

**SYNTHESIS AND ELECTRICAL PROPERTIES OF PEROVSKITE
NICKELATES**

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Dedicated to Mom and Dad.

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place at room temperature. As temperature increases, the upper limit of LNO resistance also increases, as labeled at the end of doping in each doping profile. The Raman spectra of pristine and doped LNO (H-LNO) corresponding to the doping temperature are shown by the side of each doping profile. In each Raman spectrum, the peak at $\sim 485\text{cm}^{-1}$ is from the LAO substrate. Hydrogen doping reduced the peak intensity from LNO at $\sim 400\text{cm}^{-1}$ and a new peak generated at $\sim 640\text{cm}^{-1}$ representing the formation of H-LNO phase, as indicated by the red arrow in each plot. The evolving Raman peak intensity of LNO and H-LNO after doping indicates the MIT of LNO by electron doping is closely dependent on the doping temperature. 84

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Figure 5.6. Hydrogen doping kinetics into LNO thin film. The doping rate at each temperature were fitted at the initial stages which showed exponential increase of the resistivity. The rate-temperature doping kinetics was fitted by a sigmoidal function, as indicated by the red line. The fitted saturation doping rate is $A \sim 1.22\text{min}^{-1}$. The "○" at 76°C labels the steepest slope of the fitted curve, which is $A \cdot B/4 = 0.027\text{min}^{-1}^\circ\text{C}^{-1}$ 86

Figure 5.7. Metal to insulator transition of LNO by electron doping verified by the dependance of resistivity (ρ) on temperature (T). As expected, the pristine LNO exhibits a metallic ρ - T behavior as the resistivity increases with elevated temperature. After electron doping in H_2/Ar gas at 120°C for 15 min, the ρ - T curve shows the resistivity increases with decreasing temperature, indicating an insulator phase. The resistivity for pristine and H-doped LNO thin film at 200K are 0.27 and 9743 $\text{m}\Omega\text{ cm}$, respectively, as labeled in the plot. 87

Figure 5.8. In-plane device design and fabrication with LaNiO_3 thin films. (a) A sketch of the device fabrication process. The films were patterned by ion mill into a cross shape "+" with various width and height at the cross center. The four ends were covered by 100nm Au before the deposition of Ti/Au to avoid possible contacts of the oxides and Ti. Then 100nm Pd electrodes were deposited at the film center for electron doping of LNO. (b) An optical image of the as fabricated devices with various layouts. The materials are labeled in the zoomed in view at the corresponding locations. 88

Figure 5.9. Resistive switching of devices fabricated with 0.1M-LNO/LAO and 0.2M-LNO/LAO. (a) Statistical comparison of resistive switching ratio from 50 cycles of device with 0.1M-LNO/LAO measured by two testing connections sketched in (b). Pulse conditions: +9V 500ns and -9V 1 μs referring to the Pd electrode. The scattered dots are the experimental data of switching ratios from 50 cycles, while the bar height represents the averaged switching ratio. Switching ratio is independent of the distance of the probed terminals, indicating the four Au ends are equipotential in such devices during electrical testing. (c) Statistical comparison of resistive switching ratio from 50 cycles of device with 0.2M-LNO/LAO measured by two testing connections sketched in (d). Pulse conditions: +5V 100ns and -5V 500ns referring to the Pd electrode. Similar to 0.1M-LNO

device, the switching is independent of the distance of the probed terminals, indicating the four Au ends are equipotential in such devices during electrical testing. 90

Figure 5.10. Resistance switching and potentiation measurements with LNO thin films. (a) (d) show reproducible cycling tests of 0.1M-LNO and 0.2M-LNO for over 1000 cycles. (b) (e) are the potentiation-depression behavior of devices with 0.1M-LNO/LAO and 0.2M-LNO/LAO. The training conditions are noted in the plots. For both devices, the final stabilized synaptic weight is dependent on the training pulse amplitude. (c) (f) show the retention data of multiple resistance states from the two representative devices. Four resistance states were monitored for 10^4 seconds at each state and were stable. All of the data in this figure set was collected with Pd-lower Au connection. 91

Figure 5.11. Statistics of the switching ratio and polarity for (a) 0.1M-LNO and (b) 0.2M-LNO chips with various layouts. Four different devices were measured on each chip, with the device layout sketched at the bottom of the plots corresponding to each column. The voltage polarity on the same chip is consistent from one device to another. The switching ratios were averaged through 30 cycles on each device using the Pd-lower Au connection. The edge-to-edge distance from Pd to left/right-Au electrode is $12.5\mu\text{m}$ for all layouts, and the edge-to-edge distances from Pd to upper/lower-Au electrode are 17.5, 42.5, 67.5 and $92.5\mu\text{m}$, respectively. 92

Figure 5.12. Proposed resistive switching mechanisms for (a) 0.1M-LNO and (b) 0.2M-LNO devices. (a) The thinner 0.1M-LNO is epitaxial. The grids indicate the pseudo cubic lattice, the turquoise and the dark green colors represent the pristine 0.1M-LNO and doped H-LNO, respectively. Both the lattice constant and the doped H-LNO area is exaggerated for illustration purposes. When Pd is at the negative / positive bias, the protons are attracted to / pushed away from the Pd electrode, resulting a decreased / increased spatial volume of insulating H-LNO which corresponds to the LRS / HRS. (b) The sketched lines are grain boundaries and the ones in dark green colors represents the grain boundaries with protons accumulation which are locally insulating, while the white lines represent the grain boundaries without protons which are locally conductive. The grain size is not in scale with the size of Pd electrode for illustration purpose again. At negative / positive bias on Pd, the protons are accumulated at / migrated away from the grain boundaries adjacent to the Pd electrode, blocking / forming the conductive pathways to the outer pristine LNO which corresponds to the HRS / LRS. The input pulses are too weak to drive protons to drift through perovskite lattice such that the region with dark green color representing doped H-LNO does not have any change. 93

LIST OF ABBREVIATIONS

0.1M-LNO	lanthenum nickelate (LaNiO_3) prepared from the 0.1mol/L chemical solution
0.2M-LNO	lanthenum nickelate (LaNiO_3) prepared from the 0.2mol/L chemical solution
AFM	atomic force microscopy
ALD-NNO	neodymium nickelate (NdNiO_3) thin film grown by atomic layer deposition
CSD-NNO	neodymium nickelate (NdNiO_3) thin film grown by chemical solution deposition (spin-coating)
EDS	energy-dispersive X-ray spectroscopy
FTO glass	fluorine doped tin oxide coated glass substrates
LAO	lanthanum aluminate (LaAlO_3) substrate
MIT	metal-insulator transition
PVD-NNO	neodymium nickelate (NdNiO_3) thin film grown by physical vapor deposition (sputtering)
RSM	reciprocal space mapping
SEM	scanning electron microscopy
SNO	samarium nickelate (SmNiO_3)
TEM	transmission electron microscopy
UV-VIS	ultraviolet – visible spectroscopy
XAS	X-ray absorption spectroscopy
XRD	X-ray diffraction
XRR	X-ray reflectometry

ABSTRACT

Perovskite nickelates ReNiO_3 , where Re stands for rare earth elements like La, Nd, Sm ... etc, display metal-insulator transition (MIT) due to temperature variation and/or electron doping. In this work, perovskite nickelate thin films were deposited by physical vapor deposition (PVD) and chemical solution deposition (CSD) on LaAlO_3 (LAO) substrate for epitaxial single-crystalline phase or on other substrates such as Si / SiO_2 and fluorine doped tin oxide coated glass (FTO glass) for the polycrystalline phase. Detailed deposition parameters will be discussed and the thin film characteristics by the two deposition methods will be compared.

Redox reactions between pristine conducting phase (Ni^{3+}) and correlated insulating phase (Ni^{2+}), controlling the band gap as well as the optical transparency of nickelates, lead to the electrochromic activities of NdNiO_3 (NNO) thin films in smart window applications. Both CSD-NNO and PVD-NNO thin films on LAO substrates were systematically studied by electrochemical testing, including cyclic voltammetry scans and bleaching/coloration treatments in an electrolyte. A three-electrode set up was utilized with NNO thin film as the working electrode and pH 12 KOH aqueous solution as the electrolyte. It was confirmed that both CSD-NNO and PVD-NNO are electrochemically stable in the chosen solution and the optical transmittance of the NNO films is highly tunable. One significant advantage for CSD-NNO over PVD-NNO is the stronger electrochromic activity due to the porous nature of the films prepared by CSD method.

The electron-doping induced conductivity modulation of 10^8 orders of magnitude motivates the design of electronic devices with nickelates. During the process of platinum (Pt) or palladium (Pd) assisted hydrogenation of nickelate thin films, the nickel ions in the pristine state will be reduced due to the electron doping while the protons will remain in perovskite lattice as interstitial defects. The electron doping not only opens the energy band gap of the material, but also creates a Schottky barrier at the metal-semiconductor interface simultaneously. We will present an asymmetrical memory device with two terminals, one side Pd and the other side Au, fabricated on SmNiO_3 or NdNiO_3 thin films by e-beam lithography and photo lithography. The charge carrier transport mechanisms of the devices will be discussed with the current-voltage (I-V) characteristic analysis and resistance-temperature (R-T) dependence study. In addition, collaborative work based on such micro-nano devices including X-ray absorption (XAS) mapping affirming the proton drift

under external electrical fields and more device performances with potential applications in neuromorphic computing and artificial intelligence, will be discussed.

LaNiO_3 (LNO), as the only member of rare earth nickelates which does not display thermally driven MIT, has been constructed in literature with structural modifications such as LNO/LAO superlattice or ultrathin LNO with only a few unit-cell thickness, to obtain MIT depending on temperature. Here we have successfully deposited epitaxial LNO thin films on LAO substrates by CSD method with two different solution concentrations (0.1M and 0.2M) resulting two sets of films, namely 0.1M-LNO and 0.2M-LNO, with different thicknesses. Like other nickelates such as SNO or NNO, the conductivity of LNO can also be suppressed by Pt assisted electron doping which turns the pristine metallic LNO into insulating H-LNO. LNO is so sensitive to hydrogen that its conductivity even shows response at room temperature in H_2 rich gas. A series of devices with “+” shaped LNO thin films were designed and fabricated by photo lithography, with Pd electrodes at the film center and Au electrodes at four corners. Devices fabricated on both 0.1M-LNO and 0.2M-LNO thin films showed resistive switching and synaptic behavior across Pd-LNO-Au connection, triggered by voltage pulses with a duration of hundreds of nanoseconds. The detailed resistive switching mechanisms is proposed based on the electrical testing results and thin film characterization.

1. PEROVSKITE NICKELATES THIN FILM DEPOSITION

1.1 Introduction

Perovskite rare earth nickelates have a general formula of RENiO_3 , where RE stands for a rare earth element, like La, Pr, Nd, Sm, Eu etc. They have a perovskite ABX_3 structure in which RE ions occupy A sites and Ni ions occupy B sites. Figure 1.1 gives a standard perovskite ABX_3 lattice structure, which has a perfect cubic unit cell. However, the RE ions are not large enough to sustain the perfect perovskite structure so that the NiO_6 octahedrons are slightly tilted to compensate the smaller A site space. The perovskite tolerance factor is defined to evaluate the distortion degree:

$$t \equiv \frac{d_{\text{RE-O}}}{\sqrt{2} d_{\text{Ni-O}}} \quad (1)$$

Where t is the tolerance factor, $d_{\text{RE-O}}$ and $d_{\text{Ni-O}}$ is the ionic bond distances between RE-O and Ni-O, respectively. A perfect perovskite holds a tolerance factor of 1. The first family member, LaNiO_3 , exhibits a rhombohedral structure, which has a tolerance factor slightly less than 1, at all temperatures. With the decreasing RE ions as well as the tolerance factors, the other RENiO_3 are orthorhombic at the high temperature. For some of the intermediate members, it has been observed that the symmetry change to monoclinic structure at the low temperatures.[1, 2]

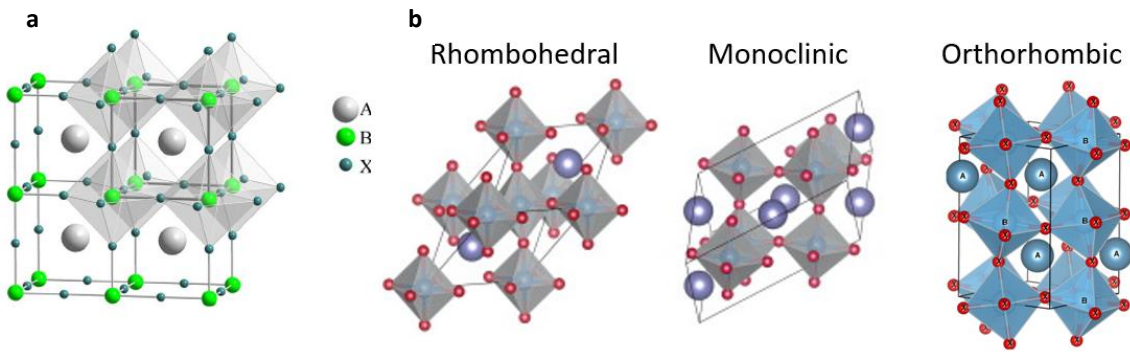


Figure 1.1. (a) A standard cubic ABX_3 structure, image from [3]. For perovskite nickelates, A sites are RE elements, B and X sites are Ni and O. (b) Rhombohedral, monoclinic and Orthorhombic lattice structures with BX_6 octahedrons illustrated. Images form [4, 5].

1.2 Metal-Insulator Transition (MIT) in Perovskite Nickelates

Ni is a transition metal with a fivefold degenerated 3d orbitals, as shown in figure 1.2(a). In a NiO₆ octahedron, these 3d orbitals will split into two degenerated higher energy e_g orbitals and three degenerated lower energy orbitals t_{2g}. The σ bonding of O 2p - Ni 3d_{z²} and O 2p - Ni 3d_{x²-y²} will form the e_g orbitals, and the π bonding of O 2p - Ni 3d_{xy,yz,zx} will form the t_{2g} orbitals (figure 1.2(c)(d)). In this case, the electron states of Ni³⁺ can be described as $t_{2g}^6 e_g^1$ and is illustrated in figure 1.3(a).

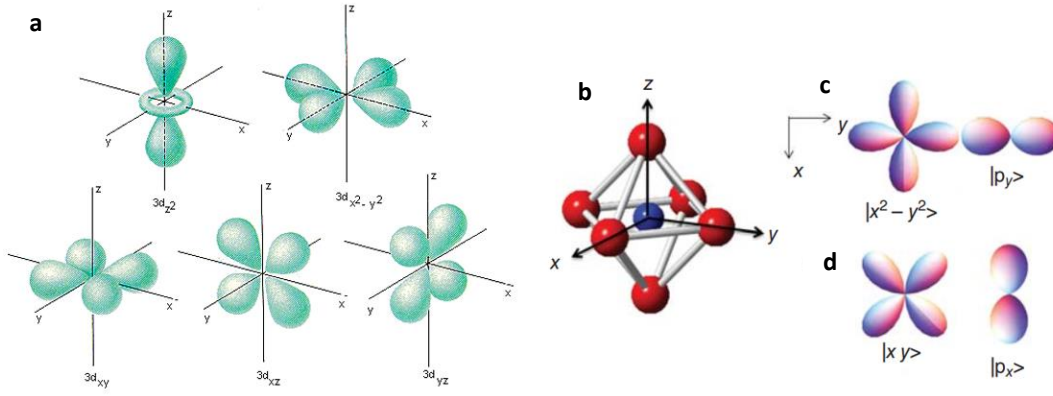
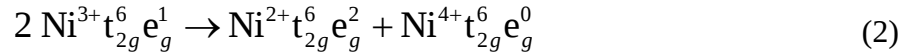


Figure 1.2. (a) Fivefold degenerated Ni 3d orbit electron clouds. Image available at [6]. (b) an NiO₆ octahedron, where x, y, z is defined from Ni ion to O ions. (c) σ bonding between Ni 3d and O 2p. (d) π bonding between Ni 3d and O 2p. Images from [7].

RENiO₃ performs a sharp MIT and it can be thermally driven. Below the MIT temperature, two adjacent NiO₆ octahedrons buckle and the charge disproportionation is proposed as:[8, 9]



As illustrated in figure 1.3(b). In Ni²⁺ the e_g orbitals are half-filled and in Ni⁴⁺ the e_g orbitals are empty, so that the RENiO₃ is insulating. While above MIT temperature, the unpaired electron at states indicates the RENiO₃ is metallic.

Similarly, the MIT can also be induced by electron doping. In J. Shi *et al.*'s work, SmNiO₃(SNO) can undergo a MIT due to electron doping by hydrogenation[8]. The SNO thin film with patterned Pt bars was annealed in a 5%H₂/95%Ar forming gas at 200°C. At the triple phase boundary of Pt/SNO/H₂, the H₂ will split into protons and electrons. The protons will be doped into SNO lattice through interstitial sites (forms H-SNO) while the electrons will occupy one of the e_g orbitals in Ni³⁺, to reduce Ni³⁺ into Ni²⁺, as shown in figure 1.3(c). This process is also

referred as proton doping or hydrogen doping. By electron doping, the resistivity of SNO at room temperature can increase several orders of magnitude.

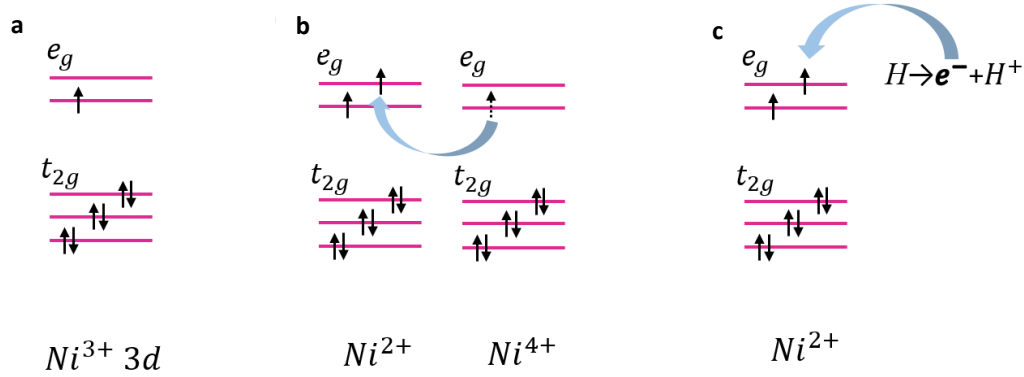


Figure 1.3. (a) Ni^{3+} 3d electron states in a NiO_6 octahedron. (b) Charge disproportionation and the resulted electron states.[9] (c) Electron doping by hydrogenation which reduces Ni^{3+} into Ni^{2+} . Images plotted from [8].

1.3 Thin Film Deposition Methods

There are many common deposition techniques in research and industry to achieve uniform and high quality thin films on desired substrates. Physical vapor deposition (PVD), including sputtering, e-beam evaporation, thermal evaporation, pulsed laser deposition are the most commonly used methods considering the quality of as-deposited films as well as the tools' handling and maintenance.

1.3.1 Rare-earth nickelates deposition by PVD-sputtering

The following are the deposition procedures for sputtering:

1. Mount and load the substrate. Before deposition, the substrate holder needs to be adjusted to a certain height and the rotation speed is usually ~ 5 rpm.
2. Plasma generation. The plasma was generated from two targets. RE target, which could be samarium (Sm) or neodymium (Nd) were powered by an RF source supply while nickel (Ni) target is connected to a DC power source. To generate the plasma, the argon (Ar) gas flow was turned on and set to 40sccm. The chamber pressure during plasma

generation was set as 25mTorr. The power for RF and DC source were ramped to the desired levels. The shutters were kept closed unless the plasma was hard to be turned on.

3. After plasma is fully on, turn on O₂ flow to 10sccm and adjust the chamber pressure to 5mTorr. Pre-sputter for at least 3min to clean up the target surface with shutters closed.
4. Open shutters for deposition. The deposition rate was usually ~1.6nm/min.
5. The as-sputtered thin films are a mixture of the oxides of Sm/Nd and Ni, such that the post-annealing process is necessary to form crystallized nickelates. For SmNiO₃ (SNO), the annealing condition is 500°C in for 24 hours at high O₂ pressure (above 1400psi). For NdNiO₃ (NNO), the annealing condition is 500°C for 24h in air.

The SNO thin films in this work were all prepared by sputtering. NNO films were prepared by both sputtering and chemical solution method, as we will discuss about this soon after.

1.3.2 Rare-earth nickelates deposition by chemical solution method

A vacuum-free deposition method was reported in literature in the past few years for its easier control of the RE:Ni ratios and low cost. [10-16] Spin-coating is usually utilized to dispense a thin layer of the chemical solution on the substrate to deposit high-quality thin films. The chemical solution deposition process is provided here:

1. The solution was prepared by dissolving neodymium/lanthanum nitrate hexahydrate (Nd(NO₃)₃·6H₂O/La(NO₃)₃·6H₂O, sigma, purity 99.9%) and nickel(II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O, sigma, purity 99.998%) in the solvent mixture of 2-methoxyethanol and acetic acid (volume ratio 4:1), preheated at 80°C.
2. The solution was heated and stirred at 80°C for 1h and then filtered. The concentration of the solution was controlled to 0.1M or 0.2M by properly adjusting the solvent volume.
3. The spin-coating method was used to deposit nickelate thin films with a spin speed of 3000rpm and duration of 30s. Then the coated films were baked at 175°C for 20min to evaporate any remaining solvent or water molecules.
4. The baked film was immediately transferred to the furnace for pyrolysis and annealing. The pyrolysis condition was 300°C for 30 min in air. Subsequently, the films were annealed at 600°C in air for 12h.

As mentioned before, NdNiO₃ thin films are prepared by both sputtering and chemical solution methods. LaNiO₃ (LNO) thin films in this work were only prepared by chemical solution methods.

Unlike PVD which could control the deposited film thickness by deposition time, CSD grows thicker films by repeating the spin-coating and baking process to add multiple layers. The film thickness was strongly reflected by the XRD peak intensities, as shown in figure 1.4. The NNO films were deposited on fluorine doped tin oxide coated glass (FTO-glass) substrate, with the peaks identified at $2\theta=33.29^\circ$, 47.76° and 59.48° . [17] The peak with highest intensity at 33.29° appeared even with the thinnest 1-layer- NNO film. As film becomes thicker with more layers coated, the rest two peaks with lower intensity gradually showed up.

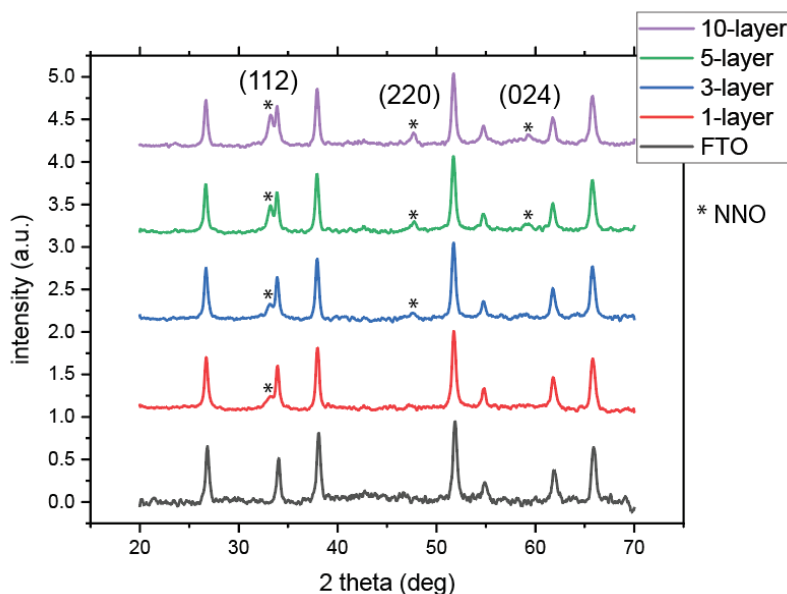


Figure 1.4. XRD peaks of CSD prepared NNO on FTO-glass substrates. NNO films with difference thicknesses resulting from 1-layer, 3-layer, 5-layer and 10-layer coating were examined. The thicker film shows higher peak intensities, as marked by “*”. The XRD pattern form a bare FTO-glass substrate is used as a reference.

The quantitative measurement of the film thickness vs. coated layers were conducted. The coated NNO films were patterned and etched by ion mill with end point detection by monitoring the count of elements neodymium and tin, meaning when NNO film is completely etched through and FTO is exposed, the etching stops. By scanning the step height at FTO-NNO, the film thicknesses of 1-layer, 3-layer, 5-layer and 10-layer NNO on FTO were ~ 60 , ~ 100 , ~ 130 , ~ 200 nm,

respectively. The relationship of film thickness and coated layers are fitted in figure 1.5, which shows that an additional layer adds ~15nm to the film, which is lower than the thickness from first coating. This is due to the slight dissolvment of the pre-coated NNO film when additional chemical solution drops are dispensed onto it and the difference in adhesion and wetting conditions of the chemical solution on bare FTO surface and on precoated NNO layer(s).

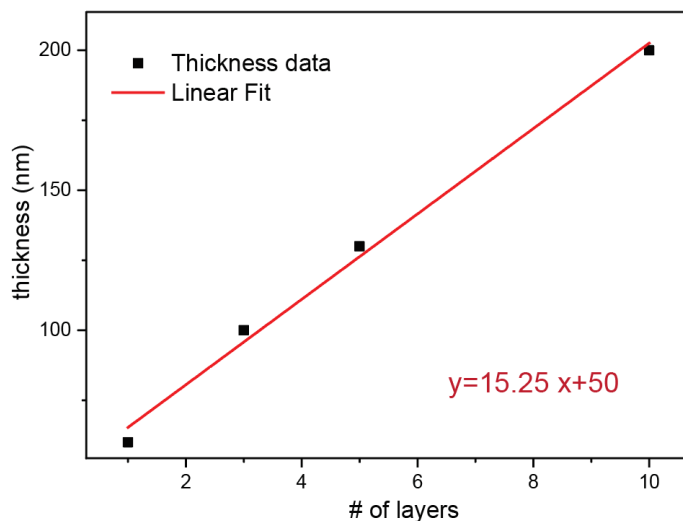


Figure 1.5. Film thickness dependence on coated layers. The expression of the fitted line is noted in the plot.

The film tomography was also affected by the film thickness deposited by CSD method. PVD is expected to deposit uniform films at a uniform deposition rate even for thick films. However, CSD method is prone to deposit porous films, as we will discuss about this soon in chapter 2. As the film prepared by CSD becomes thicker, the porosity of the film also gets higher. Figure 1.6 provides the SEM image of the film surface with various coated layers of NNO on FTO-glass substrate, with the corresponding surface porosity analyzed by ImageJ. The surface porosity for 1-layer, 3-layer, 5-layer and 10-layer NNO/FTO was calculated to be 9.65%, 12.7%, 12.9% and 14.8%.

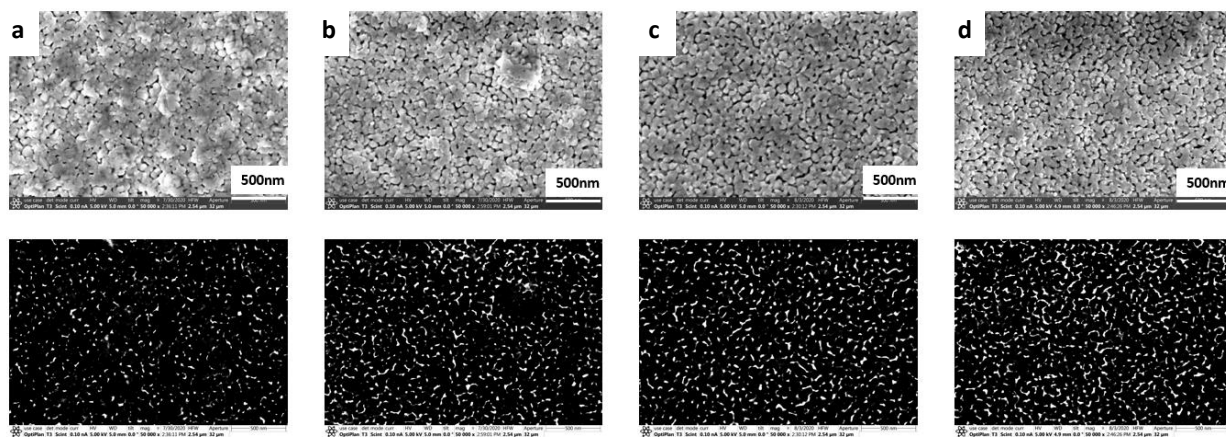


Figure 1.6. SEM images of (a) 1-layer, (b) 3-layer, (c) 5-layer and (d) 10-layer NNO/FTO thin films. The porosity analyzed by ImageJ is (a) 9.65%, (b) 12.7%, (c) 12.9% and (d) 14.8%.

1.4 Conclusions

In this chapter, phase transition properties of rare-earth nickelates were introduced. Two thin film deposition methods, physical vapor deposition and chemical solution deposition, were discussed. To avoid too much repeating, the related thin film characterizations and comparisons will be provided in the following chapters.

2. ELECTROCHROMIC PROPERTIES OF NICKELATE THIN FILMS

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2.1 Introduction

Electrochromic materials change their opacity upon application of an electrical stimulus. The change in optical properties can be non-volatile and the opacity level tuned continuously by bias voltage. Such materials are actively being researched for smart windows via controlling transparency with potential applications in energy efficient building architectures, optical shutters, and tunable optical surfaces for eye goggles, aircraft or automotive vehicles.[19] Typical electrochromic materials operate in contact with a transparent electrolyte medium sandwiched between two electrodes. The electrolyte which can be in either liquid, gel, or solid form that conducts mobile ions such as protons (H⁺) and lithium ions (Li⁺), [20, 21]. The fundamental operation principles of electrochromic inorganic oxides are based on the reversible injection of electrons and small-radius mobile cations into/out of a solid crystal lattice, accompanied with electron compensation and resulting changes in optical transparency. Time scales of interest in these diverse applications range from seconds to minutes wherein the optical transparency modulation range is controlled by electric bias over chosen time period.

To date, inorganic oxide materials including WO₃,[22] niobium oxide (Nb₂O₅),[23] titanium oxide (TiO₂),[24] nickel oxide (NiO),[25] and iridium oxide (IrO₂),[26] wherein the optical state can be switched between colored (e.g. blue, grey or opaque) and transmissive have attracted much attention owing to their diverse composition/structure, superior electrochromic performance and stability against corrosion. [27]

The most widely studied model cathodic electrochromic system of WO₃ modulates its transmittance relying on the insertion of protons and charge-compensating electrons to fill into the conduction band (t_{2g}^1) of WO₃. [28]. The material undergoes an insulator-metal transition accompanied by variation in electrical resistivity and optical transmittance between dark blue and transparent (Figure 1a). The electrochromic properties can vary depending on the microstructure

and synthesis methods. Zhao et al., synthesized quantum dots of WO_3 with an average size less than 2 nm, which showed coloration/bleaching time $< 1\text{s}$ and color efficiency of $154\text{ cm}^2\text{ C}^{-1}$. [29] Cai et al., prepared porous WO_3 film which showed an ideal optical modulation capacity of 97.7% at wavelength of 632.8 nm with switching times of 6 and 2.7 s for the coloration and bleaching, respectively. [30] Compared to crystalline WO_3 film, amorphous WO_3 may show quicker coloration and improved efficiency. Cheng et. al. reported an amorphous WO_3 prepared by photo-deposition with an optical modulation of 70% at 700 nm and coloration efficiency $> 130\text{ cm}^2/\text{C}^{-1}$. [31] Microstructure and synthesis methods are therefore important factors in optimizing performance of electrochromic materials and an active area of research.

In comparison, the most commonly used anodic oxide-based EC materials of Ni oxides are able to change from a transparent state to a neutral colored one upon extraction of protons or insertion of OH^- ions. Charge-balancing electrons are simultaneously extracted from the valence band to convert Ni^{2+} to Ni^{3+} . During operation, the films are actually in the state of mixed oxide and hydroxide at bleached state, and of oxygen-rich compounds NiOOH and Ni_2O_3 at colored state which strongly absorb visible light. [32] Similarly, NiO with diverse nanostructures such as nano-rods, nano-sheets and nano-flakes have been reported. [33] Ultrathin NiO nano-sheet was reported to have a transmittance modulation of 40% with a coloration efficiency of $43.5\text{ cm}^2\text{ C}^{-1}$. [34] Patil et al. reported one dimensional (1D) NiO nano-rods with significantly enhanced optical transmittance capability of 60%, and coloration and bleaching times of 1.55 and 1.22 s at 630 nm, respectively. Ma et al. demonstrated the synthesis of hierarchical NiO with nano-flake morphology with high optical modulation (73.2% at 550 nm), and switching time of 1.8s for coloration and 3.2s for bleaching. [35]

The ionic diffusion co-efficient in the switching medium places fundamental limits on operational characteristics of electrochromic materials. For example, crystalline WO_3 and NiO have typical proton diffusivity of the order of $10^{-8} \sim 10^{-10}\text{ cm}^2\text{ s}^{-1}$. [36, 37] Therefore, new materials that offer comparable or improved ionic diffusion coefficient and absorption over the visible spectrum are of interest and worth exploring as potential candidates for next generation electrochromic windows.

Rare earth nickelates with perovskite structure (ABO_3) are of broad research interest due to its highly sensitive electronic phase diagram with respect to orbital electron occupancy. [1, 38-41] As a representative, NdNiO_3 (NNO) shows metallic conduction behavior and is neutral grey at

room temperature with single electron occupancy in e_g orbital of Ni3d bands (e_g^1).[42-46] Upon cation intercalation accompanied with extra electron filling, the Ni state in pristine NNO experiences crossover to Ni^{2+} state that is highly localized ((e_g^2)).[47, 48] The strong carrier localization opens up an optical gap and makes the material transmissive. The ion-electron intercalation therefore leads to completely opposing effects compared with WO_3 as shown schematically in figure 1.

While hydrogen doping-driven changes in conductivity of $NdNiO_3$ have been reported in literature in the context of electronic memory device technologies[41, 43, 49], properties relevant to optical window applications are still largely unknown and forms the subject of this study. Here, we present experimental results on neodymium nickelate films synthesized by multiple methods (sputtering, chemical solution and atomic layer deposition) that display promising characteristics pertaining to optical transmittance and we further compare its properties with well-studied oxide counterparts such as WO_3 and NiO .

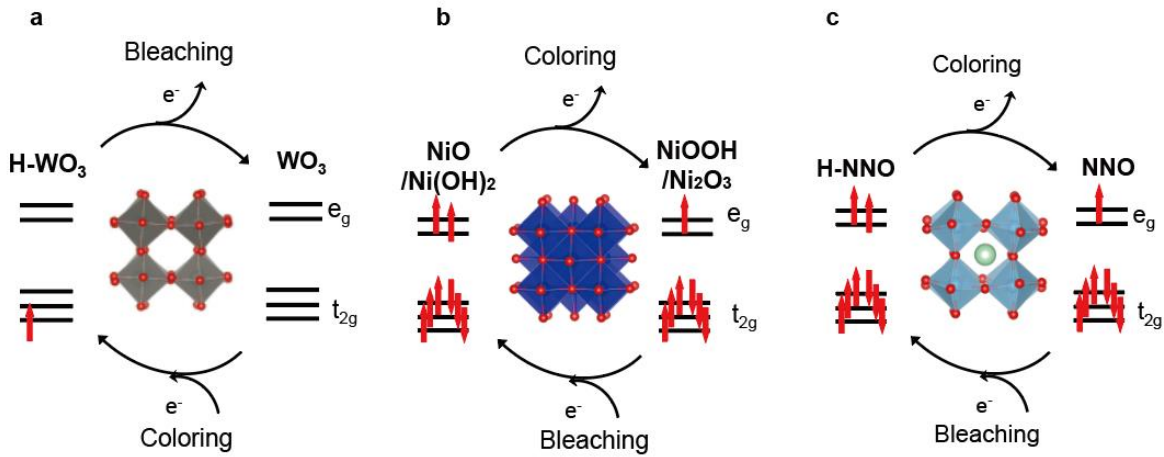


Figure 2.1. Schematic diagram of working principles of various electrochromic materials. **(a)** WO_3 working principle. The grey and red colors represent W and O atoms, respectively. The pristine WO_3 is optically transmissive (bleached state) and becomes opaque after proton insertion accompanied with extra electron filling into t_{2g} orbital (colored state). **(b)** NiO working principle. The dark blue and red colors represent Ni and O atoms, respectively. The NiO is naturally transparent at pristine state and colored while intercalated with extra OH^- or further oxidized to Ni_2O_3 . **(c)** $NdNiO_3$ working principle. The green, light blue and red colors represent Nd, Ni and O atoms, respectively. The nickelate is naturally opaque with single electron occupancy in e_g orbital and experiences a crossover to double occupancy state after proton intercalation becoming transmissive.

2.2 NdNiO₃ thin film preparation

Physical vapor deposition (PVD) of NdNiO₃ thin films (PVD-NNO): NdNiO₃ (NNO) thin films were grown on (001) LaAlO₃ (LAO) and fluorine doped tin oxide (FTO, thickness 180 nm) coated glass substrates using magnetron sputtering at room temperature combined with post-annealing in air atmosphere. The deposition condition is 40/10 sccm Ar/O₂ mixture at total pressure of 5 mTorr from two metallic Ni (DC, 70W) and Nd (RF, 170W) targets. The deposition rate is 140 nm per hour. The as-deposited samples were annealed in air at 500 °C for 24 h in a tube furnace to form the perovskite phase. Unless specifically noted, film thickness is ~50 nm prepared for the characterization studies.

Chemical solution deposition (CSD) of NdNiO₃ thin films (CSD-NNO): The solution was prepared by dissolving neodymium nitrate hexahydrate (Nd(NO₃)₃·6H₂O, sigma, purity 99.9%) and nickel(II) acetate tetrahydrate (Ni(CH₃COO)₂·4H₂O, sigma, purity 99.998%) in the solvent mixture of 2-methoxyethanol and acetic acid (volume ratio 4:1), preheated at 80°C. The solution was heated and stirred at 80°C for 1h and then filtered. The concentration of the solution was controlled to 0.2M by properly weighing the two solid precursors. The spin-coating method was used to deposit NNO thin films with spin speed of 3000rpm and duration of 30s. Then the coated films were baked at 175°C for 20min to evaporate any remaining solvent or water molecules. Then the baked film was immediately transferred to the furnace for pyrolysis and annealing. The pyrolysis condition was 300°C for 30 min in air. Subsequently, the films were annealed at 600°C in air for 12h.

Atomic layer deposition (ALD) of NdNiO₃ thin films (ALD-NNO): ALD depositions of NdNiO₃ were performed in a Veeco Savannah S200 reactor by my group mate Tae Joon Park. The deposition temperature was kept at 160 °C and pressure was 0.9 mbar, maintained by a 20 SCCM of N₂ (Indiana Oxygen, 99.9995%). Nd(iPrCp)₃ (iPrCp = i-propylcyclopentadienyl, Strem Chemicals, 99.9%) and Ni(tBu₂-amd)₂ (tBu₂-amd = N,N-di-t-butylacetamidinato, Strem Chemicals, 99.999%) were used as organometallic precursors and evaporated at 160 °C and 125 °C, respectively, while ozone (O₃) with ~concentration 200ng/mL was employed as the oxidant. Nd(iPrCp)₃ was introduced into the reactor using a “boosted” configuration where N₂ was pressurized into the cylinder prior to dosing precursor into the reactor. Ozone (O₃) was used as an oxygen precursor. Pulse and purge durations were 0.5/5 s for Nd(iPrCp)₃, 0.75/5 s for Ni(tBu₂-amd)₂, and 0.5/5 s for O₃. The NdNiO₃ film were deposited on single crystalline (001) LaAlO₃

(LAO), indium doped tin oxide (ITO) coated glass substrates, and fluorine doped tin oxide (FTO) coated glass substrates (MTI Corp.). All substrates were washed with toluene, acetone, and isopropanol and dried with Ar gas. After the deposition, the films were annealed at 600 °C for 24 hours in air for formation of perovskite phase. Extensive optimization experiments with precursors over a two-year period were carried out as this is the first report on synthesis of ALD-grown NdNiO₃ films.

2.3 Electrochromic Properties of NdNiO₃ on LaAlO₃ Substrates

2.3.1 Film characterizations

NNO thin films with nominal thickness of 40~50nm were deposited onto single crystal LaAlO₃ (LAO) substrates by PVD, CSD and ALD respectively. Figure 2.2(a-c) shows theta-2theta XRD patterns of NNO grown on LAO substrates and the insets show the enlarged patterns at $2\theta=45-50^\circ$. The diffraction pattern indicates the growth of the NNO film deposited by each method is highly [001] oriented ($2\theta_{\text{LAO}}$ at 47.98° , $2\theta_{\text{PVD-NNO}}$ at 47.47° , $2\theta_{\text{CSD-NNO}}$ at 47.48° and $2\theta_{\text{ALD-NNO}}$ at 47.54°) without any contribution from secondary phases.[17] Such an epitaxial relation can be understood based on the close matching of the pseudocubic unit cell parameter of NNO ($a_{\text{NNO}}=3.81$ Å) with the cubic unit cell parameter of LAO ($a_{\text{LAO}}= 3.789$ Å) and has been noted in literature.[50]

The morphology of representative epitaxial NNO/LAO films were analyzed by transmission electron microscopy (TEM) and shown in Figure 2.2(d-i). The high-angle annular dark field (HAADF-STEM) image and energy dispersive X-ray (EDX) mapping (Figure 2.2(d-f)) results demonstrate the uniform dispersion of Nd and Ni and the estimated atomic ratio is ~1 across the film thickness, for the three films. Compared with PVD-NNO/LAO and ALD-NNO/LAO, CSD-NNO/LAO film was relatively porous due to the nature of solution deposition followed by high temperature annealing[10, 16, 51, 52]. Cross-section high resolution TEM images of NNO/LAO films are shown in Figure 2.2(g-i), suggesting the oriented growth of NNO by all three deposition methods.

2.3.2 Raman spectroscopy

Raman spectra were collected using an inVia confocal Raman micro-spectrometer (Renishaw, UK), utilizing a 532 nm solid state laser.

Raman spectra evolution of NNO/LAO films before and after proton uptake are shown in Figure 2.3. The Raman peaks of LAO substrate between 450 and 550 cm^{-1} could be identified in all spectra. Generally, the distorted perovskite nickelate exhibits 24 Raman-active modes but only a few of them can be detected in experiment.[53] The pristine NNO films show the expected peaks at $\sim 300\text{cm}^{-1}$ (E_g mode), $\sim 410\text{cm}^{-1}$ (T_{2g} mode) and $\sim 438\text{cm}^{-1}$ (T_{2g} mode) which is consistent among all three samples.[53, 54] All peak intensity from NNO, especially the T_{2g} peak at $\sim 438\text{cm}^{-1}$, strongly decreased after the films were bleached in the basic electrolyte and later partially recovered after coloration treatment. The bleaching conditions for PVD-NNO/LAO and ALD-NNO/LAO samples were -0.7V vs. Ag/AgCl for 120s while for CSD-NNO/LAO it was -0.7V vs. Ag/AgCl for 60s. The coloration conditions for PVD-NNO/LAO and ALD-NNO/LAO films were +1V vs. Ag/AgCl for 180s, and +1V vs. Ag/AgCl for 120s for CSD-NNO/LAO sample.

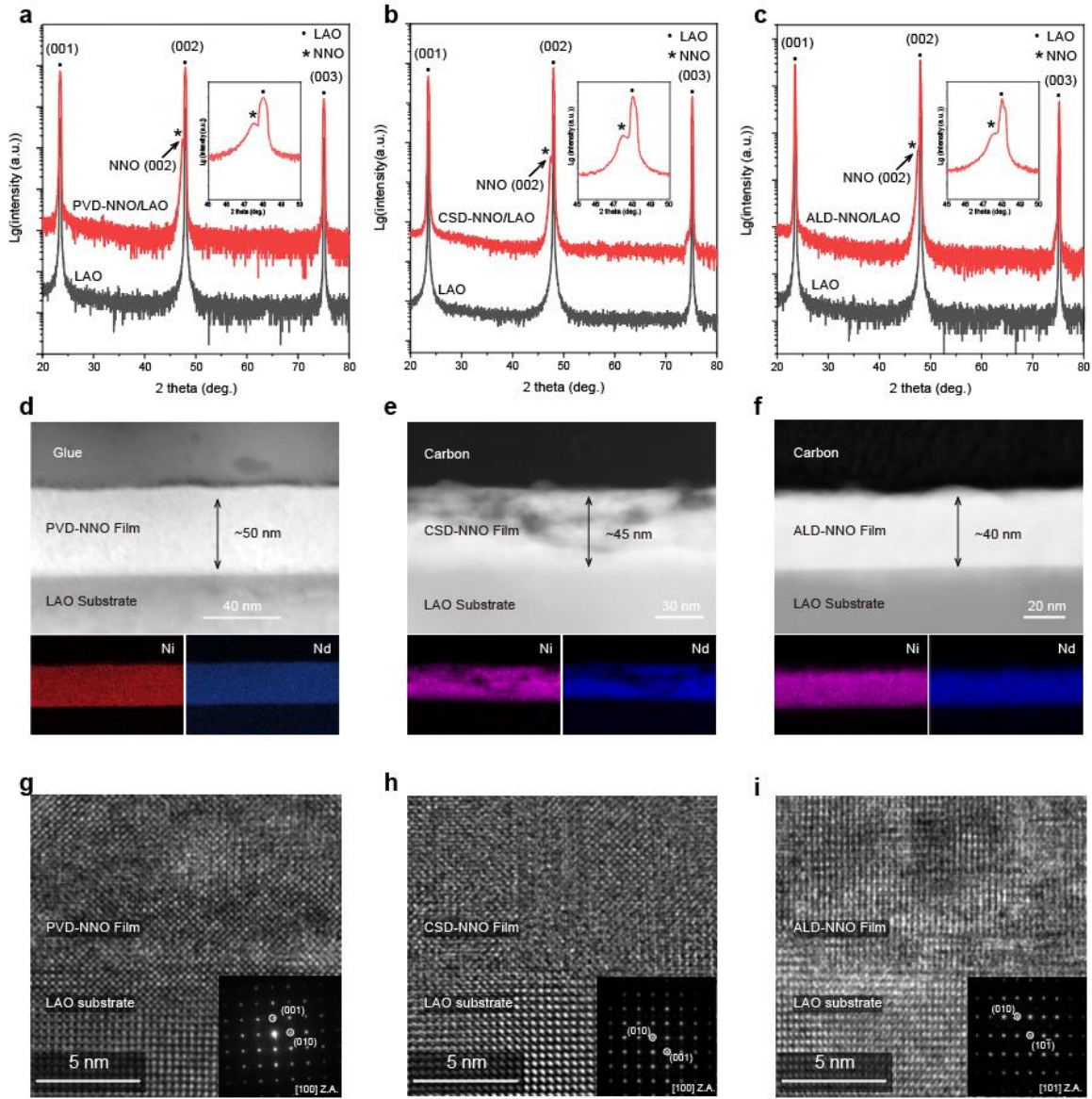


Figure 2.2. **NNO thin films on LAO substrate.** (a-c) XRD scans of NNO/LAO samples deposited by PVD, CSD and ALD. The peaks are labeled with pseudocubic notation. Insets show the enlarged scan from 45° to 50° . NNO (002) peaks were all identified, with $2\theta_{\text{PVD-NNO}}$ at 47.47° , $2\theta_{\text{CSD-NNO}}$ at 47.48° and $2\theta_{\text{ALD-NNO}}$ at 47.54° , which indicates our NNO films on LAO substrates are oriented. No peaks from any secondary phases were observed. (d-f) Cross-sectional HAADF-STEM and the corresponding EDX mappings of Ni and Nd elements, which indicate a 1:1 atomic ratio in all films. The CSD-NNO/LAO thin film is porous while the other two are dense. (g-i) High resolution TEM images of cross-sectional NNO/LAO samples at the film/substrate interface. The selected area diffraction patterns are shown in the insets, also labeled with pseudocubic notation. Figures (d)-(i) were collected by our collaborators from Argonne National Lab and Purdue Materials Engineering Department.

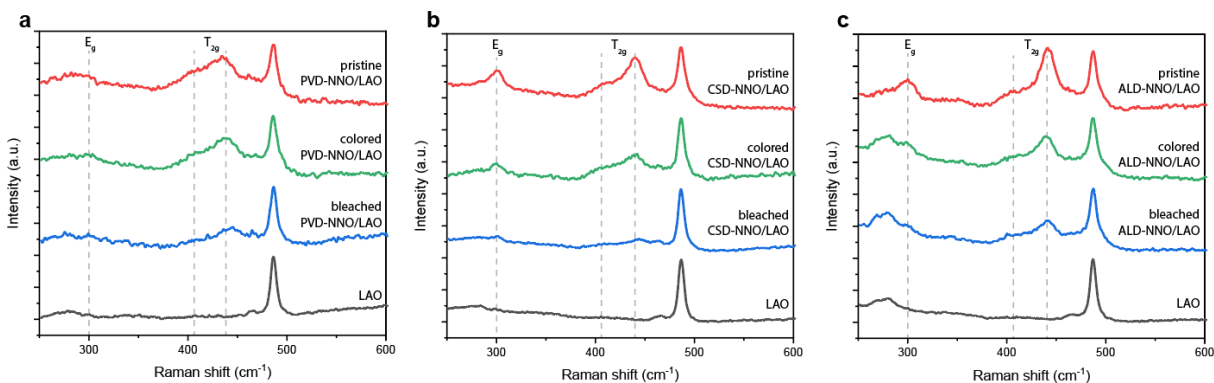


Figure 2.3. Raman spectra of NNO/LAO samples at pristine, bleached and colored states. Vibration modes from pristine NNO film noted in literature are labeled by the dashed lines.[53, 54] The NNO peak intensities decreased after bleaching (proton intercalation step) and partially recovered after coloration (proton de-intercalation step). **(a)** NNO/LAO sample prepared by PVD. Bleaching condition: -0.7V vs. Ag/AgCl for 120s. Coloration condition: +1V vs. Ag/AgCl for 180s. **(b)** NNO/LAO sample prepared by CSD. Bleaching condition: -0.7V vs. Ag/AgCl for 60s. Coloration condition: +1V vs. Ag/AgCl for 120s. **(c)** NNO/LAO sample prepared by ALD. Bleaching condition: -0.7V vs. Ag/AgCl for 120s. Coloration condition: +1V vs. Ag/AgCl for 180s. The films at bleached and colored states were treated in pH 12 electrolyte using a three-electrode setup.

2.3.3 Optical transmittance modulation

Figures 2.4 (a-c) shows the optical transmittance spectra of NNO/LAO samples in their pristine (no treatment), bleached and colored states measured in the visible wavelength range of 350–800 nm. Optical transmittance spectrum from a bare LAO substrate was used as the reference. At the wavelength of 632.8 nm, the optical transmittance modulations of NNO films are listed in Table 1. The bleaching treatment (-0.7V vs. Ag/AgCl for 30s) led to the transmittance increase of PVD-NNO/LAO, CSD-NNO/LAO and ALD-NNO/LAO by 24%, 38% and 15%, respectively. The transmittance of CSD-NNO after bleaching was higher than 90%. Further coloration treatment modulates the transmittance of PVD-NNO, CSD-NNO and ALD-NNO films by 14%, 24% and 10%, respectively. Due to the larger transmittance change in CSD-NNO after bleaching, the coloration time was slightly longer than that for PVD-NNO and ALD-NNO samples.

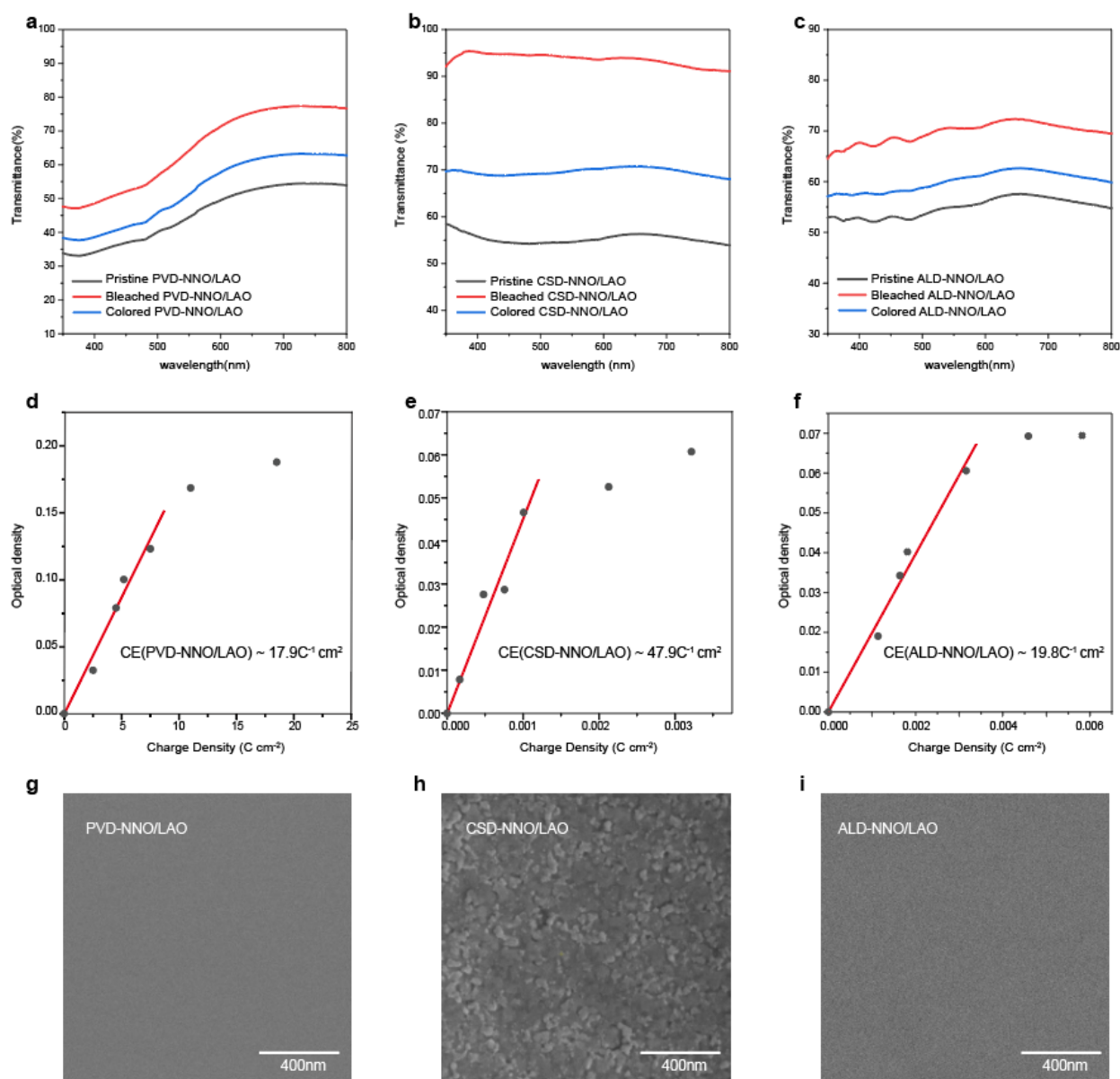


Figure 2.4. The capability of optical transmittance modulation on ~50nm NNO/LAO films and the extracted coloration efficiency. (a-c) UV-Vis spectra of NNO/LAO films prepared by (a) PVD, (b) CSD and (c) ALD in their pristine (no treatment), bleached (-0.7V vs. Ag/AgCl 30s) and colored (+1V vs. Ag/AgCl 60s for (a) and (c) and 180s for (b) due to the dramatic transmittance increase of CSD-NNO after bleaching) states in pH 12 electrolyte. (d-f) Coloration efficiency (CE) of NNO/LAO films prepared by (d) PVD, (e) CSD and (f) ALD. By linear fitting, the extracted CE values are noted in each figure. The SEM images of (g) PVD-NNO/LAO and (i) ALD-NNO/LAO indicates the films prepared by these two methods are dense, while SEM of (h) CSD-NNO/LAO shows the film is relatively porous and granular. Figures (a) (d) were collected by Yifei Sun.

Table 2.1. Optical transmittance modulation of NNO films at 632.8nm

Materials	Pristine	Bleached (-0.7V vs. Ag/AgCl 30s)	Colored (+1V vs. Ag/AgCl 60s)
50nm PVD-NNO/LAO	50%	74%	60%
50nm CSD-NNO/LAO	56%	94%	70% ^a
50nm ALD-NNO/LAO	57%	72%	62%
50nm PVD-NNO/FTO glass	48%	75%	58%
50nm CSD-NNO/FTO glass	67%	91%	74%
100nm CSD-NNO/FTO glass	55%	94%	60% ^a
50nm ALD-NNO/FTO glass	61%	72%	67%

^a. The coloration condition was +1V vs. Ag/AgCl for 180s

The coloration efficiency (CE) is defined as the change in optical density (ΔOD) per injected charge density (Q) at a specific wavelength (632.8 nm in our case). The change in optical density is obtained from equation (3-4):

$$CE = \frac{\Delta OD(\lambda)}{Q} \quad (3)$$

$$\Delta OD(\lambda) = \text{Log} \left(\frac{T_b}{T_c} \right) \quad (4)$$

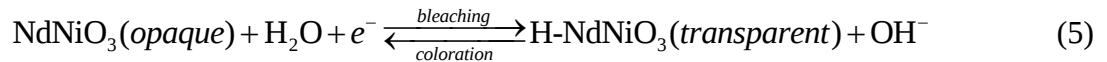
Where T_c and T_b are the transmittance in the colored and bleached states, respectively. The relationship between ΔOD and the charge density variation were shown in figure 2.4 (d-f). CE can be estimated from the slope of the linear fitting range of the curve. This method is commonly used for studying electrochromic materials[51, 55-59]. The coloration efficiency of dense films like PVD-NNO/LAO or ALD-NNO/LAO is less than $20 \text{ cm}^2 \text{ C}^{-1}$, as shown in figure 2.4 (d) and (f). The coloration efficiency for CSD-NNO/LAO could reach $47.9 \text{ C}^{-1}\text{cm}^2$ (figure 2.4 (e)). It is close to the reported values from porous WO_3 and NiO (typically around $40\sim 50 \text{ cm}^2 \text{ C}^{-1}$ [37, 57, 60]), and is $2\sim 3 \times$ the value obtained for PVD-NNO/LAO or ALD-NNO/LAO thin films. A primary reason for the difference among NNO films deposited by different methods could be the denser nature of the PVD and ALD films that limits the interfacial area between the active metal oxide grains and the protons from electrolyte, limiting the electrochromic efficiency. [61, 62] The SEM

images in Figure 2.4(g-i) confirms that CSD-NNO/LAO film has a relatively porous, granular morphology and could be suitable for further optimization of electrochromic activity.

2.3.4 Proton diffusion coefficient

0.01M (pH=12) basic (KOH) aqueous solution was utilized to study the electrochromic properties of NNO in basic aqueous environment. A three-terminal electrochemical cell were used for both electrochromic and cyclic voltammetry (CV) measurement. A silver (Ag) wire was bonded on the thin films with silver paste. The wire contact of the electrode was covered with epoxy such that the influence of Ag wire can be excluded. The NNO film was then submerged into aqueous solutions and denoted as a working electrode. The counter-electrode was a graphite rod with large surface area. Ag/AgCl (saturated KCl) was used a reference electrode. For a specific cyclic voltammetry measurement, a static electric potential (vs. Ag/AgCl) (10, 20, 50 and 100 mV s⁻¹, respectively) was applied to NNO film by a potentiostat using a Solartron 1260A electrochemical analyser. To obtain the diffusion coefficient of proton in NNO film, Randles-Sevcik (R-S) equation (i.e., $I_p/A = 268600 n^{1.5} C(D\nu)^{0.5}$) was used to fit the relation between peak current density (I_p/A , in amps/cm²) and square root of scan rate ($\nu^{0.5}$), where C is the concentration of reaction-involved species in solution (mol/mL); D is the diffusion coefficient of proton in NNO at room temperature (cm² s⁻¹); ν is scan rate (V s⁻¹); n is the number of electrons exchange in the redox process between Ni³⁺ and Ni²⁺ which is 1.[63, 64]

The CVs were measured on NNO/LAO films in 0.01M KOH (pH 12) electrolyte with a linear potential sweep at various scan rates ranging from 100mV/s to 10 mV/s to identify the insertion/extraction process of protons with a visible color change. Pairs of redox peaks (at -0.6V/-0.1V) can be observed on all three NNO/LAO films during the charge/discharge process, which indicates that the capacity behavior in CV measurement is due to Faradaic redox reactions between Ni³⁺ and Ni²⁺. The electrochromic phenomena of NNO in 0.01M KOH solution could be described as follows:



During CV measurements, specifically, the anodic current peaks at high potentials corresponding to the charge transfer as the Ni²⁺ is oxidized. This peak shifted to low-potential regime as the scan rate decreased, indicating that the reaction is kinetically limited by the charge

and mass transfer. Figure 2.5(d-f) shows the linear fitting between maximum peak anodic current density (I_p/A) and the square root of the scan rate ($v^{0.5}$) by using the R-S equation.[63] Based on the extrapolated slopes, the estimated proton diffusion coefficients of PVD-NNO/LAO, CSD-NNO/LAO and ALD-NNO/LAO was $1.14 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, $1.16 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$ and $1.30 \times 10^{-7} \text{ cm}^2 \text{ s}^{-1}$, respectively. A comparison of proton diffusion coefficient with other electrochromic metal oxides is shown in Table 2. In comparison, proton diffusion coefficient for WO_3 ranging between $\sim 2 \times 10^{-7}$ and $4 \times 10^{-10} \text{ cm}^2 \text{ s}^{-1}$ and in NiO ranging from 10^{-10} to $10^{-12} \text{ cm}^2 \text{ s}^{-1}$ have been reported in literature and is both crystallinity and electrolyte dependent.[36, 37, 65-67]

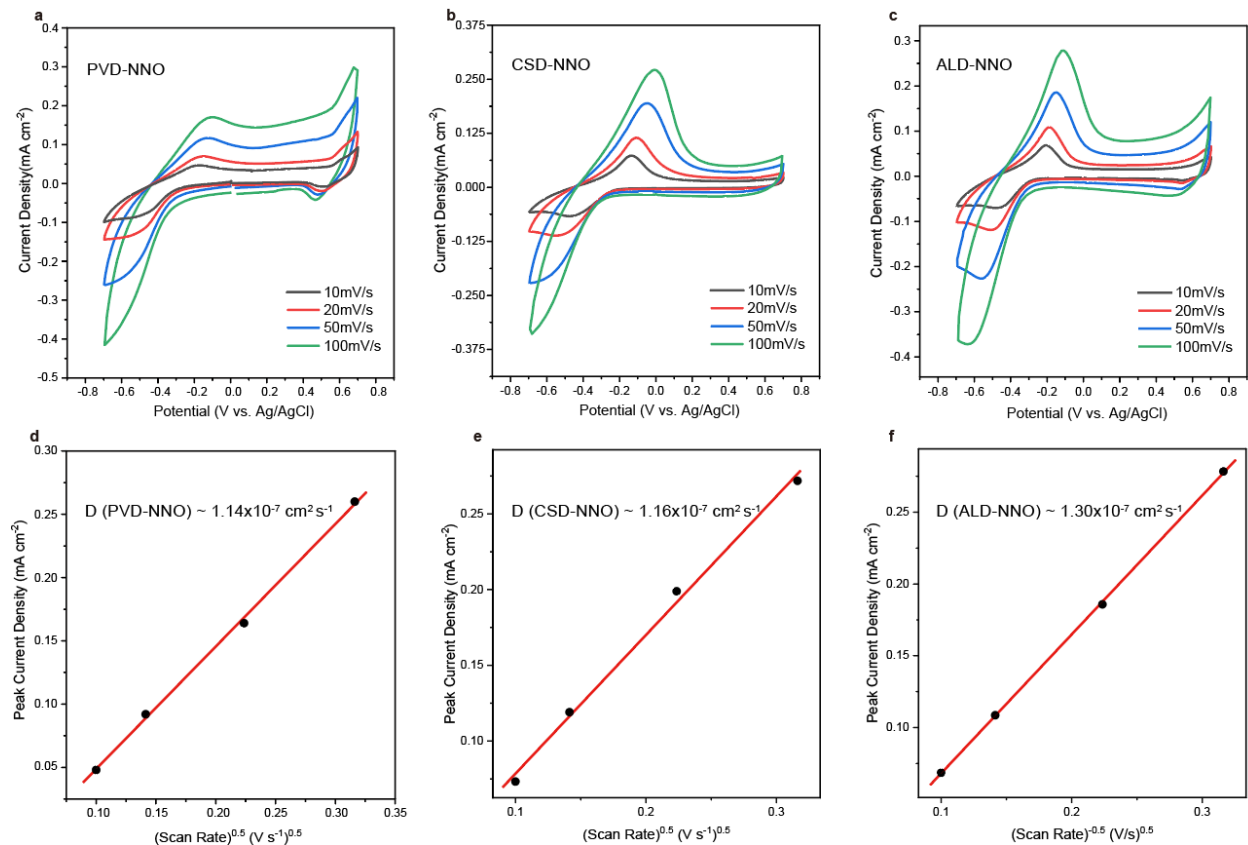


Figure 2.5. CV scans at various scan rates and the corresponding proton diffusion coefficients in NNO/LAO films. NNO films deposited by (a) PVD, (b) CSD and (c) ALD on LAO substrate were scanned by CV technique at 10mV/s, 20mV/s, 50mV/s and 100mV/s in pH 12 electrolyte. (d-f) Linear fittings between peak anodic current density (I_p/A) and the square root of the CV scan rate ($v^{0.5}$) were used to extract the proton diffusion coefficient in films, D , which are noted in the plots. In all cases, the proton diffusion coefficient was extracted to be in the similar range of $\sim 10^{-7} \text{ cm}^2 \text{ s}^{-1}$. Figures (a) (d) were collected by Yifei Sun.

Table 2.2. Diffusion coefficient of protons in representative electrochromic oxides

Materials	Electrolyte	R.T. Proton diffusion coefficient ($\text{cm}^2 \text{s}^{-1}$) ^a	Calculation Method	Preparation Method	Reference
Polycrystalline WO_3	1N H_2SO_4	4×10^{-8}	R-S equation	Evaporation	[66]
Crystalline WO_3	Poly-AMPS ^b	2×10^{-11}	AC impedance	Evaporation	[65]
Amorphous WO_3	Poly-AMPS ^b	4×10^{-10}	AC impedance	Evaporation	[65]
Amorphous WO_3	Water-based electrolyte	$2.5 \times 10^{-7} \sim 2.5 \times 10^{-9}$	N/A	N/A	[68]
Amorphous WO_3	Organic molecules	$\leq 2.5 \times 10^{-13}$	Fick's Law	N/A	[37]
Crystalline WO_3	Organic molecules	$\geq 2.5 \times 10^{-7}$	Fick's Law	N/A	[37]
$\text{Ni}_{1-x}\text{V}_x\text{O}_y$	1M KOH	2.5×10^{-16}	R-S equation	Sputtering	[36]
NiOH	1M HClO_4	4.0×10^{-11}	Finite Diffusion Model	Commercial	[67]
MoO_3	1M H_2SO_4	1.55×10^{-10}	R-S equation	CVD	[69]
TiO_2	1 M $(\text{NH}_4)_2\text{SO}_4$	2×10^{-11}	R-S equation	PVD	[70]
Single crystalline NNO by PVD	pH 12 KOH	1.14×10^{-7}	R-S equation	PVD	<i>This work</i>
Single crystalline NNO by CSD	pH 12 KOH	1.16×10^{-7}	R-S equation	CSD	<i>This work</i>
Single crystalline NNO by ALD	pH 12 KOH	1.30×10^{-7}	R-S equation	ALD	<i>This work</i>

^a. R.T.: room temperature^b. Polymerized 2-acrylamido-2-methylpropane sulfonic acid

2.3.5 Electrochemical stability of NNO/LAO

The electrochemical stability of NNO films in pH 12 environment was investigated by continuous cycling of the applied potential from -0.7 V to $+0.7 \text{ V}$ (vs. Ag/AgCl) at 100 mV s^{-1} . The change in the film electroactivity, which is represented by the charge capacity within each CV cycle, are used to evaluate the stability.[71-73] It was observed from the electrochemical stability graphs that PVD-NNO/LAO, CSD-NNO/LAO and ALD-NNO/LAO can maintain >85% of their initial electroactivities after 400 cycles (Figure 2.6). This result shows that despite the choice of

deposition method, NNO/LAO films consistently show good electrochemical stability in basic solution. This observation is similar to previous works on binary NiO.[28]

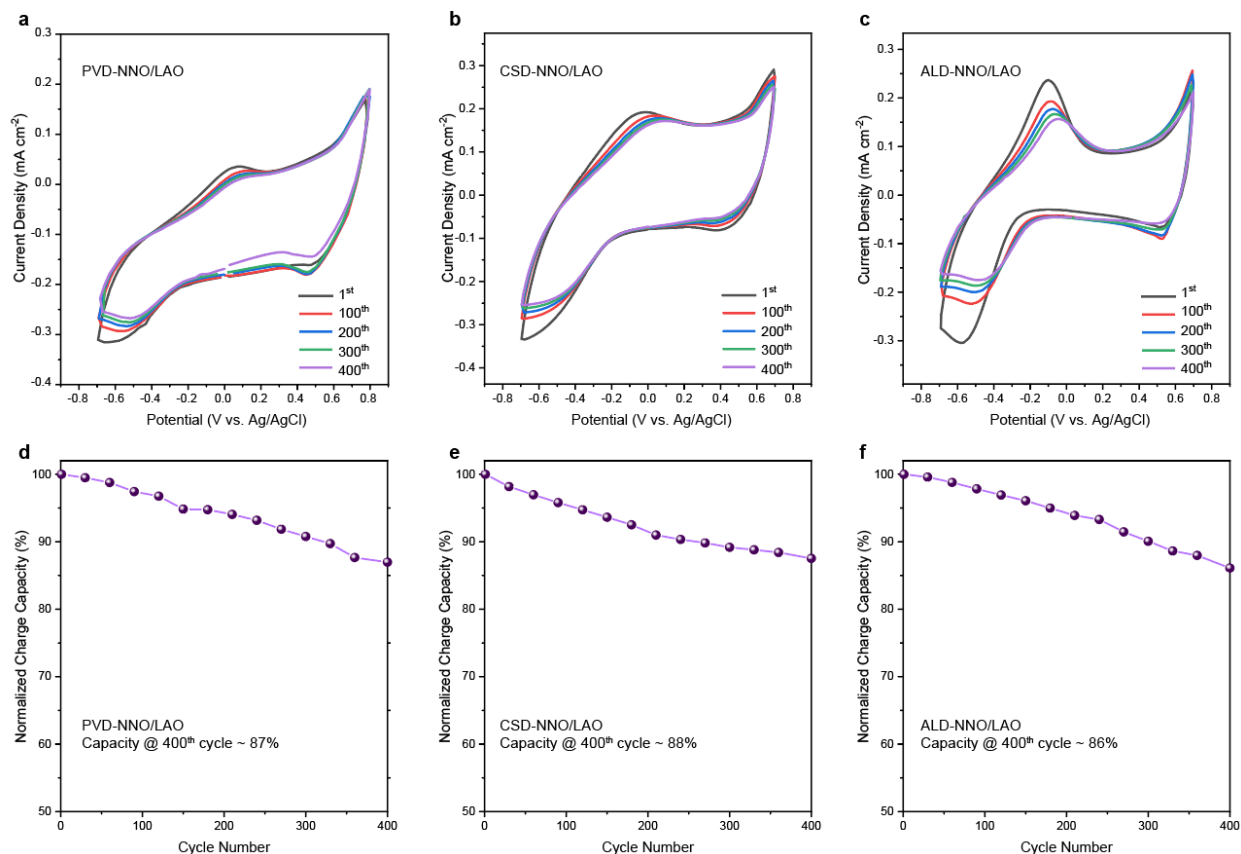


Figure 2.6. **Electrochemical stability of various NNO/LAO samples in pH 12 electrolyte.** (a) PVD-NNO/LAO, (b) CSD-NNO/LAO and (c) ALD-NNO/LAO were examined by CV scans with a scan rate of 100mV/s for 400 cycles. The initial charge capacity after 400 CV cycles for (d) PVD-NNO/LAO, (e) CSD-NNO/LAO and (f) ALD-NNO/LAO was ~87%, 88% and 86%, respectively, which indicates the NNO/LAO samples are quite stable in basic solution. Figure a were collected by Yifei Sun.

2.4 Electrochromic Properties of NdNiO₃ on FTO-Glass Substrates

The electrochemical stability of NNO/FTO films were also examined by cyclic voltammetry, which confirms that polycrystalline NNO could maintain >80% of the initial activity after 400 cycles (Figure 2.8(a-f)). We noticed the peak-to-peak separation of CVs in PVD-NNO/FTO and ALD-NNO/FTO are larger than that of corresponding NNO films grown on LAO substrates. This could be likely due to the limited diffusion as well as charge transfer in dense films deposited by

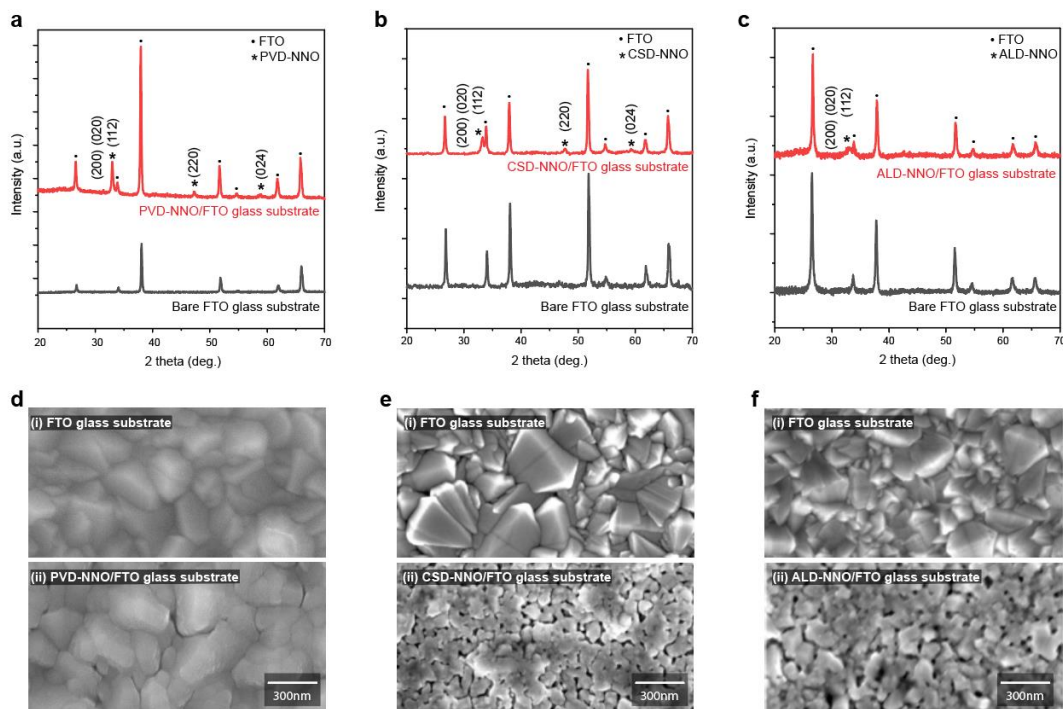


Figure 2.7. **Polycrystalline NNO/FTO samples.** (a-c) XRD patterns taken from ~200nm PVD-NNO/FTO, ~200nm CSD-NNO/FTO and ~50nm ALD-NNO/FTO and bare FTO glass substrate reference. Only one peak was identifiable in ~50nm ALD-NNO/FTO due to the thinner film. (d-f) Morphology of NNO films grown on FTO along with bare FTO substrates as reference for each case. NNO film prepared by PVD (d-(ii)) or ALD (f-(ii)) tends to follow the morphology of FTO (d-(i) and (f-(i))). The resulted polycrystalline PVD-NNO/FTO or ALD-NNO/FTO film is composed of randomly oriented small grains.

PVD and ALD, as shown in Figure 2.7(d)(f). However, CSD-NNO/FTO showed a similar CV peak potentials to single crystalline NNO/LAO films due to the microstructural differences as discussed in the above section. The transmittance change between colored and bleached states of NNO/FTO films are shown in Figure 2.8(g-i). At the wavelength of 632.8 nm, the transmittance modulation of NNO/FTO samples are listed in Table II (transmittance of a bare FTO coated glass substrate was used as the reference). The bleaching condition (-0.7V vs. Ag/AgCl for 30s) led to the transmittance enhancement of PVD-NNO, CSD-NNO and ALD-NNO, all with a thickness of ~50nm, by 27%, 24% and 11%, respectively. Note the bleaching response of CSD-NNO/FTO is limited due to the high transmittance in the pristine state (67%). The inset of Figure 2.8 (h) shows the transmittance modulation of 100nm thick CSD-NNO film grown on FTO, for which the pristine transmittance at 632.8nm (55%) is comparable to that of 50nm PVD-NNO/FTO (48%) or 50nm ALD-NNO/FTO (61%). After bleaching (-0.7V vs. Ag/AgCl for 30s) the transmittance of

100nm CSD-NNO/FTO was increased by ~40%. Further coloration treatment could modulate the transmittance of each sample back to opaque state. This result is similar to the transmittance modulation trend observed in NNO films grown on LAO substrates.

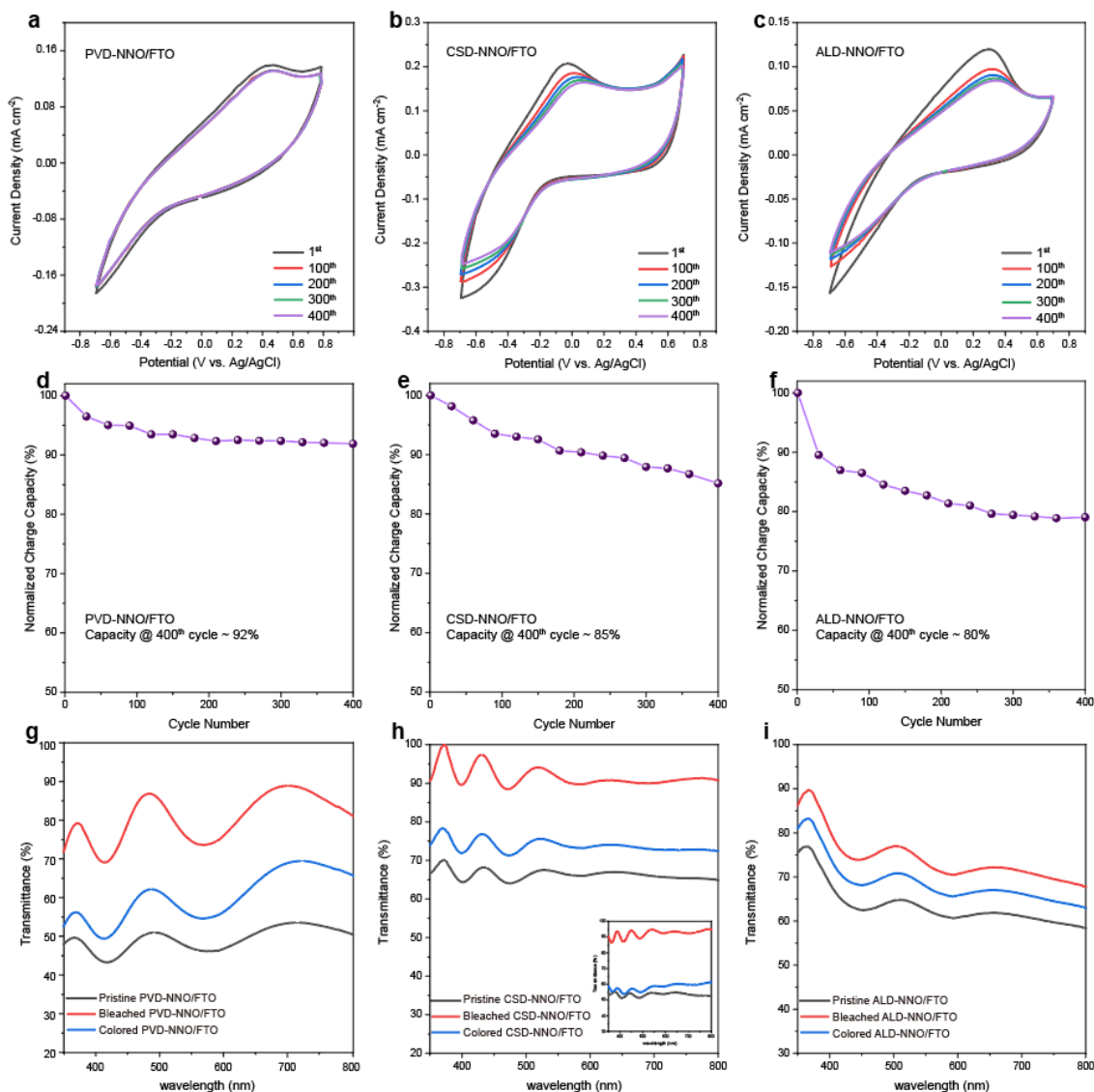


Figure 2.8. Electrochromic properties of polycrystalline NNO/FTO thin films. (a-c) CV stability test of NNO/FTO thin films in pH 12 electrolyte. (d-f) The charge capacity maintained after 400 cycles was ~92%, ~85% and ~80% for PVD-NNO/FTO, CSD-NNO/FTO and ALD-NNO/FTO, respectively. (g-i) UV-VIS spectra of pristine, bleached (-0.7V vs. Ag/AgCl for 30s) and colored (+1V vs. Ag/AgCl for 60s) NNO/FTO films with a thickness of ~50nm. The inset of (h) shows the UV-Vis spectra of 100nm CSD-NNO/FTO sample at pristine, bleached (-0.7V vs. Ag/AgCl for 30s) and colored (+1V vs. Ag/AgCl for 180s) states, which shows a much better opaque/transparent contrast based on a comparable pristine transmittance with 50nm PVD-NNO/FTO (g) or 50nm ALD-NNO/FTO (i). Figures (a) (g) were collected by Yifei Sun.

2.5 Comparison of Film Performances between Synthesis Methods

NNO thin films prepared by physical vapor deposition (PVD), chemical solution deposition (CSD) and atomic layer deposition (ALD) grew in an oriented manner on LAO substrates and were polycrystalline on FTO glass substrates (Figures 2.2 and 2.7). The films deposited in each method exhibited reversibly tunable optical transmittance due to proton (/ de-) intercalation (Figures 2.3, 2.4(a-c), and 2.8(g-i)), with a proton diffusion coefficient of $\sim 1 \times 10^{-7} \text{ cm}^2/\text{s}$ (Figures 2.5 (d-f)). Also, regardless of the deposition method, all films were stable in pH 12 basic solution, and could maintain more than 80% initial electroactivity after 400 cyclic voltammetry scans (Figures 2.6 and 2.8(d-f)). Due to the porous nature of chemical solution deposited NNO films, they are more sensitive to bleaching and coloration treatments than dense NNO films deposited by PVD or ALD. For the same bleaching condition (-0.7V vs. Ag/AgCl for 30s), CSD-NNO/LAO or NNO/FTO increased transmittance by $\sim 40\%$ (Table 1) at 632.8nm, while this value for PVD-NNO/LAO or ALD-NNO/FTO was $\sim 25\%$ (Table 1). The transmittance of bleached CSD-NNO (either deposited on LAO or FTO glass) film is higher than 90%. After bleaching, the coloration efficiency for CSD-NNO ($47.9 \text{ C}^{-1} \text{ cm}^2$) is also much higher than that of PVD-NNO ($17.9 \text{ C}^{-1} \text{ cm}^2$) and ALD-NNO ($19.8 \text{ C}^{-1} \text{ cm}^2$) (Figure 2.4(d-f)). For application in smart windows, CSD-NNO films appears to show greater degree of optical tunability compared to its denser counterparts synthesized by PVD or ALD. Similar enhancement of electrochromic performance due to microstructural aspects such as porosity has been noted in other oxides as well in literature.[25, 32, 55, 57]

2.6 Conclusions

We successfully synthesized and characterized a series of perovskite nickelate of NdNiO_3 (NNO) thin films on LaAlO_3 and FTO-coated glass substrates by PVD, CSD and ALD methods. Their electrochromic properties in basic electrolyte (0.01M KOH, pH 12) were systematically studied. The films demonstrated tunable opacity at the visible wavelength via insertion/extraction of protons from aqueous electrolytes. Cycling experiments indicated the material is stable in basic electrolyte. The high proton diffusion coefficient in NNO coupled with electrochemical stability is promising towards further exploration in smart window applications. Future directions include further optimization of microstructural features during deposition to enhance kinetics of chromic

tuning. More specifically, some potential directions to further improve the electrochemical performances of NNO are as follows. The optimization of deposition parameters of chemical solution deposition such as solution viscosity control or adding pore-generating agents can be pursued, as it will help grow granular films for enhanced charge and mass transfer. Film patterning such as etching the film into high-density arrays could be expected to create more active surface area, which would further improve the efficiency of bleaching or coloration. Chemical solution deposition is capable of depositing various nickelates including NdNiO_3 , SmNiO_3 and even alloyed rare-earth nickelates (e.g.: $\text{Sm}_{1-x}\text{Nd}_x\text{NiO}_3$) with high quality as noted in literature.[12] Considering that rare-earth nickelates should behave similarly regarding the stability in basic electrolytes, it could be promising to study the effect of chemical composition of the nickelates on electrochromic properties.

3. ELECTRONIC DEVICES DESIGN AND FABRICATION WITH PEROVSKITE NICKELATES

3.1 Introduction

Starting from the conducting-insulating phase transition of SmNiO_3 by electron-doping reported by J. Shi *et al.*, there were several attempts on electronic devices utilizing platinum (Pt) or palladium (Pd) as electrodes to generate local electronic insulating phase. C. Oh *et al.* carried out a resistive switching measurement on H_2 doped NdNiO_3 (NNO) based on an asymmetrical device[74]. Figure 3.1(a) shows a process flow of the fabrication and the proton doping. They used a shadow mask to deposit Platinum electrodes on pre-deposited NNO films, referred as H-Pt since they are for H_2 doping. The electrodes deposited after H_2 doping are referred as NH-Pt. The hysteresis loop was found when voltage sweeps are applied across H-Pt/NNO/NH-Pt and H-Pt/NNO/H-Pt, but not in NH-Pt/NNO/NH-Pt, as shown in figure 3.1(b). This indicates that it is the doped protons and electrons near H-Pt that play a role in this resistive switching behavior. They also tried with different sweeping ranges and the hysteresis loop enlarges with the increased sweeping amplitude. What is more, both the LRS and HRS resistance are inversely proportional to the H-Pt area, but not related to the distance of two electrodes. This is evidence that the resistance switching happens locally near the H-Pt rather than in between the electrodes. The proposed mechanism is that when a negative voltage is applied at the H-Pt, the protons will drift towards it and some will be stored in H-Pt electrodes as hydrogen. This operation decreases the thickness of hydrogenated NdNiO_3 (HNNO), which turns the cell into a LRS (SET operation). On the contrary, when a positive voltage is applied at the H-Pt, the protons will drift away from the it, which leads to a thicker HNNO region under H-Pt. As a result, the H-Pt/NNO/NH-Pt cell reaches a HRS (RESET operation) (figure 3.1(b)).

Further measurement in C. Oh *et al.*'s work was carried out by applying a series of different SET and RESET scans repeatedly with amplitude negatively from -1V to -9V and positively from +1V to +10V. The result shows that each I-V loop follows the previous one and drifts consistently, shown in figure 3.1(c). The resistance seems to be tunable with a proper input condition which makes it possible for the multi-level switching. Another impressive work found that switching in NNO can be triggered by a several hundred of nanoseconds voltage pulse, done by K. Ramadoss *et al.*[75]. The devices were modified with a smaller gap between two electrodes to provide a

stronger electric field. It is claimed that the resistive switching in HNNO only requires a small input energy as drifting of protons under an electric field is easy, such that the switching in HNNO is energy-efficient.

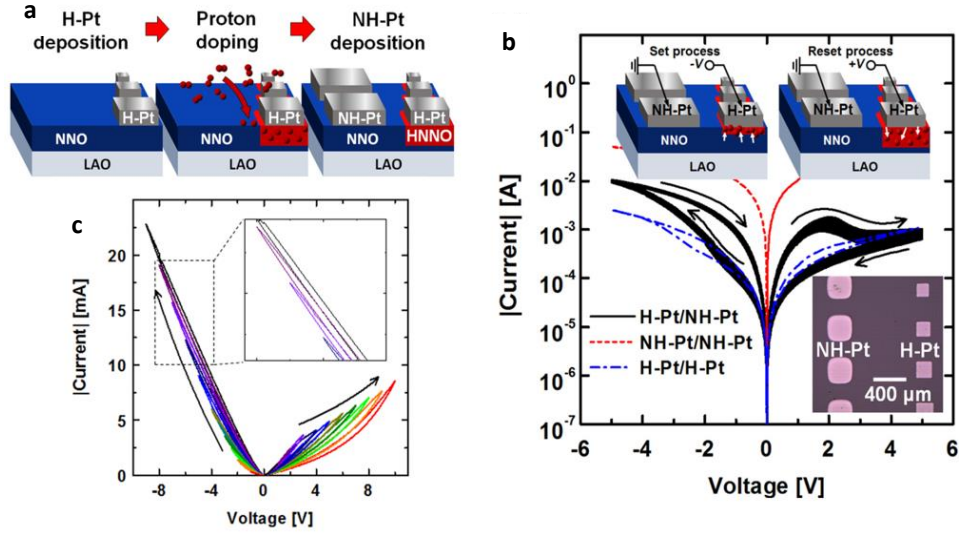


Figure 3.1. (a) The process flow of the asymmetrical device fabrication. (b) SET and RESET operation and the I-V curves of voltage sweep. Inset: top-down view of the devices. (c) Repeated voltage sweeps with different SET and RESET amplitudes. Inset: enlarged negative scan. Images from [74].

3.2 Electronic Devices Design and Processing

3.2.1 Design motivation

The electron doping process of SmNiO_3 (SNO) by Pt or Pd assisted hydrogenation is sketched in figure 3.2 (a). The film with Pd electrode is being annealed in H_2 rich forming gas (usually 5% H_2 /95%Ar). At the triple phase boundary of SNO/Pd/ H_2 , the H_2 molecules will be split into H atoms which could be stored in Pd, then into protons and electrons. The electrons will occupy the empty e_g orbitals of Ni ions, reducing Ni^{3+} into Ni^{2+} while the protons will remain in the perovskite thin film lattice as interstitial defects. As a result, the thin film close to Pd will be doped and transited into the insulating phase H-SNO, while the part far apart from Pd still remains conductive. It is more practical to finish the entire device fabrication before doping the device in case of the proton loss during fabrication. Since only Pd or Pt could help with the electron doping, we could always use another metal as the other electrode in a two-terminal device. Considering

the metal work functions and Pd is a noble metal, Au was selected as the reference electrode. Using lithography rather than shadow mask could precisely control the gap between two terminals. The asymmetric device sketch is in figure 3.2 (b), showing a gradient electronic phase from insulating H-SNO to conducting SNO between the two terminals.

This device design not only works for SNO thin films, but also works for NdNiO_3 and LaNiO_3 thin films, as we will show in the coming sections.

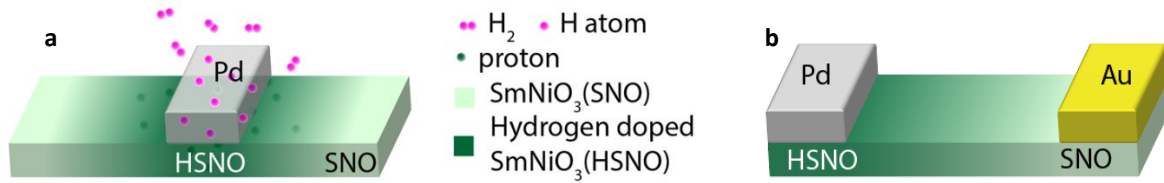


Figure 3.2. device design motivation. (a) Electron doping process of SNO thin film by Pd assisted hydrogenation. (b) Asymmetrical design of the Pd-SNO-Au two-terminal device. There is electronic phase gradient between the two electrodes.

3.2.2 1st Generation Device Fabrication

The 1st generation of devices were quite simple. The pre-deposited nickelate film was etched into rectangular islands by ion mill, then Pd and Au electrodes were deposited at the left and right side of the rectangular thin film, respectively. The device fabrication process can be found in figure 3.3 (a). However some lithography details are neglected in the plot.

For a typical photo lithography process, the steps are as follows:

1. Spin coating of photo resists. In this work LOR-3A and S1813 were used as a bilayer photo resist for easier lift off.
2. Baking for solidification. The baking condition for LOR-3A was 170°C for 5min and for S1813 was 115°C for 2min.
3. Exposure. Both mask aligner MJB3 and mask-less aligner Heidelberg were used, the exposure UV light has a wavelength of 415 nm.
4. Develop. The resist from exposed area will be developed off from the film surface. The non-exposed region will still be covered with photo resists.
5. Metal deposition. Usually e-beam evaporation was used to deposit metal electrodes.

6. Lift-off. The remaining photo resist will be removed by chemicals such as Remover-PG. After lift-off, the metal contacting the sample surface is remained while the rest of the part will be detached from the sample along with the photo resist.

Since the device fabrication process only involved photo lithography, the gap distance between two terminals were no smaller than $5\mu\text{m}$ to avoid possible shorting of the device due to the misalignment or overdevelopment of the photo resist. This is also the drawback of the 1st generation devices.

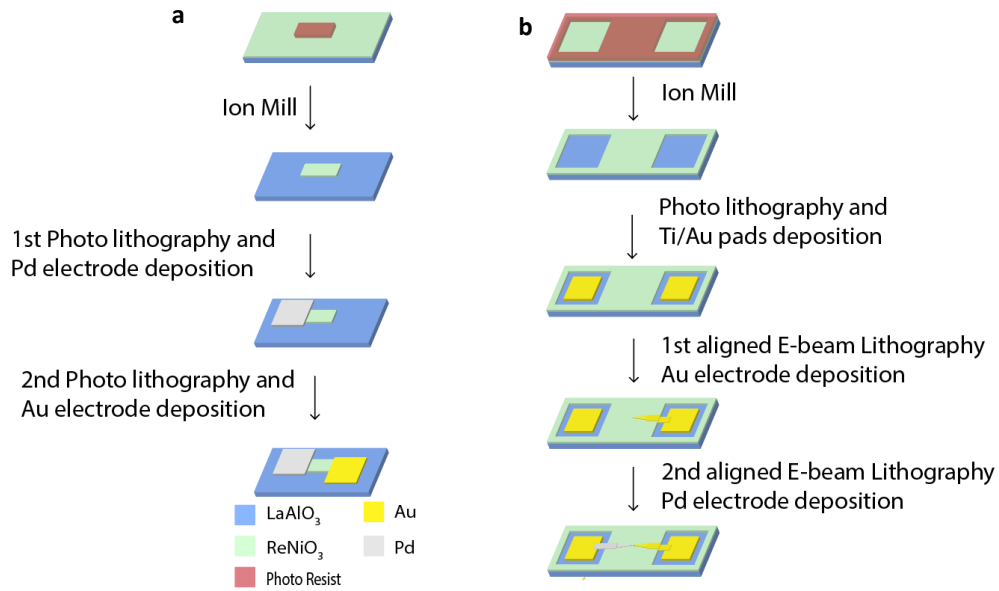


Figure 3.3. Device fabrication processes of 1st generation and 2nd generation. (a) 1st generation device only involves photo lithography in fabrication process. (b) 2nd generation device fabrication needs both photo lithography and electron-beam lithography (EBL).

3.2.3 2nd Generation Device Fabrication

To further investigate any microscopic data of proton drifting under external electrical fields, collaborating with Prof. Frano from UCSD, we were aiming at the x-ray absorption (XAS) mapping of Ni^{3+} and Ni^{2+} ions distribution before and after electrical stimuli. However, there are several requirements for the devices to be scanned under the x-ray source:

1. The gap between two terminals needs to be less than $2\mu\text{m}$ for a smaller scanning area so that the XAS mapping is efficient

2. The device needs to be wire-bonded to a PCB board so that we can apply electrical pulses outside the chamber.

For the first term, photo lithography is not capable of such a small gap so electron-beam lithography (EBL) is required. EBL needs the substrate surface to be conductive to avoid any charging issues, which indicates the thin film cannot be etched into islands anymore as the LAO substrate is very insulating. Wire-bonding requires a titanium (Ti) adhesion layer between the electrode and the oxide thin film, but there is a contact issue of Ti/SNO as the contact is often non-ohmic. In this case, the film under Ti/Au bonding pads needs to be removed. As a result, there were pairs of openings like windows etched out of the film, as shown in figure 3.3 (b). In this way, the conductive SNO still covers across the entire substrate, preventing from any electron accumulations, while it is not in direct contact with Ti at all.

Another trick in EBL is the alignment. Photo lithography uses the contrast under visible light to locate alignment marks, but EBL uses back-scattered electron signals, which depends on the atomic number Z , to identify the alignment marks from the substrate. As the nickelate film contains rare-earth elements, the background is so bright that Pd is not in good contrast with the film under back scattered electron signals. Luckily the atomic number for Au is high enough to show a decent back-scattered electron contrast on nickelate thin films. In conclusion, the deposition sequence for metal electrodes was decided as: 1. Large Ti/Au contact pads, which provides the alignment marks for the 1st aligned EBL for Au working electrodes. 2. Au working electrode patterning and deposition, which provides the alignment marks for the 2nd aligned EBL for Pd working electrodes. 3. Pd working electrodes patterning and deposition.

The fabrication process of the 2nd generation of devices is shown in figure 3.3 (b). The details of EBL process is similar to photo lithography, while the main difference is that the resist in EBL is 495 PMMA and 950 PMMA bilayer. The PMMA with a lower molecular weight (495 PMMA) will dissolve faster than the one with a higher molecular weight in the developer (MIBK:IPA=1:3), which will naturally form a larger opening at the bottom layer beneficial to the lift-off process. As the patterns written by EBL is very small, lift-off process takes a longer soaking time than photo lithography, which is usually overnight to avoid any peel-off of the metal electrodes.

3.2.4 3rd Generation Device Fabrication

There is another way to eliminate the electron charging on an insulating substrate even if the conductive nickelate thin film is etched into isolated patterns like in the 1st generation devices. The extra care here are depositing a conductive layer above PMMA bi-layer before EBL, typically 10-20nm Al layer sputtered or thermally evaporated, or commercially spin-on conductive polymers. The Al layer cannot be e-beam evaporated as the e-beam during evaporation will expose PMMA which will damage the EBL writing process. Al layer could be removed by most photo resist developers such as CD-26 or MF-26A. The commercially available conductive polymers are usually “E-spacer” and “Discharge H₂O” which are water-dissolvable.

In my practice, I tried sputtered Al layer, Discharge H₂O and E-spacer. Discharge H₂O is the worst among the three candidates as it has a horrible wetting issue on PMMA, which dose not form a uniform coating above PMMA. Al layer and E-spacer worked well but sputtering Al takes more time than spin coating E-spacer. E-spacer produces a more stable electrical conductance than sputtered Al suggested by the dose tests between difference batches, but it is so time-sensitive that the coated sample needs to be exposed within 1 hour or the electrical properties of the coated polymer would change.

The complete fabrication process of the 3rd generation devices is descirbed below as well as in figure 3.4:

1. Nickelate film was patterned by ion mill into isolated patches.
2. Photo lithography aligned to the patterned film for large Ti/Au contact pads deposition
3. Spin coating and baking of 495 and 950 PMMA bilayer, followed by spin coating of E-spacer and baking at 80°C for 90s to dry out.
4. 1st EBL aligned to Ti/Au contact pads and develop. Rinse substrate well with water for 1min to get rid of E-spacer. Then immerse into MIBK:IPA=1:3 for 1min and rinse with IPA.
5. Deposition of Au working electrodes by e-beam evaporation and lift-off
6. Repeat form step 3 to step 5 to do the 2nd EBL aligned to Au working electrodes for Pd working electrodes

The process above is not only suitable for nickelate devices but also applied to other devices processed on low-conductivity materials such as VO₂ and NbO₂. The dose tests are required every time the substrate is changed due to the scattering of electrons are affected by the elements on

substrate materials. Typically for my device layouts working with E-spacer layers, $780\mu\text{C}/\text{cm}^2$ is sufficient on LAO substrate while on sapphire or Si substrate the dose should be at least $1200\mu\text{C}/\text{cm}^2$.

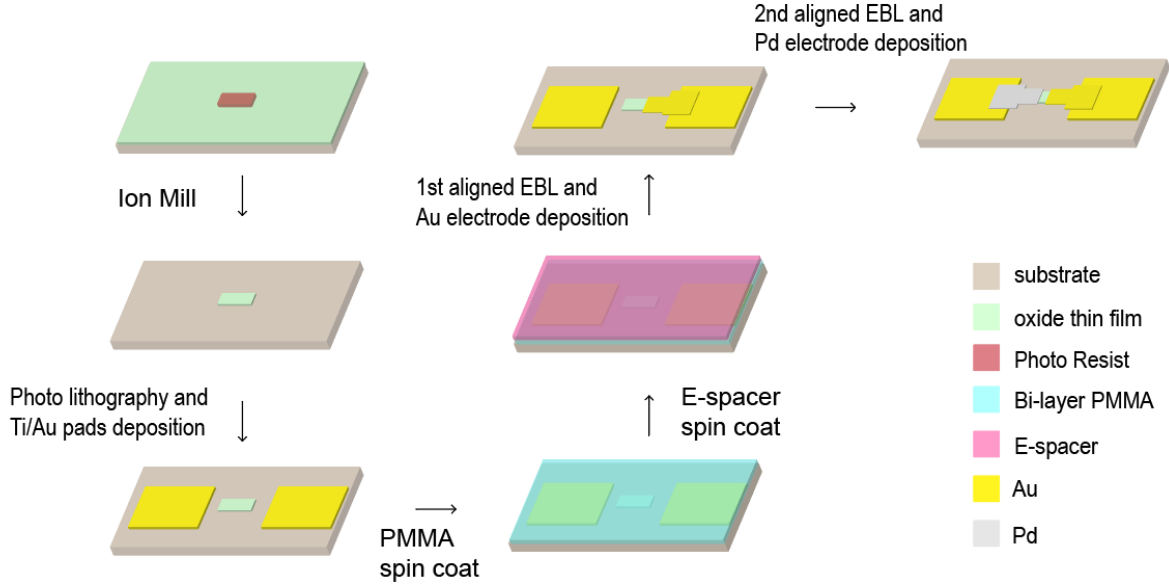


Figure 3.4. 3rd generation device fabrication process. The unique steps of E-spacer coating is specified in the sketch.

3.3 Device Performances and Applications in Neuromorphic Computing

3.3.1 Proton Redistribution

We demonstrate that electric pulses, as fast as tens of nano seconds, are effective in perturbing the proton distribution in the nickelate lattice and can tune its resistivity in a systematic fashion enabling ultrametric tree-like conductance states, as schematically shown in Fig. 3.4 (d). By applying electric pulses in consecutive and reversible manner, a tree structure of memory states can be generated as a function of number of pulses. The working in-plane devices should have a gap distances of $\sim 100\text{nm}$ or smaller. The optical and SEM images of the working devices fabricated by EBL and photo lithography on SNO are shown in Fig. 3.4 (a)-(c).

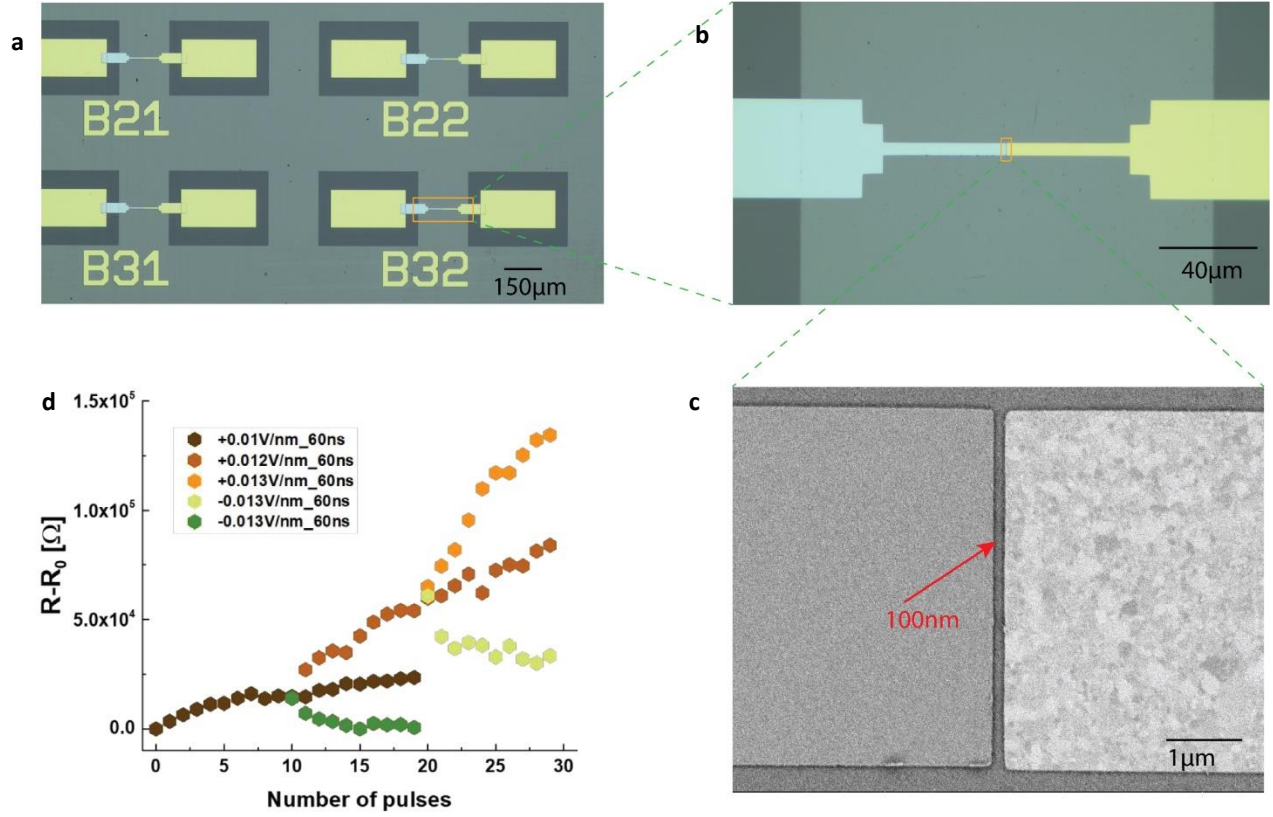


Figure 3.5. Scalability of the perovskite device down to 100 nm scale. (a)(b)(c) Optical image and scanning electron microscope (SEM) image of SmNiO_3 devices with 100 nm gap size fabricated by lithography. (d) An ultrametric tree structure of memory states can be obtained by re-distribution of the protons through 60 nanosecond pulses. This provides proof-of-principle demonstration of synaptic behavior down to 100 nm channel device. Figure (d) was measured by Tae Joon Park.

To understand the microscopic origins of tree-like memory in the hydrogen-doped nickelates, we performed in operando X-ray studies of a representative in-plane nickelate device. For this experiment, a perovskite nickelate SmNiO_3 in-plane device is catalytically doped with protons using a Pd electrode on top of the film through annealing in forming gas. We then apply electrical stimuli to the nickelate device and track the changes in the electronic structure by measuring X-ray ray absorption spectra (XAS) maps, and a schematic of the setup is shown in Fig. 3.4. The incident X-ray beam focused by a Fresnel zone plate to ~ 30 nm is used to perform the raster scan of the device between the electrodes with steps of 200 nm.

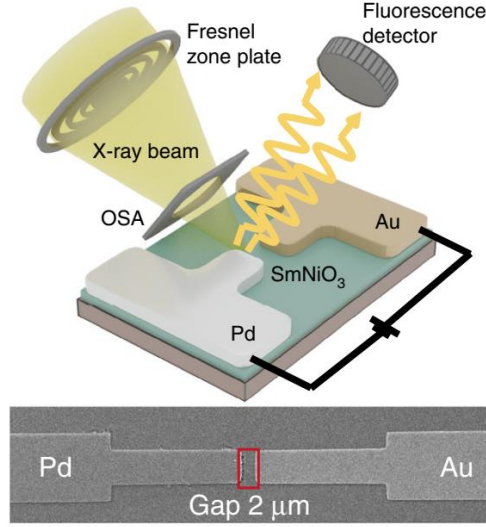


Figure 3.6. Scheme of the nanoprobe X-ray absorption imaging experiment. The incoming X-ray beam is focused by the Fresnel zone plate, and diffraction orders are filtered out by the order-sorting aperture (OSA). The fluorescence signal at the K-edge of Ni from the 30-nm spot illuminated by the X-rays is recorded by the detector positioned perpendicular to the beam. A scanning electron microscope (SEM) image of the nickelate device is shown at the bottom. The red rectangle shows the scanned area of the X-ray absorption imaging.

To reveal the spatial distribution of the hydrogen-doped areas, we fixed the energy of incoming X-ray photons at $E = 8345$ eV, which corresponds to the maximum of the Ni absorption spectrum derivative and where the shift of the absorption edge is most visible. In this case, the areas of the nickelate device doped by hydrogen are distinguishable by a more intense fluorescence signal due to the shift of the Ni K-edge toward lower energies. The normalized fluorescence map of the as-hydrogenated device is shown in Fig. 3.5(a). The yellow areas next to the Pd electrode indicate the regions with a reduced valence of Ni, while the purple areas farther away from the Pd electrode correspond to the unchanged electronic structure of pristine SmNiO_3 . To check whether the electric pulses lead to the changes in the nickelate electronic structure, we tested two different types of electrical stimuli and collected similar fluorescence maps. First, we applied several long-duration pulses (5 s) with 2 mV magnitude. The fluorescence map after this type of stimulus (Fig. 3.5 (b)) reveals only little changes compared with the initial state of the device. Subsequently, shorter 100-ns pulses of 1 V magnitude were applied to the device, which caused significant changes in the fluorescence map (Fig. 3.5 (c)). The non-uniform distribution of the fluorescence intensity with typical length scale of $1 \mu\text{m}$ appears next to the Pd electrode—the region initially doped with hydrogen. Although it is extremely challenging to detect protons directly in nanoscale

regions in a solid matrix, the electronic structure spatial maps presented here demonstrates that voltage pulses can cause migration of protons in the nickelate device from tracking the reconfiguration of Ni charge states.

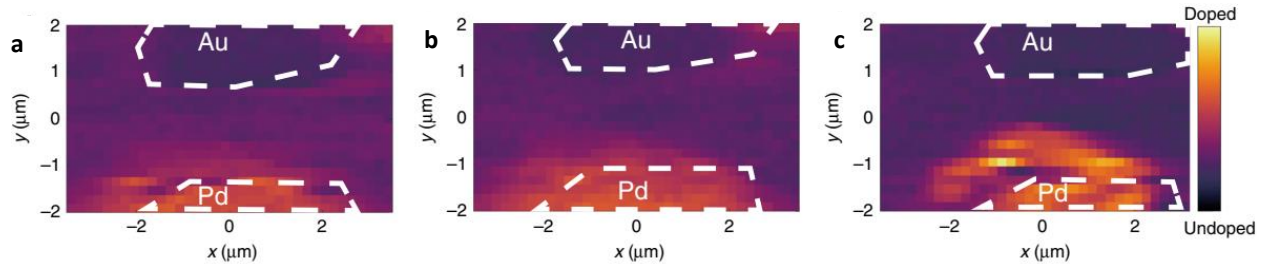


Figure 3.7. Changes in Ni K-edge fluorescence intensity of the hydrogenated nickelate device after electrical stimuli. The color corresponds to the intensity of the normalized fluorescence signal at the fixed energy of $E = 8345$ eV (where the slope of the XAS curve is highest and thus most sensitive to the energy shift) and therefore characterizes the hydrogen doping of the channel. Dashed lines denote the positions of the Au and Pd electrodes. The map of the initial sample is shown in panel (a), the map after applying several 2 mV pulses of 5 s duration time is shown in (b), and after several 1 V pulses of 100 ns duration in (c). This XAS mapping was collected by Dr. Ivan A. Zaluzhnyy in Prof. Alex Frano's Group in UCSD, conducted in Argonne and Brookhaven National Lab.

3.3.2 Reconfigurable Perovskite Nickelate Electronics

From H. T. Zhang *et al.*, "Reconfigurable perovskite nickelate electronics for artificial intelligence," *Science*, vol. 375, no. 6580, pp. 533-539, Feb 4 2022, doi: 10.1126/science.abj7943.[76]. Reprinted with permission from AAAS.

In this work, we showed that perovskite nickelates, a class of quantum materials that undergo room-temperature electronic phase transitions upon hydrogen doping, enable a versatile, reconfigurable hardware platform for adaptive computing. A single device made from H-doped NdNiO_3 (NNO), for example, could be electrically reconfigured on demand to take on the functionalities of either neurons, synapses, or memory capacitors. Such versatile tunability was distinctively enabled by the synergistic combination of a vast array of metastable configurations for protons in the perovskite lattice that can also be voltage controlled.

To demonstrate reproducible electrical reconfiguration in H-NNO, 50-nm-thick NNO films were deposited through different methods, sputtering and atomic layer deposition (ALD), as well as on

different substrates, LaAlO_3 , SiO_2 on Si and Si substrates. The fabrication processes for various devices are described below:

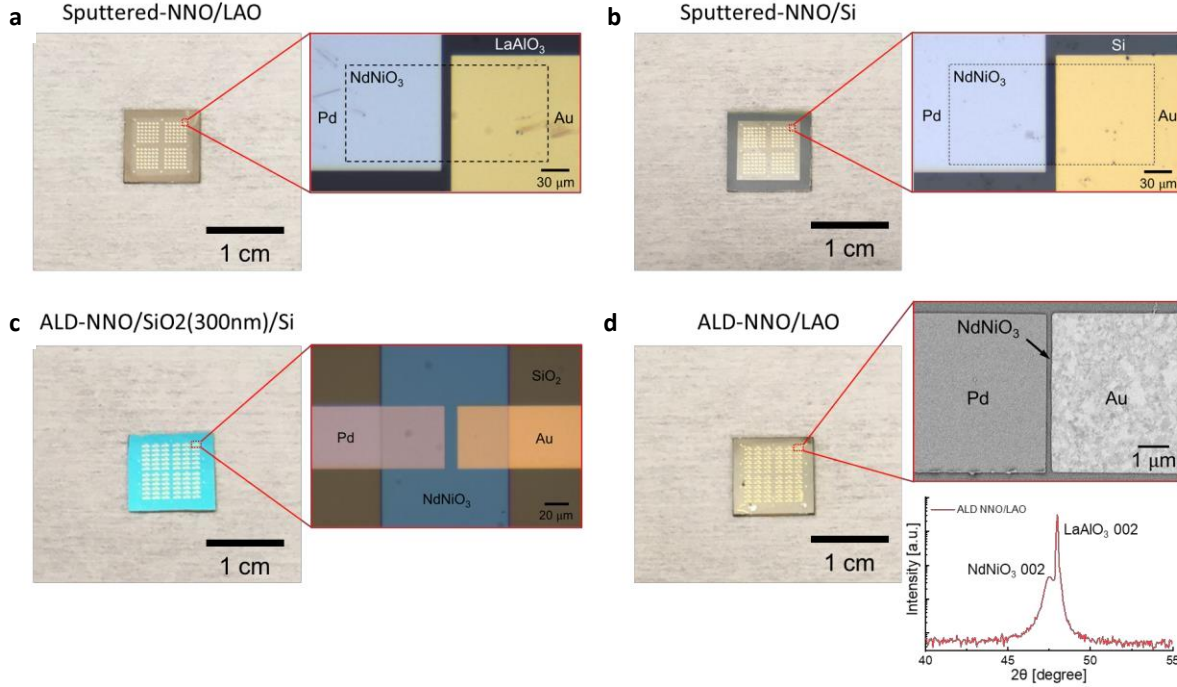


Figure 3.8. Electrically reconfigurable nickelate devices on various platforms. Various test chips with channel sizes ranging from 10 μm down to 100nm were fabricated by electron-beam lithography and photolithography and studied. Photograph of in-plane devices fabricated using (a) sputtered NdNiO_3 on LaAlO_3 , (b) sputtered NdNiO_3 on Si, (c) ALD grown NdNiO_3 on SiO_2/Si , and (d) ALD grown NdNiO_3 on LaAlO_3 . Insets in (a), (b), and (c) show optical microscope images of a single device. Scale bars are 30 μm . Inset in (d) shows a scanning electron microscope image of a single device. The scale bar is 1 μm . Below the inset is a representative Theta-2Theta XRD scan of ALD grown NdNiO_3 on LaAlO_3 . The peaks were indexed with pseudocubic notation. NdNiO_3 (002) peak was observed near the LaAlO_3 (002) peak, which indicates nickelate films are well oriented on the LaAlO_3 substrate.

NNO devices deposited by sputtering on LAO or Si: The precleaned NNO films were dry etched into islands by ion milling, followed by sequential deposition of Au and Pd electrodes at two terminals by aligned photo lithography and electron beam evaporation. The distance between Pd and Au electrodes is 10 μm .

NNO devices deposited by ALD on LAO or SiO_2/Si : The pre-cleaned NNO film on substrate was patterned by ion milling, followed by the deposition of large Ti/Au contact pads by photolithography and electron-beam evaporation. Two working electrodes, Au at one terminal and

Pd at the other, were deposited by a two-step aligned electron-beam lithography (for ALD NNO on LAO) or photo lithography (for ALD NNO on SiO₂/Si) and electron-beam evaporation. The channel length between Au and Pd working electrodes of the device on LAO and SiO₂/Si were controlled as ~100 nm and 5 μ m, respectively.

Hydrogen doping: The NNO devices studied in this work were annealed in 50 sccm forming gas flow (5%H₂/95%Ar) at 125 °C for 5 minutes.

Electrical reconfiguration of the H-NNO device is summarized in Fig. 3.8. By applying positive and negative electric pulses, the resistance state of the device could be modulated carefully, and the programmed resistance states are nonvolatile. At the electronic state i, cyclic voltage sweep measurements of the nickelate device were performed, and linear resistor behavior was observed (Fig. 3.8 (a)). The electronic state i was then switched to electronic state ii by applying a single voltage pulse, where a current-voltage (I-V) loop appeared, indicating stored energy in the device (Fig. 3.8 (b)). Next, we showed the creation of artificial neurons and synapses (that are responsible for information transfer and memory in the brain) from the same device. Spiking neuronal behavior in the H-NNO device was studied at the electronic state iii (Fig. 3.8 (c)). Consecutive electric stimuli were applied to the device, and once a critical level was reached, abrupt changes in the device resistance were observed. The nonvolatile neuronal response of the nickelate device to electric stimulus depended on both pulse voltage and pulse width.

We then demonstrated synaptic behavior at electronic state iv in the nickelate device by means of continuous voltage sweeps (Fig. 3.8(d)). At LRS, a smaller threshold pulse field (V_{th}) was sufficient to modulate the device resistance, which was suitable for analog behavior with gradual resistance changes. However, this analog update of device resistance prohibited the sudden jump in resistance necessary for spiking. At HRS, a much higher V_{th} was required to change the resistance and was beneficial for spiking neuronal behavior. Last, the linear resistor state i in Fig. 3.8 (a) could be restored by applying a single electric pulse.

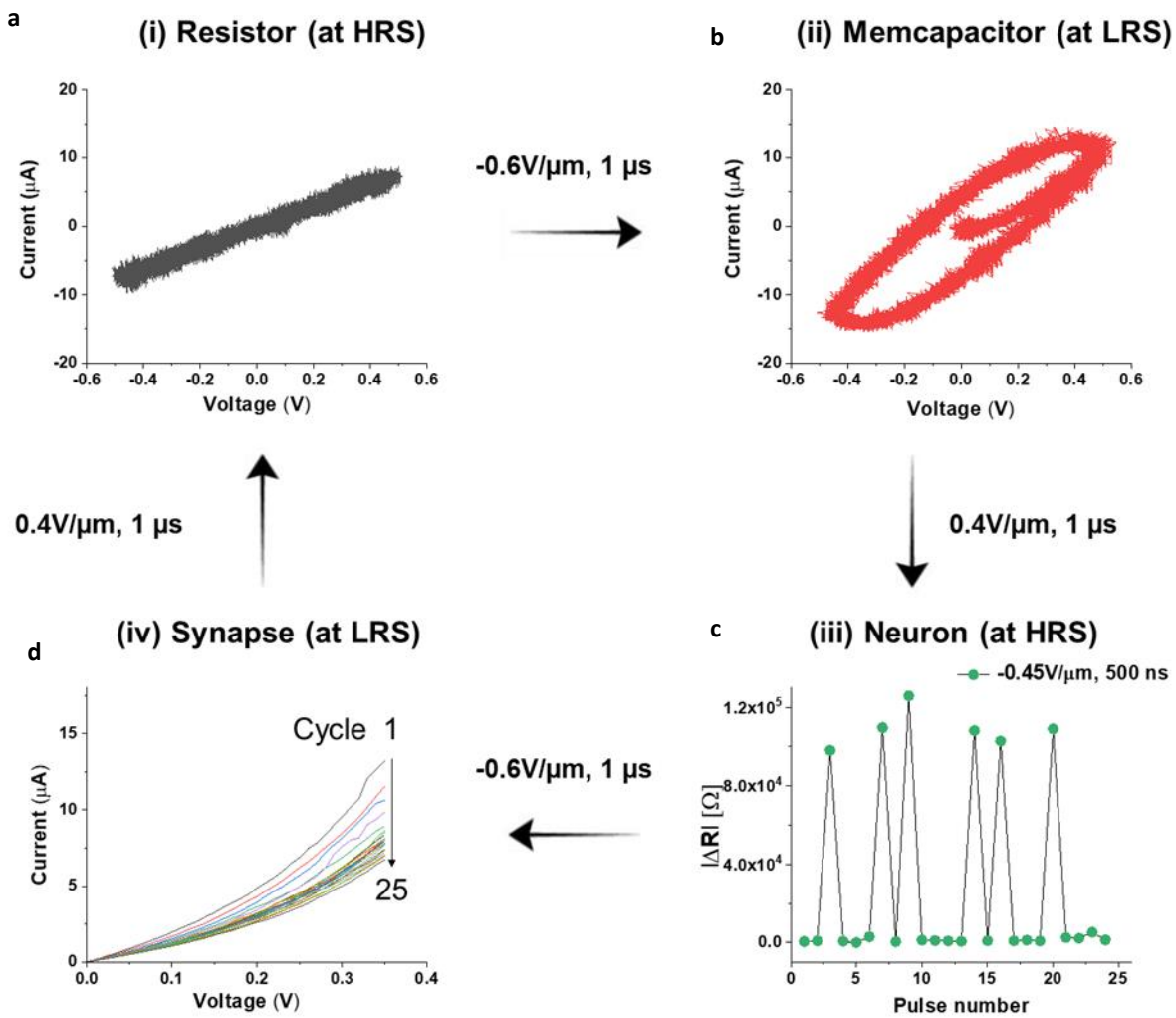


Figure 3.9. A single perovskite device can be electrically reconfigured to perform essential functions in a neuromorphic computer. (a) Nickelate device as a linear resistor under cyclic voltage sweep. (b) Nickelate device as a capacitor under cyclic voltage sweep (ii). The appearance of an I-V loop indicates stored energy in the device. (c) Nickelate device as a spiking neuron (iii). Resistance changes of the nickelate device were monitored in response to consecutive electric pulses ($-0.45 \text{ V}/\mu\text{m}$ for 500 ns). After the spike fires, the resistance of the device was restored to the original state by applying reset voltage pulse ($+0.45 \text{ V}/\mu\text{m}$ for 500 ns). (d) Nickelate device as a synapse(iv). I-V curves of nickelate devices were measured under continuous voltage sweeps. The resistance of the device increases continuously, showing analog synaptic updates. (d) to (a) Resetting the nickelate device back to initial linear resistor state. This set of data was collected by Tae Joon Park.

To understand the nanoscale mechanisms that enable electrical reconfiguration, we performed in-depth characterization on representative H-NNO devices at LRS and HRS that correspond to synapse and neuronal states, respectively. Confocal Raman spectra ranging from

300 to 550 cm^{-1} were first collected from two control samples: a pristine NNO film near the Pd electrode and a heavily doped NNO film near the Pd electrode (Fig. 3.9 (a)). The T_{2g} mode of NNO was present at $\sim 439 \text{ cm}^{-1}$ for pristine NNO, whereas it disappeared for heavily doped NNO, indicating dense proton concentration near the Pd electrode. We performed two-dimensional (2D) Raman mapping (signal to baseline mode, scan range from 320 to 470 cm^{-1}) over a rectangular region (15 by 3 mm^2) at this boundary for the H-NNO device at LRS and at HRS in Fig. 3.9 (b). The relative peak intensity of T_{2g} mode of the H-NNO device at LRS was 0.77, whereas for HRS this dropped to 0.68, indicating higher local proton distribution of H-NNO at HRS near the Pd electrode.

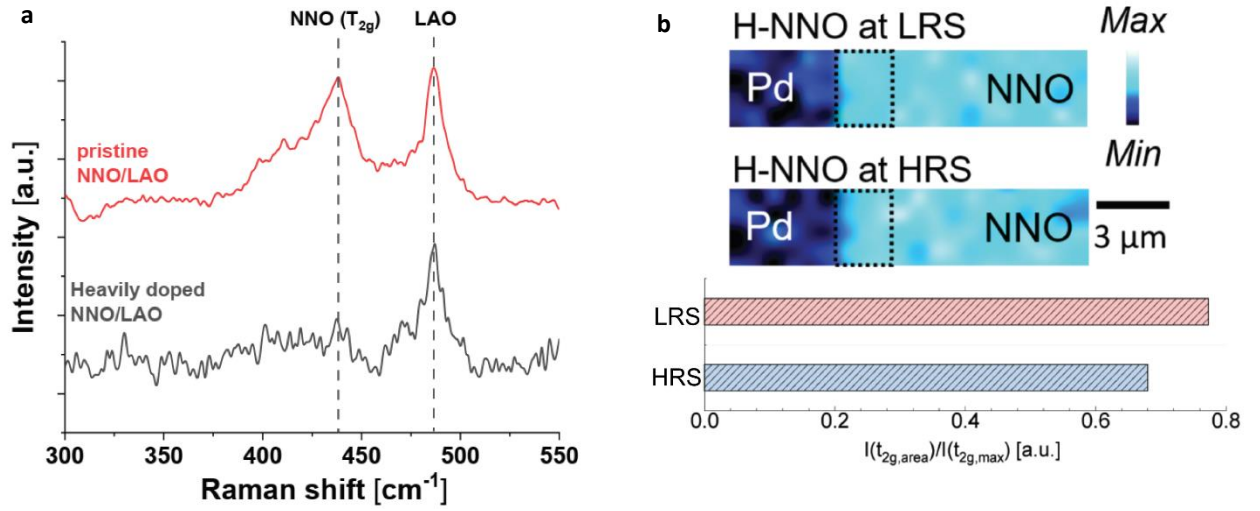


Figure 3.10. Room-temperature confocal Raman scattering analysis of pristine and heavily doped NNO/LAO. (a) Raman spectrum of pristine and heavily doped NNO/LAO. In pristine NNO sample, the strong peak of T_{2g} mode of NNO near the Pd electrode was observed at $\sim 439 \text{ cm}^{-1}$ along with the peak of LAO. The peak of T_{2g} mode of pristine NNO at $\sim 439 \text{ cm}^{-1}$ is consistent with the reported peak position[54]. However, T_{2g} mode of pristine NNO was significantly decreased in heavily doped NNO sample, indicating the hydrogen doping of NNO near the Pd electrode. (b) Spatial mapping of Raman (signal to baseline of Raman shift ranging from 320 to 470 cm^{-1}) of a 15 by 3 mm^2 rectangular area near the Pd electrode for the H-NNO device at both HRS and LRS. Scale bar, 3 μm . The bright areas correspond to NNO regions in the nickelate device, which showed strong peak intensity of T_{2g} mode at $\sim 439 \text{ cm}^{-1}$. The normalized T_{2g} peak intensity $[I(t_{2g,\text{area}})/I(t_{2g,\text{max}})]$ near the Pd electrode were obtained from the dashed rectangular area. The relative peak intensity of the H-NNO device at LRS was 0.77, whereas that of H-NNO at HRS dropped to 0.68.

Further, the carrier localization length scale of H-NNO device at HRS was 1.25nm, smaller than that at LRS which is 2.03nm, as determined from temperature-dependent electrical transport measurements (Fig. 3.10). The nanoscale cauterization of devices showed consistent results that the local proton distribution of H-NNO device at LRS and HRS near the Pd electrode were different. The temperature dependent resistivity for H-NNO at LRS and HRS was well fitted by a Mott-variable range hopping (VRH) model, which are described as:

$$\rho(T) = \rho_0 \exp\left(\frac{T_0}{T}\right)^p \quad (6)$$

where ρ_0 is the pre-factor, T_0 is the characteristic temperature, and p is the exponent dependent defined as $1/(D+1)$, which is $1/4$ for a 3D Mott-VRH model. For 3D system, T_0 is given by:

$$T_0 \equiv T_{Mott} = \left(\frac{18}{k_B N(E_F) \xi^3} \right) \quad (7)$$

where $N(E_F)$ is the density of states around fermi level, which was reported as $1.5 \times 10^{18} \text{ eV}^{-1} \text{ cm}^{-3}$ [77], and we assume it holds the same for H-NNO devices at different resistance states. The localization length ξ of the H-NNO device at LRS and at HRS was 2.03 nm and 1.25 nm, respectively. The results indicate the nickelate device at HRS shows stronger localization behavior than at LRS, consistent with the calculation about activation energy differences of the H-NdNiO₃ device at HRS and at LRS.

To further validate the resistivity-temperature fitting with VRH model, we also performed the calculations of hopping distance R_h as well as the average hopping energy W_h for both HRS and LRS devices. The expressions are given below:

$$R_h = \left(\frac{9\xi}{8\pi k_B T N(E_F)} \right)^{1/4} \quad (8)$$

$$W_h = \frac{3}{4\pi R_h^3 N(E_F)} \dots (4) \quad (9)$$

The calculated hopping distances at room temperature for HRS and LRS are 10.4nm and 11.7nm, respectively. Based on the hopping distances, the hopping energies at room temperature are 0.14eV and 0.099eV for HRS and LRS, respectively. As the criteria that $R_h/\xi > 1$ and $W_h > k_B T (@300K)$ hold true, the VRH model here is valid for the device conducting mechanism near room temperature for both HRS and LRS.

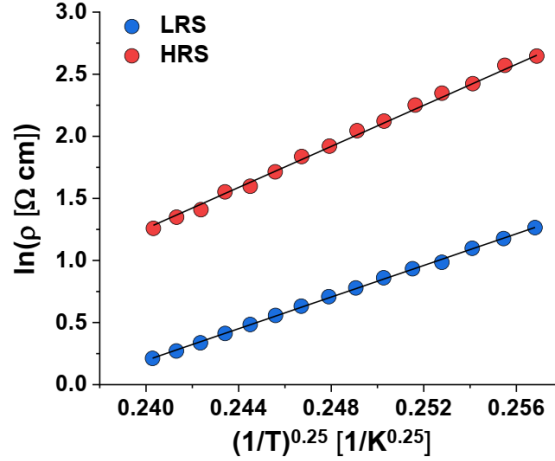


Figure 3.11. Temperature dependent electrical transport properties of the nickelate device at different resistance states. Temperature-dependent resistivity was measured to study electronic transport at different resistance states of the nickelate device. $\ln(\rho)$ vs $T^{-1/4}$ was plotted for H-NNO device at LRS (blue dot) and at HRS (red dot). Linear fittings (black lines) indicate Mott-variable range hopping (VRH). Extracted localization lengths of H-NNO device at LRS and HRS were 2.03 nm, and 1.25 nm, respectively. The transport analysis confirms the differences in carrier localization for LRS and HRS of the nickelate device at the microscopic scale.

3.4 Conclusions

Three generations of perovskite nickelate electronic devices were successfully designed and fabricated on demand. Based on the device performances, we have demonstrated ultrametric tree-like memory states in hydrogen-doped perovskite nickelates controlled by pulsed electric fields at room temperature. Controlled ion migration that can synergistically mediate highly tunable electronic structures in correlated perovskite crystals enable realization of a set of properties previously used in description of spin glasses. The results should motivate new avenues to explore use of complex synaptic behavior found in correlated semiconductors for neuromorphic learning. Then we have demonstrated artificial neurogenesis in perovskite electronic devices: the ability to reconfigure hardware building blocks for brain-inspired computers on demand within a single device platform.

4. PHYSICS OF DEVICE PERFORMANCES: RESISTIVE SWITCHING AND THE CHARGE CARRIER TRANSPORTATION MECHANISMS

4.1 Introduction

Resistive switching is a physical behavior that a material, which should be a dielectric, changes its resistance under a certain condition, usually by the effect of an applied electric field or current. An ideal resistive switching behavior requires the resistance change to be reversible and the resistance states to be stable. It has been observed that there are many materials that can show resistive switching behaviors: (1) Binary transition metal oxides (TMOs). (2) Perovskite-type complex TMOs. (3) Large band gap high-k dielectrics. (4) Graphene oxides.[78] Most resistive switching phenomena is characterized by devices fabricated with the materials mentioned above. A top electrode (TE) / dielectric / bottom electrode (BE) capacitor structure is widely used in device fabrication model. Generally there are two distinctive resistance states, namely high resistance state (HRS) and low resistance state (LRS). Some devices can also be tuned to exhibit multi resistance states by certain programmable electrical stimulations.

4.1.1 Electroforming Process

Since most of the materials that used for resistive switching are very insulating at the pristine state, a pretreatment might be necessary for the repeatable resistive switching. This pretreatment is called electroforming or forming process. Actually most of the resistive switching materials require a forming process. Electroforming process is believed to be a kind of electrical breakdown, which turns the fresh HRS into a LRS. Usually, the as-formed resistance state is the first LRS, or at least comparable to the LRSs subsequently. However, it is found that the resistance state cannot go back as high as that before the electroforming after a RESET operation.

Because of this special electrical breakdown which is reversible to some degree, the current limit, or namely the compliance current, is quite critical during the electroforming. By programming a proper compliance current, one can limit the maximum current flow through the test switching cell, which can protect the testing device from a permanent breakdown and failure.

Forming can be completed by applying either a high current or a high voltage. Such a high electrical stress can result in the ion drifting to form a conducting filament, and/or can stimulate

electrochemical reactions near the electrodes. Usually the way to find a switching voltage (current) is to apply a voltage (current) scan. If a bias voltage scan is utilized, the current will suddenly have a large increase as the voltage reaches the electroforming voltage. Again the compliance current setting is particularly desired in such a voltage scan.

Electroforming process can also be carried out by applying a constant voltage (or current), if known it is safe for electroforming. When a constant voltage is applied, the compliance current is a must for the forming process. From the current-time plot the sudden current increase can be clearly observed, which means the resistance of the cell is degraded and the forming is completed. In despite of the compliance current, it cannot be avoided that the spike current overshoot problems may occur when the current really reaches the compliance current. However, if the forming process is carried out by a current source rather than a voltage source, there is no need to set a compliance current. The resistance switching can be observed from the voltage-time plot. Moreover, the higher the constant current is, the faster the forming process can be finished.[79]

There are also lots of resistive switching systems that are “forming free”, which means the forming process is not so distinguishable with the SET operation. Also some systems are initially with a low resistance state which require a RESET operation to switch the cell into a HRS[80]. These initially ON systems are also forming free.

4.1.2 Unipolar Switching and Bipolar Switching

The resistive switching behaviors can be divided into different categories due to corresponding criteria, such as the required input conditions and the switching mechanisms etc. Considering the operation parameters, the resistive switching can be present as bipolar switching or unipolar switching. For unipolar switching, the only involved parameter is the amplitude of the applied voltages or currents, while bipolar involves the amplitude as well as the polarity. As shown in figure 4.1, we define SET (from HRS to LRS) and RESET (from LRS to HRS) operations in I-V characteristics. Unipolar switching does not require the change of polarity thus the RESET and SET voltage can be in the same quadrant of the I-V plot. Bipolar switching requires that the polarity AND the voltage must meet the proper conditions together so that the switching can happen. The SET voltage and the RESET voltage have to be different in polarity

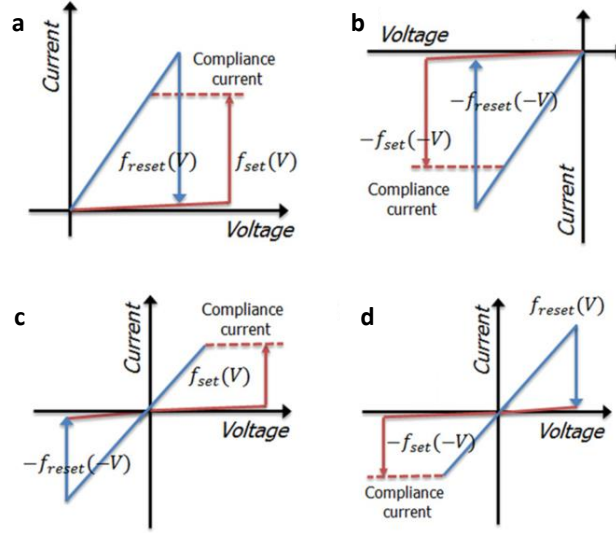


Figure 4.1. A simple illustration of unipolar and bipolar switching in I-V characteristics. In unipolar switching it is possible to observe all the four results, but for bipolar switching only (c) and (d) can happen. Images are from [78].

A wide range of transition metal oxides (TMOs) thin films have been studied during the past decades. Most popular materials are NiO[81], TiO₂[74, 79, 82], SiO_x[83, 84] and ZrO₂[85-87]. All these materials can show a unipolar switching behavior and the switching is due to the conducting filament formation and rupture. Generally the reset voltage is lower than the set voltage. Only SiO_x type is unique because their reset voltage is higher than set voltage.[88]

Bipolar switching requires the set and reset operations to be in the different polarity. If a bipolar switching needs a forming process, like in a Pt/TiO₂/Pt system, the SET and RESET voltage polarity might depend on the forming condition.[79]

People sometimes call the bipolar behavior with a positive set voltage (or current) and a negative reset voltage (or current), as indicated in figure 4.2(d) eight-wise bipolar switching. Correspondingly, the bipolar switching with a negative set voltage (or current) and a positive reset voltage, as indicated in figure 4.2(b), is called counter eight-wise bipolar switching. This is because in voltage-controlled scans, like in figure 4.1(c) and figure 4.1(d), the I-V curves of a bipolar switching run loops with an eight-wise direction or a counter eight-wise direction. Note that in the current-controlled scan, the loop running direction is in an opposite way. Also the bipolar switching may not be symmetrical. We can notice that from figure 4.2(a)(c), the electroforming

was completed faster when a negative current is applied, even the positive and negative forming current are the same in magnitude.

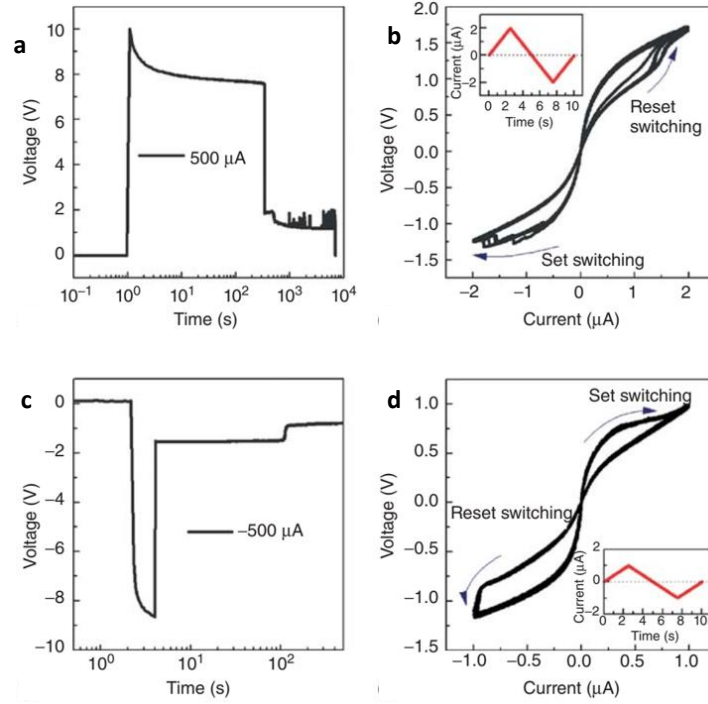
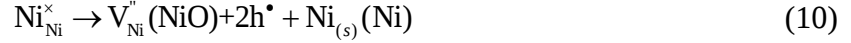


Figure 4.2. Bipolar switching schemes with the forming process. (a) The positive current, which is set as 500μA here, leading to a formed bipolar switching (b). The set and reset processes are under a negative and positive voltage, respectively. (c) Negative 500μA forming current leads to an opposite bipolar switching behavior(d). The set and reset processes are now under a positive and negative voltage, respectively. Data was from [89].

4.1.3 Conduction Filament (CF) Type Resistive Switching

It is believed that the resistance switching mechanism in this type is the formation and rupture of the CF. Almost all switching materials, that the fresh state has a high resistance, performs a unipolar resistive switching related to the conduction filament. These CFs can be formed by complex conducting phases[82], ions or vacancies[85], or pure metal atoms[86, 90]. Apparently in a metal-insulator-metal system, the dielectric insulator layer has to be very thin to let the conduction path get through. However, to make the resistive change reversibly, the insulator layer needs to be sufficiently thick so that the conduction filament may rupture. Usually the thickness of the insulator layer is 40 to 80nm.

NiO might be the most well investigated materials for unipolar switching oxides. Electroforming is required for NiO to switch. The conducting filament formed in NiO is metal phased Ni. The electrochemical reaction happened near the cathode is:[78]



This reaction leads to a phase separation, that is NiO into Ni and NiO, near the cathode. In other words, NiO near the cathode is partially reduced into metallic Ni phase, which will grow from the cathode to anode. When the Ni filament reaches the anode, the electroforming or SET process is completed. Further work done by Park *et al.* reported that NiO_x, where x is 1~1.5, can also show a unipolar switching due to the phase separation. They observed the Ni enriched region in TEM[90].

In D. S. Jeong *et al.*'s work[79], TiO₂ showed a bipolar switching behavior in vacuum with one forming process. The electrochemical reaction near the anode plays an important role:



In vacuum the oxygen gas molecules will be removed quickly so that the reaction can keep ongoing as long as the biased voltage is applied. The oxygen vacancies will diffuse from the anode to the cathode since the reaction creates an oxygen vacancy concentration gradient. In the meantime, the oxygen vacancies with positive charges will drift towards the cathode under the electric field. As a result, the oxygen vacancies will accumulate at the TiO₂/cathode interface, and a conducting oxygen vacancy enriched filament will grow all the way from there. When the conduction filament reaches the anode, the resistance between top electrode (TE) and bottom electrode (BE) will decrease dramatically. Now an electrical forming operation from HRS to LRS in a Pt/TiO₂/Pt metal-insulator-metal cell is completed. Further confirmation about CF in TiO₂ cells was done by D.-H. Kwon *et al.*[90]. The oxygen deficient region in TiO₂ was formed as a non-stoichiometric conducting Ti_nO_{2n-1} (n is typically 4 or 5) *Magneli* ' phase. It was also observed that the CF pillar was wider near TE (here as a cathode) which means the CF was grown from the cathode to the anode.

4.1.4 Interface-Type Resistive Switching

Interface-type resistive switching often happens at the interface of the metal electrode and the dielectric material. Usually the switching material is (semi)conducting in the fresh state. Ideally

the interface-type resistive switching has a clear area scaling which differs from the CF resistive switching.

Depending on the materials, the contact resistance of the electrode and the conducting oxide varies a lot. One reason is the chemical reaction between the electrode and the material, and the other is the formation of a space-charge layer. A space-charge layer is also called a depletion layer in which the majority charge carriers are strongly depleted. A considerable difference in the Fermi levels of the metal and the oxides will lead to a depletion layer. Hence, a Schottky barrier between the metal and the oxide will form which gives a high and non-linear contact resistance.

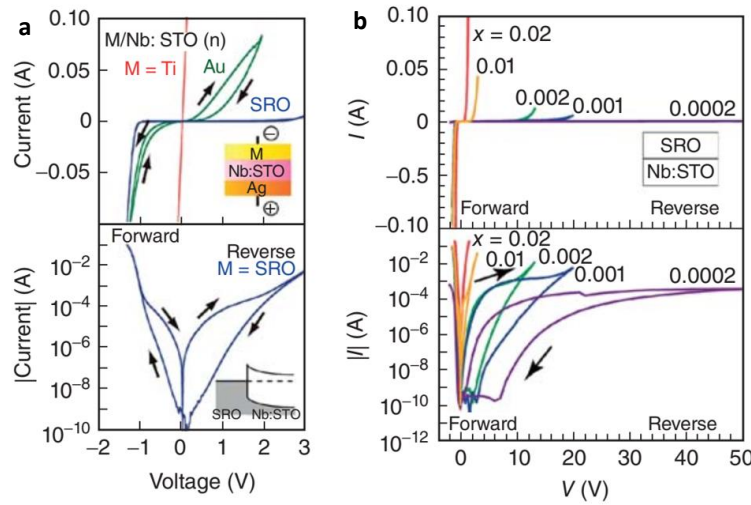


Figure 4.3. (a) I-V curves for the M/Nb:STO/Ag cell. Ti/Nb:STO shows an Ohmic contact, however the rectifying effect and the hysteresis loop appear when the top electrode is Au or SRO. (b) I-V curves of SRO / $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ / Ag cells, at different values of x . Data was reported in [91].

The most popular investigated materials involved in the interface-type switching are $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ (Nb:STO)[92-94] and $\text{Pr}_{1-x}\text{Ca}_x\text{MnO}_3$ (PCMO)[95, 96]. Figure 4.3(a) shows the I-V characteristics for the M / $\text{SrTi}_{1-x}\text{Nb}_x\text{O}_3$ / Ag cells, where the x is 0.01. Top electrode material M is Ti, Au, or SrRuO_3 (SRO), and the work function is $\sim 4.3\text{eV}$, $\sim 5.1\text{eV}$ and $\sim 5.3\text{eV}$, respectively[97]. We can clearly see that besides the rectification due to the Schottky diode, there is also a hysteresis loop in the I-V curve. Furthermore, the rectification as well as the hysteresis effects are both enhanced with the decreasing x value. When STO is heavily doped by Nb, the

contact of SRO and Nb:STO become Ohmic. This is because heavily doped semiconductors have a very thin depletion layer which the charge carrier can easily tunnel through.

The hysteresis indicates a resistive switching in the cell. It has been reported that the resistive switching mechanism in Nb:STO with a deep work function metal electrode is due to the oxygen vacancy layer under the electrode[98, 99]. S. Lee *et al.* did the simulation to see how the oxygen vacancy distribution changes the Schottky barrier structure and hence result in the resistive switching.[98] In their model, the Schottky barrier widens as the oxygen vacancies accumulate toward the interface, which corresponds to a HRS. This model also explains the eight-wise bipolar switching of the Pt/Nb:STO junction.

4.2 Electronic Transport Mechanisms in Hydrogenated Perovskite Nickelate Memristors

The device under investigation in this section was fabricated on SmNiO_3 (SNO) thin films by e-beam lithography and photo lithography. The fabrication process flow could be located in Section 3.2.3. The optical and SEM images of a single SNO device in shown in figure 4.4. The gap between Pd and Au terminals are $1\mu\text{m}$ in length. The working electrode on the left are Pd and on the right they are Au.

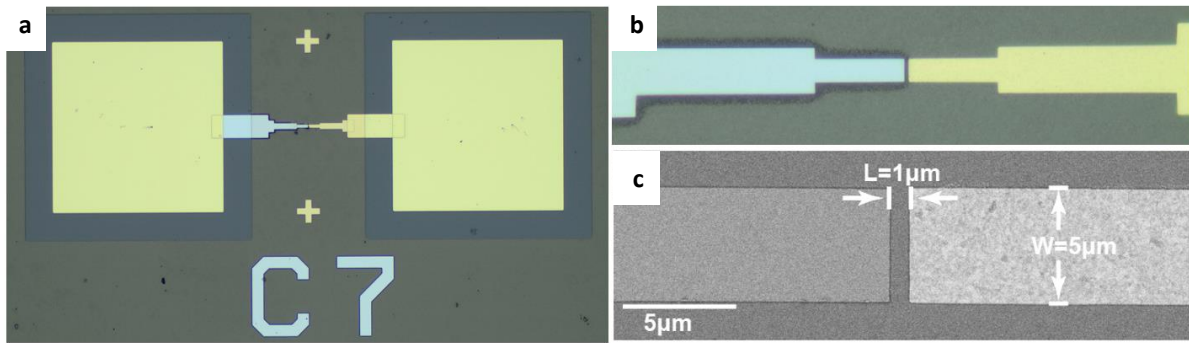


Figure 4.4. Images of electronic devices fabricated with SNO. (a) and (b) are optical images and (c) is the SEM image. In figure (b) the doped HSNO (the dark contour around Pd) is visible.

4.2.1 Resistive Switching of The Nickelate Device

The devices were measured with our probe station connected to a Keithley measurement module. All the positives and negatives in my data are referred to the Au electrode. Figure 4.5 (a)

shows the IV characteristic before and after electron doping with the sweeping range of -1V to +1V. Before doping, the linear IV, indicates both Pd/SNO and Au/SNO contacts are ohmic. The inset shows pristinely the device resistance was about 160 Ohms while after doping the resistance increased to 10^5 ohms, due to the dramatic band gap opening. The non-linear IV characteristic with hysteresis loops in figure 4.5 (b) indicates the electron doped device, could perform a stable resistive switching by continuously sweeping the voltage between -5 to +5V following a forming process (positive voltage sweep up to +6V). The inset shows the dynamic resistance during the voltage sweeping, averaged through 100 cycles. At 0V bias, it was obvious two resistance states were generated.

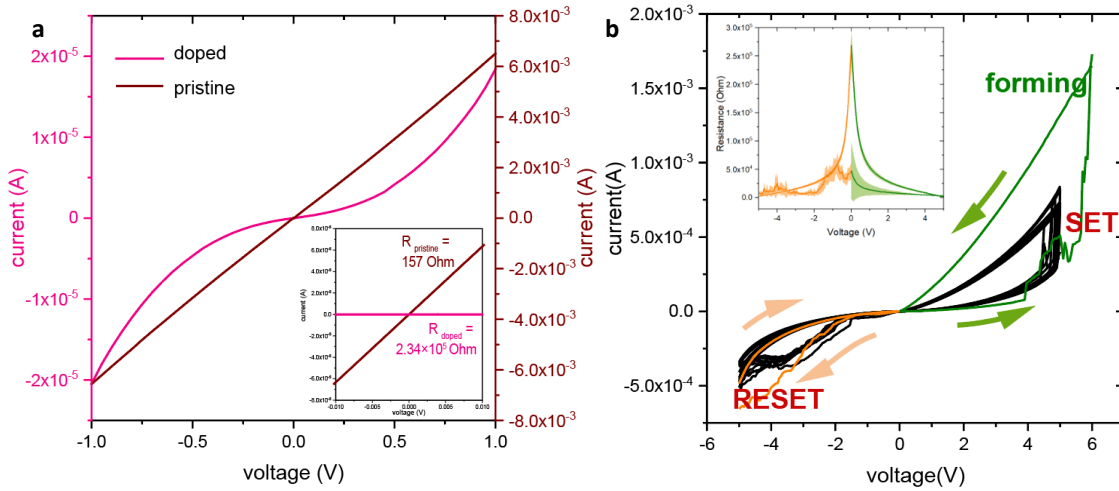


Figure 4.5. IV characteristics of pristine (undoped) and doped device. (a) Before doping, the linear IV indicated both Pd/SNO and Au/SNO contact were ohmic. After doping the IV curve became non-linear, which implied a non-Ohmic contact of metal/semiconductor due to electron doping of SNO. Inset: Resistances read at 0V bias, which increase from ~ 160 Ohms to 2.34×10^5 Ohms. (b) Continuous IV sweep between +5V and -5V after measurements in (a). The device was initially at high resistance and could repeatedly switch between high and low resistance states for over 100 cycles. Inset: dynamic resistance (dV/dI , averaged through 100 cycles, error bars indicated by the line widening) during the voltage sweeping. At 0V bias, it was obvious two resistance states were generated. HRS/LRS is about 5~6. Positive and negative biases were referred to the Au electrode.

4.2.2 Model Fitting of Non-linear I-V Conduction

To better understand the nonlinear IV characteristic which might provide a hint for the switching mechanisms, model fitting was conducted. There are several common models for such kind of non-linear I-V behaviors, such as thermionic emission, Frenkel-Poole emission, tunneling

and space-charge-limited current (SCLC) conduction.[100] Figure 4.6(a) is the positive sweep data fitting before SET, showing $\ln(\text{current})$ was linearly proportional to $\text{Voltage}^{1/4}$, which appeared to be thermionic emission over a Schottky barrier with the image force lowering effect. Such a model could be described as below:[100]

$$J_R \approx A^{**}T^2 \exp \left[-\frac{q(\phi_{B0} - \sqrt{qE_m / 4\pi\epsilon_s})}{k_B T} \right] \quad (12)$$

$$E_m = \sqrt{\frac{2qN_D}{\epsilon_s} \left(V_R + V_{bi} - \frac{k_B T}{q} \right)} \xrightarrow{V_R > 3k_B T / q} \sqrt{\frac{2qN_D}{\epsilon_s} V_R} \quad (13)$$

$$\ln(I_R) = \ln(AA^{**}T^2) - \frac{q\phi_{B0}}{k_B T} + \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s} \left(\frac{2qN_D}{\epsilon_s} \right)^{1/4} V_R^{1/4}} \quad (14)$$

Where J_R is the reverse current density; A is the contact area of the metal-semiconductor; A^{**} is the effective Richardson constant in a semiconductor material; E_m is the maximum electric field, usually at the metal-semiconductor contact interface; ϵ_s is the semiconductor permittivity; k_B is the Boltzmann's constant; N_D is the donor concentration; V_R : reverse bias.

The term $\sqrt{qE_m / 4\pi\epsilon_s}$ in equation 12 is the decreased barrier height $\Delta\phi$ by image force whenever there is electron flowing through the Schottky barrier. The equation 14 derived from equation 12 and 13 describes such a model in terms of I_R and V_R . Upper inset in figure 4.6 (a) shows the R^2 of this fitting for 100 cycles, all above 0.999, which confirmed the reliability of this fitting model. The lower inset in figure 4.6 (a) plots the intercepts and slopes of the fitted lines over 100 cycles. Both were very stable and consistent.

Figure 4.6 (b) shows the positive sweep data fitting after SET. The slopes of the fitted lines of $\ln(\text{current})$ versus $\ln(\text{voltage})$ indicated the conduction mechanism was a combination of Ohmic conduction and space charge limited current conduction. This combined conduction can be described by equation 15:[101, 102]

$$J = N_c \exp \left(-\frac{E_{ac}}{k_B T} \right) \frac{q\mu}{d} V + \frac{9\mu\epsilon_s}{8d^3} \frac{N_c}{g_n N_t} \exp \left(\frac{E_t - E_c}{k_B T} \right) V^2 \quad (15)$$

$$V_{tr} = \frac{8qd^2 g_n N_t}{9\epsilon_s} \exp \left(-\frac{E_t - E_c + E_{ac}}{k_B T} \right) \quad (16)$$

Where N_c is the density of states in semiconductor conduction band; E_{ac} is the activation energy for charge carriers; μ is charge carrier mobility; d is the distance between electrodes; g_n is

the degeneracy of energy states; N_t is the (shallow) trap density; V_{tr} is the threshold voltage above which the dominant conducting mechanism transfers from Ohmic to SCLC conduction.

The first term in equation 15 is Ohmic conduction, which results a slope regarding $\ln(I) \sim \ln(V)$ of 1, the second term is space-charge-limited-current (SCLC) conduction, which results a slope of 2. When these two terms are equal, this threshold voltage in equation 16 could be derived, above which the dominant conduction mechanism transfers from ohmic to SCLC, and the slope increases from 1 to 2. Figure 4.6 (c) is the negative voltage sweep data fitting after RESET. Similar to 4.6 (b), the conduction appeared to be a transition from SCLC conduction to Ohmic conduction as the voltage sweeps from -5V to 0V.

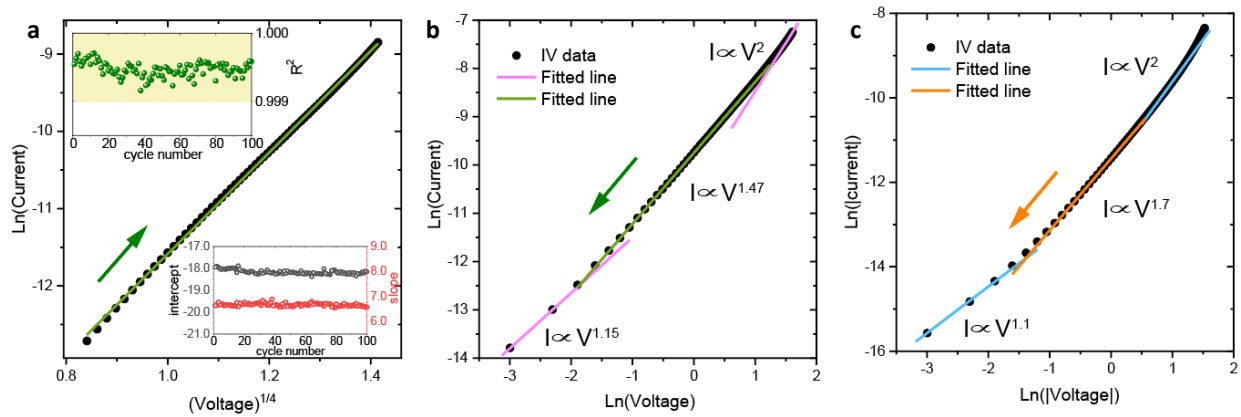


Figure 4.6. Linear fitting of the collected IV data at difference biases and different resistance states. (a) Positive voltage sweep data fitting before SET (fitting range: +0.5V to +4V), showing $\ln(\text{current})$ was linearly proportional to $\text{Voltage}^{1/4}$, which appeared to be thermionic emission over a Schottky barrier with the image force lowering effect. Upper inset: R^2 of this fitting model of IV data before SET through 100 cycles, all above 0.999, which confirmed the universality and reliability of this fitting model. Lower inset: intercepts and slopes of the fitted lines over 100 cycles. Both were very stable and consistent. The averaged slope was 6.67 and the averaged intercept was -18.14. (b) Positive voltage sweep data fitting after SET (+5V to 0V). The slopes of the fitted lines indicated the conduction mechanism was a combination of Ohmic (current proportional to V) and space charge limited current (current proportional to V^2) conduction. (c) Negative voltage sweep data fitting after RESET. Similar to (b), the conduction appeared to be a transition from space charge limited current conduction to Ohmic conduction as the voltage sweeps from -5V to 0V. However the data close to -5V showed a fitting slope higher than 2, which could possibly be the contribution of charge carrier traps.[102-104]

4.2.3 Band Diagrams Analysis

The data fitting suggests that there is a Schottky barrier formed at the Pd-HSNO contact. The band structure of SNO is shown in figure 4.7. Pristine SNO is a conducting semiconductor with a small band gap, usually less than 0.5eV at room temperature.[8] After doping the insulating HSNO has a widened band gap which is about 1eV.[105] The detailed phase transition process by electron doping of SNO can be located in section 1.2.

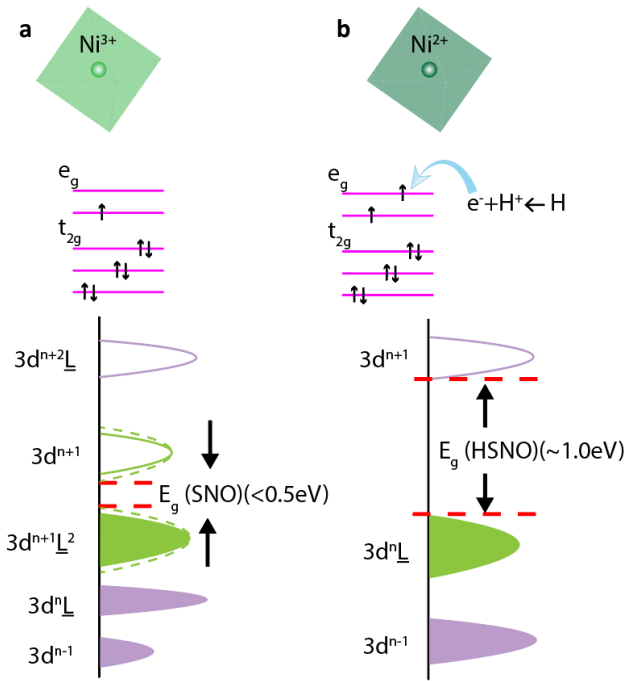


Figure 4.7. Electron-doping-driven electronic phase transition in SNO. (a) Band structure of Ni^{3+} (pristine SNO) state. The small band gap ($<0.5\text{eV}$) indicates a conducting phase. (b) Band structure of Ni^{2+} (doped HSNO) state. Due to the charge transfer and the orbitals occupation, the material is now at an insulating phase.

As a result of the phase transition with band structure evolution, the contact circumstances for Pd-HSNO and SNO-Au are quite different. Figure 4.8 shows the band diagram at the two terminals before contact. The work functions of Pd and Au are 5.12 eV and 5.10 eV, respectively, which are very close, as labeled in the diagram.[100] At room temperature, the charge carrier transportation in epitaxial SNO thin film is “hole-like” with the activation energy $\sim 0.17\text{eV}$ by the testing of Hall effect, such that the SNO is simplified here as a p-type semiconductor in vicinity of the Au electrode.[106] The work function of SNO at room temperature was reported as

$\sim 4.93\text{eV}$ by Yan *et al.*, as labeled in figure 4.8 (b) as ϕ_s . [107] We assumed that HSNO is a wide gap n-type semiconductor, with a band gap of $\sim 1.0\text{eV}$ when the SNO is fully doped (H:Ni=1:1 in atomic ratio). When the metal-semiconductor came into contact, as illustrated in figure 4.9, a Schottky barrier formed at Pd-HSNO junction while SNO-Au contact is Ohmic. The ϕ_{B0} refers to the ideal barrier height without any image force lowering effect, and the $\Delta\phi$ (exaggerated here in the plot) illustrates the lowered barrier height by the image force effect. In figure 4.9 (b), after contact there was no barrier for the charge carriers, which are holes in this case, at the SNO/Au junction, indicating that SNO/Au contact is Ohmic.

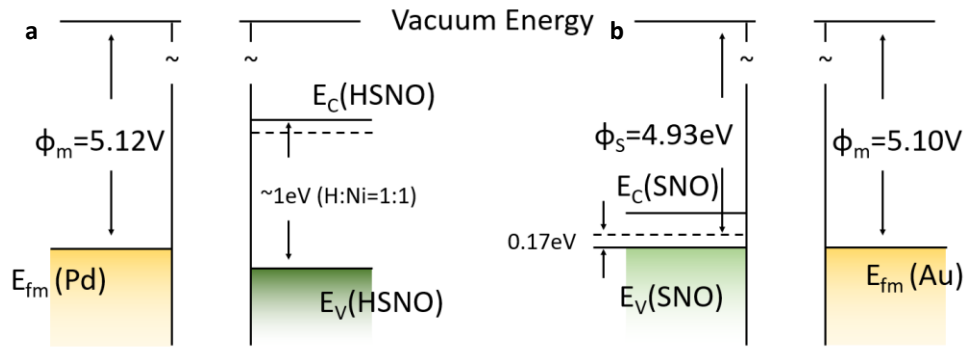


Figure 4.8. Band diagrams at Pd/HSNO junction (a) and SNO/Au junction (b) before contact.

HSNO was assumed as an n-type semiconductor with a band gap of $\sim 1.0\text{eV}$. At room temperature, the carrier transportation of pristine SNO was simplified as a p-type semiconductor with a band gap less than 0.5eV and an activation energy (for holes) about 0.17eV .

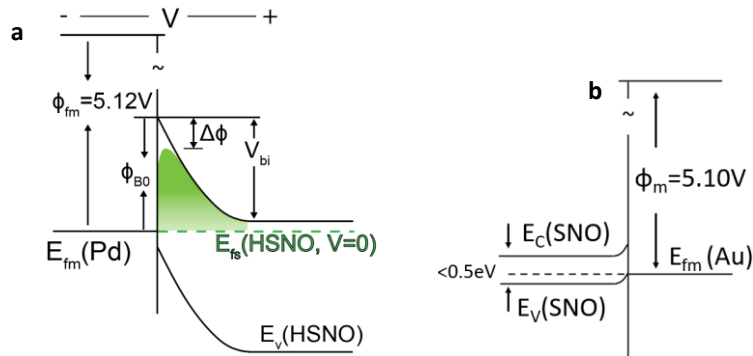


Figure 4.9. Band diagrams at Pd/HSNO junction (a) and SNO/Au junction (b) in contact.

(a) Pd/HSNO contact formed a Schottky barrier with an ideal barrier height ϕ_{B0} and a barrier decrease $\Delta\phi$ by image force lowering effect. (b) There is no barrier for charge carrier (holes) at the interface of SNO/Au, confirming the Ohmic contact.

4.2.4 Barrier Height Verification

To quantitatively analysis the Schottky barrier height at the heterojunction, we did two more sets of measurements to figure out the constants in the previous equations. Figure 4.10 (a) is the relationship between the intercepts of thermionic emission fitting versus 0 bias resistance states. This measurement was taken at room temperature and the 0 bias resistance states can be controlled by gradually removing the doped hydrogen from the device. Figure 4.10 (b) indicates the dependence of the device resistance on temperature. From the linear fitting results of a and b, the Richardson's constant A^{**} was calculated to $2.06 \times 10^{-4} \text{ Amp cm}^{-2} \text{K}^{-2}$. By plugging in the averaged intercept in figure 4.6 (a), which is -18.17, the ideal barrier height without any image force would be 0.25eV, which means around 0 voltage bias, the barrier height is almost 10 times $k_B T$ at room temperature. By further looking into the image force lowering, which involves the average slope as 6.67 in figure 4.6 (a), we find that the decreased barrier $\Delta\phi$ at +4V and +5V are 0.24eV and 0.26eV, respectively, suggesting the initial Schottky barrier height was depleted to 0 between +4V and +5V, which exactly matches the current jump in figure 4.5(b). During the above calculation, the contact area A is taken from the device design layout which is $1000 \mu\text{m}^2$. The detailed math could be located in Appendix A.

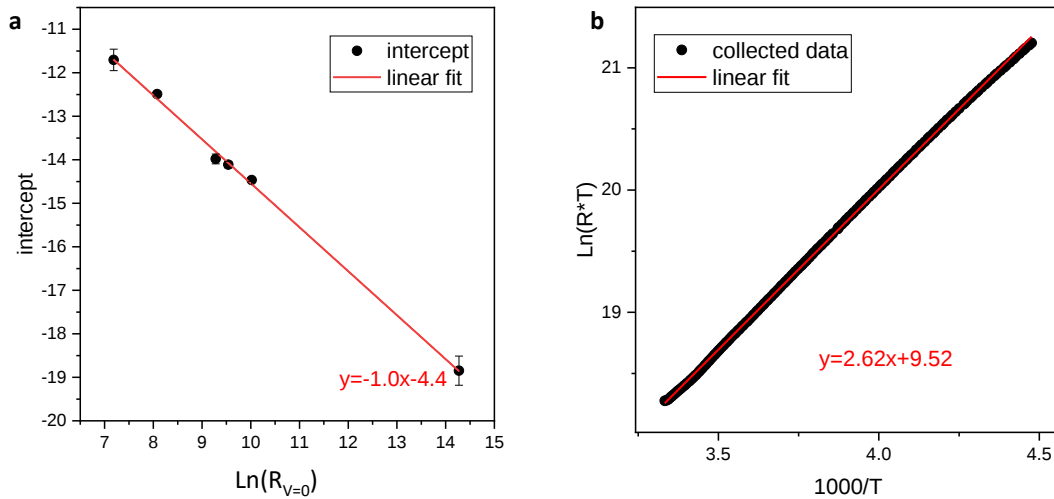


Figure 4.10. (a) The relationship between fitted intercept vs. zero-bias resistance of the device. The zero-bias resistances were measured from -0.01V to +0.01V. (b) Zero-bias resistance dependence on temperature.

4.2.5 Charger Carrier Transportation Mechanisms

The zoomed in view of such a device with a simplified device connection is shown in figure 4.11. The device is actually a connection of Pd/HSNO Schottky junction, with a huge area of the interfacial proton puddles all underneath the Pd electrode, then to insulating HSNO film, transited to conducting SNO film in gradient, then finally through the ohmic contact to Au electrode. In such a series connection, the part with the highest resistance limits the current. The complete electron transportation through the memristor device would be:

1. When the Schottky barrier at Pd-HSNO heterojunction is at the reverse bias and barrier height is not lowered to 0, thermionic emission dominates. This explains the positive conduction before SET.
2. When the Schottky barrier is decreased to 0 or at the forward bias, the conduction of HSNO-SNO gradient phase dominates, which is Ohmic+SCLC. This explains the conduction at positive bias after SET, and negative conduction after RESET.
3. We propose that the dramatic current increase after complete barrier depletion as well as the recover in negative bias is due to the spatial redistribution of interfacial proton puddles at Pd-HSNO junction. Pd works as a reservoir gates for protons and the distribution of proton puddles locally at the interface contributed to the significant resistive switching.

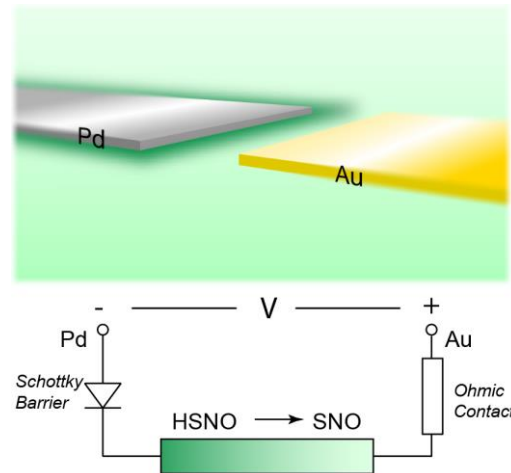


Figure 4.11. Zoomed in view of the gap between Pd and Au terminals as well as the simplified connection through the device.

4.3 Conclusion

In summary, we fabricated a non-volatile resistive memory device on SNO thin film with a 1 μ m gap between two working electrodes. The device physics was systematically studied by model fitting and band diagram analysis. There are three main conducting mechanisms involved: thermionic emission with image force lowering effect, Ohmic conduction and space charge limit current conduction. We proposed the charge carrier transportation mechanisms through the device and claimed the existence of interfacial proton puddles at Pd-HSNO contact. The electrical performance is closely related to the spatial dispersion of the interfacial proton puddles.

5. ELECTRON DOPING INDUCED METAL-INSULATOR TRANSITION IN LaNiO_3 AND MEMORY DEVICES

5.1 Introduction

Thermally driven metal-insulation transition (MIT) in perovskite rare-earth nickelate thin films has attracted wide research attention due to the tunable physical properties and unique electrical functions. The insulating state of nickelates is reported to be due to the lattice distortion caused Ni-O-Ni bending which reduces the orbital overlap.[1] Electron doping, as a temperature-independent method to induce MIT in nickelates such as SmNiO_3 (SNO) and NdNiO_3 (NNO), has been shown to modulate the resistivity over several orders of magnitude.[8, 48, 74, 75, 108] The electron doping of SNO and NNO has been studied in various electronic device applications by controlling both the doping concentration as well as the proton distribution.[18, 49, 109]

Epitaxial nickelate thin films are usually deposited on LaAlO_3 (LAO) substrates by physical vapor deposition (PVD). Some recent works on chemical solution deposition (CSD) of epitaxial nickelate thin films were reported, with comparable crystallinity and sharp MIT features.[10, 12-16] CSD as a non-vacuum deposition method, is suited to control the ratio of rare-earth elements and Ni by adjusting the weight of the solid precursors.[12, 18, 25, 51, 110] LaNiO_3 (LNO) is the only member of rare-earth nickelates which is metallic at all temperatures as it retains the rhombohedral lattice structure which maintains efficient Ni-O-Ni orbital overlap for metallic conductance even at low temperatures.[1, 111] A lot of effort has been devoted to obtaining thermally-driven MIT in LNO, such as ultra-thin films with the thickness of few unit cells, construction of superlattices, interface, orientation, or oxygen deficiency effects.[111-127] Here we demonstrate that LNO can be electron-doped into an insulator with dramatic conductivity suppression regardless of the temperature. The LNO thin films were deposited by CSD method and were systematically characterized to confirm the film quality. A series of electronic devices were fabricated with LNO channels doped with hydrogen and their resistance switching properties have been measured.

5.2 LNO Thin Film Deposition and Characterizations

5.2.1 LNO Thin film Deposition

LNO thin films were deposited by chemical solution deposition (CSD) method. To prepare the chemical solutions, lanthanum nitrate hexahydrate ($\text{La}(\text{NO}_3)_3 \cdot 6\text{H}_2\text{O}$, Sigma-Aldrich, purity 99.9%) and nickel(II) acetate tetrahydrate ($\text{Ni}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, Sigma-Aldrich, purity 99.998%), as two solid precursors, were properly weighted with atomic ratio of La:Ni=1:1, and then dissolved in the solvent mixture of 2-methoxyethanol and acetic acid (volume ratio = 9:1). The solvent mixture was preheated at 80°C. After the solid precursors were added, the solution was stirred at 80°C for 1h and then filtered. The concentration of the solution was controlled to 0.1 M and 0.2M by adjusting the solvent volumes. After the solutions were cooled down to room temperature, 20 μL chemical solutions were dropped and spin coated on LaAlO_3 (LAO) substrates with a 3000rpm spin speed for 30s. The as-coated wet films were baked at 175°C for 20min to dry out. The baked films were subsequently annealed in air at 300°C, 30min for pyrolysis followed by 600°C, 12h for crystallization.

5.2.2 X-ray Characterizations

X-ray diffraction results were collected by Panalytical Empyrean X-ray diffractometer equipped with both parallel beam and focusing optics and a high speed PIXcel 3D Medipix detector. The X-ray wavelength were $\text{Cu K}\alpha=1.5406\text{\AA}$. LNO thin films deposited from solution with concentrations of 0.1M and 0.2M, referred to as 0.1M-LNO and 0.2M-LNO respectively, were grown on LAO substrates. The XRD patterns of LNO/LAO are shown in figure 5.1, in which there are no peaks other than those from (001) orientation. All peaks in the plots are labeled in pseudo-cubic notation. Peaks from (001) oriented LNO thin films are clearly seen at all three diffraction orders. For the (002) diffraction peaks, as shown in the inset, the peak positions for LAO substrate, 0.1M-LNO and 0.2M-LNO are located at $2\theta=47.942^\circ$, 47.056° and 47.108° . [128, 129] Compared with bulk LNO with (002) diffraction angle at $2\theta=47.377^\circ$, our deposited LNO thin films are apparently strained on the LAO substrate. [129] However, thin film 0.2M-LNO is relatively less strained than 0.1M-LNO possibly due to the relaxation as film becomes thicker, especially for films prepared by CSD method. [16, 18] The small peaks at $2\theta=21.150^\circ$, 43.071°

and 66.836° are due to Cu K β which are not completely filtered out from the X-ray source, diffracted from LAO (001), (002) and (003), respectively.

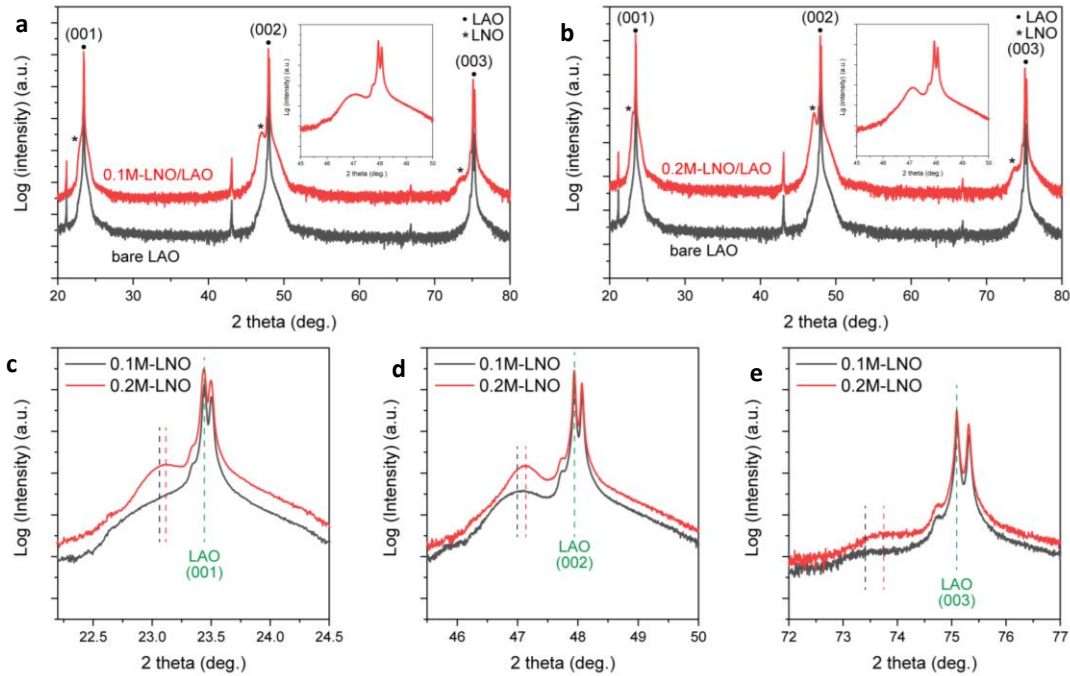


Figure 5.1. Epitaxial LNO thin films prepared by chemical solution deposition with concentrations of 0.1M and 0.2M on LAO substrates. (a) XRD pattern of 0.1M-LNO/LAO thin film. The peaks from LAO substrates are labeled by • and those from LNO thin film are labeled by * in pseudo-cubic notation. Inset: XRD pattern from 45° to 50° . The (002) peak position for LAO is located at 47.942° and the (002) peak from 0.1M-LNO thin film is located at 47.056° . (b) XRD pattern of 0.2M-LNO/LAO thin film. The peaks from LAO substrates are labeled by • and those from LNO thin film are labeled by * in pseudo-cubic notation. Inset: XRD pattern from 45° to 50° . The (002) peak position for LAO is located at 47.942° and the (002) peak from 0.2M-LNO thin film is located at 47.108° . The zoomed in XRD patterns from 0.1M-LNO and 0.2M-LNO are compared in (c)(d)(e). The thicker film showed a higher peak intensity while the diffraction peaks shifted to the higher angles. As the film thickness increased, the strain was relaxed.

Synchrotron X-ray reflectivity (XRR), and X-ray reciprocal space mapping (RSM) measurements of the LNO samples were performed on a five-circle Huber diffractometer with chi-circle geometry (where the sample horizontally placed can be rotated around the center of the diffractometer) using an X-ray energy of 20 keV (wavelength $\lambda = 0.6197 \text{ \AA}$) at the beamline 12-ID-D in the Advanced Photon Source (APS) at Argonne National Laboratory. A Si (111) monochromator with resolution $\delta E/E = 1.2 \times 10^{-4}$ was used. The X-ray beam had a total flux of

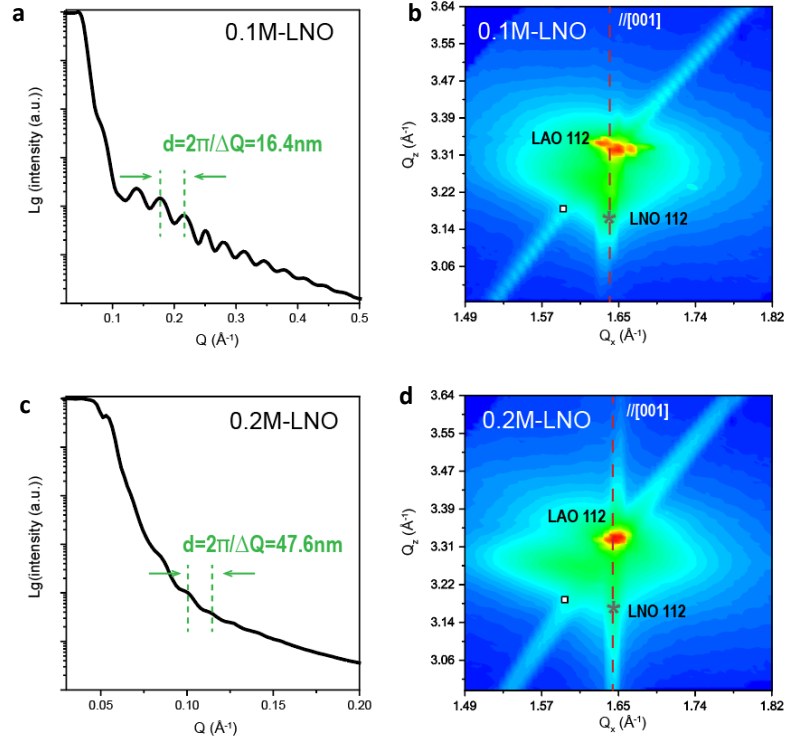


Figure 5.2. X-ray characterization of LNO thin films prepared by chemical solution deposition with concentrations of 0.1M and 0.2M on LAO substrates respectively. Figures (a) and (c) are XRR results of 0.1M-LNO/LAO (a) and 0.2M-LNO/LAO (c). The periodic oscillation indicates a film thickness as 16.4nm and 47.6nm for 0.1M LNO and 0.2M LNO, respectively. The oscillation from the thicker LNO film is less obvious, likely due to the rougher surface. Figures (b) and (d) are RSMs of 0.1M-LNO/LAO (b) and 0.2M-LNO/LAO (d) thin films scanned around (112) Bragg peak of LAO substrate. The position of the bulk LNO is labeled out by the small $\square$ in the map. The epitaxial LNO textured in (001) plane is indicated by the *. In figure (d) there is another elongation of the heat spot other than (001) orientation which suggests the relaxation of LNO as film thickness increased, which is consistent with the XRD results. The XRR and RSM data was scanned by Dr. Hua Zhou at Argonne National Lab.

$2 \times 10^{12} \text{ photons s}^{-1}$ and the beam was vertically focused by a set of beryllium-compound refractive lenses to a profile below $70 \mu\text{m}$ at 20 KeV. X-ray reflectometry (XRR) were used to analyze the film thicknesses, as indicated in figure 5.2 (a), (c). From the periodic oscillation of the XRR curves, the thickness for 0.1M-LNO and for 0.2M-LNO was estimated to be $\sim 16 \text{ nm}$ and 48 nm . The XRR oscillation feature for 0.2M-LNO was not as obvious as that from the 0.1M-LNO, which implies a rougher film surface as film grows thicker. In the reciprocal space mapping (figures 5.2 (b), (d)), both 0.1M-LNO and 0.2M-LNO are strained along the (001) surface. The positions for textured LNO/LAO (112) Bragg peaks are labeled by “*” and are off from that of bulk LNO (112) Bragg

peak in the reciprocal plane ($Q_y=1$) which is labeled by “□” in both maps. However, there is another elongation of the spot in the RSM of 0.2M-LNO, suggesting the relaxation of the thicker film.

Increasing film thickness with CSD method has a strong impact on the surface topography. Figure 3 shows the AFM and SEM images of 0.1M-LNO/LAO and 0.2M-LNO/LAO thin films. The AFM (figures 5.3 (a) (c)) scans indicate the thinner film is much more uniform and smoother than the thicker film. The insets in both maps are the height profiles along the $y = 3.5\mu\text{m}$ line (dashed lines in the maps), providing an intuitive sense of the roughness difference in the two films. The calculated roughness values from the $5 \times 5\mu\text{m}^2$ mappings are 1.174nm and 5.146nm for 0.1M-LNO and 0.2M-LNO thin films respectively. From the surface topography and grain morphology, it appears that as the LNO film grows thicker, the driving force for film epitaxy gradually weakens and the film becomes relaxed. The relaxed 0.2M-LNO is highly textured as there was no XRD peaks from other orientations. The grains on the 0.2M-LNO surface are still preferentially oriented but they were not able to form a dense film during annealing due to the nature of the chemical solution deposition method. The Atomic Force Microscopy (AFM) scans to map the thin film roughness was taken by Asylum Research, MFP-3DTM atomic force microscope under AC mode imaging. The Scanning Electron Microscopy (SEM) images were taken by a Thermo Scientific Apreo SEM.

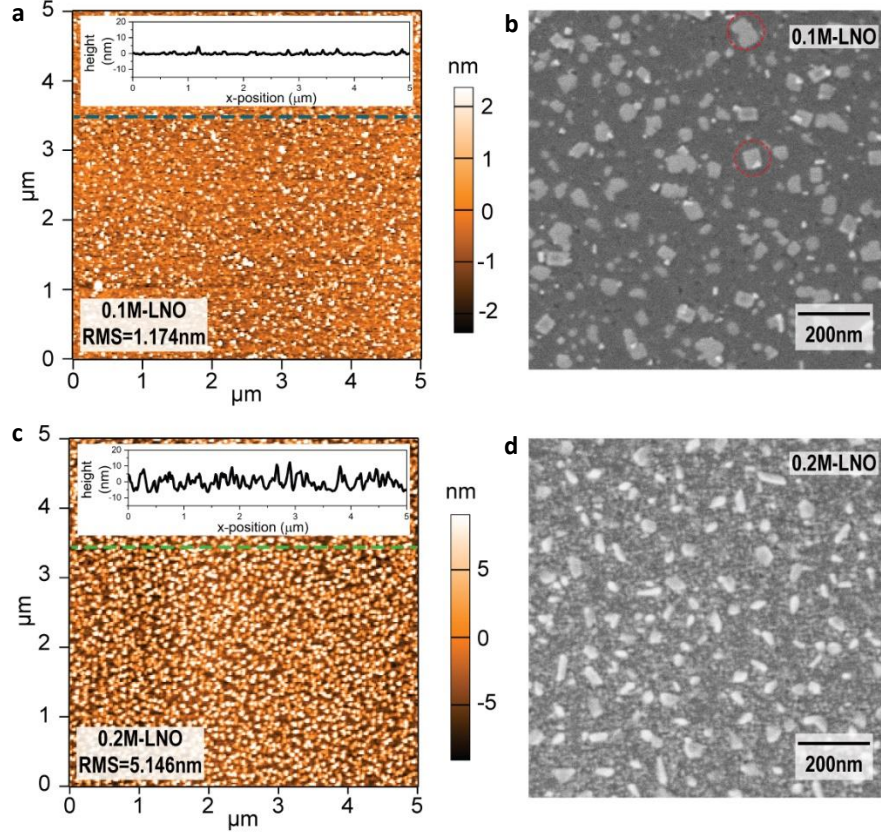


Figure 5.3. Surface topography of LNO/LAO thin films with different thicknesses. AFM height maps of (a) showed a roughness of 1.17nm of 0.1M-LNO/LAO thin film, and (c) indicates that the roughness of 0.2M-LNO/LAO is 5.14nm. The insets are height profiles at the horizontal cross section from $(x, y) = (0, 3.5\mu\text{m})$ to $(x, y) = (5\mu\text{m}, 3.5\mu\text{m})$ indicated by the dashed lines in each map, which clearly shows the surface of 0.2M-LNO is much rougher than 0.1M-LNO. (b) and (d) are the SEM images of 0.1M-LNO/LAO (b) and 0.2M-LNO/LAO (d). 0.1M-LNO (b) has a uniform matrix with some embedded large crystalline grains, mostly maintain a rhombohedral/orthorhombic crystal shape as indicated by the red circles. However, 0.2M-LNO (d) has a more disordered surface, with finer grains distributed between the larger grains and no well-defined geometric features.

5.2.3 Metal-Insulator Transition in LNO Thin Film

The electron doping induced metal-insulator transition of LNO thin films were carried out by annealing the thin films pre-patterned with Pt electrodes in 5% H_2 /95%Ar with a gas flow rate of 50sccm. The annealing was conducted in a closed chamber equipped with probes connected to Keithley model 2635A, and a hot plate with precise temperature control. During the measurements, the samples were placed on the hot plate at a certain temperature and the probes were in contacted with the adjacent Pt electrodes to read the resistances across them. Shi *et. al.* reported the electron

doping of SmNiO_3 by annealing the thin film, with Pt electrodes on top, in H_2 rich forming gas at elevated temperatures.[8] Here we have performed similar doping process at various temperatures: 25, 45, 65, 85, 105 and 125°C on six identical 0.1M-LNO/LAO samples, as shown in figure 5.4. The resistance measured across two adjacent Pt electrodes are monitored during the doping process until the maximum resistance limit is reached. The ratio of saturated resistivity over the pristine resistivity were labeled in each doping profile and it is closely related to the doping temperature, indicating that the electron doping process is thermally activated. The Raman spectra, by the side of each doping profile, were scanned immediately after doping. The Raman peak at $\sim 485\text{cm}^{-1}$ which appears in each spectrum is from LAO substrate and could be considered as a reference to compare the peak intensity between pristine and H-doped LNO thin films. As the doping temperature increases, the peak from pristine LNO at $\sim 400\text{cm}^{-1}$ decreased and a new peak at $\sim 640\text{cm}^{-1}$ emerges with a increasing intensity, representing the formation of doped LNO, namely H-LNO. The Raman peaks from LAO and pristine LNO matched well with the previous measurements, and Ramadoss *et al.* reported the similarly emerged Raman peak of hydrogen doped SmNiO_3 at $\sim 620\text{cm}^{-1}$. [77, 130] The evolution of the LNO and H-LNO Raman peaks are indicated by the red arrows and the intensity variation relative to the peak intensity from LAO substrate is plotted in figure 5.5.

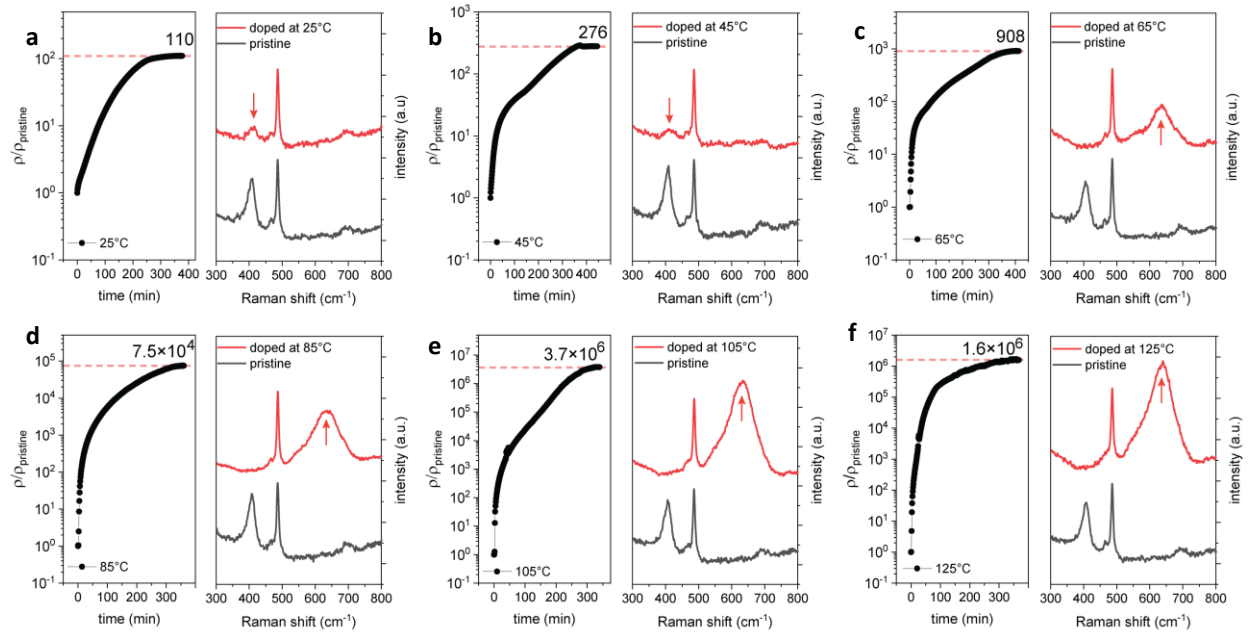


Figure 5.4. Electron doping induced MIT in LNO thin films at (a) 25°C, (b) 45°C, (c) 65°C, (d) 85°C, (e) 105°C and (f) 125°C. The LNO thin films were patterned with Pt electrodes and then annealed in 5% H_2 /95%Ar forming gas. LNO is sensitive to H_2 and the electron-doping even takes place at room temperature. As temperature increases, the upper limit of LNO resistance also increases, as labeled at the end of doping in each doping profile. The Raman spectra of pristine and doped LNO (H-LNO) corresponding to the doping temperature are shown by the side of each doping profile. In each Raman spectrum, the peak at $\sim 485\text{cm}^{-1}$ is from the LAO substrate. Hydrogen doping reduced the peak intensity from LNO at $\sim 400\text{cm}^{-1}$ and a new peak generated at $\sim 640\text{cm}^{-1}$ representing the formation of H-LNO phase, as indicated by the red arrow in each plot. The evolving Raman peak intensity of LNO and H-LNO after doping indicates the MIT of LNO by electron doping is closely dependent on the doping temperature.

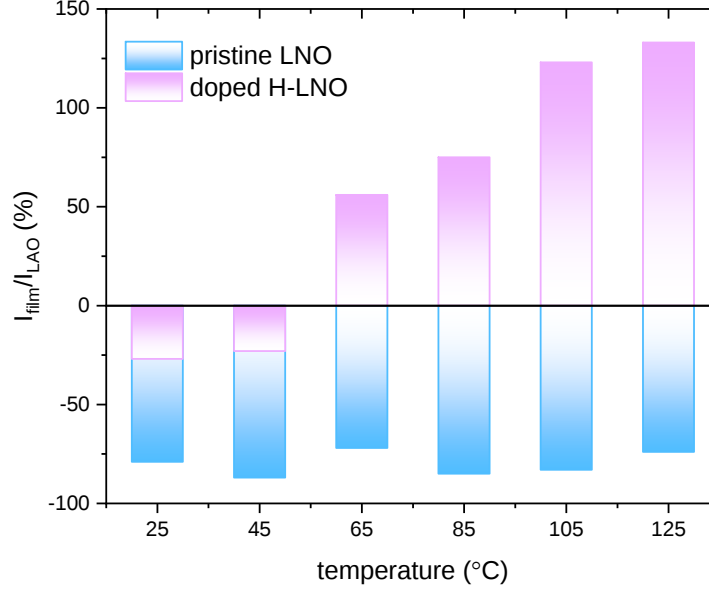


Figure 5.5. Raman peak intensity ratio from LNO thin films in comparison to the intensity of LAO substrate located at 485cm^{-1} . For ease of visualization, the relative intensity $I_{\text{film}}/I_{\text{LAO}}$ was defined as negative when I_{film} is indicated by LNO peak located at $\sim 400\text{cm}^{-1}$, and positive when I_{film} is from the peak of H-LNO at $\sim 640\text{cm}^{-1}$. The Raman peak intensity of LNO decreased and the peak from H-LNO emerged as the doping temperature increased. The relative peak intensities of the pristine LNO samples before doping are shown for reference at each temperature, indicated by the blue columns, which show nearly consistent values between -75% to -85%.

To further investigate the electron doping kinetics in relation to the doping temperature, we extracted the doping rate using an exponential fit:

$$\rho(t) = \rho_0 \exp(kt) \quad (17)$$

Where $\rho(t)$ is the material resistivity at doping time t (min), ρ_0 is the pristine material resistivity, k is the doping rate (min^{-1}). The initial exponential doping rate is fitted by $\ln(\rho(t)/\rho_0) \sim t$ and the slope is the doping rate k . The rate vs. doping temperature is plotted in figure 5.6, which shows that at low doping temperatures ($<100^\circ\text{C}$) the doping rate increases with temperature while it reaches saturation as the temperature goes above 100°C . The relationship of the doping kinetics was fitted using the sigmoid function[131, 132]:

$$\text{doping rate} = \frac{A}{1 + \exp[-B(T - T_c)]} \quad (18)$$

Where fitted $A=1.22$, indicating the saturation doping rate, regarding $\ln(\rho(t)/\rho_0) \sim t$, is about 1.22min^{-1} . T_c is fitted as 75.8°C , which implies the steepest slope of doping rate vs. temperature is located at $\sim 76^\circ\text{C}$, at which the doping rate is half the saturation value, 0.61min^{-1} . B is fitted as 0.0892 , suggesting the tangent slope at $T_c=75.8^\circ\text{C}$ is $A*B/4=0.027\text{min}^{-1}\text{ }^\circ\text{C}^{-1}$. Based on these results, the sample doping conditions for in-depth electrical studies were set at $5\%\text{H}_2/95\%\text{Ar}$ forming gas at 120°C for 15 min.

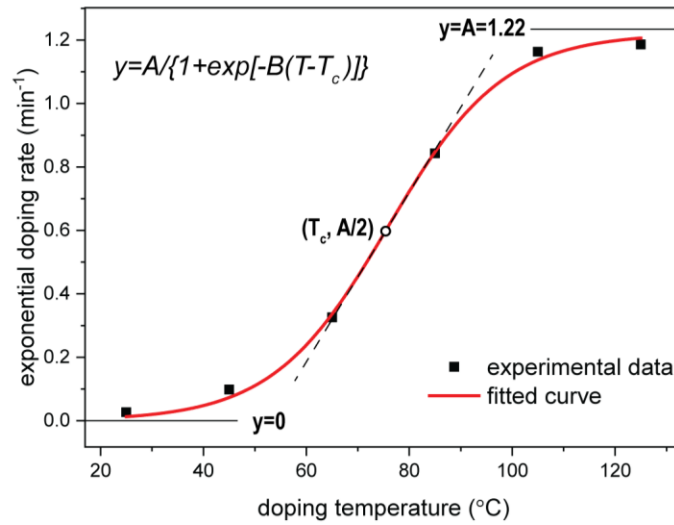


Figure 5.6. Hydrogen doping kinetics into LNO thin film. The doping rate at each temperature were fitted at the initial stages which showed exponential increase of the resistivity. The rate-temperature doping kinetics was fitted by a sigmoidal function, as indicated by the red line. The fitted saturation doping rate is $A \sim 1.22\text{min}^{-1}$. The “o” at 76°C labels the steepest slope of the fitted curve, which is $A*B/4=0.027\text{min}^{-1}\text{ }^\circ\text{C}^{-1}$.

The resistivity of pristine and doped LNO versus temperature, collected by PPMS measurement, is shown in figure 5.7. The data was collected from 0.1M-LNO thin films. DynaCool physical properties measurement system (PPMS) was used for the resistivity vs. temperature relationship (ρ - T) measurements. Both pristine and doped LNO thin films were wire bonded to the measurement puck in a 4-wire mode. The temperature was swept from 300K to about 140K at the rate of 5K per minute. The resistivity of pristine LNO is comparable with previous reports, confirming the quality of our LNO thin films deposited on LAO substrates.[118-123] As reference, resistivity data reported by Sakei *et al.* are labeled in the plot.[120] For a metal, increasing temperature results in corresponding increase in electrical resistivity while for an insulator the

trend is opposite. Clearly, the pristine metallic LNO transitioned to an insulator phase H-LNO by electron doping suggested by the distinct relationship of ρ -T for the two cases. This suggests that very similar to reports on SmNiO_3 and NdNiO_3 , LaNiO_3 can be switched from a conducting to insulating state with hydrogen doping accompanied by several orders of magnitude change in electrical resistance.

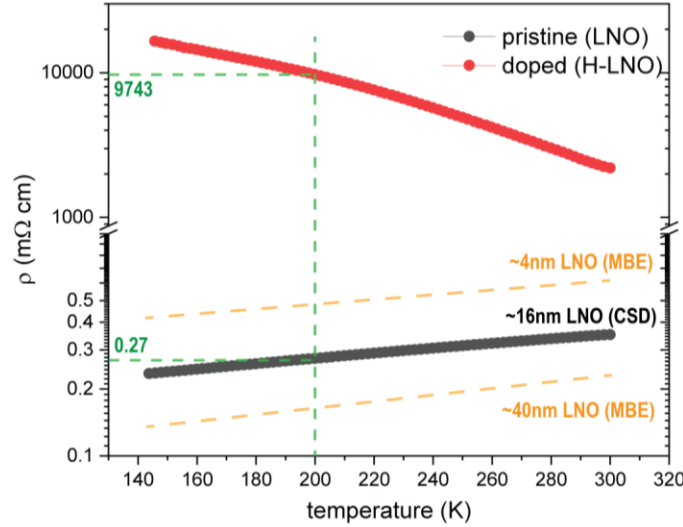


Figure 5.7. Metal to insulator transition of LNO by electron doping verified by the dependence of resistivity (ρ) on temperature (T). As expected, the pristine LNO exhibits a metallic ρ - T behavior as the resistivity increases with elevated temperature. After electron doping in H_2/Ar gas at 120°C for 15 min, the ρ - T curve shows the resistivity increases with decreasing temperature, indicating an insulator phase. The resistivity for pristine and H-doped LNO thin film at 200K are 0.27 and 9743 $\text{m}\Omega \text{ cm}$, respectively, as labeled in the plot.

5.3 LNO Memory Devices

5.3.1 Device Fabrication

Doped protons in perovskite lattice could drift under external electrical fields, leading to spatial redistribution of protons and thus contributes to the resistive switching.[49] Here we designed a series of electronic devices with Au-Ti/Au as the reference electrode and Pd as the working electrode. The device fabrication process is illustrated in figure 5.8 and is also described below:

LNO/LAO thin films were cleaned with toluene, acetone and isopropanol in a sonicator, each for 5 minutes. Then the films were patterned into “+” shapes by ion mill with SPR-220 photo resist as the etching mask. Four Au electrodes were patterned with alignment to the film and deposited by e-beam evaporation, followed by Ti/Au contact pad deposition by sputtering. The reason to deposit Au and Ti/Au separately is to avoid the contact of Ti and LNO in case of any metal-oxide contact issues. Instead, noble metal, Au, is directly in contact with LNO thin film to ensure the ohmic contact. The subsequently deposited Ti/Au pads are strong enough for wire bonding or probe contacting. In the end, Pd electrodes are deposited at the film center by e-beam evaporation. All the patterning and alignments were carried out by photo lithography.

The devices were fabricated with identical layout on both 0.1M-LNO/LAO and 0.2M-LNO/LAO thin films. After hydrogen doping, the film surrounding Pd will transition to H-LNO insulating phase while the rest of the LNO will remain metallic. The Pd electrode is designed to be smaller than the film center area. Due to the high conductivity of metallic LNO, the four Au-Ti/Au electrodes are equipotential during the electrical testing.

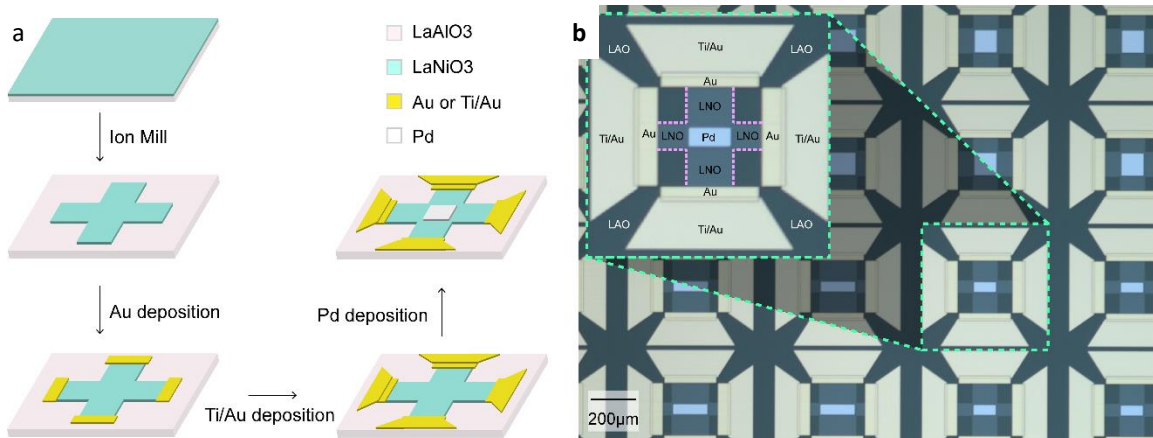


Figure 5.8. In-plane device design and fabrication with LaNiO_3 thin films. (a) A sketch of the device fabrication process. The films were patterned by ion mill into a cross shape “+” with various width and height at the cross center. The four ends were covered by 100nm Au before the deposition of Ti/Au to avoid possible contacts of the oxides and Ti. Then 100nm Pd electrodes were deposited at the film center for electron doping of LNO. (b) An optical image of the as fabricated devices with various layouts. The materials are labeled in the zoomed in view at the corresponding locations.

5.3.2 Electrical Characterizations and Performances

The devices were probed with a Micromanipulator probe station connected to a Keithley 4200A-SCS signal generator-measurement module equipped with remote preamplifier/switch modules (4225-RPM) and ultrafast pulse measurement units (4225-PMU). The pulse conditions to trigger resistive switching in figure 8 were +9V 500ns and -9V 1 μ s referring to the Pd electrode for 0.1M-LNO/LAO devices, and +5V 100ns and -5V 500ns referring to the Pd electrode for 0.2M-LNO/LAO devices. After each electrical pulses which triggered the resistive switching, the device resistance states were averaged from 10 reading voltage pulses (0.5V, 2 μ s, which does not change the device resistance).

Electrical measurements from 0.1M-LNO/LAO and from 0.2M-LNO/LAO are compared in figure 5.9, with an identical device layout, sketched in figure 5.9 (b) (d). In a top-down view of the device, the edge-to-edge distance from upper/lower Au electrode to Pd electrode is 92.5 μ m while the edge-to-edge distance from left/right Au electrode to Pd electrode is only 12.5 μ m. Both devices were switched for over 50 cycles and the corresponding statistical analyses of the 50 cycles are shown in figure 5.9 (a) (c). Regardless of the different device testing configurations referring to the distances across probed electrodes, the resistive switching ratio R_{high}/R_{low} does not appear to be affected by the testing terminals in both 0.1M-LNO and 0.2M-LNO devices.

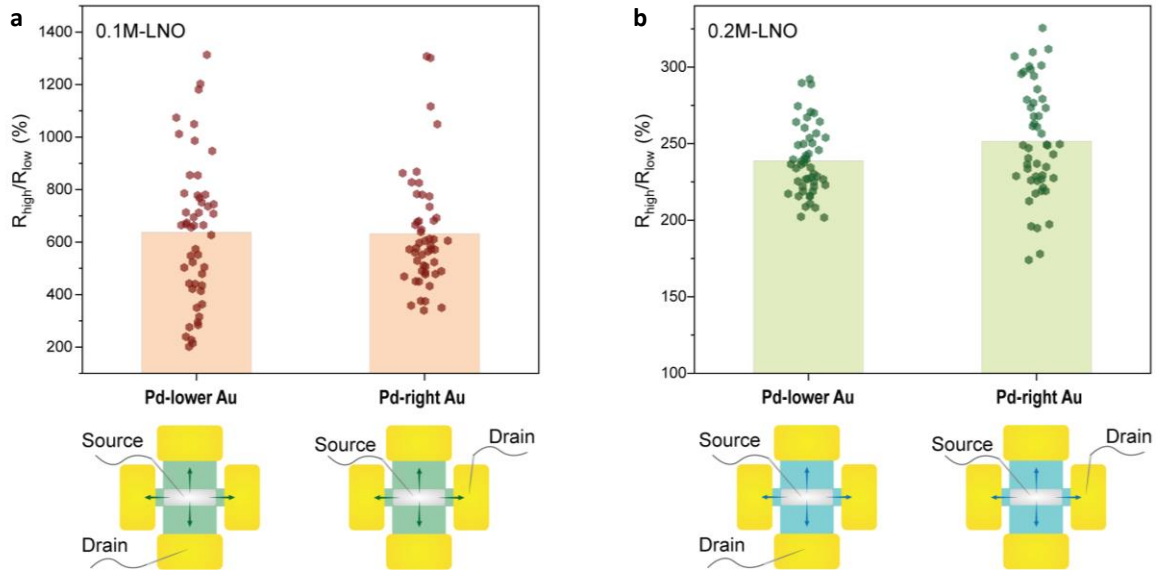


Figure 5.9. Resistive switching of devices fabricated with 0.1M-LNO/LAO and 0.2M-LNO/LAO. (a) Statistical comparison of resistive switching ratio from 50 cycles of device with 0.1M-LNO/LAO measured by two testing connections sketched in (b). Pulse conditions: +9V 500ns and -9V 1 μ s referring to the Pd electrode. The scattered dots are the experimental data of switching ratios from 50 cycles, while the bar height represents the averaged switching ratio. Switching ratio is independent of the distance of the probed terminals, indicating the four Au ends are equipotential in such devices during electrical testing. (c) Statistical comparison of resistive switching ratio from 50 cycles of device with 0.2M-LNO/LAO measured by two testing connections sketched in (d). Pulse conditions: +5V 100ns and -5V 500ns referring to the Pd electrode. Similar to 0.1M-LNO device, the switching is independent of the distance of the probed terminals, indicating the four Au ends are equipotential in such devices during electrical testing.

Figure 5.10 shows the synaptic behavior of the devices with potentiation and depression training cycles. The device stability and durability is also confirmed by switching the devices for 1000 cycles and testing the retention at multiple resistance states for 10^4 s at each state. Both 0.1M- and 0.2M-LNO devices showed tunable synaptic weights (resistances) associated with the training pulse amplitude since the final stabilized synaptic weight is highly dependent on the amplitude.

The switching polarity for 0.1M-LNO and 0.2M-LNO devices are opposite, as shown in figure 5.10 (a)(b)(d)(e) and figure 5.11. Taking 0.1M-LNO for instance, applying positive bias on Pd electrode will result in a HRS state and vice versa. On the contrary, for 0.2M-LNO devices the positive bias on Pd will draw the device to the LRS. In addition, the pulse strength for 0.1M-LNO is stronger than that required for 0.2M-LNO.

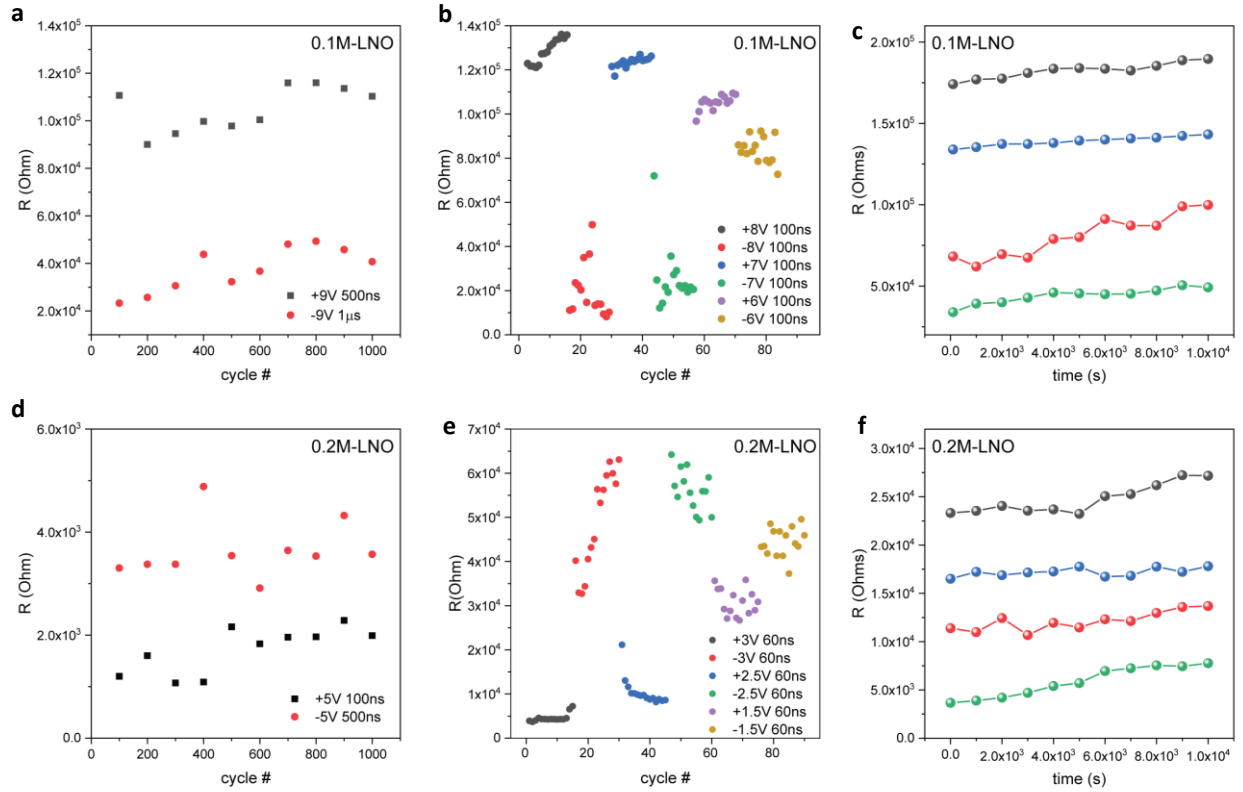


Figure 5.10. Resistance switching and potentiation measurements with LNO thin films. (a) (d) show reproducible cycling tests of 0.1M-LNO and 0.2M-LNO for over 1000 cycles. (b) (e) are the potentiation-depression behavior of devices with 0.1M-LNO/LAO and 0.2M-LNO/LAO. The training conditions are noted in the plots. For both devices, the final stabilized synaptic weight is dependent on the training pulse amplitude. (c) (f) show the retention data of multiple resistance states from the two representative devices. Four resistance states were monitored for 10⁴ seconds at each state and were stable. All of the data in this figure set was collected with Pd-lower Au connection.

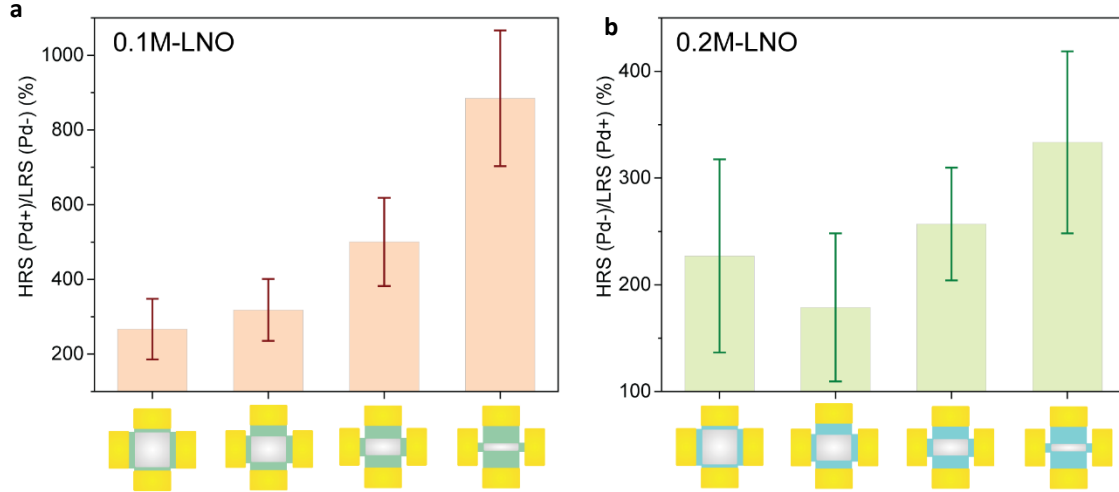


Figure 5.11. Statistics of the switching ratio and polarity for (a) 0.1M-LNO and (b) 0.2M-LNO chips with various layouts. Four different devices were measured on each chip, with the device layout sketched at the bottom of the plots corresponding to each column. The voltage polarity on the same chip is consistent from one device to another. The switching ratios were averaged through 30 cycles on each device using the Pd-lower Au connection. The edge-to-edge distance from Pd to left/right-Au electrode is 12.5 μ m for all layouts, and the edge-to-edge distances from Pd to upper/lower-Au electrode are 17.5, 42.5, 67.5 and 92.5 μ m, respectively.

5.3.3 Device Switching Mechanisms

Figure 5.12 shows the top-down view of the devices zoomed in at the Pd electrode, with substrate orientations noted. We hypothesize that the switching mechanism for 0.1M-LNO, with better epitaxial nature, is due to the drift of protons in LNO lattice under the driving force of electric fields. The drift is preferred along directions oriented along the electrodes rather than in an isotropic manner in that, based on previous reports, the energy barrier for protons to migrate in the nickelate lattice along $\langle 001 \rangle$ directions are lower than that along $\langle 110 \rangle$ directions.[49, 133] Applying negative/ positive pulses on Pd will attract/repel protons which will change the spatially distributed volume of insulating H-LNO, leading to the resistive switching of the device. However, the case for 0.2M-LNO device is different due to the distinct microstructure. At negative bias, the protons are accumulated around the Pd electrode and the device is at HRS. After a short positive pulse, the repelled protons diffuse along the grain boundaries which creates conductive paths from Pd electrode to metallic LNO film, as indicated in figure 5.12 (b), and the device is now brought to the LRS. The activation energy required for protons to migrate along grain boundaries is likely lower than that to drift through crystalline lattice, since we found the input voltage pulses triggering

the resistive responses for 0.2M-LNO devices had no impact on 0.1M-LNO at all in our experimental testing. The contribution from proton drift within lattice in 0.2M-LNO sample is less compared with the migration along grain boundaries from the electrical response. Such preferred migration of high-concentration protons along grain boundaries were also reported recently in polycrystalline nickelate thin films.[134]

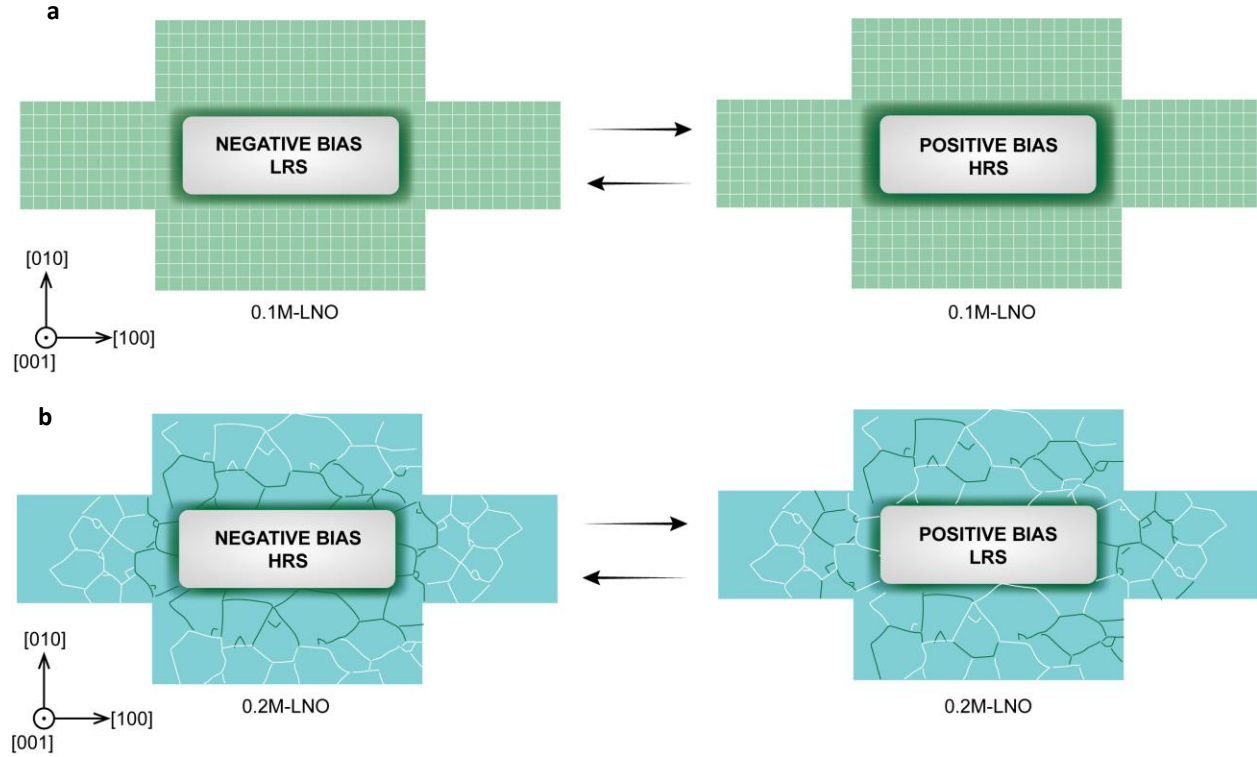


Figure 5.12. Proposed resistive switching mechanisms for (a) 0.1M-LNO and (b) 0.2M-LNO devices. (a) The thinner 0.1M-LNO is epitaxial. The grids indicate the pseudo cubic lattice, the turquoise and the dark green colors represent the pristine 0.1M-LNO and doped H-LNO, respectively. Both the lattice constant and the doped H-LNO area is exaggerated for illustration purposes. When Pd is at the negative / positive bias, the protons are attracted to / pushed away from the Pd electrode, resulting a decreased / increased spatial volume of insulating H-LNO which corresponds to the LRS / HRS. (b) The sketched lines are grain boundaries and the ones in dark green colors represents the grain boundaries with protons accumulation which are locally insulating, while the white lines represent the grain boundaries without protons which are locally conductive. The grain size is not in scale with the size of Pd electrode for illustration purpose again. At negative / positive bias on Pd, the protons are accumulated at / migrated away from the grain boundaries adjacent to the Pd electrode, blocking / forming the conductive pathways to the outer pristine LNO which corresponds to the HRS / LRS. The input pulses are too weak to drive protons to drift through perovskite lattice such that the region with dark green color representing doped H-LNO does not have any change.

5.4 Conclusion

We have successfully deposited crystalline LNO thin films on LAO substrates by CSD method. Two chemical solution concentrations, 0.1M and 0.2M, were adopted which generated distinct microstructures. The LNO thin films underwent a metal to insulator transition by electron doping upon annealing in H_2 rich forming gas. Proof-of-concept resistive switching and synaptic behavior were demonstrated with $LaNiO_3$ devices in sub-microsecond timescales. Microstructural differences between films synthesized with different chemical precursor compositions led to distinct electrical behavior suggesting future directions to optimize and tune the device behavior.

FUTURE WORK RECOMMENDATIONS

Completing this thesis is a true journey of walking through all my research experiences in the past 4 years. I made a lot of efforts to improve and validate my research results, during which there were some claims or proposals that were raised based on hypothesis. I would like to list out the potential future work that might be interesting yet challenging.

1. Determination of critical thickness in chemical solution deposition method. There is a critical thickness of ReNiO_3 thin films deposited by chemical solution deposition, above which the film becomes porous. This limitation is known to be related to the lattice constant match of the thin film and the substrate and might be also related to the ramping rate of temperature during the pyrolysis and annealing process. Theoretically the faster temperature increases to idle the better film epitaxy will be.
2. Structural engineering of nickelate thin films to enhance electrochromic performances. It has been proved that the porous NNO thin films has a significant advantage over the denser films. Further work could be carried out with detailed surface modifications like etching the film into pillar arrays to improve the surface area in the electrolyte which should result a better electrochromic activity.
3. 3rd generation device testing. The 3rd generation device was fabricated successfully and tested for some basic resistive switching by pulses. I found the electrical responses are more uniform and active among multiple 3rd generation devices compared with the situations of 1st and 2nd generations. Although I do not have the time to perform a systematic testing of this new batch of devices in my Ph.D. time, it still suggests that the nickelates might be suitable for building large-scaled network system as long as the units or building blocks are properly isolated from each other.
4. Fundamental finalization of carrier transportation mechanisms. The mechanisms raised in chapter 4 has some hypotheses. The HSNO could be tested for Hall effect to determine whether it is truly an n-type semiconductor, and the Schottky barrier height could be further verified by local measurements of work functions of HSNO near Pd electrode.
5. Resistive switching mechanisms of LNO thin film devices. The opposite resistive switching polarity related to the LNO thin film thickness is very novel. Currently the claimed mechanism of grain-boundary-type switching does not have any microscopic

data or imaging as support yet, which could be further investigated. Constructions of the LNO thin film surface topography might be a new path toward fine adjustments of the thin film responses in a device.

APPENDIX A. RICHARDSON'S CONSTANT

Starting from the reverse current by image force lowering effect:

$$J_R = \frac{I_R}{A} = A^{**}T^2 \exp \left[-\frac{q\phi_{B0}}{k_B T} + \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \left(V_R + V_{bi} - \frac{k_B T}{q} \right) \right)^{\frac{1}{4}} \right] \quad (A1)$$

$$\xrightarrow{V_R \gg 3k_B T} \ln(I_R) = \ln(AA^{**}T^2) - \frac{q\phi_{B0}}{k_B T} + \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} V_R \right)^{\frac{1}{4}}$$

From equation (A1), the intercept and slopes are extracted:

$$\text{intercept} = \ln(AA^{**}T^2) - \frac{q\phi_{B0}}{k_B T} \quad (A2)$$

$$\text{slope} = \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \right)^{\frac{1}{4}} \quad (A3)$$

The resistance at 0 bias can be derived as:

$$\begin{aligned} R_{V=0} &= \left(\frac{dI_R}{dV_R} \bigg|_{V_R=0} \right)^{-1} = (AA^{**}T^2)^{-1} \exp \left(\frac{q\phi_{B0}}{k_B T} \right) \\ &\cdot \exp \left(-\frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \left(V_{bi} - \frac{k_B T}{q} \right) \right)^{\frac{1}{4}} \right) \\ &\cdot \left(\frac{1}{4} \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \right)^{-1} \left(\frac{2qN_D}{\epsilon_s} \right)^{-\frac{1}{4}} \left(V_{bi} - \frac{k_B T}{q} \right)^{\frac{3}{4}} \end{aligned} \quad (A4)$$

Rewrite in Ln scaled format:

$$\begin{aligned} \ln(R_{V=0}) &= - \left[\ln(AA^{**}T^2) - \frac{q\phi_{B0}}{k_B T} \right] - \text{const.}(A) \\ &= -\text{intercept} - \text{const.}(A) \end{aligned} \quad (A5)$$

$$\text{const.}(A) = \ln \left[\frac{1}{4} \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \right)^{\frac{1}{4}} \left(V_{bi} - \frac{k_B T}{q} \right)^{\frac{3}{4}} \right] \quad (A6)$$

In figure 4.10(a), the const.(A) is fitted as 4.4, and the fitted slope of intercept $\sim \ln(R_{V=0})$ is exactly -1, which matches well with equation (A5).

Note the above fitting is conducted at room temperature. The temperature dependent $R_{v=0}$ is given in figure 4.10 (b), with temperature varied from 300K to 220K.

Rewrites equation (A4), sorting out terms with temperature T:

$$\begin{aligned}
R_{contact} &= \left(\frac{dI_R}{dV_R} \Big|_{V_R=0} \right)^{-1} = (AA^{**}T^2)^{-1} \exp\left(\frac{q\phi_{B0}}{k_B T}\right) \\
&\cdot \exp\left(-\frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \left(V_{bi} - \frac{k_B T}{q}\right)\right)^{\frac{1}{4}}\right) \\
&\cdot \left(\frac{1}{4} \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}}\right)^{-1} \left(\frac{2qN_D}{\epsilon_s}\right)^{-\frac{1}{4}} \left(V_{bi} - \frac{k_B T}{q}\right)^{\frac{3}{4}} \\
&= (AA^{**}T^2)^{-1} \exp\left(\frac{q}{k_B T} \left(\phi_{B0} - \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \left(V_{bi} - \frac{k_B T}{q}\right)\right)^{\frac{1}{4}}\right)\right) \\
&\cdot \left(\frac{1}{4} \frac{q}{k_B T} \sqrt{\frac{q}{4\pi\epsilon_s}}\right)^{-1} \left(\frac{2qN_D}{\epsilon_s}\right)^{-\frac{1}{4}} \left(V_{bi} - \frac{k_B T}{q}\right)^{\frac{3}{4}} \\
&\approx (AA^{**}T)^{-1} \exp\left(\frac{q\phi_{B0}}{k_B T}\right) \cdot \left(\frac{1}{4} \frac{q}{k_B} \sqrt{\frac{q}{4\pi\epsilon_s}}\right)^{-1} \left(\frac{2qN_D}{\epsilon_s}\right)^{-\frac{1}{4}} \left(V_{bi} - \frac{k_B T}{q}\right)^{\frac{3}{4}} \quad (A7)
\end{aligned}$$

The approximation at the last step is made as the image force lowering effect at $V=0$ is negligible:

$$\Delta\phi|_{V=0} = \sqrt{\frac{q}{4\pi\epsilon_s}} \left(\frac{2qN_D}{\epsilon_s} \left(V_{bi} - \frac{k_B T}{q}\right)\right)^{\frac{1}{4}} \approx 0 \quad (A8)$$

The fitting in figure 4.10 (b) is described as:

$$\ln(R_{contact} \cdot T) = -\ln(AA^{**} \cdot \text{const.}(C)) + \left(\frac{q\phi_{B0}}{k_B T}\right) \quad (A9)$$

Where:

$$\begin{aligned}
\ln(\text{const.}(C)) &= \ln\left[\left(\frac{1}{4} \frac{q}{k_B} \sqrt{\frac{q}{4\pi\epsilon_s}}\right) \left(\frac{2qN_D}{\epsilon_s}\right)^{\frac{1}{4}} \left(V_{bi} - \frac{k_B T}{q}\right)^{-\frac{3}{4}}\right] \\
&\approx \text{const.}(A) + \ln(300K) = 10.7 \quad (A10)
\end{aligned}$$

As the temperature variation was from 300K to 220K, the $k_B T/q$ term only changed from 0.026 to 0.020V, which is negligible compared to the value of V_{bi} . This is how the approximation in equation (A10) was made.

From the slope of figure 4.10 (b), the ideal barrier height of this specific device measured during R-T was:

$$2.62 = \frac{q\phi_{B0}}{1000k_B} \rightarrow \phi_{B0} = 0.226eV \quad (A11)$$

From the fitted intercept of figure 4.10 (b), the Richardson's constant A^{**} is extracted as:

$$\begin{aligned} 9.52 &= -Ln(AA^{**}) - Ln(const.(C)) \\ Ln(AA^{**}) &= -9.52 - 10.7 \approx -20 \\ A &= 1000\mu m^2 = 10^{-5} cm^2, \\ A^{**} &= 2.06 \times 10^{-4} Amp \cdot cm^{-2} K^{-2} \end{aligned} \quad (A12)$$

By plugging this A^{**} value into equation (A2) and (A3), one could figure out the barrier height calculated in section 4.2.4.

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