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Supporting Information

## Reversible Redox Control of Optoelectronic Properties of Hexagonal Tungsten Oxide Epitaxial Films Grown on YSZ Solid Electrolyte

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**Table S1.** Transmission at 1.5  $\mu$ m (*Trans.*) and the activation energy ( $E_a$ ) of the electrochemically reduced/oxidized h-WO<sub>x</sub> films. The  $E_a$  was extracted by assuming the Arrhenius-type thermal actication of  $\sigma$  as  $\sigma = \sigma_0 \exp(-E_a/k_BT)$ , where  $\sigma_0$ ,  $k_B$  and T are pre-exponential factor, Boltzmann constant, and absolute temperature, respectively.

Sample	x in WO <sub>x</sub>	<i>Trans</i> . at 1.5 μm (%)	Ea (meV)
Α	2.987	49.8	212.3
В	2.986	52.0	203.7
С	2.981	46.7	108.5
D	2.960	44.2	74.0
Ε	2.954	43.4	68.1
F	2.935	41.8	71.7
G	2.933	38.3	35.8
Η	2.931	35.4	33.3
Oxi 1	2.993	69.3	ND
Oxi 2	2.988	61.9	ND

**Table S2.** *Trans.* and *E*<sub>a</sub> of the PLD-grown h-WO<sub>x</sub> films.

Sample	x in WO <sub>x</sub>	<i>Trans</i> . at 1.5 μm (%)	E <sub>a</sub> (meV)
6 Pa	2.993	54.9	223.5
5 Pa	2.984	51.6	99.5
4 Pa	2.980	45.2	74.4
3 Pa	2.957	35.5	41.6
2 Pa	2.938	34.4	18.1



**Figure S1.** Time dependence of the current density during the electrochemical reduction treatment by applying +3 V to YSZ substrate.

![](_page_4_Figure_0.jpeg)

**Figure S2.** XPS spectra around W 4f peaks of the electrochemically redox treated h-WO<sub>x</sub> epitaxial films.

![](_page_5_Figure_0.jpeg)

**Figure S3.** Change in the out-of-plane XRD patterns of PLD-grown h-WO<sub>x</sub> epitaxial films under various oxygen pressure from 2 to 6 Pa during the film growth.

![](_page_6_Figure_0.jpeg)

**Figure S4.** Comparison of the crystallographic feature of the PLD-grown h-WO<sub>x</sub> epitaxial films under oxygen pressure of 6 Pa and 2Pa. (from left to right: out-of-plane XRD patterns, RHEED patterns, and topographic AFM images)

![](_page_7_Figure_0.jpeg)

**Figure S5.** XPS spectra around W 4f peaks of PLD-grown h-WO<sub>x</sub> epitaxial films under various oxygen pressure from 2 to 6 Pa during the film growth.

![](_page_8_Figure_0.jpeg)

**Figure S6.** Optical transmission and photographs of PLD-grown h-WO<sub>x</sub> epitaxial films under various oxygen pressure from 2 to 6 Pa during the film growth.

![](_page_9_Figure_0.jpeg)

**Figure S7.** Changes in the optical transmission spectra of the h-WO<sub>x</sub> epitaxial film after repeated electrochemical redox treatment. (From left to right: as-grown,  $1^{st}$  oxidized,  $1^{st}$  reduced, and  $2^{nd}$  oxidized)

![](_page_10_Figure_0.jpeg)

**Figure S8.** Surface morphology of the h-WO<sub>*x*</sub> epitaxial film after repeated electrochemical redox treatment. (From left to right: as-grown,  $1^{st}$  oxidized,  $1^{st}$  reduced, and  $2^{nd}$  oxidized)