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Supporting Information

for *Adv. Mater. Interfaces,* DOI: 10.1002/admi.202002257

Interaction of Water with Atomic Layer Deposited Titanium Dioxide on p-Si Photocathode: Modeling of Photoelectrochemical Interfaces in Ultrahigh Vacuum with Cryo-Photoelectron Spectroscopy

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XPS Si2p

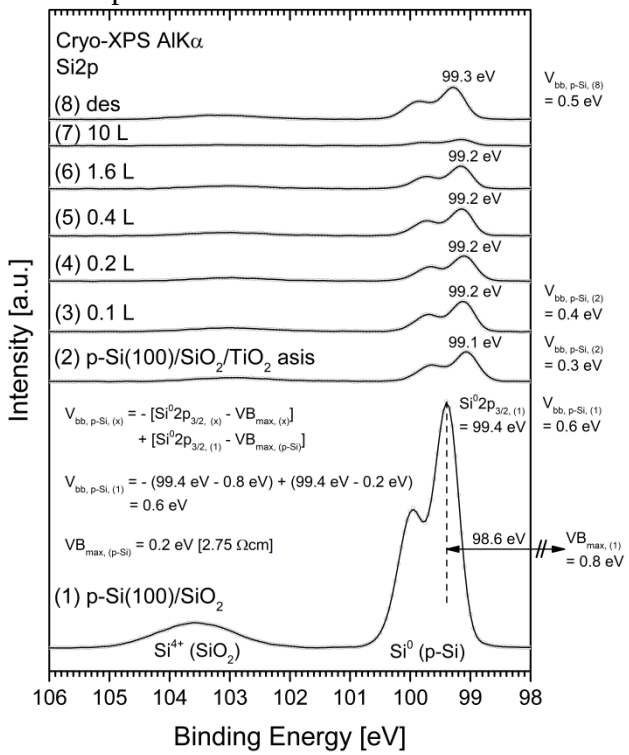

Figure S1. Cryo-XPS AlK_α Si2p spectra of the p-Si(100)/SiO_2 interface prior to the atomic layer deposition of TiO_2 as well as of the subsequential water adsorption on p-Si/SiO_2/TiO_2, followed by water desorption. Before TiO_2 deposition, the $Si2p_{3/2}$ peak of the p-Si is settled at 99.4, while the emission of Si^{4+} (SiO_2) is found at 103.6 eV. The oxidation state Si^{4+} states, that the SiO_2 layer is almost completely SiO_2. After the atomic layer deposition of TiO_2, a shift of 0.3 eV towards lower binding energies is observed. Upon water adsorption, in contrary to the TiO_2 core level in Fig. 5, a shift of 0.1 eV to higher binding energies is observed. With the equation given in the figure, the band bending $V_{bb,\ p\text{-}Si,\ (x)}$ in the p-Si at the p-Si/SiO_2 interface can be calculated for each experimental step x. $VB_{max,\ (x)}$ indicates the energy cut-off of the valence band maximum at the experimental step x, which was measured but is not shown here. For step 0 (pristine p-Si) $VB_{max,\ (0)}$ = 0.2 eV was derived from the doping concentration and the resulting specific resistance, which is known.

UPS HeII

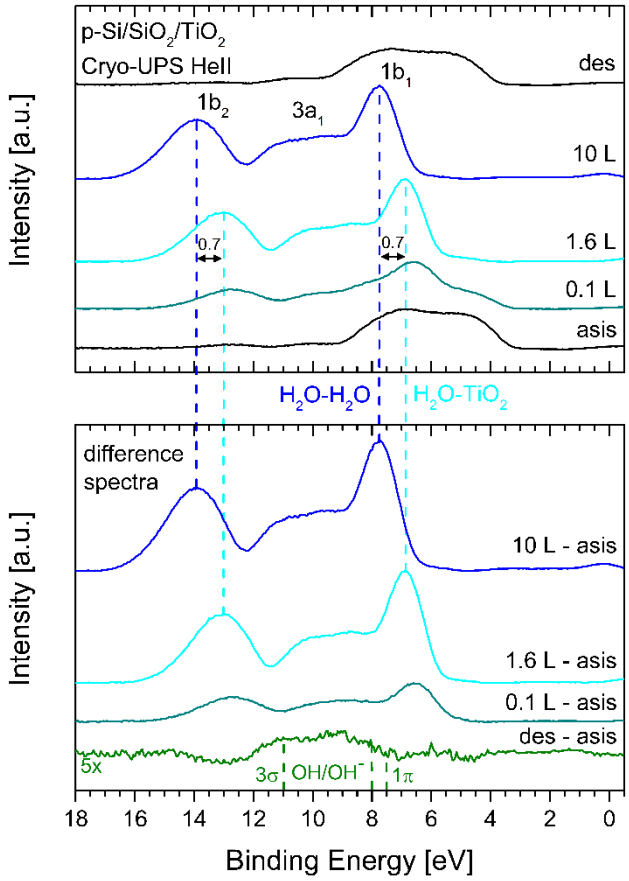

Figure S2. UPS HeII spectra and respective difference spectra for the water adsorption experiment on TiO_2. The binding energy difference between the H_2O-TiO_2 species and the H_2O-H_2O species is 0.7 eV, just as for the UPS HeI spectra in Figure 6. After desorption, chemisorbed OH and OH^- species can be detected on the surface to a very small extent. The presence of gap states in the HeII spectra could not be evaluated, since the HeII satellites directly interfere with the band gap region and satellite subtraction is more sophisticated than for HeI.