ORIGINAL ARTICLE

Electro-optical performances of nanostructured SrTiO_x films: The effect of plasma power, Ar/O₂ ratio and annealing

Eda Goldenberg^{1,2} | Turkan Bayrak² | Omid Mohammadmoradi³ ¹Sabancı University Nanotechnology Research and Application Center SUNUM, Istanbul, Turkey²Bilkent University National Nanotechnology Research Center-UNAM, Ankara, Turkey³Faculty of Engineering and Natural Sciences, Sabancı University, Istanbul, Turkey**Correspondence**Eda Goldenberg, Sabancı University Nanotechnology Research and Application Center SUNUM, TR-34956 Istanbul, Turkey.
Email: eda.goldenberg@sabanciuniv.edu**Funding information**

TUBITAK, Grant/Award Number: 113C020; Bilkent University

Abstract

The present work evaluates the effects of plasma power and oxygen mixing ratios (OMRs) on structural, morphological, optical, and electrical properties of strontium titanate SrTiO_x (STO) thin films. STO thin films were grown by magnetron sputtering, and later thermal annealing at 700°C for 1 h was applied to improve film properties. X-ray diffraction analysis indicated that as-deposited films have amorphous microstructure independent of deposition conditions. The films deposited at higher OMR values and later annealed also showed amorphous structure while the films deposited at lower OMR value and annealed have nanocrystallinity. In addition, all as-deposited films were highly transparent (~80%–85%) in the visible spectrum and exhibited well-defined main absorption edge, while the annealing improved transparency (90%) within the same spectrum. The calculated direct and indirect optical band gaps for films were in the range of 3.60–4.30 eV as a function of deposition conditions. The refractive index of the films increased with OMRs and the postdeposition annealing. The frequency dependent capacitance measurements at 100 kHz were performed to obtain film dielectric constant values. High dielectric constant values reaching up to 100 were obtained. All STO samples exhibited more than 2.5 μC/cm² charge storage capacity and low dielectric loss (less than 0.07 at 100 kHz). The leakage current density was relatively low (3×10^{-8} Acm⁻² at +0.8 V) indicating that STO films are promising for future dynamic random access memory applications.

KEYWORDS

charge storage capacity, dielectric constant, electrical properties, optical properties, oxide thin films, strontium titanate

1 | INTRODUCTION

Miniaturization of electronic components and integration with microelectronic circuits due to the rapid development of oxide thin film process technology is one of the main driving forces for future materials research. However, there are fundamental limits to the downscaling of materials involved in the current complementary metal-oxide-semiconductor technologies.¹ Metal oxide thin-films have been extensively studied for large-area flat-panel displays,

transistors, random access memory applications, charge storage devices, and sensor arrays over the past decade, because of their high carrier mobility, high transparency, excellent large-area uniformity, dielectric constants, and reasonable electrical stability and tunability. There are several types of oxide thin film materials, among them ferroelectric based oxide materials received attention based on their optical and electrical properties such as optical and dielectric constants, and density.^{1–3} They have found applications in microelectronics, energy fields as capacitors,

storage devices, temperature sensors, etc.¹⁻⁷ Among those materials, SrTiO₃ (STO) is one of the most important materials due to its chemical stability, compatibility with high temperature processes, attractive optoelectronic properties, and shows a significant promise for device applications. Especially, the field-dependent permittivity and temperature-dependent polarity of such materials are key properties in microelectronic applications.⁶⁻¹¹ Tagantsev et al.¹² and Ahmed et al.⁵ reported the use of ferroelectric materials for applications in microwave range. Moreover, in recent years CMOS-compatible memristor and tunability device applications of room-temperature (RT) grown amorphous STO thin films were intensively studied.¹³⁻¹⁵ Nonvolatile bipolar resistive switching mechanism with 10³–10⁴ switching ratios, high durability which is less than 10⁶ current-voltage sweep cycles, and over repeated 105 s long “Read cycles”, while still having retention with <1% change in resistance were obtained in oxygen deficient amorphous STO memristors.^{13,15} However, high deposition temperature is a major limitation associated with the commercialization of these materials. Therefore, low-temperature growth, and understanding its structural-properties relationship are of significant contribution to the field.^{15,16}

SrTiO₃ thin films have been deposited on variety of substrates, depending on the application. For example, the integration of STO thin films with Si substrates is highly desirable for CMOS-applications.^{17,18} In addition, the gate oxide thickness continues to decrease in metal-oxide semiconductor field-effect transistors, and the need of alternative high-*k* dielectric materials is increasing.¹⁹ In the recent years, most of the studies on STO films focused mainly on the correlation between film microstructure and optical properties including photoluminescence (PL), optical constants, or only on their electrical characteristics.²⁰⁻²⁵ To the best of our knowledge, only limited number of experimental works were reported on RT grown STO thin film (<200 nm-thick) properties vs. deposition parameters.²⁶ At the same time, there is a lot of inconsistent data, which does not always agree with reported values. Hence, the understanding of the material properties requires a systematic study to correlate the film characteristics with deposition parameters. There are many methods to produce STO thin films such as atomic layer deposition, pulsed laser deposition, sol-gel, and sputtering. Among them, the most common is a magnetron sputtering due to its simplicity, low cost, and the ability to control the material properties by tailored growth parameters.

In the present work, the effects of the oxygen mixing ratio (OMR), plasma power on STO thin film structure, optical, and electrical characteristics were systematically investigated to assess the film behavior in device structure. In addition, to the determination of the film morphology, microstructure, and optical constants (*n* and *k*), the variation of the film

dielectric constant, and the mechanisms for dielectric losses are addressed.

2 | EXPERIMENTAL PROCEDURES

SrTiO₃ thin films were deposited on Si (100) and fused silica substrates by off-plane axis NanoD—4S rf-magnetron sputtering system with 10% and 20% OMR (O₂/(Ar + O₂)). During the film deposition, two different rf-plasma power levels (75 and 100 W) were used. The chamber base pressure was <6.5 × 10⁻⁶ Torr (0.9 mPa) and kept constant at 0.67 Pa during the film deposition. Ar and O₂ were introduced into the system using separate gas lines. The depositions were performed using a stoichiometric SrTiO₃ ceramic target (50 mm, purity 99.9%). Si (2") and UV-fused silica (1") substrates were cleaned in isopropanol and later rinsed in deionized (DI) water. The distance between target and substrate was 50 mm. For each deposition conditions at least five samples were prepared and film characterization and diagnostics were performed over an area of ~2 × 2 cm located in the center of the deposited film, where the thickness non-uniformity was within ~5%. Film thickness values of STO films were extracted from ellipsometric analysis and found to be between 91 and 128 nm, depending on the deposition conditions. In order to investigate the effect of postdeposition annealing on physical properties, films were annealed at 700°C for 1 h in O₂ ambient (200 sccm) using rapid thermal annealing system. Heating rate was ~3.5°C/s, and samples were taken out from the annealing chamber after the system was cooled down to below 80°C.

X-ray diffraction (XRD) patterns were recorded with a Bruker D2 phaser XE-T diffractometer. The scanning range was 20°–60° with 0.02° scan steps for the examination of the structural characteristics of STO films. The elemental composition and bonding states of the films in the bulk were measured by X-ray photoelectron spectroscopy (XPS; Thermo Scientific 20K-Alpha spectrometer). The surface morphology was investigated with an atomic force microscope (AFM; Asylum Research MFP-3D) operating in tapping mode from a 1 × 1 μm scanned areas. Scanning electron microscope (SEM) images were acquired using a LEO Supra 35VP scanning electron microscope operated at 3 kV. A thin layer of Au/Pd sputter coated on the samples before taking SEM images.

Spectral transmission measurements were performed using a UV-VIS-NIR single beam spectrophotometer (Ocean Optics HR4000CG-UV-NIR) relative to air. Film optical constants were extracted from ellipsometric measurements using a variable angle spectroscopic ellipsometer (V-VASE, J.A. Woollam Co. Inc.) between 250 and 1200 nm spectral range, with a step of 1 nm at 65°, 70°

and 75° angles of incidence. Film refractive index (n) and extinction coefficient (k) were determined using the homogeneous Tauc–Lorentz function. The optical model consists of four-layer model including substrate, SiO₂ (2 nm), film, and surface roughness. The absorption coefficient, $\alpha(\lambda) = 4\pi k(\lambda)/\lambda$, was calculated from $k(\lambda)$ values. The optical band gap energy, E_g , was evaluated using the spectral absorption coefficient by using Tauc formula.^{26,27} The direct and indirect band gap values were determined from $(ah\nu)^2$ and $(ah\nu)^{1/2}$ vs. $h\nu$, plots respectively. Thin film PL measurements were carried out by using fluorescence spectrophotometer as a function of deposition and annealing parameters in the wavelength range of 320–605 nm using the excitation wavelength of 310 nm.

Metal/insulator/semiconductor (MIS) device structures in which STO functions as an insulator layer has been fabricated to investigate electrical properties. MIS fabrication process begins with the standard wafer cleaning of p -type Si(100) substrate which is also used as the back-side ohmic contact. To this end, 80 nm thick Al was deposited to the back side of each wafer using the VAKSIS thermal evaporation system (PVD Vapor 3S Thermal), while the top wafer side was protected with a layer of photoresist. After stripping the photoresist layers and cleaning the samples with acetone, methanol, isopropanol, and DI water, and finally drying with N₂, samples were annealed in an ATV-Unitherm (RTA SRO-704) rapid thermal annealing system at 450°C for 2 min under 100 sccm N₂ flow with a ramp rate of 15°Cs⁻¹. The top contacts of the MIS structures were formed by another thermal evaporation (~80 nm thick Ag) process, followed by lift-off. MIS capacitor structures with STO film as the insulating layer, which were fabricated using class 100 and 1000 cleanroom facilities. Ag and STO layers were patterned simultaneously to obtain MIS devices with 380.6 μm^2 active area during the development of AZ 5214E photoresist with AZ 400 K developer (Micro-Chemicals GmbH) (AZ 400 K:H₂O = 1:4). The dielectric constants of the films were calculated from the parallel plate capacitance model, and the frequency-dependent dielectric properties of the fabricated test structures were measured using Agilent E4980A Precision LCR meter from 200 Hz to 1 MHz frequency range. 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 probe station (Cascade Microtech PM-5). All electrical measurements were carried out in atmospheric conditions and in the dark environment using two probes. The dielectric constants of the films were calculated from the parallel plate capacitance model $C = \epsilon_0 \cdot \epsilon_r \cdot A/t$ where C , t , ϵ_0 , ϵ_r , and A correspond to the accumulation capacitance, film thickness, permittivity of free space (8.8542×10^{-12} F/m), dielectric constant of the film, and area of the electrodes

respectively. The film dielectric breakdown voltage (V_{bd}), dielectric breakdown field (E_{bd}), and charge storage capacity ($CSC = \epsilon_0 \epsilon_r E_{bd}$), as well as accumulation region of fabricated structure were estimated from I – V and C – V measurements.

3 | RESULTS AND DISCUSSION

3.1 | Film microstructure, composition, and morphology

The XRD patterns of as-deposited STO films are presented in Figure 1. As can be seen from the plots, the films showed amorphous phase independent of deposition conditions. The films deposited at 20% OMR value and annealed at 700°C, indicated that the films have polycrystalline cubic structure regardless of the composition giving the reflections for corresponding planes of (011) at 32.26, (111) at 39.90, (002) at 46.15, and (112) at 57.34, with the inorganic crystal structure database code (98-008-0873). In polycrystalline samples, average crystallite size was evaluated using the Scherrer equation. The crystallite size is found to be 18 nm for films annealed at 700 C for 1 h. In literature, XRD reflections of cubic STO crystal structure are stated at 22.78, 32.43, 40.00, 46.52, 52.40, 57.85, 67.91, 72.65, 77.28, 81.83, and 86.32, for planes (001), (011), (111), (002), (012), (112), (022), (122), (013), (113), and (222) respectively.

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.²⁸ However, elevated substrate temperatures might lead to the formation of interlayers, which could result in high

FIGURE 1 X-ray diffraction patterns of STO thin films deposited on n -Si(100) substrates –before and after annealing at 700°C. STO, SrTiO_x [Color figure can be viewed at wileyonlinelibrary.com]

leakage current and low dielectric constant values. Silinskas et al. also reported low quality electrical properties for strontium tantalate thin films due to formation of SiO_2 interlayer.²⁹ In addition, it is reported that crystallinity of sputtered films is improved with applied plasma power due to the energy of electron and ions in plasma.³⁰ Thus, kinetic energy of the positive ions colliding with the target increases, which enhances the energy of the sputtered atom arriving to the substrate surface, assisting further crystallization.³¹ However, in our study, we were not able to observe a considerable difference between crystallinity of 75 and 100 W samples, which indicates that aforementioned power effect is not pronounced for our RT deposited STO films. To improve the film crystallinity, RT deposition was followed by a high-temperature (700°C, 1 h) annealing process.³²

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 1. The Sr/Ti elemental ratio was found to vary between 0.45 and 1.51. 10% OMR with both deposition power results in relatively high Sr/Ti ratio. Postdeposition annealing affected the Sr/Ti ratio being reduced for films deposited at 10% OMR, while increased for films deposited at 20% OMR. XPS analyses indicated O-rich STO films. Vink et al.³³ noted that excess oxygen might originate from the presence of physically trapped oxygen. Sputtering of highly oxygenated targets such as BaTiO_3 , LiNbO_3 , and SrTiO_3 can suffer from negative ion effects.³⁴ For films deposited at RT, excess oxygen can result from physically trapped and chemically bonded oxygen in the form of hydroxyl groups originating from water vapor impurity at the vacuum reactor walls. Similar results were obtained by Noda et al.³⁵

In Figure 2A and B, 3D AFM images are presented for film deposited with 75 W plasma power at 10% OMR, 1.12 and 0.89 nm root-mean-square (rms) surface roughness for as-deposited, and annealed films respectively. Rms surface roughness of as-deposited STO films was higher for films

deposited at 75 W with 20% OMR, which can be clearly seen at Table 2. Material characteristics of thin films can be affected by surface morphology. A good example for that is the correlation between optical transmittance and surface roughness of the film. Additionally, one of the requirements of insulator films as dielectric layer in devices is that morphology of the film should be as smooth as possible. In current work, 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.^{36,37} The different behavior at higher power levels indicate that rf power effects surface morphology of sputtered thin films. Higher energy sputtered ions may cause increased surface damage, which increases surface roughness. Surface morphology of STO thin films was also examined by SEM measurements. Figure 3A,B show plane view SEM image for STO thin film, deposited at 75 and 100 W plasma power on Si (100) substrate at RT and annealed afterward at 700°C for 1 h. As it was observed in AFM analysis films deposited at lower OMR values have rough surface compare to films deposited at high OMR values.

3.2 | Optical properties

Optical transmittance spectra of as-deposited and annealed STO films are presented in Figure 4A and B, respectively. Films deposited at a power of 75 and 100 W with different OMR values showed ~80% average transmittance in visible region, independent of the deposition conditions. After annealing at 700°C, 1 h, higher transparency with respect to as-deposited films was observed. This might be due to improved film microstructure.^{38,39} The main absorption peak was around 450–500 nm and its intensity increased at lower wavelengths. All STO films showed well-defined optical band-edge in the UV spectrum. The main absorption edge slightly shifted to lower energies with increasing power.

OMR (%)	Condition	Power (W)	Sr at%	Ti at%	O at%	Ar at%	Sr/Ti
10	As-deposited	75	15.06	12.77	70.62	1.55	1.18
	Annealed		12.31	24.39	60.95	2.35	0.50
10	As-deposited	100	17.57	11.63	69.33	1.47	1.51
	Annealed		15.09	17.41	65.10	2.39	0.87
20	As-deposited	75	11.42	25.35	60.44	2.80	0.45
	Annealed		11.12	22.62	63.03	3.24	0.50
20	As-deposited	100	13.79	25.21	58.36	2.64	0.55
	Annealed		15.80	21.36	60.13	2.71	0.74

TABLE 1 Bulk elemental composition of as-deposited and annealed SrTiO_x thin films as determined by X-ray photoelectron spectroscopy survey scans. Data were collected after 30 s of in-situ Ar etching.

FIGURE 2 Atomic force microscope surface images of STO thin films deposited at 75 W plasma power with 10% oxygen mixing ratio: (A) as-deposited, and (B) annealed. STO, SrTiO_x [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 2 Thickness and Growth Rate of the as-deposited and annealed SrTiO_x thin films.

OMR (%)	Condition	Power (W)	Thickness (nm)	Growth rate (nm/min)	Surface roughness (nm)
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

Abbreviation: OMR, oxygen mixing ratio.

Optical constants of STO films were obtained by using Tauc–Lorentz oscillator model, as presented in the Experimental Methodology section. In Figure 5A,B refractive indices, and extinction coefficients are presented, as an example for films deposited with 75 and 100 W plasma power, and 10% and 20% OMR values after annealing, and the summary of the acquired data are presented in Table 3. Film refractive indices (n) were found to be between 1.83 and 2.13 for as-deposited and annealed films. The change in n values is more pronounced for the films deposited using a higher OMR values. For as-deposited films, n values increased with OMR, but the plasma power did not have significant effect on its value. Film optical band gap is determined

by using the $k(\lambda)$ values, which were obtained from ellipsometry measurements. In order to determine the direct and indirect band gap values for the as-deposited films, $(ah\nu)^{1/2}$ and $(ah\nu)^2$ vs. E data were plotted, respectively. In Figure 6A and B, the optical band gap of films deposited at 75 W plasma power with 10% OMR, and those after annealing are presented respectively (inset figure shows the direct band gap). Summary of the direct and indirect band gap values of as-deposited and annealed STO thin films are presented in Table 3. After annealing at 700°C for 1 h, indirect E_g value increased to 3.78 eV for films deposited at 75 W, while those deposited at 100 W plasma power its value did not change. Film thicknesses were also calculated from the ellipsometric

FIGURE 3 Scanning electron microscope images of STO thin films deposited with (A) 10% 100 W, (B) 20% 100 W, and annealed at 700°C. STO, SrTiO_x

data, and the corresponding deposition rates were calculated. Film deposition rates increased with increased plasma power (see Table 2).

Photoluminescence spectra of as-deposited and annealed STO films on Si substrates are presented in Figure 7A,B. All samples had three well defined luminescence peaks around at 3.44 (360), 3.26 (380), and 2.93 eV (423 nm) for as-deposited, 3.42 (363), 3.26 (380), and 2.95 eV (420 nm) 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 (391 nm) for 10% and 3.21 eV (386 nm) for 20% OMR; the second and third peaks were identified at 2.95 (420) and 2.70 eV (459 nm) for 10% and 20% OMR, respectively. After annealing, the first peak was around 3.16 eV (392 nm) for 10% and 3.19 eV for 20% OMR. The second peak is at 2.92 (424), 2.70 eV (459 nm) for 10% and 20% OMR respectively. The third peak was found at 2.70 eV (459 nm) for both samples. In addition, the peak intensities for films deposited at 100 W were higher than the 75 W counterparts. The blue PL band is observed at 2.95 (420), 2.93 (423), 2.92 eV (424 nm) and relatively weak

FIGURE 4 Optical transmission vs. wavelength plots of (A) as-deposited and (B) annealed STO thin films deposited on fused silica substrates. STO, SrTiO_x [Color figure can be viewed at wileyonlinelibrary.com]

peak at 2.70 eV (459 nm) in all samples indicated an intrinsic carrier recombination process.⁸ The blue PL reflects an intrinsic carrier recombination process above 2.9 eV. Yamada et al. also reported that a broad blue PL band is observed in bulk SrTiO_3 crystals under strong pulsed laser excitation, and the observed PL bands at 1.7 and 2.4 eV were attributed to crystal defects or impurities for STO thin films.⁴⁰ For indirect band gap SrTiO_x thin films, PL intensities of the peaks around 3.40 and 3.20 eV is reported. The intense peaks of the PL spectra reflected the main band-edge emission. The rather broad emissions generally correlated with the defects in the film and they are generally disappearing with the improved crystallinity. Our experimental result is in good agreement with the above-mentioned observations indicating that the amorphous phase might be responsible for the observed emission peaks around 3.40 and 3.20 eV, which are related to the in-gap states.⁴¹

FIGURE 5 Plots of (A) refractive index (n) and (B) extinction coefficient (k) of annealed STO thin films as a function of plasma power and oxygen mixing ratio. STO, SrTiO_x [Color figure can be viewed at wileyonlinelibrary.com]

TABLE 3 Refractive index (n), extinction coefficient (k), and optical energy band gap (E_g) values of as-deposited and annealed SrTiO_x thin films.

OMR (%)	Condition	Power (W)	N	k	E_g (eV) indirect	E_g (eV) direct
10	As-deposited	75	1.89	0	3.60	4.15
	Annealed		1.83	0	3.78	4.20
10	As-deposited	100	1.90	0.01	3.40	4.00
	Annealed		1.99	0.01	3.78	4.30
20	As-deposited	75	2.06	0.01	3.60	4.25
	Annealed		2.13	0.01	3.60	4.20
20	As-deposited	100	2.05	0.01	3.40	4.20
	Annealed		2.04	0.01	3.40	4.20

Abbreviation: OMR, oxygen mixing ratio.

3.3 | Electrical properties

To assess the basic electrical characteristics of the as-deposited and annealed STO films C - V , C - f , and I - V

FIGURE 6 Direct and indirect optical energy band gap determination of (A) as-deposited and (B) annealed STO thin films. STO, SrTiO_x [Color figure can be viewed at wileyonlinelibrary.com]

measurements of Ag/STO/p-Si MIS capacitor structures were performed in room temperature. The DC bias voltage is swept from negative voltage to positive voltage for C - V measurements. At large negative gate voltage region,

FIGURE 7 Photoluminescence spectra of (A) as-deposited and (B) annealed thin films deposited on Si substrates as a function of plasma power and oxygen mixing ratio [Color figure can be viewed at wileyonlinelibrary.com]

the capacitances of the STO dielectric films are dominant in the total capacitance, indicating accumulation.^{42,43} After the determination of the accumulation voltage, C - f of the films was measured. In strong accumulation region, using the maximum capacitance of the films, C , the dielectric constant of the film, ϵ_r , can be calculated from the formula given in the experimental section. Figure 8A,B shows the dielectric constant and dielectric loss of the MIS device structure for as-deposited (inset) and annealed film as a function of frequency. Dielectric constant values (at 100 kHz) of films deposited at 100 W increased with OMR from 10 (10% OMR) to 28 (20% OMR) for as-deposited and 51 (10% OMR) to 100 (20% OMR) for annealed. This might be due to the crystallization and improvement in the microstructure as it is observed from XRD analysis. However, its value decreased with OMR for as-deposited

FIGURE 8 (A) Dielectric constants and (B) dielectric loss values of annealed STO thin films (inset-as-deposited) as a function of plasma power and oxygen mixing ratio. STO, SrTiO_x [Color figure can be viewed at wileyonlinelibrary.com]

(75 W) and annealed films from 60 to 58 and from 62 to 49 respectively. The dielectric loss values increased slowly after 0.1 MHz and it reached to 0.4. It might be possible that the loss mechanism here mainly originates from the extrinsic loss mechanism. The reason of the high loss observed for polycrystalline STO sample at high frequencies might be due to the local polar regions induced by various defects and structural imperfections.

A quantitative analysis of the variation of the films deposited at 10% and 20% OMR (with 75, 100 W deposition power and annealing) dielectric constants as a function of Sr/Ti ratios are provided in Figure 9A,B. Regarding to the dielectric constant, shown in Figure 9A for Sr/Ti ratio between 0.45 and 1.51, the decrease is proportional to the degree of nonstoichiometry for Sr excess. The increase in dielectric constant with annealing is observed as reported in the literature.^{44,45} The increase in dielectric constant for the films deposited at 10% OMR, 100 W plasma power is much higher after annealing.

FIGURE 9 (A, B) Dielectric constants and (C, D) dielectric loss values of annealed STO thin films 10% and 20% oxygen mixing ratio for films deposited at 75 and 100 W annealed and as-deposited films as a function of Sr/Ti ratios. STO, SrTiO₃ [Color figure can be viewed at wileyonlinelibrary.com]

Similarly, the dielectric constants of the films deposited at 20% OMR, 100 W films are also increased as shown in Figure 9B. Low dielectric constants for as-deposited films may originate from higher density of defects as expected for an amorphous layer. Unlike other STO films, dielectric constant in as-deposited films (at 75 W and 20% OMR) are high before annealing.

The increase in the dielectric constants of films deposited at 100 W plasma power with increased OMR values may be due to the higher oxygen incorporation in the films and the densification of the films after the annealing process.⁴³ Furthermore, the reason for the as-deposited films having lower dielectric constant than deposited at annealed samples might be attributed to the thicker interfacial layer in as-deposited samples, or amorphous nature of the grown films. Sakabe et al. studied the grain size effects on dielectric properties of BaTiO₃ ceramics, and reported that the dielectric constant increases with crystallite size.⁴⁶ In the current research we also observed similar effect. Although higher dielectric constant values, in the range of 80–800, are

reported for high temperature epitaxial grown or doped STO thin films.^{47,48} The dielectric constant of STO obtained in the present work are in good agreement with those previously reported for films deposited at low temperatures.⁴⁷⁻⁵⁰

The STO films exhibited relatively low dielectric losses as shown in Figure 9C,D at 100 kHz, particularly at high frequencies (Figure 6B). Dielectric loss might originate from ohmic losses and can be avoided via thicker contact metal alloys.⁵¹ Figure 9C,D show stoichiometry of the films not effect on dielectric losses.

Charge storage capacity of the devices was calculated from the breakdown values of the *I*–*V* measurements. In Table 4, *V*_{bd}, *E*_{bd}, *E*_r and dielectric loss (tan (δ)) are given for as-deposited and annealed films. No breakdown voltages were observed up to ±20 V bias for films deposited with 10% OMR at 75 W and with 10% and 20% OMR at 100 W. The leakage current in all the samples are of the order of nanoampere indicating their good insulating behavior. The leakage current density for the STO based MIS capacitors are lower than 10^{−6} A/cm². It satisfies the

OMR (%)	Condition	Power (W)	V_{bd} (V)	E_{bd} (MV/cm)	ϵ_r	$\tan(\delta)$
10	As-deposited	75	—	—	59.7	0.00
	Annealed		—	—	61.7	0.03
10	As-deposited	100	—	—	10.4	0.02
	Annealed		—	—	50.8	0.03
20	As-deposited	75	7.50	0.73	57.8	0.02
	Annealed		5.30	0.58	48.9	0.07
20	As-deposited	100	—	—	28.4	0.02
	Annealed		—	—	99.3	0.02

Abbreviation: OMR, oxygen mixing ratio.

TABLE 4 Breakdown voltage (V_{bd}), breakdown field (E_{bd}), dielectric constant (ϵ_r), dielectric loss ($\tan\delta$) of as-deposited and annealed SrTiO_x thin films.

leakage current requirement for dynamic random access memory (DRAM) applications.

Breakdown field (E_b) was evaluated as 0.73 MV/cm (as-deposited) and 0.58 MV/cm (annealed) for films deposited at 20% OMR at 75 W. This might indicate more TiO₂ phases in films which caused the voltage breakdowns.⁵² The measured E_b values correspond to 3.73 and 2.51 $\mu\text{C}/\text{cm}^2$ CSC for as-deposited and annealed films at 20% OMR at 75 W respectively.

4 | CONCLUSIONS

In this study, we have obtained amorphous STO thin films on Si(100) with magnetron sputtering at room temperature. Growth rate increased from 3.6 to 5.1 nm/min with increase in plasma power. However, no significant effect was observed for films deposited at higher OMR values. All as-deposited films were amorphous. XRD data indicated that the crystallinity of films deposited at 10% OMR was higher compared to films deposited at 20% OMR. Post-deposition annealing treatment slightly improved the film crystallinity as confirmed from optical analysis, but it did not have significant influence on the elemental composition. XPS survey scans and high resolution XPS measurements confirmed the successful growth of STO films with low impurity content. Elemental analysis indicated that as-deposited films were rich in O and Ti. Sr/Ti ratio of films deposited at 10% OMR were relatively high (1.18 and 1.51 for 75 and 100 W samples, respectively), compared to films deposited at higher OMR values. AFM data revealed relatively smooth films with rms surface roughness of 1–1.5 nm. Film surface roughness values increased with plasma power due to the energetic deposition and increased deposition rate. Films exhibited refractive index of 1.89–2.05 at 550 nm, and optical band edge at 3.4–3.6 eV. The refractive indices showed an increasing trend with OMR. However, no clear correlation with plasma power was observed. Postdeposition annealing lowered film refractive indices at lower OMR values while at higher plasma power and

OMR their value did not change significantly. As-deposited films showed higher dielectric constant at lower plasma power, while with the postdeposition annealing dielectric constant values slightly decreased. However, films deposited at 100 W plasma power showed significant increase in dielectric constant with annealing. Relatively low dielectric losses at 100 kHz were obtained for STO films. According to dielectric constant values, annealed STO films deposited at high oxygen flow and power (e.g., 20% O₂ and 100 W) are promising particularly for DRAM application. This study indicates that process parameters such as plasma power, OMR, and annealing have considerable influence on the structural, optical, and electrical properties of RT sputtered STO thin films.

ACKNOWLEDGMENT

This work was performed at Bilkent University, Institute of Materials Science and Nanotechnology—UNAM. E. G. gratefully acknowledges the financial support from TUBITAK (BIDEB 2232, project no. 113C020). We thank Mr. Leghari for AFM analyses.

ORCID

Eda Goldenberg <https://orcid.org/0000-0003-4709-6591>

Omid Mohammadmoradi <https://orcid.org/0000-0001-8126-4531>

REFERENCES

- Rosa J, Kiazadeh A, Santos L, Deuermeier J, Martins R, Gomes HL, et al. Memristors using solution-based IGZO nanoparticles. *ACS Omega*. 2017;2:8366–72.
- Zhu C, Liu AO, Liu G, Jiang G, Meng Y, Fortunato E, et al. Low-temperature, nontoxic water-induced high-k zirconium oxide dielectrics for low-voltage, high-performance oxide thin-film transistors. *J Mater Chem C*. 2016;4:10715.
- Branca NC, Deuermeier J, Martins J, Carlos E, Pereira M, Martins R, et al. 2D resistive switching based on amorphous zinc-tin oxide schottky diodes. *Adv Electron Mater*. 2020;6:1900958.
- Coll M, Fontcuberta J, Althammer M, Bibes M, Boschker H, Calleja A, et al. Towards oxide electronics: a roadmap. *Appl Surf Sci*. 2019;482:1–93.

5. Ahmed A, Goldthorpe IA, Khandani AK. Electrically tunable materials for microwave applications. *Appl Phys Rev*. 2015;2:011302.
6. Van Keuls FW, Romanofsky RR, Bohman DY, Winters MD, Miranda FA, Mueller CH, et al. $\text{Yb}_{0.2}\text{Cu}_{0.3}\text{O}_{7-\delta}$, Au)/ $\text{SrTiO}_3/\text{LaAlO}_3$ thin film conductor/ferroelectric coupled microstripline phase shifters for phased array applications. *Appl Phys Lett*. 1997;71:3075–7.
7. Alzuaga S, Daniau W, Salut R, Baron T, Ballandras S, Defay E. Tunable and high quality factor SrTiO_3 surface acoustic wave resonator. *Appl Phys Lett*. 2014;105:062901.
8. Joshi PC, Krupanidhi SB. Structural and electrical characteristics of SrTiO_3 thin films for dynamic random access memory applications. *J Appl Phys*. 1993;73:7627–34.
9. Tumarkin A, Gagarin A, Odinets A, Zlygostov M, Sapego E, Kotelnikov I. Structural and microwave characterization of BaSrTiO_3 thin films deposited on semi-insulating silicon carbide. *Jpn J Appl Phys*. 2018;57:11S, 11UE02.
10. Kanemitsu Y, Yasuhiro Y. Light emission from SrTiO_3 . *Phys Status Solidi B*. 2011;248:416–21.
11. Bayrak T, Ozgit-Akgun C, Goldenberg E. Structural, optical and electrical characteristics BaSrTiO_x thin films: effect of deposition pressure and annealing. *J Non Cryst Solids*. 2017;475:76–84.
12. Tagantsev AK, Sherman VO, Astafiev KF, Venkatesh J, Setter N. Permittivity, tunability and loss in ferroelectrics for reconfigurable high frequency electronics. *J Electroceram*. 2003;115:66.
13. Nili H, Walia S, Balendhran S, Strukov SD, Bahaskaran M, Sriram S. Nanoscale resistive switching in amorphous perovskite oxide ($\alpha\text{-SrTiO}_3$) memristors. *Adv Funct Mater*. 2014;24:6741–50.
14. Rahman A, Tawfik SA, Ahmed T, Spencer MJS, Walia S, Sriram S, et al. Differential work-function enabled bifunctional switching in strontium titanate flexible resistive memories. *ACS Appl Mater Interfaces*. 2020;12:7326–33.
15. Nili H, Walia S, Kandjani AE, Ramanatran R, Gutruf P, Ahmed T, et al. Donor-induced performance tuning of amorphous SrTiO_3 memristive nanodevices: multistate resistive switching and mechanical tunability. *Adv Funct Mater*. 2015;25:3172–82.
16. Bayrak T, Goldenberg E. Growth and characterization of nanocrystalline SrTiO_x films: room temperature deposition using rf sputtering system in a pure argon environment. *Mater Res Express*. 2017;4(5):055016–23.
17. Li H, Hu X, Wei Y, Yu Z, Zhang X, Droopad R, et al. Two-dimensional growth of high-quality strontium titanate thin films on Si. *J Appl Phys*. 2003;93:4521–5.
18. Yu Z, Ramdani J, Curless JA, Overgaard CD, Finder JM, Droopad R, et al. Epitaxial oxide thin films on Si (001). *J Vac Sci Tech B*. 2000;18:2139–45.
19. Chenming HU. Silicon nanoelectronics for the 21st century. *Nanotech*. 1999;10:113–6.
20. Yasuhiro Y, Kanemitsu Y. Band-to-band photoluminescence in SrTiO_3 . *Phys Rev B*. 2010;82:121103.
21. Pizani PS, Leite ER, Pontes FM, Paris EC, Rangel JH, Lee EJH, et al. Varela JA photoluminescence of disordered ABO₃ perovskites. *Appl Phys Lett*. 2000;77:824–6.
22. Yasuhiro Y, Kanemitsu Y. Photoluminescence spectra of perovskite oxide semiconductors. *J Luminescence*. 2013;133:30–4.
23. Yasuhiro Y, Kanemitsu Y. Band-edge luminescence from SrTiO_3 : no polaron effect. *Thin Solid Films*. 2012;520:3843–6.
24. Tian Y, Adamo C, Schlom DG, Burch KS. Optical properties of SrTiO_3 on silicon(100). *Appl Phys Lett*. 2013;102:041906.
25. Yasuda H, Kanemitsu Y. Dynamics of nonlinear blue photoluminescence and Auger recombination in SrTiO_3 . *Phys Rev B*. 2008;77:193202.
26. Goldenberg E, Bayrak T, Ozgit-Akgun C, Haider A, Leghari SA, Kumar M, et al. Effect of O_2/Ar flow ratio and post-deposition annealing on the structural, optical and electrical characteristics of SrTiO_3 thin films deposited by rf sputtering at room temperature. *Thin Solid Films*. 2015;590:193–9.
27. Van Benthem K, Elsässer C, French RH. Bulk electronic structure of SrTiO_3 : experiment and theory. *J Appl Phys*. 2001;90:6156.
28. Ezhilvalavan S, Tseung-Yuen T. Progress in the developments of (Ba, Sr) TiO_3 (BST) thin films for Gigabit era DRAMs. *Mater Chem Phys*. 2000;65:227–48.
29. Silinskas M, Lisker B, Kalkofen E, Burte P. Investigation of strontium tantalate thin films for high-k gate dielectric applications. *Mater Sci Semicond Process*. 2006;9(6):1102–7.
30. Tien CL, Yu KC, Tsai TY, Liu MC. Effect of rf power on the optical, electrical, mechanical and structural properties of sputtering Ga-doped ZnO thin films. *Appl Surf Sci*. 2014;354:79–84.
31. Chaoumead A, Sung YM, Kwak DJ. The effects of rf sputtering power and gas pressure on structural and electrical properties of ITiO thin film. *Adv Cond Matter Phys*. 2012;2012:1–7.
32. Bayrak T, Kizir S, Kahveci E, Bıyıklı N, Goldenberg E. Postdeposition annealing on rf-sputtered SrTiO_3 thin films. *J Vac Sci Technol*. 2017;35:021505.
33. Vink TJ, Verbeek RGFA, Snijders JHM, Tamminga Y. Physically trapped oxygen in sputter-deposited MoO_3 films. *J Appl Phys*. 2000;87:7252–4.
34. Ishibashi K, Hirata K, Hosokawa N. Mass spectrometric ion analysis in the sputtering of oxide targets. *J Vac Sci Technol A*. 1992;10:1718–22.
35. Noda S, Nishioka M, Harano A, Sadakata M. Gas-phase hydroxyl radical generation by the surface reactions over basic metal oxides. *J Phys Chem B*. 1998;102:3185–91.
36. Franklin JB, Zou B, Petrov P, McComb DW, Ryan MP, McLachlan MA. Optimised pulsed laser deposition of ZnO thin films on transparent conducting substrates. *J Mater Chem*. 2011;21:8178–82.
37. Anthony SP, Lee JI, Kim JK. Tuning optical band gap of vertically aligned ZnO nanowire arrays grown by homoepitaxial electrodeposition. *Appl Phys Lett*. 2007;90:3.
38. Thornton JA. The microstructure of sputter deposited coatings. *J Vac Sci Technol A*. 1986;4:3059–65.
39. Lieberman MA, Lichtenberg AJ. Principles of plasma discharges and materials processing. 2nd ed. Hoboken, NJ: Wiley-Interscience; 2005.
40. Kanemitsu Y, Yamada Y. Blue photoluminescence and auger recombination of carriers in SrTiO_3 nanoparticles. *Chem Asian J*. 2020;15:709–17.
41. Rho JH, Jang SH, Ko YD, Kang SJ, Kim D-W, Chung J-S, et al. Photoluminescence induced by thermal annealing in SrTiO_3 thin film. *Appl Phys Lett*. 2009;95(24):241906.
42. Wang Z, Kugler V, Helmersson U, Evangelou EK, Konofaos N, Nakao S, et al. Characteristics of SrTiO_3 thin films deposited on Si by rf magnetron sputtering at various substrate temperatures. *Philos Mag B*. 2002;82:891–903.
43. Liu C, Tseung-Yuen T. Electrical properties of sputter deposited SrTiO_3 gate dielectrics. *J Eur Ceram Soc*. 2004;24:1449–53.
44. Kınacı B, Çetinkaya Ç, Çokduygulular E, Efkeri HI, Sönmez NA, Özçelik S. Negative capacitance phenomena in Au/

- SrTiO₃/p-Si heterojunction structure. *J Mater Sci Mater Electron*. 2020;31(11):8718–26.
45. Okhay O, Tkach A, Wu A, Vilarinho PM. Manipulation of dielectric permittivity of sol-gel SrTiO₃ films by deposition conditions. *J Phys D Appl Phys*. 2013;46:505315.
 46. Sakabe Y, Wada N, Hamaji Y. Grain size effects on dielectric properties and crystal structure of fine-grained BaTiO₃ ceramics. *J Korean Phys Soc*. 1998;32:S260–S264.
 47. Panomsuwan G, Cho SP, Saito N, Takai O. Growth and characterization of highly c-axis textured SrTiO₃ thin films directly grown on Si(001) substrates by ion beam sputter deposition. *Cryst Res Technol*. 2012;47:187–94.
 48. Baek JY, Duy LT, Lee SY, Seo H. Aluminum doping for optimization of ultrathin and high-k dielectric layer based on SrTiO₃. *J Mater Sci Technol*. 2020;42:28–37.
 49. Wang Z, Kugler V, Helmersson U, Konofaos N, Evangelou EK, Nakao S, et al. Electrical properties of SrTiO₃ thin films on Si deposited by magnetron sputtering at low temperature, temperature. *Appl Phys Lett*. 2001;79:1513.
 50. Radhakrishnan K, Tan CL, Zheng HQ, Ng GL. Preparation and characterization of rf-sputtered rf-sputtered SrTiO₃ thin films. *J Vac Sci Technol A*. 2000;18:1638–41.
 51. Al Ahmad M, Brunet M, Payan S, Michau D, Maglione M, Plana R. Wide-tunable low-field interdigitated barium strontium titanate capacitors. *IEEE Microw Compon Lett*. 2007;17:769–71.
 52. Amaral L, Tkach A, Vilarinho PM, Senos AMR. New insights into the effect of nonstoichiometry on the electric response of strontium titanate ceramics. *J Phys Chem*. 2019;123:710–8.

How to cite this article: Goldenberg E, Bayrak T, Mohammadmoradi O. Electro-optical performances of nanostructured SrTiO_x films: The effect of plasma power, Ar/O₂ ratio and annealing. *Int J Appl Ceram Technol*. 2021;18:631–642. <https://doi.org/10.1111/ijac.13705>