Correlation of Ti^{3+} States with Photocatalytic Enhancement in TiO_2 -passivated p -GaAs

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Abstract:

Recently, we reported enhanced H_2 evolution on TiO_2 -passivated GaAs. Based on density functional theory calculations (DFT) calculations, this enhancement was attributed to Ti^{3+} states, which bind reactant species and increase charge transfer across the semiconductor-liquid interface. Here, we provide a quantitative correlation between Ti^{3+} density, as measured by X-ray photoemission spectroscopy (XPS) and photoluminescence (PL) spectroscopy, and photocatalytic performance, which substantiates the hypothesis put forth previously. In the photo- I - V characteristics reported here, passivating GaAs with TiO_2 produces a shift in the onset potential of +0.35V at $1\text{mA}/\text{cm}^2$ and enhances the photocurrent by 32-fold over bare GaAs (at 0V vs. RHE), resulting in a peak photoconversion efficiency of 1.5% under AM1.5 G illumination. We find that just 1nm of TiO_2 produces the best conditions for photocatalysis. XPS spectra show that thinner TiO_2 films (1nm) have a higher density of Ti^{3+} states than thicker films (5nm), which have lower photocatalytic performance. PL spectroscopy provide further evidence for these Ti^{3+} surface states, which cause increased surface recombination. While it is apparent that the TiO_2 films cause strong electron-hole recombination, the benefit that they provide by providing catalytically active sites outweighs their detriment associated with charge recombination. No enhancement is observed for TiO_2 thicknesses above 10nm, which are crystalline and, therefore, considerably more insulating than thinner amorphous TiO_2 films.

Keywords: photocatalysis, H_2 evolution, energy conversion, GaAs, TiO_2 , solar fuel

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Photocatalytic water splitting is of great interest for its potential to store solar energy in the form of chemical bonds that can later be released without producing harmful byproducts. In the initial demonstration of photocatalytic water splitting in 1972, Fujishima and Honda used TiO_2 under ultraviolet irradiation.¹ Because of TiO_2 's wide band gap ($E_g=3.2\text{eV}$), however, very few solar photons ($\sim 4\%$) can be used to drive this photocatalyst, and thus it will never provide efficient solar energy conversion on its own. Despite this inherent limitation, the low cost, easy synthesis and chemical robustness of TiO_2 have made it by far the most extensively studied photocatalytic material.²⁻⁵ III-V compound semiconductors, such as GaAs and InP, are better candidate materials for solar utilization with band gaps of 1.42eV and 1.34eV, respectively. These band gap energies nearly match the Shockley-Queisser optimum band gap for solar energy conversion.⁶ While the Shockley-Queisser limit is typically applied to electrical solar cells, its results are general and also apply to photocatalysts.⁷ The long-standing record high applied-bias photon to current efficiency of 13.3% was obtained on *p*-type InP photocathodes covered with Pt catalysts.⁸ More recently, Ali Javey's group reported 14% efficient H_2 evolution using InP

nanopillars with a Ru catalyst.⁹ While GaAs, a more widely used material, has a band gap and electron affinity that is similar to InP, it has not been reported to provide high efficiency solar-to-hydrogen conversion. One of the main reasons for this is the extremely high surface recombination velocity (10^6 cm/s) in GaAs, which is 1 to 2 orders of magnitude higher than most other III-V compound semiconductors. The rapid electron-hole pair recombination associated with this high surface recombination velocity lowers the overall efficiency of photocatalytic energy conversion.¹⁰⁻¹² Another major problem preventing GaAs from being utilized as a photocatalyst is that its surface is not photochemically stable, like other III-V semiconductors.¹³ Several groups, including our own, have demonstrated that a very thin layer of TiO₂ can be used to make narrower band gap materials stable.^{9, 14-22} However, only Lin²³ and our groups' previous work^{19-22, 24} have reported an enhancement in the photoconversion efficiency due to the TiO₂-passivation layer, and the mechanisms of enhancement remain contradictory. In this paper, we correlate the Ti³⁺ states with photocatalytic activity using TEM, XPS, and PL spectroscopy. Also, in contrast to previous contributions by others, we investigate photocatalysts that do not contain metal co-catalyst particles, which allows us to study the semiconductor/liquid interface.

In this work, we deposit very thin layers of TiO₂ (1 to 5 nm) on GaAs by atomic layer deposition using TiCl₄ as the Ti precursor, and observe drastic enhancement in the photocatalytic efficiency compared to bare GaAs. We systematically investigate the photocatalytic performance as a function of TiO₂ thickness using gas chromatography and by measuring their photo-*I-V* characteristics as a function of reference potential. These photocatalytic surfaces are further studied using photoluminescence (PL) spectroscopy, high resolution transmission electron microscopy (HRTEM), electron energy-loss spectroscopy (EELS), and X-ray photoemission spectroscopy (XPS). To evaluate the photochemical stability of the

TiO₂-passivated GaAs surfaces, we monitor the photocatalytic yield over 48 hours under continuous illumination during the H₂ evolution reaction.

We use *p*-type (111) oriented GaAs substrates with a Zn dopant concentration of $6 \times 10^{16} \text{ cm}^{-3}$ (obtained from University Wafer, Inc.) as the photocathode for H₂ evolution. Atomic layer deposition (ALD) of TiO₂ was performed at 250°C on the *p*-GaAs wafers using TiCl₄ as the titanium source and water vapor as the oxygen source. The carrier gas during the deposition was argon with a flow rate of 20 sccm, and TiCl₄ is always used for the first half-cycle. The thicknesses of TiO₂ were measured by ellipsometry. Ohmic back contacts were made to the *p*-GaAs by evaporating 1 nm thick Ti followed by 50 nm of Au. The Ti-Au film was then connected to the external circuitry with a copper wire and coated with epoxy cement to insulate it from the electrolytic solution, as illustrated in Figure 1a. Figure 1b shows a high resolution transmission electron microscope (HRTEM) image of 3 nm amorphous TiO₂ on GaAs below a layer of electron beam deposited Pt. Here, the Pt was deposited as part of the cross section sample preparation using standard focused ion beam sample preparation techniques, and it was not used during the photoelectrochemical measurements. This high resolution TEM image confirms the thickness of the TiO₂ film, which was independently measured by ellipsometry. An HRTEM image of the GaAs surface prior to TiO₂ deposition is also shown in Figure S2 in the Supplemental Document, which shows an approximately 3 nm native oxide on GaAs, consistent with literature.²⁵ A scanning TEM (STEM) image and spatial maps of the Ti and O species obtained from EELS spectra are shown in Figure S1 of the Supplemental Document. Based on these spatial maps, it is evident that the native oxide of the GaAs has been removed during the ALD process due to the Cl⁻ ions from the TiCl₄ precursor, consistent with previous reports in the literature values.²⁵ If there were a native oxide present, the oxygen EELS signal would increase before the titanium signal. Instead, the O and Ti EELS signals increase simultaneously, corresponding to the TiO₂ interface. We measured

the photocatalytic reaction rates of two sets of samples in a pH=0 solution of 0.5 M H₂SO₄ using a three-terminal potentiostat with the prepared samples, a Ag/AgCl electrode, and a graphite electrode functioning as the working, reference, and counter electrodes, respectively. A 910 mW/cm² 532nm laser and AM1.5 G illumination solar simulator (100 mW/cm²) were used for illumination. The area of the exposed electrode surface is about 0.2 cm². H₂ evolution was verified and quantified by gas chromatography. Photoluminescence spectra were collected using a 100X objective lens, a 1800 l/mm grating, and a silicon CCD detector. A 532nm continuous-wave laser was used to excite the samples, and spectra were collected over the 750 nm to 1000 nm wavelength range. Low to moderate power excitation (10²-10⁵ mW/cm²) was used to avoid optical heating.

Figure 1c shows the photocurrent-voltage curves of *p*-GaAs photocathodes with various thicknesses of TiO₂ under an AM1.5 G illumination solar simulator, plotted together with bare GaAs. The bare GaAs (blue curve) exhibits an onset of photocurrent at a potential of approximately -0.05V vs. RHE. The TiO₂-passivated GaAs shows a clear shift in the onset potential. The sample with a nominal thickness of 1nm TiO₂ exhibits the most prominent shift, lowering the overpotential (i.e., increasing the onset potential) by 0.35V at 1mA/cm² (red curve) with a 32-fold enhancement of photocurrent over bare GaAs (at 0V vs RHE). It is interesting that such a large shift in the onset potential is obtained from such a thin layer of material. Nevertheless, these results were reproduced consistently in several different sets of samples. We observe no improvement over bare GaAs for TiO₂ thicknesses above 10nm, as shown in Figure S3 of the Supplemental Document. This is because amorphous TiO₂ is far more conductive than crystalline TiO₂, which is insulating and, therefore, impedes charge transfer to the ions in solution.²⁴ The hydrogen evolution efficiency (η) was evaluated by computing the

applied-bias photon to current efficiency of the photocatalytic reaction according to the following equation²⁶

$$\eta = \left(\frac{(E_{in} - E_{out}) * I}{P_0} \right) 100\% \quad (1)$$

where E_{in} is the applied reference potential vs. RHE, E_{out} is the voltage of the redox couple (H^+/H_2) vs. RHE (which is 0V in this case), I is the photocurrent density (mA/cm^2) observed, and P_0 is the incident optical power density (100 mW/cm^2). This equation gives the electrode efficiency for the H_2 evolution half-reaction.^{9, 27} The maximum applied-bias photon to current efficiency for p -GaAs with a 1nm TiO_2 passivation layer reaches approximately 1.5% at an applied potential of +0.2 V vs. RHE, as shown in Figure 1d. It should be noted that the photocatalysts measured in this study do not contain metal co-catalyst particles (typically consisting of precious metals), which are known to speed up the reaction kinetics. This allows us to explore the semiconductor/liquid interface, which has largely gone unstudied in these TiO_2 /semiconductor heterojunctions. It is clear from these photo- I - V characteristics that the surface kinetics of the thinnest TiO_2 film (1nm) provide the fastest kinetics. Our hypothesis is that this enhancement is due to a high density of Ti^{3+} defect states, which are more pronounced in the nominally 1nm film. The light absorption by the 5nm TiO_2 in visible range is negligible, and instead, we believe the reason for the slight decrease in performance seen for 5 nm films compared to 1 nm films is due to the defect density of the TiO_2 material which decreases with film thickness. In order to substantiate this claim, we have performed XPS spectroscopy and photoluminescence spectroscopy, as shown in Figures 2 and 3, respectively.

Figure 2 shows X-ray photoemission spectroscopy (XPS) of these TiO_2 deposited GaAs samples. Figure 2a shows the core level binding energies of $Ti \ 2p_{1/2}$ and $Ti \ 2p_{3/2}$ in the TiO_2 film at 464.7 and 459.0 eV, respectively. Additional XPS peaks with lower binding energy of 457.1 eV (red fit curve) are assigned to Ti^{3+} . The area ratios of Ti^{3+} to $Ti \ 2p_{1/2}$ are 0.15, 0.09, and 0.061 for

the 1nm, 3nm, and 5nm TiO₂ films, respectively, indicating a larger Ti³⁺ state density in thinner TiO₂ films. Figure 2b shows the O 1s core level peaks for samples with 1nm, 3nm, and 5nm thick TiO₂ deposited on GaAs. Since the native oxide of the GaAs is removed during the ALD process, as is evident from the HRTEM data (see Figure S1 of the supporting information), both O peaks in these XPS spectra are believed to originate from the TiO₂ thin layers. The O 1s core level peaks are fitted with two symmetric Gaussian curves denoted as Oa and Ob. The Oa peak is ascribed to oxygen atoms of stoichiometric TiO₂ while the Ob peak corresponds to oxygen vacancies.²⁸ The area ratios of Ob to Oa are 2.4, 1.6, and 1.4 for the 1nm, 3nm, and 5nm TiO₂ films respectively, indicating that the ratio of Ob to Oa decreases as the thickness increases. This implies that there are higher densities of oxygen vacancies in thinner TiO₂ films, which is consistent with the results of the Ti³⁺ XPS peaks. Thus, a higher concentration of O vacancies correspond to more active sites, resulting in a higher hydrogen generation efficiency and, hence, higher onset potentials. The dark *I-V* characteristics of TiO₂-passivated GaAs (Figure S4 in the Supplemental Document) also shows a large shift in the onset potential indicating that the catalytically active sites are primarily responsible for the enhanced H₂ evolution reaction. XPS data of GaAs with 3nm TiO₂ passivation after a 12 hour reaction (see Figure S6 of the Supplemental Document) shows the presence of Ti³⁺ peaks after the reaction.

In order to further explore the role of this TiO₂ (or TiO_{2-x}) surface layer, we also measured the photoluminescence (PL) spectra of these GaAs samples with various thicknesses of TiO₂. These spectra are plotted in Figure 3. Here, we find that the sample with the highest PL efficiency (i.e., bare GaAs) has the lowest photocatalytic efficiency, and vice versa, the sample with the lowest PL efficiency (1nm TiO₂) has the highest photocatalytic efficiency. Initially, this was somewhat surprising, since materials with strong photoluminescence efficiencies typically make good solar cells and photocatalysts. However, it is apparent that the catalytically active

surface states also cause strong electron-hole recombination, which limits the PL efficiency. However, the benefit that these surface states provide by lowering the potential barrier of the reaction and promoting charge transfer outweighs their detriment associated with charge recombination. For the sample with nominally 1nm TiO₂, we observe a 5-fold reduction in the photoluminescence intensity (efficiency), indicating a high density of surface states, which act as non-radiative recombination centers, thus lowering the PL efficiency. GaAs with slightly thicker (3nm and 5nm) TiO₂ exhibits higher PL intensities than 1 nm TiO₂, by reducing the effects of these surface states. We have also seen this inverse correlation between PL intensity and photocatalytic activity for InP passivated with various TiO₂ thicknesses.²¹

From thermodynamic considerations alone, GaAs (either p- or n-type) is known to be unstable under both anodic and cathodic conditions.²⁹ In our previous work of H₂ evolution on TiO₂-passivated GaP³⁰, atomic force microscopy (AFM) as well as the photo-*I-V* characteristics showed that thin layers of TiO₂ protect the underlying GaP from corrosion in the strongly acid electrolytic solution. We observe similar findings for TiO₂-passivated GaAs. Figure S5a of the Supplemental Document plots the time dependent photocurrent of bare GaAs and TiO₂-passivated GaAs, which shows that bare GaAs corrodes readily while TiO₂-passivated GaAs is stable. We performed measurements extending over several hours monitoring H₂ evolution produced by GaAs coated with 3nm TiO₂ under 532nm wavelength illumination with an applied potential of +0.1V (vs. RHE) in a 0.5M H₂SO₄ solution. The yields of H₂ were measured by gas chromatography after 12, 24, and 48 hour illumination times and are plotted in Figure 4a. The H₂ peak appears at a GC retention time of 2.1 min, and the integrated area increases linearly with the illumination time. After calibration, the yields of H₂ in μmol was plotted as a function of time, as shown in Figure 4b. The linear relationship of the H₂ yield versus time indicates that the TiO₂-passivated GaAs is photochemically stable in this strongly acidic electrolyte (pH=0). Also,

the time dependence of the photocatalytic current taken over a 48-hour period is plotted in Figure S5b of the Supplemental Document, which shows that this photocatalyst is stable over 48 hours of illumination. The Faraday efficiencies of the 12, 24 and 48 hour reactions are around 92%, as summarized in Table 1. We also measured the Faraday efficiency of bare GaAs to be only 6%, which is 15X lower than the TiO₂-passivated Faraday efficiency. This is most likely due to the photoelectrochemically-driven corrosion of the GaAs crystal structure that is circumvented by the TiO₂ layer.

In conclusion, we observe enhanced photocatalytic H₂ evolution on TiO₂-passivated GaAs. The TiO₂ layer hosts active surface states on the GaAs, which increase the recombination rate of photogenerated electron-hole pairs. The benefit of these active sites in lowering the potential barrier for this reaction outweigh the unfavorable effects of charge recombination, resulting in a net enhancement in the photocurrent density. The highest efficiency is obtained from GaAs with a 1nm TiO₂ passivation layer under AM1.5 G illumination, which reaches 1.5% at an applied voltage of approximately +0.2V vs. RHE. We observe no improvement over bare GaAs for TiO₂ thicknesses above 10nm, where the insulating nature of the TiO₂ eventually outweighs its benefits. The TiO₂ passivation layer prevents photocorrosion of the GaAs surface, providing a viable, long-term stable photocatalyst. Moreover, the Faraday efficiency of TiO₂-passivate GaAs reaches 92%, 15X higher than that of bare GaAs which is only 6%.

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Figures

Figure 1. (a) Schematic diagram of sample geometry. (b) TEM Image of 3nm TiO₂ on GaAs. Note that for TEM sample preparation and imaging purposes, the surface of the substrate is coated with a thick layer of Pt. (c) Photocatalytic current-potential curves and (d) corresponding photon-energy conversion efficiency calculated by using Equation 1 for GaAs photocatalysts with various thicknesses of TiO₂ under an AM1.5 G illumination in a 0.5M H₂SO₄ pH=0 solution.

Figure 2. (a) Ti 2p and (b) O 1s core level XPS spectra of various thickness of TiO₂ on GaAs.

Figure 3. Photoluminescence spectra of GaAs photocatalysts with various thicknesses of TiO₂ under 532nm excitation.

Figure 4. (a) Gas chromatograph (GC) data taken after 12, 24, and 48-hour reactions on GaAs with 3nm TiO_2 under 532nm illumination in a 0.5M H_2SO_4 solution. (b) H_2 yield plotted as a function of time.

Table 1. H_2 yields and Faradaic efficiencies of the 12, 24, and 48-hour reactions on GaAs with 3nm TiO_2 under 532nm illumination in a 0.5M H_2SO_4 solution.

Reaction Time (0.1V vs. RHE)	H_2 (μmol)	Faraday Efficiency
12hr	42.7	91.2%
24hr	78	92.3%
48hr	135	93.1%