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Photocurrent Enhancement of Hematite Nanowires by Gold
Underlayer Deposition and Ti Doping

A thesis submitted in partial satisfaction of the requirements for the
degree Master of Science
in
Electrical Engineering (Nanoscale Devices and Systems)

by
Paniz Allameh

Committee in Charge:
Professor Deli Wang, Chair
Professor Shadi Dayeh
Professor Sungho Jin

2014
The Thesis of Paniz Allameh is approved and it is acceptable in quality and form for publication on microfilm and electronically:

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Chair

University of California San Diego

2014
I dedicate this thesis to my parents, Atousa Majd and Kouros Allameh. Their unconditional love and words of encouragement always helped me to get through rough times.

I also dedicate this work to my grandfather Hossein Majd and aunt Faranak Majd who took me to my first grade class 20 years ago and never stop supporting me during this journey.

I dedicate this thesis to my aunt Fariba Sedaghat who has been there for me through all of the transitions in my life.
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ABSTRACT OF THE THESIS

Photocurrent Enhancement of Hematite Nanowires by Gold Underlayer Deposition and Ti Doping

By

Paniz Allameh

Master of Science in Electrical Engineering (Nanoscale Devices and Systems)

University of California, San Diego 2014

Professor Deli Wang, Chair

Iron oxide is an extensively studied semiconductor material in the field of renewable energy and hydrogen production due to its
versatile properties such as visible light absorption, small bandgap, stability in solutions with variety of pH and most importantly being cheap and abundant. Although it has a maximum theoretical solar to hydrogen efficiency of about 16%, its intrinsic properties such as low oxygen evolution reaction, short carrier life time and diffusion length prevented from achieving such efficiencies and being commercially available.

In this paper Iron oxide nanowires were created using a facile and cost effect solution growth. Carrier concentration, charge separation and Oxygen evolution reaction kinetics of the device was improved by simple sputtering method of gold as an underlayer and Ti as a dopant. Calcination to temperatures up to 800 °C results in additional Sn doping by diffusion from FTO layer as well as crystal structure improvement.

All though XRD measurements show no evidence on existence of TiOₓ more detailed measurements such as XPS is required to validate the results.

The exact mechanism of charge separation, surface passivation and carrier concentration as a result of Ti and Au deposition can be investigated in the future work by Mott Shottky measurements.
Fossil fuels vs. Hydrogen

Fossil fuels formed over hundreds of millions of years under extreme pressure and temperature; however it took humans only a few hundred years to consume an incredible amount of them. Figure 1 shows that combined known sources of Oil, Gas and Coal can only serve us until about 2088.

Figure 1. Amount and lifetime of some Fossil Fuels.
Having a limited source is not the only drawback of fossil fuels. Combustion of fossil fuels releases enormous amounts of Carbon dioxide, CO$_2$ into the atmosphere. CO$_2$ is a heat trapping gas and causes the Infrared Radiation (IR) to stay in the atmosphere, increasing the temperature. This increased temperature is directly involved in disappearing of Arctic sea ice, followed by rising sea levels, heat waves and declining yields of food production.$^2$ Figure 2 shows the increasing rate of CO$_2$ production over the past decades.

![Global Carbon Dioxide Emissions from Fossil Fuel Burning, 1751-2012](image)

Figure 2. Global CO$_2$ emissions until the year 2012.$^2$
To prevent more CO₂ emission and provide more energy for the growing demand of today’s world, a less pollutant more efficient substitute is needed. Hydrogen is the lightest element and most abundant chemical substance of the universe (constituting about 75% of all matter). The heat content of hydrogen gas is 141.80 MJ/Kg that is 3 times higher than Gasoline (47.30 MJ/Kg) and about 4.3 times higher than high quality Coal (32.50 MJ/Kg).

\[
2\text{H}_2(g) + \text{O}_2(g) \rightarrow 2\text{H}_2\text{O}(g), \quad \Delta H = -484 \text{ kJ mol}^{-1}
\]

Having water as its sole waste product and with its high energy content, Hydrogen is a promising alternative for Fossil Fuels.

Among several other methods of hydrogen production--such as steam reforming, Plasma reforming, Electrolysis, Thermolysis and Photobiological water splitting--Photocatalytic water splitting is a promising and renewable method. In a typical Photoelectrochemical (PEC) cell, water splits into hydrogen and oxygen upon light illumination on photocatalytic material such as semiconductors.
Chapter 2 Photoelectrochemical cells (PEC)

2.1 Semiconductors

A material with electrical conductivity between metals and insulators is called a semiconductor. Pure semiconductors have poor conductivity that can be increased upon doping with electron donor or electron acceptor elements. If the semiconductor is doped with electron donor element it has excess negatively charged electrons (charge carrier) and is called n-type semiconductor. If the semiconductor is doped with an electron acceptor element it will have vacancy energy level in its valance band that act as a positive charge carrier (holes) and is called a p-type semiconductor. For example, when Silicon (Si) with 4 valance electrons is doped with Antimony (SB) with 5 valance electrons, 4 out of 5 electrons of phosphorous bond with 4 adjacent Si atoms leaving 1 free negatively charged electron, thus forming an n-type Si. On the other hand when Si is doped with Boron (B) with 3 valance electrons, all of the Boron’s valance electrons bond with three adjacent Si atoms leaving the 4th Si atoms electron deficient. This electron deficiency is a positively charged carrier. Figure 3 demonstrates the effect of Sb and B dopants on Si respectively.
The small conductivity of semiconductors is due to their small but non-zero bandgap. In other words, there is a small energy gap (forbidden states) between the top of the valance band and bottom of the conduction band. The electrons in semiconductor can absorb energy that is equal or larger than its specific bandgap and jump from valance band to conduction band. This property is the basis of the semiconductor electrodes in photoelectrochemical cells.

2.2 PEC Device

PEC cell is a type of solar cell in which water decomposes into oxygen and hydrogen, a process called artificial photosynthesis. It can produce electrical energy and hydrogen gas that can be used as fuel.
alternative to gasoline. Figure 4 shows a schematic of a typical PEC device. A PEC cell has 2 different electrodes: Photonode and Photocathode. In principle, there are three different cell types:

- n-type semiconductor photoanode and metal photocathode
- n-type semiconductor photoanode and p-type semiconductor photocathode
- metal photoanode and p-type semiconductor photocathode

![Schematic Diagram of a Photoelectrochemical cell.](image)

For a typical n-type photo anode and p-type photocathode cell, Photons with equal or higher energy of the bandgap of the photo anode create electron hole pairs in the photo anode. The holes transfer to the semiconductor/electrolyte interface and oxidize O$_2$ to O while the electrons migrate to the photo cathode through the
external circuit to reduce H\(^+\) to H\(_2\). The water splitting reaction contains two half reactions. The required energy of each reaction is measured against Normal Hydrogen Electrode (NHE).

Oxidation: \(2H_2O \rightarrow 4H^+ + 4e^- + O_2\) \(E^0 = 1.23\) V vs. NHE

Reduction: \(4H^+ + 4e^- \rightarrow 2H_2\) \(E^0 = 0.00\) V vs. NHE

Overall: \(2H_2O \rightarrow 2H_2 + O_2\) \(E^{\text{cell}} = 1.23\) V vs NHE

\[\Delta G = 475\ \text{kJ/mol}\]

The half reaction potential values are measured at pH=0 and can shift with pH according to the following equation:

\[E = E_0 - 0.059(v) \times \text{pH}\]

Since both half reaction potentials change with a same amount, the total energy difference stays as 1.23 V vs. NHE. This is the minimum energy for water splitting however energy lost due wire connection or heat should also be considered for precise calculation.

### 2.3 Photo ELECTRODE

The photo electrode should satisfy the following requirements simultaneously,
**Bandgap:**

The most important characteristic of the photo electrode is its bandgap. It should be larger than the energy required for oxidation of water that is 1.23 eV and at the same time not too large to be able to absorb light in the visible range. Table 1 lists the bandgap energy and minimum bias requirement of several oxide anodes.

Table 1. Bandgap energy and minimum bias of some oxides.  

<table>
<thead>
<tr>
<th>Material</th>
<th>$E_g$ (eV)</th>
<th>$qV^*_b$ (eV)</th>
<th>$E_g + qV^*_b$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ta$_2$O$_5$</td>
<td>4.0</td>
<td>$-0.4$</td>
<td>3.6</td>
</tr>
<tr>
<td>SnO$_2$</td>
<td>3.5</td>
<td>0</td>
<td>3.5</td>
</tr>
<tr>
<td>KTaO$_3$</td>
<td>3.5</td>
<td>$-0.2$</td>
<td>3.3</td>
</tr>
<tr>
<td>Nb$_2$O$_5$</td>
<td>3.4</td>
<td>0</td>
<td>3.4</td>
</tr>
<tr>
<td>BaTiO$_3$</td>
<td>3.3</td>
<td>$-0.1$</td>
<td>3.2</td>
</tr>
<tr>
<td>SrTiO$_3$</td>
<td>3.2</td>
<td>$-0.2$</td>
<td>3.0</td>
</tr>
<tr>
<td>ZnO</td>
<td>3.2</td>
<td>0</td>
<td>3.2</td>
</tr>
<tr>
<td>TiO$_2$</td>
<td>3.0</td>
<td>+0.1</td>
<td>3.1</td>
</tr>
<tr>
<td>PbO</td>
<td>2.8</td>
<td>+0.4</td>
<td>3.2</td>
</tr>
<tr>
<td>Bi$_2$O$_3$</td>
<td>2.8</td>
<td>+0.7</td>
<td>3.5</td>
</tr>
<tr>
<td>WO$_3$</td>
<td>2.7</td>
<td>+0.5</td>
<td>3.2</td>
</tr>
<tr>
<td>YFeO$_3$</td>
<td>2.6</td>
<td>+0.5</td>
<td>3.1</td>
</tr>
<tr>
<td>Pb$_2$Ti$<em>3$W$</em>{13}$</td>
<td>2.4</td>
<td>+0.4</td>
<td>2.8</td>
</tr>
<tr>
<td>CdFe$_2$O$_4$</td>
<td>2.3</td>
<td>+0.8</td>
<td>3.1</td>
</tr>
<tr>
<td>PbFe$<em>{12}$O$</em>{19}$</td>
<td>2.3</td>
<td>+1.0</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>2.2</td>
<td>+0.7</td>
<td>2.9</td>
</tr>
<tr>
<td>FeTiO$_3$</td>
<td>2.2</td>
<td>+1.1</td>
<td>3.3</td>
</tr>
<tr>
<td>Fe$_3$TiO$_4$</td>
<td>2.1</td>
<td>+1.2</td>
<td>3.3</td>
</tr>
<tr>
<td>Hg$_2$Ta$_2$O$_7$</td>
<td>1.8</td>
<td>+1.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Hg$_2$Nb$_2$O$_7$</td>
<td>1.8</td>
<td>+1.1</td>
<td>2.9</td>
</tr>
</tbody>
</table>

*Flat band potential vs. H$_2$/H$_2$O at pH = 14.*
A negative bias means the semiconductor's bandgap is large enough to split water and the valance and conduction bands are positioned below and above the Oxygen and hydrogen potentials, thus require no external bias. It is easy to see that most of the oxides with negative or 0 bias requirement have bandgap energies of at least 3.2 eV that corresponds to the wavelength of 387nm. Exclusion of photon energies between 1.23 and 3.2 ev from water splitting reaction results in the decrease of the overall performance.

**Band Edge position:**

The energy band edge position is also a determining factor in water splitting. Ideally the bottom of the conduction band should be below the oxidation energy of the oxygen and the top of the valance band should be above the hydrogen reduction energy. Figure 5 shows the band position of some semiconductors and their relative band position with respect to the normal hydrogen electrode (NHE) at pH=1.
**Stability:**

Resistance to chemical and photo corrosion is another determining factor in choosing the photoelectrode material. The reactions at the solid/liquid interface could change and destroy the electrode properties. Unfortunately many of the semiconductors with suitable bandgap energy are not resistant to the damage cause by photo illumination. Gerischer showed that photo anodes and photocathodes should satisfy the following criteria in order to be resistant against corrosion:
E(O₂/H₂O) < E_{p,d}

E(H⁺/H₂) > E_{n,d}

E(O₂/H₂O) is the energy of the redox couple (H₂/O₂), E(H⁺/H₂) is the energy of the redox couple H⁺/H₂, E_{p,d} is the free enthalpy of oxidation reaction and E_{n,d} is the free enthalpy of reduction reaction for one electron. Figure 6 shows the decomposition potentials of several semiconductors at pH=2.  

Figure 6. Decomposition potentials of several semiconductors.
TiO$_2$ is one of the best known oxides for corrosion resistant as well as SnO$_2$ and WO$_3$. Their $E_{n,d}$ is above $E(H^+/H_2)$ meaning they reduce hydrogen before reducing themselves. Their $E_{p,d}$ is below $E(O_2/H_2O)$ meaning they oxidize O2 before getting oxidized themselves. A semiconductor such as ZnO is stable only as a cathode while Cu$_2$O is not stable at all. The great corrosion resistant of TiO$_2$ trades off by its poor light absorption spectra (UV range).

To this date, research has shown no single material that can satisfy all of the requirements to serve as an electrode for complete water splitting. A heterostructure of a low bandgap semiconductor mixed with a corrosion resistant large bandgap semiconductor, would be an ideal structure that meets all three requirements of bandgap energy value, band edge location and stability.
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5. No Title. at <http://hyperphysics.phy-astr.gsu.edu/hbase/solids/dope.html>


8. MARUSKA, H. P. & GHOSH, A. K. A STUDY OF OXIDE-BASED HETEROSTRUCTURE PHOTOELECTRODES H . Paul M A R U S K A and Amal K . GHOSH Although investigations have now been conducted on more than 50 different materials that have shown promise for use as sunlight absorbers in water photo- elec. 1, 411–429 (1979).

Chapter 3 Iron Oxide Photoanode

3.1 Introduction

Iron is the 26th element and belongs to the first transition metal series of the periodic table. It forms most of the outer and inner core of our planet. 32.1% of the mass of the earth is composed of Iron, thus it is the most abundant material on planet earth¹ and the 6th most common element in the Universe.² ³ Iron is refractory element and maintain its structure and properties at high temperature making it a very stable material. ³

Iron forms wide range of oxidation states from -2 to +6 with +2 and +3 being the most common states. Among 16 known oxide an oxyhydroxide structures, Iron (III) oxide also known as ferric oxide, is of particular interest.

Iron (III) oxide exist in several phases: Epsilon, Beta, Gamma and Alpha phase.

3.2 Iron(III) Oxides Structure

The epsilon phase (ε-Fe₂O₃) has an orthorhombic structure (Pna₂₁) and is considered to be an intermediate phase between
alpha and Gamma. It is mostly mixed with these two phases and hard to find in a pure form. It is a metastable phase and transforms to alpha phase at temperature higher than 500 up to 750. It has a very large coercive field and can be used to make permanent magnets used in magnetic recording.  

Figure 7. Orthorhombic structure of epsilon phase (ε-Fe2O3).
The Beta phase (\(\beta\-Fe_2O_3\)) has a body centered cubic structure, bixbyite, and is a metastable phase of iron oxide below 770K and transforms to alpha phase and higher temperatures.\(^8\)

![Beta phase structure](image)

Figure 8. Body centered cubic structure Beta phase (\(\beta\-Fe_2O_3\)).\(^7\)

The Gamma phase (\(\gamma\-Fe_2O_3\)) has a spinel structure with ferrimagnetic behavior with a Curie temperature \((T_C)\) of 928 K.\(^9,10\) due
to its strong magnetic behavior it is used widely in magnetic recording (recording tapes) industry.

Figure 9. Spinel structure of Gamma phase (γ-Fe2O3).  

The alpha phase (α-Fe2O3) is the most common form of the Fe2O3 with rhombohedral, corundum structure. It has an antiferromagnetic behavior below 260K and weak ferromagnetic property between 260 and 950K.  

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3.3 \( \alpha{-}\text{Fe}_2\text{O}_3 \) Hematite Photoanode Properties

\( \alpha{-}\text{Fe}_2\text{O}_3 \) also known as hematite is one of the most studied metal oxide semiconductors for water splitting for several reasons including but not limited to: being a non-toxic inexpensive and abundant semiconductor, visible light absorption due to narrow indirect band gap of 2.0-2.2 ev, stability in aqueous solutions and
finally valence -band edge position for water oxidation.\textsuperscript{11,12,13} An estimated maximum theoretical solar to hydrogen (STH) efficiency of 15\% (based on bandgap) makes Hematite an excellent candidate for photoanode.\textsuperscript{14}

On the other hand hematite has intrinsic limitations such as poor surface oxygen evolution reaction kinetics, poor conductivity, short minority carrier lifetime in the order of 10ps, Short hole diffusion length of (2 to 20 nm) and long penetration depth of visible light because of its indirect bandgap transition (100nm for $\lambda=500nm$).\textsuperscript{15-21} The two later suggest that most of the minority carrier charges (holes) would recombine within the bulk structure before being transferred to the surface of the hematite and reach the liquid surface. Strategies such as elemental doping, nano-structuring, integration of oxygen evolving catalysts, surface modification and heating treatment have been employed to increase the overall efficiency of hematite devices and overcome the previous drawbacks.

3.3.1 Doping effects

For a semiconductor crystal with low conductivity and charge carrier mobility, introduction of an impurity can alter the structure of the crystal and improve the conductivity significantly. Donor impurities
create states near the conduction band of the semiconductor while acceptor impurities create energy states near the valence band of the semiconductor. The small gap between these induced states and their closet energy band edge (of the semiconductor) is called dopant-site binding energy. Because of this, it takes a very small energy to ionize the dopant atom and release its free charge carriers into the conduction or valence band of the semiconductor, thus improving the conductivity. Figure 11 shows the effect of doping on Valence and Conduction band in the semiconductor.

![Figure 11. Effect of doping on Valence and Conduction band energy levels.](image)

The semiconductor conductivity due electron/hole concentration n/p and electron/hole mobility μₑ and μₚ is defined respectively by the following formulas:
\[ \delta = n*e*\mu_e \]

\[ \delta = p*e*\mu_p \]

Dopants can also shift the energy bands relative to the Fermi level. These can be useful in semiconductors with improper band edge for continuous water splitting\(^{23}\). The Fermi level after doping can be calculated with respect to the intrinsic Fermi level before doping using the impurity doping concentration \(n_0\) and intrinsic carrier concentration of the semiconductor \(n_i\) using:

\[ E_f - E_i = kT \ln \left( \frac{n_0}{n_i} \right) \]

Research shows that doping hematite with electron donors such as Zr, Ti, Sn, Si and electron acceptors such as Cu and Mg improved the overall performance photoanode.\(^{24-26}\)

### 3.3.2 Nanostructuring effects

As was mentioned before, hematite has short hole diffusion length compared to its visible light penetration depth suggestion recombination minority charge carriers before reaching the electrolyte interface. This limitation can be reduced by engineering the structure of photoanode. Figure 12A shows that for a film
morphology the photogenerated hole has to travel the entire length of the film \(1/\alpha\) , \(\alpha\) being the absorption coefficient) to perform water oxidation. In contrast, Figure 12B shows that with nanowire morphology the light still travels the length of the nanowire \(1/\alpha\) but the photogenerated hole only needs to travel the radial distance of the nanowire.

![Figure 12](image)

Figure 12. Hole diffusion path in (A) film and (B) nanowire. 27

The maximum minority carrier diffusion before recombination is related to the minority carrier life time \(\bar{\tau}\) and Diffusion coefficient \(D\) by

\[
L = \sqrt{D \cdot \bar{\tau}}
\]

If the diameter of the nanowire is less than \(L\) then most of holes can reach the electrolyte before recombination.
3.3.3 Surface treatment effects

Water splitting efficiency increases with increasing the density of the holes on the surface to participate in the oxidation reaction. When holes reach the semiconductor /liquid interface they can either oxidize water or recombine with surface electrons. Hematite known to have low oxidation kinetics for 2 reasons: Complex 4 step electron transfer for water oxidation and high density surface states. Attempt to improve either limitation can enhance solar water splitting efficiency.

Surface states:

Sudden crystal transition from bulk to the surface (termination of crystal structure) would affect the electrical properties of the material at the surface. Atoms at the surface develop energy states within their bandgap; these states will not be formed in bulk atoms. Figure 13 shows a schematic of these states at the semiconductor liquid interface.
Hematite is known to have low oxygen evolution kinetics due to these surface states. The extreme large over potential (about 1 V compared to its flatband potential of 0.4) may the result of these states. Le Formal et al showed that thin layer deposition of Al₂O₃ passivates these states and decrease the overpotential by about 100mV.²⁹

Another strategy to prevent hole recombination and increase OER kinetics is introducing catalysts such as CO on the surface of hematite to decrease activation energy of the oxygen evolution reaction. ³⁰
References


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Chapter 4 Methods and Measurements

4.1 Device Fabrication

In order to investigate the effect of Gold and Titanium on Iron oxide nanowires, the following procedure was adopted from Vayssieres with small modification.\textsuperscript{1} Fluorine-doped tin oxide (FTO, TEC 15, Pikington glass) glass substrate was cut into 0.64 cm\(^2\) squares, sonicated for 5 minutes in acetone, isopropanol and DI water respectively. The samples were then rinsed with deionized water and blown dry with air. Small portion of the edge of the FTO samples (approximately 0.16 cm\(^2\)) was covered with Kapton Tape BGA High Temperature Heat Resistant Polyimide (up to 280 °C) to prevent nanowire growth and maintain an Ohmic contact.

For samples with intermediate layer between FTO and nanowires, 3nm Au/Ti was sputtered on the substrate using a Denton Discovery 18 Sputtering system. The active pressure of argon was 2.5 mT with 200W RF bias for Au and 400W bias for Ti.

A solution of 1.21 g ferric chloride (FeCl\(_3\).6H\(_2\)O), 2.54 g sodium nitrate (NaNO\(_3\)) and 30 ml deionized water [17.6 M\(\Omega\)·cm] was made and sonicated for 5 minutes. The solution and the substrate were then
transferred into a stainless still autoclave and placed in an oven at temperature 108 °C for 4 hours. The autoclave cooled down in room temperature for 2 hours and samples were washed with DI water and Dried in air. 8nm Ti was sputtered on the samples using the same sputtering device and condition using different deposition time. Finally the heat resistant tape was removed and samples were heated in high temperature laboratory oven to be activated. The heating profile was as follow: the sample were heated from room temperature to 550 °C at a rate of 17.5 °C/min. temperature was kept at 550 °C for 2 hours to convert Iron Oxy Hydroxide (FeOOH) to Iron Oxide. The temperature was raised to 650 at a rate of 25 °C/min and kept constant for another 20 minutes. Finally the temperature rose from 650 to 800 at a rate of 25 °C/min. The samples were immediately taken out of the oven and cooled down in room temperature naturally. Figure 14 shows the heating profile of as prepared samples.
Figure 14. Heating Profile for hematite activation.
Figure 15. Schematic diagram of hematite samples a) 3nm Au underlayer b) 3nm Ti underlayer c) 3nm Au underlayer with 8nm Ti top deposition d) 3nm Ti underlayer with 8nm Ti top deposition e) no intermediate layer deposition f) 8nm Ti top deposition.
4.2 Performance and characterization

4.2.1 PEC and IPCE measurements

Photocurrent measurements were conducted in a three electrode configuration in 1 M NaOH as the electrolyte with pH 13.6. A platinum coil was used as a counter electrode, Hg/HgO as a reference electrode and as prepared hematite nanowires on FTO substrates as a working electrode. A wire was attached to the surface of the FTO, that was covered with tape before annealing, using a silver paste. The sample was then covered with epoxy to control the illumination area. The exposed area was calculated using PhotoShop comparing the Pixel numbers of the selected sample compared to pixels of the known 1 cm² square as shown in Figure 16.

Figure 16. Schematic of a typical sample next to 1 cm² square for area measurements by Photoshop.
The samples were illuminated by a Newport 67015 solar simulator and a 150 W xenon lamp equipped with 1.5 AM filter and approximately 100mW/cm² light intensity on the sample. Electrodes were connected to a Digi-Ivy potentiostat for Current density measurements with a scan rate of 50 mV/s swept between -0.5 to 0.67 V vs Hg/HgO. The potentials vs. Hg/HgO were converted to the reversible hydrogen electrode (RHE) using Nernst equation:

\[ E_{\text{RHE}} = E_{\text{Hg/HgO}} + 0.059 \text{pH} + E_0 \]

E₀ for the Hg/HgO electrode in 1M NaOH is 0.14v at room temperature and \( E_{\text{Hg/HgO}} \) were potentials applied to working electrode.

For Incident photon-to-current conversion efficiency (IPCE) measurements same setup was used. The light would pass through a iHR 550 monochromator to be breakdown into desired wavelengths. Calibration of the monochromatic light was done using a Newport 818-UV silicon photodiode. The IPCE was calculated using the following formula:

\[ \text{IPCE} = \frac{J_{\text{phS}}(\lambda)}{J_{\text{phD}}(\lambda)} \cdot \frac{\text{R}(\lambda) \cdot 1240}{\lambda} \]
\( \lambda \) is the wavelength of incident light in nm. \( \frac{J_{\text{phS}}(\lambda)}{J_{\text{phD}}(\lambda)} \) is the ratio of Sample to the photo diode current density (both mA cm\(^{-2}\)). \( R(\lambda) \) is the Si photodetector responsivity provided by the supplier in A W\(^{-1}\).

### 4.2.2 SEM and XRD measurements

The samples were characterized by a Phillips XL30 scanning electron microscope with working distance of 10mm and 10kV. The XRD measurements were done using Cu-Ka1 radiation. Step angle size was 0.2 degree with dwell time of 7 seconds.
Reference

Chapter 5 Results and discussions

This study involved synthesis, structural and performance analysis of hematite nanowires grown on FTO substrate with different metal under and over layer deposition.

5.1 Morphology

Figure 17 presents the SEM images of the Au bottom/Ti top deposition sample as FeOOH phase, Fe2O3 phase (heat at 550 °C for 2 hours) and after sintering up to 800 °C at different magnifications. The samples got denser with heating 2 hours in 550 °C and the crystallinity improved more with heating samples all the way to 800 °C. The results are similar with other hydrothermal growth mechanisms reported before\(^1\). The samples didn’t change their morphology at 800 °C as they have been kept in that temperature for only few minutes.
The nanowires are approximately 70 nm wide and 200 nm long. The Top metal deposition did not change the morphology because it was not initially involved in the growth procedure as a precursor. The bottom contact deposition altered the growth of nanowires. Figure 18 compares the Au and Ti bottom deposition samples. The nonuniform growth of nanowires on the sample with Ti underlayer results in
inconsistence I-V characteristics, Figure 19, thus the sample was excluded from the rest of the experiment.

Figure 18. Comparison of hematite growth on Ti (left) and Au (right) underlayer.

5.2 Performance

As mentioned before, a three electrode system was used to measure the photoactivity of samples. It should be noted that efficiencies calculated by this setup are not precise because the voltage is measured between working and counter electrode whereas the potential is measured between working and reference electrode.

Photocurrent activity of samples are shown in Figure 20.
Figure 19. Current density under illumination for several samples with Ti underlayer.

Figure 20. Current density under illumination (left) and dark (right).
The sample without heat treatment shows a large dark current compared to others. It is known that imperfect crystal structures present crystallographic defects in grain boundaries and reduce hematite into Fe$_3$O$_4$\textsuperscript{2}. The Semimetal behavior of Fe$_3$O$_4$ attributed to elevated dark current that is in agreement with our findings. The undoped sample with heat treatment showed higher photocurrent compared to the undoped sample that was not heated. The increase in conductivity and carrier concentration is due to diffusion of Sn atoms from the FTO glass upon annealing as reported previously.\textsuperscript{3} The low onset potential of about 0.7V vs. RHE (Reversible Hydrogen Electrode) is also in agreement with as prepared hematite nanowires in the past.\textsuperscript{3,4} The sample with gold underlayer shows same onset potential but higher current density. The first explanation of comes from Shottky barrier that is formed at the gold and hematite interface. The barrier height is the difference between the work function of gold (4.2-4.7)\textsuperscript{5} and electron affinity of hematite (4 ev )\textsuperscript{6} which is between 0.2 to 0.7 V. When the voltage is applied, the electrons from hematite will flow down to gold and effectively separated from the holes resulting in less recombination and higher current. Au showed similar behavior with other material such as BiFeO$_3$ and BiVO$_4$.\textsuperscript{7,8} The thin layer of gold can also melt and diffuse into hematite and increase carrier
concentration and conductivity of hematite to improve the photocurrent. Another possible explanation for improvement of photocurrent by Au deposition could be suppression of Sn diffusion. If majority of Sn atoms diffuse from the FTO layer, conductivity of FTO would decrease dramatically and cannot transfer electrons to the external circuit fast.

The sample with Ti top deposition shows a larger current density compared to undoped and Au underlayer. A positive shift of onset potential with Ti doping is observed. This is in agreement with some previous reports\textsuperscript{9,10} while contradicting others.\textsuperscript{11,12} This difference could be related to different annealing time. It seems that calcination of samples at high temperatures (500-800) would diminish the “deep trap states” thus reducing the onset potential.\textsuperscript{12-13} The Sample with Au underlayer and Ti overlayer shows maximum current density while having slightly lower onset potential compare to Ti overlayer sample without Au underlayer deposition.

Ti is an active metal and upon exposure to heat or highly oxidative solution (pH=13.6) is expected to oxidize it to TiO\textsubscript{2}. Figure 21 shows the XRD measurements for 2 samples with and without Ti top deposition.
Figure 21. XRD peaks of undoped (blue, bottom) and Ti doped (red, top) hematite.

The thickness of the FTO glass was more than of the XRD sample holder thus a shift in the peaks is observed. The SnO2 peaks are in good agreement with those previously reported (JCPDS no. 33-0664). The SnO2 peaks shift (about 2θ= 0.5 degrees) can be used to adjust the 2θ axis. After shifting the peaks backward by 0.5 degrees they both show a dominant peak of high index (104) at 2θ= 35 and characteristic peak at 2θ= 37 that is indexed to (110). The results are similar to the previously reported values obtained by slightly modified hydrothermal growth mechanism. No peaks of titanium or its oxides are captured within detection limit of the device. There are two
possible explanations for this observation. First, the thickness of the deposited Ti layer was so thin that the peaks could not be detected. It is also possible that upon heating up to 800 °C, the Ti layer was melted and diffused completely into the hematite crystal structure.

A simple experiment comparing 12nm TiO2 and 8 nm Ti top layer was performed. The thicker thickness of TiO2 is chosen to roughly represent same amount of Ti atoms in both samples. Figure 22 shows much larger photocurrent activity for TiO2 layer compared to Ti layer. One possible explanation for dramatic difference between the TiO2 and Ti top sputtered is the TiOₓ form of oxide that is less active than TiO₂. A more detailed analysis such as X-ray photoelectron spectroscopy (XPS) is needed to check for existence of Ti-O binding if any to validate formation of any TiOₓ.
5.3 Incident photon to Current efficiency (IPCE)

The light that reaches the sample will have less intensity due losses through solution and setup. To calculate the actual intensity of light on the sample the following attenuation coefficient was considered:

$$\alpha = -\frac{1}{L} \ln \frac{I_{\text{out}}}{I_{\text{in}}}$$

$L$ is the distance between the cell quartz window and the other end of the cell, $I_{\text{in}}$ is the light intensity collected by the Si photodiode at the quartz window position, and $I_{\text{out}}$ is the light intensity exiting the cell at the other end. The light intensity on the sample and IPCE (%) is calculated by:
\[ I_{Si} = I_{in} e^{\alpha L_s} \]

\[ \text{IPCE} = R_s \frac{q}{h \nu} = R_{Si} \frac{1240 I_s A_l}{\lambda I_{Si} A_S} \times 100 \]

\( L_s \) is the distance between the cell quartz window and the sample and \( R_{Si} \) is the responsivity of the Si photodiod. Figure 23 shows the calculated IPCE (\%) at voltage 1.5 vs. RHE for three different samples.

![Figure 23. IPCE comparison of undoped (black, square), doped (red, circle) and doped with gold underlayer (green, triangle)](image)

Both samples with Ti top overlayer and one with Au underlayer show improvement in IPCE (\%). On the other hand the sample with Au underlayer shows no significant difference compare to the one without. This suggest that Au has no plasmonic effect and the
enhancement is only due integration of Ti. It is suggested that IPCE(%) improvement by Ti is the result of formation of Ti$^{4+}$ that can donate a free electron and improve carrier concentration and conductivity.\textsuperscript{15} This will decrease recombination rate and enhance photo activity. The IPCE pattern does not follow the current difference for samples with and without Au underlayer.

5.4 Current vs. Time measurements

Figure 24 shows the Photo response of samples at potential 1.23 Vs RHE. The current spikes are the result of rapid hole migration and accumulation at the surface upon illumination. Due to the Low oxygen evolution reaction kinetics at the surface of hematite the phogenerated holes recombine in bulk or surface states.\textsuperscript{2,16} Au underlayer and Ti top deposition show significant decrease in recombination rate until reaching the equilibrium.
Figure 24. Current vs time for graphs at potential 1.23 V vs RHE.
References


Chapter 6 Conclusion

The purpose of this research was to improve the hematite nanowires photocurrent by sputtering gold underlayer and Titanium overlayer. Cheap solution growth and doping mechanism via sputtering was sued to minimize the cost of fabrication. Photocurrent enhancement by Au deposition was attributed to decreasing hole and electron recombination rate and effective charge separation as seen in Current vs Time measurements. It is also hypothesized that Au prevents excessive diffusion of tin elements from FTO thus improving conductivity of the contact between hematite nanowires and FTO surface. Photocurrent enhancement by Ti was attributed to formation of unknown TiO\textsubscript{x} that is less conductive than TiO\textsubscript{2}. Increasing carrier concentration via doping is also considered as a reason for current improvement.

The future work for this experiment will be aimed on more detailed analysis of the structure of the nanowires. An XPS spectra and elemental mapping analysis would provide better insight on the exact mechanism Ti overlayer and gold underlayer improve the hematite structure. Furthermore, Flat potential, Carrier concentration and
possible surface passivation by Ti overlayer can be investigated by Mott Shottky measurements.