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 μm (*Trans.*) and the activation energy (E_a) of the electrochemically reduced/oxidized h-WO_x films. The E_a was extracted by assuming the Arrhenius-type thermal actication of σ as $\sigma = \sigma_0 \exp(-E_a/k_B T)$, where σ_0, k_B and T are pre-exponential factor, Boltzmann constant, and absolute temperature, respectively.

Sample	x in WO_x	*Trans.* at 1.5 μm (%)	E_a (meV)
A	2.987	49.8	212.3
B	2.986	52.0	203.7
C	2.981	46.7	108.5
D	2.960	44.2	74.0
E	2.954	43.4	68.1
F	2.935	41.8	71.7
G	2.933	38.3	35.8
H	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_a of the PLD-grown h-WO_x films.

Sample	x in WO_x	*Trans.* at 1.5 μm (%)	E_a (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

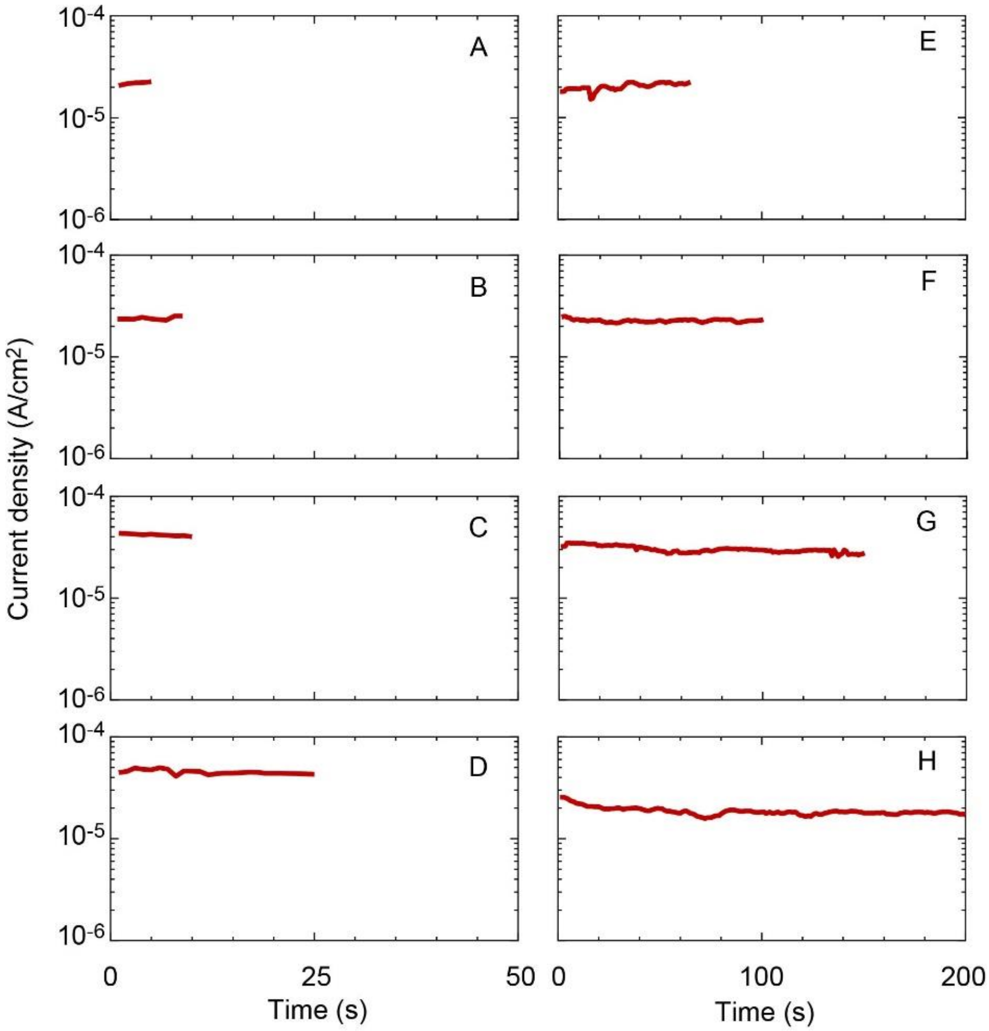

Figure S1. Time dependence of the current density during the electrochemical reduction treatment by applying +3 V to YSZ substrate.

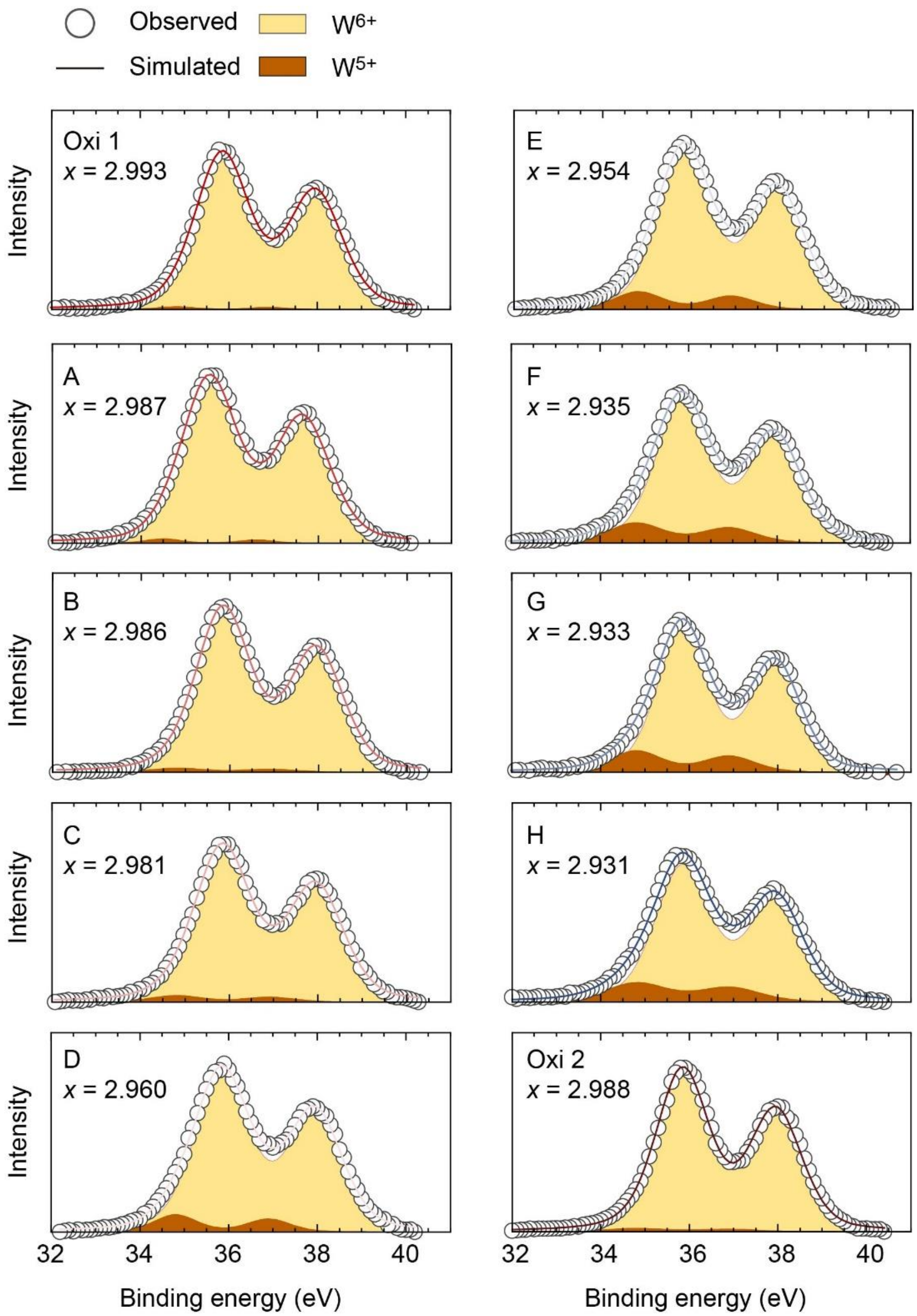

Figure S2. XPS spectra around W 4f peaks of the electrochemically redox treated h-WO_x epitaxial films.

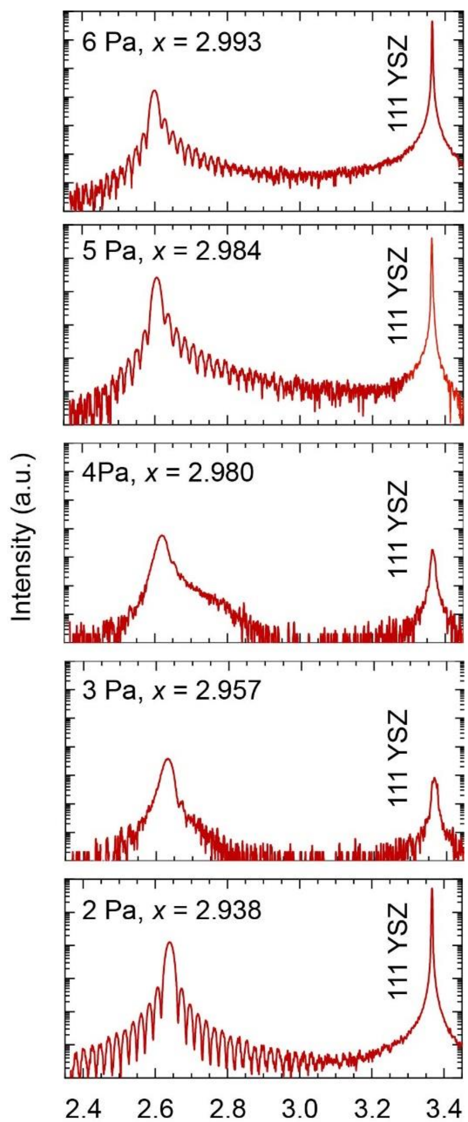

Figure S3. Change in the out-of-plane XRD patterns of PLD-grown h-WO_x epitaxial films under various oxygen pressure from 2 to 6 Pa during the film growth.

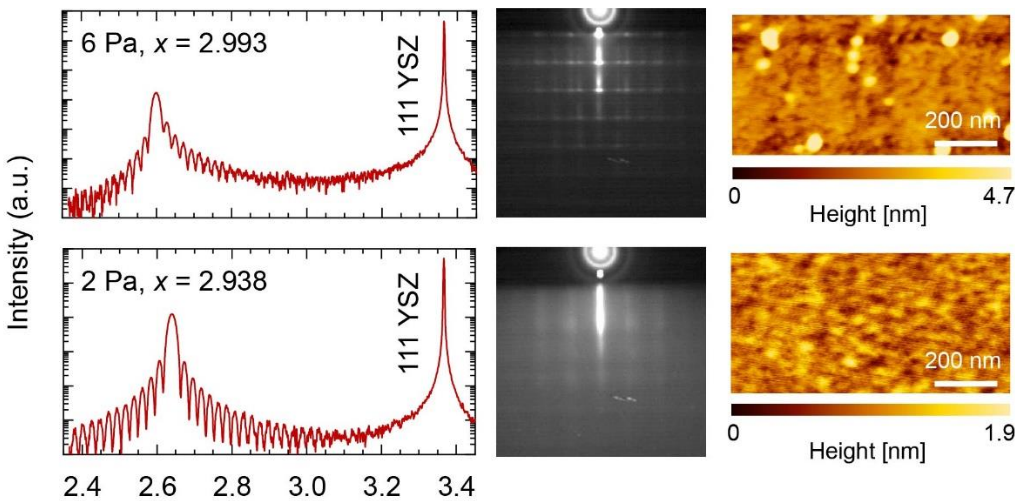

Figure S4. Comparison of the crystallographic feature of the PLD-grown h-WO_x epitaxial films under oxygen pressure of 6 Pa and 2Pa. (from left to right: out-of-plane XRD patterns, RHEED patterns, and topographic AFM images)

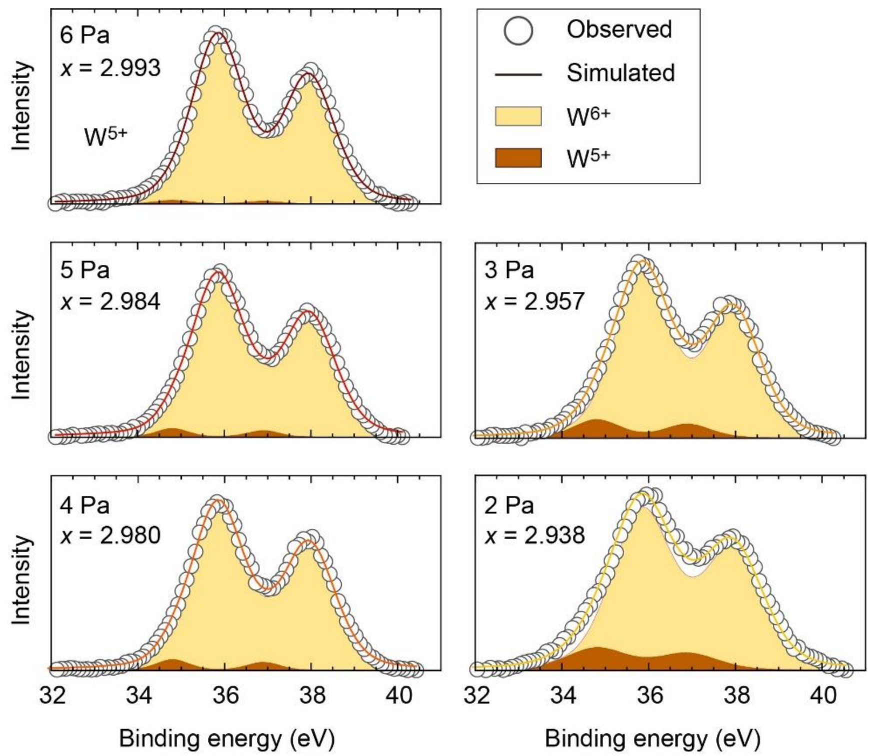

Figure S5. XPS spectra around W 4f peaks of PLD-grown h-WO_x epitaxial films under various oxygen pressure from 2 to 6 Pa during the film growth.

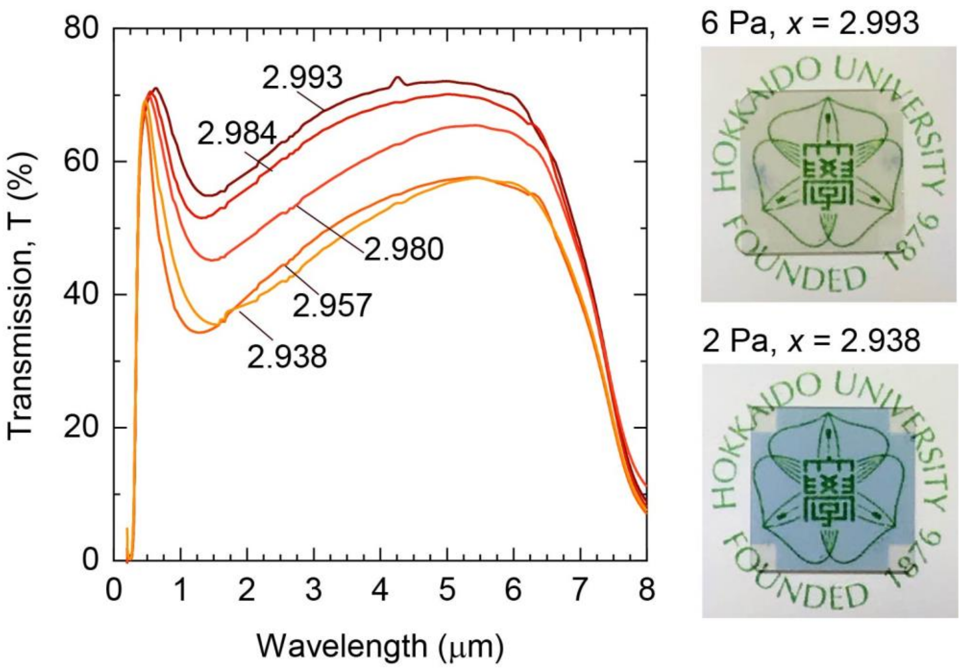

Figure S6. Optical transmission and photographs of PLD-grown h-WO_x epitaxial films under various oxygen pressure from 2 to 6 Pa during the film growth.

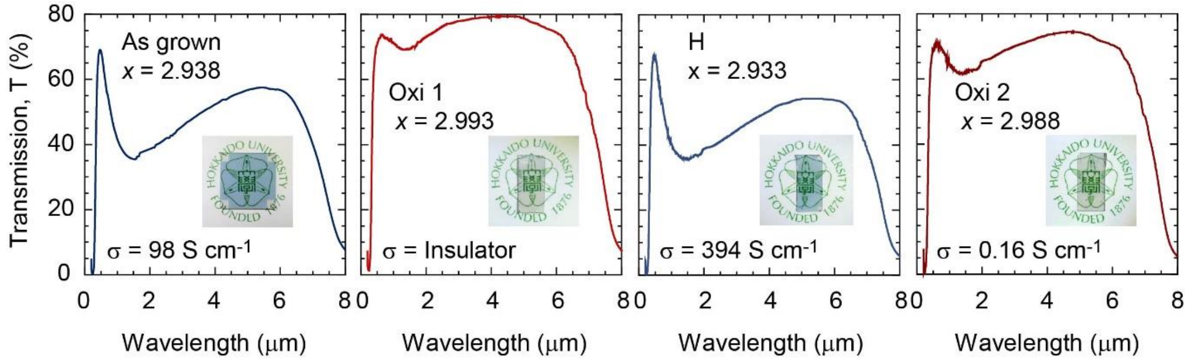

Figure S7. Changes in the optical transmission spectra of the h-WO_x epitaxial film after repeated electrochemical redox treatment. (From left to right: as-grown, 1st oxidized, 1st reduced, and 2nd oxidized)

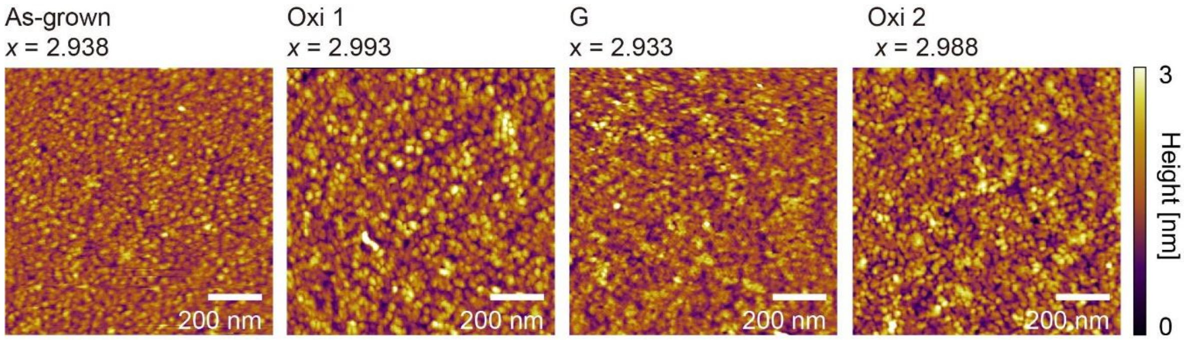

Figure S8. Surface morphology of the h-WO_x epitaxial film after repeated electrochemical redox treatment. (From left to right: as-grown, 1st oxidized, 1st reduced, and 2nd oxidized)