**Abstract:**

Heterojunctions between TiO₂ 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 2000 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 traverse through the TiO₂.

**Introduction**

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.

**Results, Highlights, and Accomplishments**

**Section 1: Formation of n-Si/TiO₂ Heterojunctions**

Variable-temperature dark J–V transport behavior of n-Si/TiO₂ heterojunctions. Mott–Schottky plots for n-Si/TiO₂

TiO₂ 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: ~0.2 V
- Richardson constant A* = 1.87 A cm⁻²K⁻²

(2 orders of magnitude less than for a typical n-Si/metal junction, agrees with 1.1 to 10 cm⁻²K⁻² defect state density)

**Section 2: Band Energetics of n-Si/TiO₂ 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 SiO₂ from 3.8 eV for SiO₂ to 3.0 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/TiO₂ interfacial layer
(d) TiO₂ overlayer

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

**Section 3: Band Energetics of an semiconductor liquid junction**

Schematic energy diagram of the TiO₂ liquid junction:

(a) Band shifting in the TiO₂
(b) Ideal semiconductor region band bending in the TiO₂ with no PD in the EDL
(c) Fermi level pinned to the defect states, PD occurs in the EDL
(d) Ideal behavior is once again observed.

**Outlook**

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0014353. Research was in part carried out at the Molecular Materials Research Center of the Beckman Institute of the California Institute of Technology.

**Acknowledgments**

This work was supported by the DOE under Award Number DE-SC0014353. Research was in part carried out at the Molecular Materials Research Center of the Beckman Institute of the California Institute of Technology.

**Investigation of the Interfacial Energetics of Electrolyte/Metal/a-TiO₂/Si interfaces**

Matthias H. Richter, Shu Hu, Michael F. Lichterman, Paul Núñez, Ethan J. Crumlin, Hans-Joachim Lewerenz, Bruce S. Brunschwig, and Nathan S. Lewis

**Introduction**

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 shown 1000s 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, p'-Si, or p'-Si and TiO₂. X-ray photoelectron spectroscopic data allowed formulation of the energy band diagrams for the n-Si/TiO₂ heterojunctions and p'-Si/TiO₂ interfaces. Operando Ambient Pressure X-ray photoelectron spectroscopy investigations provided quantitative understanding of the energy bands of these parameters that make these photoelectrochemical conductions.

**Results, Highlights, and Accomplishments**

**Section 1: Formation of n-Si/TiO₂ Heterojunctions**

Variable-temperature dark J–V transport behavior of n-Si/TiO₂ heterojunctions. Mott–Schottky plots for n-Si/TiO₂

TiO₂ 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: ~0.2 V
- Richardson constant A* = 1.87 A cm⁻²K⁻²

(2 orders of magnitude less than for a typical n-Si/metal junction, agrees with 1.1 to 10 cm⁻²K⁻² defect state density)

**Section 2: Band Energetics of n-Si/TiO₂ 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 SiO₂ from 3.8 eV for SiO₂ to 3.0 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/TiO₂ interfacial layer
(d) TiO₂ overlayer

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

**Section 3: Band Energetics of an semiconductor liquid junction**

Schematic energy diagram of the TiO₂ liquid junction:

(a) Band shifting in the TiO₂
(b) Ideal semiconductor region band bending in the TiO₂ with no PD in the EDL
(c) Fermi level pinned to the defect states, PD occurs in the EDL
(d) Ideal behavior is once again observed.

**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**

This material is based upon work performed by the Joint Center for Artificial Photosynthesis, a DOE Energy Innovation Hub, supported through the Office of Science of the U.S. Department of Energy under Award Number DE-SC0014353. Research was in part carried out at the Molecular Materials Research Center of the Beckman Institute of the California Institute of Technology.