 mTorr film) roughness value could be positive factor for tunability.



Figure 4.28: Figure of merit for BST thin films as a function of frequency.

4.3 Post Deposition Annealing SrTiO₃ Thin Film

For ease of discussion, films annealed at 300, 600, 700, 800, 900 °C are referred as STO-300, STO-600, STO-700, STO-800, and STO-900 respectively. For time dependent study of 700°C annealed samples for 15, 30, and 45 min are referred as STO-700/15, STO-700/30 and STO-700/45, respectively. As-deposited sample is referred as STO-RT.

4.3.1 Film Microstructure, Composition, and Surface Morphology

Figure 4.29 (a) and (b) show the GIXRD patterns of STO films are deposited by RF-sputtered on Si as a function of annealed temperature with the annealing duration of 60 min and as a function of annealing time annealed at 700°C, respectively. STO-RT was found to be an amorphous-like nanocrystalline film with an amorphous broad diffraction peak observed between 2Theta positions of 25° to 35°.



Figure 4.29: GIXRD patterns of annealed STO thin films (a) with different annealing temperatures (b) as a function of annealing at fixed 700°C.

(012) reflection might be related to the nanocrystalline phase of the STO which appeared after 300°C annealed. Crystallization started when annealing temperature is reached 600°C with (011), (111), (002), (012), (112) and (022) reflections. However, broad nano-crystal peak still remained at this temperature. The complete crystallization of the films were observed only after 700°C and annealing at 800°C caused further accentuating of crystalline planes and the film became highly crystalline. The XRD spectra pointed out to be cubic STO (ICSD code: 01-086-0178) with (001), (011), (111), (002), (012), (112), (022), (013), (113), and (222) reflections appearing at 22.92°, 32.59°, 40.14°, 46.67°, 50.91°, 57.94°, 67.92°, 72.51°, 77.28°, 81.82° and 86.11° 2Theta positions, respectively. The crystallinity started to slightly degrade at 900°C, and (012) reflection additionally appeared. Interestingly, the (012) reflection is present in the samples STO-300, STO-600 and STO-900, however it vanished for STO-700 and STO-800. Slightly degradation at 900°C annealing process was observed from the reduced intensity of the polycrystalline reflections when compared to STO-800. We noted above that the crystallization of the films was pronounced significantly at 700°C. However, time dependent annealing at 700°C shows us that crystallization started in the first 15 min of annealing process. On the other hand, amorphous/nanocrystalline phases remained: the broad diffraction peaks are observed at STO-700/30 and STO-700/45 and disappered at STO-700.

Interplanar spacing for (011) was calculated from the Bragg's law as described at experimental methodology section from the most intense peak, i.e., d_{011} and it is found to be 2.7454 Å. Lattice parameter (a) values of the cubic STO unit cells were calculated to be 3.8826 Å. The the crystallite sizes of the films were calculated from the (011) reflection using Scherrer formula for the films, STO-700, STO-800, STO-900 and STO-700/15, STO-700/30, STO-700/45 which are given by the Fig. 4.30 (a) and (b). The maximum crystallite size was found to be 16.00 nm for STO-800. However, the crystallite sizes are a bit smaller than reported values of 20 to 30 nm. The reason of that the reported values were acquired for films deposited at different substrate temperature and/or annealed with the similar temperatures after the deposition [51,59].

Survey and high-resolution XPS scans of STO films were recorded as a function of annealing temperature and time (just for the film annealed at 700°C). The data revealed the presence of Sr, Ti, O, and Ar, which are presented in Table 4.9. The XPS scans show us nearly stoichiometric STO films which were deposited at RF sputtering with 7 mTorr deposition pressure in pure argon environment at RT and with annealing treatment.

Sample Name	Sr at.%	Ti at.%	O at.%	Ar at.%	$\mathrm{Sr/Ti}$
STO-RT	22.66	16.52	56.58	4.24	1.4
STO-300	18.19	18.12	59.16	4.54	1.1
STO-600	22.87	19.02	54.88	3.22	1.2
STO-700	23.08	19.68	54.09	3.15	1.2
STO-70015	22.16	18.53	57.14	2.17	1.2
STO-70030	23.01	17.98	56.69	2.32	1.3
STO-70045	23.27	17.93	56.20	2.66	1.3
STO-800	22.36	18.54	56.80	2.29	1.2
STO-900	20.25	22.30	54.39	3.07	0.9

Table 4.9: Sr, Ti, O, and Ar compositions of the as-deposited and annealed film STO thin films as determined by XPS survey scans. Data were collected after 30 s of in—situ Ar etching.

The surface morphology of STO thin film was investigated by using AFM. In Figure 4.31, surface morphology of as-deposited and annealed STO films were shown. It is obvious that surface roughness was strongly depending on the an-



Figure 4.30: Crystallite size as a function of (a) annealing temperature and (b) annealing time for STO-700.

nealing temperature and crystallinity. Therefore, polycrystalline films showed higher roughness than the amorphous and nanocrystalline films.



Figure 4.31: AFM images at (a) RT, rms: 0.17 nm (b) 300°C, rms: 0.16 nm (c) 600°C, rms: 0.15 nm (d) 700°C, rms: 0.87 nm (e) 800°C, rms: 0.66 nm (f) 900°C, rms: 0.98 nm (g) 700°C for 15 min, rms: 0.87 nm (h) 700°C for 30 min, rms: 0.36 and (i) 700°C for 45 min, rms: 0.31 nm.

Plan-view SEM images are given in Fig. 4.32 (a) and (b) for STO-RT film and STO-800, respectively. In Figure 4.32 (c) cross sectional image of STO-800 is given which indicated around 80 nm thick STO film. STO-RT sample is relatively smooth as expected for thin film amorphous STO. With increasing annealing temperature to 800°C, the grains appeared and some void formations were observed which might be related to the densification of the film. This might be one of the reasons for the increased surface roughnesses.



Figure 4.32: SEM images of the (a) as-deposited, (b) annealed at 800° C and (c) cross-section of the annealed sample at 800° C

TEM and HR-TEM images with SAED pattern of the STO-800°C are presented in Fig. 4.33. Polycrystalline STO, silicon substrate, silicon oxide, and platinum layers are labelled as STO, Si, SiO₂, and Pt in TEM and HR-TEM images for convenience. Deposited and annealed at 800°C STO film was observed to be in the form of 15 nm particles (Fig. 4.33 (a) and (c)). Fig. 4.33 (b) shows that material was deposited in a continuous manner. HR-TEM image shows in Fig. 4.33 (d) and (e), as well as SAED pattern in Fig. 4.33 (f) confirmed polycrystalline nature of STO film after 800°C annealing. The large bright spots on the diffraction pattern is related to the Si substrate. The bright spots on the diffraction rings indicate STO crystalline planes.



Figure 4.33: (a)-(c) Cross-sectional TEM and (d)-(e) HR-TEM images, and (f) SAED pattern of the STO thin film annealed at 800°C.

4.3.2 Optical Properties

Figure 4.34 presents transmission spectra of as-deposited and annealed at 300 and 900°C of STO films on quartz. All films show sharp fundamental absorption edges which at the near-UV region and transparent zone are in visible to near IR zone with >75% transmittance.

The main absorption edge shifted towards the higher wavelength with annealing temperature. Shift in the absorption edge is clearly observed with 700°C annealing temperature after 30 min (STO-700/30) and further temperatures. STO-900 shows the lowest transmittance in near IR region and relatively good transmittance in near visible region. STO-800 shows the lowest transmittance in visible region and it shows nearly same transmittance with STO-900. The optical



Figure 4.34: Transmission spectra of as-deposited and annealed STO thin films at 300°C and 900°C.

transmission spectra depends on three factors in general: oxygen deficiency, surface roughness, and impurity centers. Low transmittance of STO-900 might be attributed to increase of roughness. Large grain size in stoichiometric film should result in higher transmittance than as-deposited film [127]. While increasing the grain size, surface roughness increased and void formations were appeared. These are the reasons why we see decrease in the optical transmission spectra with annealing process.

Tauc-Lorentz oscillator model was used for the determination of the optical constants, i.e., extinction coefficients and refractive indices. Figure 4.35 shows refractive indices of STO-RT, STO-300, STO-600, STO-700, STO-800, and STO-900 as a function of wavelength. The summary of the refractive indices and extinction coefficient at 550 nm are presented in Table 4.10. Refractive indices of STO films increased with the annealing temperature up to 900°C. At 800°C, the value of refractive index is close to the value of STO single crystal (2.39). It is a well known fact that the refractive index increases with crystalline quality and this observation confirms this correlation.



Figure 4.35: Spectral refractive indices of as-deposited and annealed STO films.

Direct band gap energies (E_g) of the as-deposited, annealed with different temperatures, and annealed at 700°C as a function of a time STO thin films were estimated by extrapolation of the linear portion of square of absorption coefficient multiplying with photon energy (hv) in Fig. 4.36 (a) and (b). Figure 4.36 (a) shows the direct band gap values of STO-700, STO-800, and STO-900 and also the inset figure shows the STO-RT, STO-300 and STO-600. The direct band gap of the STO thin films decreased with annealing temperature. Figure 4.36 (b) shows direct band gap (E_g) energies for STO thin films annealed at 700°C with a function of time for 15 min, 30 min, 45 min, and 60 min.

The sharpness of the absorption edge energy increased with time and the direct band gap values increased from 4.20 to 4.40 eV for reduced annealing time from 60 to 15 min. The direct band gap of STO-RT is 4.50 eV and it decreased to 4.10 eV for STO-900. In the literature, the direct and indirect band gap values were found to be in the range of 3.32 to 3.80 eV [51] and 4.25 eV [17] for the polycrystalline STO films. The higher direct band gap values of STO can be attributed to the strain induced defects or nanocrystalinities which is remained in the polycrystalline film. In this study, the higher direct band gap energies than noted values in the literature of STO-700, STOO-800, and STO-900 might be attributed to the strain induced defects. However, STO-700, STOO-800 and

Sample Name	n	k	E_g direct (eV)
STO-RT	1.81	0.000	4.50
STO-300	1.82	0.000	4.50
STO-600	1.79	0.000	4.55
STO-700	2.11	0.002	4.20
STO-70015	1.90	0.000	4.40
STO-70030	2.15	0.000	4.22
STO-70045	2.05	0.000	4.22
STO-800	2.16	0.001	4.18
STO-900	2.09	0.000	4.10

Table 4.10: The summary of the refractive index, extinction coefficient at 550 nm and optical band gap values of the as-deposited and annealed STO thin films.

STO-900 showed lower direct bad gap energies than STO-RT, STO-300 and STO-600 due to the vanished (012) reflection for these films which confirmed by XRD analysis. The summary of the direct band gaps of as-deposited and annealed STO films were given in Table 4.10.

4.3.3 Electrical Properties

Ferroelectrics are well known materials due to their high dielectric constant. STO-RT, STO-300 and STO-800 were chosen to observe a dielectric constant and dielectric loss differences of amorphous, nanocrystalline, and polycrystalline STO thin film in MIS (Ag/STO/Si(higly doped)) structure. Dielectric constants were observed to increase for STO-RT and STO-300 at lower frequencies which were shown in Fig. 4.37 (a) and (b). Dielectric constant of STO-RT decreased gradually with frequency until 20 kHz, after this frequency dielectric constant stayed at 7. The low dielectric constant might be attributed to the lattice mismatch between sputtered STO and Si substrate. Additionally, poor adhesion of the contact metal (Ag) on STO thin film might be imposed to the dielectric constant as well as defects and structural imperfections in STO film. The highest dielectric



Figure 4.36: Direct band gap of the annealed STO film (a) at high temperatures (inset shows low temperature annealed films) and (b) as a function of time at 700°C.

constant was revealed with the polycrystalline STO-800 from the 1 kHz to 3 MHz (46.77 to 44.89). However, the dielectric constant of STO-800 decreased after the 3 MHz (26.18). Dielectric loss of the STO-800 increased sharply after 1 MHz and it reached 2 at 4 MHz due to the reason of the conductivity (G) increased sharply.

The origin of the high dielectric permittivity observed from the polycrystalline STO-800 is that compensation of the microscopic forces in polycrystalline regions that maintains the material in non-polar phase in the zero electric field.



Figure 4.37: (a) Dielectric constants and (b) dielectric loss values of STO thin film annealed at different temperatures as a function of frequency.

Restoring force opposing the poling action of the applying field is weak due to the compensation of the microscopic forces. This is the reason of the high dielectric permittivity in ferroelectric polycrystalline material. Small crystallite size, interface layer, and well known lattice mismatch between Si substrate and STO might be the reason of the low dielectric constant of the STO thin film as comparison of the noted dielectric constant of the literature. Dielectric constant and loss values of STO thin films depend on many factors i.e., annealing and measurement temperature, bottom electrodes, local polar regions, random field defects, composition, thickness etc. [5]. The loss mechanism here mainly originate from extrinsic loss mechanism. Charge defects move with AC electric field resulting in a formation of the acoustic waves at the frequency of the applied field [5]. Additionally, the reason of the high loss at polycrystalline STO-800 at high frequencies might be due to the local polar regions induced by various defects and structural imperfections which can be seen from SEM images on the surface. However, the dielectric constant and loss of the STO films future promising values while considering only 100 nm thick STO films for microelectronic applications.

4.4 SrTiO₃ Deposition with Different Pressure for 100 and 120 W Deposition Power

Figure 4.38 shows the thickness of deposited STO thin films as a function of the deposition pressure. It is a general rule that in sputtering, deposition rate increases with reduced deposition pressure.



Figure 4.38: Thicknesses of the STO films deposited under different pressures for 100 and 120 W deposition.



Figure 4.39: Transmission spectra of the STO film deposited at 100 W with different deposition pressures.



Figure 4.40: Refractive indices of the STO film deposited at 100 W with different deposition pressures.



Figure 4.41: Indirect band gap of the STO thin film depicting an absorption between 3.2 to 3.8 eV.

However, sputter deposition systems are different from each other which depends on the chamber geometry, configuration and pumping schemes etc. Therefore, deposition recipes should be carefully tested for different vacuum systems. As can be seen in Fig. 4.38, in our sputtering system, deposition rate increased not only with RF power, but also with pressure as well.

At 120 W, deposition rate increased with the deposition pressure. However, at 100 W deposition rate increased until 7 mTorr and it decreased with 10 mTorr, finally increased again at 15 mTorr. Well-adhered and uniform films were deposited with rotational substrate at both power levels. The experiment should continue with the further deposition pressures i.e., 20 and 25 mTorr. Probably,

deposition rate might show a tendency to reduce with further increased deposition pressures. Transmission spectra for the films deposited at 100 W as a function of the deposition pressure are given in Fig. 4.39.

The main band gap is shifting towards higher wavelength with deposition pressure. There is an exception here: 10 mTorr shifted to higher wavelength with respect to 15 mTorr sample. The films show high transparency: $\sim 90\%$ in visible and $\sim 80\%$ in near IR range. In near IR range, transmission decreased with deposition pressure and there is an exception again that 7 mTorr and 15 mTorr show the same transmission in this range. For determination of the optical constant, ellipsometric data analysis was used. Four layer model which includes Si, geneoscillator, simple grading, and surface roughness, was used and additionally some films showed nonuniformity. Figure 4.40 shows the spectral refractive indices as a function of deposition pressure for 100 W samples. Refractive indices increased with deposition pressure until 10 mTorr and decreased for 15 mTorr sample. The indirect band gap of the samples are presented in Fig. 4.41 which was deposited at 15 mTorr and 10 mTorr with 100 W.
4.5 Photocatalytic Activity of SrTiO₃

Schematic diagram which is given Fig. 4.43 depicting the fabrication of TiO_2 nanofibers/STO heterostructure were fabricated using a three step fabrication process:

1-) TiO₂ coated PVP-ZnAc (PVP-ZnAc-TiO₂) nanofibers were fabricated by electrospinning.

2-) STO was deposited on PVP-ZnAc-TiO₂ nanofibers by RF-sputter deposition. (Fig. 4.42)



Figure 4.42: Schematic illustration of RF sputter deposition of STO on TiO2 nanofibers with various time; 3 min, 5 min, and 240 min, respectively.

3-) STO dposited onto PVP-ZnAc-TiO₂ nanofibers were calcinated at 500° C for 3h in order to remove polymeric cores.(Fig. 4.43)



Figure 4.43: Schematic illustration of the STO/TiO_2 nanofibers after the calcination process (a) 3 min (b) 5 min and (c) 240 min STO deposition.

SEM images of the 3 and 5 min STO deposition on TiO₂ nanofibers are shown in Fig. 4.44 (a)-(c) before the calcination process. Electrospun nanofibers show wide range of diameters and additionally can be observed depending upon the solvent and its characteristics. STO/TiO₂/STO width after 3 and 5 min deposition are in the range of 250 to 400 nm and after 240 min deposition of STO on TiO₂ nanofiber is in the range of 400 nm to 1.5 μ m. The following TEM analyzes are in good agreement with SEM observation. STO/TiO₂/STO heterostructure can be seen clearly with TEM images for 3, 5 and 240 min deposition in Fig. 4.45.

EDX analyzes show that C% concentration after the 3 and 5 min STO deposition are found to be around 75%. However, only 2% is found after 240 min deposition. Recorded detailed EDX spectra from TEM shows the signal of Sr, Ti,





Figure 4.44: SEM images of the STO/TiO_2 nanofibers (a) and (b) 3 min and (c) 5 min STO deposition before the calcination process.

O, C, and Cu, which come from the TEM grid, concentration is given in Table 4.11. Therefore, further characterizations continued with the 240 min deposited STO/TiO_2 fiber templates.

It is known fact that sputter deposition is a physical vapor deposition technique, and does not provide uniform and conformal deposition when compared to CVD or ALD method. Because one side of the nanofibers directly see the plasma, STO atoms can easily reach onto one-side of TiO_2 nanofibers, while depositing less on the other side. Due to the lack of conformity, STO film thicknesses are measured to be in the range of 40 to 500 nm.





Figure 4.45: TEM images of (a) 3 min, (b) 5 min and (c) 240 min STO deposited TiO_2 nanofibers

The crystalline phases of TiO_2 was identified by XRD. Anatase phases of TiO_2 were identified of the $STO/TiO_2/STO$ heterostructure. The anatase phase of tetragonal TiO_2 with (011), (004), (020), (015), (121), (024), (116), (220), (125), (224) reflections appearing at 25.342°, 37.960°, 48.044°, 53.992°, 55.093°, 63.945°, 69.112°, 70.245°, 75.034°, 82.866° 2Theta positions (ICSD code:98-017-2914), respectively. (Fig. 4.46)

The photocatalytic (PC) activity of the STO/TiO₂/STO heterostructures prepared are tested using methylene blue (MB) in an aqueous solution. In Figure 4.47 plots of the photodegradation fraction of the MB as a function of presence of the photocatalyst of STO/TiO₂/STO template is compared with pure TiO₂.

Table 4.11: EDX spectra from TEM analysis.



Figure 4.46: XRD spectra of the STO/TiO_2 heterostructure after the calcination process.

MB PC degredation is an interface reaction on a photocatalyst. The expected photogenerated e⁻ and h⁺ under UV recombine inside the photocatalyst can be described as follows: h⁺ in VB of the STO react with OH⁻ and producing hydroperoxy radicals HO. e⁻ in the CB of TiO₂ creates superoxide O_2^{-} . (Detailed explanation is given section 2.5.1) MB solution react with these oxidazing agents and degrade to inorganic compounds of CO₂ and H₂O. PC decomposition principle in a heterostructured STO/TiO₂/STO nanofibrous template was illustrated in Fig. 2.13. Photogenerated e⁻ might easily transfer from CB of STO to CB to TiO₂ and h⁺ from VB of TiO₂ to VB of STO due to the slightly higher potential of flat—band of STO when compered to TiO₂.

On the other hand, experimental results of STO/TiO_2 template showed lower

PC activity then pure TiO_2 nanofibers (Fig.4.47 (d)). It might form as a protective layer for nanofibers.

For further research on STO/TiO_2 nanofibrous templete and photocatalytic activity of SrTiO_3 might be possible with Sr doped TiO_2 nanofibers or atomic layer deposition (ALD) of SrTiO_3 on TiO_2 nanofibers due to the ALD provides usually more controllable growth of thin films. Thus, ALD might provide possible deposition of nucleated STO, not as a thin film structure.



Figure 4.47: UVvis spectra of the (a) MB solution, (b) $\text{STO}/\text{TiO}_2/\text{STO}$ heterostructured nanofibers, (c) TiO₂ nanofibers and (d) degradation rate (C/C₀) of the MB solution with and without $\text{STO}/\text{TiO}_2/\text{STO}$ nanofibers by exposing 365 nm UV light.

Chapter 5

Conclusion and Future Work

In this thesis, we report STO and BST thin films deposited on Si, UV-FS, and quartz substrates at RT by RF-magnetron sputtering process. STO and BST thin film microstructure, elemental composition, surface morphology, optical, and electrical properties were studied as a function of oxygen concentration (for STO), deposition power (for STO), and reactor pressure (for STO and BST). Influence of post-deposition annealing temperature and time was also investigated on STO samples, while BST sample was just at 800°C for 1 h.

GIXRD measurements showed that the transition of amorphous phase to nanocrystalline phase start at 300°C for 1 h annealing. Some polycrystal grains appeared at 600°C for 1 h with nanocrystallinity. Polycrystalline phase transition started at 700°C annealing for 15 min and the polycrystal peak intensities reached the maximum at 800°C. The formation of the STO polycrystalline phase was strongly dependent on the annealing temperature. With the increase of annealing temperature until 800°C, STO grains formed and grain size increased to the highest value (16 nm) at this temperature, which indicated on improvement in the crystalline quality. However, at 900°C the intensity of polycrystalline peak decreased and the grain growth depicted a saturated grain size. Annealing at different temperatures and time at 700°C for 1 h under O_2 ambient leads to crystallization of the STO layer and also significantly affected the optical and electrical characteristics of the resulting thin films.

Amorphous behavior with some nanocrystallinity was observed for the asdeposited BST films. Post-deposition annealing at 800°C under O_2 ambient led to crystallization of the films, and significantly influenced the optical and electrical characteristics of the BST samples.

Highly transparent and well-adhered films were achieved with RT-deposition. Amorphous behavior with some nano-crystallinity was observed for the assputtered thin films irrespective of the O_2 flow rate. While as-deposited STO films had very smooth surfaces, rms values of the annealed films, particularly the ones deposited using high oxygen concentration, were slightly higher than those of their as-deposited counterparts. Additionally, due to the increased deposition rate, surface roughness values increased as well with plasma power. Average optical transmissions of the as-deposited films improved in the VIS and NIR spectral regions with increasing O_2 flow rates.

As-deposited STO and BST films had very smooth surfaces while increased surface roughnesses were noted upon annealing, especially for BST samples. The annealing study on STO showed us that the major grain growth started at 700°C in 15 min and further temperatures, resulting in porous films, which causes a degradation in its optical and structural properties as can be seen with rms results which taken by AFM.

Refractive indices of STO films slightly increased with the post-deposition annealing treatment and OMR. However, no clear correlation with plasma power was observed. By increasing the annealing temperature the main absorption edge shifted towards higher wavelengths. This result also determined by the spectroscopic ellipsomety measurements until 900°C, at which high porosity resulted in decreasing of the direct band gap of the STO-900 film. The refractive index values showed on increasing trend with film crystallinity as expected. For BST samples, film transmissions decreased with post-deposition annealing and exhibited an increased optical loss due to scattering. SEM and AFM measurements also indicated significantly increased surface roughness upon annealing. Dielectric constants increased with crystallinity. Therefore, STO-800 showed relatively high dielectric constant when compared to its amorphous (STO-RT) and nanocrystalline (STO-300)counterparts. Also, STO-800 showed stable dielectric constant around 46 until 3 MHz but it drastically degreased to 27 after this frequency. However, relatively high dielectric constants in the range of 30 to 99 at 100 kHz was obtained for ;300 nm-thick STO films deposited at RT. Calculated dielectric constants and relatively low losses are promising for microelectronic applications as relatively thin (\sim 100 nm) STO thin films were considered here. This study demonstrates that post deposition annealing temperature and annealing time have considerable influence on the structural, optical, and electrical properties of room-temperature sputtered amorphous-grown STO thin films. On the other hand, dielectric constants of BST films were found to be relatively lower (i.e., 46-72), compared to the values reported in literature (Table 2.2).

Processing parameters such as deposition pressure, O_2 concentration, and deposition and annealing temperatures have significant influence on the structural, optical and electrical properties of sputtered STO thin films.

Our experimental studies showed that RF sputtering deposition features a good potential for the fabrication of transparent ferroelectric oxide films with good adhesion and homogeneity. Moreover, dielectric constants, tunability, and dielectric loss values are promising with RT deposition on Si substrates. Our achievements might lead to further studies including material and device development. Possible future directions are listed below:

- Investigation of STO and BST with different substrate temperatures at different deposition power, OMR, and higher pressure (>7 mTorr).
- Zr, Nb, Ta doped STO and BST studies with different recipies to optimize tunability performance.
- Investigation of annealing temperature and time on RF sputtered BST films.
- Demonstration of the electronic and optoelectronic device applications of

RF sputtered STO and BST tihn films and their doped counterparts; i.e.; resistive memories, photodedectors, tunable capacitors.

- Investigation of photocatalytic properties of STO.
- Investigation of the substrate impact on room temperature RF sputtered STO and BST; i.e.; Si(111), MgO.
- Investigation of room-temperature RF sputtered STO-BST thin film alloys.

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"ich lebe mein leben in wachsenden ringen

die sich ber die dinge ziehen

den letzten werd' ich vielleicht nicht vollbringen

aber versuchen will ich ihn"

Rainer Maria Rilke