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Effect of oxygen vacancy distribution on the thermoelectric properties of La-doped SrTiO₃ epitaxial thin films

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A detailed study of the role of oxygen vacancies in determining the effective mass and high temperature (300–1000 K) thermoelectric properties of La-doped epitaxial SrTiO₃ thin films is presented. It is observed that at intermediate temperatures, a transition from degenerate to non-degenerate behavior is observed in the Seebeck coefficient, but not electrical conductivity, which is attributed to heterogeneous oxygen non-stoichiometry. Heikes formula is found to be invalid for the films with oxygen vacancies. By fitting the spectroscopic ellipsometry (SE) data, obtained in the range 300–2100 nm, using a Drude-Lorentz dispersion relation with two Lorentz oscillators, the electrical and optical properties of the films are extracted. Using the excellent agreement between the transport properties extracted from SE modeling and direct electrical measurements, we demonstrate that an increase in concentration of oxygen vacancies results in a simultaneous increase of both carrier concentration and electron effective mass, resulting in a higher power factor. © 2012 American Institute of Physics. [<http://dx.doi.org/10.1063/1.4767840>]

I. INTRODUCTION

SrTiO₃ (STO) exhibits a host of interesting phenomena ranging from being a quantum paraelectric insulator¹ to a ferroelectric under strain² and a metal³ or superconductor⁴ when doped and hence has been one of most extensively studied perovskite oxides. These diverse properties make it an attractive choice for many applications such as oxide-based electronics,⁵ photocatalysis, and as electrodes⁶ in solid oxide fuel cells. Recently, the presence of a two-dimensional electron gas at the bare surface of STO⁷ and at the interface of the polar STO with non-polar LaAlO₃ (LAO) has been demonstrated,⁸ triggering intense research from both fundamental and applications points of view.⁹ STO also holds huge promise as a thermoelectric material,¹⁰ due to its high effective mass (m^*) and tunable carrier density (n).¹¹ Since the discovery¹² of a high figure of merit (defined as $ZT = S^2\sigma T/\kappa$, where S , σ , and κ are, respectively, the Seebeck coefficient, electrical conductivity, and thermal conductivity)¹³ in p -type Na_xCoO₂, the search for an n -type counterpart has intensified, and electron doped STO has been regarded as a potential candidate. However, the high thermal conductivity¹⁴ of STO (3–10 W m⁻¹ K⁻¹) limits ZT , with a best reported value of 0.37 in 20% Nb doped STO bulk.¹⁵

The strategies to improve ZT of STO based thermoelectric materials involve enhancement of the electronic transport properties (referred to as the power factor, $S^2\sigma T$) and/or engineering the material to impede the phonon propagation to reduce κ . The former route relies on the tunable m^* of mobile electrons in STO, which is reported to be an order of magnitude higher than that of conventional semiconductors¹⁶ while the electrical conductivity can be varied by doping

with substitutional elements¹⁷ or by introducing oxygen vacancies (SrTiO_{3- δ}).¹⁸ While undoped STO is a wide band gap (~ 3.2 eV) insulator,¹⁹ doping with appropriate elements (e.g., La or Nd for Sr and/or Nb or Ta for Ti) or oxygen vacancies make the material semiconducting or metallic. However, substitutional doping is found to enhance carrier concentration only at the expense of Seebeck coefficient.

Though the role of oxygen vacancies in enhancing carrier concentration of oxides is well established, there has been no consensus on how oxygen vacancies affect m^* and hence the Seebeck coefficient. Recently, it has been reported²⁰ that oxygen vacancies enhance the low temperature mobility of STO thin films depending upon the thickness of the doped layer. However, for oxygen-deficient bulk undoped and La-doped STO, an enhancement of Seebeck coefficient at high temperatures has also been reported.²¹ Using *ab-initio* studies based on density functional theory, Wunderlich *et al.*²² showed that electronic effects in STO depend strongly on oxygen vacancy concentration. With smaller concentration of oxygen vacancies, m^* was shown to increase, while an opposite trend was predicted for higher concentrations. By assuming a scattering parameter, $r = 1$ (scattering by polar optical phonons), Ravichandran *et al.*²³ have deduced m^* from Boltzmann transport equation using the measured transport properties of double-doped STO films and concluded that m^* decreases with an increase in carrier concentration. For arriving at the results, they have assumed that oxygen vacancies lift the six-fold degeneracy of the conduction band to a four-fold one. This assumption, however, is valid only for high concentration of oxygen vacancies. By analyzing the transport properties, assuming a six-fold degenerate conduction band and $r = 2$ (scattering by impurity ions), Okuda *et al.*²⁴ have concluded that m^* increases with carrier concentration for bulk STO doped with La. To resolve the obvious contradictions in the literature as to the

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exact dependence of m^* on carrier concentration, further studies on elucidation of m^* are required, preferably with more than one technique.

Conventionally, m^* of semiconductors have been determined by the Shubnikov-de Hass effect,²⁵ optical methods,²⁶ photoemission spectroscopy,²⁷ and cyclotron resonance techniques,²⁸ or by solving the Boltzmann transport equation using a four coefficients method.²⁹ Alternatively, m^* may also be determined using spectroscopic ellipsometry (SE).³⁰ We have used SE in conjunction with high temperature (300–1000 K) thermoelectric measurements to bring out the dependence of m^* of carriers on the oxygen vacancy concentration in La-doped STO (LSTO) thin films grown by pulsed laser deposition (PLD). SE being a non-destructive technique was used to extract the optical as well as electrical properties of the double-doped films in a non-contact way. The results obtained by the two methods were compared and analyzed to bring forth the underlying physical mechanisms that govern m^* as well as the optical and thermoelectric properties of the films.

II. EXPERIMENTAL METHODS

LSTO films were prepared by pulsed laser deposition at a substrate temperature of 700 °C. A KrF excimer laser (248 nm wavelength, 20 ns pulse width, and 10 Hz repetition rate) was used for ablation using a $\text{Sr}_{0.98}\text{La}_{0.02}\text{TiO}_3$ target. A constant laser fluence of 6 J/cm^2 was maintained for 30 000 shots to complete the deposition after a 1000 shot pre-ablation of the target surface. The substrates were single side polished (100) oriented LAO of size $10 \times 10 \times 0.5\text{ mm}^3$. The substrates were cleaned ultrasonically in deionized water and isopropyl alcohol and jet-dried using high purity (5N) nitrogen gas. The deposition chamber was evacuated to a base pressure of less than 10^{-8} mbar, and the films were grown oxygen deficient by introducing 20 mTorr of high purity (5N) argon gas into the chamber using a mass flow controller.

The structure and phase purity of the films were identified using high resolution X-ray diffraction (HRXRD, Bruker-AXS D8 Discover) in the θ - 2θ geometry with $\text{Cu K}\alpha$ radiation and using a step size of 0.001° . The composition of the films was determined by Rutherford backscattering spectrometry (RBS, Kobelco), after depositing an identical film on Al_2O_3 substrate. SE parameters, ψ and Δ , were measured in the spectral range 300–2100 nm using an ellipsometer (UVISSEL ER, Horiba-Jobin Yvon). Measurements were performed at 295 K in air at three incident angles (60° , 65° , and 70°) using a Xe lamp. To fit the SE data, a mean-square algorithm was used, assuming a thin roughness layer/LSTO/LAO stack. The skin depth of incident electromagnetic radiation in a conducting film is expressed as $d = \sqrt{\rho\lambda_0/\pi\mu_0c}$, where ρ is the resistivity, λ_0 is the wavelength of the electromagnetic radiation in free space, μ_0 is the permeability of free space, and c is the velocity of light.³¹ For the LSTO films (with $\rho = 4\text{ m}\Omega\text{ cm}$), d varies from 160 to 420 nm in the spectral range 300 to 2100 nm. Since the thickness of the films ($\sim 215\text{ nm}$) is lower than d at higher wavelengths, the influence of the substrate had to be taken into account while fitting the SE data. The LAO substrate has a high band gap

($\sim 5.6\text{ eV}$)³² and is transparent in the range 300–2100 nm. However, the use of single-side polished substrates ensured that stray reflections from the sample stage are completely eliminated. For accurately representing the substrate, a reference spectrum of bare LAO was collected and used in the fitting procedure.

Hall effect measurements were carried out at 300 K with a four probe configuration (Physical Property Measurement System, Quantum Design). High temperature electrical conductivity and Seebeck coefficient were measured using linear four probe and differential methods, respectively, in the range 300–1000 K with a commercial setup (RZ2001i, Ozawa Science). Prior to the measurements, current-voltage (I-V) linearity checks were conducted at both low and high temperatures to ensure proper ohmic contacts. The high temperature measurements were performed in Ar/H_2 (4% H_2) and Ar gas. Since the total time taken for one complete high temperature measurement is $\sim 20\text{ h}$, the films may be considered as annealed in the ambient gas used for the measurement. In order to have a systematic study of the role of oxygen vacancies in determining the transport properties, SE and Hall effect measurements were carried out on films grown simultaneously. In addition, a clean laser window was used for every experiment to eliminate any run-to-run variation in laser fluence at the target due to coating on the laser window.³³ The thermoelectric films were then subjected to two cycles of thermoelectric measurement in Ar/H_2 (denoted by film A) and Ar gas (denoted by B).

III. RESULTS AND DISCUSSION

A. Structural and compositional characterizations

The epitaxial growth of the film on the lattice matched LAO substrate is evident from the strong (100) orientation of the films as observed in the out of plane (c -axis) HRXRD pattern in Bragg-Brentano (θ - 2θ) geometry shown in Fig. 1. The lattice constant of the as-grown film is $3.910\text{ \AA}$. A shift (shown as inset to Fig. 1) in the XRD peaks is observed for films A and B suggesting that annealing in Ar/H_2 and Ar

FIG. 1. Out-of-plane (c -axis) HRXRD pattern in θ - 2θ geometry for LSTO films. The epitaxial growth of films is clearly seen. Inset shows the shift in (200) peak position for films A and B annealed, respectively, in Ar/H_2 and Ar ambients.

influence the unit cell parameters of LSTO. The lattice constant of film A is found to be larger (3.911 Å) compared to that (3.906 Å) of B and can be explained based on oxygen vacancies. It has been reported in the *ab-initio* studies by Luo *et al.*³⁴ that Ti-Ti bond length is significantly greater than that of Ti-O-Ti and hence the oxygen vacancies bring forth a tetragonal distortion of the lattice. Annealing in Ar/H₂ creates more oxygen vacancies in film A, leading to an enhanced Coulomb repulsion of cations, which results in an increase in lattice parameter.³⁵ The crystallite size of the films is calculated to be ~50 nm, using the Scherrer formula and is found to be independent of annealing.

The RBS spectrum of the as-grown film on Al₂O₃ substrate is shown in Fig. 2 along with the simulated curve. The edges corresponding to the elements of the film are marked. Since the substrate is thick, signal from Al extends to lower energies and the oxygen peaks from the film as well as the substrate are superimposed on the Al plateau. The composition of the film is estimated to be 21.5% Sr, 0.5% La, 21.4% Ti, and 56.6% O. Since the La ions substitute for the Sr ions in LSTO films, the film is best represented as Sr_{1.07}La_{0.025}Ti_{1.07}O_{3-δ}, δ being 0.17. The small deviation from target stoichiometry is evidently due to the presence of Ar gas during film growth, which can affect the growth process by introducing oxygen vacancies.

B. Transport properties

The temperature dependence of electrical conductivity of the films is shown in Fig. 3. Electrical conductivity decreases with temperature, revealing a degenerate semiconducting nature. Heating in the forming gas ambient (Ar/H₂) leads to an outward diffusion of oxygen (reduction) leading to an increase in the concentration of oxygen vacancies in film A. The earlier *ab-initio* studies^{22,34} had predicted that the introduction of small oxygen vacancies would create an additional donor band about 0.3–0.4 eV below the conduction band minima. Hence, it is reasonable that an increase in concentration of oxygen vacancies results in an increase in carrier density and a corresponding decrease in electrical

FIG. 2. RBS spectra of the LSTO film. The symbols correspond to the experimental data, and the solid line to the simulated curve. The high energy edges corresponding to the constituent elements of the film are marked.

FIG. 3. Temperature variation of electrical conductivity of the films.

resistivity. However, during heating in the presence of Ar, presence of trace oxygen inside the measurement setup results in an inward diffusion of oxygen (oxidation) into the volume of film B through the film surface. The diffusing oxygen atoms occupy the grain boundaries, forming carrier trapping acceptor states, thereby reducing the itinerant carrier density. It is well established³⁶ that each ionized oxygen vacancy can account for two conduction electrons and hence the carrier density (n) decreases when the vacancy is filled by oxidation, resulting in a decrease in conductivity. The difference in conductivity of the films at 295 K after the high temperature measurements (see Table I) suggests that the changes effected by the ambient after a heating cycle are irreversible.

The carrier density and mobility of the films at 295 K are presented in Table I. The high carrier density of the films suggests that in addition to La dopants, ionized oxygen vacancies also contribute electrons to the conduction band. The influence of oxygen vacancy concentration to the transport properties is evident from the higher carrier density of film A compared to that of film B. The higher oxygen vacancy concentration also contributes scattering centers that limit the mobility of the films. For a highly degenerate electron gas, the mean free path of the carriers³⁷ is given by $l = (3\pi^2)^{1/3} \left(\frac{h}{2\pi} \right) \left(\frac{\sigma n}{e^2} \right)^{1/3}$, where h is the Planck's constant, σ is the electrical conductivity, and n , the carrier density. The electron mean free path of the films is evidently much smaller (see Table I) than the crystallite size of the films suggesting that in-grain scattering is predominant over grain boundary scattering. Since the carrier densities of the films are well in excess of 10^{20} cm^{-3} , the major scattering centers are doubly ionized oxygen vacancies and La ions, which contribute to scattering of carriers by ionized impurities. In semiconductors, the dominant scattering mechanisms are different at different regimes of temperature.³⁸ Much below the Debye temperature (513 K for undoped STO),³⁹ ionized impurity scattering dominates. Even at 300 K, acoustic phonon scattering can gradually set in and can become dominant at higher temperatures. For the LSTO films, the irreversible oxidation or reduction depending on the annealing ambient brings in additional changes to the underlying physical mechanisms that determine the transport properties and hence are to

TABLE I. Thermoelectric and optical properties of LSTO films at 295 K. The optical band gap (E_g), electrical conductivities measured directly (σ_{DC}) and extracted from SE modeling (σ_{opt}), ratio of effective mass to rest mass of electron (m^*/m_0), carrier density (n), mobility (μ), relaxation time (τ), mean free path of carriers (l), density of states of the conduction band (N_c), and Seebeck coefficients (S) are presented.

Film	E_g (eV)	σ_{DC} (S cm ⁻¹)	σ_{opt} (S cm ⁻¹)	m^*/m_0	n ($\times 10^{21}$ cm ⁻³)	μ (cm ² V ⁻¹ S ⁻¹)	τ (fs)	l (nm)	N_c ($\times 10^{19}$ cm ⁻³)	S (μ V K ⁻¹)
A	3.24	258	260	7.8	2.8	0.58	2.6	0.17	9.57	-230
B	3.24	133	137	3.2	0.9	0.96	1.8	0.19	2.52	-210

be considered as well. Taking all these into account, it is reasonable to expect different mechanisms driving the observable physical properties at different temperature regimes in LSTO films. High temperature mobility studies can bring forth further details in this regard, the absence of which makes it unproductive to comment further on the scattering processes.

Figure 4 shows the variation of Seebeck coefficient of the films with temperature. Absolute values of Seebeck coefficient increase with temperature for both the films and asymptotically approach a stable high temperature value. Such a non-monotonic temperature dependence is often explained using Heikes formula.⁴⁰ For perovskite titanates, the thermopower at the high temperature limit is expressed as⁴¹

$$S = -\frac{k_B}{e} \left(\frac{1 - \rho}{\rho} \right), \quad (1)$$

where k_B is the Boltzmann constant, e is the electronic charge, and ρ is the ratio of number of Ti³⁺ ions to that of Ti⁴⁺. For the LSTO films, the presence of two sources of doping, viz. La dopants and oxygen vacancies, has to be taken into account. Since both films A and B were simultaneously deposited, the La concentration is the same for both the films. Film A, with a higher oxygen vacancy concentration, should possess higher values of ρ and hence a lower absolute value of Seebeck coefficient compared to film B. However, the opposite is observed, implying that the Heikes formula, though qualitatively agreeing well with the observed asymptotic behavior of Seebeck

coefficient, is not valid for the films with oxygen vacancies. Moreover, a deviation from the saturation value is also observed in Fig. 4, at higher temperatures for both the films, at the regime where oxidation/reduction of the films sets in. Heikes formula cannot be used to explain the temperature variation of Seebeck coefficient since it gives only the high temperature limit wherein the configurational entropy is maximum. Additionally, Heikes formula does not show the trade-off between conductivity and Seebeck coefficient and cannot be used to predict the power factor.⁴²

Interestingly, the temperature dependence of Seebeck coefficient can be explained using an alternative mechanism, invoking non-homogenous distribution of vacancies and dopants. Since the electrical conductivity follows a degenerate semiconducting behavior, it is reasonable to assume that the Seebeck coefficient also follows the degenerate Fermi gas model. For a degenerate semiconductor, assuming parabolic band and an energy independent scattering, Seebeck coefficient varies with temperature as⁴³

$$S_T = \frac{8\pi^{8/3} k_B^2 m^* n^{-2/3}}{3^{5/3} h^2 e} (r + 1) T, \quad (2)$$

where n is the carrier density, k_B is the Boltzmann constant, h is the Planck's constant, e is the electronic charge, and r is the scattering parameter, which varies with the scattering mechanism under consideration. However, the Seebeck coefficient is not linear in T for the entire temperature range. Assuming $r = 2$ (ionized impurity scattering) for the LSTO films, the m^* of the carriers around 300 K can be estimated from the slopes of the linear fits to the S - T curves below 375 K. Clearly, oxygen vacancies play a crucial role in determining m^* of the films. Film B, with higher mobility as a direct consequence of having lower oxygen vacancy concentration, has the lowest m^* and hence the lowest Seebeck coefficient (see Table I). However, a complete understanding of the exact dependence of m^* on the mobility of the films is rather difficult and would require high temperature Hall effect studies. Nevertheless, the dependence of m^* on oxygen vacancies and hence the mobility can be explained by considering the lower lattice parameter in film B. In LSTO, the bottom of the conduction band is mainly comprised of Ti 3d orbitals³⁴ and the screening of Coulomb repulsion of Ti ions due to the presence of oxygen atoms in the TiO₂ plane leads to an increase in the Ti 3d- t_{2g} orbital overlapping. Hence the band curvature increases and the carriers become "light."

At temperatures above 375 K, the Seebeck coefficient slowly deviates from the degenerate semiconducting nature and assumes a non-degenerate state. As shown as inset to

FIG. 4. Temperature dependence of Seebeck coefficient of the films. The linear fits to the low temperature region based on Eq. (2), assuming a degenerate conduction mechanism are also shown. Inset shows the variation of Seebeck coefficient with $\log T$. The slopes of the linear fits are around $-298 \mu\text{V K}^{-1}$ decade⁻¹ due to the setting in of a non-degenerate conduction mechanism at intermediate temperatures. The deviation at higher temperatures is due to the oxidation/reduction of the films depending on the ambient.

Fig. 4, S varies linearly with $\ln(T)$, for film B, in accordance with the relation⁴⁴

$$S \propto \frac{-3K_B}{2e} \ln(T), \quad (3)$$

which is valid for a non-degenerate semiconductor. The slope obtained is in excellent agreement with the expected value of $-298 \mu\text{V K}^{-1} \text{ decade}^{-1}$. For film A, we observe deviations from the linear behavior at lower and higher temperatures. A non-degenerate Seebeck coefficient above 700 K has been previously reported in La-doped bulk STO ceramics.⁴⁵ It is to be noted here that there was no corresponding metal-semiconductor transition reflected in the temperature dependence of electrical conductivity of the films shown in Fig. 3. A possible reason may be the heterogeneous oxygen non-stoichiometry³⁶ within the volume of the film. Additionally, a non-homogeneous distribution of La dopants cannot also be ruled out. The oxygen vacancies partially ionize by localizing the conduction electrons and clustering of such vacancies, which is common in STO films grown by PLD,⁴⁶ and can act as localizing sites for the itinerant electrons.⁴⁷ The randomly distributed and clustered nature of oxygen vacancies in LSTO has been previously reported¹⁴ to influence the phonon transport. Hence it is reasonable that the co-existence of differently reduced regions in the films dictates the observed degenerate electrical conductivity and non-degenerate Seebeck coefficient. If the above argument is true, it would also imply that if the lightly reduced regions become more reduced or if the highly reduced regions become less reduced, the heterogeneous oxygen non-stoichiometry must vanish and the Seebeck coefficient should deviate from the non-degenerate behavior. At very high temperatures, a deviation from the non-degenerate behavior is indeed observed and can be attributed to the oxidation/reduction of the differently reduced regions of the films in the particular gaseous ambient, consistent with the changes observed in electrical conductivity at these temperatures.

C. Spectroscopic ellipsometry and validation of effective mass

The optical properties of the films vary as the wavenumber ($\tilde{\nu}$) of the radiation and can be described by the complex refractive index $n^*(\tilde{\nu}) = n(\tilde{\nu}) + ik(\tilde{\nu})$ or the complex dielectric function $\epsilon(\tilde{\nu}) = \epsilon_1(\tilde{\nu}) + i\epsilon_2(\tilde{\nu})$, where n is the refractive index, k is the extinction coefficient, and ϵ_1 and ϵ_2 are, respectively, the real and imaginary parts. n^* and ϵ are related by the expression $\epsilon(\tilde{\nu}) = n^{*2}(\tilde{\nu})$. In the wavelength under consideration (300–2100 nm), the dielectric function is determined by the electronic properties of the films. While absorption of radiation by free carriers is prominent at the near infra-red frequencies, absorption by bound electron-ion pairs determine the optical properties near the band gap⁴⁸ (ultraviolet-visible region) of the films. Hence, a linear combination of Drude model for free carriers and Lorentz oscillator model for the bound electrons can be used to completely describe the optical properties of the films in the region of

wavelengths probed. A complex dielectric function (ϵ^*) incorporating the two different models can be expressed as⁴⁹

$$\epsilon^* = \epsilon_\infty - \frac{\omega_p^2}{\omega^2 + i\omega\Gamma_\tau} + \sum_{k=1}^N \frac{A_k^2}{E_k^2 - \omega^2 - i\omega C_k}, \quad (4)$$

where the first two terms represent the Drude dispersion and the last term the Lorentz harmonic oscillator. In Eq. (4), ϵ_∞ is the high frequency dielectric constant, ω_p is the plasma frequency, Γ_τ is the damping constant (inverse of relaxation time, τ), and A_k , E_k , and C_k are, respectively, the amplitude, resonance energy, and damping of the k th harmonic oscillator.

SE spectra for the films are shown in Fig. 5. Using a mean square algorithm, the experimental data were fitted and best fits (by minimization of χ^2) could be obtained by considering $k=2$. The parameters used in the fitting are listed in Table II. Considerable differences in ω_p , Γ_τ , and E_k confirm the variation of oxygen concentration in the films. The extracted n and k for the films are shown in Fig. 6. For film B, the filling up of oxygen vacancies makes the film denser, and hence the refractive index is higher. For film A, the presence of more oxygen vacancies and hence the higher carrier concentration is reflected in the higher extinction coefficient due to the enhanced free carrier absorption, at longer wavelengths. It is important to note that optical band gaps of the films extracted from the SE analysis show negligible dependence on concentration of oxygen vacancies. In n-type semiconductors, at carrier densities higher than the density of states of the conduction band (N_c), the lowest states of the conduction band are occupied, leading to the broadening of the band gap

FIG. 5. Measured and simulated SE curves in the range 300–2100 nm for films A and B. Open circles correspond to the measured ψ , open rectangles to the measured Δ , while the lines correspond to the simulated curves for the three different incident angles (60° , 65° , and 70°).

TABLE II. Fitting parameters for the Drude-Lorentz dispersion relation (Eq. (5)) with two Lorentz oscillators for the films. The high frequency dielectric constant (ϵ_∞), plasma frequency (ω_p), damping constant (Γ_τ) of plasmons and amplitude (A_k), energy (E_k), and damping (C_k) of the k th harmonic oscillator are presented.

Film	Thickness (nm)	ϵ_∞	SE fitting parameters							
			Drude Part		Lorentz oscillator 1			Lorentz oscillator 2		
			ω_p (eV)	Γ_τ (eV)	A_1 (eV)	E_1 (eV)	C_1 (eV)	A_2 (eV)	E_2 (eV)	C_2 (eV)
A	214.7	2.004	0.704	0.256	174.176	4.589	1.621	144.003	1.525	0.894
B	214.5	2.008	0.619	0.376	176.646	4.621	1.608	139.634	1.499	0.910

FIG. 6. Extracted n and k as a function of wavelength for the films.

(the positive Burstein-Moss (BM) effect).⁵⁰ For LSTO films, the carrier densities are much higher than calculated using the relation $N_c = 2[(2\pi m^* kT)/\hbar^2]^{3/2}$ and hence a positive shift in band gap with increasing carrier density is to be expected. However, since the carrier densities are much higher than the Mott critical density⁵¹ ($\sim 10^{18} \text{ cm}^{-3}$), the positive BM effect is accompanied by a band gap shrinkage due to many body effects, and evidently these two effects largely cancel out each other in LSTO films, leaving the band gap unaltered.

Using the Drude parameters (ω_p and Γ_τ) extracted from the SE modeling, electrical conductivity, carrier density, and mobility of the films can be calculated using respectively the relations

$$\sigma_{opt} = \frac{\epsilon_0 \omega_p^2}{\Gamma_\tau}, \quad (5)$$

$$n_{opt} = \frac{m^* \epsilon_0 \omega_p^2}{e^2}, \quad (6)$$

$$\mu_{opt} = \frac{e}{m^* \Gamma_\tau}, \quad (7)$$

where ϵ_0 is the permittivity of free space and e is the electronic charge. Since Eq. (5) does not contain any microscopic transport parameters, the excellent agreement (see Table I) obtained between the calculated electrical conductivities and those obtained by direct electrical measurements (σ_{DC}) at 295 K, suggest the validity of the SE modeling and offers a pathway for extracting m^* by comparing the carrier concentrations and mobilities obtained from SE analysis and direct Hall measurements. The values of m^* thus extracted match exactly with those obtained from the analysis of

Seebeck coefficient, implying that grain boundary scattering is negligible in the films.⁵² Hence the validity of the earlier discussion on transport properties of the films based on predominant ionized impurity scattering at temperatures below the Debye temperature is established. From the consistency of the results, it is clear that m^* increases with oxygen vacancies demonstrating the prediction by Wunderlich *et al.*²² and confirming the findings on bulk LSTO by Okuda *et al.*²⁴ It is to be noted here that the growth conditions of our films are entirely different from what has been reported by Ravichandran *et al.*²³ and hence their observation that m^* decreases rapidly and remains nearly constant with increasing carrier concentration is not applicable to our films. The transport properties of the PLD grown STO films depend strongly on cation stoichiometry, which in turn varies with the deposition conditions⁵³ and hence a more meaningful comparison is not possible.

Evidently for the given growth conditions, by increasing the oxygen vacancy concentration by post deposition annealing, the carrier density as well as Seebeck coefficient of LSTO films can be increased, but only at the expense of mobility, which limits the electrical conductivity. Hence, from a thermoelectric perspective, for LSTO films with a fixed La concentration, there exists an optimum oxygen vacancy concentration for which the power factor is maximum. The power factor of the films as a function of temperature is plotted in Fig. 7. It is seen that film A has the highest power factor ($0.47 \text{ W m}^{-1} \text{ K}^{-1}$ at 510 K). It has been reported that oxygen vacancies effectively scatter phonons in STO, bringing in a marked reduction of lattice thermal conductivity¹⁴

FIG. 7. Calculated power factor-temperature product of the films as a function of temperature.

and hence the enhanced power factor will help improve ZT of STO based thermoelectrics. Further improvements may be possible by fine tuning m^* either by controlling the deposition parameters or by *ex-situ* annealing.

IV. SUMMARY

In summary, we have demonstrated the influence of oxygen vacancies on effective mass and the thermoelectric and optical properties of epitaxial SrTiO₃ films. By introducing oxygen vacancies, the carrier density and the effective mass of carriers are found to increase, which improve the electrical conductivity and Seebeck coefficient of the films. However, the simultaneous decrease in mobility of the carriers affects the electrical conductivity and hence limits the enhancement in power factor. The electrical transport properties of the films are dominated by scattering from ionized impurities. While electrical conductivity of the films follows a degenerate model in the entire temperature range of 300–1000 K, the Seebeck coefficient follows a degenerate model at temperatures below 375 K and a non-degenerate model at intermediate temperatures, which can be attributed to the heterogeneous oxygen non-stoichiometry.

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