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ABSTRACT

We report the spectroscopy ellipsometry study for LaCoO$_3$ epitaxy thin films grown on different SrTiO$_3$ substrates [LCO/STO(001) and LCO/STO(111)]. Reciprocal space mapping measurements show that the as-prepared LCO/STO films are fully strained at the interface. The optical constants (the refractive index and the extinction coefficient) of LCO films from 300 K to 800 K are obtained based on the ellipsometry measurements. The optical absorption at the near-infrared region increases with heating and sharply enhances around 500 K due to the occurrence of insulator–metal transition. The observed isosbestic point reveals the evolution of the band structure along with the insulator–metal transition. The red shift of the isosbestic point from the (001) sample to the (111) sample indicates the important role interfacial strain plays in affecting the spin states. We also provide the optical conductivity and the relative effective number of interband transition electrons for different energy regions.

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Perovskite cobalt oxide LaCoO$_3$ (LCO) is a nonmagnetic insulator with rhombus distortion.$^1$–$^3$ Most of its properties are fascinating and lead to many potential applications including gas sensors and solid oxide fuel cells.$^4$ The $3d$ orbital of cobalt splits into the triple degenerate $t_{2g}(d_{xy}, d_{xz}, d_{yz})$ low state and the double degenerate $e_g(d_{z^2}, d_{x^2-y^2})$ upper state in the crystal field. The Co$^{3+}$ ions show a $3d^6$ electron configuration with a low spin diamagnetic ground state, fully occupying the $t_{2g}$ level ($t_{2g}^6S = 0$). The properties of LCO could be modulated by the interaction among the crystal field, Hund exchange energy, multiple state effect, and spin-orbital coupling. With the increase in temperature, the electrons at the $t_{2g}$ ground state can be thermally excited to the $e_g$ state, which makes the Co$^{3+}$ ions transform from the low spin state to the magnetic intermediate spin state ($t_{2g}^5e_g^1S = 1$) or the high spin state ($t_{2g}^4e_g^2S = 2$),$^5$–$^8$ consequently leading to a major change in electronic and magnetic properties. LCO transfers into the paramagnetic state, accompanied by a sharp increase in magnetic susceptibility at 100 K, and further undergoes an insulator–metal transition at 500 K.$^{12,13}$

So far, it has been disputed whether the nature of the cobalt ion spin state at high temperature is the high spin state or the intermediate spin state.$^{14}$–$^{20}$ On the one hand, the paramagnetic transition at 100 K was considered as a crossover from low spin to high spin. On the other hand, by means of local density approximation (LDA) with Hubbard $U$, the low spin to intermediate spin crossover was suggested.$^{17}$ The experimental and theoretical supports for these two points of view have been extensively reported. Such a long-standing
divergence reveals the complexity of LCO, which requires a better understanding of the nature of high temperature transition.

Spectroscopic ellipsometry (SE) is a clean, fast, and powerful optical method to characterize the optical properties and the electronic structure with strong electron correlation, especially for materials with an electric phase transition (e.g., insulator–metal transition).21,22 The SE data ($\Psi, \Delta$) can be expressed using the following formula:

$$\rho = \frac{R_p}{R_s} = \tan \Psi e^{i \Delta},$$  

where $R_p$ and $R_s$ are the reflection coefficients for $p$- and $s$-polarization, respectively. Combining SE data and the appropriate physical model, the optical constants and the dielectric function can be extracted, and then, the band structure in the UV/visible region and absorption in the infrared region can be obtained for some materials. However, until now, SE works for LCO were rarely reported.23,24 In this work, we performed an SE study on LCO thin films grown on SrTiO$_3$ (STO) substrates with (001) and (111) orientations. The optical constants through insulator–metal transition were obtained for LCO films at different temperatures. We also show the optical conductivity and the relative effective number of interband transition electrons in different energy regions separated by the observed isosbestic points.

LCO thin films were grown with the pulsed laser deposition (PLD) method on STO substrates with different orientations of (001) and (111). X-ray diffraction (XRD) with Cu K$_\alpha$ radiation (Rigaku, TTR III) was introduced to identify the phase and growth orientations of as-prepared samples. Reciprocal space mapping (RSM) was employed to study the interfacial strain between STO substrates and LCO films. X-ray reflection (XRR) was used to determine the thickness of the LCO thin films.

Temperature dependent SE data from 300 K to 800 K were measured using a rotating-polarizer SE (J.A. Woollam Co., Inc. M-2000U). The incident angle was kept at $70^\circ$. Because the LCO film is not affected by oxygen during heating, the experiment was performed under an air condition.

Figure 1(a) shows the XRD patterns for LCO epitaxial films grown on STO(001) and STO(111). Some groups reported that both the perovskite LCO and STO bulk materials possess a cubic structure with the space group $Pm-3m$, and the experimental measured lattice constants are 3.820 Å and 3.899 Å, respectively.25,26 In this picture, the LCO epitaxial films show noticeable (001) and (111) diffraction peaks along with the peak of STO substrates. The LCO diffraction peaks appear at higher angles, indicating smaller lattice constant formation. The patterns clearly identify that LCO films are epitaxially grown on the STO single crystal substrate along with the same orientation.

Figure 1(b) shows the small angle XRR results for as-prepared LCO/STO samples. The period of finite size Fresnel oscillation around the diffraction peak allows us to calculate the thickness of the films using the fundamental Bragg equation:

$$2d \sin \theta = n\lambda,$$  

where $d$ and $\lambda$ represent the thickness of the LCO film and the x-ray wavelength, respectively. The calculated thicknesses are 12.43 nm for the LCO/STO (001) film and 9.80 nm for the LCO/STO (111) film, as seen in Fig. S1.

The RSM technique is employed to study the interfacial strain for LCO films on STO substrates with different orientations. The (311) and (211) planes were chosen for measurements of LCO/STO(001) and LCO/STO(111) samples, respectively. Figures 1(c) and 1(d) display the corresponding RSM images. The
two pictures illustrate that the (0LL) direction shows no obvious difference between LCO and STO, suggesting that the LCO growth is in the plan lattice parameters, similar to the STO substrates, and can be considered as fully strained. However, the LCO (H00) direction gives a broad diffraction profile for both films, which confirms the formation of a highly strained interface between the substrate and epitaxial films. Based on these results, the calculated lattice constants of LCO films on STO(001) and STO(111) are 3.765 Å and 3.751 Å, respectively. The smaller lattice constants a for LCO films as compared to 3.820 Å for bulk LCO indicate the fully strained state in nature.

Next, we turn to the analysis of SE measurement data. Considering the optical response of LCO/STO films, we established an optical model containing the LCO sample layer and the STO substrate layer. Surface roughness is neglected from a contrast fit with and without roughness. The optical constants of the STO substrate are obtained by a separate measurement, as shown in Fig. S2.

The optical constants of the LCO layer were parameterized by a B-spline function. The B-spline curve is defined by a series of monotone non-decreasing knots, and the knot recursive polynomial is expressed as follows:

\[ B^k_i(x) = \begin{cases} 1 & (t_i \leq x < t_{i+1}) \\ 0 & \text{otherwise} \end{cases}, \]

\[ B^k_i(x) = \left( \frac{x - t_i}{t_{i+k} - t_i} \right) B^{k-1}_{i} + \left( \frac{t_{i+k+1} - x}{t_{i+k+1} - t_{i+1}} \right) B^{k-1}_{i+1}(x), \]

where \( t_i \) is the \( i \)th knots, and \( B^k_i(x) \) represents the \( k \)th B-spline basis function for the \( i \)th knots. By addition of every knot polynomial, the B-spline curve \( S(x) \) can be expressed as

\[ S(x) = \sum_{i=1}^{n} c_i B^k_i(x). \]

In order to guarantee that the optical constants are consistent with the Kramers–Kronig analysis, B-spline with applied Kramers–Kronig analysis is used in this analysis.\textsuperscript{27}

The experimentally measured and model fitted SE data \((\Psi, \Delta)\) for LCO/STO(001) and LCO/STO(111) at 300 K and 800 K agree with each other well, as seen in Fig. 2. The \((\Psi, \Delta)\) data evidently display a different profile between 300 K and 800 K due to the insulator–metal transition.

The obtained optical constants for LCO/STO samples at different temperatures are shown in Fig. 3. With the increase in temperature, the refractive index decreases for wavelengths higher than 600 nm. At the same time, the extinction coefficient increases at the near-infrared region, heralding the occurrence of band gap closing. Infrared optical absorption directly connects to the behavior of low energy free carriers. This phenomenon reveals the increases in carrier concentration and mobility in LCO upon heating, which represents a typical signal for insulator–metal transition.\textsuperscript{26,29} The optical absorption near IR abruptly elevates around 500 K, as seen in Fig. 3, concluding that the transition occurs at this temperature and is consistent with the previous report.\textsuperscript{31} Drude and Gaussian oscillators fitting of the dielectric functions provide the quantitative analysis support, as shown in Fig. 4. The fitting parameters of Drude oscillators are shown in Table I. The decreasing dc resistivity \( \rho \) accompanies with the increasing mean scattering time \( \tau \) from 300 K to 800 K, implying the decrease in resistivity and scattering of carriers. When cooling back to 300 K, the optical constants recover to the initial state, indicating that the insulator–metal transition is reversible.

Noticeably, the extinction coefficient curves at different temperatures intersect at one point. Such a type of point is defined as an isosbestic point, which is a fingerprint for insulator–metal transition.\textsuperscript{26} This isosbestic point in LCO emerges due to the spectral weight transfer from a higher-lying interband transition region to the lower-energy free carrier absorption region. Essentially, this is caused by the change in the band structure. The isosbestic points for LCO/STO(001) and LCO/STO(111) are located at 515 nm and 600 nm, respectively. The wavelength shift between two isosbestic points connects with the detailed band structure variation, which comes from the small difference in the interfacial strain and the spin state in LCO, as mentioned.\textsuperscript{31}
FIG. 3. Optical constants as a function of wavelength for as-prepared samples at different temperatures: (a) the refractive index and (b) the extinction coefficient for the LCO/STO (001) sample and (c) the refractive index and (d) the extinction coefficient for the LCO/STO (111) sample. The arrows indicate the isosbestic points for two different samples.

FIG. 4. Oscillator fitting of the LCO dielectric functions: (a) and (b) represent fitting for LCO/STO (001) at 300 K and 800 K, respectively and (c) and (d) represent fitting for LCO/STO (111) at 300 K and 800 K, respectively.

TABLE I. Drude oscillator fitting parameters for LCO films.

| LCO/STO Sample | $\rho$ (Ω/cm) | $\tau$ (fs) |
|-----------------|--------------|------------|
| (001) 300 K     | 0.004 144    | 0.031      |
| (001) 800 K     | 0.001 109    | 0.203      |
| (111) 300 K     | 0.004 317    | 0.025      |
| (111) 800 K     | 0.001 050    | 0.259      |

To have a deep insight into the variation of the band structure in LCO upon insulator–metal transition, we calculate the optical conductivity through the obtained optical constants according to the formula

$$\sigma = \frac{\varepsilon_2 \omega}{4\pi},$$

where $\varepsilon_2 = 2nke_0$ is the imaginary part of the dielectric function, and $\omega$ is the photonic frequency. The calculated optical conductivity spectra for LCO/STO(001) and LCO/STO(111) at different...
temperatures are shown in Figs. 5(a) and 5(b). These spectra can be clearly divided into four regions according to the three observed isosbestic points at around 1.5 (2.05) eV, 4 eV, and 4.5 eV. Based on the density functional theory (DFT) and dynamical mean field theory (DMFT) calculation of band structure, we assign an optical absorption at 0.7 eV ∼ 1.5 eV (0.7 eV ∼ 2.05 eV) for the interband transition from Co $t_{2g}$ to $t_{2g}$ and $t_{2g}$ to $e_g$ and an optical absorption at 1.5 eV ∼ 4 eV (2.05 eV ∼ 4 eV) for the interband transition from O 2$p$ to Co $e_g$. The increase in the low energy region interband transition indicates the increase in transition from $t_{2g}$ to $e_g$, which is a signal of the increase in Co ions from low spin states to high spin states.

To quantitatively analyze the results, we consider the effective number of electrons $N_{\text{eff}}$ associated with the particular interband transition, which is defined as

$$N_{\text{eff}} = \frac{2m_0}{\pi e^2 N} \int_{E_1}^{E_2} \sigma(E) \, dE,$$

where $m_0$ represents the mass of a free electron, and $N$ is the number of Co atoms per unit volume. To pay more attention to the spectral weight transfer, the relative effective number of interband transition electrons $R_{\text{eff}}$ is introduced by comparing with that at 300 K, which can be defined by the following equation:

$$R_{\text{eff}}(T, E_1 \sim E_2) = \frac{N(T, E_1 \sim E_2) - N(300K, E_1 \sim E_2)}{N(300K, E_1 \sim E_2)}.$$

The calculated relative effective number of electrons as a function of temperature is shown in Figs. 5(c) and 5(d) for both LCO/STO(001) and LCO/STO(111). There is a clear increase in the effective number of interband transition electrons at 0.7 eV ∼ 1.5 eV (0.7 eV ∼ 2.05 eV) and a decrease in the effective number of interband transition electrons at 1.5 eV ∼ 4 eV (2.05 eV ∼ 4 eV), which is consistent with our observation. On the other hand, the increase in higher energy regions may be related to the transition to higher energy bands of the $e_g$ orbital, which needs further consideration.

In summary, we investigated the optical properties of LCO epitaxial thin films on STO with (001) and (111) orientations through high temperature insulator-metal transition. The RSM images confirm the fully strained interface between LCO and STO. Based on the temperature dependent SE data, we obtained the optical constants of LCO films at different temperatures. The optical absorption increases with the increase in temperature in the low energy region due to the increase in free carrier concentration and mobility. A significant spectral weight transfer is observed across the isosbestic point, which is related to band structure variation. The shift in the isosbestic point between different orientation samples reveals the strain effect on the spin states. The optical conductivity and the relative effective number of interband transition electrons are also provided for different energy regions, which are divided by the three observed isosbestic points.

See supplementary material for the fitting of XRR results and the optical constants of STO.

**AUTHORS’ CONTRIBUTIONS**

Q.C. and X.W. contributed equally to this work.

This work was financially supported by the Science Challenge Project (Grant No. TZ2016001).

**DATA AVAILABILITY**

The data that supports the findings of this study are available within the article [and its supplementary material].

**REFERENCES**

1. P. M. Raccah and J. B. Goodenough, Phys. Rev. 155, 932 (1967).
2. K. Asai, P. Gehring, H. Chou, and G. Shirane, Phys. Rev. B 40, 10982 (1989).
3. M. Itoh, M. Sugahara, I. Natori, and K. Motoyoi, J. Phys. Soc. Jpn. 64, 3967 (1995).
4. S. Yamaguchi, H. Okimoto, H. Taniguchi, and Y. Tokura, Phys. Rev. B 53, R2926 (1996).
5. R. Mahendiran and A. K. Raychaudhuri, *Phys. Rev. B* **54**, 16044 (1996).
6. C. H. Chen, H. J. M. Bouwmeester, R. H. E. van Doorn, H. Kruithof, and A. J. Burggraaf, *J. Solid State Ionics* **98**, 7 (1997).
7. N. Orlovskaya, K. Kleveland, T. Grande, and M. A. Einarsrud, *J. Eur. Ceram. Soc.* **20**, 53 (2000).
8. G. H. Jonkar and J. H. VanSanten, *Physica* **19**, 120 (1953).
9. V. G. Bhade, D. S. Rajoria, C. N. R. Rao, G. R. Rao, and V. G. Jadhao, *Phys. Rev. B* **12**, 2832 (1975).
10. G. Thornton, F. C. Morrison, S. Partington, B. C. Tofield, and E. Williams, *J. Phys. C: Solid State Phys.* **21**, 2871 (1988).
11. M. A. Senaris-Rodriguez and J. B. Goodenough, *J. Solid State Chem.* **118**, 323 (1995).
12. G. Thornton, F. C. Morrison, S. Partington, B. C. Tofield, and E. Williams, *J. Phys. C: Solid State Phys.* **21**, 2871 (1988).