Microscopic Study of Atomic Layer Deposition of TiO$_2$ on GaAs and Its Photocatalytic Application

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ABSTRACT: We report a microscopic study of p-GaAs/TiO$_2$ heterojunctions using cross-sectional high resolution transmission electron microscopy (HRTEM). The photocatalytic performance for both H$_2$ evolution and CO$_2$ reduction of these heterostructures shows a very strong dependence on the thickness of the TiO$_2$ over the range of 0–15 nm. Thinner films (1–10 nm) are amorphous and show enhanced catalytic performance with respect to bare GaAs. HRTEM images and electron energy loss spectroscopy (EELS) maps show that the native oxide of GaAs is removed by the TiCl$_4$ atomic layer deposition (ALD) precursor, which is corrosive. Ti$^{3+}$ defect states (i.e., O vacancies) in the TiO$_2$ film provide catalytically active sites, which improve the photocatalytic efficiency. Density functional theory (DFT) calculations show that water molecules and CO$_2$ molecules bind stably to these Ti$^{3+}$ states. Thicker TiO$_2$ films (15 nm) are crystalline and have poor charge transfer due to their insulating nature, while thinner amorphous TiO$_2$ films are conducting.

Since Fujishima and Honda initially demonstrated photocatalytic water splitting using TiO$_2$ in 1972, the study of photocatalysis has received worldwide interest due to its potential applications in solar fuel generation either through water splitting or CO$_2$ reduction. While TiO$_2$ is a widely studied material, its theoretical photocurrent density under one-sun illumination is only about 1 mA/cm$^2$. Narrower band gap materials like Si, InP, and GaAs are more promising candidates, since their theoretical photocurrent densities are 44, 35, and 32 mA/cm$^2$, respectively. However, one of the primary problems, which prevents these narrower band gap materials from being utilized as photocatalysts, is that their surfaces are not photochemically stable. Therefore, passivating their surfaces to protect them from photocorrosion without sacrificing their photoconversion efficiency will enable more efficient photocatalytic systems to be developed.

Recently, several groups have demonstrated that a very thin layer of TiO$_2$ can be used to make these narrower band gap materials stable. Chen et al. first showed that TiO$_2$ deposited by atomic layer deposition (ALD) can stabilize silicon photoanodes for water oxidation. Hu et al. also reported that amorphous TiO$_2$ coatings stabilize Si, GaAs, and GaP photoanodes for efficient water oxidation. For the study of photocathodes, it is also reported that TiO$_2$ can be used to protect p-InP from corrosion and provide efficient solar-driven H$_2$ production. Our group’s previous work showed that, in addition to making GaP and InP photocathodes photochemically stable, a thin layer of TiO$_2$ can also provide substantial enhancement in the photoconversion efficiency for both H$_2$ evolution and CO$_2$ reduction. More recently, Lin et al. has also discussed similar enhancement in photocatalytic H$_2$ evolution using InP and TiO$_2$ films deposited with various ALD precursors, including TDMAT (i.e., [(CH$_3$)$_2$N]$_4$Ti) and titanium isopropoxide (i.e., C$_3$H$_5$O$_3$Ti). While these previous works are very encouraging, a detailed microscopic picture of these TiO$_2$-passivated heterostructures is lacking.

In this report, we provide a detailed study of TiO$_2$ layer growth on GaAs by atomic layer deposition using high resolution transmission electron microscopy (HRTEM) and electron energy-loss spectroscopy (EELS), as well as plane wave density functional theory (PW-DFT) calculations, which are carried out to provide a detailed picture of the p-GaAs/TiO$_2$ interface and explore the role of surface binding of reactants and intermediate species to the TiO$_2$ surface. In this work, p-type (111) oriented GaAs substrates with a Zn dopant concentration of 6 × 10$^{16}$ cm$^{-3}$ (obtained from University Wafer, Inc.) are used as the photocathode. There is approximately 3 nm of native oxide on the GaAs surface.

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Atomic layer deposition 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. TiCl₄ is used for the first half-cycle, and argon was the carrier gas with a flow rate of 20 sccm during deposition. Figure 1a–c shows HRTEM images of TiO₂ films deposited with 25, 75, and 500 cycles of atomic layer deposition on GaAs. These films have nominal thicknesses of 1, 3, and 15 nm, respectively. Pt was deposited in order to enable cross section sample preparation using focused ion beam milling and was not used in the photocatalysis measurements described below. Figure 1d–f shows EELS spatial profiles of the Ti and O species for the 25, 75, and 500 cycle TiO₂ on GaAs samples, respectively. In Figure 1d, the oxygen signal increases approximately 0.5 nm before the Ti signal, indicating the presence of the GaAs native oxide underneath the TiO₂ layer. Therefore, on the basis of these EELS spectra, there is both native GaAs oxide and amorphous TiO₂ on the GaAs surface after the 25 cycle ALD process. It should be noted that the thickness of GaAs’s native oxide is substantially lower than the 3 nm native oxide observed on bare GaAs (without TiO₂ deposition), as shown in the inset diagram in Figure 2b. After 25 ALD cycles, the native oxide of the GaAs was partially removed due to the Cl⁻ ions from the TiCl₄ precursor. Figure 1e shows the EELS spatial maps of GaAs with 75 cycles of atomic layer deposition of TiO₂. Here, both the O and Ti signals increase together, indicating that the native oxide of GaAs has been completely removed during the ALD process. With further growth of 500 cycles, the amorphous TiO₂ becomes crystalline as shown in Figure 1f. This layer of TiO₂ is in the anatase phase with clear lattice planes along the 101 direction, identified by the interplane distance of 3.5 ± 0.1 Å, as indicated in Figure S2. Shi et al.’s work also shows anatase phase TiO₂ formed by high temperature atomic layer deposition.¹²

Figure 2a shows the H₂ evolution photocurrent–potential curves of p-GaAs photocathodes with various thicknesses of TiO₂ and (b) GaAs with 10 nm TiO₂ before and after annealing under 532 nm illumination in a 0.5 M H₂SO₄ pH = 0 solution. The dark curves are for bare GaAs. Inset shows schematic diagram of the GaAs/TiO₂ sample geometry.
TiO2 under 910 mW/cm2 532 nm illumination in a 0.5 M H2SO4 electrolyte, plotted together with bare GaAs. The bare GaAs (blue curve) exhibits an onset of photocurrent at a potential of approximately −0.05 V vs RHE. The TiO2-passivated GaAs shows a clear shift in the onset potential. The sample with a nominal thickness of 1 nm TiO2 exhibits the most prominent shift, lowering the overpotential from −0.75 V (blue curve) to 0.32 V (at 10 mA/cm2) (red curve) with a 120×-fold enhancement of photocurrent over bare GaAs at 0 V vs RHE. This potentials shifts can be seen more clearly from the log–linear plot of the photo-I−V data shown in Figure S7. These results were reproduced consistently in several different sets of samples. The enhancement is attributed to the oxygen vacancies (Ti3+ states), which provide the photocatalytically active site for H2 evolution, which is consistent with the results from PW-DFT calculations shown in Figure 4b. At the same time, we observe no improvement when the TiO2 thickness reaches 15 nm, as shown by the orange curve. 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. In the works of Chen et al.4 and Viswanathan et al.13 it was assumed that electrons were tunneling through a high-quality ALD layer,13 whereas in the work of Hu et al.5 it was reported that electronically leaky annealing, due to the crystallization of the TiO2 during annealing. The photocurrent decreases dramatically after annealing, which is due to the crystallization of TiO2 during annealing. Photocatalytic production of CO from CO2 reduction was analyzed using gas chromatography, as shown in Figure S3b.

It is widely accepted that the reduction of H2O to form H2 occurs predominantly at the Ti3+-O vacancy sites due to the reaction of adsorbed H+ ions.15,16 Thus, a higher concentration of O vacancies correspond to more active sites, resulting in a higher hydrogen generation efficiency. Similarly, these Ti3+-O vacancy sites can also provide the catalytically active sites for CO2 reduction.17–19 As was previously done,20 plane wave density functional theory (PW-DFT) calculations were performed on a supercell of anatase composed of 16 TiO2 units exposing the 101 surface. The Quantum Espresso package was used with the most recently available ultrasoft pseudopotentials with scalar relativistic corrections,21–24 and spin-unrestricted calculations were done employing the Perdew–Burke–Ernzerhof (PBE) functional.25 Kinetic energy cutoffs of 435.2 (4.352) eV were applied to the wave functions (charge density) with a 1 × 1 × 1 Monkhorst-Pack k-point grid centered at Γ. A DFT+U approach was instituted with Grimme’s method26 for dispersion forces (+D) and a Hubbard U parameter of 3.6 eV (+U). An explanation for this approach was provided in our previous study.20 Clean, stoichiometric anatase and defective anatase with a surface oxygen vacancy were both investigated in this study. Adsorption energies were calculated by subtracting energies of the two components (H2O and surface) from the energy of the adsorbed system:

$$E_{\text{ads}} = E[\text{surf} + \text{H}_2\text{O}] - E[\text{surf}] - E[\text{H}_2\text{O}]$$
where the surface was stoichiometric anatase or defective anatase with a surface oxygen vacancy.

A manual search was performed to determine the global minimum of adsorbed H$_2$O to the anatase support reproducing the same geometries found in Tiloca et al.’s study on water on anatase. Adsorption energies were favorable between neutral H$_2$O adsorbed to stoichiometric (~1.26 eV as indicated in Figure S5) and defective anatase (~1.50 eV). These energies differ from those of Tiloca et al. due to possible interactions across our smaller supercell and the additional consideration of dispersion forces, which lowered the adsorption to stoichiometric anatase significantly (Tiloca et al. reported ~0.74 eV) and to defective anatase minimally (Tiloca et al. reported ~1.48 eV). As in our findings with CO$_2$, molecules adsorbed to defective anatase tend to fill the surface oxygen vacancy. In Figure 4b, the water molecule attempts to both fill the oxygen vacancy with its oxygen (colored green) and retain a hydrogen bond to the neighboring surface oxygen on the oxide support. Moreover, the hydrogen bond might be considered an “activated” bond with a length of 1.71 Å as compared to 1.89 Å on the stoichiometric support, indicating that the system is approaching the proton transfer to the O atom of the support. In a molecular dynamics study, Tiloca et al. estimated the activation barrier from adsorption of H$_2$O to dissociation of the H$_2$O to two hydroxyls to be ~0.1 eV. Moreover, Fujimori et al. maintained that hydroxylation of their MgO support provided the pathway for two mechanisms of hydrogen evolution: the direct redox process and the water oxidation reaction in the presence of CO. This indicates that Ti$_3^+$–O sites are more energetically favorable for H$_2$O adsorption, which results in higher H$_2$O evolution efficiencies, consistent with previous reports in the literature. This calculation combined with our previous finding of spontaneous CO$_2$ reduction on defective anatase (a charge transfer of 0.897 e from the support to CO$_2$) indicates that the O vacancies provide catalytically active sites for CO$_2$ and H$_2$O absorption, and no overpotential is required to form the CO$_3^{2-}$ intermediate.

In conclusion, we have carried out a microscopic study of GaAs photocathodes passivated with various thicknesses of TiO$_2$ using atomic layer deposition. High resolution transmission electron microscopy (HRTEM) and electron energy-loss spectroscopy (EELS) show that the native oxide of GaAs is removed by the TiCl$_4$ precursor during the TiO$_2$ growth. The photocatalytic performance for both H$_2$ evolution and CO$_2$ reduction of these heterostructures shows a very strong dependence on the thickness of the TiO$_2$ over the range of 0–15 nm. Thinner TiO$_2$ films are amorphous and show enhanced catalytic performance with respect to bare GaAs, whereas thicker TiO$_2$ films (15 nm) are single crystal and have poor charge transfer due to the insulating nature of crystalline TiO$_2$. DFT calculations show that the water and CO$_2$ molecules bind stably to TiO$_2$, which can further improve the photocatalytic charge transfer process.

**EXPERIMENTAL METHODS**

Ohmic back contacts were made for the p-GaAs by evaporating 5 nm of 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 the inset diagram in Figure 2b. High resolution transmission electron microscope images of TiO$_2$ on GaAs were taken with a JEOL JEM-2100F TEM equipped with a Gatan Quantum SE Gif quantum energy filter. A layer of Pt was deposited on the surfaces of samples as part of the cross section sample preparation using standard focused ion beam sample preparation techniques. TiO$_2$ films were annealed in a furnace at 450 °C for 30 min while flowing N$_2$ gas. The photocatalytic H$_2$ evolution measurements were carried out in a pH = 0 solution of 0.5 M H$_2$SO$_4$ 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. The area of the exposed electrode surface is about 0.1 cm$^2$. A 532 nm continuous-wave laser was used to excite the samples, and low to moderate power excitation (910 mW/cm$^2$) was used to avoid optical heating. The nonaqueous solution (for CO$_2$ reduction) was prepared using acetonitrile (AcN, 99.99%), dimethyl sulfoxide (DMSO, 99.96% D, Sigma-Aldrich), and 1-ethyl-3-methylimidazolium tetrafluoroborate ([EMIM][BF$_4$] 99.0%, HPLC, Sigma-Aldrich). An anion exchange membrane (Selemon AMV, Anion Exchange Membrane, AGC Inc.) was used to separate the working and counter electrodes to prevent oxidation of the reduced CO$_2$ products. This anion exchange membrane only allows negative ions to transfer through the membrane, which prevents the oxide intermediate from participating in the oxygen evolution half-reaction at the counter electrode. A three-terminal potentiostat was used with the prepared semiconductor samples as the working electrode, a Ag/AgNO$_3$ reference electrode, and a Pt wire as the counter electrode. The Ag/AgNO$_3$ electrode was made of a silver wire immersed in 0.01 M silver nitrate dissolved in 0.1 M TEAP/AcN. Also, the reference electrode was calibrated against a ferrocene/ferrocenium (Fc/Fc$^+$) redox couple to confirm that it gave the right potential with respect to NHE. A detailed discussion of the calibration can be found in our previous work. Before each measurement, CO$_2$ was purged through the solution on the working electrode side for 30 min. H$_2$ evolution and the gaseous products from the CO$_2$ reduction reaction were analyzed with a gas chromatograph (GC) (Bruker GC-450) equipped with a thermal conductivity detector (TCD) and a carbon-plot column (Agilent). The produced CO was quantified by integrating the area of the CO peak, and this was related to the calibration data (Figure S4).

**ASSOCIATED CONTENT**

3 Supporting Information

The Supporting Information is available free of charge on the ACS Publications website at DOI: 10.1021/acs.chemmater.5b03246.

TEM images of bare GaAs and 10 nm TiO$_2$ on GaAs, gas chromatography data for product after reaction, schematic diagram of H$_2$O adsorption on stoichiometric anatase, and additional photocatalytic current–potential curves. (PDF)
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■ AUTHOR INFORMATION

Notes
The authors declare no competing financial interest.

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