Investigation of the Interfacial Energetics of Electrolyte/Metal/a-TiO_2/Si interfaces

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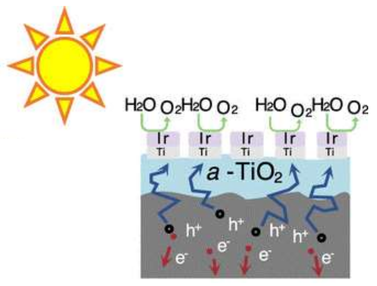
Abstract:

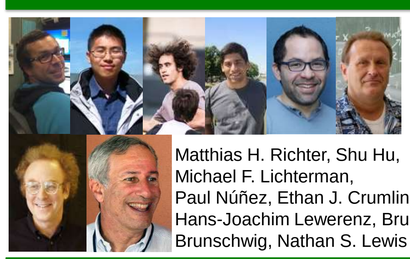
Photoelectrochemical cells based on semiconductor-liquid interfaces provide a theoretically ideal structure for converting solar photons into electricity or chemical fuels. Unfortunately, the stability of the photoelectrodes is a major impediment to the realization of deployable devices. Recently semiconductor photoelectrodes stabilized with TiO2 coatings have show 1000's of hours of stability and the ability to conduct charge between the semiconductor and the solution. Solid-state electrical, photoelectrochemical, and photoelectron spectroscopic techniques have been used to characterize the behavior, conduction, and electronic structure of interfaces between n-Si, n^+-Si, or p^+-Si and TiO_2. X-ray photoelectron spectroscopic data allowed formulation of the energy band-diagrams for the n-Si/TiO_2, n^+-Si/TiO_2, and p^+-Si/TiO_2 interfaces. Operando Ambient Pressure X-ray photoelectron spectroscopy investigations provided quantitative understanding of the energy bands the the parameters what make these photoelectrochemical conduction.

Introduction



Heterojunctions between TiO_2 and small-band-gap semiconductors have been shown to be stable against photocorrosion while in contact with 1.0 M KOH(aq) and under simulated solar illumination for up to 2200 h of continuous water oxidation. Solid-state and photoelectron spectroscopy experiments described here provide a detailed picture of the energetics of the heterojunctions between the various layers in n-Si, "leaky" amorphous TiO2, and the KOH electrolyte. We present a detailed picture of the band energetics for the interfaces that explains how holes can travers move through the TiO2.

Team



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Outlook

The interfacial chemistry, device physics, and photoelectron spectroscopic insights provide directions for improving the energy-conversion performance of such heterojunctions. This work makes possible the engineering of the protection layer's interfacial dipoles, energy of the defect states, and control of interfacial recombination. Further, the use of TiO2 protection layers for photoelectrodes makes possible the development of deployable devices

Acknowledgments

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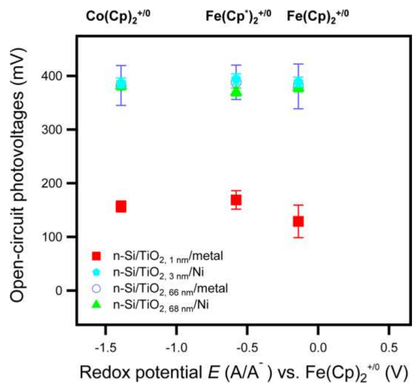
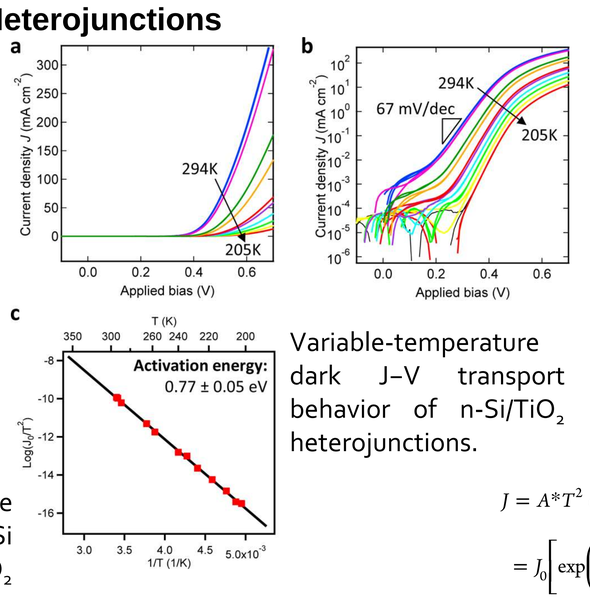
Results, Highlights, and Accomplishments

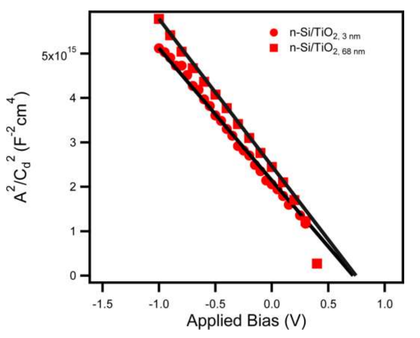
Section 1: Formation of n-Si/TiO_2 Heterojunctions



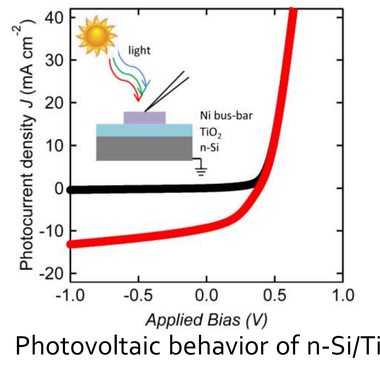
Open-circuit photovoltage versus the electrochemical potential for n-Si photoelectrodes coated with TiO_2 overlayers.



Variable-temperature dark J–V transport behavior of n-Si/TiO_2 heterojunctions.



Mott–Schottky plots for n-Si/TiO_2 heterojunctions.

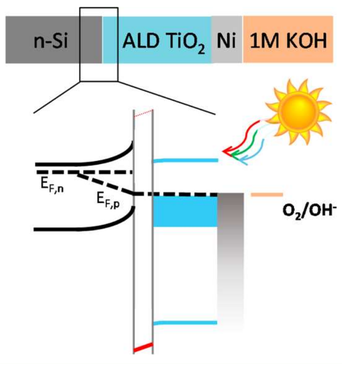


Photovoltaic behavior of n-Si/TiO_2 heterojunctions evaluated in a typical solar-cell-measurement configuration.

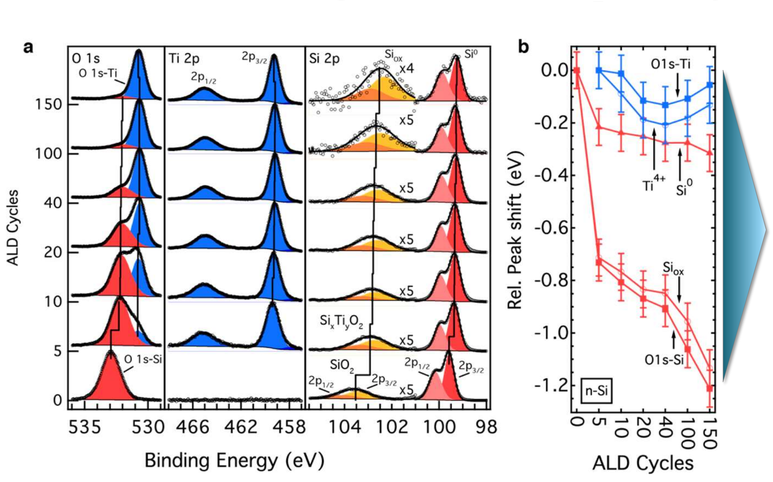
$$J = A^{*}T^{2}\exp\left(-\frac{q\Phi_B}{kT}\right)\left[\exp\left(\frac{qV}{nkT}\right)-1\right]$$
$$= J_0\left[\exp\left(\frac{qV}{nkT}\right)-1\right]$$

TiO_2 overlayer acts as a charge-transfer layer for n-Si to form a buried heterojunction with the n-Si photoelectrode:

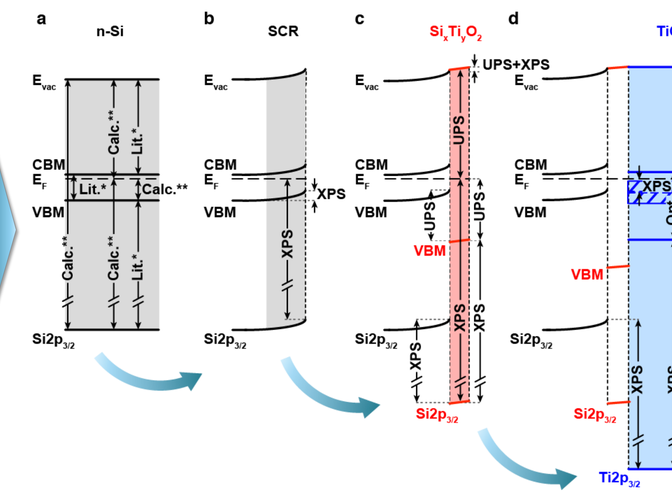
- Photovoltage: ~0.4 V
- Built-in voltage: ~0.7 V
- Richardson constant A* = 1.87 A cm² K^{-2}
  (2 orders of magnitude less than for a typical n-Si/metal junction, agrees with 1.1 × 10^{20} cm^{-3} defect state density)



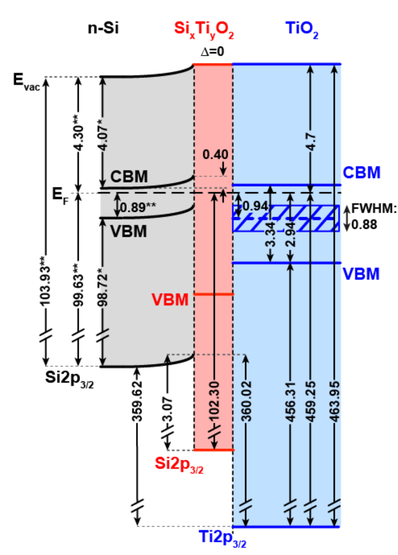
Section 2: Band Energetics of n-Si/TiO_2 Heterojunctions



Raw data and fitted peaks for (a) the O 1s, the Ti 2p, and the Si 2p core-level emissions of incremental ALD cycles on n-Si substrates.
A change of chemical shift for Si_{ox} from 3.8 eV for SiO_2 to 3.09 eV ± 0.1 eV was observed.

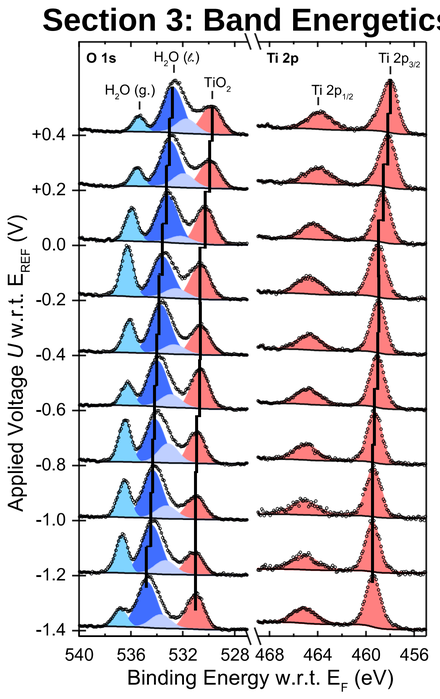


The development of an interfacial band diagram from UPS and XPS measurements is illustrated progressively:
(a) bulk silicon;
(b) space-charge (SCR) region of Si
(c) $Si_xTi_yO_2$ interfacial layer
(d) TiO_2 overlayer

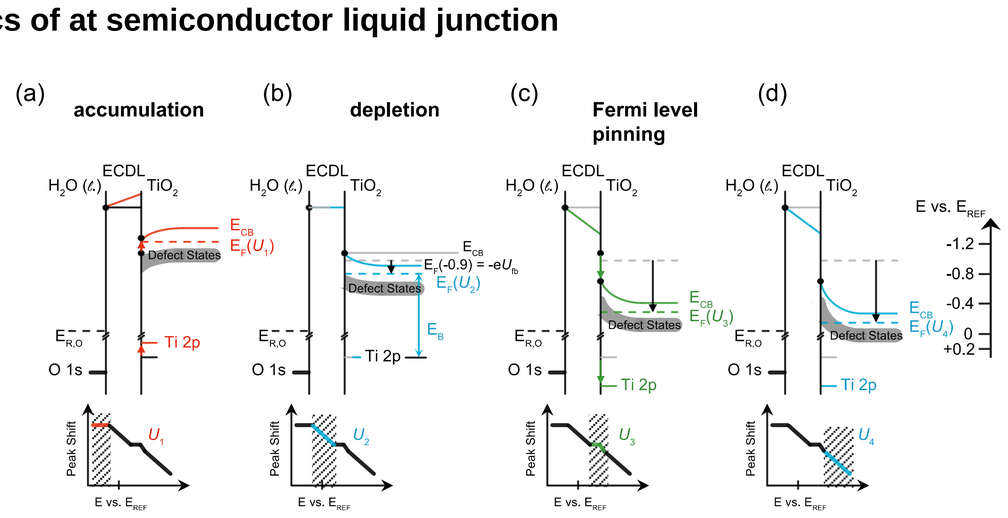


Band-energy diagrams of n-Si surfaces after RCA-2 treatments and deposition of TiO_2 by ALD. The dashed blue region illustrates the position of the TiO2 defect band.

Section 3: Band Energetics of at semiconductor liquid junction



Raw data and fitted peaks for the O 1s and Ti 2p core-level emissions under different applied potentials.



Schematic energy diagram of the TiO_2/liquid junction:

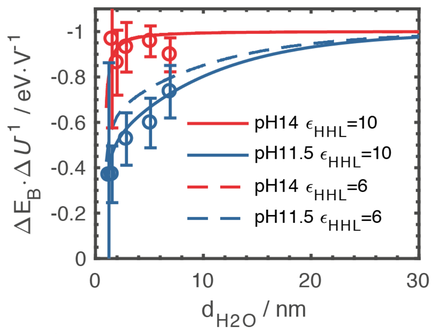
(a) Band shifting in the TiO_2

(b) Ideal semiconductor region band bending in the TiO_2 with no PD in the EDL

(c) Fermi level is pinned to the defect states, PD occurs in the EDL

(d) Ideal behavior is once again observed.

Electrochemical double layer



Slope of change in binding energy with potential, $\Delta E_B/\Delta U$, vs thickness of electrolyte, for the water O 1s peak at pH 11.5 and 14, respectively. A HHL thickness of 0.8nm, with values of ε_{HHL} = 10 (solid lines) and ε_{HHL} = 6 (dashed lines), and ε_{DL} = 80 was used for the calculations.

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