STUDY OF THE METAL-INSULATOR TRANSITION IN $LaCoO_{3-x}$ EPITAXIAL FILMS

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by
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ABSTRACT

Materials with temperature-dependent metal-to-insulator transitions (MIT) have gained attention for the abrupt collapse of the band gap during the transition. Various novel transistor structures which utilize MITs have been suggested and realized to produce more energy efficient transistors. To achieve practical operation temperatures for device applications, however, MIT materials with transition temperatures below 400 K are unsuitable. This work focuses on one MIT material with a high temperature transition, $LaCoO_3$. Using oxide molecular-beam epitaxy (MBE) a series of $LaCoO_{3-x}$ thin films with varied La and Co compositions were grown. All films were grown on $LaAlO_3$ $(001)_p$ substrates, which like $LaCoO_3$, has a pseudocubic perovskite structure. The lattice mismatch is less than 0.9%. X-ray diffraction θ-2θ measurements were used to assess the structure of the films; the out-of-plane lattice constant of each film was calculated using a Nelson-Riley analysis. The temperature-dependent resistivity of each film was measured and each shows a change in electrical resistivity of more than two orders of magnitude in the MIT temperature range of 400 - 600 K, which is similar to that of bulk single crystal $LaCoO_3$. The abruptness and magnitude of the MIT is found to be insensitive to the film composition for samples ranging from $La_{1.1}CoO_{3-x}$ to $LaCo_{1.1}O_{3-x}$.

BIOGRAPHICAL SKETCH

Lindsey E. Noskin received her Bachelor of Science degree from Cornell University in May of 2017 with a thesis entitled, "Growth of NbO_2 by Molecular-Beam Epitaxy and Characterization of its Metal-Insulator Transition." During her undergraduate career, she spent one semester on the Neubauer Exchange Program at the Technion in Haifa, Israel. As an undergraduate student, Lindsey was given the Milton Fisher Scholarship for Innovation and Creativity and was a Hunter R. Rawlings III Cornell Presidential Research Scholar. Upon acceptance to the accelerated Master of Science program offered by the department of Materials Science and Engineering at Cornell, Lindsey was also awarded the Intel Corporation/Semiconductor Research Corporation Fellowship for her Master's Degree.

This thesis is dedicated to my parents: when the going gets tough, the tough get going.

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MIT materials are an exciting class of materials for their potential to improve the efficiency of transistor devices. These materials can be triggered by an external stimulus, e.g. temperature change, pressure change, or induced current, to have an abrupt collapse of the band gap and cause the material to go from an insulator to a metal.[1] The temperature-dependent metal-insulator transitions of single crystal MIT materials have been extracted from the literature and plotted in Figure 1(a).[2-26] This data was selected from the literature for being the MITs with the largest relative change in electrical resistivity during the transition of the material. Restrictions for the selected data were that only intrinsic behavior of high-quality single crystal were shown, that is, not due to the formation of filaments, chemical reactions or recrystallization.

Large, sharp changes of several orders of magnitude of resistivity can be seen in Figure 1(a) and are further quantified in Figure 1(b) where the relative magnitude of the transition is plotted with the transition temperature for each material. The end points of the transition region were determined to be the extrema of the second derivative and marked with an "x" in Figure 1(a). For NbO_2, the bounds of the transition region were determined based on an earlier study using x-ray diffraction to identify the temperature range of dimerization, which is the mechanism of the MIT for this material.[27]

Special interest has been taken in this class of materials for their potential to be utilized in transistor devices for more abrupt and efficient transitions.[28] Attempts to reduce the sub-threshold slope of metal-oxide-semiconductor field-effect transistors (MOSFETs) and beat the 60 mV/decade Boltzmann limit using MITs were successful. Previous work on VO_2 has shown this capability by integrating the MIT material in series and electrically triggering the transition at a temperature below the transition temperature.[28]

One material selection limitation for MOSFET devices is the necessity to perform reliability at temperatures at high as 400 K.[29] Due to the limitation that an MIT-integrated MOSFET device is only operational at sub-MIT temperatures, many of the MIT materials (those with T_{MIT} < 400 K) shown in Figure 1 have no potential for utilization in real MOSFET device applications. Therefore, the list of potential materials (referred to as high-temperature MIT materials) is reduced to: $LaCoO_3$, V_3O_5, Ti_2O_3,

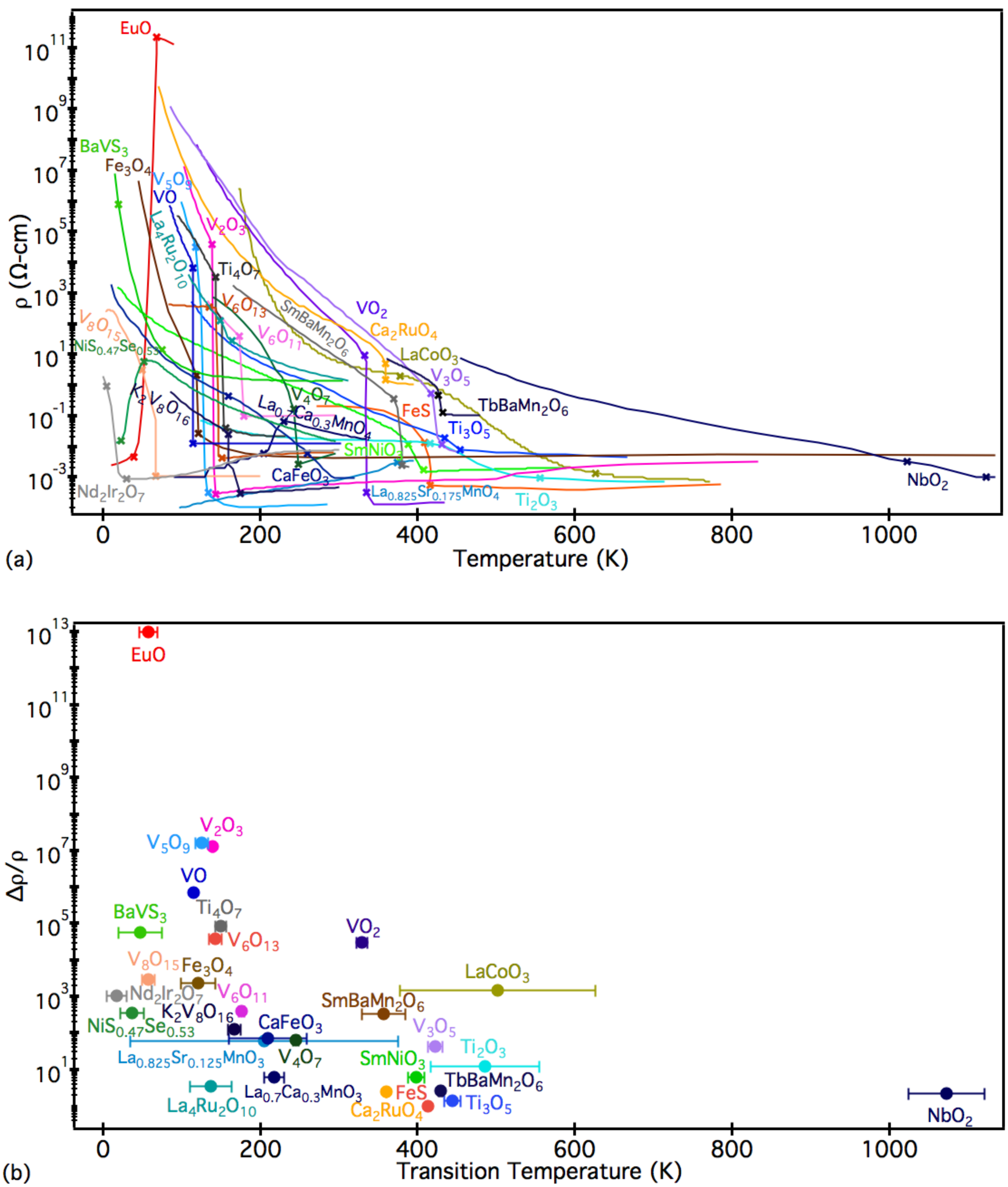

FIG. 1. (a) Electrical resistivity versus temperature of common MIT materials. X-symbols denote the start and end to the MIT of each given material. (b) Relative change in electrical resistivity versus temperature of common MIT materials. Data for the resistivity versus transition temperature of each material was extracted from separate publications[2-26] featuring the largest transitions of reported bulk crystal data to make these comprehensive plots.

$TbBaMn_2O_6$, FeS, Ti_3O_5 and NbO_2. Of these seven remaining materials, $LaCoO_3$ has the greatest potential for future devices because of having the largest relative change in resistivity of high-temperature MIT materials. During the MIT of $LaCoO_3$ the resistivity changes over three orders of magnitude. Despite the high potential for this material, no significant MIT has been reported for a $LaCoO_3$ thin film. [30]

In this work, we present the synthesis of $LaCoO_{3-x}$ thin films with varied La and Co relative concentrations by oxide molecular-beam epitaxy (MBE). All films in this study were grown on $LaAlO_3$ $(001)_p$ substrates, where the p subscript denotes pseudocubic indices. $LaCoO_3$ and $LaAlO_3$ have the same space group symmetry, $R\bar{3}c$, at room temperature, with a lattice mismatch within 0.9% in this orientation.[31,32] $LaCoO_{3-x}$ thin films were characterized with x-ray diffraction and resistivity measurements at a temperature range of 220 K – 700 K. Our results suggest high potential for a $LaCoO_3$-based transistor devices.

Single-phase epitaxial $La_{1+y}CoO_{3-x}$ and $LaCo_{1+z}O_{3-x}$ thin films were synthesized in a distilled ozone ambient at 600 °C. The doses of lanthanum and cobalt were matched using *in situ* reflection high energy electron diffraction (RHEED) intensity oscillations to determine the period required for a monolayer dose of each molecular-beam, a process described by Haeni, *et al*.[33] In addition to alternating between layering of La atoms followed by Co atoms, a 20 second wait period was introduced to allow Co to oxidize to form Co_2O_3, the desired oxidation state. After determining deposition periods required for a 1:1 ratio of La to Co, 105 unit cells of each film of the $La_{1+y}CoO_{3-x}$ and $LaCo_{1+z}O_{3-x}$ series were deposited on individual substrates as a rate of approximately 12 nm/h.

X-ray diffraction θ-2θ scans show that the films grown are all the desired phase of $LaCoO_3$ and can be seen in Figure 2(a). Using these spectra, Nelson-Riley analysis was conducted to determine the out-of-plane lattice constants for each film.[34] The stoichiometric film has an out-of-plane lattice constant of 3.854 Å, which can be seen in comparison to the other four films in Figure 2(b). These out-of-plane lattice constants were calculated using the Nelson-Riley method based on four peaks in x-ray diffraction spectra.[34] There is an asymmetric trend in Figure 2(b) which shows a decrease in out-of-plane lattice constant as the degree away from stoichiometric increases. The lattice constant values can be compared to values for reported bulk lattice parameters when applied in plane for a commensurate film according to the following equation[35]:

$$\varepsilon_{out-of-plane} = \frac{-2\upsilon}{1-\upsilon}\varepsilon_{in-plane} \quad (1)$$

Based on this calculated value for the out-of-plane lattice constant, the value reported in this work is slightly smaller, however, closer in value than any thin film of $LaCoO_{3-x}$ previously reported.[36-42]

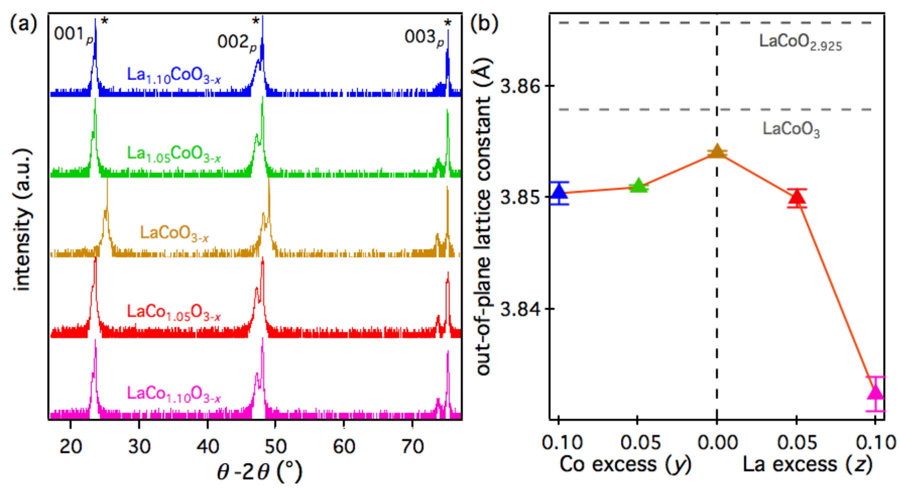

FIG. 2 (a) θ-2θ x-ray diffraction spectra of each of the five $La_{1+y}CoO_{3-x}$ and $LaCo_{1+z}O_{3-x}$ films where "*" denotes peaks of $LaAlO_3$ $(001)_p$ substrates and film peaks are labeled with their corresponding index. (b) out-of-plane lattice constant versus composition showing a size for the stoichiometric film that is closest in value to the expected size based on bulk crystal data.[31,32,43]

Additionally, x-ray diffraction rocking curves were measured. The rocking curve for the stoichiometric $LaCoO_{3-x}$ shows high similarity to the substrate and the full width half maximum (FWHM) of the film peak is 0.0045 °, the lowest ever reported for a $LaCoO_{3-x}$ film.[36-42,44] This curve shows a low degree of mosaicity and high similarity to the substrate. To continue the study of the quality of the stoichiometric film, a reciprocal space map (RSM) taken on the off axis of (103) is shown in Figure 3. The RSM shows thickness fringes and peaks for both the film and substrate along the same Q_x position, conveying a fully commensurate film and indicating no signs of relaxation.

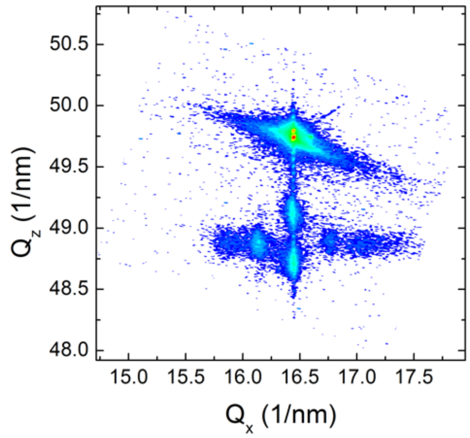

FIG. 3 Reciprocal space mapping (RSM) of $LaCoO_{3-x}$ (103) and $LaAlO_3$ (103).

Scanning transmission electron microscopy (STEM) images in Figure 4 show the epitaxy of the film to the substrate. These results convey low atomic scale defects. Additionally, the results confirm that an epitaxial, commensurate film was grown. Dark rows near the substrate-film interface are likely due to oxygen loss due to the vacuum atmosphere of the instrument.

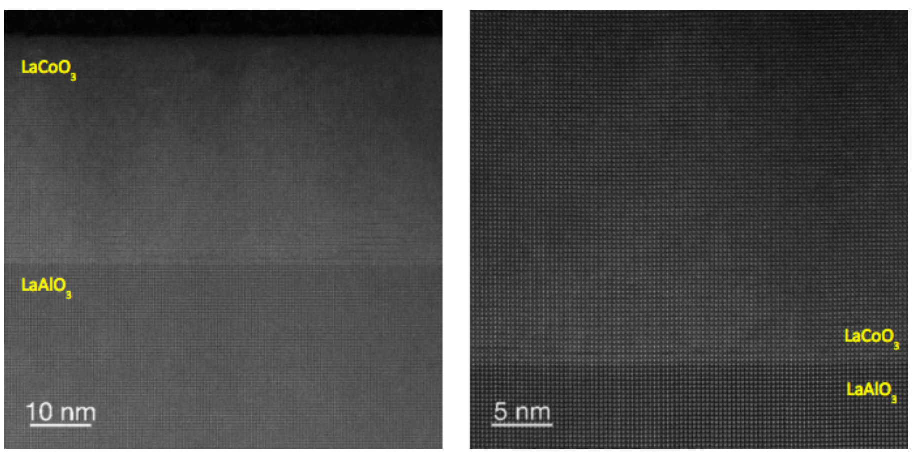

FIG. 4 Transmission electron microscopy (STEM) images of a $LaCoO_{3-x}$ film on $LaAlO_3$ $(001)_p$.

For high and low temperature electrical resistivity measurements, all films were patterned in a linear geometry, as seen in Figure 4(a) first with a 10 nm adhesion layer of chromium followed by 200 nm of platinum by evaporator deposition. After patterning the electrodes, the films were capped with an amorphous layer of MgO to prevent oxygen loss, which was shown in initial tests. All films in this work were first measured at low temperature from 200 K– 295 K followed by high temperature measurements from 295 – 700 K, the heating and cooling results of which are shown in Figure 4(b). Of the films in this series, the stoichiometric film shows character in curvature most like published bulk data.[26] Off-stoichiometry films have less defined curved regions for the start and end of the transition regions. The stoichiometric film is most conductive at all temperatures and has the lowest relative change in resistivity, as shown in Figure 4(c). The relative change in resistivity for the stoichiometric film is 1116, two orders of magnitude improved from the best value reported for thin film $LaCoO_3$.[30]

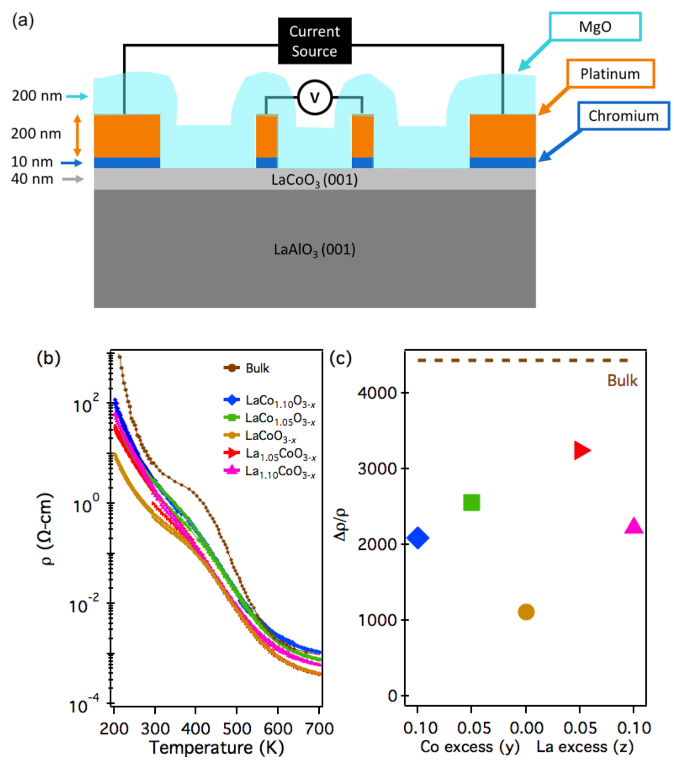

FIG. 4. (a) Diagram of the 4-point electrical resistivity contacts used to measure $LaCoO_{3-x}$ films (b) Temperature-dependent metal-insulator transitions of five films in this work. (c) Relative change in resistivity during the MIT of each of the five films compared to that of a previously published bulk crystal $LaCoO_3$.[26]

In conclusion, the MIT of $LaCoO_3$ is not strongly influenced by a less than 0.1 variation of the [La]/[Co] ratio. This work shows the highest quality $LaCoO_3$ thin film ever reported.[36-42,44] Additionally, this work shows the largest MIT of any film ever reported with an MIT transition temperature above 400 K.[44,45]

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