Anisotropic electronic properties of $a$-axis-oriented Sr$_2$IrO$_4$ epitaxial thin-films

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Abstract

We have investigated the transport and optical properties along the $c$-axis of $a$-axis-oriented Sr$_2$IrO$_4$ epitaxial thin-films grown on LaSrGaO$_4$ (100) substrates. The $c$-axis resistivity is approximately one order of magnitude larger than that of the $ab$-plane. Optical absorption spectra with $E \perp c$ polarization show both Ir 5$d$ intersite transitions and charge-transfer transitions (O 2$p$ to Ir 5$d$), while $E//c$ spectra show only the latter. The structural anisotropy created by biaxial strain in $a$-axis-oriented thin-films also changes the electronic structure and gap energy. These $a$-axis-oriented, epitaxial thin-films provide a powerful tool to investigate the highly anisotropic electronic properties of Sr$_2$IrO$_4$.

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A layered iridate compound, $\text{Sr}_2\text{IrO}_4$, which is an antiferromagnetic insulator ($T_N \sim 240 \text{ K}$),\textsuperscript{1,2} has recently attracted substantial interest due to its exotic electronic state. Coexisting electronic correlations and strong spin-orbit coupling of $5d$ electrons has led to the formation of the $J_{\text{eff}} = 1/2$ Mott state in $\text{Sr}_2\text{IrO}_4$ (SIO-214).\textsuperscript{3} Even though debate continues concerning its ground state (i.e., Mott insulator vs. Slater insulator\textsuperscript{4,5}), this compound has unprecedented potential for electronic device applications. For example, unconventional superconductivity is theoretically predicted in doped SIO-214\textsuperscript{6} and the strong spin-orbit interaction is expected to result in novel electronic states such as topological insulators\textsuperscript{7} and Weyl semimetals.\textsuperscript{8,9} Recently, SIO-214 thin films have been grown and characterized,\textsuperscript{10-12} resulting in a better understanding of the underlying physics of SIO-214 and providing impetus for developing device applications. However, only $c$-axis-oriented SIO-214 thin films have been synthesized thus far, which limits experimental access primarily to in-plane ($ab$-plane) properties. Hence, thin film studies of SIO-214 have produced results that are quite similar to those obtained for bulk SIO-214 crystals, whose naturally cleaved surfaces are also $ab$-planes. Since characterization of the $c$-axis of a number of layered oxides have revealed important physical information (e.g., the pseudo-gap energies in high-$T_c$ cuprates\textsuperscript{13}), the fabrication of SIO-214 thin films with large $ac$-planes (or $bc$-planes) will permit investigations of important physical properties that are not readily accessible in typical bulk crystals and $c$-axis-oriented thin films.

In this Letter, we report the structural, transport, and optical properties of $a$-axis-oriented SIO-214 thin films, whose large surfaces ($5 \times 5 \text{ mm}^2$) are $bc$-planes (or $ac$-planes). We have grown $a$-axis-oriented SIO-214 epitaxial thin films on LaSrGaO$_4$ (100) single-crystal substrates, where the [100]-direction is the surface-normal direction. In a similar study of layered $3d$ transition-metal oxides, $a$-axis-oriented thin films were grown on LaSrAlO$_4$ (100),\textsuperscript{14} which has
the same $K_2NiF_4$-structure as LaSrGaO$_4$ (LSGO). Due to differences in the tetragonal lattice parameters for SIO-214 (5.4979 Å and 25.798 Å)$^{15}$ and LSGO (3.852 Å and 12.68 Å)$^{16}$, the [110] and [110] directions of the SIO-214 thin films are parallel to the [100] and [010] directions of LSGO, respectively, and the thin film’s $c$-axis lies parallel to the [001]-axis of the substrate, as schematically illustrated in Fig. 1. The [100], [010], and [001]-directions of the LSGO substrate are labeled as $a$, $b$, and $c$, respectively, and we use this notation in the following paragraphs.

Since the lattice mismatches between the substrate and the SIO-214 thin films are calculated as –0.92 % and –1.73 % along the $b$- and $c$-axes (Table 1), there is biaxial compressive strain along the $b$- and $c$- axes of the thin films. We have measured the transport and optical properties along the $ab$-plane and the $c$-axis of the SIO-214 thin films, which clearly show its anisotropic insulating nature. In particular, the $c$-axis optical spectrum has no absorption peaks except for the charge-transfer transition peak (from O 2$p$ to Ir 5$d$) above 2 eV. Our observation confirms that the low-energy optical transitions that exist near 0.5 eV and 1.0 eV in SIO-214 are due to inter-site optical transitions between Ir 5$d$ orbitals that lie in the $ab$-plane.

We have grown $a$-axis-oriented, epitaxial SIO-214 thin films using a custom-built pulsed laser deposition system with in-situ reflection high-energy electron diffraction (RHEED) and in-situ optical spectroscopic ellipsometry.$^{17}$ Optimal growth parameters are oxygen partial pressure ($P_{O_2}$) of 10 mTorr, substrate temperature of 700 °C, and laser (KrF excimer, $\lambda = 248$ nm) fluence of 1.2 J/cm$^2$. We have monitored the thin film growth using RHEED, which shows a “layer-by-layer + island” growth mode, presumably due to the large surface energy of the film. A total film thickness of about 20 nm has been estimated by using 4 to 5 oscillations of the RHEED specular spot intensity during the initial growth.
The structure of these $a$-axis-oriented, epitaxial SIO-214 thin films has been identified using X-ray diffraction. The (220) and (440) thin-film peaks are only visible very near to the (200) and (400) substrate peaks in the $\theta-2\theta$ scan in Fig. 2 (a), ensuring that the films have an $a$-axis orientation. The FWHM of the rocking curves of the thin-film diffraction peaks are less than 0.07° (data not shown) suggesting that the samples have good crystallinity. In addition, the $bc$-plane epitaxy has been confirmed by pole figures and $\phi$-scans (data not shown). In order to obtain lattice-strain information, X-ray reciprocal space maps have been measured near the (310) and (303)-reflections of the LSGO substrate for the $ab$- and $ac$-planes, respectively, as shown in Fig. 1(b) and 1(c). Note that there is biaxial compressive strain in the $bc$-plane resulting in the elongated $a$-axis of the SIO-214 thin film, even though strain relaxation easily occurs along the $b$-axis. The lattice parameters, lattice strain, and the Poison ratio are summarized in Table 1. It is noteworthy that artificial $ab$-plane anisotropy has been created by biaxial lattice stain in this sample geometry, i.e. the $a$-axis lattice parameter is longer than the $b$-axis. Therefore, the $a$-axis-oriented, epitaxial SIO-214 thin films have orthorhombic rather than tetragonal structure.

Figure 3 shows the electrical resistivity of the SIO-214 thin films for two current orientations: Samples were sliced and patterned into bar shapes to measure the temperature-dependent resistivity along the $b$-axis ($\rho_{ab}$) and $c$-axis ($\rho_c$) using conventional four-probe methods. Insulating behavior is clearly evident in both directions; however, the $c$-axis resistivity is about an order of magnitude larger than the $b$-axis resistivity. This anisotropy is also present in the Arrhenius plot shown in Fig. 3(b), where the dashed lines are fits to $\rho (T) = \rho_0 \exp (\Delta/2k_BT)$, where $\rho$, $\rho_0$, $\Delta$, and $k_B$ are the resistivity, proportionality constant, gap energy, and Boltzmann constant, respectively. Note that the values of $\Delta$ are estimated to be 97 meV (77 meV) at high temperature and 27 meV (24 meV) at low temperature for current applied along the $c$-axis ($b$-
axis). A similar temperature-dependent behavior has been reported for bulk SIO-214 crystals, where the temperature dependence of the gap is primarily attributed to additional magnetic ordering below the magnetic transition temperature.\(^{18}\)

Figure 4(a) shows optical absorption spectra of the SIO-214 thin films, which also exhibit anisotropy. The optical absorption coefficients are measured at room temperature with a Fourier-transform infrared spectrometer for energies in the range of 0.05 – 0.6 eV, and a grating-type spectrometer for energies in the range of 0.5 – 6 eV, using polarized incident light with E\(_{\perp c}\) or E\(_{\parallel c}\). A schematic illustration of the measurement setup is presented in the inset of Fig. 4(a), where LSGO and SIO-214 are blue and red, respectively. Two absorption peaks at around 0.5 eV (\(\alpha\)) and 1.0 eV (\(\beta\)) are clearly visible in the E\(_{\perp c}\) spectra, while no absorption peak is present at these energies in the E\(_{\parallel c}\) spectra. The \(\alpha\) and \(\beta\) peaks have been already observed in the \(ab\)-plane of SIO-214 bulk crystals\(^{19}\) and \(c\)-axis-oriented thin films\(^{12}\). They are interpreted as Ir 5\(d\) optical transitions between \(J_{\text{eff}} = 1/2\) and \(J_{\text{eff}} = 3/2\) states,\(^3,^{20}\) as schematically illustrated in Fig. 4(b). Note that the Ir 5\(d\) optical transitions reflect electron hopping between Ir sites in the \(ab\)-plane. The absence of the \(\alpha\) and \(\beta\) peaks in the E\(_{\parallel c}\) optical spectrum confirms that inter-site optical transitions are forbidden in the E\(_{\parallel c}\) polarization (Fig. 4(c)). However, both the E\(_{\perp c}\) and E\(_{\parallel c}\) spectra exhibit a relatively isotropic feature at around 3 eV (A) due to charge-transfer optical transitions from O 2\(p\) states to Ir 5\(d\) states.

Note that the optical peak widths of the \(\alpha\) and \(\beta\) transitions in the E\(_{\perp c}\) spectrum are quite similar to those of SIO-214 thin films under isotropic \(ab\)-plane tensile strain with a compressed \(c\)-axis lattice. In the recent study of \(c\)-axis-oriented SIO-214 thin films (i.e., SIO-214 \(c\)-axis
normal to substrate surface) deposited on various substrates with both \(ab\)-plane tensile and compressive strain,\(^{12}\) the optical peak widths and positions exhibit a systematic dependence on lattice strain. The \(E_{\perp c}\) optical spectrum (Fig. 4(a)) is similar to that for \(c\)-axis-oriented SIO-214 thin films grown on SrTiO\(_3\) (100) and GdScO\(_3\) (110) substrates, which are under isotropic tensile strain in the \(ab\)-plane with a decreased \(c\)-axis lattice parameter. Since there is \(ab\)-plane anisotropy in the \(a\)-axis oriented thin films discussed in this letter (Table 1), it is hard to draw a concrete conclusion concerning these data. However, the similarity of these two spectra suggests that changes in the \(c\)-axis lattice parameter (involving elongation or flattening of IO\(_6\) octahedra) play an important role in changing the electronic structure of SIO-214. It is also noteworthy that an optical gap energy (\(\Delta_{op}\)) of about 0.2 eV is estimated from the onset of the \(E_{\perp c}\) optical absorption spectrum, which is approximately two-thirds of the values obtained in Refs.\(^{12}\) and \(^{19}\). This optical gap suppression, which is not observed in \(c\)-axis-oriented SIO-214 thin films, might be related to the \(ab\)-plane anisotropy in \(a\)-axis-oriented SIO-214 thin films. Since it is not clear how the artificial \(ab\)-plane anisotropy, i.e., strain-induced, different \(a\)- and \(b\)-axes lattice parameters, distorts the IrO\(_6\) octahedra in \(a\)-axis-oriented thin films, microscopic characterizations such as scanning transmission electron microscopy\(^{21,22}\) and resonant X-ray diffraction\(^{23,24}\) will provide additional important information.

In summary, we have synthesized \(a\)-axis-oriented, epitaxial SIO-214 thin films with artificial \(ab\)-plane anisotropy and a flattened \(c\)-axis lattice on LSGO (100) substrates. We have observed that these thin films are insulating along both the \(b\)- and \(c\)-axes, but the \(c\)-axis resistivity is an order of magnitude larger than the \(b\)-axis resistivity. We have observed optical absorption spectra where the two optical peaks at 0.5 eV and 1.0 eV are only observed for \(E_{\perp c}\), which
supports the view that these peaks originate from inter-site Ir 5d transitions. Since the large surface area (bc-plane) of these samples is orthogonal to the naturally cleaved surface of this compound, our sample geometry provides an important way to investigate the in-plane anisotropy and c-axis properties, which are not easily accessible in bulk crystals.

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Table 1. Lattice parameters and strain of \( \alpha \)-axis-oriented epitaxial thin films of Sr\(_2\)IrO\(_4\) (SIO-214).

| Crystallographic direction | LSGO lattice parameters (Å) | SIO-214 film pseudo-cubic lattice parameters (Å) | Lattice mismatch (%)* | Lattice strain (%)** |
|----------------------------|----------------------------|-------------------------------------------------|-----------------------|----------------------|
| \( a \) [100]\(_{\text{sub}} \) // [110]\(_{\text{film}} \) | 3.852                      | 3.91                                            | —                     | + 0.65               |
| \( b \) [010]\(_{\text{sub}} \) // [1\( \bar{1} \)0]\(_{\text{film}} \) | 3.852                      | 3.88                                            | – 0.92               | – 0.1                |
| \( c \) [001]\(_{\text{sub}} \) // [001]\(_{\text{film}} \) | 12.68                      | 12.7                                            | – 1.73               | – 1.4                |

* Lattice mismatch is calculated from the pseudo-cubic lattice parameters of bulk SIO-214 \( (d_{\text{bulk}}) \) and substrates \( (d_{\text{sub}}) \) by \( (d_{\text{sub}} - d_{\text{bulk}}) / d_{\text{sub}} \times 100 \) (%).

** Lattice strain is estimated by using \( \varepsilon = (d_{\text{film}} - d_{\text{bulk}}) / d_{\text{bulk}} \times 100 \) (%).

Poisson’s ratio, \( v = \varepsilon_a / (\varepsilon_a - \varepsilon_b - \varepsilon_c) = 0.30 \).
Figure Captions

FIG. 1  Schematic diagram of the sample geometry with the $a$-axis-oriented SIO-214 thin-film grown on the LSGO (100) substrate, where the IrO$_6$ octahedra are red and the Sr atoms are blue. The [110], [1$ar{1}$0], and [001] directions of the SIO-214 thin film are parallel to the $a$: [100], $b$: [010], and $c$: [001] directions of LSGO, respectively. The large colored arrows represent the direction of crystal strain: compressive (green) along the $b$- and $c$-axes and tensile (orange) along the $a$-axis.

FIG. 2  X-ray diffraction data for SIO-214 thin-films on LSGO:  (a) $\theta$-2$\theta$ scan of a thin film for which the ($l00$) film peaks are clearly visible and confirm the $a$-axis orientation of the film. Reciprocal space maps of (b) the SIO-214 (420) film peak (black $\times$) near the LSGO (310) substrate peak (white cross), and (c) the SIO-214 (336) film peak (black $\times$) near the LSGO (303) substrate peak (white cross).

FIG. 3  (a) Temperature dependence of the electrical resistivity of a SIO-214 thin-film on LSGO for current applied along the $b$-axis (red) and $c$-axis (blue). (b) Arrhenius plot of the resistivity data, where the dashed lines are fits to $\rho(T) = \rho_0 \exp(\Delta/2k_BT)$ for two distinct temperature regions.

FIG. 4  (a) The optical absorption coefficient for SIO-214 thin films on LSGO where the incident light is polarized such that $E_{\perp c}$ (red) and $E//c$ (blue). Schematic band structure and optical transitions (arrows) for (b) the $E_{\perp c}$ polarization and (c) the $E//c$ polarization. The dotted lines indicate the Fermi energy.
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Figure 1
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Figure 2
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$\rho_c$ and $\rho_{ab}$ as functions of temperature $T$.

$\Delta_{c1} = 97$ meV, $\Delta_{c2} = 27$ meV, $\Delta_{ab1} = 77$ meV, $\Delta_{ab2} = 24$ meV.

$\rho = \rho_0 \exp(\Delta/2k_B T)$.

Figure 3
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Figure 4
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