Supplemental Information for:

Chemical and Electronic Structure Analysis of a $SrTiO_3$ (001) / *p*-Ge (001) Hydrogen Evolution Photocathode

Kelsey A. Stoerzinger[1,*], Yingge Du[1], Steven R. Spurgeon[2], Le Wang[1], Demie Kepaptsoglou[3,4,5], Quentin M. Ramasse[3,6,7], Ethan J. Crumlin[8], Scott A. Chambers[1,*]

[1] Physical and Computational Sciences Directorate, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland WA 99352, USA

[2] Energy and Environment Directorate, Pacific Northwest National Laboratory, 902 Battelle Blvd, Richland WA 99352, USA

[3] SuperSTEM, SciTech Daresbury Campus, Daresbury, WA44AD, UK

[4] Jeol Nanocentre, University of York, Heslington, York, YO10 5BR, UK

[5] Department of Physics, University of York, Heslington, York, YO10 5BR, UK

[6] School of Chemical and Process Engineering, University of Leeds, Leeds, LS2 9JT, UK

[7] School of Physics, University of Leeds, Leeds, LS2 9JT, UK

[8] Advanced Light Source, Lawrence Berkeley National Laboratory, Berkeley, California 94720, USA

***kelsey.stoerzinger@pnnl.gov; sa.chambers@pnnl.gov**

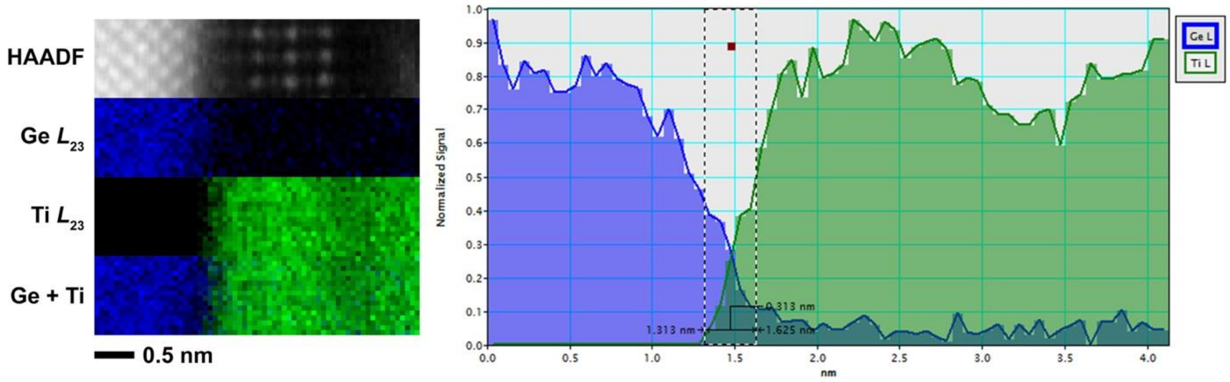

Figure S1: Left: STEM-EELS composition maps of a 5 u.c. $SrTiO_3$ / *p*-Ge (001) film measured at 60 kV, showing the integrated Ge $L_{2,3}$ and Ti $L_{2,3}$ edge signals along the Ge [100] zone-axis. Right: Line profiles extracted from the maps, highlighting the sharp interface between the film and substrate. The maps have been normalized to the signal extrema on either side of the interface. Some beam damage has occurred near the surface (right side) of the map.

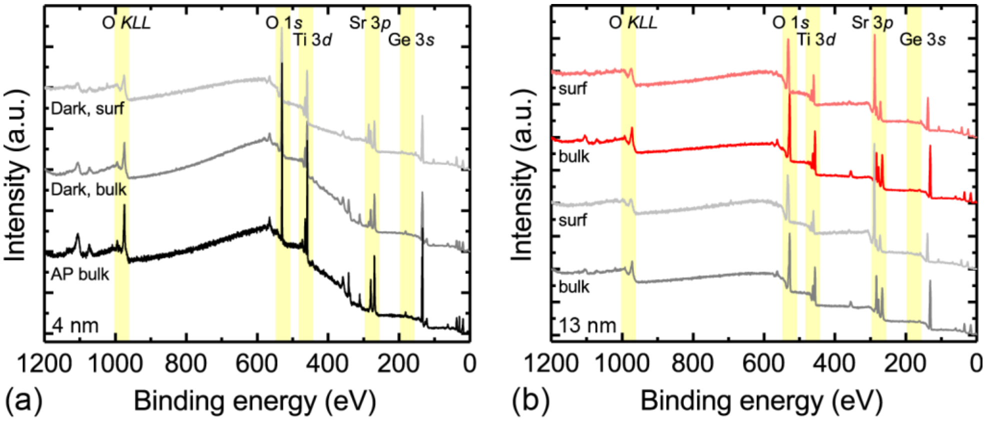

Figure S2: Surveys with an Al K-alpha source (IPE *hν* = 1486 eV) at 90° (bulk) and 20° (surf) incidence. highlighting some of the key core level and Auger features. (a) For 4 nm $SrTiO_3$ / Ge, a small amount of Ge intensity (core levels and Auger features) can be observed through the thickness of the 4 nm film due to the large information depth of high kinetic energy photoelectrons. (b) For 13 nm $SrTiO_3$ / Ge, no Ge is observed. On both films, carbon is present after measurements in both the dark (gray) and light (red).

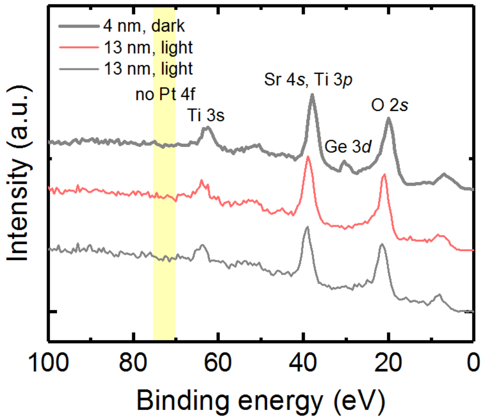

Figure S3: Narrowed region of surveys with an Al K-alpha source (IPE *hν* = 1486 eV) at 20° incidence to obtain more signal from the film surface. For the 4 nm $SrTiO_3$ after cycling in the dark (bold gray) and the 13 nm film after cycling in the dark (thin gray) and light (thin red), the lack of a peak in the highlighted region of the Pt 4f indicates no Pt is deposited during cycling.

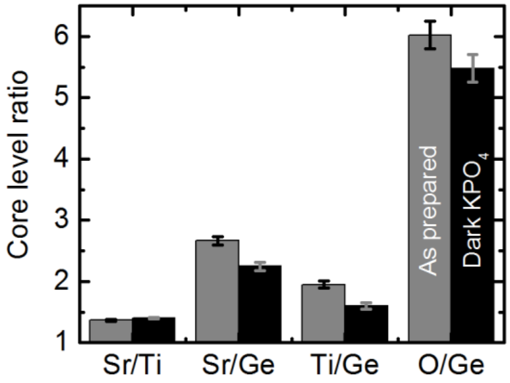

Figure S4: Core level ratios probed with Al K-alpha source in UHV: Sr 3d, Ti 2p, Ge 3d, and O 1s for 4 nm $SrTiO_3$ / Ge. Error bars obtained from compounded standard deviations in CasaXPS. Compared to the 'as prepared' film measured directly after growth, the film HER cycled in 0.1 M potassium phosphate buffer (pH 7) maintains the same Sr/Ti ratio, giving no indication of preferential Sr leaching. However, the cycled film shows some reduction in the film peaks relative to the Ge substrate, indicating stoichiometric removal of the film during cycling – possibly due to corrosion of the underlying substrate at pinhole defects.

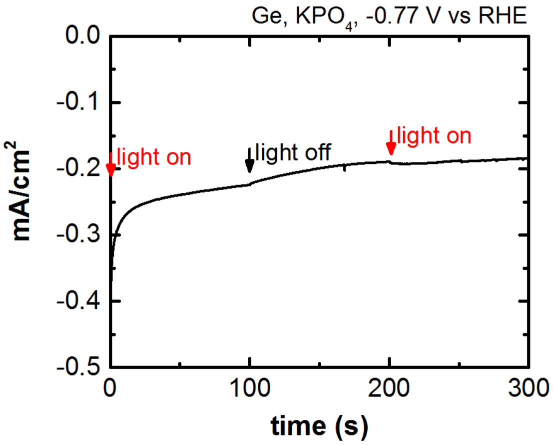

Figure S5: Chronoamperometry of bare Ge wafer at -0.77 V vs RHE in pH 7, 0.1 M phosphate buffer. The HER current decreases with time, and no change in current is observed with illumination by a 630 nm red LED.

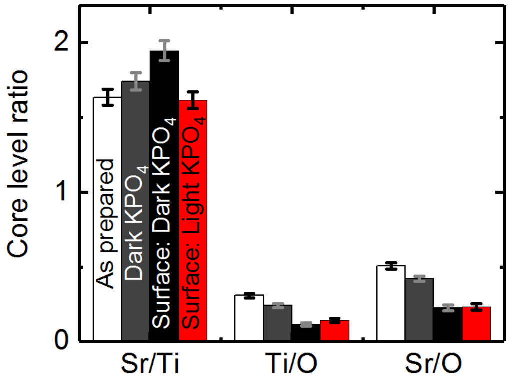

Figure S6: Core level ratios probed with Al K-alpha source in UHV: Sr 3d, Ti 2p, and O 1s for 13 nm $SrTiO_3$ / Ge. Error bars obtained from compounded standard deviations in CasaXPS. Compared to the 'as prepared' film measured directly after growth measured at 90° (white), the film HER cycled in 0.1 M potassium phosphate buffer (pH 7) in the dark maintains the same Sr/Ti ratio when measured at 90° (dark gray), giving no indication of preferential Sr leaching. After cycling under illumination (20°, red), the Sr/Ti ratio at the surface decreases, potentially indicative of slight Sr leaching. The decrease in the Ti/O and Sr/O ratios decrease upon cycling is likely due to the formation of oxygen adsorbates from interaction with H_2O and/or the electrolyte.

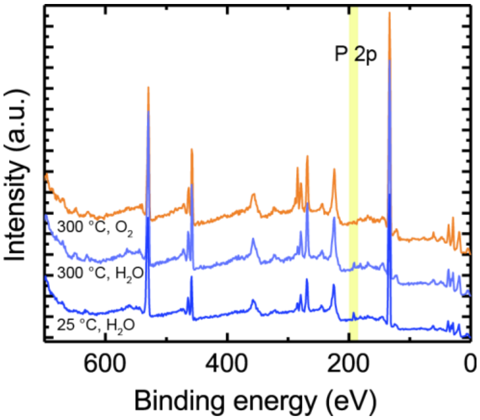

Figure S7: Surveys at an IPE of $h\nu$ = 735 eV. The $SrTiO_3$ surface exhibits only the expected features from Sr, Ti, O and trace C at the noted temperature and 100 mTorr of the noted atmosphere, aside from a small intensity in the P 2p region likely attributed to PO_4 formation in H_2O.

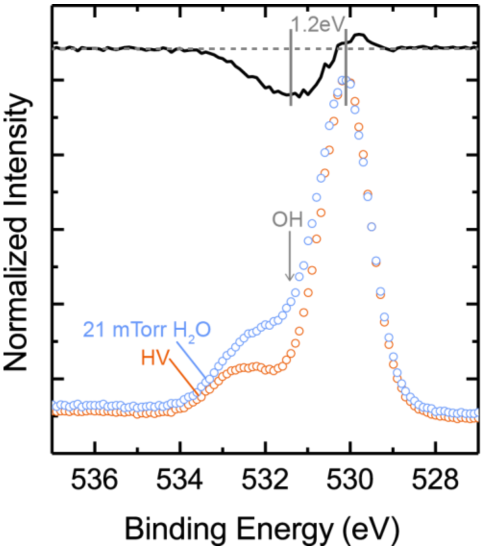

Figure S8: O 1s spectra at 300 °C in high vacuum after O_2 exposure (orange) and while dosing H_2O, at ~21 mTorr H_2O (blue), probed with an IPE of *hν* = 690 eV. The difference spectra (black) illustrate that the OH species formed by H_2O dissociation on the surface are at ~1.2 eV above the bulk BE. The BE scale was calibrated using the Au 4f of a foil pressed onto the surface.

Table S1: O 1s fitting parameters in CasaXPS. GL indicates the percent Lorentzian component to a mixed Gaussian-Lorentzian line shape. The position of the surface feature was not constrained, but we note the fit for both O_2 and H_2O environments resulted in the component locating at ~532.7 eV. For OH and CO_3, the location was fixed relative to that of the bulk oxygen component. The BE scale was calibrated using the Au 4f of a foil pressed onto the surface.

	Bulk Ox	**Surf**	**OH**	**CO_3**	**H_2O_{vap}**
GL	40	50	0	0	0
FWHM	1-1.5	1.4-1.7	1.5-1.7	1.5-1.7	<1
Pos.		~532.7	+1.2	+2.35	

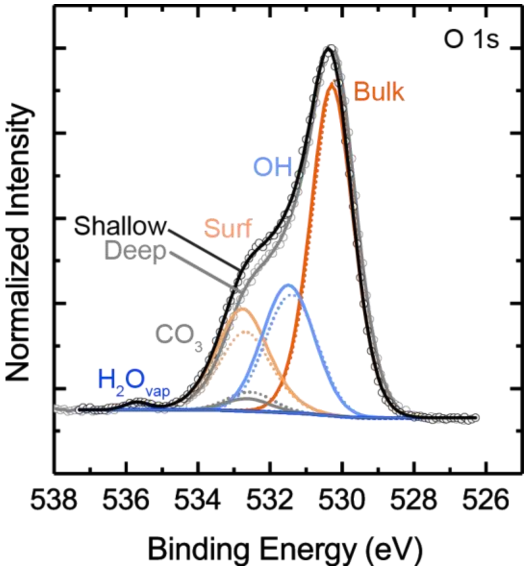

Figure S9: Depth profiling of the O 1s core level at 300 °C in 100 mTorr H_2O, Shirley-background subtracted and normalized to the maximum intensity. Using a shallow incident photon energy (IPE, black/solid) of *h*ν = 690 eV highlights species located on top of the bulk component (orange) – the "surface" peak (peach) and OH (light blue) – compared to the deep IPE (gray/dashed) of *h*ν = 735 eV.

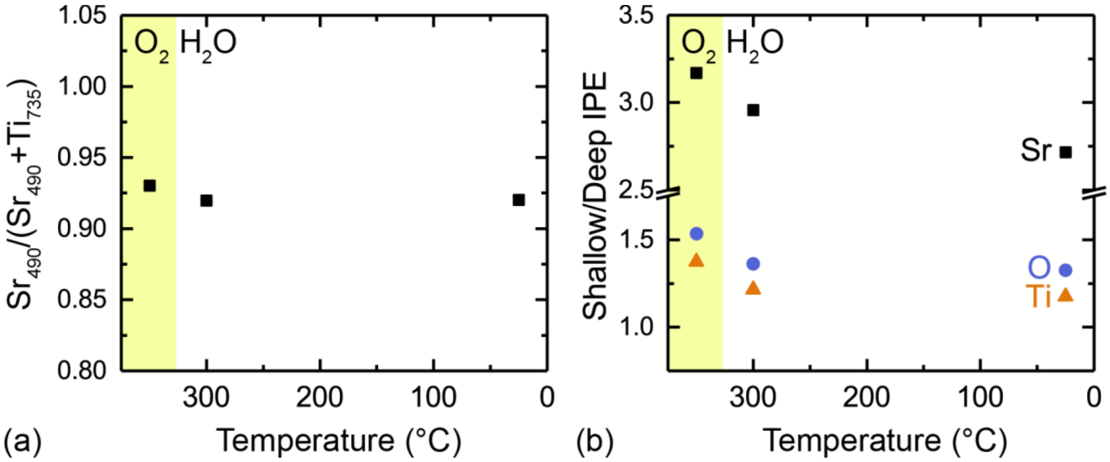

Figure S10: Quantification of surface stoichiometry during AP-XPS, measured at 300 °C in 100 mTorr O_2 (yellow bar) and at noted temperature in 100 mTorr H_2O (white region). (a) Cation ration: Sr 3d/(Sr 3d + Ti 2p), measured with an incident photon energy (IPE) of *h*ν = 490 and 735 eV, respectively, to give comparable kinetic energies and thus inelastic mean free paths. (b) Ratio of shallow/deep IPE of Sr (black, 490 eV/690 eV), O (blue, 690 eV/735 eV), and Ti (orange, 690 eV/735 eV). All ratios remain similar regardless of sample temperature and environment, showing no indication of e.g. Sr segregation.