Supplementary Material

Stable and tunable phosphonic acid dipole layer for band edge engineering of photoelectrochemical and photovoltaic heterojunction devices

René Wick-Joliat¹, Tiziana Musso¹, Rajiv Ramanujam Prabhakar¹, Johannes Löckinger², Sebastian Siol², Wei Cui¹, Laurent Sévery¹, Thomas Moehl¹, Jihye Suh¹, Jürg Hutter¹, Marcella Iannuzzi¹, S. David Tilley^{1*}

- Department of Chemistry, University of Zurich, Winterthurerstrasse 190, CH-8057 Zürich, Switzerland
- (2) EMPA, Überlandstrasse 129, CH-8600 Dübendorf, Switzerland
- * Email: <u>david.tilley@chem.uzh.ch</u>

Contents

Experimental	2
Sample fabrication	2
Characterization	3
Computational details	4
' Supporting tables	5
Supplementary Figures	6
Supporting References	26

Experimental

Sample fabrication

Si wafer cleaning and etching. p-Si wafers were bought from Sil'Tronix, France, (Boron doping, 10-30 Ohm·cm, single side polished) and cut into 1x1cm pieces, which were then cleaned by ultrasonicating for 10 min each in acetone, soapy water (Deconex), water and ethanol, followed by 10 min at 50 °C in $H_2O/H_2O_2/NH_4OH$ (5:1:1) solution, 10 min at 50 °C in $H_2O/H_2O_2/HCI$ 5:1:1 solution and 30 s in 2% HF solution at room temperature. Samples were then rinsed with water, dried in N₂ stream and immediately used for the next steps.

Anchor layer deposition. All anchor layers were deposited by ALD onto freshly cleaned and etched Si wafer pieces using a Picosun R-200 machine. TiO₂ deposition was carried out at 120 °C using sequential pulses of tetrakis(dimethylamino)titanium (T precursor: 85 °C) and H₂O (T precursor: 25 °C). Ten cycles were used for anchor layer yielding amorphous TiO₂ films with a thickness of 0.5 nm (0.52 Å/cycle), as determined by ellipsometry. Al₂O₃ deposition was done at 120 °C using pulses of trimethylaluminium (T precursor: 25 °C) and H₂O (T precursor: 25 °C). Unless stated otherwise, 5 cycles were deposited yielding Al₂O₃ thicknesses of 0.5 nm. For Ga₂O₃ deposition, a higher temperature of 160 °C was used with pulses of tris(dimethylamido)gallium (T precursor: 150 °C) and H₂O (T precursor: 25 °C). 10 cycles were used to obtain Ga₂O₃ thicknesses of 0.5 nm.

PA spin coating, annealing and rinsing. Solutions of phosphonic acid (**PA**, H₃PO₃, 99%, Sigma-Aldrich) in EtOH were spin coated onto Si wafer pieces at 2000 rpm for 20-30 s with an acceleration of 500 rpm/s. Typically, 0.1 ml of PA solution was used. After spin coating, the samples were annealed on a hot plate in air at 120 °C for 10 min, allowed to cool down to ~80 °C on the hot plate (ca. 30 min) and then quickly cooled to room temperature by removing them from the hot plate. The samples were then rinsed under a stream of EtOH for 2-3 s and then dried in a stream of N₂.

Different phosphonic acids. Layers of methylphosphonic acid (MPA, CH_5O_5P , 98%, Sigma-Aldrich), phosphoric acid (H_3PO_4 , 99.999%, Sigma-Aldrich), fluorophosphoric acid (FPA, H_2FO_3P , 70 wt% in H_2O , Sigma-Aldrich), hydroxybenzylphosphonic acid (HBPA, $C_7H_9O_4P$, 97%, Sigma-Aldrich) were spin coated from 10 mM ethanolic solutions, annealed and rinsed with the same procedure used for PA.

TiO₂ ALD. ALD of the protective layer was carried out analogously to TiO_2 anchoring layer but using 930 cycles, yielding 50 nm of TiO_2 .

Pt sputtering. To finalize the PEC cells, 1 nm of Pt was sputtered using a Safematic CCU-010 device.

AZO/Ni. For PV cells, the front contact was fabricated by sputtering 260 nm of Al:ZnO (2% at Al, 1.8 W cm⁻²) and 105 nm of MgF₂. A 4 μ m Ni/Al grid was deposited by e-beam evaporation.

Sb₂Se₃ fabrication. Sb₂Se₃ thin films were prepared by selenization of electrodeposited Sb as reported elsewhere.¹ Briefly, Sb metal was electrodeposited on Au coated FTO substrates using an electrolyte of antimony potassium tartarate and citric acid with the pH adjusted to 1.3 by addition of concentrated sulfuric acid. After electrodeposition the samples were annealed in a tube furnace at 350 °C in the presence of Se.

Cu₂O fabrication. Electrodeposition substrates were prepared by sputtering 100 nm of Au onto FTO coated glass. Cu₂O was electrodeposited at 30 °C in galvanostatic mode at a current density of -0.1 mA/cm² for 100 min using a Keithley source meter. The aqueous copper sulfate solution was prepared with the following initial concentrations: 0.2 M CuSO₄ (Sigma-Aldrich, \geq 99%), 0.5 M K₂HPO₄ (Sigma-Aldrich, \geq 99.5%), 3 M lactic acid (Fisher Scientific, 85%). The pH was adjusted to 12 by adding 2 M KOH (Honeywell, extra pure).

Characterization

Ellipsometry. Thicknesses of PA layers as well as TiO_2 , Al_2O_3 , Ga_2O_3 layers deposited by ALD were measured using a J.A. Woollam Co. alpha-SE ellipsometer with standard scan speed at 65° and 70°. The layers were modeled with a Si substrate and transparent film on top.

JV, CA (PEC). Electrochemical measurements were conducted in 1 M H_2SO_4 using a Biologic SP-200 potentiostat equipped with impedance module. Pt wire was used as counter electrode and Hg/HgSO₄ as reference electrode (+0.634 V vs RHE). Current-Voltage sweeps were recorded at scan velocities of 10 or 20 mV/s, in the dark, under 1 sun illumination (AM1.5, LOT mercury lamp solar simulator) or under chopped illumination (1 sec chopping). The photocathode n-Si/TiO₂/Ni was measured in 1 M KOH using Ag/AgCl as reference. Chronoamperometric measurements were performed by applying 0 V_{RHE} under 1 sun illumination.

JV, EQE, stability (PV). A Keithley 2400 source meter with four-terminal sensing was used to record J-V curves under standard test conditions (1000 W m⁻², 298 K, ABA solar simulator). External quantum efficiency (EQE) spectra were recorded at 298 K using a triple-grating monochromator with a chopped white light source and a lock-in amplifier with 100 W m⁻² white light bias. Data was referenced to a monocrystalline Si solar cell certified by Fraunhofer ISE. Stability of the PV cells was tested in a heat-light soaking experiment at 80 °C under 1 sun illumination at maximum-power-point in dry N₂ atmosphere. An I-V curve was recorded every 30 min.

Electrochemical Impedance Spectroscopy (EIS). The space charge capacitance (C_{sc}) was obtained from EIS measurements. From C_{sc} in the depletion region the doping density, flat band potential and n- or p-type character of a semiconductor can be obtained using Mott-Schottky analysis. The measurements on PV cells were performed on solar cells using a BioLogic SP-200 potentiostat in two electrode configuration in the dark and light with frequencies from 1 MHz to 0.1 Hz with potential steps of 25 or 50 mV with a waiting time of 10 s after each potential step. FTO/TiO₂/PA samples were measured in PEC mode with three electrode configuration in 1 M H₂SO₄ (pH 0) or 1 M Na₂SO₄ (pH 2) with mercury sulfate reference electrode in the dark. A frequency range from 200 kHz to 0.1 Hz and potential steps of 25 mV or 33 mV were used. For both cases (PV and PEC) a voltage perturbation of 10 mV was applied. The data was fitted with ZView software. A constant phase element (CPE) was used to model the space charge capacitance and the CPE was then converted to C_{sc} using equation 1:

$$C_{sc} = \frac{\left(R_{ct} \times Q\right)^{\binom{l}{n}}}{R_{ct}}$$
(1)

with R_{ct} being the charge transfer resistance, Q the charge from the CPE and n as the CPE exponent. The flat band potential (E_{fb}) and doping density (N_A) were obtained by plotting $1/C_{sc}^2$ versus the applied potential, giving E_{fb} as the x-axis intercept and the doping density as the slope according to the Mott-Schottky equation (eq 2):

$$\frac{1}{C_{sc}^2} = \frac{2}{N_A \varepsilon \varepsilon_0 q} (E - E_{fb} - \frac{kT}{q})$$
(2)

with q as the electron charge, ε as the dielectric constant of the material, ε_0 as permittivity of free space, and N_A as acceptor density (for p-type materials, N_D for n-type semiconductors), E is the applied potential, k is the Boltzmann constant and T is the temperature.

Atomic force microscopy (AFM, VEECO E-Scope) was performed to retrieve information about the surface topography of the sample. The measurement was performed in tapping mode using a Pt–Ir metal coated tip with a nominal spring constant $k = 2.8 \text{ Nm}^{-1}$ and a resonance frequency of 100 kHz.

X-ray photoelectron spectroscopy (XPS) was conducted using a Physical Electronics (PHI) Quantum 2000 spectrometer featuring monochromatic Al-K α radiation, generated from an electron beam operated at 15 kV and 35.8 W. The energy scale of the instrument was calibrated using Au and Cu reference samples. The analysis was conducted at 2 E⁻⁹ mbar, with an electron take off angle of 45° and a pass-energy of 23.5 eV for all samples. The measurements were conducted without charge neutralization. Spectra of select samples were fitted using Voigt profiles (GL30) after Shirley background subtraction. A doublet splitting of Δ E = 0.63 eV was used for the Si 2p core level emission, whereas a single Voigt profile was used to fit the Al 2p.

Electrospray-ionisation mass spectroscopy (ESI-MS). High-resolution mass spectra were acquired on a QExactive instrument (ThermoFisher Scientific) equipped with a heated electrospray ionization source. PA was spin coated onto p-Si/Al₂O₃, annealed and then rinsed with EtOH and dried in N₂ stream. The sample was then ultrasonicated in 1 ml of 1 mM NaOH to remove the compounds bound to the Si surface, and the obtained solution was analyzed by HR-ESI-MS.

SEM-EDX. SEM images were obtained from a Zeiss Supra 50 VP equipped with EDX detector Oxford X-MAX80. An electron beam voltage of 10 kV was used. Images were recorded using the in-lens detector.

Computational details

Kohn-Sham level DFT simulations with the Gaussian and plane wave (GPW) formalism have been carried out with the CP2K/QUICKSTEP package.^{2,3} Triple-zeta valence plus polarization basis (TZVP) have been employed for all atomic kinds. Goedecker-type pseudopotentials⁴ have been used, respectively with 12, 6, 1, 5 valence electrons for Ti, O, H and P. Convergence of the basis set, surface energy and cut-off values have been carefully checked. The Perdew-Burke-Ernzerhof (PBE)⁵ exchange-correlation functional, based on the general gradient approximation (GGA), has been used. Dispersion interactions have been accounted for with the Grimme's D3 correction.⁶ The dipole correction⁷ has been used for all dipole computations. Periodic boundary conditions have always been applied.

To simulate the multilayer structures, a crystalline model of PA⁸ approximately 6.5 Å thick, was equilibrated for few picoseconds at 300 K, with *ab-initio* molecular dynamics simulations, on top of the titania with a maximum coverage of PA molecules.

The work function (Φ) is generally defined as the difference between the vacuum level (V_0) and the Fermi energy (E_f) of the system under study: $\Phi = (V_0 - E_f)$. In the case of thin slabs, this definition becomes problematic, as Φ can be affected by size related quantum oscillations, showing a slow convergence with slab thickness.⁹ For finite-size slabs, Φ can alternatively be computed as the difference between the electrostatic potential in vacuum, V_0^{slab} , and the averaged electrostatic potential inside the slab, V_m^{slab} , referenced to the Fermi energy of the oxide:

 $\Phi = (V_0^{slab} - V_m^{slab} - E_f^{bulk})$

where E_{f}^{bulk} is computed from a bulk calculation.^{9,10} With this macroscopic averaging technique it is possible to obtain accurate work function values for thin slabs, since quantum-size effects are reduced.⁹

Supporting tables

Table 1: Performance of PV cells in Figure 1E.

sample	PCE (%)	V _{oc} (V)	J _{sc} (mA/cm ²)	FF (%)
p-Si/TiO ₂	2.6	0.237	31.9	34.4
p-Si/dipole/TiO ₂	6.2	0.430	32.2	45.1

Table 2: Performance of PEC cells in Figure 1E. The onset potential was defined as the potential where the photocurrent reaches 0.5 mA/cm².

sample	ABPE (%)	V _{onset 0.5mA/cm2} (V _{RHE})	J at 0 V RHE (mA/cm ²)
p-Si/TiO ₂	1.5	0.190	23.9
p-Si/dipole/TiO ₂	4.8	0.404	24.6

Supplementary Figures

S1: Different anchor layers



Supplementary Figure 1. A: J-V plots of devices with the general structure p-Si/anchor layer/TiO₂/Pt (Blank) or p-Si/anchor layer/dipole/TiO₂/Pt (Dipole) recorded in 1M H_2SO_4 under 1 sun illumination. B: J-V plots of devices with varied Al_2O_3 anchor layer thickness. Scy denotes that the layer was deposited using 5 subsequential pulses of trimethylaluminium and water in the ALD process. Illumination was chopped once per second.

Discussion: We tried a variety of oxides that are available in our lab. We assume that the biggest shift is obtained on Al_2O_3 for one of the following reasons (and maybe a combination of both): Firstly, a very thin anchor layer is desired to assure a low series resistance and the $AlMe_3/H_2O$ ALD process for Al_2O_3 is very well behaved, likely giving a uniform ultrathin film, as compared to the TDMAT/H₂O process for TiO₂, which is less well behaved, necessitating thicker layers to be completely blocking.¹¹ Therefore, we can expect a more uniform binding of PA. Secondly, Al_2O_3 is known for its good surface passivation properties,¹²⁻¹⁴ and we argue that the biggest shifts can only be obtained on substrates with low surface state concentration.



Supplementary Figure 2. J-V plots of different devices recorded in 1M H₂SO₄ under 1 sun illumination.

Discussion: The onset potential of p-Si/TiO₂ device is +190 mV (vs. RHE). The introduction of a thin AI_2O_3 layer decreases V_{onset} to +80 mV, while retaining the slope of the J-V curve. This effect could be caused by a parasitic dipole induced by the AI_2O_3 , which is known to passivate Si surfaces through the field passivation effect, where fixed negative charges are present in the AI_2O_3 .^{12–14} If that is the case, those negative charges interacting with the p-Si substrate would shift the bands up and therefore decrease the photovoltage of the p-Si/Al₂O₃/TiO₂ system as compared to p-Si/TiO₂. On the other hand, a PA layer increases V_{onset} by 100 mV to +280 mV even if no anchor layer was deposited. We assume, that in this case a very thin layer of native silicon oxide acts as anchor layer. The presence of a silicon oxide layer, even after HF etching, was also observed in XPS. The SiO₂/PA interface would then act as a dipole as explained in the main text and figure S7 below.



S3: Band diagrams p-Si/n-TiO₂ with and without dipole

Supplementary Figure 3. Band diagrams of p-Si/n-TiO₂ heterojunction without modification (A-D) and with PA dipole layer (E-H). A and E show the bands in flat band condition, B and F after contact and C and G show a full PEC device with increased photovoltage due to the dipole layer in F. D and H show the corresponding J-V curves under illumination for p-Si/TiO₂ and p-Si/PA/TiO₂, respectively.

S4: XPS Phosphorous



Supplementary Figure 4. XPS core level spectra for P 2p (A) and P 2s (B) for p-Si/Al₂O₃/PA (top) and p-Si/Al₂O₃ reference (bottom). The P $2p_{3/2}$ core level binding energy for PA reported in the NIST database¹⁵ (134.30 eV) is marked as black dashed line in A.

S5 : SEM and EDX



Supplementary Figure 5. SEM images (left) and EDX analysis of a small section of the same area (right). A: etched p-Si surface. B: etched p-Si surface with 0.5 nm Al_2O_3 layer. C: p-Si/ Al_2O_3 with PA spin coated. D: p-Si/ Al_2O_3 /PA after annealing, rinsing with EtOH and drying in N_2 stream. Note that the white spots visible in samples A, B and D are dust particles showing a high C content in EDX.

S6: AFM



Supplementary Figure 6. AFM mapping of p-Si with 1 nm TiO_2 layer (A) and p-Si/TiO_2/PA (B). The RMS roughness is <0.5nm for both samples. No increase in surface roughness could be observed after PA treatment suggesting the formation of a uniform and homogeneous PA layer.

S7: ESI-MS



Supplementary Figure 7. High resolution electron spray ionization mass spectrum (HR-ESI-MS). PA was spin coated onto p- Si/Al_2O_3 , annealed and then rinsed with EtOH and dried in N_2 stream. The sample was then ultrasonicated in 1 ml of 1 mM NaOH to remove the compounds bound to the Si surface and the obtained solution was analyzed by HR-ESI-MS, showing that PA is not oxidized during annealing and not washed away by EtOH rinsing.

S8: EQE measurement



Supplementary Figure 8: Quantum efficiency measurements of p-Si/TiO₂ (blank) and p-Si/Al₂O₃/PA/TiO₂ (Dipole) samples.

S9: Dipole Formation



Supplementary Figure 9: A: Schematic representation of -OH terminated TiO_2 with increasing PA surface coverage and PA multilayer. B: Electron withdrawing effect increases from bare TiO_2 to full monolayer. DFT calculations suggest that going from PA mono- to multilayer induces changes at the anchor layer/PA interface, resulting in an increased dipole. These combined effects add up to an increasing dipole over the range of sub-monolayer to full monolayer to multilayer. C: Dipole (Δ) represented as a step in the vacuum energy, with increasing magnitude going from sub-monolayer to multilayer.

S10: PA different binding modes



Supplementary Figure 10. Adsorption energies of different PA binding modes on rutile $TiO_2(110)$. M stands for monodentate, B for bidentate. Pink trends are referred to this work, while violet ones are taken from Luschtinetz et al.¹⁶ The atomic PA structures are shown in the insets. In the B2 mode 2 H atoms of PA form a bond with two adjacent titania O atoms, remaining coordinated to the O atom of PA.

S11: XPS Si/SiO₂



Supplementary Figure 11. A: Comparison of Si, SiO₂ and Al₂O₃ binding energies between reference p-Si/Al₂O₃ and p-Si/Al₂O₃/PA. Compared to the reference sample, the relative binding energies increase more for layers closer to the surface of the sample (i.e. a stronger shift of the core level binding energy is observed for Al₂O₃ and SiO₂ than for Si). These results indicate a strong surface band bending in the PA modified sample. Annealing of the PA layer only has a minor influence on the observed band bending. B: XPS core level spectra for Si 2p and Al 2p for p-Si/Al₂O₃ reference sample (bottom) and p-Si/Al₂O₃/PA sample before (middle) and after annealing and rinsing with ethanol (top). C: Band diagram (only E_{vac} shown, but all other band should have the same shape) without and with PA modification in order to explain why the binding energy difference is biggest for layers closer to the surface. The band bending in the base case is unknown and we only measure the relative band bending difference induced by the PA. The band bending of the blank samples is therefore set to zero in A and C.



Supplementary Figure 12. Current-Voltage plot of n-Si/TiO₂/Ni (red) and n-Si/anchor layer TiO₂/PA dipole/TiO₂/Ni (blue). Cyclic voltamograms recorded in 1 M KOH electrolyte under 1 sun illumination at 10 mV s⁻¹ scan speed. The redox pair before the water oxidation onset shows reduction/oxidation of the Ni catalyst. Both, Ni redox peaks and water oxidation onset, are shifted by 200 mV to more positive voltages, indicating a smaller photovoltage upon PA modification of the heterojunction.

S13: Band diagram n-Si/PA/TiO₂



Supplementary Figure 13. Band structure of $n-Si/TiO_2$ (A-C) and $n-Si/PA/TiO_2$ (D-E) before contact (or under flat band conditions), in equilibrium in the dark, and under illumination.



Supplementary Figure 14. Linear sweep voltametry of homojunction pn-Si/TiO₂ (red) and pn-Si/PA/TiO₂ (blue), recorded in $1M H_2SO_4$ at a scan speed of 10 mV s⁻¹ under chopped illumination.

S15: band diagrams pn-Si/PA/TiO₂



Supplementary Figure 15. Band diagrams for $pn-Si/TiO_2$ before contact (A) and in equilibrium (B) and for $pn-Si/PA/TiO_2$ before contact (C) and in equilibrium (D). Note that the photovoltage (red arrow) is generated within the Si homojunction and its magnitude is not affected by a dipole layer placed outside the homojunction. However, a slightly better fill factor is observed in the dipole modified sample (Fig S11), which we attribute to a narrow parasitic barrier between n-Si and TiO_2 which the excited photoelectrons have to tunnel through. This barrier becomes smaller when the pn-Si bands are shifted closer to the TiO_2 bands, therefore explaining the smaller series resistance and better fill factor in the dipole modified device.

S16: different phosphonic acids



Name	Structure	DFT structure	Dipole direction	Dipole along Z direction
Phosphonic acid PA	H −P: OH OH		1	-0.3 D
Methylphosphonic acid MPA	H ₃ C O OH OH		Ļ	+0.6 D
Fluorophosphonic acid FPA	F − − − − OH	→	1	-1.1 D
Hydroxybenzyl phosphonic acid HBPA	O OH		Ļ	+4.8 D
Phosphoric acid H ₃ PO ₄				0.0 D

Supplementary Figure 16: Top: J-V plots of devices with the general structure p-Si/anchor layer/dipole layer/TiO₂/Pt (blank) with different phosphonic or phosphoric acids acting as dipole layers recorded in 1 M H₂SO₄ under 1 sun illumination or chopped illumination (for H₃PO₄, pink). Bottom: Comparison of the structures of the phosphonic acid structures and their calculated gas phase dipole moment along the vertical z-axis (i.e. along the P-R bond) calculated from DFT relaxed structures with the direction and magnitude of the gas phase dipole moment.

Discussion: The gas phase dipole is one of several secondary factors that also contribute to the overall dipole, some other factors being: size of the PA and therefore closeness of packing; degree of tilt on the surface; binding mode; thickness of the PA layer (which varied for all PAs tested).

S17: Stability of PA in pH 2 electrolyte



Supplementary Figure 17: Mott-Schottky plots for 50 nm TiO_2 (black). EIS measured in 1 M Na_2SO_4 at pH 2 in the dark. Capacitance was calculated at a frequency of 1.2 Hz. The same sample was then modified with PA and EIS measured 3 times successively (red, green, blue) followed by a CV measurement to -0.25 V_{RHE} and then another EIS measurement (pink).

Discussion: It should be noted that the data shown here were obtained from one single frequency as fitting with an appropriate equivalent circuit was not possible since the resistance of the relevant charge transfer process would always approximate infinity. Knowing that charge transfer processes are very slow (Hz range), we chose to show the capacitance at 1.2 Hz in the figure above. For those reasons, we want to emphasize that the data presented should be interpreted qualitatively, not quantitatively.

The data shows that the flat band shift is biggest in the first measurement and then slowly decreases. When negative voltages of -0.25 V_{RHE} are applied, the PA layer is completely removed and the measured flat band potential corresponds to bare TiO₂. At those potentials, the surface Ti⁴⁺ ions are reduced to Ti³⁺ resulting in a weaker bond to PA and bond breakage eventually.

S18. Dewetting of PA layer when unprotected



Supplementary Figure 18. SEM (left row) and AFM images (right row) of aged p-Si/Al₂O₃ (A, B) and p-Si/Al₂O₃/PA (C, D, E). AFM images were recorded 5 days after PA deposition and SEM images 3-5 weeks after deposition.

Discussion: As expected, the blank sample (A, B) is still flat after aging, whereas the PA modified samples (C, D) show PA structures of coagulated spheres (200 - 400 nm in diameter and up to 100 nm in height) which formed in the first few days after PA deposition (without protection by TiO₂). Panel E shows another sample which aged for 5 weeks and shows a very different pattern of PA islands of 200 - 1000 nm in diameter. Thus, the PA layer should be protected immediately (within hours) after deposition.

S19: PV stability



Supplementary Figure 19. Figures of merit of four solar cells during heat-light soaking experiments. JV curves were automatically recorded every 30 min and the full experiment lasted for 6 days (samples Blank 1 and Dipole 1) or 2.5 days (Blank 2 and Dipole 2). A: output power at maximum power point, B: development of the open circuit voltage V_{oc} , C: short-circuit current (J_{sc}), D: fill factor (FF), E: Stability factor (P after time t divided by initial P).

S20: Impedance, band diagrams impedance



Supplementary Figure 20. Mott-Schottky plots for 50 nm ALD-TiO₂ on FTO (A) and PA on 50 nm ALD-TiO₂ on FTO (B) and 2 nm ALD-TiO₂ on PA on 50 nm ALD-TiO₂ on FTO (C). The values for the flat band potential obtained by linear fitting of the data are given in the graphs. D: qualitative band structure of TiO₂ in flat band conditions. E: qualitative band diagrams of PA modified TiO₂. The PA layer results in a step in the vacuum energy level, therefore shifting the TiO₂ bands to more positive values. The dipole induced shift is reflected in the difference between bare TiO₂ (A) and PA modified TiO₂ (B). F: The PA layer is protected by a 2 nm TiO₂ layer. This layer is too thin to have a bulk and is not probed by impedance. Mott-Schottky still gives the flat band energy of the underlying 50 nm TiO₂ layer. The E_{fb} shift is smaller than in (E) due to partial dipole screening induced by the second PA-TiO₂ interface, which counteracts the dipole of the first TiO₂/PA interface and therefore leads to a smaller overall dipole.

Supporting References

- (1) Prabhakar, R. R.; Septina, W.; Siol, S.; Moehl, T.; Wick-Joliat, R.; Tilley, S. D. J. Mater. Chem. A **2017**, *5*, 23139.
- (2) Hutter, J.; Iannuzzi, M.; Schiffmann, F.; VandeVondele, J. *Wiley Interdiscip. Rev. Comput. Mol. Sci.* **2014**, *4*, 15.
- (3) VandeVondele, J.; Krack, M.; Mohamed, F.; Parrinello, M.; Chassaing, T.; Hutter, J. *Comput. Phys. Commun.* **2005**, *167*, 103.
- (4) Goedecker, S.; Teter, M.; Hutter, J. Phys. Rev. B 1996, 54, 1703.
- (5) Perdew, J. P.; Burke, K.; Ernzerhof, M. Phys. Rev. Lett. 1996, 77, 3865.
- (6) Grimme, S.; Antony, J.; Ehrlich, S.; Krieg, H. J. Chem. Phys. 2010, 132, 154104.
- (7) Bengtsson, L. Phys. Rev. B **1999**, 59, 301.
- (8) Persson, K. A.; Skinner, D.; Chen, W.; Cholia, S.; Hautier, G.; Gunter, D.; Ong, S. P.; Dacek, S.; Richards, W. D.; Jain, A.; Ceder, G. *APL Mater.* **2013**, *1*, 011002.
- (9) Fall, C. J.; Binggeli, N.; Baldereschi, A. J. Phys. Condens. Matter 1999, 11, 2689.
- (10) Shan, B.; Cho, K. Phys. Rev. B 2004, 70, 233405.
- (11) Moehl, T.; Suh, J.; Sévery, L.; Wick-Joliat, R.; Tilley, S. D. ACS Appl. Mater. Interfaces **2017**, *9*, 43614.
- (12) von Gastrow, G.; Alcubilla, R.; Ortega, P.; Yli-Koski, M.; Conesa-Boj, S.; Fontcuberta i Morral, A.; Savin, H. *Sol. Energy Mater. Sol. Cells* **2015**, *142*, 29.
- (13) Hoex, B.; Schmidt, J.; Pohl, P.; van de Sanden, M. C. M.; Kessels, W. M. M. *J. Appl. Phys.* **2008**, *104*, 044903.
- (14) Hoex, B.; Heil, S. B. S.; Langereis, E.; van de Sanden, M. C. M.; Kessels, W. M. M. *Appl. Phys. Lett.* **2006**, *89*, 042112.
- (15) Alexander V. Naumkin, Anna Kraut-Vass, Stephen W. Gaarenstroom, C. J. P. *NIST X-ray Photoelectron Spectroscopy Database*; Gaithersburg MD, 20899, 2012.
- (16) Luschtinetz, R.; Oliveira, A. F.; Frenzel, J.; Joswig, J.; Seifert, G.; Duarte, H. A. Surf. Sci. **2008**, 602, 1347.