Supporting Information

Optimizing Pulsed Laser Deposition of Crystalline $BiVO_4$ Thin Film on Yttrium-stabilized Zirconia (110) Substrates

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Methods

Thin Film Photoanode Preparation

$BiVO_4$ (BVO) thin film photoanodes are fabricated on YSZ (110) single crystalline substrates (MTI Corp.) by PLD, using a KrF excimer laser (λ = 248 nm). Typically, a 50-nm-thick ITO film is first deposited over the YSZ substrate at 600˚C, under the base pressure of 6 × 10^{-7} Torr. Unless otherwise noted, BVO thin film is subsequently deposited above the ITO layer under an oxygen pressure of 10 mTorr, using a two-step deposition (TSD) method. In the first step, the substrate temperature is ramped up to 675 ˚C in a rate of 30 ˚C min^{-1}, before the deposition of a BVO seeding layer with 1000 laser pulses at a repetition rate of 5 Hz. After the seeding layer formation, the bulk of BVO film is deposited with 9000 laser pulses at a repetition rate of 1 Hz, with the substrate temperature maintained at 675 ˚C and oxygen pressure at 10 mTorr. Finally, the sample is cooled down to room temperature with a ramping rate of 10 ˚C min^{-1}. The ITO laser ablation target is obtained from Kurt J. Lesker, while the BVO target is prepared by a conventional ceramic sintering method, using commercial $BiVO_4$ powder (Alfa Aesar).

Microstructural, Chemical and Optical Characterization

Lattice structures of the thin films are characterized by X-ray diffraction (XRD, Rigaku SmartLab), using Cu K_α radiation (λ = 1.5418 Å). The surface morphology is investigated using scanning electron microscopy (SEM, Hitachi S-4800). Ultraviolet-visible (UV-Vis) absorption spectra are collected by a PerkinElmer Lambda 25 UV/Vis spectrophotometer, from 400 nm to 800 nm. TEM lamellas are made using the in-situ lift-out method with a FEI Helios G5 UX Dual Beam FIB/SEM. STEM is measured by ThermoFisher F200X Talos S/TEM.

Photoelectrochemical Characterization

The photoelectrochemical (PEC) characterization is performed using a potentiostat (PAR VersaStat 4) in the three-electrode configuration, with the BVO thin film photoanode as the working electrode, Ag/AgCl/saturated KCl as the reference electrode, and a Pt wire as the counter electrode. The electrolyte is a pH = 7 phosphate buffer with hole-scavengers (sodium sulfite) added. The pH is confirmed with a pH meter (Fisher Scientific Accumet XL 20). The electrode potential is converted from the Ag/AgCl reference to the reversible hydrogen electrode (RHE) reference following the equation below:

$$E_{RHE} = E_{Ag/AgCl} + E^{o}_{Ag/AgCl} + 0.05962\ [V] \cdot pH$$

$$E^{o}_{Ag/AgCl} = 0.1976\ [V_{RHE}]$$

The photoanodes are illuminated from the back, i.e., through the ITO back contact, by simulated solar radiation from a 150 W xenon lamp equipped with an AM 1.5G filter (Newport). The incident light power is adjusted to a nominal power of 100 mW cm^{-2}, according to the measurement by a calibrated Si solar cell (Newport). For linear scan voltammetry (LSV), the scan rate is kept at 0.05 V/s. All PEC results shown here are average values obtained from two times of scan.

Electrochemical impedance spectroscopy (EIS) was performed at a DC bias of 0.5 V under AM 1.5 G illumination (frequency range: 100 kHz ~ 1 Hz).

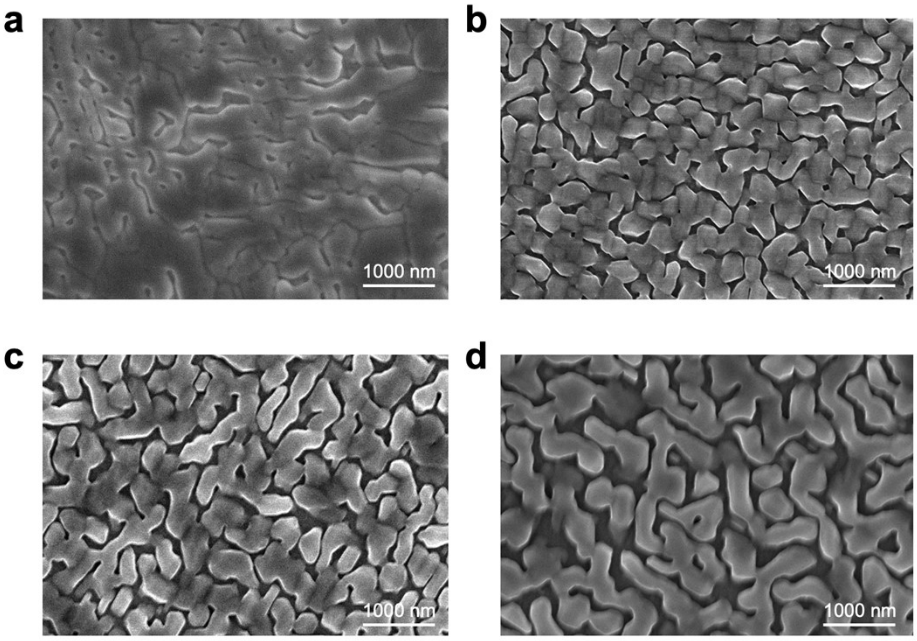


Figure S1. SEM images of BVO film deposited over YSZ (110), using the one-step method, at the substrate temperatures of (a) 650°C, (b) 675°C, (c) 700°C, and (d) 725°C. The BVO coverages of the 4 panels are respectively 83.2%, 81.1%, 87.7%, and 82.8%.

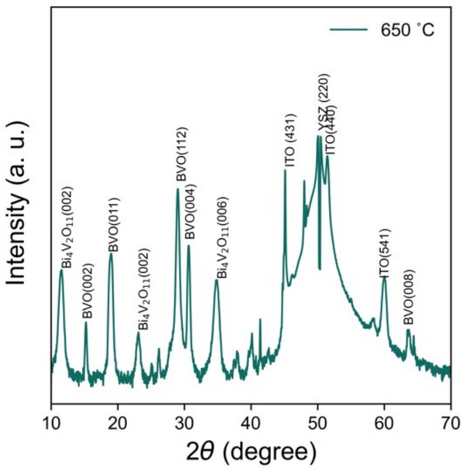


Figure S2. XRD pattern of BVO over YSZ (110) with one step deposition, at the substrate temperature of 650°C.

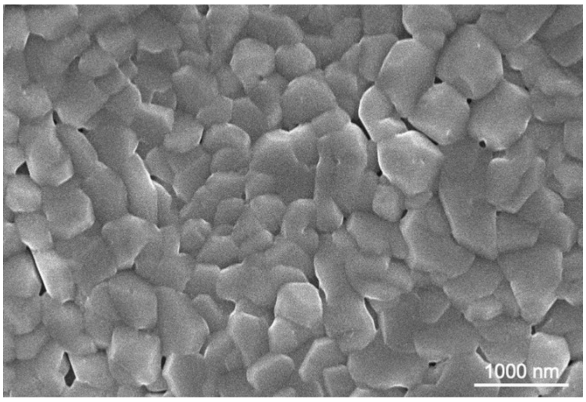


Figure S3. SEM images of BVO film deposited over YSZ (110) at 675°C using the one-step method, with 10000 laser pulses at 1 Hz repetition rate.

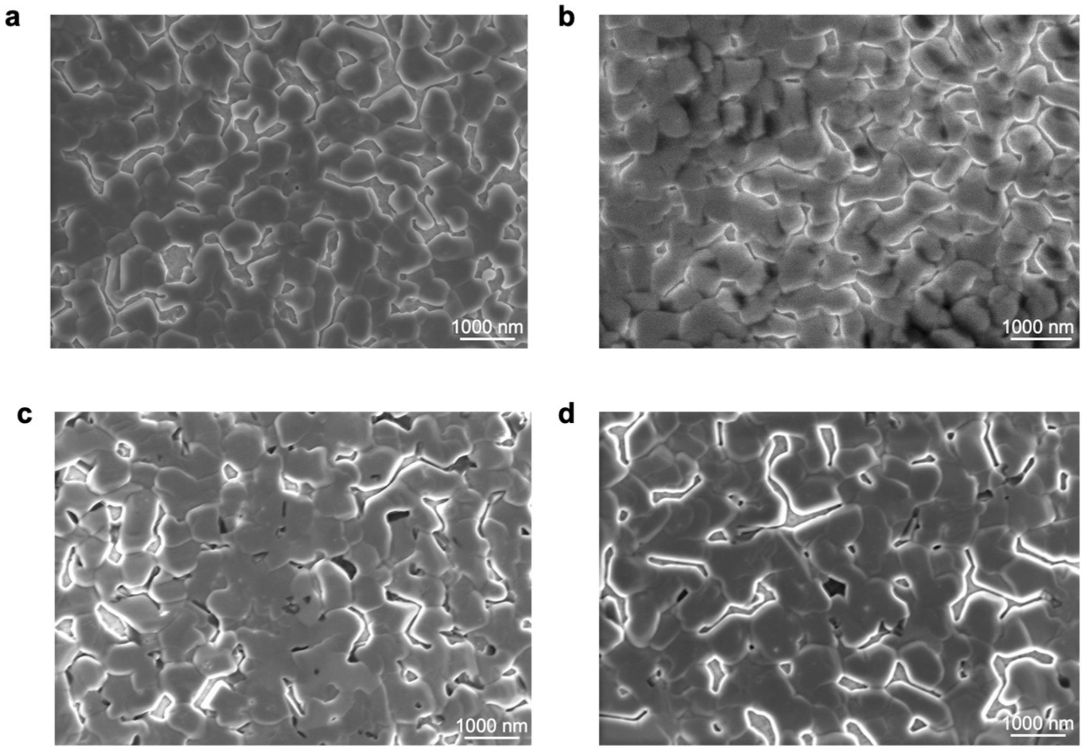


Figure S4. SEM images of BVO over YSZ (110) by two-step-deposition (TSD) method, with different temperature decreasing rate after the deposition is finished: (a) 5 ˚C min^{-1}; (b) 10 ˚C min^{-1}; (c) 20 ˚C min^{-1}, and (d) 25 ˚C min^{-1}.

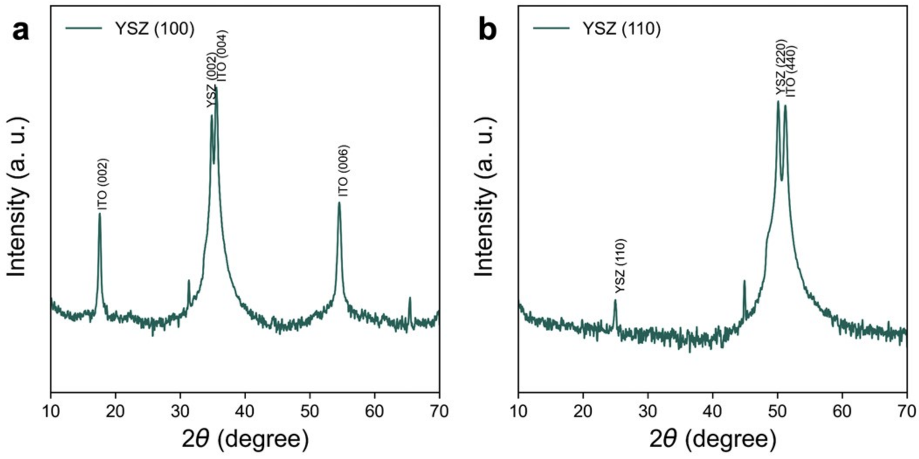


Figure S5. XRD patterns of ITO over YSZ substrates (a) ITO/YSZ (100), and (b) ITO/YSZ (110).

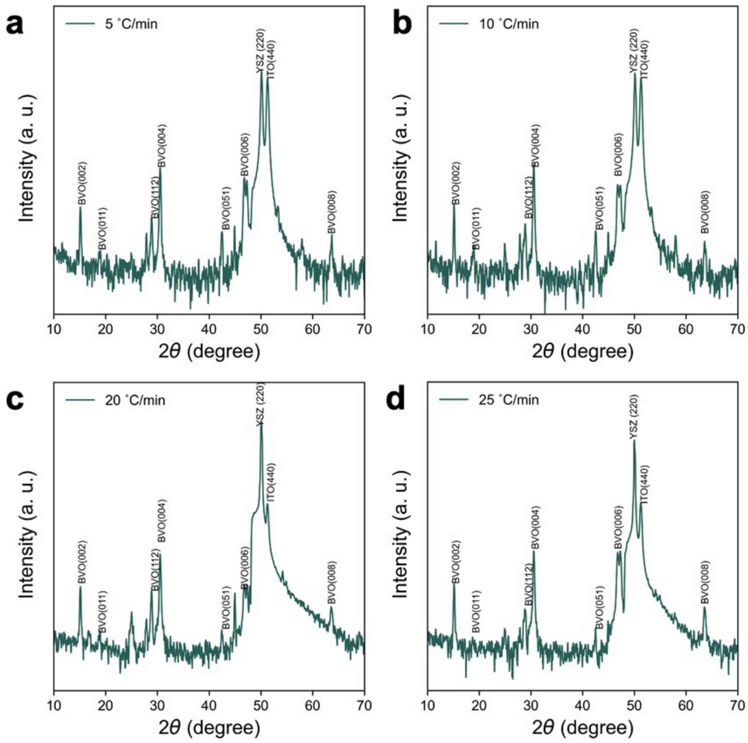


Figure S6. XRD patterns of BVO thin films deposited over YSZ (110) substrates using the TSD method, with post-growth cooling rates of (a) 5°C min^{-1}, (b) 10°C min^{-1}, (c) 20°C min^{-1}, and (d) 25°C min^{-1}.

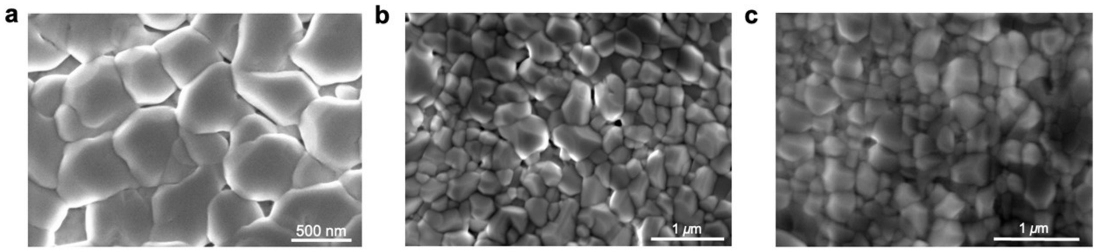


Figure S7. SEM images of BVO/ITO/YSZ (110) by the TSD method, with different oxygen pressure during deposition: (a) 15 mTorr; (b) 30 mTorr and (c) 60 mTorr.

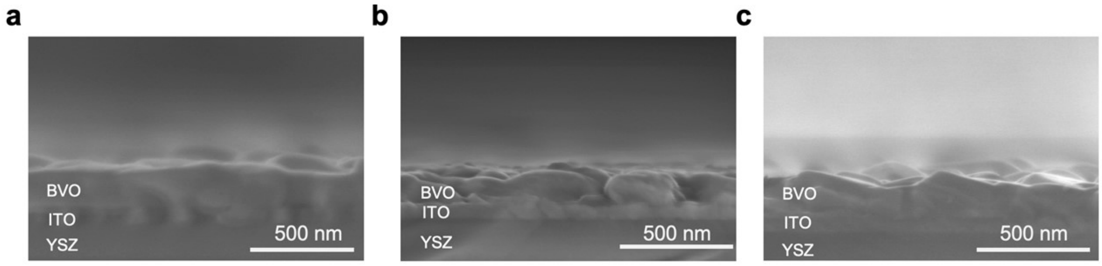
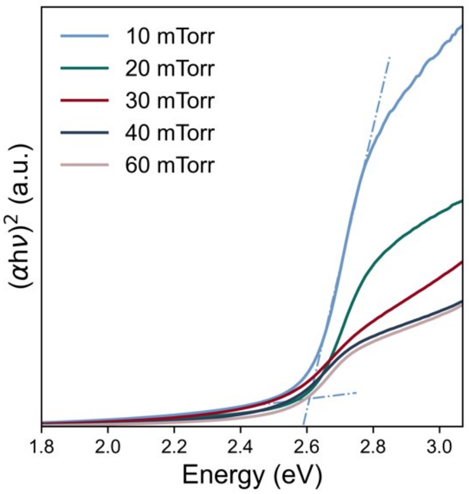


Figure S8. Cross-section SEM images of BVO thin film over YSZ (110) with two step deposition, under (a) 10 mTorr; (b) 20 mTorr; (c) 40 mTorr.



Oxygen Pressure /mTorr	**Band gap/ eV**
10	2.60
20	2.60
30	2.55
40	2.54
60	2.54

Figure S9. Tauc-plot of BVO fabricated by TSD method under different oxygen pressure from 10 mTorr, 20 mTorr, 30 mTorr, 40 mTorr, and 60 mTorr, and their according band gaps achieved from Tauc-plot (right Table).

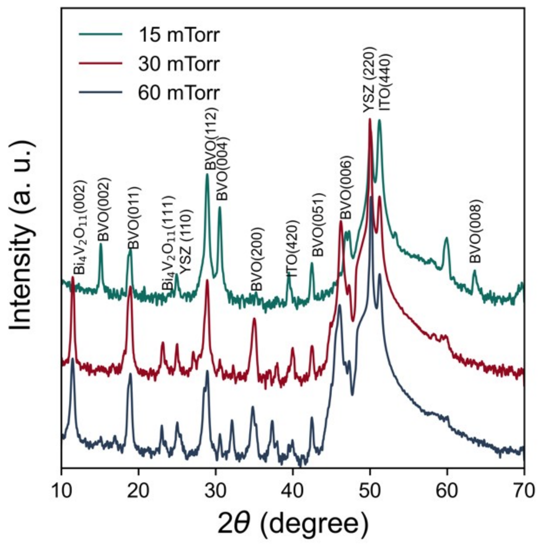


Figure S10. XRD pattern of BVO thin film over YSZ (110) with two step deposition (TSD) under conventional deposition condition, with different oxygen pressure during deposition, from top to bottom, 15 mTorr, 30 mTorr and 60 mTorr, respectively.

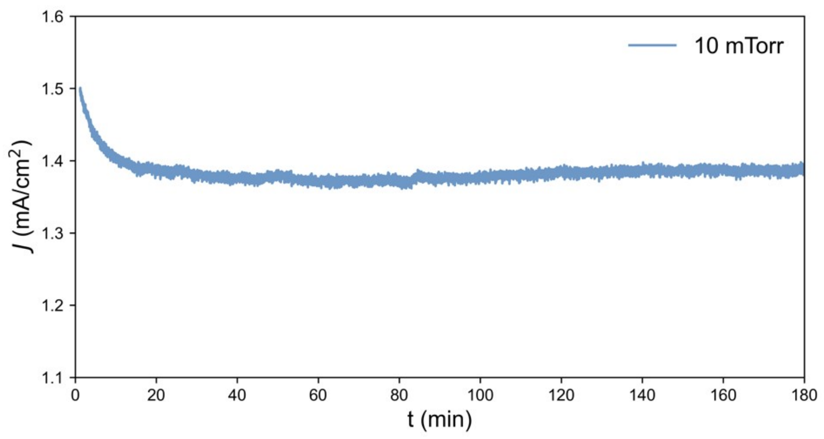


Figure S11. J-t plot of BVO/ITO/YSZ (110) photoanode with two step deposition (TSD) grown under 10 mTorr oxygen pressure.

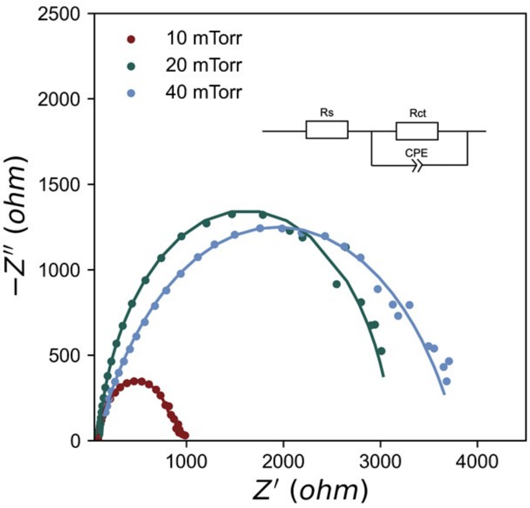


Figure S12. Nyquist plot of TSD BVO/ITO/YSZ (110) photoanodes grown under different oxygen pressure.

Table S1. R_s and R_{ct} resistance values from EIS of BVO photoanodes with TSD under different oxygen pressure.

Oxygen Pressure/mTorr	R_s/Ω	R_{ct}/Ω
10	88	785
20	95	3031
40	84	3711