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Modeling the transport properties of epitaxially grown thermoelectric oxide thin films using spectroscopic ellipsometry

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The influence of oxygen vacancies on the transport properties of epitaxial thermoelectric (Sr,La)TiO₃ thin films is determined using electrical and spectroscopic ellipsometry (SE) measurements. Oxygen vacancy concentration was varied by *ex-situ* annealing in Ar and Ar/H₂. All films exhibited degenerate semiconducting behavior, and electrical conductivity decreased (258–133 S cm⁻¹) with increasing oxygen content. Similar decrease in the Seebeck coefficient is observed and attributed to a decrease in effective mass (7.8–3.2 *m_e*), as determined by SE. Excellent agreement between transport properties deduced from SE and direct electrical measurements suggests that SE is an effective tool for studying oxide thin film thermoelectrics.

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SrTiO₃ (STO) is a cubic perovskite possessing a wide variety of interesting properties which make it attractive for diverse technological applications.^{1–3} Stoichiometric STO is a band insulator with a wide band gap of ~3.2 eV.^{4,5} In addition, undoped STO exhibits a high Hall mobility⁶ of >10⁴ cm² V⁻¹ s⁻¹ and a high dielectric constant and hence is investigated for its dielectric, piezoelectric, and optoelectronic properties. By introducing oxygen vacancies^{4,7} or by doping with La³⁺ or Nb⁵⁺ ions,^{8,9} STO can be made n-type semiconducting or degenerate.^{10–13} Owing to its structural and chemical stability at high temperatures⁹ and a high electron effective mass,¹⁴ electron doped STO thin films are considered as excellent candidates for high temperature thermoelectric applications.^{3,15,16}

For accurate description of Seebeck coefficient of thin films, the effective mass of carriers and scattering parameter need to be determined together with the transport properties such as electrical conductivity, carrier concentration, and mobility. Traditional methods for probing the Fermi surface and determining the carrier effective mass using de-Haas-van Alphen and other resonance techniques require that the mobility and relaxation time of the carriers be quite large, which is not applicable for doped STO films that possess low mobility and short relaxation time. Another method to determine the effective mass is to solve the Boltzmann transport equation using the measured values of electrical conductivity, Hall, Seebeck, and Nernst coefficients that requires special instruments and careful sample preparation.¹⁷ For STO based thin film thermoelectric materials, the effective mass is often determined from the temperature variation of Seebeck coefficient, using suitable theoretical models,¹⁸ assuming the scattering parameter.⁹ Large effective mass has been calculated for doped STO using *ab-initio* methods.^{14,19} Optical methods such as spectroscopic ellipsometry (SE) is used to determine effective mass and scattering effects in conduct-

ing thin films, for example degenerate transparent conducting oxides.^{20,21} SE, being a non-destructive and non-invasive technique, can be effectively used in extracting the thickness, composition, and phase of the films. By employing suitable theoretical dielectric functions to fit the ellipsometry data, contactless determination of electrical properties of the films is possible.²² Hence, it is worthwhile to investigate the possibilities of extracting effective mass of doped STO films using SE and applying it in determining the Seebeck coefficient. Here, we report the transport properties of La doped STO (LSTO) films determined by SE and direct electrical methods and compare the measured Seebeck coefficients with that calculated using an appropriate theoretical model.

LSTO films have been prepared by pulsed laser deposition technique on LaAlO₃ ⟨100⟩ (LAO) substrates (10 × 10 × 0.5 mm³) held at a temperature of 700 °C. A KrF excimer laser (248 nm wavelength, 20 ns pulse width, and 10 Hz repetition rate) was used for ablation from a Sr_{0.98}La_{0.02}TiO₃ target. A constant laser fluence of 6 J cm⁻² was maintained for 30 000 shots to complete the deposition, following a pre-ablation of 1000 shots to clean the target surface. The films were grown oxygen deficient by introducing 20 mTorr of high purity (5 N) Ar into the chamber using a mass flow controller. As-deposited films (denoted by A) were annealed *ex-situ* in Ar/H₂ (4% H₂) and Ar gas (denoted by B and C, respectively), the former gas help trap residual oxygen in the furnace, making the films oxygen deficient while the latter cannot trap oxygen, resulting in films with more oxygen concentration.

The structure and phase purity of the films were identified using high resolution x-ray diffraction (HRXRD) technique (Bruker-AXS D8 Discover) employing the θ - 2θ geometry with Cu K α radiation and using a step size of 0.001°. The growth of epitaxial LSTO film on the LAO ⟨100⟩ substrate can be observed from the HRXRD pattern shown in Fig. 1. The lattice parameter of films A and B was identical (3.911 Å) and larger compared to that (3.906 Å) of film C and can be explained based on oxygen vacancies.

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FIG. 1. HRXRD pattern in the θ - 2θ geometry for the LSTO film on LAO (100) substrate.

Films A and B contain more oxygen vacancies which lead to enhanced Coulomb repulsion of cations in the TiO_2 or SrO planes, resulting in an increase in lattice parameter.²³ The crystallite size of the films is calculated to be ~ 50 nm, using the Scherrer formula. The composition of the films was determined by Rutherford backscattering spectroscopy yielding La concentration identical to that of the target. Electrical conductivity and Hall effect were measured at 295 K with a four probe configuration using a physical property measurement system (Quantum Design Physical Property Measurement System). High temperature electrical conductivity and Seebeck coefficient were measured using linear four probe and steady state techniques, respectively, in the temperature range 300–700 K using a commercial setup (Ozawa RZ2001i). To ensure that the contacts are ohmic, systematic I-V linearity checks were conducted at low and high temperatures.

SE parameters I_C and I_S were measured *ex situ* in the range 300–2100 nm at room temperature using an ellipsometer (Horiba-Jobin Yvon UVISSEL ER). The parameters I_C and I_S are linked to the ellipsometric angles ψ and Δ by the relations $I_C = \sin 2\psi \cdot \cos \Delta$ and $I_S = \sin 2\psi \cdot \sin \Delta$. Measurements were performed at 295 K in air at three incident angles (60, 65, and 70°) using a Xe lamp. The skin depth in a conducting film with high density of carriers is expressed as $\delta = \sqrt{\rho \lambda_0 / \pi \mu_0 c}$, where ρ is the resistivity, λ_0 is the wavelength of the electromagnetic radiation in free space, μ_0 , the permeability of free space, and c , the velocity of light. For the LSTO films, δ varies from 160 to 420 nm in the spectral range 300 to 2100 nm. Since the thickness of the films (~ 215 nm) is lower than δ at higher wavelengths, the influence of the substrate had to be taken into account while fitting the SE data. To incorporate the substrate and to model the film/substrate interface, a reference spectrum for the bare LAO substrate was used and an air/roughness layer/LSTO/LAO stack having three interfaces was considered in the modeling to accurately represent the samples under test.

The optical properties of the films depend on the wave-number ($\tilde{\nu}$) of the radiation and can be described by the complex dielectric function $\epsilon(\tilde{\nu}) = \epsilon_1(\tilde{\nu}) + i\epsilon_2(\tilde{\nu})$, where ϵ_1 and ϵ_2 are, respectively, the real and imaginary parts. In the

wavelength range of 300–2100 nm, electronic properties of the films dominate the dielectric function. A combination of Drude and Lorentz oscillator models can be used to fully describe the optical properties of the films, the former model being more prominent at higher wavelengths where free carriers absorb the radiation and the latter at lower wavelengths, near the band gap of the material.²⁴ For the LSTO films, we use a complex dielectric function (ϵ^*) given by

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

where the first two terms represent the Drude dispersion due to free carrier absorption and the last term the Lorentz oscillator model. In Eq. (1), ϵ_∞ is the high frequency dielectric constant, ω_p is the plasma frequency, Γ_τ is the damping constant whose inverse is the relaxation time, and A_k , E_k , and C_k are, respectively, the amplitude, energy, and damping of the harmonic oscillator.

Figure 2 shows the measured SE spectra (I_C and I_S) for the films. The data were fitted using a mean square algorithm

FIG. 2. (Color online) SE spectra of the films measured at three angles of incidence. The symbols correspond to the experimental data and the lines correspond to the fit using Eq. (1).

TABLE I. Parameters used for fitting the SE data using Eq. (1) with two Lorentz oscillators. ϵ_∞ is the high frequency dielectric constant, ω_p is the plasma frequency, Γ_τ is the damping constant, and A_k , E_k , and C_k are, respectively, the amplitude, energy, and damping of the k^{th} harmonic oscillator.

Sample	SE fitting parameters								
	Drude			Lorentz Oscillator 1			Lorentz Oscillator 2		
	ϵ_∞	$\omega_p(\text{eV})$	$\Gamma_\tau(\text{eV})$	$A_k(\text{eV})$	$E_k(\text{eV})$	$C_k(\text{eV})$	$A_k(\text{eV})$	$E_k(\text{eV})$	$C_k(\text{eV})$
A	2.036	0.734	0.286	177.285	4.609	1.677	141.886	1.433	0.873
B	2.004	0.704	0.256	174.176	4.589	1.621	144.003	1.525	0.894
C	2.008	0.619	0.376	176.646	4.621	1.608	139.634	1.499	0.910

and best fits (by minimization of χ^2) could be obtained by considering two Lorentz oscillators. The parameters used for the fit are listed in Table I. The electrical conductivity, carrier concentration, and mobility of the films can be extracted from the Drude model by using, respectively, the relations

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

$$n = \frac{m^* \epsilon_0 \omega_p^2}{e^2}, \quad (3)$$

$$\mu = \frac{e}{m^* \Gamma_\tau}, \quad (4)$$

where $m^* = x m_0$ is the effective mass of the electrons, x being a constant and m_0 , the rest mass of electrons, ϵ_0 is the permittivity of free space, and e is the electronic charge. The mean free path of the carriers was also determined using the relation $l = (3\pi)^{1/3} \left(\frac{h}{2\pi} \right) (\sigma / e^2 n^{2/3})$, which is true for a highly degenerate electron gas.²⁵

For electron concentration above 10^{20} cm^{-3} , the Hall mobility is dominated by scattering due to ionized impurities.²⁶ Since the mean free path (l) of electrons is much smaller (see, Table II) than the crystallite size ($\sim 50 \text{ nm}$) in the films, in-grain (ionized impurity) scattering dominates Γ_τ and hence the optical mobility. Also, the Debye temperature²⁷ (θ_D) of STO is 513 K and scattering by ionized impurities is the predominant mechanism at temperatures below θ_D . Hence, it is reasonable to assume that grain boundary scattering is negligible in the films and mobility determined from Hall effect and SE measurements are identical, leading to the extraction of effective mass of the carriers. The transport properties of the films determined from SE modeling and direct electrical measurements are presented in Table II and excellent agreement of the properties is obtained for the extracted values of effective mass, which validates the assumption of predominant grain boundary scattering. The effective mass determined for the films match well with

those reported for doped STO.^{14,19} High carrier concentration of films A and B is due to oxygen vacancies, each of which donates two electrons, in addition to the La dopants that donate one electron each to the conduction band. Due to oxidation, film C has the lowest value of carrier concentration and resistivity, even though mobility is higher due to the filling up of oxygen vacancies which otherwise act as defect centers and scatter the carriers. The effective mass of film C is much lower and can be explained based on the decrease in lattice parameter, i.e., decrease in the distance between the two neighboring Ti ions, which leads to an increase in the Ti $3d-t_{2g}$ orbital overlapping.

Figure 3 shows electrical conductivity and Seebeck coefficient of the films in the temperature range 300–1000 K. Electrical conductivity decreases with temperature, which is characteristic of a degenerate semiconductor. The negative value of the Seebeck coefficient implies that electrons serve as the majority carriers. The measured Seebeck coefficients are slightly higher than those reported for molecular beam epitaxy grown LSTO films with similar carrier concentrations, but since the carrier mobility was not reported,²⁸ a meaningful comparison is not possible. For a highly degenerate semiconductor with parabolic bands, S is given by^{29,30}

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

where k_B is the Boltzmann constant, h is the Planck's constant, and r is the scattering parameter. For scattering by ionized impurities, $r = 2$. With the extracted value of effective mass from the combined SE and Hall effect studies, Seebeck coefficient at 295 K is calculated for the films using Eq. (5) and the results are presented in Table II. The excellent agreement between the calculated (S_{cal}) and measured values validates the determination of effective mass from SE modeling.

In summary, we have determined the transport properties of LSTO films by SE modeling, using a complex dielectric function, and compared those to that obtained by

TABLE II. Electrical properties and Seebeck coefficient of the films at 295 K, measured directly and calculated using SE parameters. σ_{DC} and σ_{Opt} are, respectively, the conductivities measured directly and calculated using SE data. m^* is the effective mass extracted assuming identical carrier concentration (n) and mobility (μ) from SE and Hall measurements. l is the mean free path, while S and S_{cal} are, respectively, the Seebeck coefficients measured directly and calculated using Eq. (5).

Sample	$\sigma_{\text{DC}}(\text{S cm}^{-1})$	$\sigma_{\text{Opt}}(\text{S cm}^{-1})$	m^*/m_0	$n(\times 10^{21} \text{ cm}^{-3})$	$\mu(\text{cm}^2 \text{ V}^{-1} \text{ s}^{-1})$	$l(\text{nm})$	$S(\mu\text{V K}^{-1})$	$S_{\text{cal}}(\mu\text{V K}^{-1})$
A	247	253	7.6	2.9	0.53	0.16	−227	−219
B	258	260	7.8	2.8	0.58	0.17	−230	−233
C	133	137	3.2	0.9	0.96	0.19	−210	−206

FIG. 3. (Color online) Electrical conductivity and Seebeck coefficient of the films measured as a function of temperature.

electrical measurements. Excellent agreement has been obtained for carrier concentration, electrical conductivity, and Seebeck coefficient measured directly and calculated assuming highly degenerate conduction. The results suggest that SE can be an effective tool in determining the transport properties of degenerately doped oxide thermoelectric thin films.

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