

# Electronic property modulation of transition metal oxides by electrochemical and strain engineering

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## Abstract

Transition metal oxides (TMOs) are of great importance as an active material for future electronic/energy devices because of several potential characteristics over conventional semiconductor-based electronic materials. Since the properties of TMOs are strongly dependent on the electronic structures of TM *d* bands, further unique properties can appear and functional switching devices can be developed by controlling the Fermi level and local structure distortion. In this paper, we will introduce two topics: (1) electrochemically switchable electromagnetic phase switching device based on SrCoO<sub>x</sub> using our developed leakage free alkaline electrolyte and (2) giant thermoelectric power factor enhancement by epitaxial strain induced phonon-drag effect in LaNiO<sub>3</sub>.

## 1. Introduction

Transition metal oxides (TMOs) are of great importance as an active material for future electronic/energy devices. Since the electronic properties of TMOs are strongly dependent on the electronic structures of TM *d* bands, the appearance of further unique properties can be expected by controlling the Fermi level and local structure distortion. In addition, due to the flexible valence state of TM ion in TMOs, the rich variety of physical properties, can be switched by their non-stoichiometry, i.e. oxygen excess/deficiency and protonation. However, the switching classically needs high-temperature heating or electrochemistry in liquid electrolyte, which is unsuitable for device applications. In this paper, we will introduce two topics: one is electrochemically switchable electromagnetic phase switching device based on SrCoO<sub>x</sub> using our developed solid-state thin-film-transistor (TFT) structure with leakage free alkaline electrolyte, and second is extremely large thermoelectric power factor enhancement by epitaxial strain induced phonon-drag effect in LaNiO<sub>3</sub> thin films.

## 2. General Instructions

### 2.1. Electromagnetic phase switching device using SrCoO<sub>x</sub>

Electrical switching of electro-magnetic phase in a non-volatile manner is a key technology for advanced spintronics. Especially, robust conversion from antiferromagnetic (AFM) insulator to ferromagnetic (FM) metal remains challenging issue for low-energy magnetic memory device. Although

AFM/FM state of a magnetic oxide can be switched by redox reactions through thermal annealing at high-temperatures in oxygen/vacuum atmosphere or liquid-electrochemistry, the electromagnetic switching should be operatable in solid-state device at room temperature (RT) for the practical applications.

Here we introduce RT-operatable electromagnetic phase switching device based on SrCoO<sub>x</sub>, using our-developed water-incorporated amorphous (a-) NaTaO<sub>3</sub> nanopillar array glass as a gate insulator [1].

A TFT structure was fabricated on AFM-insulator SrCoO<sub>2.5</sub> (brownmillerite phase) film as an active material (Fig.1) by pulsed laser deposition (PLD). The SrCoO<sub>2.5</sub> epitaxial film was fabricated on SrTiO<sub>3</sub> (001) substrate. A leakage-free alkaline electrolyte a-NaTaO<sub>3</sub> nanopillar array glass was deposited at RT under high O<sub>2</sub> pressure of 11 Pa for a solid gate insulator. The film porosity is 60%, where the liquid water is confined in the nanospace of the a-NaTaO<sub>3</sub> film and no leakage of the liquid water occurs because of the large surface tension between the water and nanopillar array [2]. A bilayer of a-WO<sub>3</sub> film and Ti film was used for the counter layer/ gate electrode. The Cr/Au bilayer film is used for the

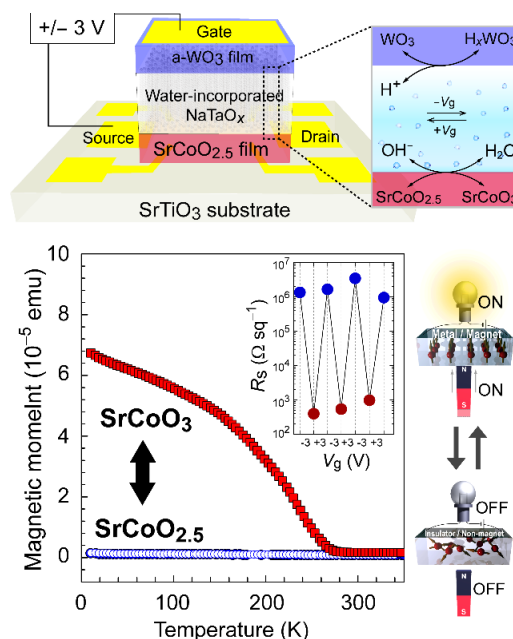


Fig.1 Schematic image and electro-magnetic phase switching of SrCoO<sub>x</sub>-based TFT using water-incorporated NaTaO<sub>x</sub> nanopillar glass as the gate insulator.

source and drain electrodes for ohmic contact.

For negative gate voltage application, electrochemical oxidation of  $\text{SrCoO}_{2.5}$  occurs at RT, leading to the 100% phase conversion into FM- $\text{SrCoO}_3$  (perovskite) with  $T_c = 275$  K. For positive gate voltage application, electrochemical reduction of FM- $\text{SrCoO}_3$  leads to the conversion into AFM- $\text{SrCoO}_{2.5}$ . The AFM/FM phase switching and sheet resistance switching (ON/OFF ratio  $\sim 10^4$ ) are simultaneously and reversibly controlled under a small DC voltage ( $\pm 3$  V) within a very short time (2–3 s) at RT in air.

## 2.2. Strain-induced large power-factor enhancement by breaking thermoelectric trade-off relation in $\text{LaNiO}_3$

Thermoelectric conversion is an energy harvesting technology that directly converts waste heat into electricity by the Seebeck effect of thermoelectric materials. Compared to state-of-the-art thermoelectric materials based on heavy metal chalcogenides, TMOs have several merits such as high-temperature stability and abundant resources, but the further enhancement of the conversion efficiency is necessary for thermoelectric applications. The conversion efficiency is generally evaluated in terms of a dimensionless figure of merit ( $ZT = S^2 \cdot \sigma \cdot T \cdot \kappa^{-1}$ ), where  $Z$  is the figure of merit,  $T$  is the absolute temperature,  $S$  is the Seebeck coefficient,  $\sigma$  is the electrical conductivity, and  $\kappa$  is the thermal conductivity of thermoelectric materials. One strategy to enhance  $ZT$  is an improvement of the power factor ( $PF = S^2 \cdot \sigma$ ). However, it has been difficult to improve  $PF$ , because the tuning of  $PF$  is restricted by the well-known trade-off relationship between  $S$  and  $\sigma$ ; when the  $\sigma$  is increased by carrier doping,  $|S|$  decreases at the same time.

Here, we discovered the large  $PF$  enhancement by breaking trade-off relation in compressively strained epitaxial thin films of strongly correlated TMO,  $\text{LaNiO}_3$ .

To systematically introduce strain to (001)  $\text{LaNiO}_3$ , epitaxial films (25 nm in thickness) were deposited at 700 °C under

high  $\text{O}_2$  pressure of 25 Pa by PLD onto lattice-mismatched substrates with in-plane lattice mismatch ( $\Delta a/a$ ) from  $-4.0\%$  to  $+3.4\%$ .

As the strain ranged from tensile (+) to compressive (−), the out-of-plane and in-plane lattice constant ratio ( $c/a$ ) increased from 0.966 to 1.025. In association with the  $c/a$  change, the  $\text{LaNiO}_3$  films showed the increase both of  $\sigma$  from  $1.3 \times 10^3$   $\text{S cm}^{-1}$  to  $3.8 \times 10^4$   $\text{S cm}^{-1}$  and  $S$  from 7  $\mu\text{V K}^{-1}$  to 22  $\mu\text{V K}^{-1}$  at the same time (Fig.2). As the result, the  $10^3$ -times enhancement of  $PF$  with maximum value of 18  $\mu\text{W / K}^2\text{cm}$  was achieved under the compressive strain at RT. Although  $\sigma$  of all the films showed the metallic temperature dependence,  $S$  for the film under compressive strain state showed large phonon drag thermopower ( $S_g$ ), which is expressed as  $S_g = (m^* v_F l_h / \tau_e q T)$  in the non-degenerated regime. It is known that, if the electron-phonon interaction is predominant, phonons can drag electrons following the temperature gradient and the  $S_g$  independently enhances the total  $S$  over the conventional carrier-diffusion thermopower. Although  $m^*$  is almost unchanged by the strain, phonon mean-free-path ( $l_h$ ) is largely enhanced by the compressive strain of  $-2\%$ , which strongly suppresses Umklapp scattering. The phonons with long  $l_h$  remain even at RT under compressive strain, which should contribute RT phonon drag  $S_g$  to enhance  $PF$  by breaking the trade-off relation.

## 3. Conclusions

Electrochemically switchable electromagnetic phase switching device with water incorporated a- $\text{NaTaO}_3$  nanopillar array film was demonstrated by RT oxidation/reduction of the  $\text{SrCoO}_x$  channel. The present all-solid-state device with leakage free alkaline electrolyte provides a novel electrical conversion approach to realize functional devices by switching electronic, optical, and magnetic properties of TMOs [3].

Extremely large thermoelectric  $PF$  enhancement was demonstrated in  $\text{LaNiO}_3$  by epitaxial strain induced phonon-drag effect. This finding reveals novel strategies for developing trade-off-free thermoelectric materials.

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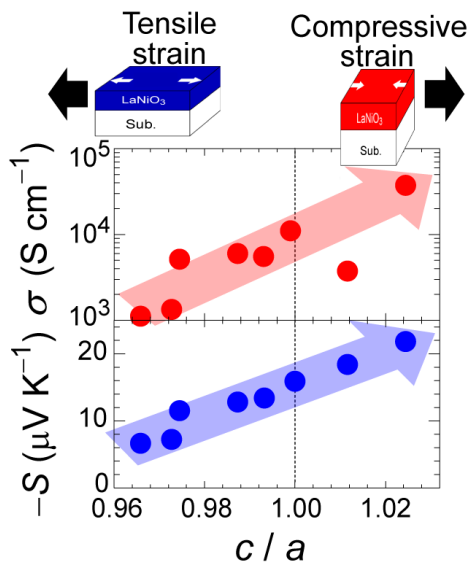


Fig.2 Trade-off free interdependence of electronic conductivity ( $\sigma$ ) and thermopower ( $S$ ) for  $\text{LaNiO}_3$  films under epitaxial strain.