Infrared optical properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$ epitaxial films

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The reflectance of La$_{0.7}$Ca$_{0.3}$MnO$_3$ epitaxial thin films on perovskite substrates with a range of lattice constants is studied in the frequency range 50–5000 cm$^{-1}$. The complex dielectric functions of the bare La$_{0.7}$Ca$_{0.3}$MnO$_3$ films are obtained by modeling the measured reflectivity spectra of the two-layer La$_{0.7}$Ca$_{0.3}$MnO$_3$/substrate system with separately measured dielectric functions of the bare substrate. The results thus derived indicate that the internal optical phonon modes of the MnO$_6$ octahedra are strongly affected by the substrate-induced lattice distortion. © 1997 American Institute of Physics.

The origin of the colossal negative magnetoresistance (CMR) recently observed in perovskite manganites La$_{1-x}$A$_x$MnO$_3$ (A: divalent alkaline ions) have been a subject of intense experimental and theoretical studies. Recent theoretical investigations have revealed that the lattice effects and the strong electron–phonon interaction due to the Jahn-Teller coupling play an important role in the occurrence of the CMR in manganites. Many aspects of the magnetic and resistivity data can be successfully explained in terms of the scenario of lattice polaron conduction. In order to further verify the mechanism of the CMR effect and the correlation of lattice distortion with the magnetic and transport properties, infrared data are needed for providing direct information of the optical phonon modes and the electron–phonon interaction.

The investigations of the electrical transport and magnetic properties of La$_{0.7}$Ca$_{0.3}$MnO$_3$ (LCMO) films on perovskite substrates with different lattice constants indicate that larger lattice distortion induced by the substrates gives rise to larger zero-field resistivity and larger negative magnetoresistance. In the present work we report our experimental investigations of the infrared properties of LCMO epitaxial films on various perovskite-based substrates: LaAlO$_3$(LAO), SrTiO$_3$(STO) and YAlO$_3$(YAO). Infrared (IR) reflectivity spectra of single crystalline LAO, STO and YAO are also measured. Using the dielectric functions obtained directly from the bare substrate, we have fitted the measured reflectivity spectra of LCMO films on the substrates by modeling the complex dielectric functions of bare LCMO. Our work indicates that the optical conductivity of LCMO and the observed Mn-O stretching and Mn-O–Mn bending phonon modes are strongly affected by substrate induced lattice distortion.

The LCMO epitaxial films are grown by pulsed laser deposition using a stoichiometric target of La$_{0.7}$Ca$_{0.3}$MnO$_3$ in 100 mTorr of oxygen. The temperature of the substrates is 700 °C. The growth is followed by annealing in 1 atm oxygen at 900 °C for 2 h, and the epitaxy of the films is confirmed by the x-ray rocking curves. The thickness of the films is 200±10 nm. The lattice constants $a$, $b$, and $c$ (c sampled surface) of all samples are determined using high resolution x-ray diffraction spectroscopy. The results are tabulated in Table I. As shown in Table I, the lattice distortion induced by the substrates yields the mismatch lattice strain, defined as $(\Delta a_0/a_0)$, where $a_0$ is the lattice constant of the bulk perovskite, and $\Delta a_0$ is the difference between the lattice constant of the film and that of the bulk LCMO. The substrate-induced lattice strain has important effects on the optical phonon modes. Therefore the infrared spectroscopy of films on different substrates can provide direct comparison of the phonon frequency shifts with the lattice strain, determined from x-ray diffraction measurements.

Near normal incidence reflectivity is measured against a reference Al mirror with a Fourier-transform spectrometer in the entire IR spectral region 50–5000 cm$^{-1}$. The temperature of the sample is varied with a liquid He-cooled cryostat.

The large contribution of the substrate to the reflectance of LCMO thin films prevents direct derivation of the LCMO complex conductivity from the standard Kramers–Kronig (KK) transformations of the measured spectra. It is necessary to know the substrate dielectric function with high accuracy in order to model the optical spectra of the thin films. The complex dielectric functions of single crystalline LAO, STO, and YAO are obtained by means of KK analysis of the measured substrate spectra. For the analysis of the substrate spectra,

<table>
<thead>
<tr>
<th>Compound</th>
<th>$\Delta a_0/a_0$</th>
<th>$\Delta b_0/b_0$</th>
<th>$\Delta c_0/c_0$</th>
</tr>
</thead>
<tbody>
<tr>
<td>LCMO/LAO</td>
<td>0.05</td>
<td>-0.93</td>
<td>1.58</td>
</tr>
<tr>
<td>LCMO/YAO</td>
<td>0.57</td>
<td>-0.10</td>
<td>1.01</td>
</tr>
<tr>
<td>LCMO/STO</td>
<td>1.07</td>
<td>0.95</td>
<td>-0.39</td>
</tr>
</tbody>
</table>

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tra, we assume the constant reflectivity below 50 cm$^{-1}$ and a single oscillator approximation above 5000 cm$^{-1}$. To avoid the KK transformation error due to the uncertainty in the extrapolation of the reflectivity spectra from zero to infinity, we perform analytical dispersion analysis of the measured spectra. A model based on the following factorized form of the complex dielectric function$^7$ is applied:

$$\bar{\varepsilon}_s = \varepsilon_s \prod_j \frac{\omega^2 - \omega_j^2 + i \gamma_j \omega}{\omega^2 - \omega_j^2 - i \gamma_j \omega}. \quad (1)$$

The model has been successfully used to fit IR reflectivity spectra of several oxidic perovskites.$^{8,9}$ The adjustable parameters for $j$th complex pole $p$ and zero $z$ in this description uniquely determine four phonon mode parameters for $j$th transverse optical (TO) and longitudinal optical (LO) pair: the frequencies $\omega_{jT}$, $\omega_{jL}$ and damping terms $\gamma_{jT}$, $\gamma_{jL}$. The assumption of different parameters for the TO and LO modes is necessary when the TO and LO modes have different phonon decay channels and different damping rates. The phonon mode parameters of the substrates and the high-frequency dielectric constant $\varepsilon_s$ are initially evaluated from the KK analysis and then used as starting values for the least-squares fit of the reflectivity spectra to the factorized expression (1).

By this means the complex refractive indices $\sqrt{\bar{\varepsilon}_s} = n_s + i k_s$ for the perovskite substrates are obtained and used in the two-layer (LCMO/substrate) modeling. Notice that good agreement between the optical quantities which yield the best fit to reflectivity data and those obtained from a KK analysis is observed above 150 cm$^{-1}$.

Near normal incidence reflectivity $R = |\bar{r}|$ of a film of thickness $d$ on a semiinfinite substrate is related to the complex refractive indices of the film $\sqrt{\bar{\varepsilon}_f} = n_f + i k_f$ and of the substrate $\bar{n}_s$ by the following equations for the reflectance amplitude $\bar{r}$:

$$\bar{r} = \frac{\bar{r}_f + \Gamma}{1 + \bar{r}_f \Gamma}, \quad \Gamma = \frac{\bar{r}_f \bar{r}_s - 1}{\bar{r}_f \bar{r}_s - 1} \exp(2i\psi), \quad (2)$$

where

$$\bar{r}_f = \frac{1 - n_f - ik_f}{1 + n_f + ik_f}, \quad \bar{r}_s = \frac{1 - n_s - ik_s}{1 + n_s + ik_s}.$$
There are three main phonon modes in the spectra: the Mn-O stretching mode around 580 cm$^{-1}$, the Mn-O-Mn bending mode around 350 cm$^{-1}$ and the La(Ca)-site external mode, located around 160 cm$^{-1}$.\(^\text{11,13}\) The bending mode is found to be split due to the orthorhombic distortion in LCMO. As shown in Fig. 2, the stretching and bending phonon modes shift significantly to lower frequencies, as the mismatch lattice strain (see Table I) increases. On the other hand, the external phonon frequency is nearly independent of the lattice constant. If the dependence of the phonon frequency on lattice constant is approximated as $\omega \sim a^{-\alpha}$, the power $\alpha$ is roughly estimated to be 8 for the stretching mode and 5 for the bending mode. Similar strong $\alpha$ dependence of the stretching mode frequency is observed in layered cuprates and related materials.\(^\text{14}\) This fact indicates that both of the highest frequency phonon modes may be strongly affected by the interaction with electronic system, and the latter might also be modulated by the change in the Mn–O bond length and Mn–O–Mn bond angle. It should be noted that lineshapes of the phonon peaks in Fig. 2 are nearly independent of the lattice distortion induced by the substrates. It suggests that the LCMO epitaxial films under study are structurally homogeneous throughout the entire film thickness.

In summary, an analysis of the reflectance of LCMO epitaxial films on various substrates with an extended range of lattice constants has been performed by taking into account the substrate contributions. Our results provide evidence for a strong dependence of the Mn–O–Mn bending and Mn–O stretching phonon mode parameters on the lattice distortion induced by the substrates. An extension of the present investigation to studying the variations of LCMO phonon modes with temperature and the analysis of the mid-IR reflectance and transmittance spectra may provide further understanding of the role of the lattice distortion and polaron conduction in the occurrence of the CMR effects in perovskite manganites.

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