

Supporting information

Electrochromic properties of perovskite NdNiO₃ thin films for smart windows

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S1. Atomic Layer Deposition Process Details

Process conditions and deposition temperature windows were evaluated for NiO_x and NdO_x oxides independently to confirm ALD behavior and to select appropriate deposition temperature conditions for the mixed oxide. Nd(iPrCp)₃ was heated in 5 °C steps to confirm volatility for introduction into the reactor; 160 °C

was chosen as the final vaporization temperature. Due to the hygroscopic nature of $\text{Nd}[\text{OH}]_x$ and a lack of reactivity of $\text{Nd}(\text{iPrCp})_3$ with water, O_3 was employed as the oxidant. A narrow plateau of ALD growth of NdO_x was observed in the temperature range from 160 to 180 °C. (Fig. S1a) At deposition temperatures above 180 °C, the deposition rate of NdO_x increases, indicating another reaction mechanism – likely decomposition of the Nd precursor. A process window of NiO_x was also confirmed over 160 °C using $\text{Ni}(\text{tBu}_2\text{-amd})_2$ and O_3 as the oxidant. In Fig. S1b, growth rates of NdO_x and NiO_x were evaluated by varying the dose time of Nd precursor and Ni precursor. The result demonstrates that the growth rate of NdO_x and NiO_x saturates at a dose time of 0.5 and 0.75 s, respectively. At a deposition temperature of 160 °C a linear growth rate was confirmed by plotting the thickness of NdO_x and NiO_x as a function of number of cycles. (Fig. S1c) At this temperature, growth rates of NdO_x and NiO_x films are 0.438 Å/cycle and 0.212 Å/cycle, respectively.

The NNO film was deposited using the pulsing sequence $[m \times (\text{Nd}(\text{iPrCp})_3 + \text{O}_3) + n \times (\text{Ni}(\text{tBu}_2\text{-amd})_2 + \text{O}_3)] \times N$, where m is the pulsing number of NdO_x -deposition basic cycles, n is the pulsing number of NiO_x -deposition basic cycles, and N is the repeating cycles. The composition of as-deposited NNO_x films was measured by EDS to establish the relationship between the deposited Nd/Ni and pulsed Nd/Ni ratios (m/n), as shown in Fig. S1d. A 2/1 ratio of pulsed Nd/Ni cation precursor results in ~1/1 stoichiometric Nd/Ni cation ratio in as-deposited NNO_x films. The linear relation between deposited Nd/Ni ratio and pulsed Nd/Ni ratio demonstrates high controllability of cation ratio and deposition process.

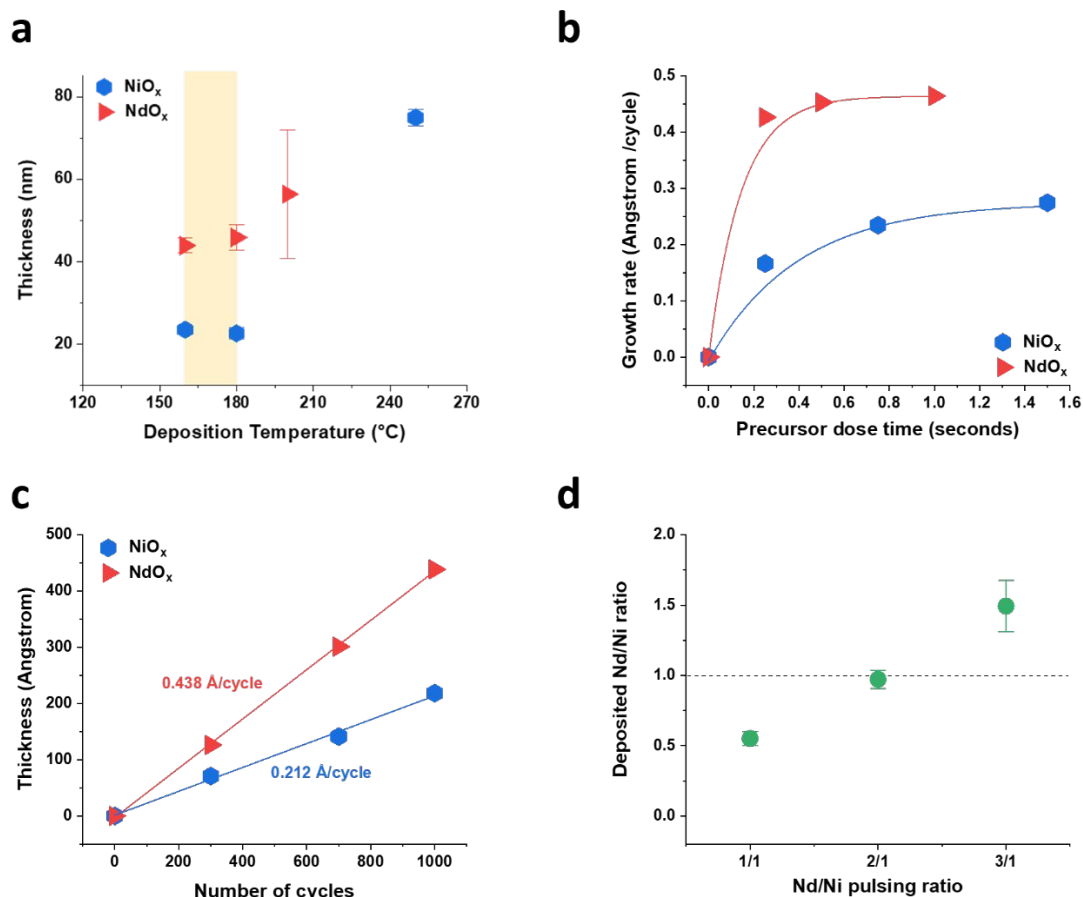


Figure S1. ALD process optimization experiments. (a) Dependence of the film thickness on the deposition temperature for NiO_x (hexagons) and NdO_x (triangles) films. (b) Growth rate as a function of precursor dose time for NiO_x (hexagons) and NdO_x (triangles) films at 160 $^{\circ}\text{C}$. (c) Dependence of the thickness on the number of cycles for NiO_x (hexagons) and NdO_x (triangles) films at 160 $^{\circ}\text{C}$. (d) Deposited Nd/Ni cation ratio determined by EDS as a function of pulsed Nd/Ni cation precursors. The black dashed line indicates the stoichiometric Nd/Ni cation ratio. The films were grown on Si substrates.

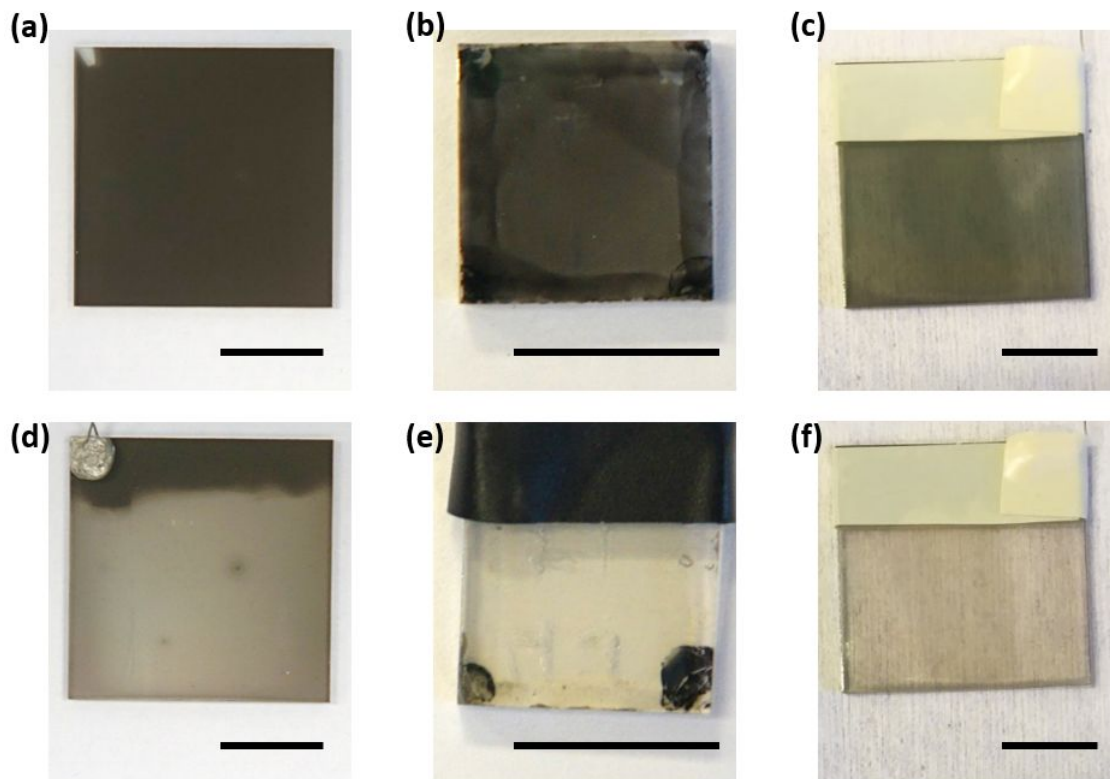


Figure S2. Optical images of NNO/FTO samples in pristine (a-c) and bleached (d-f) states. (a) and (d): optical images of ~150nm PVD-NNO/FTO. The pristine sample was bleached by applying -1.5V vs. Ag/AgCl for 2 min. **(b) and (e):** optical images of ~150nm CSD-NNO/FTO. The pristine sample was bleached by applying -1V vs. Ag/AgCl for 1 min. **(c) and (f):** Optical images of ~50nm ALD-NNO/FTO. The pristine sample was bleached by applying -1V vs. Ag/AgCl for 3 min. *Scale bars, 1 cm.* The desired transmittance through the film in any particular state can be further optimized by choice of film thickness and strength/duration of electrical bias based on application needs. To avoid undesirable chemical reactions during coloration/bleaching due to over oxidation/reduction of NNO films, the maximum bias in our experiments was limited to ± 1.5 V vs. Ag/AgCl.

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