Tunnel barrier photoelectrodes for solar water splitting

Lian Guo,1 David Hung,1 Weigang Wang,2 Weifeng Shen,3 Leyi Zhu,2 Chia-Ling Chien,1,2 and Peter C. Searson1,2,a

1Department of Materials Science and Engineering, Johns Hopkins University, Baltimore, Maryland 21218, USA
2Department of Physics and Astronomy, Johns Hopkins University, Baltimore, Maryland 21218, USA
3Department of Physics, Brown University, Providence, Rhode Island 02912, USA

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Tunnel barrier photoelectrodes, with a thin inorganic tunnel barrier layer that isolates the semiconductor electrode from the electrolyte while allowing current flow across the interface, are a possible solution to the problem of photocorrosion in solar water splitting. In this approach, selection of the semiconductor for the light absorber is decoupled from selection of the tunnel barrier material that provides chemical stability. Here we demonstrate a proof-of-principle of this approach with TiO2/MgO tunnel barrier photoelectrodes. © 2010 American Institute of Physics. [doi:10.1063/1.3479055]

The development of a practical photoelectrochemical system that can use sunlight to convert water into hydrogen and oxygen remains a major challenge.1 Photoelectrochemical water splitting utilizes a semiconductor photoanode to absorb light and generate electron hole pairs such that the holes at the surface of the photoanode oxidize water to oxygen and the photogenerated electrons reduce protons to molecular hydrogen at a conventional metal cathode. As a result of the reactions involved, the photoanode operates under strongly oxidizing conditions, at highly acidic or basic pH, and with vigorous gas evolution. Despite the fact that semiconductors with appropriate band gaps for efficient water splitting are well known, photocorrosion has been a fundamental limitation for technologically viable photoelectrochemical cells. Wide band gap semiconductors have excellent photostability but only harvest a small fraction of the solar spectrum.2 To overcome this problem, three main strategies have been explored: (1) decreasing the band gap of wide band gap semiconductors, (2) tandem cells,3 or (3) searching for new materials.4–6

An alternative approach to the photocorrosion problem is to isolate the light absorbing semiconductor from the aqueous environment by introducing a surface layer. However, there are several major challenges associated with this approach: the surface layer must allow current flow across the interface, it must be chemically stable under operating conditions, and it must be defect free to avoid exposing the light absorbing semiconductor to the aqueous environment. Here we investigate tunnel barrier photoelectrodes with a thin inorganic tunnel barrier layer that isolates the semiconductor electrode from the electrolyte. In this way, selection of the semiconductor is decoupled from selection of the tunnel barrier material that provides chemical stability.

Over the past 30 years there has been remarkable progress in the fabrication of inorganic tunnel junctions, beginning with the development of Josephson junctions and more recently with the development of magnetic tunnel junctions.7,8 As a result of these technological developments, Al2O3 or MgO tunnel junctions are routinely deposited on the wafer scale without defects and with layer thicknesses of 0.5–2 nm with a precision of better than 0.5 nm. These advances in processing make it possible to consider efficient tunnel junction photoelectrodes for solar energy conversion. The chemical deposition of thin wide band gap oxide layers has been explored as a method to inhibit the back electron transfer reaction in dye sensitized solar cells.9,10 However, in this system it is not necessary to eliminate nonuniformities and defects since photocorrosion is not a problem.

In this paper, we report a proof-of-principle demonstration of this approach with MgO tunnel barriers on single crystal TiO2. The rationale for selecting this system is: (1) although TiO2 is a wide band gap semiconductor, its photoelectrochemical properties have been widely studied and (2) the deposition of wafer scale, high-quality MgO tunnel barriers is routinely used in the fabrication of magnetic tunnel junctions.11 MgO is a good insulator with a band gap of 7.8 eV.12

The MgO films deposited on the single crystal (100) rutile TiO2 wafers were characterized by x-ray photoelectron spectroscopy (XPS).13 Figure 1 shows the Ti 2p and Mg 2s spectra for as-deposited TiO2 and TiO2/MgO tunnel barrier photoelectrodes with 1 nm or 2 nm MgO. The dramatic decrease in the Ti 2p peak after the deposition of a 1 nm MgO layer is due to the attenuation of photoelectrons from the TiO2 substrate. When the MgO thickness is increased to 2 nm, the Ti 2p peak is barely detected. A well-defined Mg 2s peak is only seen after MgO deposition.

The thickness and uniformity of the tunnel barriers were determined by angle resolved XPS. The film thickness is related to the intensity ratio between the film and the substrate (If/Isub) measured at different take-off angles by:14

$$\ln \left( 1 - \frac{I_s}{I_{sub}} \right) = \frac{d}{\lambda} \sec \theta,$$

where If and Isub are the intensities of the Mg 2s and Ti 2p peaks, respectively, K is a factor that takes into account the different photoelectron cross-sections or atomic sensitivity factors (ASF), θ is the angle between emitted photoelectrons and the surface normal, λ is the inelastic mean free path (IMFP) of the photoelectrons, and d is the MgO tunnel bar-
barrier thickness. We take $\lambda \approx 3.1$ nm (Ref. 15) for Ti $2p$ and Mg $2s$ photoelectrons in MgO, and $K=0.19$ taking ASF $=2.001$ for Ti ($2p$) and 0.252 for Mg ($2s$). The XPS data show excellent agreement with Eq. (1) [Fig. 1(c)] and extrapolate to the origin, indicating the good uniformity of the MgO layers. From the slopes of the fits we obtain thicknesses of 1.2 and 2.4 nm in good agreement with the nominal thickness of 1 nm and 2 nm, respectively.

Figure 2(a) shows I-V curves for TiO$_2$ and TiO$_2$/MgO tunnel barrier electrodes under white light illumination in 1 M KOH solution. The photocurrent onset for TiO$_2$ occurs at $-0.7$ V and the photocurrent rapidly reaches a plateau at about $-0.2$ V. The TiO$_2$/MgO photoelectrodes exhibit similar I-V curves although the photocurrent onset shifts to more positive potentials. The smaller photocurrent for the 2 nm MgO layer is consistent with a decrease in the probability of hole penetration across the tunnel barrier. The inset in Fig. 2(a) shows oxygen evolution at a TiO$_2$/MgO (2 nm) tunnel barrier photoanode. We note that a pH gradient or an external bias is required to achieve simultaneous hydrogen evolution at the platinum counter electrode with the tunnel barrier photoelectrodes or bare TiO$_2$.

Figure 2(b) shows photocurrent-time transients for TiO$_2$ and TiO$_2$/MgO tunnel barrier photoelectrodes in a two-electrode configuration in 1 M KOH under white light illumination showing oxygen gas evolution ($i_h \approx 15$ mA cm$^{-2}$). (b) Photocurrent-time transients for TiO$_2$ and TiO$_2$/MgO tunnel barrier photoelectrodes under the same condition as (a).

FIG. 2. (a) Current-voltage curves for TiO$_2$ and TiO$_2$/MgO tunnel barrier photoelectrodes in 1 M KOH under white light illumination (300 mW cm$^{-2}$). The dashed line is the dark current on bare TiO$_2$. Experiments were performed in a two electrode configuration with a platinum counter electrode at a scan rate of 50 mV s$^{-1}$. (Inset) Photograph of a TiO$_2$/MgO(2 nm) tunnel barrier photoanode in a two electrode cell configuration in 1 M KOH under white light illumination showing oxygen gas evolution ($i_h \approx 15$ mA cm$^{-2}$). (b) Photocurrent-time transients for TiO$_2$ and TiO$_2$/MgO tunnel barrier photoelectrodes under the same condition as (a).

FIG. 3. (a) IPCE vs wavelength for TiO$_2$ and TiO$_2$/MgO tunnel barrier photoelectrodes in 1 M KOH solution under open circuit conditions. The IPCE for TiO$_2$ is attenuated by the high reflectivity of the polished surface resulting from immersion in KOH solution.

Figure 3 shows incident photon-to-electron conversion efficiency (IPCE) measurements for TiO$_2$ and TiO$_2$/MgO tunnel barrier electrodes. These measurements were reproducible over multiple cycles. The IPCE for TiO$_2$ photoelectrodes increases at wavelengths less than about 400 nm. Consistent with Fig. 2, the IPCE decreases with increasing tunnel barrier thickness. The IPCE for the 2 nm MgO tunnel barrier is about three times smaller than the IPCE for TiO$_2$ at photon energies close to the band gap but is about an order of magn-

FIG. 3. (a) IPCE vs wavelength for TiO$_2$ and TiO$_2$/MgO tunnel barrier photoelectrodes in 1 M KOH solution under open circuit conditions. The IPCE for TiO$_2$ is attenuated by the high reflectivity of the polished surface and the indirect band gap of rutile. (Inset) Tauc Plot showing that the band gaps are 3.03 eV irrespective of the tunnel barrier thickness.
nitude smaller at shorter wavelengths. A Tauc plot of the IPCE data (inset) for TiO₂ and the TiO₂/MgO photoelectrodes shows an indirect band gap of 3.03 eV, very close to the value of 3.02 eV for rutile TiO₂ reported in the literature.¹⁷

The ability to isolate a light absorbing semiconductor from the strongly acidic or basic conditions used for water splitting, while allowing reasonable levels of charge transport across the interface, is highly challenging. We have fabricated TiO₂/MgO photoelectrodes and show that the MgO tunnel barrier is stable in strong base, at least for the time scale of the experiments. Although the photocurrent is attenuated by the presence of the tunnel barrier, the incorporation of an oxygen evolution catalyst should improve the performance. These proof-of-principle results for a model system indicate that tunnel barrier photoelectrodes with light absorbers well matched to the solar spectrum may be a route to efficient water splitting.

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¹³See supplementary material at http://dx.doi.org/10.1063/1.3479055 for details of sample preparation, sample characterization, and photoelectrochemical measurements.