



HOKKAIDO UNIVERSITY

Title	Study on the Solid-State Electrochemical Thermal Transistors with High Electrical Conductivity Active Layers
Author(s)	卞, 志平
Degree Grantor	北海道大学
Degree Name	博士(工学)
Dissertation Number	甲第16174号
Issue Date	2024-09-25
DOI	https://doi.org/10.14943/doctoral.k16174
Doc URL	https://hdl.handle.net/2115/93476
Type	doctoral thesis
File Information	BIAN_Zhiping.pdf



**Study on the Solid-State Electrochemical
Thermal Transistors with High Electrical
Conductivity Active Layers**

高電気伝導性活性層を用いた固体電気化学
熱トランジスタに関する研究

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AUGUST 2024

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Chapter 1. General Introduction

1.1 Background of this thesis

The world's energy consumption is on a continuous upward trajectory year by year.

While there are concerns that future energy supply may surpass consumption, leading to the depletion of energy resources, a significant amount of energy loss still occurs due to waste heat discarded in power generation and industrial processes, as well as minor heat emissions from electronic devices. To achieve an energy-efficient society and enhance sustainability, reducing wasteful energy discharged as unused heat is essential. The reuse of waste heat resulting from the low conversion rate of primary energy is crucial for sustainable development (**Figure 1-1**)[1-6]. Low- to medium-

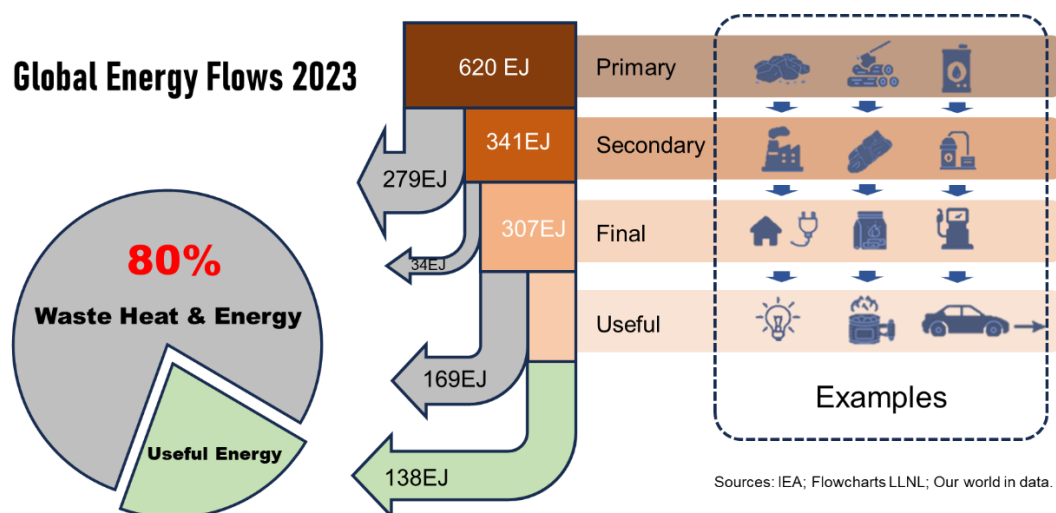


Figure 1-1 Global energy flow of primary to useful energy. Including conversion losses (waste and rejected energy), in EJ for 2023. When the primary energy become useful energy, 80 % of the energy will become waste heat and waste energy.

temperature (100–300 °C) waste heat is particularly challenging to reuse because the temperature is too low to generate jet steam for power generation. Although thermoelectric energy conversion technology presents a potential solution, its efficiency is too low in this temperature range in air.

In recent years, efforts to harness thermal energy through thermoelectric conversion and thermotronics have been spreading. Thermotronics attempts to control the flow of heat itself and apply it to devices, rather than converting it into electrical energy. Derived from the concept of electronics, thermotronics focuses on the heat flow carried by acoustic phonons, which are vibrational molecules responsible for thermal conduction in crystals. However, controlling phonons is challenging, and methods to control heat flow are yet to be established due to physical limitations such as phonon speed and interfacial thermal resistance, making dynamic modulation like that of electrical properties difficult.

Despite these challenges, thermal management technologies[7] such as thermal diodes[8-10] and thermal transistors[11-18] have recently attracted attention. Thermal diodes rectify the heat flow, while thermal transistors electrically switch the heat flow ON and OFF. Concepts such as thermal transistors have been proposed, but they have

not yet reached practical application, necessitating further research. We expect that thermal displays visualizing heat contrast using infrared cameras can be realized using thermal transistors (see **Figure 1-2**), which may prove useful for the reuse of waste heat. The development of these technologies is essential to reduce wasteful energy and promote sustainability.

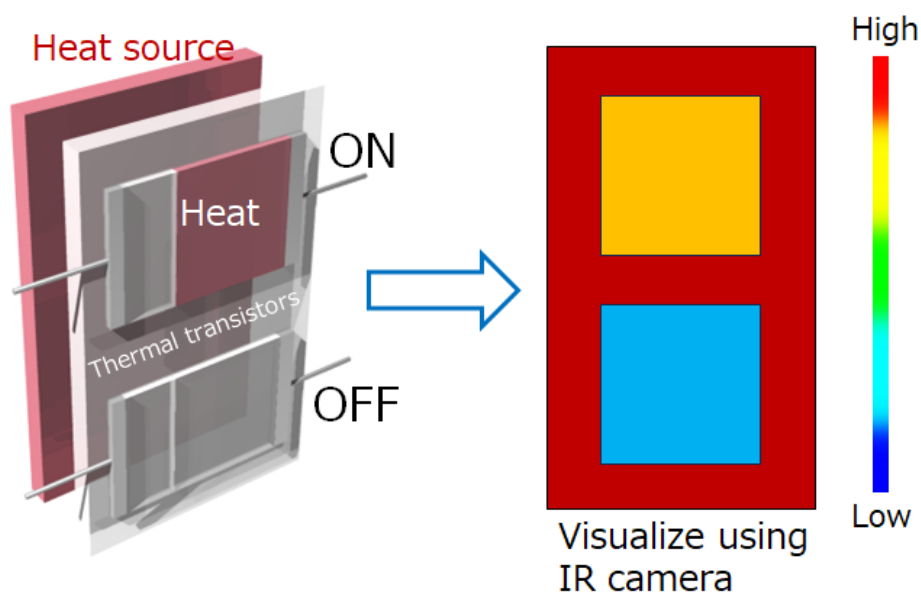


Figure 1-2 The concept of thermal display. Thermal transistors will be placed above a heat source, and its ON/OFF state will be controlled through an electrical gate. As a result, different contrasts will appear on the IR camera, reflecting the transistor's switching behavior.

1.2 Introduction of thermal transistors

1.2.1 The concept and demonstration of thermal transistors

The thermal transistor is a type of thermotronics technology that aims to switch heat flow in a manner similar to how semiconductor transistors switch electric current. In

electronic circuits, transistors are crucial components, adjusting the conductivity of the active layer by applying a gate electric field to switch the current between the source and drain (see **Figure 1-3**, left). Analogously, thermal transistors modulate the thermal conductivity of the active layer using an electric gate, defining the OFF state as having low thermal conductivity and the ON state as having high thermal conductivity (see **Figure 1-3**, right). This innovation in thermal management

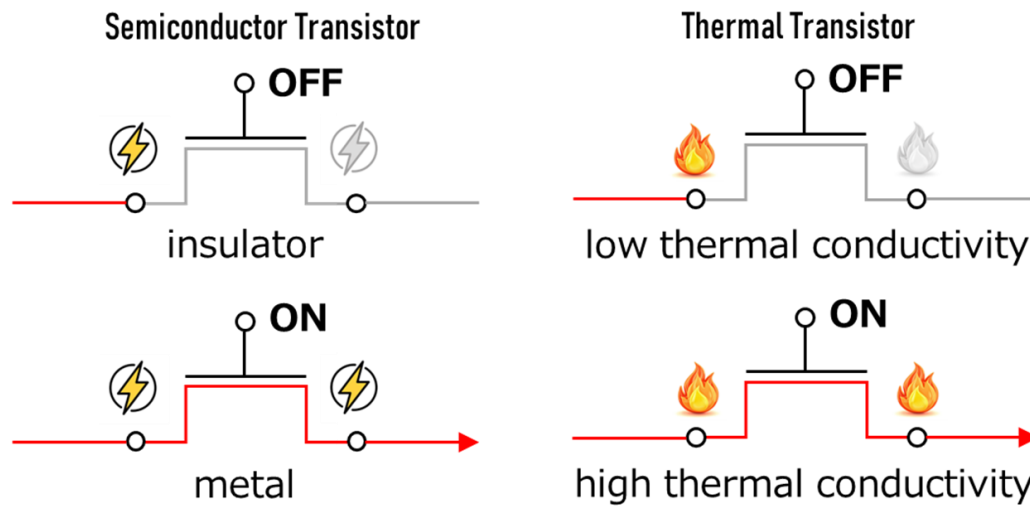


Figure 1-3 (Left) Semiconductor transistor with electrical gate and (Right) proposed thermal transistor with electrical gate. Just as semiconductor transistors switch the ON/OFF state of electric current, thermal transistors can switch the ON/OFF state of heat flow.

technologies holds promise for controlling heat at the nanoscale, such as in thermal shutters and new non-contact thermal circuits for information processing using phonons instead of electrons.

The realization of thermal transistors would not only enable the effective reuse of small waste heat emitted from electronic devices but also lead to the development of novel thermal devices. These could include heat control devices for semiconductor integrated circuits, thermal shutters that can switch the transmittance of infrared (thermal) rays, and thermal displays that utilize differences in infrared transmittance. The concept of a "thermal transistor" has been theoretically proposed and has garnered attention for its potential applications in these areas[16].

By integrating thermal transistors into thermal management systems, we can significantly advance the efficient reuse of waste heat and promote sustainability. These devices are expected to play a crucial role in the development of innovative thermal management technologies, enabling better control and utilization of heat, thus contributing to a more energy-efficient and sustainable future.

1.2.2 The history of thermal transistors

The history of experimental validation of thermal transistors is relatively recent. In 2014, Cho and Cahill from the University of Illinois Urbana-Champaign fabricated a thin film of LiCoO_2 , widely used as a cathode material in lithium-ion batteries, and measured its thermal conductivity using the time-domain thermoreflectance (TDTR)

method, comparing the discharged state (LiCoO_2) with the charged state ($\text{Li}_{0.6}\text{CoO}_2$)[17]. They found that the thermal conductivity of the Li_xCoO_2 thin film could be reversibly changed from $5.4 \text{ W m}^{-1} \text{ K}^{-1}$ to $3.6 \text{ W m}^{-1} \text{ K}^{-1}$, marking the first thermal transistor. In 2018, Sood and Cui from Stanford University reported using an electrolyte (LiPF_6 salt, EC/DEC solvent) and inserting/extracting Li electrochemically in the active layer of MoS_2 to alter its thermal conductivity[13], dubbing it an "electrochemical thermal transistor." However, these thermal transistors, essentially lithium-ion batteries using non-aqueous electrolytes, required sealing in containers, posing practical limitations. The active layer must be stable in air.

Some transition metal oxides stable in air exhibit significant changes in crystal structure due to oxidation-reduction (or protonation). For instance, the crystal structure of SrCoO_x ($2.5 \leq x \leq 3$) changes from a brownmillerite structure at $x = 2.5$ to a perovskite structure at $x = 3$. It is also possible to protonate compounds like $\text{H}_y\text{SrCoO}_{2.5}$ ($0 \leq y \leq 2$) using residual water in ionic liquids or porous insulators as electrolytes[18,19]. In 2020, Lu and Yildiz and Chen from Massachusetts Institute of Technology measured the thermal conductivity of $\text{H}_y\text{SrCoO}_{2.5}$, $\text{SrCoO}_{2.5}$, and SrCoO_3 thin films, reporting values of $0.5\text{--}0.8 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{H}_y\text{SrCoO}_{2.5}$, $1.5\text{--}1.8 \text{ W m}^{-1} \text{ K}^{-1}$ for $\text{SrCoO}_{2.5}$, and $3\text{--}6 \text{ W m}^{-1} \text{ K}^{-1}$ for SrCoO_3 , with an ON/OFF ratio of thermal

conductivity (SrCoO_3 to $\text{H}_y\text{SrCoO}_{2.5}$) of 10 ± 4 [18]. However, they also used ionic liquids as electrolytes for electrochemical oxidation and protonation, requiring sealing in containers. Moreover, the electrode, electrolyte, and active SrCoO_x thin film were not integrated, necessitating the removal of the electrolyte after oxidation/protonation and deposition of a metal Al thin-film transducer on the SrCoO_x surface for thermal conductivity measurement, preventing repeated protonation-oxidation cycles.

1.2.3 The first all-solid-state thermal transistor

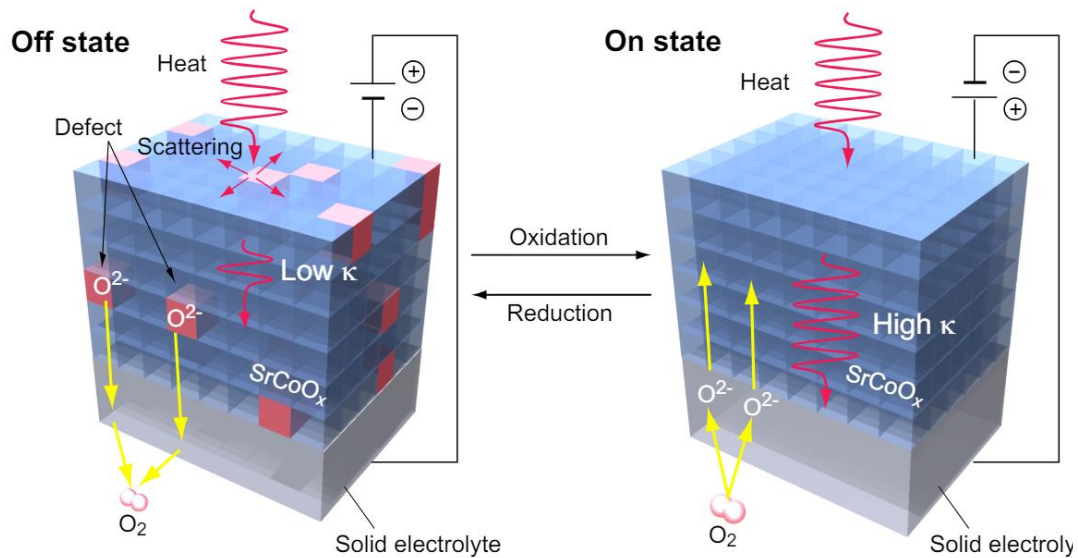


Figure 1-4 The world's first all-solid-state thermal transistor. (Left) Off state. Oxygen defects are generated in the SrCoO_x layer via the electrochemical reduction treatment. Resultant SrCoO_2 layer (defect perovskite) contains $1/3$ oxygen defects against SrCoO_3 , and the defects scatter the heat flow, reducing the thermal conductivity. (Right) On state. Electrochemical oxidation treatment causes the oxygen defects to disappear, increasing the thermal conductivity.

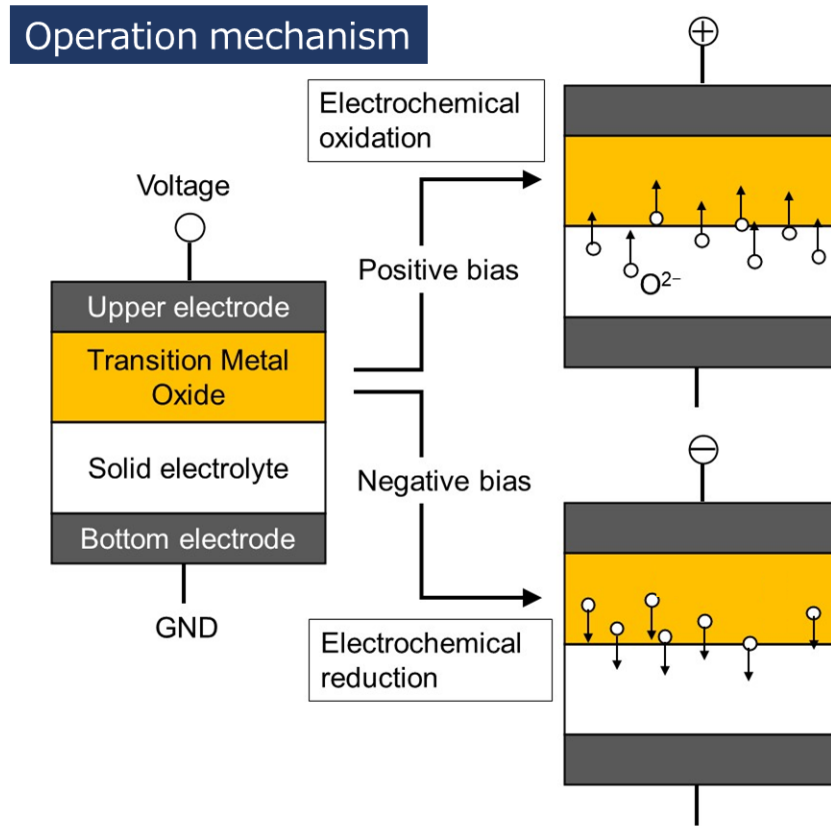


Figure 1-5 Operation mechanism of the all-solid-state thermal transistor. Oxygen defects are generated in the SrCoO_x layer via the electrochemical reduction treatment and the defects scatter the heat flow. Then the transistor shows off state. When it be oxidized, the defects disappear and shows heat flow on state.

To address these issues, in 2023, our team successfully demonstrated the world's first all-solid-state thermal transistor made from solid electrolytes and transition metal oxides (see **Figure 1-4**) [20], garnering significant attention domestically and internationally. Specifically, we fabricated a layered structure consisting of an upper electrode, transition metal oxide SrCoO_x ($2 \leq x \leq 3$), solid electrolyte YSZ, and a

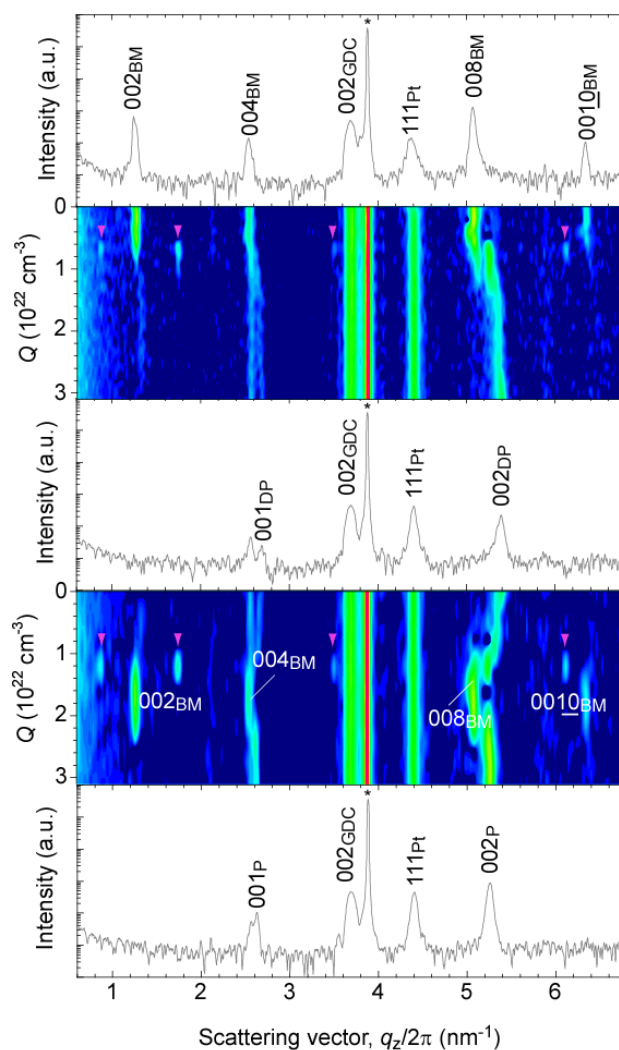


Figure 1-6 Topotactic crystal structure change of the SrCoO_x film upon electrochemical reduction/oxidation treatment. Out-of-plane XRD patterns for the as-grown $\text{SrCoO}_{2.5}$, reduced SrCoO_2 , and oxidized SrCoO_3 . 002 YSZ is marked as *.

lower electrode on a single-crystal solid electrolyte substrate. The operation mechanism is shown in **Figure 1-5**. Topotactic crystal structure change of the SrCoO_x film upon electrochemical reduction/oxidation treatment is shown in **Figure 1-6**. The electrochemical redox treatment began by applying a negative current to reduce brownmillirite- $\text{SrCoO}_{2.5}$ into defect perovskite- SrCoO_2 . Next the

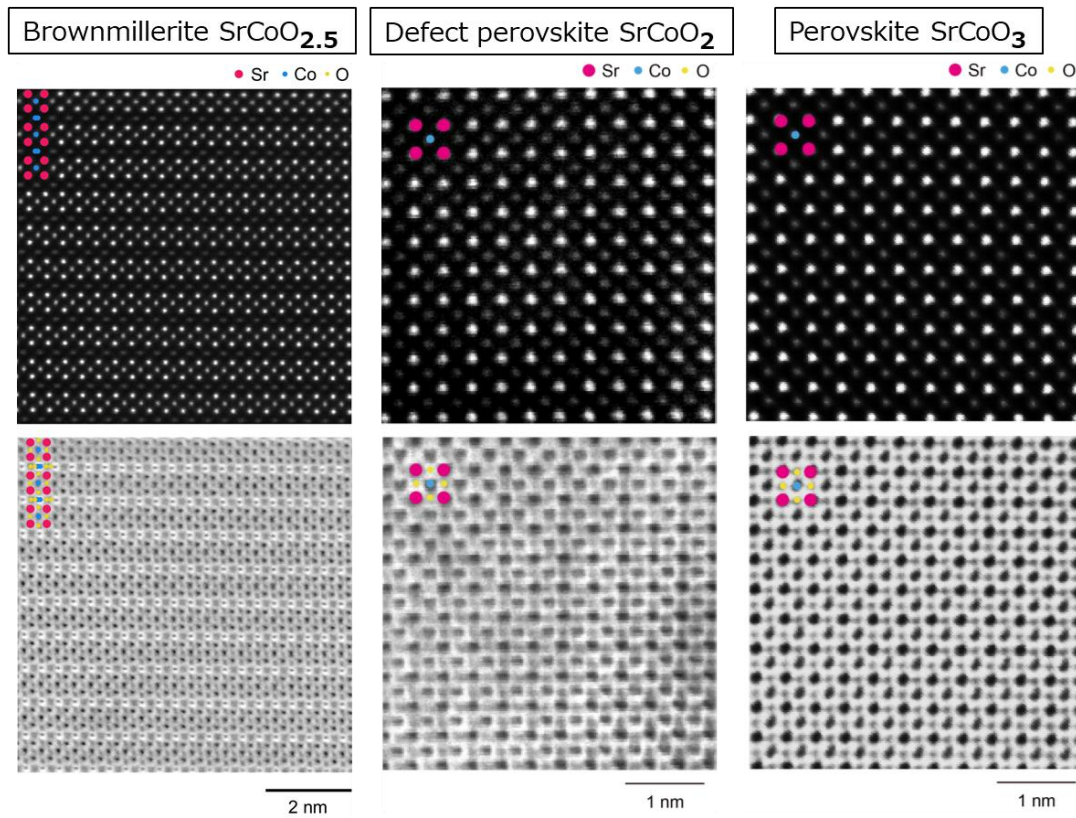


Figure 1-7 Cross-sectional STEM images (HAADF and ABE) of the as-fabricated $\text{SrCoO}_{2.5}$, reduced SrCoO_2 and oxidized SrCoO_3 . HAADF-STEM images show that the heavier atomic column has a brighter contrast. Square lattice composed of Sr and Co is clearly visualized. Brighter dots are Sr (atomic number, $Z = 38$) and darker dots are Co ($Z = 27$).

device was oxidized electrochemically to perovskite - SrCoO_3 . Cross-sectional STEM images (HAADF and ABE) of the as-fabricated $\text{SrCoO}_{2.5}$, reduced SrCoO_2 and oxidized SrCoO_3 are shown in **Figure 1-7**. By applying voltage, we utilized the significant change in thermal conductivity due to oxidation-reduction of the transition metal oxide to achieve a repeatable ON/OFF ratio of 4 for the thermal conductivity in the all-solid-state thermal transistor.

1.3 Different solutions of thermal transistors

Electrical control of κ in the active materials of thermal transistors is paramount. It necessitates a switch between the on-state (high κ) and off-state (low κ). Electrochemical (current driven) and electrostatic (voltage driven) approaches offer pathways to govern the κ of active materials.

1.3.1 Voltage driven thermal transistors

When discussing the electrostatic (voltage-driven) thermal transistor, we refer to a novel device that utilizes electric fields to control thermal conduction. Its operation revolves around adjusting the thermal conductivity within the transistor via an applied electric field, thereby modulating the heat transfer under the influence of voltage signals. An important characteristic of this transistor is that it does not alter the crystalline structure of the material during operation. Representative research achievements in this field include ferroelectric/antiferroelectric thermal transistors[12] and graphene molecular thermal transistors[11].

1.3.2 Current driven thermal transistors

Current-driven thermal transistors, particularly prominent in current research, are a type of thermal transistor where heat conduction is controlled by electric currents.

These devices often involve the insertion and extraction of ions during operation, resulting in changes to the crystalline structure of the active materials. This characteristic enables dynamic modulation of thermal conductivity, making them suitable for applications requiring tunable thermal management and efficient heat flow control in electronic devices and energy systems. Research in this area focuses on optimizing material compositions and device architectures to enhance thermal performance and durability while managing structural changes induced by ion dynamics.

1.4 TMOs as active layer materials of thermal transistors

TMOs exhibit a diverse range of functional behaviors, including magnetic, electrical, and optical properties. These properties can be finely tuned by adjusting the composition and crystal structure of the materials[21-25]. Such versatility enables the development of thermal transistors capable of dynamically modulating heat flow in response to electric currents, catering to the needs of advanced electronic applications. Moreover, TMOs have been studied extensively for their potential in advanced memory devices[26-28] and for exhibiting various switching phenomena[29-31]. These capabilities, including electrical, superconducting, and magnetic switching, are

pivotal for achieving precise control over thermal management in complex electronic systems.

The TMOs used as active layers of thermal transistors in this thesis, including strontium cobaltite (SrCoO_x), strontium ferrite (SrFeO_x), and lanthanum nickelate (LaNiO_x), all belong to the common perovskite-type structure TMOs. These materials exhibit changes between metallic and insulating states concurrent with variations in the valence states of transition metal ions[32-46], leading to alterations in their crystal structures. Importantly, these structural changes directly impact the electrical conductivity, thereby enabling modulation of thermal conductivity. This relationship forms the core focus of investigation in this study.

1.5 Objective of this thesis

The primary aim of this thesis is to explore the mechanisms for enhancing the thermal conductivity ON/OFF ratio and the width of thermal conductivity switching based on the world's first all-solid-state thermal transistors: SrCoO_x -based thermal transistor. By understanding these mechanisms, the selection of active materials can be optimized, leading to the development of more advanced all-solid-state thermal transistors with superior performance.

In this thesis, I first utilize the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ solid solution system to clarify the underlying mechanism responsible for the κ of SrCoO_x -based thermal transistors. I find the electron thermal conductivity plays a significant role in certain metallic transition metal oxides.[47] Then, LaNiO_x , as a material that meets these criteria, was identified as a suitable candidate for fabricating thermal transistors with an exceptional κ switching width of $4.3 \text{ W m}^{-1} \text{ K}^{-1}$. The fully oxidized LaNiO_3 (on-state) produced a κ of $6.0 \text{ W m}^{-1} \text{ K}^{-1}$, primarily attributed to a substantial contribution from electron thermal conductivity ($3.1 \text{ W m}^{-1} \text{ K}^{-1}$).[48] This thesis is composed of the following chapters:

In Chapter 1, a comprehensive background on thermal transistors is introduced.

In Chapter 2, experimental methods are introduced.

In Chapter 3, based on our all-solid-state SrCoO_x thermal transistor, I clarified the systematic modulation of κ of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ ($0 \leq x \leq 1$, $2 \leq y \leq 3$) solid solutions.[9]

Hence, I found materials that show a high electrical conductivity (means high electron thermal conductivity) and highly ordered lattices in the ON state, but display

electrical insulating properties and disordered lattices in the OFF state should improve the ON/OFF κ ratio.

In Chapter 4, based on my collaborate work on protonation and deprotonation of nickel oxides using ionic liquids, I confirmed the validity of the strategies outlined in Chapter 3 for finding suitable active materials and enhancing thermal transistor performance. Additionally, I have discovered that LaNiO_x is a promising candidate as an active material. I fabricated the all-solid-state thermal transistor using LaNiO_x .^[10] This work presents a breakthrough with LaNiO_x -based electrochemical thermal transistors, with an exceptional κ switching width of $4.3 \text{ W m}^{-1} \text{ K}^{-1}$. The LaNiO_x -based electrochemical thermal transistor demonstrated κ cyclability while maintaining the structural integrity of the LaNiO_x crystalline lattice, making it a promising candidate for integration into next-generation devices, particularly thermal displays.

In Chapter 5, the above studies are summarized.

In conclusion, this thesis has discovered a method to achieve high ON/OFF κ ratio and wide κ switching widths by modulating electron thermal conductivity. Based on this discovery, a highly promising LaNiO_x -based thermal transistor has been

fabricated. It underscores the significance of κ control for improving energy efficiency and enabling novel applications in thermal management and beyond.

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Chapter 2. Experimental Methods

2.1 Thin film fabrication

Thin film growth is generally categorized into two major types: 1. Physical Vapor Deposition (PVD) and 2. Chemical Vapor Deposition (CVD). This distinction is based on whether the material undergoes a physical or chemical transformation from the target to the substrate. The epitaxial single-crystal films used in the fabrication of the all-solid-state thermal transistor in this study were prepared using Pulsed Laser Deposition (PLD), a technique that falls under PVD. Therefore, this paper will only introduce PVD and its main techniques, without delving into other methods.

Physical vapor deposition (PVD) is further divided into vacuum evaporation and sputtering deposition. In these processes, thin film materials are primarily transported to the substrate surface through physical means, typically using solid or molten sources. The characteristics of PVD include a high vacuum requirement, low deposition temperature, and relatively simple equipment. Following the rapid development of vacuum coating technology in the 20th century, several new thin film preparation techniques have emerged.

Based on evaporation deposition, electron beam evaporation and molecular beam epitaxy (MBE) were developed. Techniques such as ion beam sputtering deposition, pulsed laser deposition (PLD), magnetron sputtering, ion beam-assisted deposition (IBAD), and low-energy ion beam deposition were developed from the interaction of energy beams with solids.

Here, I systematically introduce pulsed laser deposition (PLD).

2.1.1 Pulsed Laser Deposition (PLD)

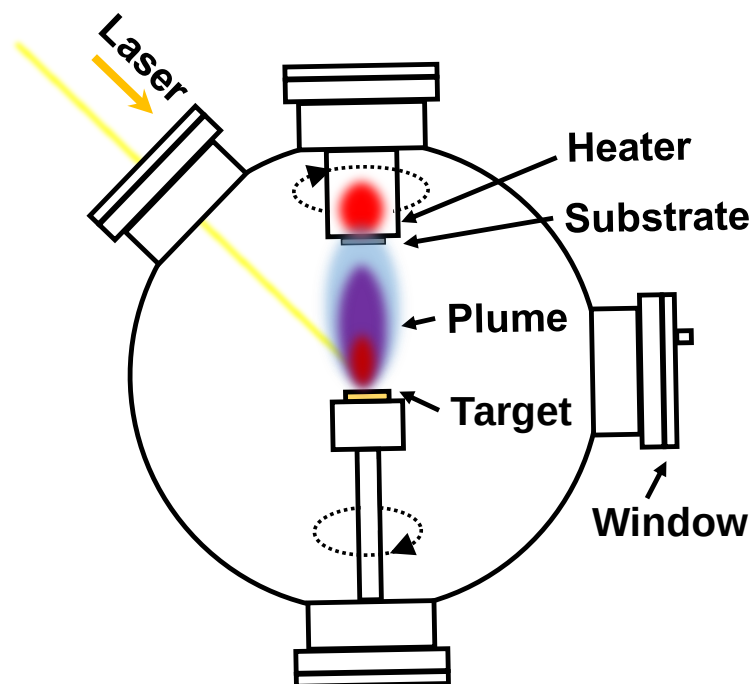


Figure 2-1 Schematic of PLD. A pulsed laser is focused onto the target material to achieve a forward-directed plume. The plasma state of this plume provides the material flux necessary for film growth.

In 1960, the invention of the world's first ruby laser marked a significant advancement

in the study of laser-matter interactions. The first experiments in laser deposition were conducted in the 1960s, with continuous efforts by scientists extending into the 1970s and 1980s. Pulsed laser deposition (PLD) only gained widespread attention and development after it was successfully applied to the in-situ epitaxial growth of high-temperature superconducting films, thereby being promoted as a technique for oxide film growth.[1]

In this technique, as shown in **Figure 2-1**, a pulsed laser is focused onto the target material to achieve a sufficiently high laser energy density. Each laser pulse evaporates or ablates a small amount of the material. The ablated material is ejected from the target surface as a forward-directed plume. The plasma state of this plume provides the material flux necessary for film growth. In PLD, the forward-directed, ellipsoidal shape of the plume can lead to a certain distribution of deposition thickness. The material distribution from the plume is symmetric relative to the normal of the target surface and can be described by a $\cos^n(\theta)$ distribution, where n can range from ~4 to 30.[2] Due to factors such as textures generated on the ablated target surface, spatial non-uniformities in the laser spot, and laser absorption by the plasma, the deposition from the plume may also become non-uniform.[3] However, issues like these can be addressed by rastering the target and rotating the substrate, allowing for

the achievement of uniform film coverage over a large area. Similar to evaporation, PLD can control the thin film growth process at an atomic level.

Pulsed laser deposition (PLD) offers several significant advantages:[4]

Excellent Stoichiometry Control: PLD can easily produce multicomponent thin films with desired stoichiometry. The high-power pulsed laser ablation creates a plume whose composition matches the target material. Maintaining an appropriate oxygen environment prevents oxygen volatilization, ensuring accurate stoichiometry in oxide films.

- (1) High Efficiency and Short Duration: The ablation process generates high-energy particles (10 eV to 100 eV), promoting surface diffusion on the substrate and requiring lower substrate temperatures, thus enhancing deposition efficiency.
- (2) Flexible Parameter Adjustment: The laser in a PLD system operates independently of the chamber, allowing for flexible adjustment of laser parameters. PLD is compatible with various materials that can be ablated into a plume.
- (3) High Compatibility and Scalability: Modern PLD systems integrate auxiliary devices like in-situ reflective high-energy electron diffraction (RHEED) and rotating inlets, promoting uniform film growth and real-time monitoring.

- (4) Ease of Cleaning and Material Switching: The directional nature of the ablation plume minimizes chamber contamination, making PLD suitable for frequent material changes, which is ideal for research environments.

The excimer laser's high pulse energy, short wavelength, and low divergence have significantly expanded PLD's applicability. Its ability to break chemical bonds directly creates highly reactive fragments, enhancing PLD's versatility for various materials. The epitaxial thin films used in the all-solid-state transistors discussed in this thesis were all prepared using a PLD system (**Figure2-2**) equipped with a Coherent COMPexPro 102 excimer laser ($\lambda = 248$ nm).

2.1.2 Direct Current (DC) Sputtering

DC sputtering is a cost-effective thin film deposition technique ideal for electrically conductive materials. It involves a vacuum chamber with the target material and substrate positioned parallel to each other, filled with high purity argon gas. When a pulsed DC current ionizes the argon, the metal target (cathode) and substrate (anode) facilitate the process. The ionized argon collides with the negatively charged target, dislodging metal ions into the plasma. These ions are then attracted to the positively charged substrate, where they condense to form a thin film coating.

In this thesis, I used a DC sputtering system to prepare the Pt top (which is also used as transducers for thermal conductivity measurement) and bottom electrodes for the all-solid-state thermal transistor.

2.2 Crystallographic analyses

2.2.1 X-ray diffraction (XRD)

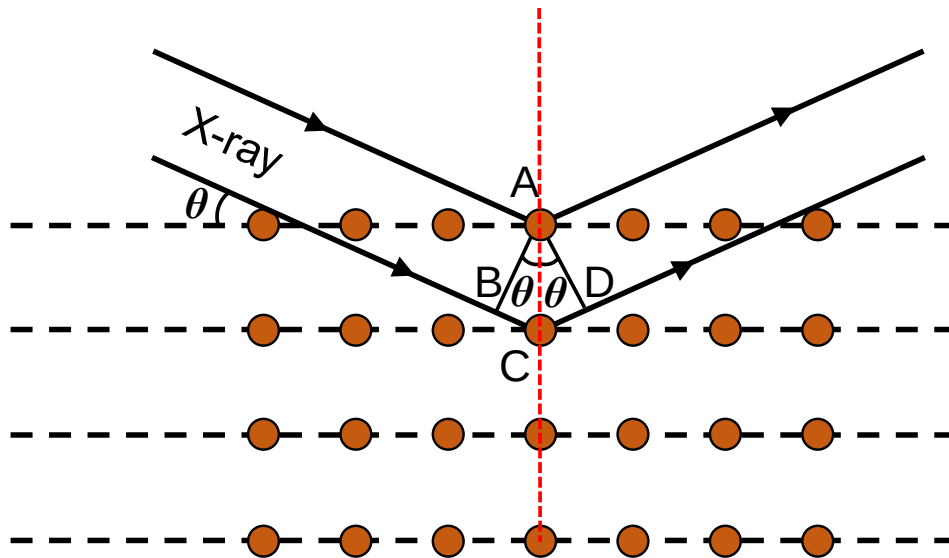


Figure 2-2 Geometric diagram of X-ray diffraction for a crystal. Bragg's law can be figured out by the geometric diagram.

In 1895, German physicist Wilhelm Röntgen discovered a type of highly penetrating light, which was named X-rays. In 1912, P.P. Ewald proposed a formula in his doctoral thesis describing the process of light waves passing through an ordered array of scattering atoms, based on the hypothesis that crystals are composed of particles in a spatial lattice. Building on discussions with Ewald, Max von Laue realized that X-

rays might have the suitable wavelength to achieve lattice diffraction. In June 1912, von Laue published the first diffraction pattern in the Proceedings of the Royal Bavarian Academy of Science. Inspired by this, the Bragg father-son duo developed the famous Bragg equation.

When X-rays interact with a crystal, the atoms at the lattice points act as independent scattering sources. Significant diffraction occurs when the path difference between adjacent outgoing rays is an integer multiple of the wavelength. The geometric relationship involved is shown in **Figure 2-2**, leading to the derivation of:

$$\Delta = BC + CD = 2 \cdot d \cdot \sin \theta = n \cdot \lambda \quad (2.1)$$

where d is the interplanar spacing, θ is the Bragg angle, and n is the order of

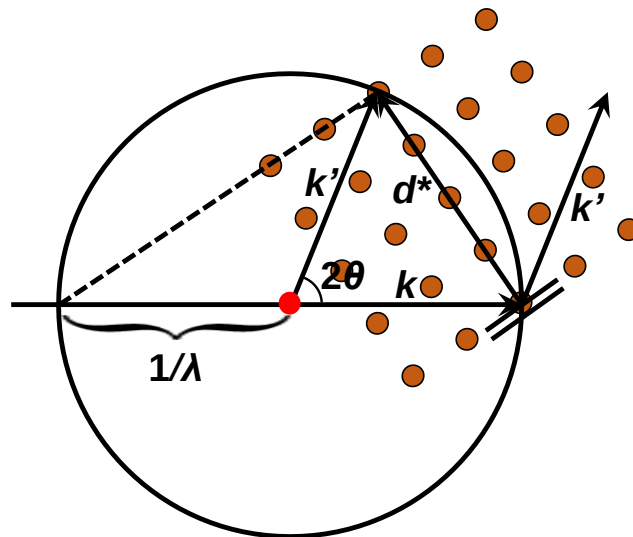


Figure 2-3 Diagram of Ewald sphere. k is the incident wave vector, k' is the outgoing wave vector, and d^* is the reciprocal lattice vector.

diffraction.

The concept of reciprocal space is often introduced when describing crystals. Reciprocal space and real space have a transformation relationship. Let the basis vectors in reciprocal space be $\mathbf{a}^*$, $\mathbf{b}^*$ and $\mathbf{c}^*$, then they have the following relationships with the real space basis vectors $\mathbf{a}$, $\mathbf{b}$, $\mathbf{c}$:

$$\mathbf{a}^* = 2\pi \cdot \frac{\mathbf{b} \times \mathbf{c}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{b}^* = 2\pi \cdot \frac{\mathbf{c} \times \mathbf{a}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad \mathbf{c}^* = 2\pi \cdot \frac{\mathbf{a} \times \mathbf{b}}{\mathbf{a} \cdot (\mathbf{b} \times \mathbf{c})} \quad (2.2)$$

The Bragg equation can also be expressed in reciprocal space, using the Ewald sphere method to understand crystal diffraction. As shown in **Figure 3.4**, where $\mathbf{k}$ is the incident wave vector, $\mathbf{k}'$ is the outgoing wave vector, and $\mathbf{d}^*$ is the reciprocal lattice vector, the diffraction condition is:

$$\mathbf{d}^* = \mathbf{k}' - \mathbf{k} \quad (2.3)$$

In this thesis, to study the crystal structure of the active layer of thermal transistors, I used a four-circle diffractometer (ATX-G, Rigaku, Japan). The fundamental techniques involved are detailed below.

X-ray Reflectivity (XRR) is a non-destructive technique that probes the surface and interface information of samples. It is commonly used to fit thin film thickness and surface/interface roughness. The resulting reflectivity curve exhibits periodic

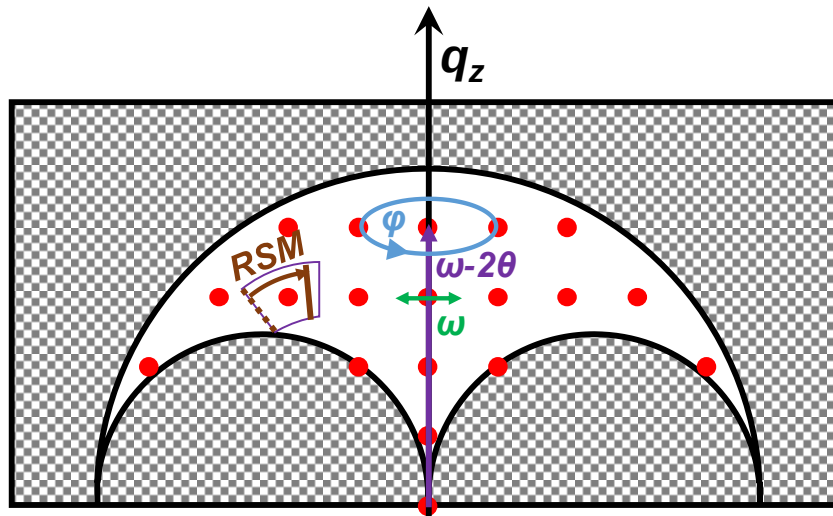


Figure 2-4 Schematic diagrams of ω - 2θ scan, ω scan, ϕ scan, and RSM. The areas marked with gray dots represent regions where the Ewald's sphere does not intersect with the diffraction peak positions. Therefore, the diffraction peaks in these regions cannot be detected using a diffractometer.

oscillations, where the period T can approximate the film thickness, and the decay slope reflects the surface/interface roughness. The approximate film thickness can be derived using the Bragg equation:

$$H \approx \frac{\lambda}{2} \cdot \frac{1}{\theta_{m+1} - \theta_m} = \frac{\lambda}{2} \cdot \frac{1}{T} \quad (2.4)$$

ω - 2θ scanning is one of the most common diffraction techniques. By synchronizing ω and 2θ , it performs a one-dimensional scan in reciprocal space along a specific direction. When epitaxial films grow on single-crystal substrates with specific orientations, ω - 2θ scanning combined with the Bragg equation is used to determine the lattice constants of the epitaxial films.

When a sample meets the diffraction condition with X-rays, an ω scan at a specific 2θ

angle is performed, known as ω scanning. This method provides information on the broadening of the diffraction spot in the ω direction. The full width at half maximum (FWHM) of the ω scan is often used to assess the crystallinity of the sample.

Scanning along the normal direction of a specific crystal plane is known as φ scanning. It is typically used to determine the epitaxial relationship and symmetry of the film and substrate. By selecting a set of diffraction spots with in-plane components and performing φ scanning, the number of peaks and the distribution of corresponding substrate peaks over a 360° rotation can reveal the epitaxial relationship and symmetry.

Often, the aforementioned line scan methods can only determine the position of a specific diffraction spot, with the search process being time-consuming and the results less intuitive. Reciprocal Space Mapping (RSM) can easily solve these issues, providing a direct view of the relative positions and contour shapes of the substrate and film peaks. It facilitates the analysis of stress and defect states. In reciprocal space, the components of the diffraction vector $\mathbf{q}$ in the in-plane and out-of-plane directions are:

$$\begin{cases} q_x = |\mathbf{q}| \cdot \sin(2\theta/2 - \omega) \\ q_y = |\mathbf{q}| \cdot \cos(2\theta/2 - \omega) \end{cases} \quad (2.5)$$

2.2.2 X-ray spectroscopy (XAS)

One significant aspect of the interaction between X-rays and matter is the absorption of X-rays by the material. X-ray Absorption Spectroscopy (XAS) provides elemental information by measuring the system's response to varying incident photon energy. XAS techniques typically offer elemental specificity and are applicable to nearly all atoms. They can be used for various sample types, including solids (crystalline or amorphous), liquids, and gases. Non-transmission XAS collects experimental data by detecting total electron yield (TEY) or total fluorescence yield (TFY). These methods ensure that sample concentration does not need to be uniformly distributed. Overall, XAS testing has minimal sample requirements and does not damage the sample during the process.

2.2.3 Scanning Transmission Electron Microscopy (STEM)

High-Angle Annular Dark Field scanning transmission electron microscopy (HAADF-STEM) was conducted to examine the film structure in detail. When the incident electron beam interacts with the sample, it scatters both elastically and inelastically, altering the electrons' direction and energy. The HAADF-STEM image is obtained by detecting inelastically scattered electrons or thermal diffuse scattering (TDS) at high angles using an Annular Dark-Field (ADF) detector.

In ADF mode (range of θ_2), elements with larger atomic numbers (Z-values) appear brighter, while elements with smaller Z-values are less visible[5,6]. To visualize lighter atoms, annular bright-field (ABF, range of θ_3) STEM[7] and low-angle annular dark-field (LAADF) STEM[8] is used. Within the range of θ_1 , signals come from incoherently scattered electrons at very high incident angles, resulting in HAADF Z-contrast micrographs, which are highly dependent on the atomic number (Z-value)[9].

Additionally, STEM can analyze the film's electronic structure using electron energy loss spectroscopy (EELS) and determine the chemical composition through micro-area energy dispersive spectroscopy (EDS).

In this thesis, the atomic arrangements of the active layers of thermal transistors were visualized using a STEM (JEM-ARM200CF, JEOL) operated at 200 keV.

2.3 Electrical transport properties

Electrical transport properties are intrinsic characteristics of materials, used to determine whether a film behaves as a semiconductor, metal, or insulator. These properties are crucial for understanding the behavior of materials in various electrical

and electronic applications.

2.3.1 Electrical conductivity

Electrical conductivity testing of thin films often involves either the two-electrode method or the four-electrode method, each with its own advantages and disadvantages.

The traditional two-electrode method is convenient to operate and significantly reduces the probability of signal loss due to poor electrode contact compared to the four-electrode method. However, because of the inherent resistance of the wires, the two-electrode method can introduce errors when measuring low-resistance samples.

The four-electrode method, on the other hand, corrects for this error, improving measurement accuracy. The sheet resistance (R) can be calculated by following equations:

$$\begin{aligned} R_1: \quad R_{12,43} &= \frac{V_{2(43)} - V_{1(43)}}{I_{12} - I_{21}}, & R_2: \quad R_{23,14} &= \frac{V_{2(14)} - V_{1(14)}}{I_{23} - I_{32}} \\ R_3: \quad R_{34,21} &= \frac{V_{2(21)} - V_{1(21)}}{I_{34} - I_{43}}, & R_4: \quad R_{41,32} &= \frac{V_{2(32)} - V_{1(32)}}{I_{41} - I_{14}} \end{aligned} \quad (2.6)$$

The series measurements are used to calculate the resistivity (ρ) based on the following equations:

$$\rho_1 = \frac{\pi}{\ln 2} \frac{R_1 + R_2}{2} f\left[\frac{R_1}{R_2}\right] d \quad (2.7)$$

Four possible configurations are: ρ_1 - R_1, R_2 ; ρ_2 - R_2, R_3 ; ρ_3 - R_3, R_4 ; ρ_4 - R_4, R_1 . Here d is

the thickness of film, and f is the geometrical factor, which is 1 for perfect symmetry.

In this thesis, the four-electrode method is used to measure the electrical conductivity of the active layer in the all-solid-state thermal transistor.

2.3.2 Thermopower

Thermopower (S) is a technique used to investigate the electronic density of states (DOS) around the Fermi level (E_F). For single-band semiconductors, the S value can be described by the Mott equation:

$$S = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left\{ \frac{d[\ln(\sigma(E))]}{dE} \right\}_{E=E_F} = \frac{\pi^2}{3} \frac{k_B^2 T}{e} \left\{ \frac{1}{n} \cdot \frac{dn(E)}{dE} + \frac{1}{\mu} \cdot \frac{d\mu(E)}{dE} \right\}_{E=E_F} \quad (2.8)$$

Here, k_B , e , n , and μ are the Boltzmann constant, electron charge, carrier concentration, and carrier mobility, respectively. This equation simplifies to the slope of the DOS around the E_F . In this study, S was utilized to monitor changes in the electronic structure of materials. The thermopower of the films was measured using a standard steady-state method at room temperature. The sample was placed between two Peltier devices about 3 mm apart, which created a temperature difference by applying forward or reverse current to each side. The temperature gradient (ΔT) and the thermoelectromotive force (ΔV) were recorded simultaneously, and thermopower was determined from the slope of the linear fit of $\Delta T - \Delta V$.

2.4 Time-domain thermoreflectance (TDTR)

The reflectivity of the sample surface is linearly related to temperature, and this relationship can be expressed by the photothermal reflectance coefficient (dR/dT). The TDTR method measures the change in the photothermal reflectance coefficient of the sample surface to determine the temperature change, which is then used to study the heat conduction process on a femtosecond to nanosecond timescale.

The implementation of the TDTR method involves the following steps:

- (1) A femtosecond pulsed laser is split into two beams: the pump beam and the probe beam.
- (2) The pump beam is directed onto the sample surface, inducing a transient thermal response.
- (3) The probe beam is directed onto the sample surface with a time delay relative to the pump beam, controlled by a long-travel delay stage.
- (4) As the delay stage moves, the time delay changes, allowing measurement of the sample surface's photothermal reflectance coefficient over time.
- (5) This allows indirect determination of the sample surface temperature as a function of time.
- (6) The resulting temperature change curve is fitted to a corresponding theoretical

thermal model to obtain the thermal properties of the sample.

The schematic of TDTR measurement setup I used is shown in **Figure 2-5**.

In TDTR experiments for measuring thermal properties of nanostructured materials, a common setup includes a surface metallic layer (Pt was used in this thesis) of tens of nanometers thickness. This layer serves dual roles: rapidly converting optical energy

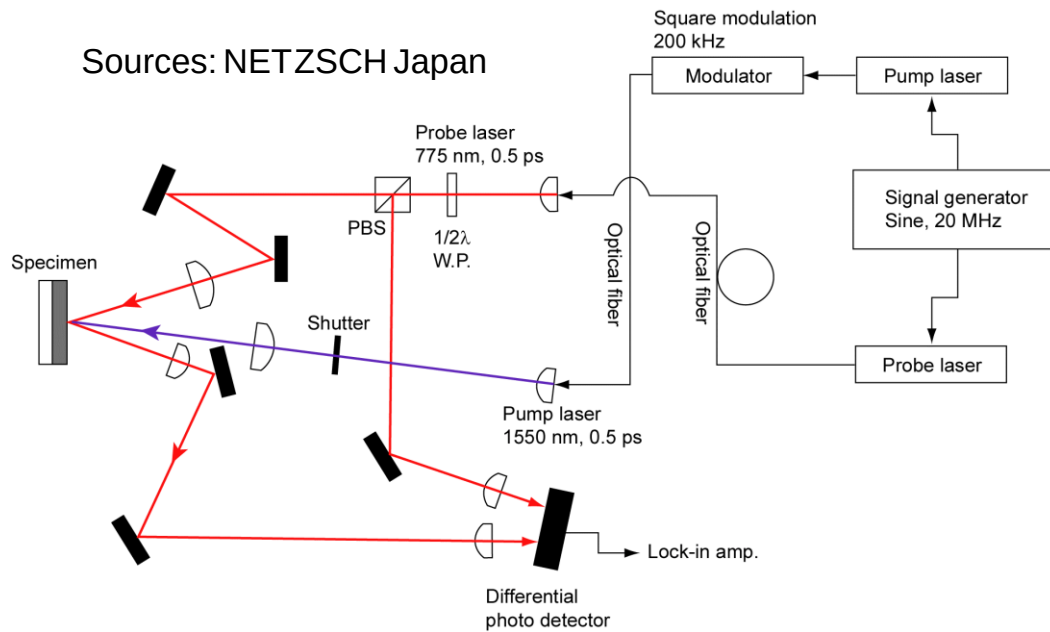


Figure 2-5 Schematic of TDTR system (PicoTR). TDTR is an optical pump–probe technique in which the pump beam thermally excites a sample surface, and the probe beam measures the time-resolved thermorefectance of bulk materials, nanostructures, and thin films.

from laser pulses into heat and acting as a temperature sensor due to its linear reflectance-temperature relationship. At short timescales, the non-equilibrium thermal

conduction within the metallic layer defies classical Fourier models, reflecting its unique energy absorption and redistribution dynamics.

The thermal reflection signal V is composed of an in-phase signal V_{in} and an out-of-phase signal V_{out} , expressed as $V = V_{in} + iV_{out}$, where i is the imaginary unit. Therefore, its amplitude and phase can be defined as:

$$A = \sqrt{V_{in}^2 + V_{out}^2}$$

$$\varphi = \tan^{-1}(V_{out}/V_{in}) \quad (2.9)$$

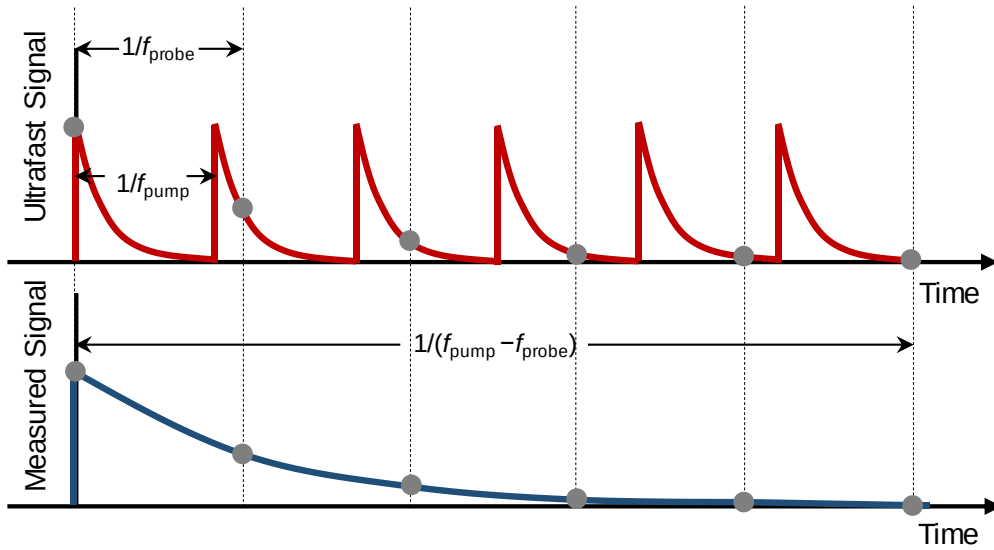


Figure 2-6 The signal detection mechanism. The curves shown on the top of represent the surface temperature of the sample in response to the pump input, which has a repetition rate of f_{pump} and a period of $1/f_{\text{pump}}$. Each successive probe pulse, represented by the dots, is delayed with respect to the pump pulse by the time $\Delta t = \Delta f / (f_{\text{pump}} f_{\text{probe}})$, where $\Delta f = f_{\text{pump}} - f_{\text{probe}}$ is also known as the beat frequency.

Here, A represents the amplitude signal, and φ represents the phase signal, determined by the in-phase V_{in} and out-of-phase V_{out} signals, respectively. The phase signal is

less susceptible to noise, vibrations, and background interference compared to the amplitude signal to some extent. Therefore, in this graduation thesis, the phase signal is used to fit the thermal conductivity of the sample. In this thesis, the results were simulated using the packaged software developed by the manufacturer, PicoTherm corporation (Now is NETZSCH).

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Chapter 3. Solid-State Electrochemical Thermal Transistors with Strontium Cobaltite – Strontium Ferrite Solid Solutions as the Active Layers

3.1 Objective of this chapter

In Chapter 1, I already state that we realized the world's solid-state electrochemical thermal transistors that exhibit ON/OFF thermal conductivity (κ) ratio of ~ 4 at room temperature[1]. Compared to previously reported thermal transistors, our solid-state electrochemical thermal transistors offer clear advantages, including the absence of liquids and the ability to withstand high temperatures due to their inorganic structure. Practical thermal transistors would be realized when the properties such as the ON/OFF ratio are improved. Thus, it is crucial to clarify the underlying mechanism responsible for the κ of SrCoO_y -based thermal transistors.

In this chapter, I will introduce strontium cobaltite – strontium ferrite solid solutions $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ ($0 \leq x \leq 1$, $2 \leq y \leq 3$) as the active layer of solid-state electrochemical thermal transistors (**Figure 3-1**). There are several similarities and differences in the crystal structure and electron transport properties between SrCoO_y and SrFeO_y . The

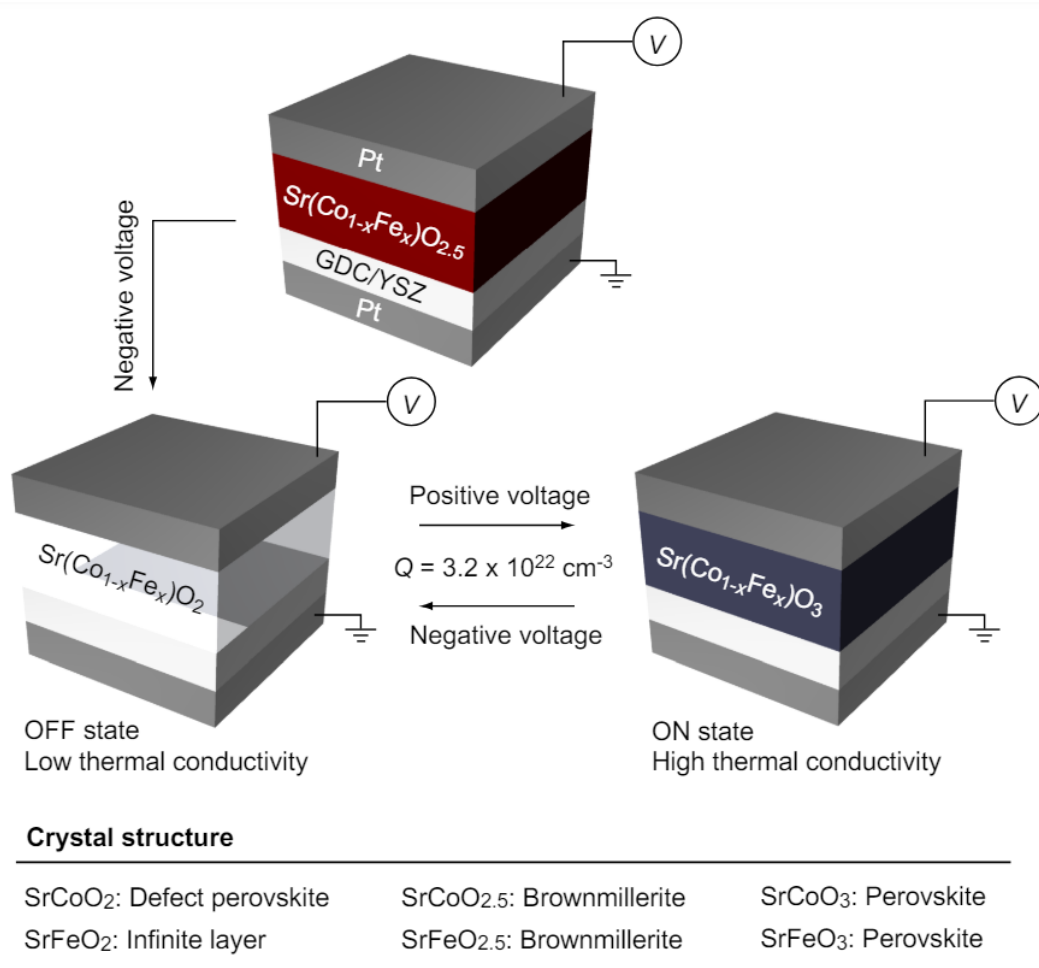


Figure 3-1 Schematic device operation of the solid-state electrochemical thermal transistors using $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ ($0 \leq x \leq 1$, $2 \leq y \leq 3$) as the active layer. Applying positive and negative voltages at 280 °C controls the state switching. When the thermal transistor is in the on state, the thermal conductivity of the active layer is high in the on state of the thermal transistor due to the well-ordered crystal structure but is low in the off state due to the oxygen defect structure.

crystal structure of both SrCoO_y and SrFeO_y is brownmillerite (BM) when $y = 2.5$ and perovskite (P) when $y = 3$. When $y = 2$, the crystal structure of SrCoO_y is defect perovskite (DP) and that of SrFeO_y is infinite layer (IL). BM and IL phases of SrCoO_y and SrFeO_y are electrical insulators. Both P- SrCoO_3 and P- SrFeO_3 are metallic conductors but the

electrical conductivity of SrCoO_3 ($\sigma_{\text{RT}} \sim 1.4 \times 10^3 \text{ S cm}^{-1}$ [2]) is higher than that of SrFeO_3 ($\sigma_{\text{RT}} \sim 50 \text{ S cm}^{-1}$ [3]). Since the difference in the crystal structure affects the lattice thermal conductivity and the difference in the electrical conductivity affects the electron thermal conductivity, we expected that κ of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ ($0 \leq x \leq 1, 2 \leq y \leq 3$) solid solutions is modulated by both controlling x and y .

I fabricated solid-state electrochemical thermal transistors using $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ as the active layers and measured the thermal conductivity after the electrochemical redox treatments. When $y = 3$, the lattice thermal conductivity of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ (P-phase) was insensitive to x , around $2.8 \text{ W m}^{-1} \text{ K}^{-1}$. When $x = 0$ (SrCoO_3), the κ increased to $\sim 3.8 \text{ W m}^{-1} \text{ K}^{-1}$ due to the contribution of the electron thermal conductivity ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$). When $y = 2$, the κ of the DP-phase ($x \leq 0.5$) was $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$, whereas the κ of the IL-phase ($x > 0.5$) was $\sim 1.2 \text{ W m}^{-1} \text{ K}^{-1}$, due to their higher periodicity in the atomic arrangement. The present results clearly indicate that the materials with the following characteristics are suitable to improve the ON/OFF κ ratio; Materials that are high electrical conductors with highly ordered lattices when the transistor is on, and electrical insulators with disordered lattices when the transistor is off.

3.2 Experimental

SrCo_{1-x}Fe_xO_y solid solutions films were heteroepitaxially grown on 10%-Gd-doped CeO₂ (GDC) buffered (001)-oriented YSZ substrates by pulsed laser deposition (PLD) technique. First, ~10-nm-thick GDC was heteroepitaxially grown on a YSZ (10 mm × 10 mm × 0.5 mm, double-sided polished, Crystal Base) substrate at 750 °C in an oxygen atmosphere (10 Pa). Focused KrF excimer laser pulses ($\lambda = 248$ nm, fluence ~ 2 J cm⁻² pulse⁻¹, repetition rate = 10 Hz) were irradiated onto the ceramic target of GDC and different SrCo_{1-x}Fe_xO_y. After films growth, the sample was cooled to room temperature in the PLD chamber in an oxygen atmosphere (10 Pa). Then ~40-nm-thick Pt film was sputtered on the top surface of the SrCo_{1-x}Fe_xO_y epitaxial film followed by low density Pt film sputtering on the backside of the YSZ substrate. Pt sputtering was performed at room temperature. Finally, the sample was cut into four squares (~5 mm × 5 mm). The thermal transistor (~5 mm × 5 mm) was put on a Pt-coated glass substrate, which was heated at 280 °C in air. Then the electrochemical redox treatment was performed by applying a constant current of ± 50 μ A. After applying the current, the sample was immediately cooled to room temperature. The crystalline phase, orientation, and lattice parameters of the resultant films were analyzed by high-resolution X-ray diffraction (XRD) (Cu K α_1 , $\lambda = 1.54059$ Å, ATX-G, Rigaku). The out-of-plane Bragg diffraction

patterns were measured at room temperature to clarify the changes in the crystalline phase of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$. The lattice parameters were calculated from the diffraction peaks. The atomic arrangement of the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ films were visualized using scanning transmission electron microscopy (STEM, JEM-ARM200CF, JEOL) operating at 200 keV. κ of the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ films perpendicular to the substrate surface was measured by time-domain thermoreflectance (TDTR, PicoTR, PicoTherm). The top Pt film was used as the transducer. The decay curves of the TDTR signals were simulated to obtain κ . The specific heat capacities of the layers used for the TDTR simulation were Pt, $132 \text{ J kg}^{-1} \text{ K}^{-1}$; SrCoO_y , $485 \text{ J kg}^{-1} \text{ K}^{-1}$; SrFeO_y , $536 \text{ J kg}^{-1} \text{ K}^{-1}$ and YSZ, $460 \text{ J kg}^{-1} \text{ K}^{-1}$. The specific heat capacities of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ solid solutions were calculated by Kopp-Neumann law[4]. Details of the TDTR method is described in Chapter 2. Soft X-ray absorption spectroscopy (XAS) of the Fe L- and O K-edges was performed at the 2A beamline in the Pohang Accelerator Laboratory. The direction of the incident X-rays was normal to the sample plane, and a circular polarization was used. The XAS spectra of these samples were measured in the total electron yield (TEY) mode at room temperature. The base pressure of the system was 10^{-9} Torr. Also, the electrical conductivity and thermopower was conducted. Compared with other characterizations, no Pt films were deposited on the surface of the samples here, and only low-density Pt films are deposited on the backside

of the samples. Oxidation of the samples was achieved by inverting the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ films side on gold foil. The electrical conductivity (σ) of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ films was measured by the DC four-probe method at room temperature in air. Thermopower of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ films was measured by the standard steady-state method. The film sample was placed in the gap (~ 3 mm) between two Peltier devices. By applying the current to Peltier device, a temperature difference was generated in the sample. We measured the temperature difference (ΔT) and the thermo-electromotive force (ΔV) simultaneously at room temperature. The thermopower was calculated as the linear slope of the ΔT – ΔV plot.

3.3 Result and discussion

Solid-state electrochemical thermal transistors with $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ solid solution films as active layers were fabricated in the previously reported way (See Experimental section). The electrochemical redox treatment was performed at 280 °C in air by applying a constant current of ± 50 μA . During the redox reaction, we controlled the flown electron density $Q = (I \cdot t)/(e \cdot V)$ by the current applying time, where I is the flown current, t is the

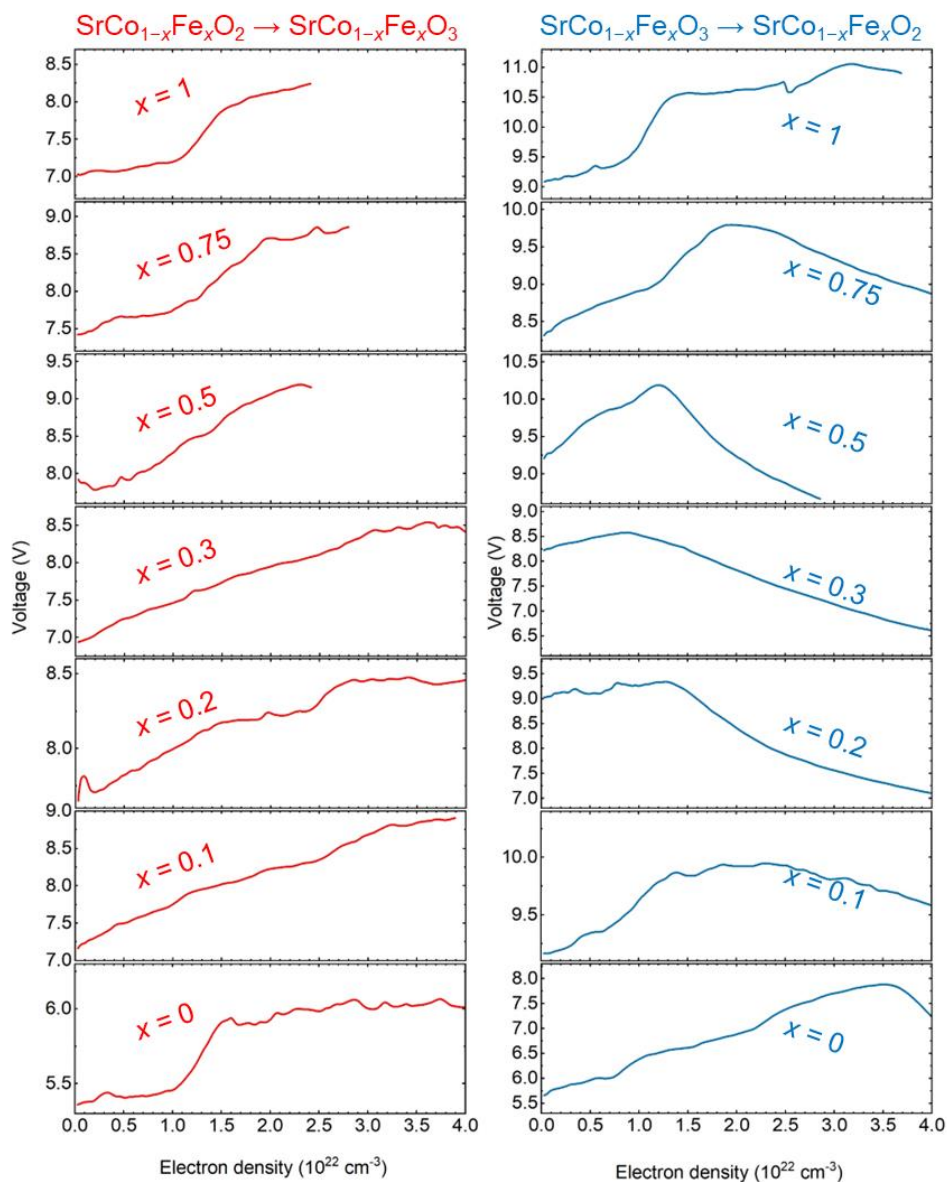
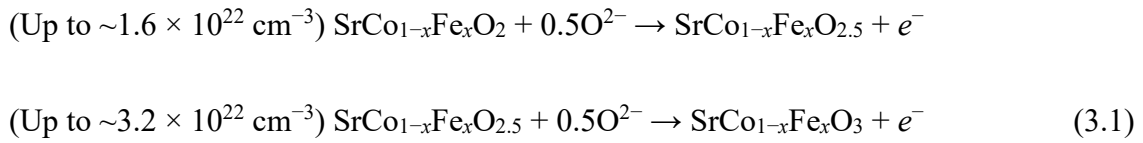


Figure 3-2 Changes in the required DC voltage of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ thermal transistors during oxidation from $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_2$ to $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ (left panel) and reduction from $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ to $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_2$ (right panel).

applied time, e is the electron charge, and V is the volume of the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ layer in thermal transistors. **Figure 3-2** shows the Q - V curves of each solid solution thermal

transistor's active layer. From this figure, it is evident that when a small amount of Fe ($x = 0.1, 0.2, 0.3$) is doped, the oxidation process requires a higher electron density or longer time to reach the inflection point. Conversely, the reduction process reaches the inflection point with a lower electron density and shorter time. The change in the out-of-plane X-ray diffraction (XRD) patterns of the resultant devices (**Figure 3-3**) reveal that the following electrochemical redox reactions occurred according to Faraday's laws of electrolysis in all cases.



In **Figure 3-3**, the clear phase transition process from as grown BM phase $\text{SrFeO}_{2.5}$ (**Figure 3-3a**) to reduced infinite layer SrFeO_2 (**Figure 3-3b**) and finally to oxidized SrFeO_3 (**Figure 3-3c**) is shown. The infinite layer SrFeO_2 appeared ($\sim 1.6 \times 10^{22} \text{ cm}^{-3}$) almost at the same time of beginning of reduction of GDC. At this point, further increasing the electron density does not continue to reduce SFO but instead leads to the continuous reduction of GDC, causing the 002 diffraction peaks of GDC to change continuously. As for the study of phase transitions in SrCoO_x , it has already been covered in the research on SrCoO_x -based thermal transistors and is not within the scope of this thesis. Therefore, it is not elaborated here.

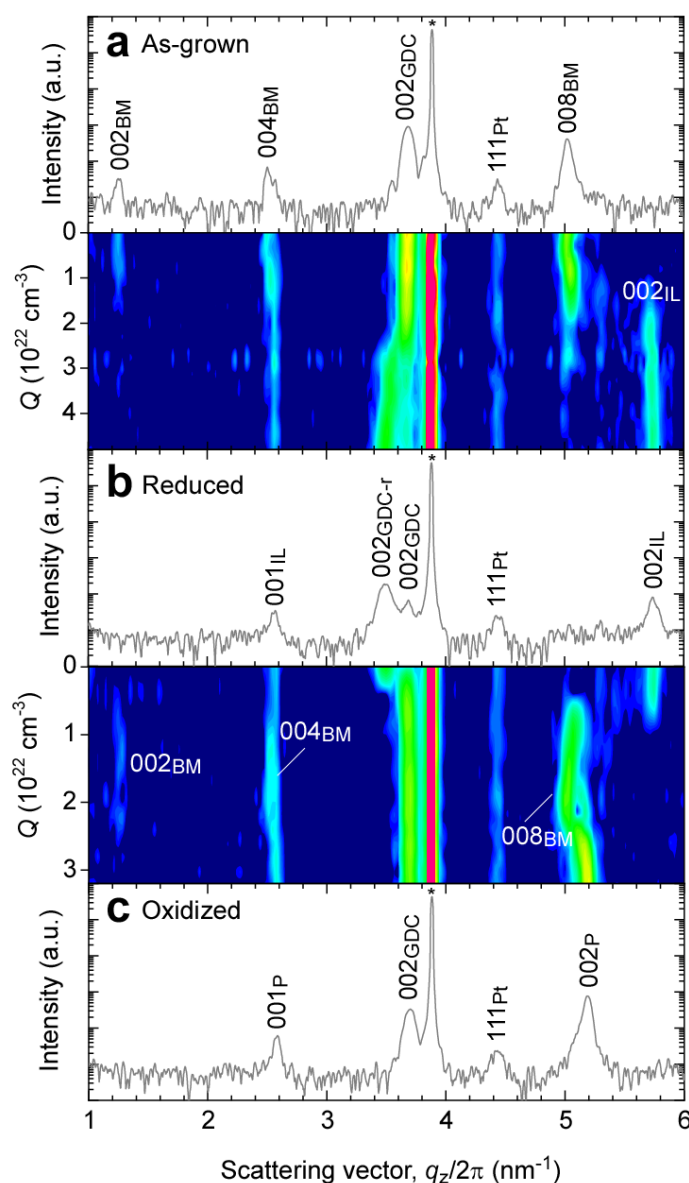


Figure 3-3 Change in the out-of-plane XRD pattern of the solid-state electrochemical thermal transistor using SrFeO_y as the active layer. (a) As-grown state: only intense Bragg diffraction peaks of the 00l brownmillerite (BM) $\text{SrFeO}_{2.5}$ appear with 002 GDC, 111 Pt, and YSZ substrates (*). (b) Reduced state: Bragg diffraction peaks of the 00l infinite layer (IL) SrFeO_2 are observed. A diffraction marked with # is originating from the YSZ substrate. (c) Bragg diffraction peaks of 00l perovskite (P) SrFeO_3 are seen.

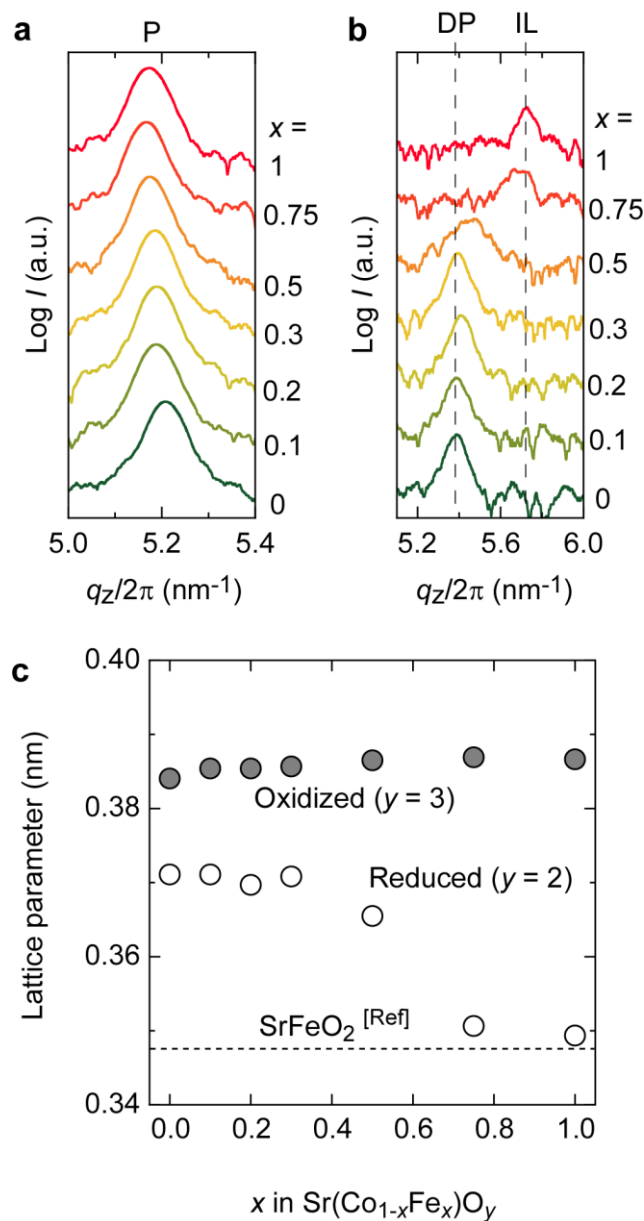


Figure 3-4 Out-of-plane XRD patterns of (a) ON state and (b) OFF state $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ based solid-state electrochemical thermal transistors. (c) Changes in the lattice parameters as a function of x . Structural phase transformation from DP to IL is clearly seen.

Figure 3-4 shows the changes in the crystal lattice of the fully oxidized $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ (ON state) and the fully reduced $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_2$ (OFF state). The diffraction peak position

of $y = 3$ phases (**Figure 3-4a**) is insensitive to x , always showing the perovskite (P) phase. On the other hand, the peak position of $y = 2$ phases (**Figure 3-4b**) changes when x exceeds 0.5, indicating that the defect perovskite (DP) structure is stable when $x \leq 0.5$ and the infinite layer (IL) structure[5-7] is stable when $x > 0.5$. Using the XRD patterns, we extracted the lattice parameters (**Figure 3-4c**). The lattice parameter of the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ films slightly increases with x since the ionic radius of Fe^{4+} (58.5 pm) is slightly larger than Co^{4+} (53 pm)[8]. On the other hand, the lattice parameter of the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_2$ films drops when x exceeds 0.5 due to the structural phase transformation from DP to IL. The observed lattice parameter of SrFeO_2 is close to the reported values.

The changes in the atomic arrangement of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ ($x = 1, y = 2, 2.5$, and 3) were confirmed by scanning transmission electron microscopy (STEM) observations (**Figure. 3-5**). Atomic arrangements of the perovskite SrFeO_3 , brownmillerite $\text{SrFeO}_{2.5}$, and infinite layer SrFeO_2 are clearly visualized. This is the first time that the infinite-layer structure of SrFeO_2 has been observed using STEM under all-solid-state electrochemical reduction conditions. Since SrFeO_x is often susceptible to corrosion in humid atmospheric environments, this observation can only be achieved by rapidly preparing and examining

the STEM samples. The X-ray absorption spectroscopy (XAS) spectra of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$

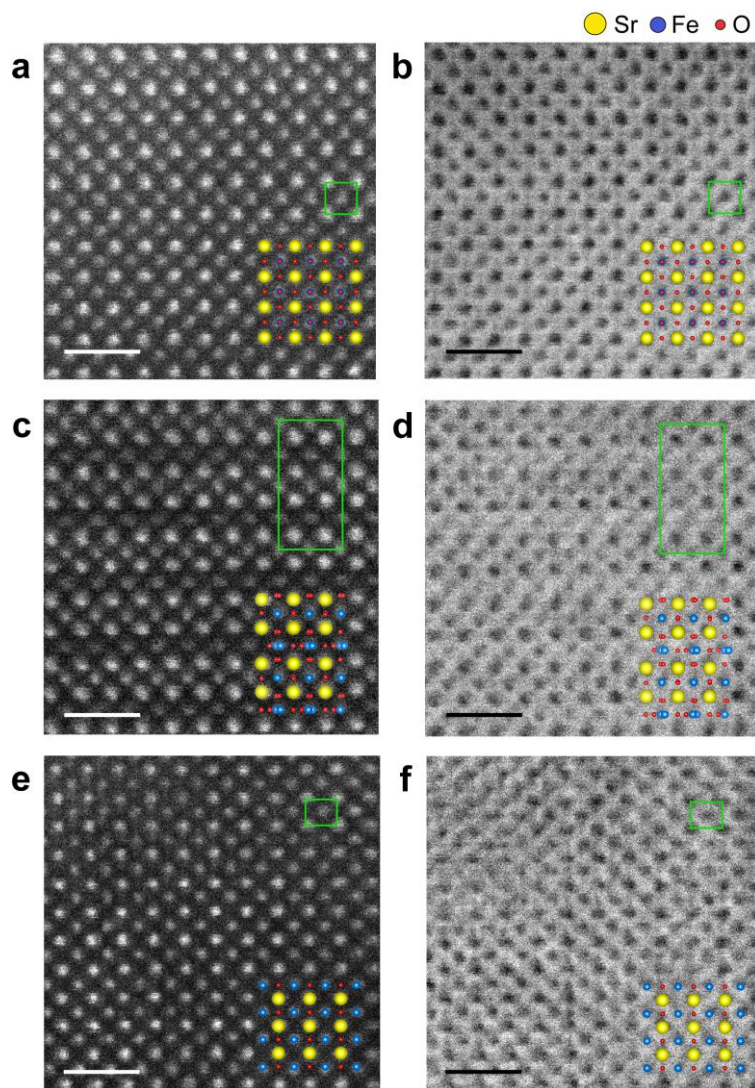


Figure 3-5. Cross-sectional STEM images of the SrFeO_y layers in the solid-state electrochemical thermal transistors. (a, c, e) HAADF-STEM images of (a) SrFeO_3 , (c) $\text{SrFeO}_{2.5}$, and (e) SrFeO_2 . Brighter dots are Sr (atomic number, $Z = 38$) and darker dots are Fe ($Z = 26$). (b, d, f) ABF-STEM images of (b) SrFeO_3 , (d) $\text{SrFeO}_{2.5}$, and (f) SrFeO_2 . Green squares represent the unit cell. Scale bar is 1 nm.

($x = 1$) was also measured (**Figure. 3-6**). Fe L-edge slightly shifts to lower energy with

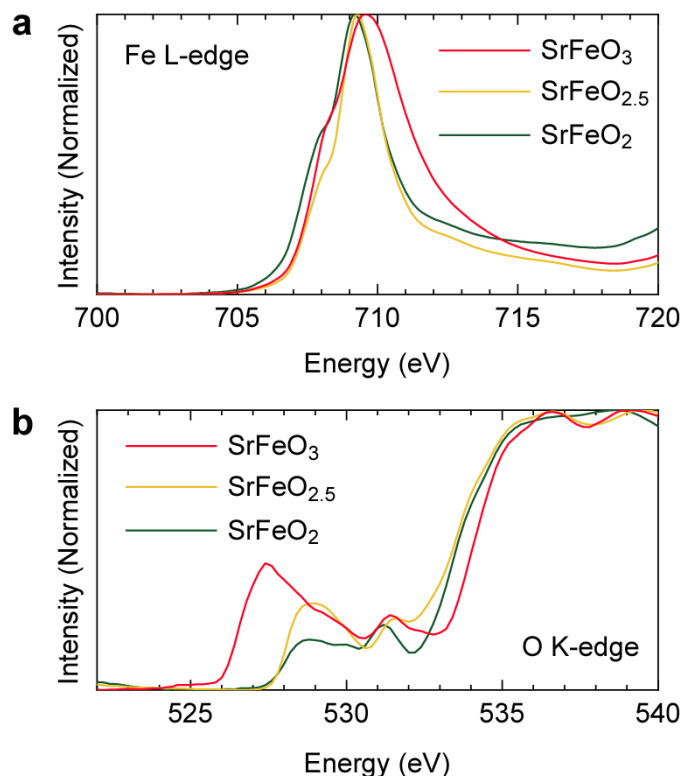


Figure 3-6 Soft X-ray absorption spectrum of SrFeO_x . (a) Soft X-ray absorption spectrum of Fe L_3 -edge of SrFeO_3 (red line), $\text{SrFeO}_{2.5}$ (yellow line), and SrFeO_2 (green line). (b) Soft X-ray absorption spectrum of O K-edge of SrFeO_3 (red line), $\text{SrFeO}_{2.5}$ (yellow line), and SrFeO_2 (green line).

decreasing y . On the other hand, O K-edge shifts to higher energy side with decreasing y .

Since SrFeO_x is often susceptible to corrosion in humid atmospheric environments, the XAS results can only indicate the trend of changes in the valence state of Fe, but cannot quantitatively confirm the information. This result can indicate that the valence state of Fe in the SrFeO_2 is 2.

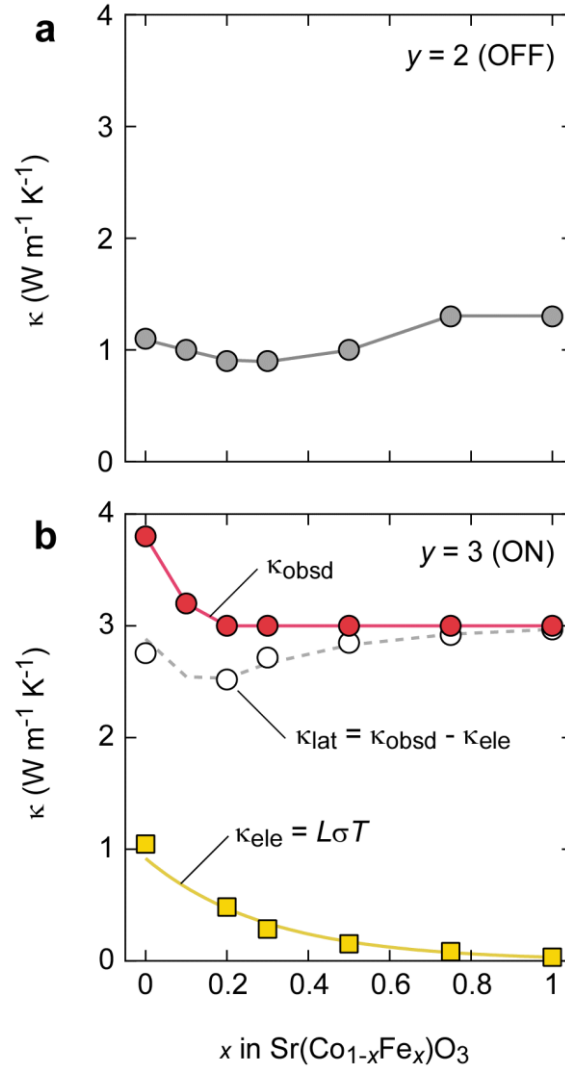


Figure 3-7 Changes in the thermal conductivity of (a) OFF state and (b) ON state of the solid-state electrochemical thermal transistors. (a) When the transistor is off ($y = 2$), κ slightly decreases from 1.1 to 0.9 as x increases from 0 to 0.5 and then increases to 1.2 $\text{W m}^{-1} \text{K}^{-1}$. (b) When the transistor is on ($y = 3$), κ_{obsd} dramatically decreases from ~ 3.8 to ~ 3.0 $\text{W m}^{-1} \text{K}^{-1}$ as x increases from 0 to 0.2 and then becomes saturated at ~ 3.0 $\text{W m}^{-1} \text{K}^{-1}$. Electron thermal conductivity (κ_{ele}) is calculated from $\kappa_{\text{ele}} = L\sigma T$, where L is the Lorentz number, σ is the electrical conductivity, and T is the absolute temperature. Lattice thermal conductivity (κ_{lat}) is calculated from $\kappa_{\text{lat}} = \kappa_{\text{obsd}} - \kappa_{\text{ele}}$.

Next, we measured the thermal conductivity (κ) of the thermal transistors when it is ON

and OFF at room temperature in air (**Figure 3-7**, **Figure 3-8**). When the transistor is off ($y = 2$) (**Figure 3-7a**), the κ slightly decreases from 1.1 to 0.9 with increasing x from 0 to 0.5, and increases to $1.2 \text{ W m}^{-1} \text{ K}^{-1}$ after that. The well-ordered oxygen defect arrangement in the IL structure (MO_6 octahedra $\rightarrow$ MO_4 square planar, $M = \text{Co}$ and Fe) would cause the IL structured films to exhibit slightly higher κ than those of the DP structures films. On the other hand, when the transistor is on ($y = 3$) (**Figure 3-7b**), the κ dramatically decreases from $\sim 3.8 \text{ W m}^{-1} \text{ K}^{-1}$ to $\sim 3.0 \text{ W m}^{-1} \text{ K}^{-1}$ with increasing x from 0 to 0.2, and saturates $\sim 3.0 \text{ W m}^{-1} \text{ K}^{-1}$ after that.

As for the ON state, since their structures remain perovskite structure and both Co and Fe atoms have similar atomic masses, the change in κ is evidently due to factors other than the lattice. In the case of ceramics, quantized lattice vibration (phonon) dominantly carries heat, while in the case of metals, electron carrier dominantly carries heat. Therefore, observable thermal conductivity is a summation of the lattice thermal conductivity κ_{lat} and electron thermal conductivity κ_{ele} .

In order to estimate κ_{ele} , we separately measured the electrical conductivity (σ) and thermopower (S) of the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ layers at room temperature (**Figure 3-9**). The σ

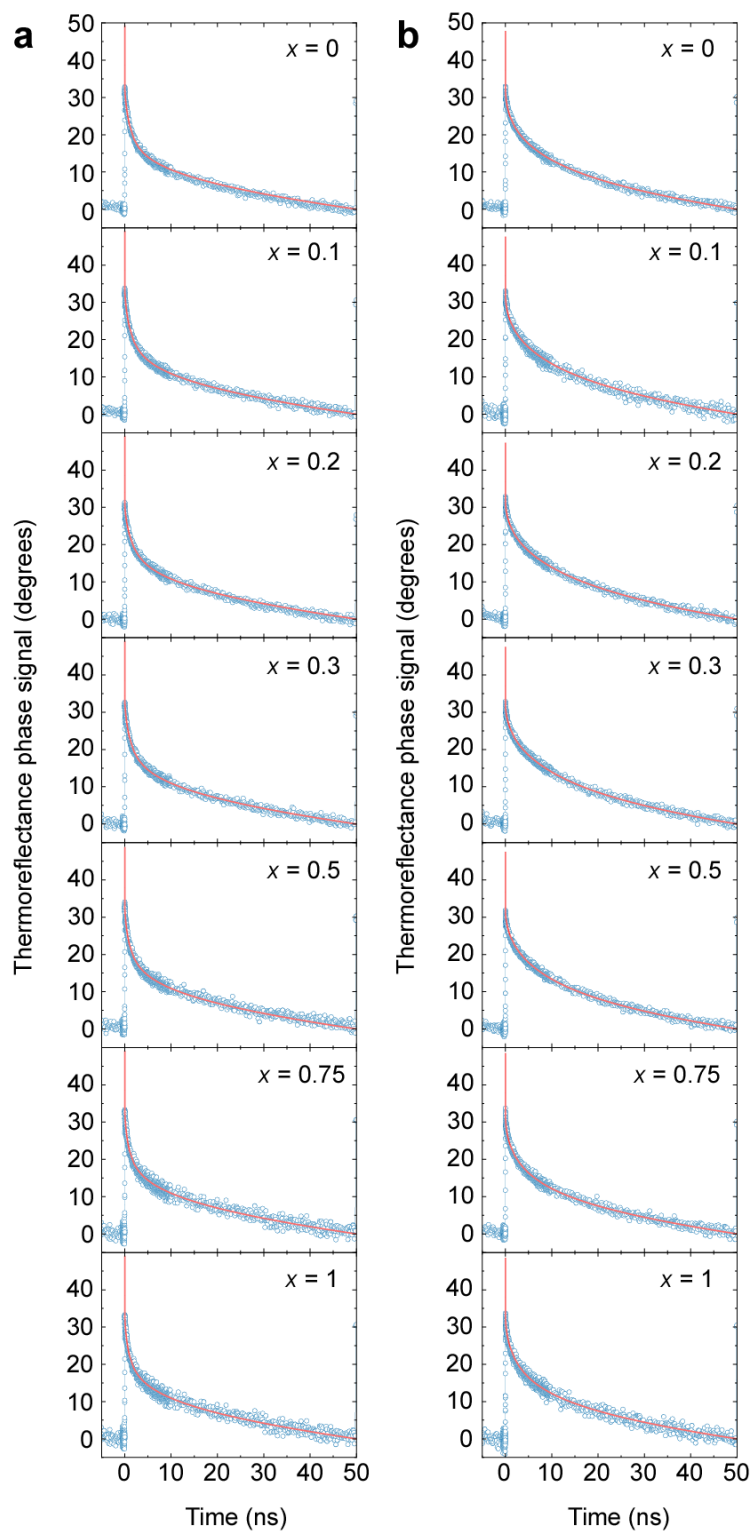


Figure 3-8 Decay curves of the thermorefectance phase signal for the $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ thermal transistors. (a) ON state ($\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$) and (b) OFF state ($\text{SrCo}_{1-x}\text{Fe}_x\text{O}_2$).

dramatically decreased with increasing x . We found that there is a linear relationship between $\log \sigma$ and x :

$$\text{Log } \sigma (\text{S cm}^{-1}) = 3.101 - 1.45 x \quad (3.2)$$

On the other hand, S values of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ are all negative, and their absolute value increases with increasing x . Generally, when the Fermi level is closer to the band edge, the absolute value of the partial differential of the density of states (DOS) at the Fermi level is larger, the absolute value of its thermal power is larger and the conductivity tends to be lower[9].

Then, we calculated κ_{ele} of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ layers using the relationship between $\log \sigma$ and x by assuming Wiedemann-Frantz law[10]:

$$\kappa_{\text{ele}} = L \cdot \sigma \cdot T \quad (3.3)$$

where L is the Lorentz number ($2.44 \times 10^{-8} \text{ W } \Omega \text{ K}^{-2}$). The κ_{ele} gradually decreased with x and has a similar tendency with κ_{obsd} . We then extracted κ_{lat} as $\kappa_{\text{lat}} = \kappa_{\text{obsd}} - \kappa_{\text{ele}}$. The κ_{lat} of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ ($x = 0$) was $\sim 2.8 \text{ W m}^{-1} \text{ K}^{-1}$, and the κ_{lat} firstly decreased then returned and saturated $\sim 2.9 \text{ W m}^{-1} \text{ K}^{-1}$ with increasing x , most likely due to alloying effect.

The present results clearly indicate that the materials with the following characteristics are suitable to improve the ON/OFF ratio; Materials that are high electrical conducto with

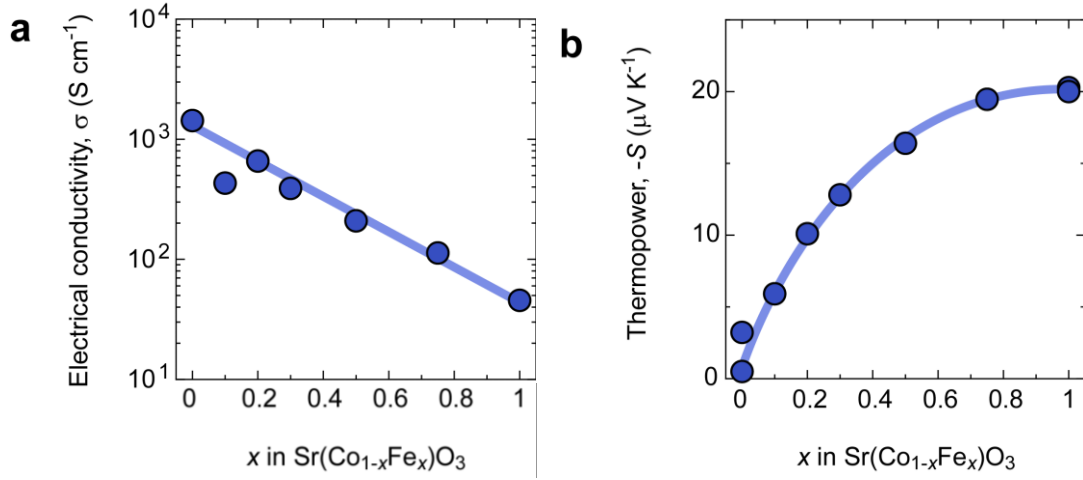


Figure 3-9 Change in the electron transport properties of the SrCo_{1-x}Fe_xO₃ layers measured at room temperature. (a) Electrical conductivity (σ) and (b) thermopower (S). We found that there is a linear relationship between $\log \sigma$ and x : $\log \sigma (\text{S cm}^{-1}) = 3.101 - 1.45x$. The $-S$ tends to increase with increasing x in SrCo_{1-x}Fe_xO₃

highly ordered lattices when the transistor is on, and electrical insulators with disordered lattices when the transistor is off. Since the electrical conductivity of SrCoO₃ is not as high as some other metal oxides (e.g. SrRuO₃: $6.6 \times 10^3 \text{ S cm}^{-1}$ [11], SrNbO₃: $1 \times 10^4 \text{ S cm}^{-1}$ [22]), there would be still room for improvement. The present results would boost the development of practical solid-state thermal transistors.

3.4 Conclusion

In summary, the systematic modulation of the κ of SrCo_{1-x}Fe_xO_y ($0 \leq x \leq 1$, $2 \leq y \leq 3$) solid solutions has been clarified. I fabricated solid-state electrochemical thermal transistors using SrCo_{1-x}Fe_xO_y as the active layers and measured the thermal conductivity

after the electrochemical redox treatments. When $y = 3$, the lattice thermal conductivity of $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ (P-phase) was insensitive to x , around $2.8 \text{ W m}^{-1} \text{ K}^{-1}$. When $x = 0$ (SrCoO_3), the κ increased to $\sim 3.8 \text{ W m}^{-1} \text{ K}^{-1}$ due to the contribution of the electron thermal conductivity ($\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$). When $y = 2$, the κ of the DP-phase ($x \leq 0.5$) was $\sim 1 \text{ W m}^{-1} \text{ K}^{-1}$, whereas the κ of the IL-phase ($x > 0.5$) was $\sim 1.2 \text{ W m}^{-1} \text{ K}^{-1}$, due to their higher periodicity in the atomic arrangement. The present results clearly indicate that the materials with the following characteristics are suitable to improve the ON/OFF ratio; Materials that are high electrical conductors with highly ordered lattices when the transistor is on, and electrical insulators with disordered lattices when the transistor is off. The present results would boost the development of practical solid-state thermal transistors.

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Chapter 4. Solid-State Electrochemical Thermal Transistors with Large Thermal Conductivity Switching Widths

4.1. Objective of this chapter

In the last chapter, through my exploration of all-solid-state thermal transistors based on $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_y$ solid solutions, I discovered that the high electron thermal conductivity (κ_{ele}) brought about by high electrical conductivity (σ) contributes to the overall thermal conductivity (κ) in certain specific material systems. This implies that by exploring a series of high σ crystalline phases of transition metal oxides (TMOs), there is a probability of finding more suitable active layer materials for all-solid-state thermal transistors.

This is not an easy exploration. In addition to the aforementioned goals, the following points should be considered when selecting suitable active layer materials:

1. The material must be able to be epitaxially grown on the oxygen ion conductors relied upon in this study, specifically, on 10%-Gd-doped CeO_2 (GDC)-buffered (001)-oriented YSZ substrates. In other words, the lattice must have a high degree of compatibility with the substrate and exhibit good wettability with the substrate material.
2. The material must have the potential for redox reactions, and the crystalline phase presented during the redox process must still maintain a high degree of lattice match with the substrate.

3. The material must have high chemical stability, meaning it should not easily react with environmental factors such as moisture to form new substances.

There are not many materials that simultaneously meet the above conditions. I have made numerous attempts with material systems such as SrVO_x , SrMoO_x , and CuO_x , but none of them could fully satisfy all the conditions to become qualified active layer materials for all-solid-state thermal transistors.

In subsequent collaboration with Tanaka-Lab at Osaka University, we conducted a series of studies on the thermal conductivity during the protonation/deprotonation process of rare earth nickelate (ReNiO_3) materials. The research revealed that LaNiO_3 , which has the highest σ among various ReNiO_3 , also possesses very high κ . I also found that, bulk LaNiO_3 also has comparably high electrical and thermal conductivity[1], indicating its potential for thermal conductivity modulation (**Table 4-1**). As a result, I chose LaNiO_3 as the active material for solid-state electrochemical thermal transistors.

Table 4-1 The electrical conductivity (σ) and the thermal conductivity (κ) of bulk ReNiO_3 ($\text{Re} = \text{La}, \text{Nd}, \text{and Sm}$) at room temperature.[1]The ionic radius data is from Shannon's report.[2]

J.-S. Zhou <i>et al.</i> , <i>PRB</i> 67 , 020404(R) (2003)	LaNiO_3	NdNiO_3	SmNiO_3
Ionic radius of Re^{3+} ion ($\text{\AA}$) (C.N. = 12)	1.36 ²	1.27 ²	1.24 ²
Electrical conductivity at RT (S cm^{-1})	10500	3400	---
Total thermal conductivity, κ ($\text{W m}^{-1} \text{K}^{-1}$)	10.7	6.5	4.0
Electron thermal conductivity, κ_{ele} ($\text{W m}^{-1} \text{K}^{-1}$)	7.6	2.5	0
Lattice thermal conductivity, κ_{lat} ($\text{W m}^{-1} \text{K}^{-1}$)	3.1	4.0	4.0

Therefore, before formally introducing the development details of the LaNiO_x all-solid-state thermal transistor, I intend to dedicate a section to our research on ReNiO_3 and their κ during the protonation/deprotonation process. This research laid a very important foundation for my development of the LaNiO_x all-solid-state thermal transistor.

4.2 Wide-range thermal conductivity modulation based on protonation of LaNiO_3

Electric gate can be applied to control the proton diffusion and induce the resistance change of ReNiO_3 for application such as artificial synapse[3,4]. In this research, the ReNiO_3 thin films were grown on LSAT(001) by pulsed laser deposition conducted by Tanaka-Lab at Osaka University. Protonation of ReNiO_3 is achieved by ionic liquid

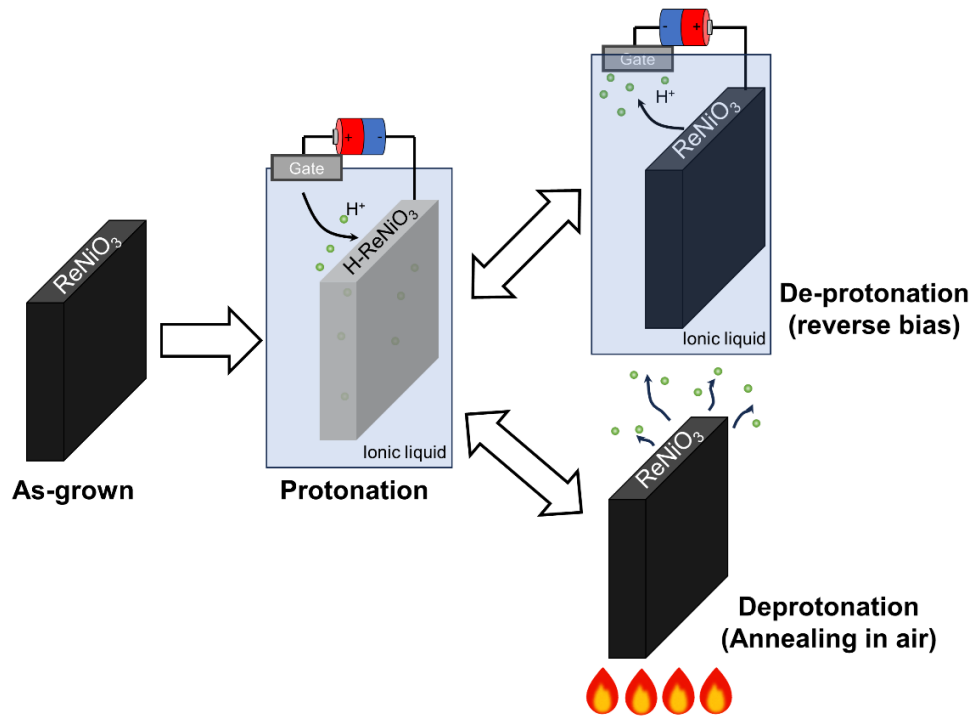


Figure 4-1 The protonation by ionic liquid gating and two reversible approaches to realize deprotonation.

gating at room-temperature as shown in **Figure 4-1**. The water molecules are decomposed at the thin film surface and proton diffuses into $ReNiO_3$ due to chemical potential difference [5]. Deprotonation can be realized by two approaches, (1) ionic liquid gating with reversed voltage and (2) annealing the $H-ReNiO_3$ in the air at 400 °C. The room-temperature κ of $ReNiO_3$, $H-ReNiO_3$ and deprotonated $ReNiO_3$ series are evaluated at room-temperature by time domain thermos reflectance (TDTR) as described in the Chapter 2. By fitting the decay curve of phase signal of TDTR, the

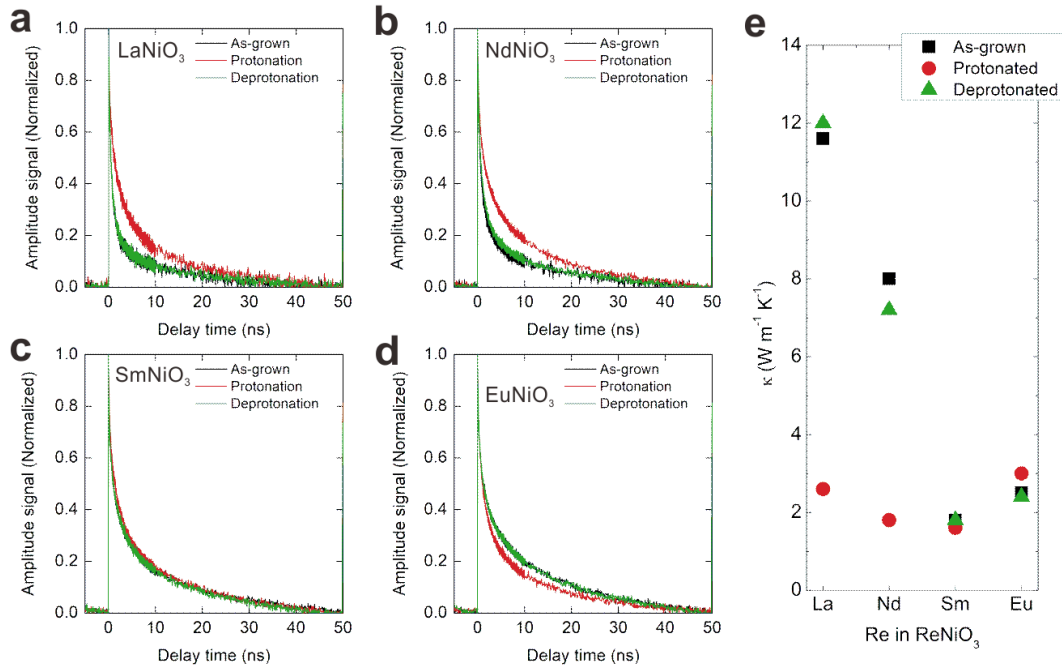


Figure 4-2. TDTR decay curves of as-grown, protonated and deprotonated $ReNiO_3$ ($Re = La, Sm, Nd, Eu$) measured by the process mentioned in method section. The original data of each material is demonstrated in (a)-(d). (e) is a summary of the thermal conductivity modulation of $ReNiO_3$ before and after protonation and the reproducibility is verified. Among all, $LaNiO_3$ exhibits wide-range modulation of thermal conductivity.

total κ of as-grown $ReNiO_3$ ($Re = La, Nd, Sm, Eu$) thin films are estimated to be 11.6 $W m^{-1} K^{-1}$, 8.0 $W m^{-1} K^{-1}$, 1.8 $W m^{-1} K^{-1}$ and 2.5 $W m^{-1} K^{-1}$, respectively (**Figure 4-**

2a-d). After performing protonation by ionic liquid gating, the measured curves of LaNiO_3 exhibit clearly difference from as-grown state and the thermal conductivities are greatly suppressed to $2.6 \text{ W m}^{-1} \text{ K}^{-1}$ for LaNiO_3 . Besides, similar to the structural modulation, κ 's of the as-grown status is recovered after deprotonation (**Figure 4-2e**), implying the reversibility of the wide-range thermal regulation in LaNiO_3 by controllable protonation and deprotonation which is crucial for future device applications.

It is known that LaNiO_3 is always metallic, while NdNiO_3 , SmNiO_3 and EuNiO_3 exhibits metal-insulator transition at $\sim 200 \text{ K}$, $\sim 400 \text{ K}$ and $\sim 450 \text{ K}$, respectively[6-8]. By summarizing the relationship of thermal conductivity and electrical conductivity of ReNiO_3 and H-ReNiO_3 , it is found that at 300 K the wide-range thermal conductivity regulation only occurs in the material that is in metallic status. Hence, for LaNiO_3 , the high κ in their pristine states could be mainly governed by κ_{ele} . Since LaNiO_3 is metallic at room temperature, it is assumed that the total κ of LaNiO_3 could be roughly estimated by Wiedemann–Franz law which has already been introduced in Chapter 3.

After protonation, the Ni^{3+} is reduced to Ni^{2+} , and the electrons become localized due to strong repulsion between two e_g electrons in Ni^{2+} . Thus, the dominating κ_{ele} in LaNiO_3 is great suppressed and electrical conductivity decreases by ~ 3 orders of magnitude. Then, in the H-LaNiO_3 , the intrinsic κ_{lat} becomes dominant instead and the

wide-range modulation of thermal conductivity can be observed. As comparison, it is known that the oxygen content can also result in metal-insulator transition in perovskite oxides. This provided me with significant insight. If LaNiO_3 is used as the active layer in all-solid-state thermal transistors, utilizing oxygen vacancy control to regulate its metal-insulator transition could offer substantial advantages. Therefore, I conducted further research on LaNiO_x -based all-solid-state thermal transistor.

4.3 Experimental

LaNiO_x films were heteroepitaxially grown on $\text{SrCoO}_x/\text{GDC}$ -buffered (001)-oriented YSZ substrates using pulsed laser deposition (PLD). First, approximately 10 nm-thick GDC was heteroepitaxially grown on a YSZ (10 mm $\times$ 10 mm $\times$ 0.5 mm, double-sided polished, crystal base) substrate at 770 °C in an oxygen atmosphere (10 Pa). Approximately 2-nm-thick SrCoO_x was grown on GDC in the same conditions. Focused KrF excimer laser pulses ($\lambda = 248$ nm, fluence ~ 2 J cm $^{-2}$ pulse $^{-1}$, repetition rate = 10 Hz) were irradiated onto the ceramic target of GDC. Subsequently, an approximately 80-nm-thick LaNiO_3 film was heteroepitaxially grown on the GDC film at 625 °C in an oxygen atmosphere (25 Pa). The laser fluence was approximately 1.6 J cm $^{-2}$ pulse $^{-1}$. After film growth, the sample was cooled to room temperature in a PLD chamber in an oxygen atmosphere (25 Pa). An approximately 50-nm-thick Pt film was sputtered on the top surface of the LaNiO_3 epitaxial film, followed by an approximately 50-nm-thick Pt film sputtered on the backside of the YSZ substrate. DC sputtering of

Pt was performed at room temperature. The samples were cut into four squares ($\sim 5 \text{ mm} \times 5 \text{ mm}$). After that, thermal transistor ($\sim 5 \text{ mm} \times 5 \text{ mm}$) was placed on a Pt-coated glass substrate and heated at 280°C in air. Electrochemical redox treatment was performed by applying a constant current of $\pm 10 \text{ }\mu\text{A}$, after which the sample was immediately cooled to room temperature. During the redox treatment, we controlled the flown electron density $Q = (I \cdot t)/(e \cdot V)$ through the current application time. The crystalline phase, orientation, and lattice parameters of the resultant films were analyzed using high-resolution x-ray diffraction ($\text{Cu K}\alpha_1$, $\lambda = 1.54059 \text{ }\text{\AA}$, ATX-G, Rigaku). Out-of-plane Bragg diffraction patterns and reciprocal space mappings (RSMs) were measured at room temperature to clarify changes in the crystalline phase of LaNiO_x . The lattice parameters were calculated from the diffraction peaks. The atomic arrangements of the LaNiO_3 films were visualized using a STEM (JEM-ARM200CF, JEOL) operated at 200 keV . To measure the electrical conductivity (σ) of the LaNiO_x layers after redox treatment, we mechanically attached Au foil on the film surface while Pt films were deposited only on the backside of the YSZ substrate. The LaNiO_x films were oxidized and reduced electrochemically at 280°C in air using the Au foil as the electrode. The σ of the LaNiO_3 (on state) and $\text{LaNiO}_{2.72}$ (off state) films was measured using the DC four-probe method with a van der Pauw electrode configuration at room temperature in air. The κ of the LaNiO_3 layers perpendicular to the substrate surface was measured through time-domain thermoreflectance (TDTR, PicoTR, Netzsch Japan). The top Pt film was used as the transducer. The decay curves of the TDTR signals were simulated

to obtain κ . The specific heat capacity of the LaNiO_3 ceramic target was measured by differential scanning calorimetry (DSC, DSC200, Hitachi High-Tech Co.). The specific heat capacities of the layers used for the TDTR simulation were Pt: $132 \text{ J kg}^{-1} \text{ K}^{-1}$ [9]; LaNiO_3 : $420 \text{ J kg}^{-1} \text{ K}^{-1}$ (measured) (*cf.* $448 \text{ J kg}^{-1} \text{ K}^{-1}$ [10]), and YSZ: $460 \text{ J kg}^{-1} \text{ K}^{-1}$ [11]. Note that we simulated the TDTR decay curves by assuming the interfacial resistance due to 2-nm-thick SrCoO_x and 10-nm-thick GDC layers is constant ($1 \times 10^{-9} \text{ K W}^{-1}$). We confirmed this assumption works by measuring the thermal conductivity of the thicker (151-nm-thick) LaNiO_3 active layer. In the treatment of the thermal conductivity values, as there were uncertainties such as the position of the baseline, position of time zero, and noise in the signal, we used error bars for $\pm 15\%$ of the obtained values.

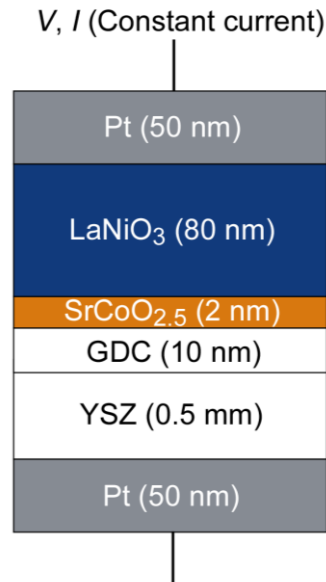


Figure 4-3 Structure of the thermal transistor that is composed of six layers. 50-nm-thick Pt film, 80-nm-thick LaNiO_x film, 2-nm-thick SrCoO_x film, 10-nm-thick Gd-doped CeO_2 (GDC) film, 0.5-mm-thick (001) YSZ single-crystal substrate, and 40-nm-thick Pt film.

4.4 Results and Discussion

4.4.1 Electrochemical Thermal Transistor Fabrication and Operation

Figure 4-3 shows a schematic of the thermal transistor device structure, which is similar to those of our previous thermal transistors[12-14] In this study, we inserted an

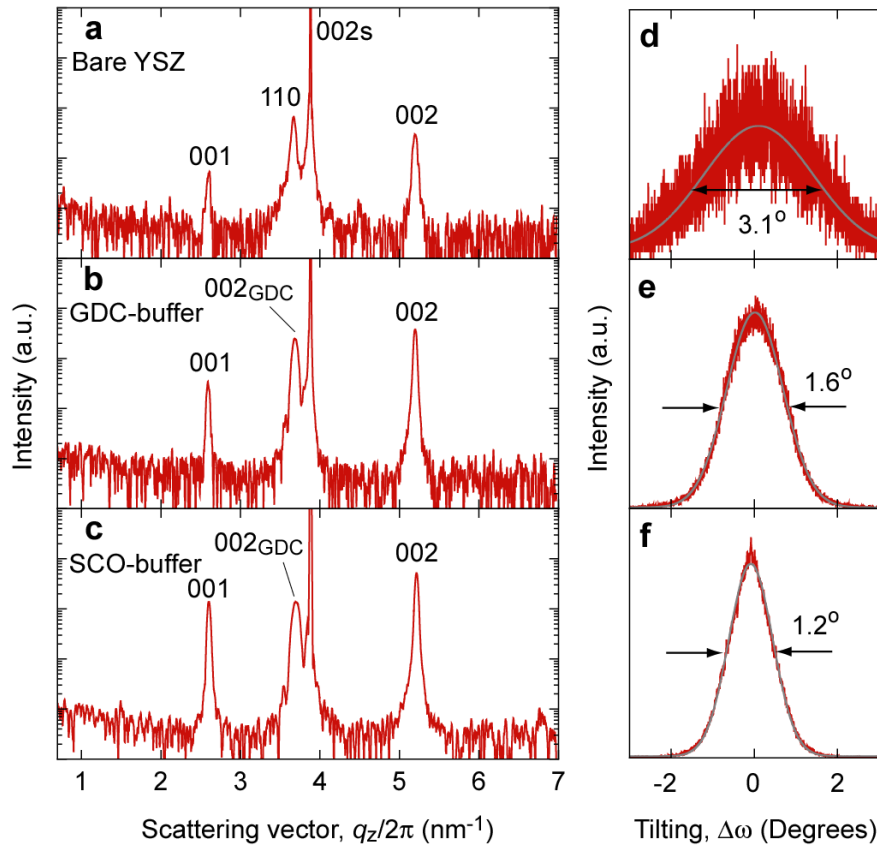


Figure 4-4 XRD patterns of the LaNiO_3 films grown on various substrates. (a)-(c) Out-of-plane Bragg diffraction patterns of the LaNiO_3 films grown on (a) bare (001) YSZ substrate, (b) GDC-buffered (001) YSZ substrate, and (c) $\text{SrCoO}_x/\text{GDC}$ -buffered (001) YSZ substrate. (d)-(f) Out-of-plane rocking curves of 002 LaNiO_3 of the films on (d) bare (001) YSZ substrate, (e) GDC-buffered (001) YSZ substrate, and (f) $\text{SrCoO}_x/\text{GDC}$ -buffered (001) YSZ substrate.

extremely thin SrCoO_x layer between the LaNiO_3 and solid electrolyte (Gd-doped

CeO₂/YSZ) (**Figure 4-4**). As shown in **Figure 4-4**, When LaNiO₃ is grown on bare YSZ, a single-orientation, pure epitaxial film cannot be obtained, and the rocking curve

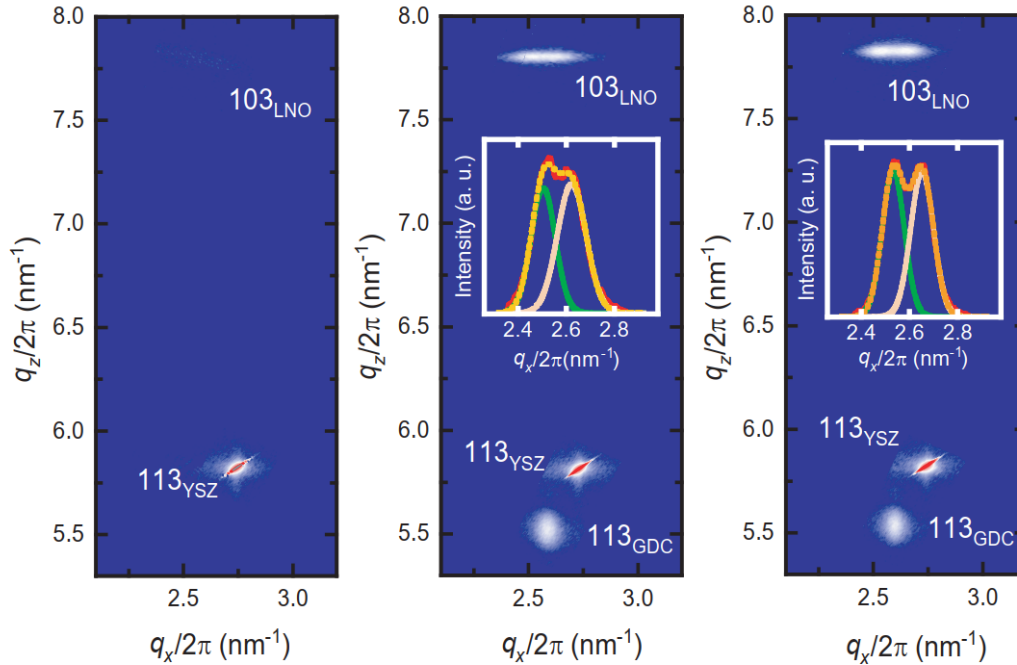


Figure 4-5 X-ray reciprocal space mappings (RSMs) around 113 YSZ diffraction spots. Left panel is LaNiO₃ grows directly on (001) YSZ, 103 LaNiO₃ shows very low intensity. Using ~10nm GDC as a buffer layer can decrease the lattice mismatch between substrate and film (5.5% to -0.5%). Single-oriented LaNiO₃ can be grown but shows wide and split 103 diffraction spots (Middle panel). The FWHM of each peak is 0.1181 nm⁻¹ (green) and 0.1407 nm⁻¹(light pink). Based on this, inserting ~2nm SrCoO_x as a buffer, the width of 103 peak decreases but still splitting. The FWHM of each peak is 0.1077 nm⁻¹ (green) and 0.1114 nm⁻¹(light pink). Using ~2 nm SrCoO_x and ~10 nm GDC as a buffer layer can effectively improve the quality of LaNiO₃ film. The lattice parameter of LaNiO₃ on SrCoO_x/GDC/YSZ is $a = 0.386$ nm and $c = 0.383$ nm. The volume of lattice is 0.05706 nm³.

exhibits a relatively broad (3.1°) full width at half maximum (FWHM). However, when LaNiO₃ is grown on YSZ with a GDC buffer layer, a single-orientation epitaxial film can be achieved, and the FWHM of the rocking curve narrows (1.6°). Nevertheless, the film quality is still insufficient for fabricating thermal transistors. When LaNiO₃ was

grown on the $\text{SrCoO}_x/\text{GDC}$ -buffered (001) YSZ, the crystallographic orientation was stronger than that without a buffer layer. X-ray reciprocal space mapping (RSM) around 113 YSZ diffraction spots (**Figure 4-5**) confirmed that LaNiO_3 grown on $\text{SrCoO}_x/\text{GDC}$ -buffered (001) YSZ demonstrated the highest quality. As shown in **Figure 4-5**, the in-plane lattice constant of the GDC film is larger than that of YSZ. With a thickness of 10 nm, the GDC film exceeds its critical thickness, allowing the lattice to fully relax. This is highly beneficial in reducing the lattice mismatch with common perovskite materials. It is noteworthy that the 113-diffraction spot of LaNiO_3 exhibits splitting, whether grown on YSZ with only a GDC buffer layer or on YSZ with both a GDC and an additional SCO buffer layer. This splitting may be caused by the tilting of different LaNiO_3 crystal domains during the growth process. Additionally, after using SCO as an extra buffer layer, the splitting of the 113-diffraction spot becomes noticeably closer, and the FWHM of each split peak also narrows. This leads me to believe that selecting a better buffer layer could potentially further optimize the preparation of LaNiO_3 thermal transistors. Specifically, it may eliminate the splitting of the 113-diffraction peak and narrow the FWHM, resulting in LaNiO_3 films with properties more closely resembling those of bulk LaNiO_3 . This could further enhance the thermal conductivity switching range of the thermal transistor. Moreover, there was a positive correlation between the quality of LaNiO_3 and its thermal conductivity (**Table 4-2**). Thus, the use of the thermal transistor structure shown in **Figure 4-3** is crucial.

Table 4-2 Electrical and thermal conductivity of the LaNiO₃ films grown on the three different substrates.

	Bare YSZ	GDC-buffered	SCO-buffered
Electrical conductivity, σ (S cm ⁻¹)	500	1200	4200
Thermal conductivity, κ (W m ⁻¹ K ⁻¹)	1.6	4	5.7
Electron thermal conductivity, κ_{ele} (W m ⁻¹ K ⁻¹)	0.36	0.88	3.0
Lattice thermal conductivity, κ_{lat} (W m ⁻¹ K ⁻¹)	1.2	3.1	2.7

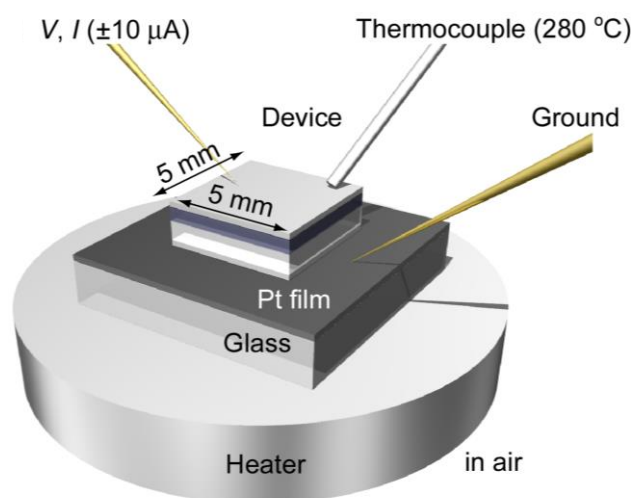
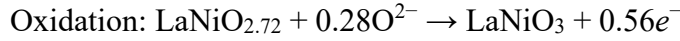
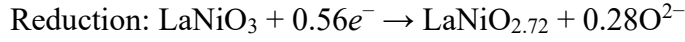


Figure 4-6 Schematic of LaNiO_x thermal transistor. The transistor was placed on a Pt-coated glass substrate and heated at 280 °C in air. A K-type thermocouple was used to monitor the switch surface temperature. The switch measured 5 mm × 5 mm. A constant negative current (−10 μA) was applied for reduction; a constant positive current (+10 μA) was applied for oxidation.

The setup for the operation of the LaNiO_x thermal transistor is shown in **Figure 4-6**.

Electrochemical redox treatment was performed at 280 °C in air by applying a constant current of ±10 μA. During the redox reaction, we controlled the flown electron density $Q = (I \cdot t)/(e \cdot V)$ through the current application time (**Figure 4-7**), with a step of $Q = 2 \times 10^{21} \text{ cm}^{-3}$ marked as A – K, where I is the flown current, t is the application time, e is the electron charge, and V is the volume of the LaNiO_x layer in the thermal transistor.

In this study, electrochemical redox treatments were performed according to Faraday's law of electrolysis.



The conductivity of the reduced state of $\text{LaNiO}_{2.72}$ (9 S cm^{-1}) also confirmed its identity as $\text{LaNiO}_{2.72}$ [15].

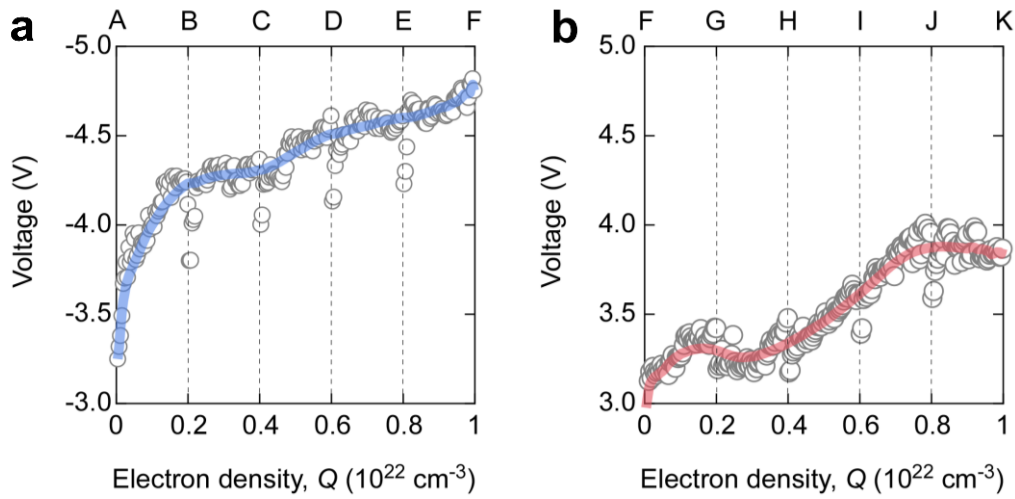


Figure 4-7 Changes in observed DC voltage of thermal transistor during (a) reduction from LaNiO_3 to $\text{LaNiO}_{2.72}$ and (b) oxidation from $\text{LaNiO}_{2.72}$ to LaNiO_3 with a step of $Q = 2 \times 10^{21} \text{ cm}^{-3}$.

Electrochemical redox treatment was initiated by applying a negative current to reduce LaNiO_3 to $\text{LaNiO}_{2.72}$ **Figure 4-7a**). As Q increased, the absolute value of the voltage increased. The slope decreased after $2 \times 10^{21} \text{ cm}^{-3}$ and slightly increased after $2 \times 10^{21} \text{ cm}^{-3}$. When the current became positive, $\text{LaNiO}_{2.72}$ was oxidized to LaNiO_3 (**Figure 4-7b**). As Q increased, fluctuations occurred at $2 \times 10^{21} \text{ cm}^{-3}$ and $8 \times 10^{21} \text{ cm}^{-3}$. Overall, there was still an increasing trend and an absolute value between 3 V and 5 V,

with minimal variations. The absence of steps in the process curve indicates that there were no new thermodynamically stable phases.

4.4.2 Crystalline Lattice and Thermal Conductivity Changes during Redox Treatment

Redox treatment induced reversible changes in the crystalline lattice of LaNiO_x step by step (reduction $A \rightarrow F$, oxidation: $F \rightarrow K$), as evidenced by the out-of-plane x-ray diffraction patterns (**Figure 4-8a**). Slight shifts in the 002 diffraction peak indicated

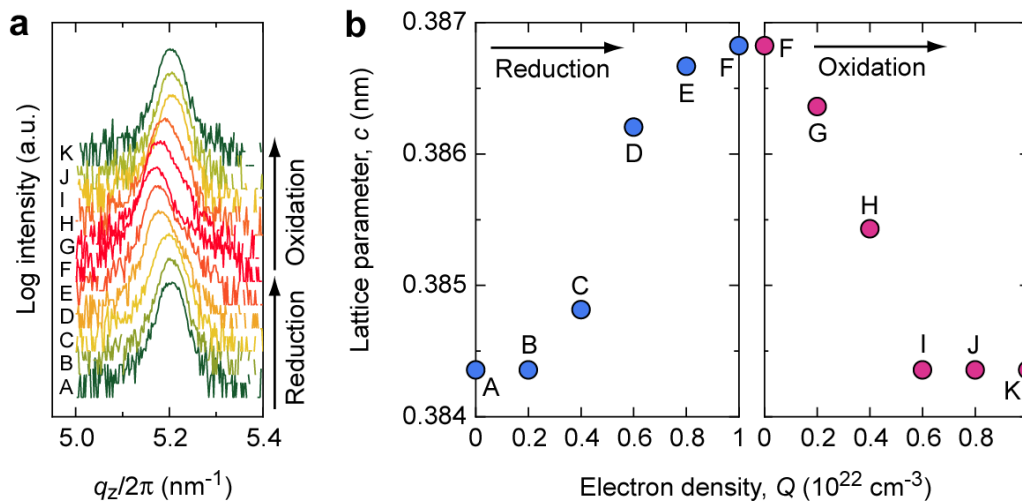


Figure 4-8 Change in the crystalline lattice of the LaNiO_x layer after redox treatment. a) Change in out-of-plane XRD patterns after redox treatment with a step of $Q = 2 \times 10^{21} \text{ cm}^{-3}$. The 002 diffraction peak shifted to a smaller q_z side after reduction and a larger q_z side after oxidation. These shifts were entirely reversible. b) Changes in lattice parameter c of LaNiO_x as a function of Q . A lattice expansion of $\approx 0.6\%$ occurred after reduction.

modulations in the crystal structure, with lattice expansion observed after reduction and shrinkage observed after oxidation. The change in the lattice parameter c is shown in

Figure 4-8b.

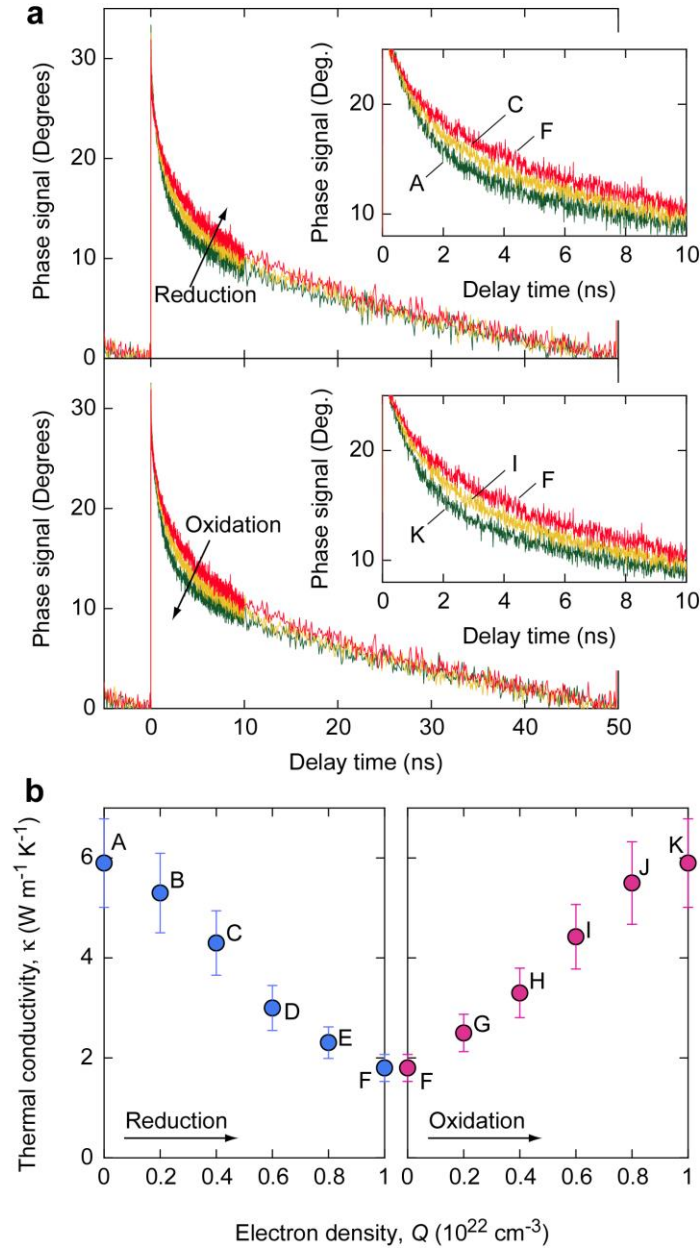


Figure 4-9. Changes in thermal conductivity (κ) of LaNiO_x layer after redox treatment. a) TDTR decay curves of the thermal switch after (upper) reduction and (lower) oxidation treatment. b) Changes in κ of LaNiO_x layer after (left) reduction and (right) oxidation treatment with a step of $Q = 2 \times 10^{21} \text{ cm}^{-3}$. The κ of LaNiO_3 was $5.9 \text{ W m}^{-1} \text{ K}^{-1}$; it decreased almost linearly with Q after reduction. After oxidation, the κ increased almost linearly with Q and returned to $5.9 \text{ W m}^{-1} \text{ K}^{-1}$.

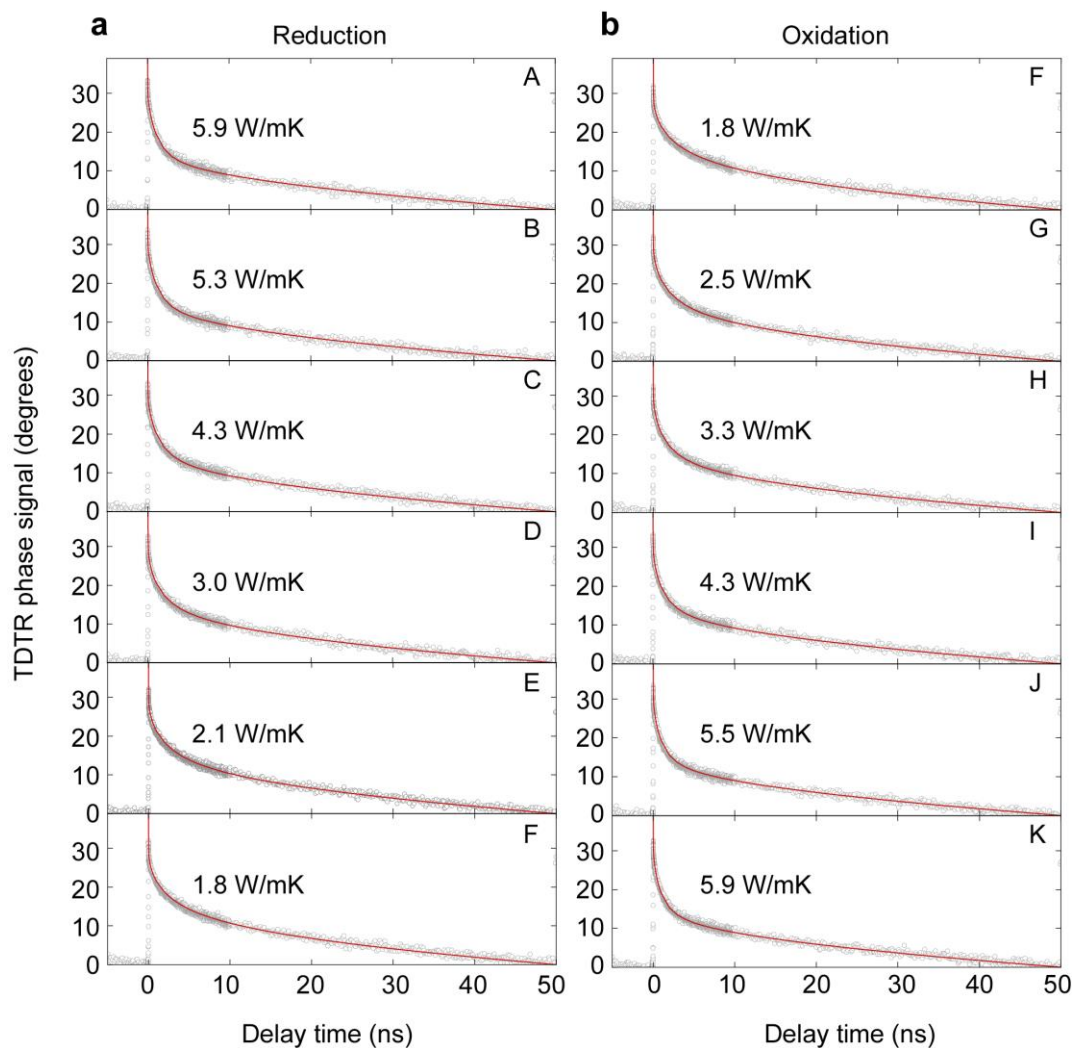


Figure 4-10 TDTR phase signal decay curves during (a) reduction and (b) oxidation.

Figure 4-9 illustrate the significant changes in the κ of the LaNiO_x during redox treatment. Time-domain thermoreflectance (TDTR) decay curves show a decrease in κ from $5.9 \text{ W m}^{-1} \text{ K}^{-1}$ to $1.8 \text{ W m}^{-1} \text{ K}^{-1}$ after reduction ($A \rightarrow F$) and an increase from $1.8 \text{ W m}^{-1} \text{ K}^{-1}$ to $5.9 \text{ W m}^{-1} \text{ K}^{-1}$ after oxidation ($F \rightarrow K$). Both the reduction and oxidation processes exhibited a nearly linear change in thermal conductivity. The slight variations in lattice constants between the oxidized and reduced states are attributed to the

disappearance and generation of oxygen vacancies. Through phonon scattering, oxygen vacancies contribute to a decrease in the lattice thermal conductivity. **Figure 4-10** shows the TDTR fitting results for **Figure 4-9**.

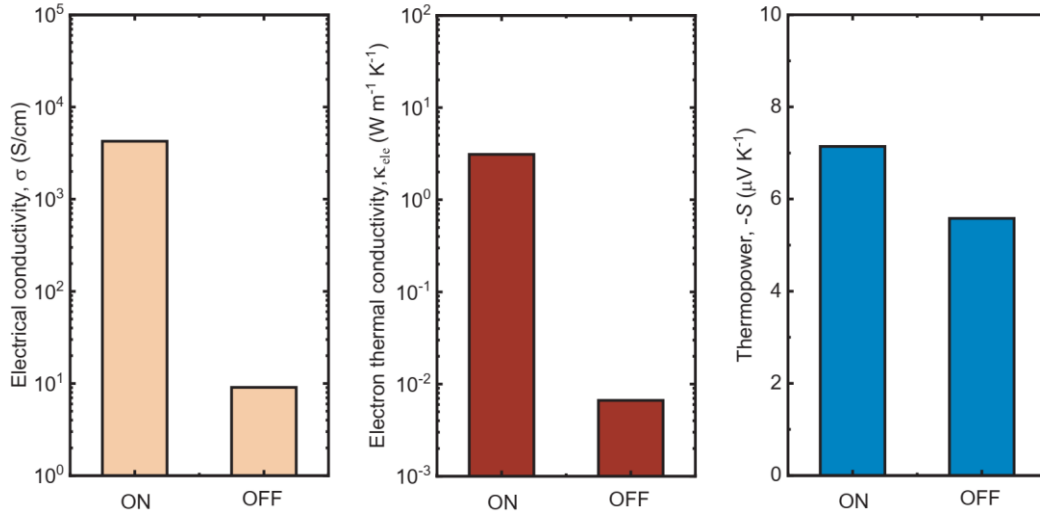


Figure 4-11 Change in the electron transport properties of the LaNiO_x films (on and off states) of the thermal transistor measured at room temperature.

However, there is a significant contrast in electrical conductivity (σ) between the oxidized (4250 S cm^{-1}) and reduced (9 S cm^{-1}) states (**Figure 4-11**). We estimated the electron thermal conductivity (κ_{ele}) by assuming the Wiedemann–Franz law which has been already introduced in Chapter 3. The κ_{ele} of the oxidized state reached $3.1 \text{ W m}^{-1} \text{K}^{-1}$. According to the principle that observable thermal conductivity is the sum of lattice thermal conductivity (κ_{lat}) and κ_{ele} [16], we estimated the κ_{lat} of LaNiO_3 (on-state) to be $2.9 \text{ W m}^{-1} \text{K}^{-1}$. This value aligns with previously reported values for bulk LaNiO_3 [1], confirming the consistency of our findings. This substantial difference enabled the LaNiO_x thermal transistor to modulate its thermal conductivity over a wide

range. Furthermore, the linear and reversible changes in thermal conductivity indicate the potential of the LaNiO_x -based thermal transistor for precise thermal modulation.

4.4.3 Cycle Properties of Thermal Transistor

As shown in **Figure 4-12**, the LaNiO_x -based thermal transistor exhibits cycling properties. The on-state (LaNiO_3) has a higher average thermal conductivity ($6.0 \text{ W m}^{-1} \text{ K}^{-1}$) than the off-state ($\text{LaNiO}_{2.72}$, $1.7 \text{ W m}^{-1} \text{ K}^{-1}$). Seven cycles are shown in the figure. The TDTR decay of LaNiO_3 was faster than that of $\text{LaNiO}_{2.72}$ (**Figure 4-12a**). The TDTR curves for each cycle overlapped significantly, indicating good repeatability.

Figure 4-13 shows the TDTR fitting results for **Figure 4-12**.

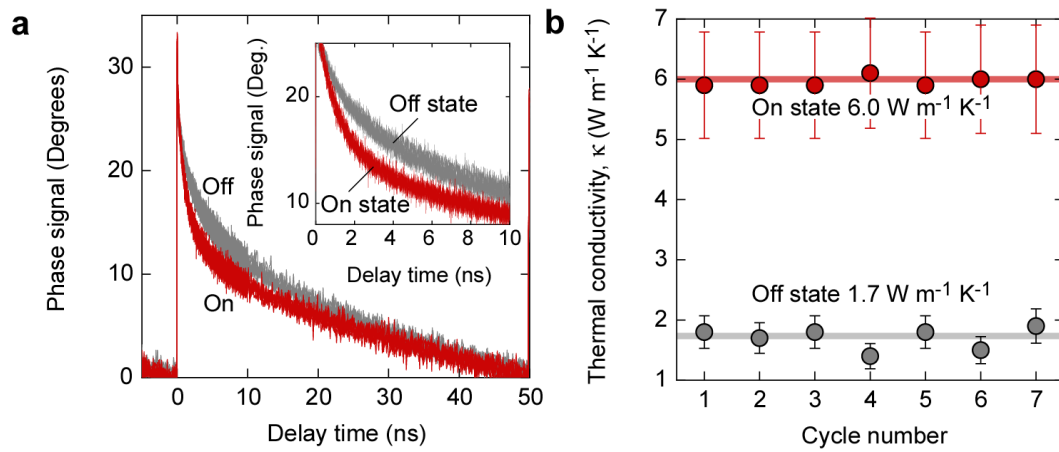


Figure 4-12 Cycle properties of LaNiO_x -based thermal transistor. a) Changes in TDTR decay curves (seven cycles overlapped). The TDTR decay of the LaNiO_3 layer was faster than that of the $\text{LaNiO}_{2.72}$ layer. b) Change in κ of LaNiO_3 and $\text{LaNiO}_{2.72}$ layers after redox cycling. The average κ of the LaNiO_3 (on-state) layer and $\text{LaNiO}_{2.72}$ (off-state) layer were 6.0 and $1.7 \text{ W m}^{-1} \text{ K}^{-1}$, respectively. The κ_{ele} of the LaNiO_3 (on-state) layer was high ($3.1 \text{ W m}^{-1} \text{ K}^{-1}$). The κ_{ele} of the $\text{LaNiO}_{2.72}$ (off-state) layer was negligible.

4.4.4 Comparison with Other TMO Thermal Transistors

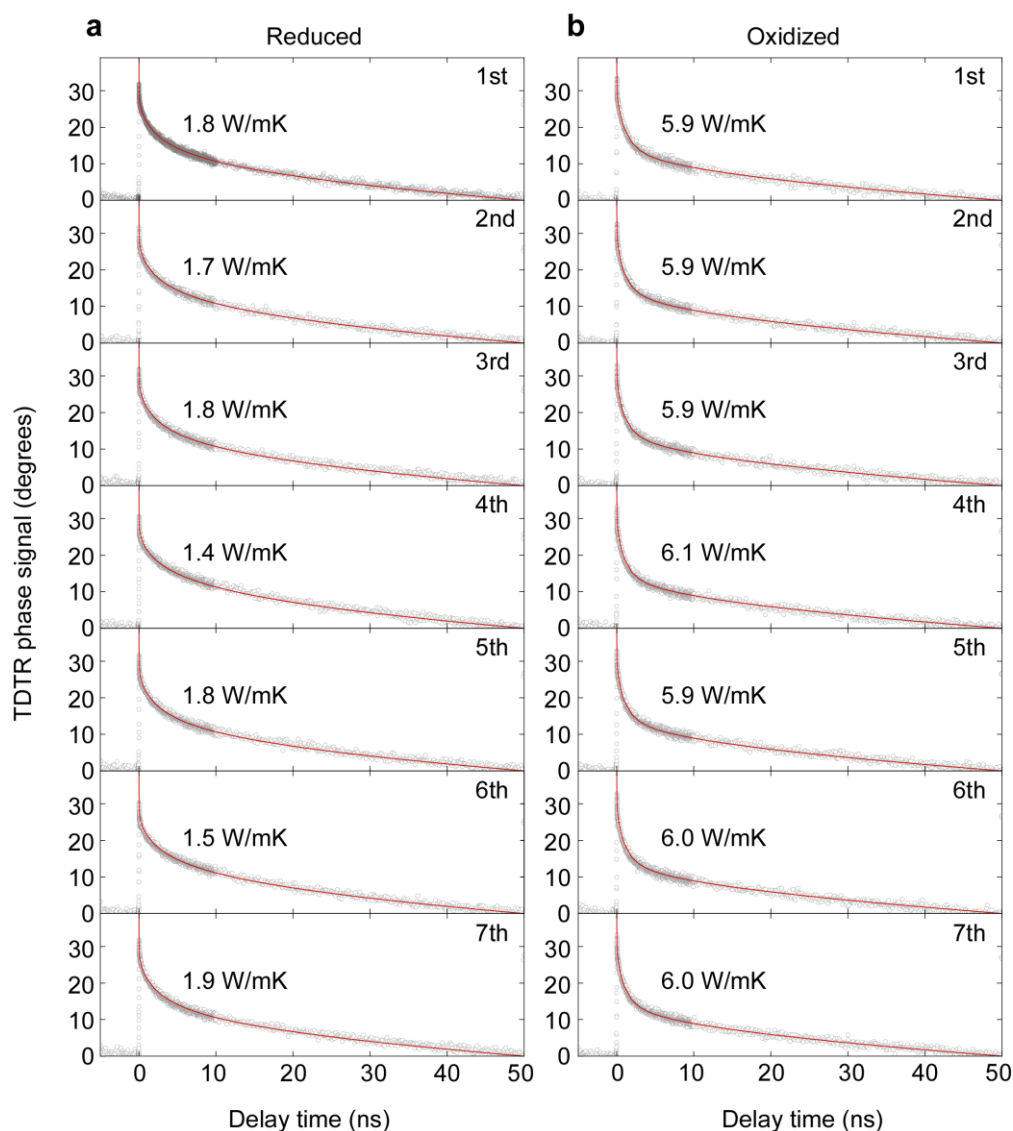


Figure 4-13 TDTR decay cycle of the LaNiO₃ layer in the thermal transistor.

Figure 4-14 compares the thermal conductivity switching widths of different TMOs, indicating the unparalleled performance of LaNiO_x-based thermal transistors, with a thermal conductivity switching width of approximately $4.3 \text{ W m}^{-1} \text{ K}^{-1}$, significantly greater than that of other TMOs. The wide switching range indicates the exceptional versatility of LaNiO_x in modulating its thermal conductivity. The inherent ability of

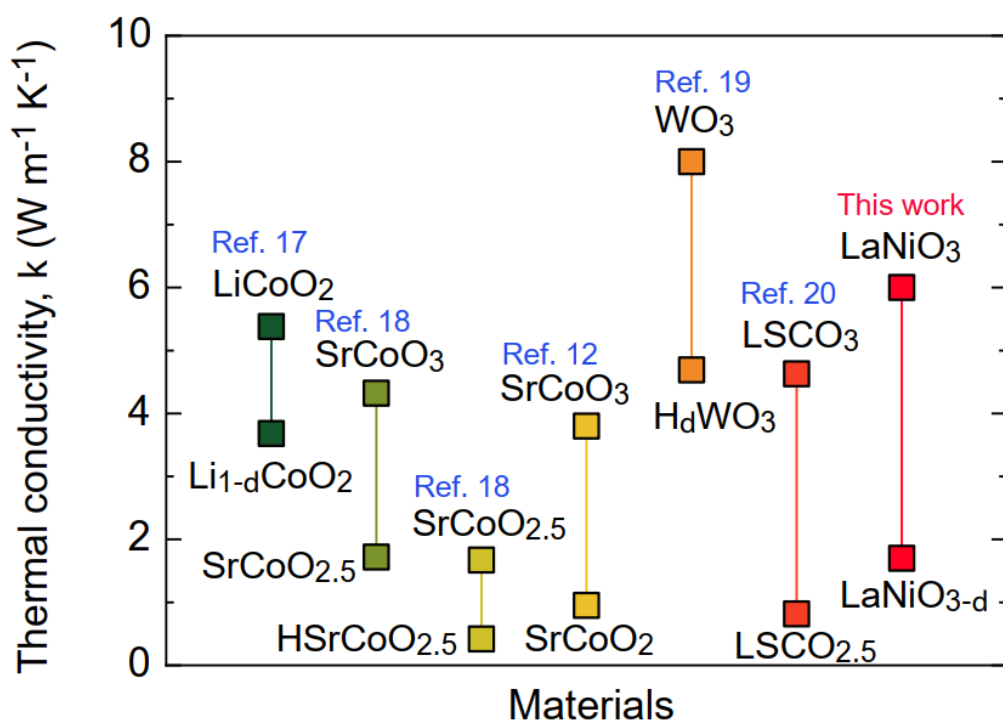


Figure 4-14 Comparison of thermal conductivity switching widths of several transition metal oxides. LaNiO_x-based thermal transistors exhibited large thermal conductivity switching widths ($\sim 4.3 \text{ W m}^{-1} \text{ K}^{-1}$). Data for LiCoO₂ $\leftrightarrow$ Li_{1- δ} CoO₂ are from Ref. 17, SrCoO₃ $\leftrightarrow$ SrCoO_{2.5} and SrCoO_{2.5} $\leftrightarrow$ HSrCoO_{2.5} are from Ref. 18, SrCoO₃ $\leftrightarrow$ SrCoO₂ are from Ref. 12, WO₃ $\leftrightarrow$ H _{δ} WO₃ are from Ref. 19, and La_{0.5}Sr_{0.5}CoO₃ (LSCO₃) $\leftrightarrow$ La_{0.5}Sr_{0.5}CoO_{2.5} (LSCO_{2.5}) are from Ref. 20.

LaNiO_x-based thermal transistors to linearly transition between high thermal conductivity in the fully oxidized state and low thermal conductivity in the reduced state positions them at the forefront of TMOs for thermal management applications. The nuanced control over thermal conductivity and the stability demonstrated in the cycling properties (**Figure 4-12**) underscore the potential of LaNiO_x-based thermal transistors for application in next-generation thermal displays and other advanced thermal management systems.

4.5 Conclusion

This study presents a breakthrough with LaNiO_x -based electrochemical thermal transistors, with an exceptional κ switching width of $4.3 \text{ W m}^{-1} \text{ K}^{-1}$. The fully oxidized LaNiO_3 (on-state) produced a κ of $6.0 \text{ W m}^{-1} \text{ K}^{-1}$, primarily attributed to a substantial contribution from electron thermal conductivity ($3.1 \text{ W m}^{-1} \text{ K}^{-1}$). In contrast, the reduced $\text{LaNiO}_{2.72}$ (off-state) had a low κ of $1.7 \text{ W m}^{-1} \text{ K}^{-1}$ due to negligible electron thermal conductivity ($0.007 \text{ W m}^{-1} \text{ K}^{-1}$) and phonon scattering caused by oxygen vacancies. The LaNiO_x -based electrochemical thermal transistor demonstrated κ cyclability while maintaining the structural integrity of the LaNiO_x crystalline lattice, making it a promising candidate for integration into next-generation devices, particularly thermal displays.

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Chapter 5. Summary

This given doctoral research investigated the high performance all-solid-state thermal transistor by the strategy of the active layer material with high electrical conductivity. Based on our development of the world's first all-solid-state thermal transistor, I obtained the aforementioned strategy through a series of further studies. Using this strategy, I successfully developed an LaNiO_x all-solid-state thermal transistor with a large thermal conductivity (κ) modulation range.

First, due to the extremely similar redox pathways of SrFeO_x and SrCoO_x , and the similar valence state changes and atomic/ionic radii of Fe and Co elements, I combined these two materials to prepare a series of solid solution active layer thermal transistors. The aim was to enhance the ON/OFF κ switching ratio or modulation width of SrCoO_x -based all-solid-state thermal transistors. I measured $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ thermal conductivity after electrochemical redox treatments. For $\text{SrCo}_{1-x}\text{Fe}_x\text{O}_3$ (perovskite phase) with $y = 3$, the lattice thermal conductivity (κ_{lat}) remained nearly constant around $2.8 \text{ W m}^{-1} \text{ K}^{-1}$ regardless of the value of x . However, for SrCoO_3 ($x = 0$), the κ increased to approximately $3.8 \text{ W m}^{-1} \text{ K}^{-1}$ due to an electron thermal conductivity contribution (κ_{ele}) of about $1 \text{ W m}^{-1} \text{ K}^{-1}$. For the defect perovskite phase with $y = 2$ and $x \leq 0.5$, the κ was approximately $1 \text{ W m}^{-1} \text{ K}^{-1}$, while for the infinite layer phase with $x > 0.5$, it was around $1.2 \text{ W m}^{-1} \text{ K}^{-1}$, attributed to higher atomic arrangement periodicity. These results indicate that materials which are excellent electrical conductors with highly ordered

lattices when the transistor is ON, and electrical insulators with disordered lattices when the transistor is OFF, are optimal for improving the ON/OFF κ ratio.

As mentioned above, by exploring a series of high σ crystalline phases of transition metal oxides (TMOs), there is a probability of finding more suitable active layer materials for all-solid-state thermal transistors. I conducted a series of studies on the κ during the protonation/deprotonation process of rare earth nickelate ($ReNiO_3$) materials with Osaka University's collaborators. The research revealed that $LaNiO_3$, which has the highest σ among various $ReNiO_3$, also possesses very high κ . This provided significant insight. By using $LaNiO_x$ as the active layer in all-solid-state thermal transistors and controlling oxygen vacancies to regulate its metal-insulator transition, substantial advantages could be achieved. Therefore, I conducted further research on $LaNiO_x$ -based all-solid-state thermal transistors.

Then I focused on the use of $LaNiO_x$ -based electrochemical thermal transistors to address the limitations in κ switching width. My investigations indicated a κ switching width of $4.3 \text{ W m}^{-1} \text{ K}^{-1}$. Fully oxidized $LaNiO_3$ (on-state) exhibited a high κ of $6.0 \text{ W m}^{-1} \text{ K}^{-1}$, primarily attributed to the contribution of electron thermal conductivity ($3.1 \text{ W m}^{-1} \text{ K}^{-1}$). Conversely, reduced $LaNiO_{2.72}$ (off state) had a low κ of $1.7 \text{ W m}^{-1} \text{ K}^{-1}$ due to scattering of phonons by oxygen vacancies. Both the reduction and oxidation processes exhibited a nearly linear change in thermal conductivity.

The schematic depicted in **Fig. 5-1** introduces LaNiO_x as the active layer, offering a wide κ switching width. In the on state, LaNiO_3 has heightened electrical conductivity when fully oxidized, resulting in a significant contribution from the electron thermal conductivity. Conversely, the off state achieved through electrochemical reduction leads to oxygen vacancies, reduced electrical conductivity, and negligible electron thermal conductivity. Scattering of phonons by these vacancies manifests as a low

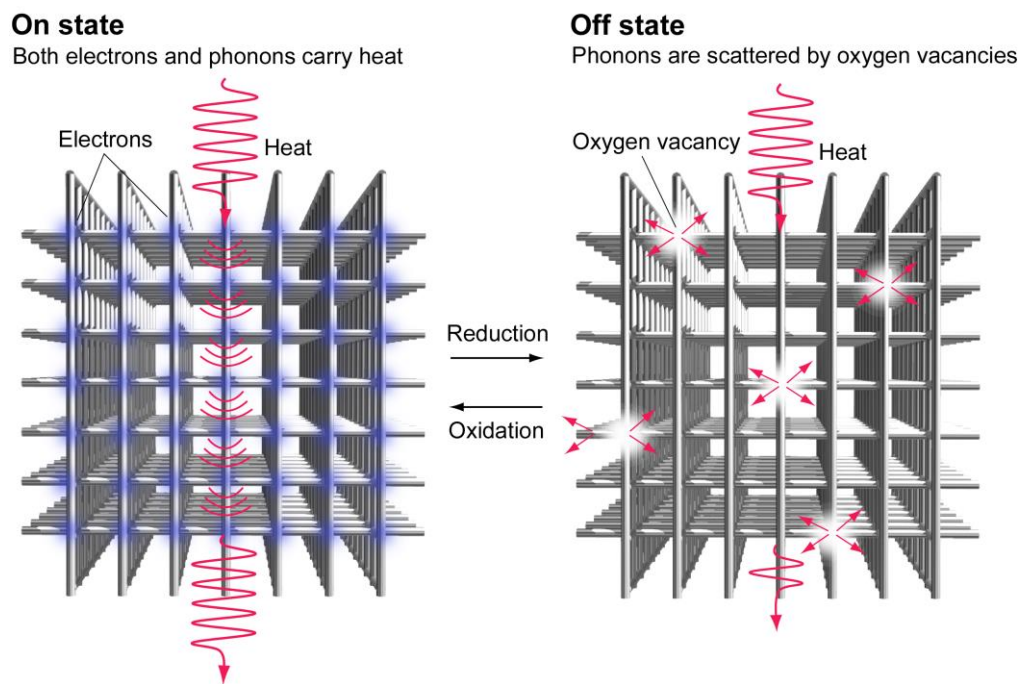


Figure 5-1 Strategy of electrochemical thermal transistors with transition metal oxide active layer with large thermal conductivity switching width. (Left) Diagram of on state. Fully oxidized TMOs show high electrical conductivity. Both electrons and phonons carry heat. The thermal switch shows high κ . (Right) Diagram of off state. Electrochemical reduction treatment produces oxygen vacancies. The reduced TMOs show low electrical conductivity. The κ_{ele} is negligible. Phonons are scattered by oxygen vacancies. The thermal switch shows low κ .

thermal conductivity.

Overall, the emergence of LaNiO_x -based all-solid-state thermal transistors has linked

the modulation of thermal conductivity with the regulation of electrical conductivity. This approach reduces the potential for lattice structure damage that could occur during cyclic experiments when κ is controlled by changes in lattice structure. This development will become an independent research direction for enhancing the performance of thermal transistors.

Acknowledgements

As I write this, I am filled with emotion. This marks the end of my doctoral journey and the conclusion of the research path I once loved. Despite my deep reluctance, I have no regrets.

I still vividly remember how distressed I was when others failed to keep their commitments. At that time, Prof. Ohta extended a helping hand without hesitation. This marked the beginning of my journey to Japan and my research life at Hokkaido University. Therefore, I have always been deeply grateful to Prof. Ohta. He not only provided significant assistance in my research but also offered encouragement and support during the difficult times I faced due to COVID-19.

Here, I would also like to express my gratitude to Prof. Tanaka and Assistant Prof. Li from Osaka University for their help, encouragement, and support during our collaborative research. Additionally, I extend my thanks to Prof. Jeon from Pusan National University and Associate Prof. Feng from University of Tokyo for their care and concern.

I would like to thank Prof. Matsuo and Assistant Prof. Endo for their assistance in TEM data collection. I am also grateful to Ms. Hirai and Ms. Mori from the Technical Department of RIES for their support. I would also like to thank Dr. Lin and Dr. Yang, former members of the University of Tokyo. They put in a lot of effort for my TEM

samples.

Additionally, I want to thank all the members of the laboratory who have helped me. In particular, I want to express special thanks to the following members: I am grateful to Associate Prof. Katayama, who is an exceptionally approachable and kind professor. I also thank former Assistant Prof. Cho for explaining TDTR-related knowledge to me. I appreciate Assistant Prof. Magari's kindness and gentleness. I am thankful for the continuous help from Secretary Ozaki, who is a very kind and thoughtful person. I am thankful to Yoshimura, who has always worked diligently and hard. She is my first and only Japanese friend so far. I am grateful to Kang for his warmth and generosity. His calm demeanor is something I greatly admire and strive to learn from. I am thankful to Dr. Gong, Dr. Chen, Dr. Yang (exchange student), Yu, Wu, Liu, Zhou, and Chen. Being in a foreign country, it is truly a blessing to meet so many kind and friendly compatriots. I am grateful to Dr. Jeong, whose perpetually optimistic attitude has had a profound impact on me. I am thankful to Dr. Ghediya. We have shared many job-seeking experiences with each other.

I want to give special thanks to my wife, Ms. Zhang, who is also a doctoral student at IST. It is she who has accompanied me through countless difficulties, and it is she with whom I have shared the joys of life. I hope that in the days to come, we can continue to support each other and grow old together (同舟共济、白头偕老).

My doctoral journey, from beginning to end, has been filled with thrills and excitement.

I believe these experiences have shaped me in unique ways and strengthened my resilience. Therefore, I am also thankful to destiny for this journey of personal growth and learning.

Finally, I would like to conclude with a quote from Lu Xun (鲁迅/魯迅) and share it with everyone for mutual encouragement:

“May the youth of China rid themselves of coldness and march onward, without paying heed to the babble of those who indulge in self-pity. Let those who can do something, do it; let those who can speak up, speak up. With every ounce of warmth, shed a ray of light; even a firefly's glow can illuminate the darkness, without waiting for a torch.”

“愿中国青年都摆脱冷气，只是向上走，不必听自暴自弃者流的话。能做事的做事，能发声的发声。有一分热，发一分光，就令萤火一般，也可以在黑暗里发一点光，不必等候炬火。”

「中国の若者たちが冷たさを振り払い、ただ前に進むことだけに専念し、自暴自棄になる者のおしゃべりには耳を貸さないでほしい。物事ができる者はそれを行い、声を発することのできる者は発するべきである。一片の熱さがあれば、一片の光を放つことができる。萤火の光でも暗闇を照らすことができる。たいまつを待つ必要はない。」

Zhiping Bian

Sapporo, Japan

2024.06

List of Publications

Publications related to this thesis

- (1) **Z. Bian**, M. Yoshimura, A. Jeong, H. Li, T. Endo, Y. Matsuo, Y. Magari, H. Tanaka, H Ohta, “Solid-State Electrochemical Thermal Transistors with Large Thermal Conductivity Switching Widths”, *Advanced Science* Vol.xx, pp.2401331 (2024)
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- (2) **Z. Bian**, Q. Yang, M. Yoshimura, H. Cho, J. Lee, H. Jeon, T. Endo, Y. Matsuo, H. Ohta, “Solid-State Electrochemical Thermal Transistors with Strontium Cobaltite – Strontium Ferrite Solid Solutions as the Active Layers”, *ACS Appl. Mater. Interfaces* Vol.15, pp.23512-23517 (2023)
- (3) H. Li, **Z. Bian**, M. Yoshimura, K. Shimoyama, C. Zhong, K. Shimoda, A. Hattori, K. Yamauchi, I. Hamada, H. Ohta, H. Tanaka, “Wide-range thermal conductivity modulation based on protonated nickelate perovskite oxides” , *Appl. Phys. Lett.* Vol.124, pp.191901 (2024).

Other publications

- (1) M. Yoshimura, Q. Yang, **Z. Bian**, H. Ohta, “Significant Reduction in the Switching Time of Solid-State Electrochemical Thermal Transistors”, *ACS Appl. Electron. Mater.* Vol.5, pp.4233-4239 (2023).
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- (1) **Zhiping Bian**, Mitsuki Yoshimura, Ahrong Jeong, Haobo Li, Takashi Endo, Yasutaka Matsuo, Yusaku Magari, Hidekazu Tanaka, Hiromichi Ohta, “Solid-State Electrochemical Thermal Transistors with Large Thermal Conductivity Switching Widths”, 2024 年 第 71 回 応用物理学会春季学術講演会, 東京都市大学 世田谷キャンパス, 東京, 2024 年 3 月 22 日-25 日.
- (2) **Zhiping Bian**, Mitsuki Yoshimura, Ahrong Jeong, Hiromichi Ohta, “Absence of High On-to-Off Thermal Conductivity Ratio in the $\text{LaSr}_{1-x}\text{Co}_x\text{O}_y$ -based Thermal Transistors”, MRM2023, Kyoto, Japan, December 11-16, 2023. (Oral)
- (3) **Zhiping Bian**, Mitsuki Yoshimura, Qian Yang, Hai Jun Cho, Joonhyuk Lee, Hyoungeen Jeon, Takashi Endo, Yasutaka Matsuo, Hiromichi Ohta, “Solid-State Electrochemical Thermal Transistors with Perovskite Cobalt Oxide-based Solid Solutions as the Active Layers”, The 2023 RIES-CEFMS (Research Institute for Electronic Science – Center for Emergent Functional Matter Science) Joint International Symposium, Rusutsu Resort Hotel and Convention Center, Japan, December 7-8, 2023. (Poster)
- (4) **Zhiping Bian**, Mitsuki Yoshimura, Qian Yang, Hai Jun Cho, Joonhyuk Lee, Hyoungeen Jeon, Takashi Endo, Yasutaka Matsuo, and Hiromichi Ohta, “Solid-State Electrochemical Thermal Transistors with Perovskite Cobaltate-based Solid Solutions as the Active Layers”, The 24th RIES-HOKUDAI International Symposium 開 [kai], Hokkaido University, Sapporo, Japan, December 6-7, 2023.(Poster)

- (5) **Zhiping Bian**, Mitsuki Yoshimura, Qian Yang, Hai Jun Cho, Joonhyuk Lee, Hyoungjeen Jeon, Takashi Endo, Yasutaka Matsuo, and Hiromichi Ohta, “Solid-state electrochemical thermal transistors with perovskite cobalt oxide-based solid solutions as the active layers”, The Mini Workshop on Functional Materials Science (Organizers’ meeting), Sapporo, Japan, December 1-2, 2023. (Poster)
- (6) **Zhiping Bian**, Mitsuki Yoshimura, Qian Yang, Hai Jun Cho, Joonhyuk Lee, Hyoungjeen Jeon, Takashi Endo, Yasutaka Matsuo, and Hiromichi Ohta, “Solid-State Electrochemical Thermal Transistors with Perovskite Cobalt Oxide-based Solid Solutions as the Active Layers”, 29th International Workshop on Oxide Electronics (iWOE29), Busan, Korea, October 15-18, 2023. (Poster)
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- (8) **Zhiping Bian**, Qian Yang, Mitsuki Yoshimura, Hai Jun Cho, Joonhyuk Lee, Hyoungjeen Jeon, Takashi Endo, Yasutaka Matsuo, and Hiromichi Ohta, “Thermal Conductivity Modulation of $\text{SrCoO}_x - \text{SrFeO}_x$ Solid Solution in Solid-State Electrochemical Thermal Transistors”, The 4th Workshop on Functional Materials Science (FMS2023), Busan, South Korea, June 18-21, 2023. (Poster)
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- (11) Zhiping Bian, Qian Yang, Mitsuki Yoshimura, Hai Jun Cho, Hiromichi Ohta, “Solid-state Electrochemical Thermal Transistors using $\text{SrCoO}_y\text{--SrFeO}_y$ Solid Solutions”, 7th International Conference on Advances in Functional Materials (AFM 2023), Fukuoka, Japan, January 9-12, 2022 (Oral)

- (12) Zhiping Bian, Qian Yang, Mitsuki Yoshimura, Joonhyuk Lee, Hyoungjeen Jeon, Jinghuang Lin, Bin Feng, Yuichi Ikuhara, Hai Jun Cho, and Hiromichi Ohta, “Thermal Conductivity Modulation in $\text{SrCoO}_y\text{--SrFeO}_y$ Solid Solution by Electrochemical Redox Reaction” , The 23rd RIES-Hokudai International Symposium 拓 [Taku], Sapporo, Japan, December 5-6, 2022. (Poster)

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