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## Title

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Permalink https://escholarship.org/uc/item/8jp9f8zb

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Publication Date 2009-07-24

# High Density n-Si/n-TiO<sub>2</sub> Core/Shell Nanowire Arrays with Enhanced Photoactivity

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#### ABSTRACT

There are currently great needs to develop low-cost inorganic materials that can efficiently perform solar water splitting as photoelectrolysis of water into hydrogen and oxygen has significant potential to provide clean energy. We investigate the Si/TiO<sub>2</sub> nanowire heterostructures to determine their potential for the photooxidation of water. We observed that highly dense Si/TiO<sub>2</sub> core/shell nanowire arrays enhanced the photocurrent by 2.5 times compared to planar Si/TiO<sub>2</sub> structure due to their low reflectance and high surface area. We also showed that n-Si/n-TiO<sub>2</sub> nanowire arrays exhibited a larger photocurrent and open circuit voltage than p-Si/n-TiO<sub>2</sub> nanowires due to a schottky barrier at the heterojunction.

KEYWORDS: Solar water splitting, Si, TiO<sub>2</sub>, heterojunction, core/shell nanowire

#### MANUSCRIPT TEXT

Direct solar energy conversion to storable fuels such as hydrogen offers a promising route towards less reliance on fossil fuels.<sup>1-4</sup> For example, photoelectrolysis of water to generate H<sub>2</sub> on a semiconductor/electrolyte interface has the attractive advantages of clean processing and energy savings over steam reforming of natural gas. One of the most critical issues in solar water splitting is the development of a photoanode with high efficiency and long term durability in an aqueous environment. TiO<sub>2</sub> has been extensively studied as a photoanode due to its high resistance to photocorrosion.<sup>5-10</sup> However, its conversion efficiency of solar energy to hydrogen is still low (less than 4 %)<sup>6</sup> due to its large bandgap (3.0 ~3.2 eV). TiO<sub>2</sub> requires an external bias to reduce water for H<sub>2</sub> production to overcome the chemical over potential.<sup>5, 11</sup> Si (E<sub>g</sub> = 1.12 eV), on the other hand, can absorb sunlight efficiently. It is however challenging to use Si for photoelectrolysis since it readily corrodes in water. Moreover, it is thermodynamically impossible for Si to oxidize water spontaneously due to its high

valence band maximum (VBM) energy. Therefore, a composite semiconductor electrode composed of a semiconductor heterojunction has been proposed to compensate these shortcomings. In these cases, the photoanode is composed of a small band gap semiconductor that is protected by a stable semiconductor.<sup>12-14</sup>

Semiconductor heterojunctions can absorb different region of the solar spectrum.<sup>15-18</sup> The advantage of composite structures is that each semiconductor need to satisfy one energetic requirement: matching the conduction band minimum (CBM) or VBM with either the H<sub>2</sub> reduction or O<sub>2</sub> oxidation potential. Single semiconductor materials typically can not satisfy the requirements of suitable bandgap energies for efficient solar absorption and meantime with band-edges aligned with both the H<sub>2</sub> and O<sub>2</sub> redox potential of water.<sup>3,19</sup> Here, we prepared TiO<sub>2</sub> coated Si nanowire arrays and studied their photo-oxidative properties. We observed that Si/TiO<sub>2</sub> core/shell nanowire arrays showed higher photocurrent than the planar Si/TiO<sub>2</sub>. A semiconductor heterojunction of n-Si/n-TiO<sub>2</sub> or p-Si/n-TiO<sub>2</sub> has different band bending properties near the junction.<sup>12, 20</sup> The n/n heterojunction has a potential energy barrier between the two semiconductor regions that reflects minority holes in the TiO<sub>2</sub> similar to the back surface field in solar cell.<sup>21</sup> Using photocurrent and open circuit voltage measurements, we show that the n/n heterojunction is more promising for photoelectrochemical (PEC) cell application.

Highly oriented Si nanowire arrays on the silicon wafers were synthesized by an aqueous electroless etching method.<sup>22</sup> These Si nanowire arrays significantly suppress reflection which has the potential to provide a higher efficiency of PEC cell. We prepared n-type and p-type Si electroless etched nanowire (EENW) arrays from n-Si(100) (P doped, 0.6~0.8  $\Omega$ cm) and p-Si(100) (B doped, 1~5  $\Omega$ cm) wafers with dopant concentrations of ~10<sup>16</sup> cm<sup>-3</sup>. A clean silicon wafer was immersed into the etching solution containing 0.04 M AgNO<sub>3</sub> (99.999%, Aldrich) and 5M HF (49%, Honeywell) at room temperature. The length of the EENW was controlled by the etching time (0.2 µm/min growth rate).

 $TiO_2$  was grown both on the Si EENW arrays and the planar Si wafer by a home-built atomic layer deposition (ALD) system with  $TiCl_4$  (99.990%, Alfa) and pure water as the precursors. Si samples were cleaned with a buffered HF solution to remove the native oxide layer right before loading into the ALD

vacuum chamber. The ALD system deposits polycrystalline anatase  $TiO_2$  layer with an average growth rate of 1.2 Å per cycle on the planar Si wafer and 0.7 Å per cycle on our Si EENW arrays at 300 °C. On the Si EENW array, diffusion of the gas precursors is reduced due to the high density of the nanowire arrays, which leads to slower growth rate than the planar substrate. Care was taken to ensure that the TiO<sub>2</sub> thickness on the EENW arrays and planar substrates were equivalent.

Typical cross sectional scanning electron microscope (SEM) and the transmission electron microscope (TEM) images of Si EENW and the ALD TiO<sub>2</sub> coated Si EENW (Si EENW/TiO<sub>2</sub>) are shown in Figure 1a-d. The Si EENW and Si EENW/TiO<sub>2</sub> arrays are produced vertically on the Si wafer with high density. Si EENW maintains the same crystallinity as the starting Si wafer.<sup>22</sup> and their diameters are in the range of  $20 \sim 200$  nm. Figure 1d shows polycrystalline TiO<sub>2</sub> deposition on the EENW. Figure 1e and f show the top view SEM images of Si EENW/TiO<sub>2</sub> arrays and TiO<sub>2</sub> thin film on the Si(100) wafer with average thickness of 35 nm. The nanocrystalline nature of the TiO<sub>2</sub> coating is similar for deposition on the nanowire surface and on the flat wafer surface. The X-ray diffraction (XRD) characterization indicates that the ALD grown  $TiO_2$  layer has an anatase structure both on the Si(100) wafer and on the Si EENW array, as shown in Figure 2. For photoelectrolysis of water, anatase TiO<sub>2</sub> has the advantage of a flat band potential ( $U_{fb}$ ) that is 200 mV more negative than that of the rutile TiO<sub>2</sub>. This allows anatase TiO<sub>2</sub> to have sufficient cathodic potential for hydrogen reduction from water.<sup>23</sup> The carrier concentration (N<sub>D</sub>) of TiO<sub>2</sub> layer by ALD was determined by capacitance versus voltage measurement. 90 nm TiO<sub>2</sub> thin film was deposited on the highly doped n-Si wafer (As doped,  $0.001 \sim 0.004 \ \Omega cm$ ), and Ni was deposited on the TiO<sub>2</sub> thin film. From the Mott-Schottky relation, N<sub>D</sub> was found to be 2.76 x  $10^{17}$  cm<sup>-3</sup>. The TiO<sub>2</sub> becomes n-type semiconductor because of defects such as oxygen vacancies and titanium interstitials, and their carrier concentration varies from  $\sim 10^{17} \text{cm}^{-3}$  to  $\sim 10^{20}$  cm<sup>-3</sup> depending on synthesis.<sup>24-26</sup>

Photocurrent measurements were performed in a 1M KOH electrolyte with three electrodes configuration (EG&E Pinceton Applied Research Potentiostat, VersaStat II): Si/TiO<sub>2</sub> photoanode as a working electrode, Pt gauze as a counter electrode, and a saturated calomel electrode (SCE, Pine

Research Instrumentations, AFREF1) as a reference electrode. All three electrodes are in a glass cell which has a 1 inch quartz window, and Ar gas was bubbled through to remove the dissolved oxygen during the measurement. The current versus potential measurements were carried out at a 10 mV/s sweep rate. A constant light intensity of 100mW/cm<sup>2</sup> from a 450 W Xe lamp (Oriel, 6266) illuminated our samples, and a liquid filter (Oriel, 6123NS) was used to avoid solution heating by infrared light.

Figure 3a shows the photocurrent versus bias potential characteristics for Si/TiO<sub>2</sub> composite photoanodes. Under illumination, oxidation of water takes place on the photoanode.

$$4OH^{-} + 4h^{+} \rightarrow 2H_2O + O_2$$
  $E^{0} = +0.160 \text{ V (vs SCE)}$ 

The photocurrent versus bias potential curves have three regions: low photocurrent density region at negative bias potential (region I), plateau of the photocurrent density at more positive bias potential (region III), and increasing photocurrent density region (region II) between regions I and III. No photocurrent passes through the semiconductor and electrolyte interface when the negative bias voltage is close to the flat band potential because any created excess holes and electrons are recombined before holes transfer into the electrolyte (region I).<sup>27</sup> The photocurrent plateau appears as the bias potential sweeps to more positive direction (region III), where the photocurrent is limited by the number of the holes excited by illumination.

Our planar Si/TiO<sub>2</sub> samples show comparable photocurrent density to those reported in the literature. The reported value<sup>9</sup> for a 15  $\mu$ m thick film of P-25 TiO<sub>2</sub> on Ti foil is 0.1 mA/cm<sup>2</sup> under the same illumination conditions (Xe lamp, 100 mW/cm<sup>2</sup>) even though the thickness of our ALD grown TiO<sub>2</sub> film is only 35 nm. At region III, 20  $\mu$ m long Si EENW/TiO<sub>2</sub> samples show 2.5 times higher photocurrent density than planar Si/TiO<sub>2</sub> samples for both n-type and p-type Si. The Si EENW/TiO<sub>2</sub> composites have higher photocurrent mainly because of lower reflectance and larger surface area than the Si planar/TiO<sub>2</sub>.

Figure 3a also shows that  $n-Si/n-TiO_2$  composites have 20~25 % higher photocurrent density and more negative onset potential than those of p-Si/n-TiO<sub>2</sub> for both nanowire and planar structures. Higher photocurrent is expected for the n/n junction since band bending at the junction helps charge separation.

The band bending of the semiconductors at the junctions were shown in Figure 3b and c. The Fermi energy (E<sub>F</sub>) of our n and p type silicon are -4.25 eV, and -4.97 eV (relative to the vacuum level), respectively. E<sub>F</sub> of TiO<sub>2</sub> was calculated <sup>28-29</sup> from the reported electron effective mass in anatase (m<sub>e</sub><sup>\*</sup> = 1m<sub>e</sub>)<sup>30</sup> and the measured carrier concentration (N<sub>D</sub> = 2.76 x 10<sup>17</sup> cm<sup>-3</sup>). Figure 3b illustrates the charge flow in n-Si/n-TiO<sub>2</sub> junctions under illumination. The e<sup>-</sup>/ h<sup>+</sup> pairs are created inside both the Si and TiO<sub>2</sub> because the TiO<sub>2</sub> shell is transparent under visible light. Visible light can be harvested by the core Si. Under the illumination, Fermi energies of the electrons and holes, so-called quasi-Fermi energies ( $E_F^*$ ), differ from  $E_F$  in dark,<sup>19</sup> and the quasi Fermi energies of minority holes ( ${}_{p}E_{F}^*$ ) in the n-Si and n-TiO<sub>2</sub> are shown. The photogenerated hole in TiO<sub>2</sub> ( ${}_{\pi O_2}h^+$ ) moves toward the n-TiO<sub>2</sub>/electrolyte interface and oxidizes OH<sup>-</sup> to oxygen, while photogenerated electrons in the n-TiO<sub>2</sub> ( ${}_{\pi O_2}e^-$ ) move away from the front surface due to the schottky barrier at the interface with the electrolyte.

In addition to this charge separation, the interface between the n-Si and n-TiO<sub>2</sub> reduces the loss of holes in the TiO<sub>2</sub> region which results in an increase of the photoanodic current. The potential barrier seen by the holes at the n-Si/n-TiO<sub>2</sub> junction reflects holes back into the TiO<sub>2</sub> layer (Figure 3b). This is analogous to the back surface field of a solar cell which has shown larger photocurrent and larger output voltage by adding a heavily doped region adjacent to the contact.<sup>31</sup> To complete the circuit, the photogenerated electrons in the n-Si ( $_{si}e^-$ ) move to the counter electrode where the reduction reaction takes place. The photogenerated hole in n-Si ( $_{si}h^+$ ) moves toward the n-Si/n-TiO<sub>2</sub> junction and recombines with the  $_{TiO_2}e^-$ . Therefore, n-Si/n-TiO<sub>2</sub> core/shell structure shows the largest increase in photocurrent since its band alignment at the junction helps reduce recombination under illumination. In the case of p-Si/n-TiO<sub>2</sub> junctions, the flow of electrons and holes at the junction of p-Si/n-TiO<sub>2</sub> is opposite to the desirable direction. Figure 3c shows that  $_{TiO_2}h^+$  can move either to the electrolyte or to the p-Si in p/n junction. The p-Si/n-TiO<sub>2</sub> junction, therefore, has smaller observed photo-anodic current density than n-Si/n-TiO<sub>2</sub>.

The larger photocurrent in the n-Si/n-TiO<sub>2</sub> leads to a larger negative onset potential. This is a result of the n/n junction's effective charge separation that leads to a larger short circuit current  $(J_{sc})$ .<sup>31</sup> Both n-Si EENW/TiO<sub>2</sub> and p-Si EENW/TiO<sub>2</sub> have similar dark current values  $(5\mu A/cm^2)$ . Also, higher V<sub>oc</sub> is expected for n-Si/n-TiO<sub>2</sub> since the  $E_F$  and band energies of the n-Si and n-TiO<sub>2</sub> shift upward at open circuit under the illumination. The V<sub>oc</sub> of n-Si/n-TiO<sub>2</sub> photoanode is V<sub>oc</sub> = V<sub>oc</sub>(TiO<sub>2</sub>/electrolyte) + V<sub>oc</sub>(Si/TiO<sub>2</sub>).<sup>20</sup> For the p-Si/n-TiO<sub>2</sub>, the band energies of the n-TiO<sub>2</sub> shift upward but the band energies of the p-Si shift downward. The photovoltage at the p-Si/n-TiO<sub>2</sub> junction is in the opposite direction to the photovoltage at the n-TiO<sub>2</sub>/electrolyte interface due to the downward band bending. The V<sub>oc</sub> of p-Si/n-TiO<sub>2</sub> photoanode is V<sub>oc</sub> = V<sub>oc</sub>(TiO<sub>2</sub>/electrolyte) - V<sub>oc</sub>(Si/TiO<sub>2</sub>).

We can take the advantage of the higher  $V_{oc}$  of the n/n junction for the PEC cell. Enhanced  $J_{sc}$  and  $V_{oc}$  will provide a higher efficiency PEC cell. Also, for the solar water splitting, larger  $V_{oc}$  provides high enough cathodic potential to reduce the water to hydrogen. It is important that the flat band potential of the semiconductor is lower than the hydrogen reduction potential. For example, Fe<sub>2</sub>O<sub>3</sub> (E<sub>g</sub> = 2.1 eV) and WO<sub>3</sub> (E<sub>g</sub> = 2.6 eV) have been studied due to higher stability and lower band gap than TiO<sub>2</sub>. However, both need an external bias voltage to complete the water splitting since their CBMs are lower than hydrogen reduction potential by 0.2 V and 0.1V.<sup>6</sup> Therefore, the n/n composites have the potential for the spontaneous photoelectrolysis of water.

Stability is another important requirement for the PEC cell. By coating the Si with  $TiO_2$ , we can make the photoanode stable in the 1M KOH aqueous solution. The n and p type Si EENW/TiO<sub>2</sub> core/shell structures have shown constant photocurrent levels while testing for one hour (Supporting information Figure S1). In contrast, planar Si wafers and Si EENW arrays generate vigorous H<sub>2</sub>(g) bubbles in the KOH electrolyte and as a result they are etched.

Figure 4 demonstrates the photocurrent density depending on the length of the n-Si EENW/TiO<sub>2</sub> arrays. We prepared 5  $\mu$ m, 10 $\mu$ m, and 20 $\mu$ m long n-type Si EENW/TiO<sub>2</sub> arrays and planar n-Si/TiO<sub>2</sub>. We observed that the longer Si EENW/TiO<sub>2</sub> arrays have higher photocurrent although the photocurrent density normalized by the length of the nanowires decrease as shown in Figure 4b. All of the three Si

EENW/TiO<sub>2</sub> arrays had significantly lower reflectance than Si planar/TiO<sub>2</sub> sample (supporting information Figure S2). The Si EENW/TiO<sub>2</sub> sample can effectively trap the light by extending the path length due to multiple reflection in a high density array structures similar to textured surfaces.<sup>32</sup> When the wires are  $5 \sim 20 \mu m$  long, their reflectance values are nearly the same. All of the three different length Si EENW/TiO<sub>2</sub> arrays have about  $1\sim 2\%$  of reflectance in the UV region (200~350 nm), and about 5 % of reflectance in the visible region (450 ~900 nm). In addition to low reflectance, the high surface area of Si EENW is also expected to contribute the higher photocurrent since it increases the interface area with the electrolyte as well as the overall amount of TiO<sub>2</sub>. Lower reflectance and higher surface area of the Si EENW/TiO<sub>2</sub> contribute to higher absorption and higher photocurrent density than the planar samples.

In order to ascertain the contribution of the core Si, we measured the photocurrent and  $V_{oc}$  of the Si/TiO<sub>2</sub> photoanodes under the visible light illumination. The light was passed through a 441.6 nm edge filter to cut off the UV region from the Xe lamp so that carriers are generated only in the Si. We observed that there was no photocurrent under the visible light for all Si/TiO<sub>2</sub> composites. Photogenerated holes in Si cannot be transferred to the valence band of TiO<sub>2</sub> since there is a significant barrier at the junction (Figure 5c and d). Instead, the photogenerated e<sup>-</sup>/h<sup>+</sup> pairs in the Si recombine so that there is no net charge flux.<sup>19, 33</sup> Therefore, photo-oxidation cannot take place at the TiO<sub>2</sub> surface unless carriers are photogenerated in the TiO<sub>2</sub> shell.

The V<sub>oc</sub> shifts under visible light illumination as shown in Figure 5a and b. For n-Si/n-TiO<sub>2</sub>, the photogenerated holes in the Si move toward the TiO<sub>2</sub> and recombine with electrons in TiO<sub>2</sub> due to an electric field in space charge region. The charge separation shifts the  $E_F$  and the band energies of the n-Si upward, so that the space charge region diminishes. When flat band is attained, there will be no more charge separation. Therefore, the V<sub>oc</sub> of the n-Si/n-TiO<sub>2</sub> photoanode becomes more negative (Figure 5a). For p-Si/n-TiO<sub>2</sub>, the band bending of the p-Si diminishes similar to n-Si/n-TiO<sub>2</sub>, but the reduced band bending shifts the band energies of p-Si downward which reduces the V<sub>oc</sub> under visible light (Figure 5b).

From the change of the  $V_{oc}$  under visible light, we confirmed that the core Si absorbs the visible light and it contributes shift of the band energies.

In conclusion, we compared the photocurrent density of the planar Si and Si EENW coated by ALD  $TiO_2$  thin film. The Si EENW/TiO\_2 has 2.5 times higher photocurrent density than the planar Si/TiO\_2 due to lower reflectance and higher surface area. We also observed an increase of the photocurrent by using n-Si/n-TiO\_2 heterojunctions because n/n junctions enhance the charge separation and minimize recombination. The n/n heterojunction is a promising structure for solar water splitting since the photovoltage at the junction can compensate the lower energy level of the conduction band of the shell semiconductor. Also, the n/n heterojunction could potentially increase the efficiency of the photovoltaic cell due to a higher open circuit voltage and higher photocurrent.

**ACKNOWLEDGMENT** This work was supported by the Director, Office of Basic Energy Sciences, Chemical Sciences, Materials Sciences and Engineering Division, of the U.S. Department of Energy under Contract No. DE-AC02-05CH1123. We thank Prof. Nate Lewis and his group for helpful discussion and assistance in the initial testing of our samples.

**Supporting Information Available**. This material is available free of charge via the Internet at http://pubs.acs.org.



**Figure 1.** Characterization of Si EENW and Si/TiO<sub>2</sub> core/shell structures. (a) Cross sectional SEM of 20  $\mu$ m long Si EENW arrays, demonstrating vertical alignment and high density. (b) Typical TEM image of a Si EENW. (c) Cross sectional SEM images of Si EENW arrays coated with TiO<sub>2</sub> by ALD at 300 °C. (d) Typical TEM image of Si EENW/TiO<sub>2</sub> core/shell nanowire, showing that polycrystalline TiO<sub>2</sub> covers the Si EENW. (e) Top view SEM images of Si EENW/TiO<sub>2</sub> array. (f) Top view SEM image an ALD grown TiO<sub>2</sub> thin film on a Si wafer, showing nanometer size grains of TiO<sub>2</sub>.



**Figure 2.** X-ray diffraction pattern of  $TiO_2$  layer grown by ALD at 300 °C. 25~40 nm  $TiO_2$  deposited on Si EENW arrays (red line), 35 nm  $TiO_2$  thin film on a Si planar substrate (black line). Both  $TiO_2$  layers index to polycrystalline anatase.



**Figure 3.** (a) Photocurrent density versus bias potential (vs SCE) of Si/TiO<sub>2</sub> photoanodes: n-Si EENW array coated by TiO<sub>2</sub> (blue), n-Si(100) planar substrate coated by TiO<sub>2</sub> (green), p-Si(100) planar substrate coated by TiO<sub>2</sub> (purple). Schematic representation of band energies and charge transfer (b) for n-Si/n-TiO<sub>2</sub> and (c) for p-Si/n-TiO<sub>2</sub> under the illumination. Si EENW/TiO<sub>2</sub> samples have 2.5 times larger photocurrent density than Si planar/TiO<sub>2</sub>. n-Si/n-TiO<sub>2</sub> photoanodes have more negative onset potential than p-Si/n-TiO<sub>2</sub> both for planar and nanowire structures.



**Figure 4.** (a) Variation of photocurrent density versus potential depending on the length of n-Si EENW/TiO<sub>2</sub> arrays: 20  $\mu$ m (blue line), 10  $\mu$ m (green line), 5  $\mu$ m (red line) long NW arrays and n-Si planar/TiO<sub>2</sub> (black line). (b) Relationship between photocurrent density versus the length of n-Si EENW/TiO<sub>2</sub>, illustrating longer wire arrays have higher photocurrent. The axis to the right is the current density normalized by the length of the nanowire.



**Figure 5.** Open circuit voltage ( $V_{oc}$ ) versus elapsed time for (a) n-Si EENW/TiO<sub>2</sub> and (b) p-Si EENW/TiO<sub>2</sub> arrays under visible light illumination(< 420 nm, ON) and in dark (OFF), and schematic diagram of band bending and  $V_{oc}$  for (c) n-Si EENW/TiO<sub>2</sub> and (d) p-Si EENW/TiO<sub>2</sub> arrays under visible light illumination, demonstrating that n-Si EENW/TiO<sub>2</sub> increase  $V_{oc}$  the while the p-Si EENW/TiO<sub>2</sub> decrease the  $V_{oc}$  under visible light.

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