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C.S. Blair
(Ph.D. Thesis)

March 1984

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The Photoelectrochemical Properties of Plasma Deposited Iron Oxide Thin Films

Christopher Scott Blair
Ph.D. Thesis

Lawrence Berkeley Laboratory
University of California
Berkeley, California 94720

March 1984
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Iron Oxide Thin Films

Christopher Scott Blair

Abstract

Thin films of iron oxide were produced by the RF glow discharge
decomposition of iron pentacarbonyl in the presence of oxygen.
Optical emission spectroscopy was used to investigate the chemistry
of the glow discharge. Emission spectra showed the presence of
oxygen atoms, FeO, Fe(I), CO, Ar and N₂. An actinometry technique
was utilized to determine how the concentration of each of these
species varied with changes in RF power level and O₂/Fe(CO)₅ ratio.

Film composition was investigated using elemental analysis, Auger
electron spectroscopy (AES), secondary ion mass spectrometry (SIMS)
and electron spectroscopy for chemical analysis (ESCA). Stoichiometric Fe₂O₃ was noted with deposition temperature greater
than 300°C and O₂/Fe(CO)₅ feed ratios greater than 1. Carbon was
detected in films deposited at temperatures of 250°C or less.

Film structure was investigated using x-ray diffraction and
scanning electron microscopy (SEM). Amorphous films were produced
at temperatures less than 200° C. At higher temperatures, \( \alpha \)-Fe, wustite (FeO), magnitite (\( \text{Fe}_3\text{O}_4 \)) and hematite (both \( \alpha \) and \( \gamma \)) were detected. Crystallite size and degree of preferred orientation varied with deposition temperature and RF power level.

Optical transmittance and reflectance were measured for the plasma deposited films. The absorption depth was less than 100 nm for light from 200 to 500 nm.

Capacitance–voltage measurements were performed to determine electron concentration in the films. Resistivities and dielectric constants were determined from current–voltage and capacitance measurements, respectively. Electron mobility and depletion layer thickness were calculated from these data. Carrier concentrations were approximately \( 10^{16} / \text{cm}^3 \) for all deposition conditions.

The photoelectrochemical properties of the films were measured in 1 M NaOH. Photocurrents were observed at anode potentials greater than \(-0.5 \) V vs. SCE. The highest quantum efficiency noted was 45\% using 250 nm light at 0.6 V vs. SCE. Surface recombination and depletion layer recombination played a role in limiting quantum efficiency at short wavelength. Long wavelength quantum efficiency was low due to the nature of the electronic transition of iron oxide. Quantum efficiency was greater than other types of iron
oxide thin films tested. A theoretical solar energy conversion efficiency was calculated to be 0.6%. 
Acknowledgments

I would like to thank my research director, Dennis W. Hess, for the opportunity to work on this project. The help and advice he gave me throughout my graduate education was sincerely appreciated. I would also like to thank the other members of my thesis committee, Charles W. Tobias and Eugene E. Haller for their efforts in reviewing this work.

Several individuals were responsible for performing analyses on the thin films produced in this project. In particular, Tom Allen of Optical Coatings Laboratory, Inc. provided reflectance data and John F. Evans of the University of Minnesota contributed surface analyses. The staff of Lawrence Berkeley Laboratory and the College of Chemistry Analytical Laboratory likewise provided valuable services.

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Chapter 1

Introduction

1.1 Iron Oxide Thin Films

Iron oxide thin films are used in a number of applications. Perhaps the most widely known is in magnetic recording and memory applications. Iron oxide is ideal for a recording medium because it combines a high saturation magnetization with a high degree of chemical stability (1). For most recording and memory applications, small particles of iron oxide are mixed with an organic binder and spread in a thin film on the tape or disk.

Iron oxide is also useful as a transparent photomask in the integrated circuit (IC) processing industry (2). While iron oxide is transparent to some visible light, it strongly absorbs light at wavelengths shorter than about 550 nm. Since most photoresists respond only to light in the shorter wavelength region (< 450 nm), iron oxide can be used to generate resist patterns. Here the unique
advantage over other materials is that the operator can see through the iron oxide photomask and insure proper mask alignment.

Finally, iron oxide is useful as a liquid junction solar cell. By absorbing shorter wavelengths of visible light (< 560 nm), photons are utilized in electronic processes that make available chemical or electrical energy. Since iron oxide combines high light absorption with a bandgap well within the visible spectrum (2.2 eV, 560 nm) iron oxide thin films have been studied as possible solar energy conversion materials (3). Solar energy applications of iron oxide will be discussed in more detail later.

1.2 Production of Iron Oxide Thin Films

A number of techniques have been utilized to produce thin films of iron oxide. Perhaps the easiest method is to oxidize the surface of pure iron. This can be done thermally, either with a flame or in a furnace under an oxygen atmosphere, or electrochemically, where the iron metal is anodically biased in an electrolyte solution. While both methods result in a surface oxide layer, the thermal film always results in a surface layer of α-Fe₂O₃, with an inner layer of Fe₃O₄ (4). The anodic oxide also has an inner layer of Fe₃O₄, but
the surface is always $\gamma$-$\text{Fe}_2\text{O}_3$ (5).

Iron oxide films can also be deposited from the gas phase. Reactive evaporation was used recently in an effort to produce epitaxial films of magnetite for magnetic recording purposes (6). In this case, pure iron metal was evaporated in an oxygen atmosphere and deposited onto NaCl and iron substrates.

Iron oxide films can be formed by sputtering (7,8). An iron oxide target is made the cathode in an RF glow discharge at moderate vacuum, with $O_2$ and an inert gas used as the sputtering atmosphere. Both amorphous and crystalline films can be produced in this manner. The $\alpha$, $\beta$ and $\gamma$ crystalline phases of iron oxide can all be obtained, depending upon the deposition conditions used.

Chemical vapor deposition (CVD) has been used to produce iron oxide thin films. In CVD, gas phase materials which contain iron and oxygen undergo a chemical reaction to produce a solid film of iron oxide. The gas phase iron sources used to date have been iron pentacarbonyl (9,10,11), iron chloride (12), and iron acetylacetonate (13,14,15). In all cases, the substrate upon which the film is deposited must be heated to high temperature ($>200^\circ\text{C}$) in order to activate the chemical reaction. The films produced can
be either crystalline or amorphous, depending on the deposition temperature.

1.3 Properties of Iron Oxide

As mentioned previously, iron oxide has a number of useful properties. A summary of reported studies on this material can be found in Ref. 16. Some of the key properties of iron oxide that are relevant to the current study are described below.

Iron oxide can exist in many structural forms. The "Powder Diffraction Files" list 9 distinct crystal structures (17), and amorphous iron oxide has also been reported (2,11,18). The most stable crystalline forms of iron oxide are magnetite, Fe₃O₄, and hematite, Fe₂O₃. The crystal structures of these two oxides are shown in Fig. 1. Magnetite has a cubic inverse spinel structure, and is the iron oxide most commonly found in nature (19). Hematite, Fe₂O₃, exists in several modifications, the most stable being the α form, a corundum structure (20). All other forms are currently thought to be metastable: γ (tetragonal structure), β (cubic bixbyite structure), ε (monoclinic), and other forms not completely characterized: δ, η (unknown). In addition, a non-stoichiometric
Fig. 1. Lattice structures for magnetite and hematite.
oxide, wustite ($\text{Fe}_{0.84}^0$ to $\text{Fe}_{0.95}^0$) can be formed at high temperatures, and a perovskite structure has been observed at high pressure (16).

Magnetite and hematite differ in many important respects. The magnetic properties of iron oxide have been studied for years (19). Magnetite is ferrimagnetic, as is the metastable $\gamma$ phase of hematite. Indeed, $\gamma$-$\text{Fe}_2\text{O}_3$ is easily produced by oxidation of $\text{Fe}_3\text{O}_4$ at moderate temperature in the presence of water (21). This is the procedure used when $\gamma$-$\text{Fe}_2\text{O}_3$ is produced for magnetic recording applications (19). On the other hand, $\alpha$-$\text{Fe}_2\text{O}_3$ is antiferromagnetic (22).

The electrical properties of iron oxides have also been the subject of many studies (23-31). $\alpha$-$\text{Fe}_2\text{O}_3$ is a semiconductor, and can be either n or p type, depending on processing conditions (23, 27-28). Likewise, the resistivity of pure $\alpha$-$\text{Fe}_2\text{O}_3$ can vary over many orders of magnitude ($10^3$-$10^{10}$ ohm-cm) (30,31), and can be readily changed by oxidation or reduction (24,31). Electron and hole room temperature mobilities can vary from $10^{-1}$-$10^{-5}$ cm$^2$/v-s, depending upon doping level and degree of crystallinity (27-29).

Electrical properties of iron oxide are also very sensitive to
impurities in the crystal lattice (25,26). The conductivity mechanism of n-type \( \alpha-Fe_2O_3 \) has been studied, and is thought to be a "hopping" mechanism: electrons hop from \( Fe^{2+} \) to \( Fe^{3+} \) (26). Thus, the existence of \( Fe^{2+} \) sites seems to be essential for n-type conductivity (30). Ultra pure stoichiometric \( \alpha-Fe_2O_3 \) has a resistivity of over \( 10^6 \) ohm-cm, and lower resistivities are due to either oxygen vacancy or impurity incorporation (25,26).

The mechanism of oxygen vacancy formation may be expressed as:

\[
O_o^x \rightarrow 1/2O_2(g) + V_o'' + 2e' \quad [1]
\]

Further increases in conductivity may be the result of the reduction of iron atoms in the iron oxide lattice:

\[
2Fe_{Fe}^x + 2e' \rightarrow 2Fe_{Fe}' \quad [2]
\]

Finally, the incorporation of an impurity into the \( Fe_2O_3 \) lattice, of +4 valence, may increase the conductivity by the following mechanism:

\[
M(IV) \rightarrow M(IV)Fe' + e' \quad [3]
\]

The impurity ion is simply incorporated substitutionally, causing
Fe$^{3+}$ to donate an electron to the iron oxide conduction band. Metals showing this phenomena in previous studies are Ti(27,31), Sn(32) and Zr(33).

P-type conductivity is not well understood. In iron oxide, p-type carriers are less mobile, and the mobility is more temperature sensitive than for n-type carriers (26). Intrinsic p-type conductivity occurs upon either high temperature oxidation of iron oxide (27), or incorporation of divalent ions into the lattice (25,34). Oxidation probably results in the production of Fe$^{4+}$, which acts as an electron acceptor (23), although the alternative possibility, O$^-$ ion formation, has also been suggested (26). Divalent metal ions incorporated substitutionally would result in Fe$^{4+}$ sites at an adjacent location in the lattice. Indeed, Cu, Mg and Ni have been used to produce p-type Fe$_2$O$_3$ (25,26,34).

The optical properties of Fe$_2$O$_3$ have also been studied extensively. Absorption bands have been noted at 1.4, 1.9, 2.2, and 3.2 eV (16). The transition at 2.2 eV is of greatest interest, since this is the transition involved with charge transfer to an electrolyte solution in photoelectrolysis. The nature of this transition is complex, however. Evidence for both a direct (30) and an indirect, or phonon assisted (31) transition has been reported.
Kennedy and Frese suggest that direct measurement of optical transitions may be misleading in Fe$_2$O$_3$ due to an overlap of the 1.9 eV and the 2.2 eV transitions (31). Their photocurrent measurements would suggest that the 2.2 eV transition is indirect.

1.4 Principles of Photoelectrochemistry

Photoelectrochemistry involves the use of light to drive a thermodynamically uphill chemical reaction. The practical aspects lie in solar energy conversion technology, in that sunlight can be converted into chemical energy through photoelectrochemical processes. The most extensively studied chemical reaction proposed for photoelectrochemical solar energy conversion is photoelectrolysis, where sunlight is used to split water into hydrogen and oxygen. Since hydrogen is useful both as a fuel and as a chemical feedstock, an efficient photoelectrolysis process would indeed be an important development. The chemical and electrical processes involved in photoelectrolysis have been extensively reviewed (35-42).

Photoelectrolysis exploits the unique properties of the semiconductor-electrolyte interface. When a semiconductor is
immersed in an electrolyte, a liquid junction is formed and charge transfer occurs across the solid-liquid interface in order to equalize the electrochemical potentials of the semiconductor and the electrolyte. The electrochemical potential of the semiconductor is called the Fermi level. The potential of the electrolyte is taken to be the liquid redox potential, or the potential of the half cell reaction occurring at the electrode (37). For an n-type semiconductor, for example, with the Fermi level initially greater than the electrolyte potential, electrons cross the interface to combine with ions in solution until an equilibrium between electron concentration and electric field in the semiconductor is reached. This results in a net deficiency of electrons in the region near the surface of the semiconductor, called the depletion region. This layer can range in thickness from 10 nm to several microns, and contains a positive space charge due to electron deficiency. This space charge region causes a bending of the conduction and valence bands near the surface and further electron migration is inhibited. The liquid junction has been analyzed extensively, and has characteristics similar to a Schottky junction (35,42). In fact, this type of photoelectrochemical cell is commonly called a Schottky cell.

Since the surface environment is electrically quite different from
that in the semiconductor bulk, the position of the bands at the surface is a function only of electrolyte composition, or in the case of water electrolysis, pH. The band positions in the bulk are a function of the electrode potential. If the semiconductor is connected to a metal counter electrode by an external circuit, equilibrium is established throughout the system. The Fermi level is assumed to be constant, and equal to both the electrolyte redox potential and the metal electrode potential.

Upon irradiation, electron-hole pairs are produced in the semiconductor (Fig. 2). The electric field resulting from junction formation sweeps electrons into the semiconductor bulk, making them available to the cathode for reducing water to hydrogen gas by the reaction:

\[ 2e^- + 2H_2O \rightarrow H_2(g) + 2OH^- \]  \[ 4 \]

The hole, in turn, accepts an electron, thus evolving oxygen:

\[ 2h^+ + 2OH^- \rightarrow 1/2O_2 + H_2O \]  \[ 5 \]

When a photon is absorbed in the semiconductor space charge region, an electron is elevated from the valence band to the conduction band of the semiconductor as shown in Fig. 2. More light absorption
Fig. 2. Semiconductor-electrolyte junction
yields other energetic electrons which raise the Fermi level of the semiconductor to a more negative value, and decrease the amount of band bending. The maximum (or most negative) value of the Fermi level occurs when the conduction and valence bands are flat. This is referred to as the flat band potential, and is only a function of pH for a given semiconductor (35, 38). Since it is the Fermi level under illumination that determines the potential of the metal counter electrode in a photoelectrolysis cell, water splitting can only occur if the flatband potential is greater than the hydrogen evolution potential. When this is not the case, an external bias is required.

The alternative to a Schottky cell is a p/n cell, which instead uses two different photoelectrodes in the same electrolysis bath: a p-type cathode and an n-type anode (35). Fig. 3 shows how this method can transfer electrons to and from the electrolyte. Not only does a p/n cell not require an external bias to electrolyze water, but a lower bandgap semiconductor can be used, thus increasing the possible conversion efficiency.

The first photoelectrochemical experiment was performed in 1839 by Becquerel, who showed that a silver/silver chloride electrode in solution produced a voltage when illuminated (43). Further progress was not possible until the development of methods to produce
Fig. 3. Semiconductor-electrolyte junctions for a p/n liquid junction solar cell.
materials of high purity. In 1954, Brattain and Garrett used germanium as an electrode in electrochemical cells, and they were able to explain that the photoinduced surface reactions were responsible for producing an electrical potential (44).

Utilization of these methods for energy conversion and storage was not considered until Fujishima and Honda built the first photoelectrolysis cell in 1975, using an n-type TiO$_2$ anode connected to a platinum cathode (45). They found that oxygen and hydrogen were evolved, but with a low quantum efficiency, estimated to be 0.1% for the total light from a xenon lamp. This was due in part to the fact that the conduction band for TiO$_2$ is only slightly more negative than the $\text{H}^+/\text{H}_2$ redox potential, despite the large band gap (3.0 eV). In most practical situations, external biasing would be required. Moreover, the large band gap means that only ultraviolet light is utilized.

In general, only metal oxides are stable as pure n-type photoanodes in electrolysis baths: non-oxide materials become oxidized themselves, rather than splitting water molecules (35). Nearly two dozen n-type metal oxides have been studied as photoanodes, and most of them are stable in solution. Unfortunately, none of them have been shown to be ideal: either the
band gap is too large for efficient sunlight utilization, or external biasing is required to evolve hydrogen.

1.5 Iron Oxide Photoanodes

As mentioned earlier, iron oxide is an n-type semiconductor, with a bandgap of about 2.2 eV. This energy value corresponds to a photon wavelength of 560 nm, well within the range of visible light (400-700 nm). Thus, iron oxide could ideally utilize about 1/2 of the total solar spectrum, shown in Fig. 4.

Many attempts have been made to construct iron oxide photoanodes. Hardee and Bard deposited thin films of iron oxide onto heated titanium and platinum substrates using iron acetylacetonate as the source gas (46,47). The films were deposited in layers, with each successive deposition being followed by a 1 minute Meeker burner anneal. Quantum efficiencies were not reported, but observed photocurrents were rather low. The authors reported that photocurrents occurred up to wavelengths of 550 nm, and that the anodes were stable in solutions of pH > 4.5.

Quinn et al. reported results for bulk single crystal α-Fe₂O₃ grown by a flux technique (48). Quantum efficiencies up to 35% were
Fig. 4. Solar energy flux for AM1 conditions.
obtained, but only with large anodic bias. The flatband potential (−0.67 at pH = 13.6) was not sufficiently negative to produce any hydrogen without the application of an external bias.

Kennedy et al. made photoanodes from pressed, sintered pellets of α-Fe₂O₃ (48-51). Quantum efficiencies and flatband potentials were approximately the same as those reported for the single crystal photoanodes. Hackerman et al. prepared thin films of iron oxide by thermal oxidation of pure iron in a Fisher burner (52,53). Also, films of γ-Fe₂O₃ were produced by anodic oxidation in this study. Quantum efficiencies were not reported, but photocurrents for the α-Fe₂O₃ films were substantially less than those reported for single crystal α-Fe₂O₃. The anodic oxide had a somewhat lower bandgap (1.9 eV), but produced even smaller photocurrents.

Clearly, results published for iron oxide photoanodes are not encouraging. Though all reports indicate the photoanodes are stable in basic solution, quantum efficiencies are low compared to other materials, particularly for thin film photoanodes. Flatband potentials are not sufficiently negative to evolve hydrogen without an external bias.

Efforts to improve the properties of iron oxide photoanodes have
been reported recently. Sammells and Ang found that a thin platinum dispersion on the surface of thermally grown iron oxide films resulted in increased photocurrent, as did additions of peroxide to the electrolyte (55). Kennedy et al. found that α-Fe₂O₃ pellets doped with up to 2 a/o silicon performed substantially better than pure Fe₂O₃ photoanodes, particularly with regard to flatband potential (50). Titanium doping did not have this effect.

Other dopants have been incorporated into sintered pellets of iron oxide in order to decrease the flatband potential to more cathodic values: SnO₂ and CaO (56); GeO₂, SnO₂ and PbO₂ (51); and ZrO₂, CeO₂, HfO₂, V₂O₅, Nb₂O₅, Ta₂O₅, and Al₄C₃ (52). In all cases, n-type conductivity greater than that with pure Fe₂O₃ pellets was observed, and flat-band potentials varied somewhat for the different atoms incorporated into the iron oxide lattice. In no case, however, was the resulting flatband potential sufficiently cathodic to evolve hydrogen without an external bias. It is important to note that with all dopants, photoanode performance was a strong function of dopant concentration (52).

Although iron oxide photoanodes have some activity in the visible part of the solar spectrum, efficiencies gradually decrease in the range 400–560 nm, after which no photoresponse is seen. Therefore,
some work has been directed at extending the visible wavelength response of this material. In particular, Merchant et al. used Cr$_2$O$_3$ doping, but the resulting photoresponse was poor, due to high bulk resistivity (30).

Liou et al. attempted to solve the problem of positive flatband potential by producing a "heterojunction" electrode (57). In this case, a 120 nm layer of TiO$_2$ was deposited onto a thermally grown iron oxide film. It was thought that this technique might combine the favorable flatband potential of TiO$_2$ with the more optimal wavelength response of Fe$_2$O$_3$. Unfortunately, visible wavelength photocurrent was seen only at high anodic bias.

Other work reported recently has attempted to utilize iron oxide photoanodes in p/n photoelectrolysis cells. Mette et al. reported such a cell using thermally grown Fe$_2$O$_3$ in series with zinc doped GaP (58). Cell energetics were such that water was electrolyzed without an external bias, but at low (0.1%) efficiency. Leygraf et al. have reported on a "homojunction" p/n cell, which utilized a Si doped Fe$_2$O$_3$ photoanode (n-type) in series with a Mg doped Fe$_2$O$_3$ photocathode (p-type) (34). The p-type photocathode was not completely stable under reaction conditions and required periodic
reoxidation in solution. The reaction proceeded without an external bias. Efficiencies were again quite low (0.035%).

Due to the advantages of low bandgap and high chemical stability, a great deal of work has been directed at improving the efficiencies and flatband potentials of iron oxide photoanodes. This work has consisted mostly of adding chemical dopants to bulk iron oxide (30,50-52,55). Few experiments have been performed with iron oxide thin films, and no comprehensive study has determined how film deposition processes affect Fe₂O₃ photoanode performance. This is surprising, because iron oxide thin film properties are known to vary widely with changes in formation method and processing conditions (2,3,6-15).

More importantly, thin film photoanodes have advantages over photoanodes constructed from the bulk material. From an engineering standpoint, photoanodes with surface areas appropriate for large scale solar collection would be more economical using a thin film active layer above an inexpensive substrate. Thin films can be formed over large areas with present processing technology.

Fundamental considerations also suggest that thin film photoanodes may be better suited to an improved solar energy conversion system. With a bulk semiconductor, most of the material is not used in the
energy producing process: only in the depletion region can photon absorption result in electron-hole pair separation and resulting chemical/electrical energy production. Once generated, the electron must travel through the semiconductor bulk, where it is subject to ohmic losses and to recombination/trapping phenomena. A thin film, conversely, can be made approximately the same thickness as the depletion region, so that no bulk energy losses can occur.

1.6 Plasma Enhanced Deposition

Plasma enhanced deposition (PED) is a process wherein a glow discharge is used to enhance the formation of thin film materials made from gas phase reactants. The advantage of PED lies in its ability to activate gas phase chemical reactions independently of other deposition parameters, e.g. temperature. Thus, thin films can be produced at near ambient temperatures using gases that ordinarily display large activation energies for reaction (59,60).

Chemical reactions are activated in plasma deposition by the interaction of gas phase molecules with high energy (1-10 eV) electrons. Electrons are accelerated by electric fields established in the glow discharge, and collide with neutral gas molecules. This
results in ions, electrons, free radicals, and metastable species. These chemically reactive species are then free to react with other molecules, resulting in increased reaction rates. Of course any side reaction may be activated as well as the reaction of interest and this can result in unique modifications in the properties of the deposited films.

Production of a glow discharge requires relatively unsophisticated equipment. The usual operating pressure range of 10 to 1000 mtorr is easily achieved with mechanical pumping. Electrical power to initiate and maintain the glow discharge (usually RF) can vary from 0.1 to 1.0 watt/cm$^2$ of electrode area. Other parameters, such as reactant flow rate and composition, RF frequency, and substrate temperature can all be varied. The fact that chemical reactions normally requiring thermal activation can proceed at reasonable rates at any temperature means that deposition temperature can be used as an operating parameter to modify film structure. Indeed, the large number of process parameters available for modification, particularly considering the huge processing "window" available for modification, is the primary advantage of plasma deposition. Previous work has indicated that all processing variables affect the final properties of the deposited films (59,61-65). Thus, judicious manipulation of these variables allows one to "tailor" the
properties of the deposited films for particular applications. Some materials made by plasma deposition are reported to have properties which are unattainable by other deposition techniques (66-69).

Plasma deposition has been used to produce a large number of different materials (59-61), and much work has been devoted toward gaining a better understanding of the deposition process (70-72). Most of this work has been directed at materials other than iron oxide, and toward applications other than thin film photoanodes. In fact, only one investigation using glow discharge deposition to produce iron oxide has appeared in the literature: Secrist and Mackenzie deposited Fe$_2$O$_3$ thin films using iron carbonyl and oxygen in a microwave discharge (73). The film was identified as a mixed phase of α-Fe$_2$O$_3$ and Fe$_2$O$_3$-H$_2$O by Debye-Scherrer x-ray powder diffraction patterns. The iron oxide films were not directed toward any particular application. The only work devoted to plasma deposition of thin film photoanodes has been in this laboratory, using PED to produce TiO$_2$ thin films (74). The results of this work showed that photoanode performance varied with deposition conditions, but that the best plasma deposited films performed substantially better than TiO$_2$ photoanodes made by other means.

While much work has been reported in incorporating dopants into
bulk iron oxide photoanodes, relatively little has been directed towards novel methods of iron oxide thin film formation and modification. Noting the potential advantages of thin film photoanodes and the plasma deposition process, research was undertaken to utilize this technique for the fabrication of iron oxide photoanodes. The goals of this project were to:

1. Deposit thin films of iron oxide by PED

2. Characterize the chemical, electrical and physical properties of the films as a function of deposition conditions

3. Determine the suitability of PED Fe$_2$O$_3$ for use in photoelectrolysis

4. Relate the performance of PED Fe$_2$O$_3$ photoanodes to the plasma deposition process in order to better understand that process
Chapter 2

Experimental Methods

2.1 Plasma Deposition System

Two deposition systems were utilized in this study. The first, shown in Fig. 5, was enclosed by a pyrex bell jar (10 in. dia. by 12 in. ht.) sealed to a flat stainless steel baseplate (12 in. dia.) with a viton L gasket. Inside, two circular parallel stainless steel electrodes (5 in. dia.) were used to couple the RF power to the gas phase reactants. The top electrode was the "driven" electrode, or the electrode to which RF power was applied. For this reason, the top electrode was supported by two insulating alumina rods.

The top electrode also served as the gas feed/distributing system. The gases used to produce iron oxide were iron pentacarbonyl (Alfa Products) and oxygen (commercial grade, 99.96%). Oxygen was fed into the system through the base plate via a glass
Fig. 5. Parallel plate plasma deposition reactor.
tube which connected to the tube at the center of the top electrode. The iron carbonyl, likewise fed through the baseplate, flowed into the hollow portion of the top electrode, and flowed out through four holes in the bottom of the upper electrode. The $\text{Fe(CO)}_5$ tube was well insulated with asbestos and glass wool inside the alumina tube. To provide further insulation, a pyrex sleeve containing glass wool was placed over the alumina tube. This precaution prevented thermal decomposition of the $\text{Fe(CO)}_5$ before reaching the top electrode. The gas feed system prevented mixing of the two gases before injection into the region between the two electrodes. Inside the hollow upper electrode, stainless steel cooling coils were welded to the bottom surface. The cooling fluid (either air or water) was fed through the baseplate to the electrode through stainless steel and teflon tubing (not shown).

The lower electrode was electrically grounded and supported by 3 stainless steel legs bolted to the baseplate. The lower electrode could be heated with a ring heater up to $500^\circ C$ (Chromalox, A-20 135394). Substrates were placed on top of the lower electrode for all depositions, and temperature was monitored with an iron-constantan sheath thermocouple (Omega, 1/8 in. by 18 in.). Temperature monitoring can be a problem in systems of this nature, since a differences can exist between the surface temperature of the
substrate and the temperature of the thermocouple (placed inside a blind hole in the bottom of the bottom electrode, 1/16 in. from the top surface.) However, previous work with this system suggests such discrepancies are less than 20 °C (68).

Exhaust gases were pumped through a 1 3/4 in. diameter hole in the center of the base plate, through a stainless steel liquid N\textsubscript{2} cooled cold trap, to a corrosion resistant vacuum pump (Alcatel Model 2063 C). A butterfly valve between the reactor and the cold trap was used to control the residence time independent of reactant flow rate.

Pressure was monitored with a McLeod gauge and a capacitance manometer (MKS Baratron Gauge Model 222A). Oxygen was metered with a mass flow controller (Tylan Model FC-260). Iron carbonyl, a moderate vapor pressure liquid at room temperature, was stored in a pyrex flask maintained a 20 °C by a water bath. A rotameter was used to meter the Fe(CO)\textsubscript{5} flow through a stainless steel micrometering valve.

RF power was supplied by a variable frequency signal generator (Tektronix 190B), through a power amplifier (ENI A150). Power was monitored with a power/SWR meter (Heathkit HM-102) and was electrically coupled to the reactor via a matching network (Heathkit
Antenna Tuner).

A second reactor was also used to deposit films and to study gas phase chemical reaction and film formation mechanisms. This reactor is pictured in Fig. 6. A quartz tube (3.0 in. O.D., 2 ft. length) was sealed on one end by a 2 in. I.D. vacuum quick disconnect which was welded to the vacuum pump piping system previously mentioned. The other end was sealed by a stainless steel baseplate with a groove-o-ring-flange connection. Pressure and temperature were monitored in the same manner as in the other system. Substrates were placed on a stainless steel susceptor (2 in. square) which was in turn placed on a 1/4 in. thick quartz plate. The susceptor was heated by two 200 watt cartridge heaters (Tempco).

RF power was supplied with the aforementioned generating equipment and was coupled via two external copper ring electrodes (1 in. wide). Iron carbonyl flow was monitored by a Molecular Flow Element (MKS FE-0.5) and differential pressure transducer (MKS Baratron Model 220B). This arrangement easily allowed Fe(CO)$_5$ flow rates of less than 0.5 sccm to be measured. Oxygen was metered as before. A tubular Pyrex ionization chamber (2 in. dia., 12 in. long) was connected to the above reactor via an L-shaped 0.5 in. O.D. Pyrex tube. The ionization chamber used external copper electrodes similar to those used in the main reactor. The inside of the
Fig. 6. Tubular plasma deposition reactor.
Fig. 6a. Base plate of tubular reactor showing viewport used for OES.
ionization chamber and connecting Pyrex tube were both coated with phosphoric acid prior to use to prevent the surface recombination of oxygen atoms produced in the chamber. A Plasma Scan System (Plasmatherm PSS-2M) was used to monitor visible/UV light emission from the glow discharge region of the reactor during deposition.

2.2 Experimental Procedure

Film deposition procedures were essentially the same for both reactors. In a typical deposition, the system was pumped down to a low pressure (less than 20 mtorr) while the lower electrode was heated to the desired temperature. (In the tubular reactor, heating did not commence until after substrates were placed on the susceptor, and the reactor was pumped down.) When that temperature was reached, substrates were placed on the lower electrode and the system was again evacuated to less than 20 mtorr.

The substrates used depended upon the type of analysis desired. In this study, pure iron (Alfa Products, Puratronic), titanium foil (Alfa Products, 99.7%), glass cover slips, stainless steel, NaCl single crystal (Barnes Analytical), quartz slides, and silicon wafers (100 or 111) were used. Iron and titanium substrates were
first degreased with methanol, then rinsed with deionized (DI) water (> 17 x 10^6 ohm-cm), etched in dilute (2%) HF solution, and rinsed again in DI water.

Once base pressure (20 mtorr) was reached, O_2 gas flow was initiated, and the RF glow discharge was ignited. The RF power level was set and matched to the reactor by reducing SWR to 1. The pressure was increased by throttling the pump. A 5 minute O_2 plasma was always used to clean the substrates of organic contaminants. During the cleaning process, temperature, power and oxygen partial pressure were maintained at the level used for the particular deposition. A thin oxide layer was formed on the iron substrate during this step, but the thickness was not determined.

Work by Hussey et al. suggest that a thermally grown oxide film such as that produced here would consist of a layered structure: a thin outer layer of α-Fe_2O_3 and a thicker Fe_3O_4 inner layer. The α-Fe_2O_3 would probably be a few tens of nm thick (4). The Fe_3O_4 layer would be thicker, but this material has metal-like conductivity. Therefore, the semiconducting properties of the overall structure should not be significantly influenced by this cleaning procedure.
After the 5 minute plasma preclean, the Fe(CO)$_5$ flow rate was set at the desired value, and the pump throttle adjusted if necessary to achieve a pressure of 200 mtorr. Adjustment of the matching network to obtain the desired power and SWR was sometimes necessary at this point. When sufficient time had elapsed to deposit a film of desired thickness, the Fe(CO)$_5$ flow was terminated. After 1 minute, the O$_2$ flow was stopped as well, and the throttle valve was opened completely. RF power was turned off at this time. The system was vented to atmosphere, and the substrates were removed.

When depositing films by the indirect plasma method, a flow rate of 30 sccm O$_2$ (with 5% N$_2$) was always used. For these films RF power was only applied to the ionization chamber of Fig. 6. A power of 250 watts was used for all depositions. Under these conditions, a production ratio of oxygen atoms, [O]/[O$_2$], was approximately 0.20. The proportion of oxygen atoms was determined by the well known titration of the reaction gas by NO$_2$ (94). A mass flow meter (Tylan model FM 260) measured the flow of NO$_2$ into the reaction zone of the tubular deposition chamber. Upon initiation of NO$_2$ flow, a greenish-yellow glow appeared in the reactor, due to the reaction sequence:
\[0 + \text{NO}_2 \rightarrow \text{NO} + \text{O}_2\] \[6a\]

\[0 + \text{NO} \rightarrow \text{NO}_2 + \text{hv}\] \[6b\]

The glow was observed visually in a darkened room. When the flow rate of \( \text{NO}_2 \) was equal to that of the oxygen atoms, the glow disappeared. This was because no excess \( \text{O} \) was available to react with \( \text{NO} \), and the second reaction of this sequence could not take place.

2.3 Thickness/Density Measurement

The mass of the deposited film was easily obtained by weighing thin glass cover slips (about 0.15 g) before and after deposition using a microbalance. (Mettler Instruments Corp., Type M5) Unfortunately, iron oxide film density often varied with deposition conditions. Film thickness was then obtained by depositing the film on glass or silicon, masking approximately 1/2 of the film by dipping a portion of the film and substrate into photoresist solution (AZ20), and baking the photoresist at about 100°C in a vacuum oven for 1 hour. At that point, the film was etched in 33% HCl solution (sometimes heated to boiling), and rinsed in DI water.
The photoresist was then easily stripped by an acetone rinse, leaving a sharp step in the oxide film. The step height was measured using an Alpha-Step Profiler (Tencor 10-00020). Steps made by masking a portion of a glass or silicon substrate with another substrate during deposition were not as sharp as the etched steps, and thus film thickness could not be determined as accurately as with the etching procedure.

2.4 Chemical Analysis

The thin films were analyzed for iron and carbon by bulk analytical techniques. (All analyses of this type were performed by the Analytical Chemistry Laboratory in the College of Chemistry, University of California, Berkeley.) Films deemed for chemical analysis were deposited on thin glass cover slips. Weights of the slips were determined before and after deposition as previously mentioned. The iron content of the film was determined by atomic absorption spectroscopy after dissolving the sample in sulfuric acid. Carbon content was determined after high temperature (850° C) oxidation of another film sample, by using gas chromatography to analyze the effluent gas for CO₂. Oxygen content was determined by
difference, assuming only iron, oxygen and carbon were present in the films.

In addition, film composition was analyzed using Auger Electron Spectroscopy (AES), Electron Spectroscopy for Chemical Analysis (ESCA), and Secondary Ion Mass Spectrometry (SIMS). These measurements were performed at the NSF Regional Facility in Surface Analysis, University of Minnesota. Additional AES and SIMS measurements were made at Lawrence Berkeley Laboratory, Materials and Molecular Research Division.

2.5 Film Structure Determination

An X-ray diffractometer (Picker Model 3488) was used to determine the nature of crystallinity in the deposited films. A monochromatic radiation source (copper Kα, 1.54 nm) was directed onto the samples. After diffraction by the film, the beam was detected by a thallium activated NaI detector. Intensity was plotted as a function of twice the incident angle (2θ) on a chart recorder. Determination of crystal type and degree of orientation was made by comparing the diffraction pattern obtained for a particular film with that in the Powder Diffraction File (17).
Scanning Electron Microscopy (Hitachi Model S-310A) was also used to ascertain film structural characteristics. In most cases, a thin (10nm) layer of gold or palladium was sputter deposited (Hummer) atop the iron oxide film to minimize problems of surface charging.

2.6 Optical Property Measurement

Reflectance measurements were made using a Gier-Dunkle integrating sphere attachment in conjunction with a Perkin Elmer 330 Spectrophotometer. Tom Allen of the Optical Coatings Laboratory, Inc. in Santa Rosa, California performed the reflectance measurements. Transmittance measurements were made using a Perkin-Elmer Spectrophotometer (Model 571, double beam, 1 nm bandpass slit) for films deposited on 2 mm thick quartz plates.

2.7 Electrical Measurements

Film resistivity was determined by performing resistance measurements under DC conditions (Keithley 179 Digital Multimeter) and at 1 KHz (General Radio 1650A Impedance Bridge) on iron oxide films deposited on iron substrates. Electrical contact was made to
the film by evaporating aluminum dots (0.46 mm²) atop the Fe₂O₃ through a shadow mask. Capacitance measurements (Boonton capacitance meter 71A) on this structure allowed calculation of the dielectric constant at 1 MHz.

For films deposited on glass substrates, a four-point probe (Alessi Model A4P series) was used to measure resistivity. The films were degreased with isopropanol, rinsed with deionized water (> 17 x 10⁶ ohm-cm) and dried in a dry nitrogen gas stream. For very high resistivity films (> 10⁵ ohm-cm), a picoampere source (Keithley Model 261) was connected across the probe, and an electrometer (Keithley Model 610C) with 10¹⁴ ohm input resistance was used to determine the corresponding voltage drop. The four point probe was encased in a light-proof enclosure to prevent photogeneration of charge carriers. The range of currents used was 5-20 nA, resulting in a voltage drop of 1-20 volts for the various films. Under these conditions, a linear current-voltage relationship always resulted.

Capacitance-voltage (CV) measurements were made to determine film carrier concentrations. For this purpose, metal-insulator-semiconductor (MIS) structures were built by electron beam evaporation of a layer (60-300 nm) of quartz on top of
iron oxide films (Temescal electron gun operated at 7 KV and 400 mA). Electrical contact was made by evaporating aluminum dots on top of the quartz as before. A schematic diagram of the structures used for electrical measurements is shown in Fig. 7.

Capacitance was measured at 1 MHz with the Boonton meter. A voltage ramp was used to apply DC bias across the film (-10 to 10 volts) at a scan speed of 0.04 volts/second. Small signal capacitance versus applied voltage was recorded on a Hewlett-Packard 7045A X-Y recorder. A schematic of the C-V measurement system is shown in Fig. 8.

2.8 Photoanode Fabrication

Figure 9 shows the technique for constructing a photoanode from an iron oxide film above an iron substrate. The backside of the metal was scrapped with a knife edge to ensure good electrical contact. A wire was then attached to the back side using silver epoxy (TRA-CON Bipax BB 2902). After the silver epoxy was allowed to set (24 hours), the structure was attached to a glass microscope slide section (1 in. square) using insulating (Devxon "5 minute") epoxy, such that only the iron oxide film was exposed to the electrolyte.
Fig. 7. Schematic of structures made for electrical measurements of films.
Fig. 8. Equipment for electrical measurements.
Fig. 9. Photoelectrode structure.
Another photoanode structure was built using a transparent, conductive substrate. The substrate was 1 cm x 2 cm x 0.2 cm Pyrex, covered with a 200 nm layer of antimony doped SnO₂. This substrate was made by Dr. Werner Kern at RCA Laboratories. This structure allowed illumination of the photoanode from either the front or back side. Electrical connections to the SnO₂ were made by physically masking a portion of the SnO₂ surface during film deposition, and attaching a wire to the exposed portion using the silver epoxy mentioned above. The insulating epoxy was then used to seal the SnO₂/silver epoxy connection from the solution. A photoanode of this type is shown in Fig. 10.

2.9 Photoelectrochemical Equipment

Figure 11 shows the equipment used to test the photoelectrochemical performance of iron oxide photoanodes. The cell (4 in. cube) was fabricated of UV absorbing 1.25 cm thick polyacrylic (Polycast Technology Corporation). A quartz window (2 in. dia., 1/8 in. thick) allowed transmission of all UV-visible wavelengths into the cell. The electrolyte, 1 M NaOH, was mixed from reagent grade NaOH and DI water. A saturated calomel reference
Fig. 10. Photoelectrode for illumination from the back side.
Fig. 11. Equipment for electrochemical testing of photoanodes.
electrode was placed within 3 cm of the front surface of the film, and a 10 cm$^2$ platinum foil served as the counterelectrode. A teflon coated stirring bar kept the electrolyte mixed during experiments, and nitrogen gas was bubbled continuously through the solution to exclude air and electrolysis products.

UV/visible light was produced by a 200 watt mercury arc lamp (Oriel Corporation model 8510-4 power supply, model 6137 housing) focused with a f/1.0 fused silica lens. A grating monochrometor (Oriel 7240 housing and 7270 grating) with 1 nm, 10 nm and 20 nm bandpass slits was driven by a 100 nm/minute wavelength scanning drive. This system allowed determination of photoresponse as a function of wavelength. Determination of quantum efficiency was carried out by measuring the lamp flux with a radiometer (Optronics Laboratory, Inc. 730A) and dividing this value into the measured current density. Figure 12 shows a typical lamp spectrum using the 20 nm slit.

A PAR model 173 potentiostat was used to control photoanode potential, and voltage ranges could be scanned by using a PAR model 175 function generator. Output current, from which anode photocurrent was determined, was monitored with a PAR model 176 current follower. A Hewlett-Packard model 7045A X-Y recorder was used for current-voltage and current-wavelength data recording.
Fig. 12. Typical output from mercury lamp (20 nm slits).
Chapter 3

Film Deposition

3.1 Deposition Uniformity

Uniform deposition of film material over a large area can sometimes be a problem in plasma deposition systems. Earlier work using the parallel plate reactor from which the system in Sec. 2.1 was built reported a strong radial dependence of film deposition rate (68). This problem was particularly severe at higher power levels (100 watts). Deposition nonuniformity was substantially mitigated by using the gas feed distributing upper electrode described in Sec. 2.1. Figure 13 shows the profile of deposition rate over the lower electrode area for two power levels. Deposition temperature was 250° C for this data, with both Fe(CO)$_5$ and O$_2$ flow rates at 1 sccm. RF frequency was 13.56 MHz and pressure was 200 mtorr. Using the hollow upper electrode described in Sec. 2.1, depositions of reasonable uniformity were obtained over 3-4 cm of
Fig. 13. Deposition profile for parallel plate reactor. Conditions were 250°C, 13.6 MHz, O₂/Fe(CO)₅ = 1 at the power levels indicated.
the lower electrode diameter. This allowed uniform film deposition over multiple substrates, and accurate calculation of bulk film density for a single substrate.

3.2 Deposition Rate

Film deposition rate was measured under a variety of conditions, both in order to produce films of the desired thickness, and to ascertain the effect of deposition parameters on deposition rate. For the latter objective, one parameter was varied while all others were held constant. It was hoped that this procedure would yield information on reaction kinetics and mechanisms. The parameters investigated were Fe(CO)₅ flow rate, O₂ flow rate, substrate temperature, RF power and RF frequency.

Determination of deposition rate was usually accomplished simply by measuring the thickness of the deposited film and the time taken to deposit it. (See Sec. 2.7.)

\[ R = \frac{t_f}{t} \]  

[7]

where \( t_f \) is the actual film thickness, and \( t \) is the deposition
time. In this case, data were reported in the form of nm/minute. Unfortunately, the density of iron oxide can vary under some experimental conditions. Bulk density of the films varied from 2.5 to 5.1 g/cm$^3$ with the range of parameters used in this study. (See Sec. 5.1.) When film density varies with variation in an experimental parameter, results must be reported in terms of a mass flux to the film surface. In this case, results are reported as:

$$R' = \frac{w}{At}$$  \[8\]

where $w$ is the weight of the deposited film, $A$ the area of the substrate, and $t$ the deposition time. This form of the deposition rate would tend to better represent reaction rates involved in film formation. For example, both density and deposition rate varied with substrate temperature. Figure 14 shows film deposition rate, in nm/minute, from 30$^0$ to 300$^0$ C. This is with 10 watts RF power at 13.57 MHz and with a 1:1 ratio of iron carbonyl to $O_2$. At temperatures greater than 150$^0$ C, deposition rate appears to decrease with further increases in temperature. But because film density increases with temperature (Sec. 5.1), deposition rate based on film mass presents a more accurate representation of deposition reaction rate.
Fig. 14. Deposition rate variation with temperature. Conditions were 250°C, 13.6 MHz, \( \frac{O_2}{Fe(CO)_5} = 10 \) at 10 W RF power.
The variation of mass deposition rate with temperature is presented in the form of an Arrhenius plot in Fig. 15. It is clear that two regimes are present. At temperatures greater than 150° C, deposition rate does not vary significantly with temperature. At lower temperatures, the deposition rate does vary with temperature, with an activation energy of 1.6 Kcal/g-mole (0.07 eV). Comparison with activation energy values obtained from CVD (chemical vapor deposition) using iron carbonyl and oxygen without a plasma (8-12.7 Kcal) (10, 11) indicates that the plasma substantially lowers the activation energy of iron carbonyl oxidation. Still, deposition of iron oxide from iron carbonyl without a plasma shows no temperature dependence above 200° C (75).

In atmospheric pressure CVD of Fe₂O₃ by Fe(CO)₅, it is thought that surface processes dominate reaction kinetics at temperatures less than 200° C (10). It is likely that surface processes are involved in plasma deposition as well. The lower activation energy for plasma deposition may be related to the effects of the plasma environment on the growing film surface. Charged species in the plasma, electrons and ions, continuously bombard the film surface during deposition. Such bombardment transfers energy to surface bonds and to species adsorbed on the surface, and may thus promote
Fig. 15. Arrhenius plot for plasma deposition. Deposition conditions: 13.6 MHz at 10 W RF power, $O_2/Fe(CO)_5$ ratio = 10.
adsorption and activate chemical reactions. At higher temperatures, both plasma and non-plasma deposition rates appear to be limited by reactant flow rate.

Film deposition rate was found to depend strongly upon iron carbonyl flow rate. Figure 16 shows this dependence for constant oxygen flow rate (10 sccm) at 500°C. It is clear that at low Fe(CO)$_5$ flow rates, the deposition rate varies much more strongly with iron carbonyl than at higher iron carbonyl flow rates. In an attempt to better understand this behavior, the data of Fig. 16 were replotted on a log-log scale, Fig. 17. The approximate rate expression for iron oxide deposition rate is:

$$R = 2.8 \times 10^2 X^{0.74}$$  \hspace{1cm} [9]

for iron carbonyl concentrations greater than 0.9. In this expression, $R$ is the deposition rate in nm/minute, and $X$ is the mole fraction of Fe(CO)$_5$ in the reactor feed. The data taken at very low flow rates do not fit this relationship. This may be due to a different reaction mechanism, or to problems involved in monitoring Fe(CO)$_5$ flow at this low flow rate (about 0.5 sccm). The reaction coefficient varies from the values of 1.525 - 1.34 obtained by Mason with atmospheric pressure CVD from Fe(CO)$_5$ (10). This is not
Fig. 16. Deposition rate dependence on iron carbonyl flow rate. Deposition conditions: 13.6 MHz at 10 W RF power. The \( \text{O}_2 \) flow rate was constant at 10 sccm.
Fig. 17. Deposition rate dependence on Fe(CO)$_5$ mole fraction. Deposition conditions were as in Fig. 16.
unreasonable, because Mason hypothesized that the atmospheric CVD reaction took place through a homogeneous nucleation process which will be discussed in Sec. 3.3. On the other hand, a purely molecular reaction mechanism:

\[ \text{Fe(CO)}_5(g) + \frac{1}{2}\text{O}_2(g) \rightarrow \text{FeO(g)} + 5\text{CO(g)} \]  

[10]

would be first order in iron carbonyl. But the exponent in Eqn. [9] is lower than this value as well. Carbon dioxide may play a role. There is evidence that \( \text{CO}_2 \) inhibits iron carbonyl oxidation at larger concentrations (10). It is likely that some \( \text{CO}_2 \) is produced in a glow discharge containing CO and \( \text{O}_2 \). According to Brown and Bell, the reaction has a very high activation energy. Their results suggest that conversion to \( \text{CO}_2 \) would only be about 10%. However, metal carbonyls are known to catalyze gas phase oxidation reactions, so its concentration here may be considerably higher. Unfortunately, detecting \( \text{CO}_2 \) in the presence of large amounts of CO is difficult. Even the "persistent" \( \text{CO}_2 \) bands were not noted in this study using OES (86). However, it is likely that more \( \text{CO}_2 \) would be formed in a glow discharge environment than with atmospheric CVD.
Deposition rate variation with oxygen concentration is noted from Fig. 18, for a constant total pressure of 0.2 mtorr, at 250°C, 10 watts RF power. While the relationship appears to be substantial, it is again largely superficial. With greater oxygen content in the gas phase during deposition, film composition changes from pure iron to Fe$_2$O$_3$, with a corresponding change in film density. (See Sec. 5.1.) Figure 19 shows the mass deposition rate for these films, which appears to increase more slowly with oxygen concentration. The reason for this effect may be that oxygen gas is not involved in a rate limiting reaction step, but merely oxidizes the iron present in the gas or on the solid surface. By this process, oxygen gas would become incorporated into the film as determined by its gas phase concentration, while the same amount of iron would be deposited in each case. Oxygen content would determine the structure and density of the film, but would change film mass to a lesser degree (since Fe$_2$O$_3$ is only 30% oxygen by weight).

The effects of the electrical parameters of the plasma do not have a significant effect on the deposition rate. Figure 20 indicates how RF power level has little effect on film deposition rate for two iron carbonyl flow rates. This is probably due to the nature of Fe-CO bonding in iron carbonyl. The activation energy for decomposition of iron carbonyl is 20 Kcal/mole (0.87 eV) (75). Since
Fig. 18. Deposition rate dependence on oxygen reactor content. Deposition conditions were 250° C at RF power = 10 W, 13.6 MHz. Iron carbonyl flow rate was held constant at 1 sccm.
Fig. 19. Deposition rate dependence on oxygen reactor content. Same deposition conditions as in Fig. 18.
Fig. 20. Deposition rate dependence on power for two Fe(CO)$_5$ flow rates. Films were deposited at room temperature, with a constant O$_2$ flow rate of 10 sccm. Frequency was 13.6 MHz.
in a glow discharge electron energies typically range from 1-10 eV, even a lower power plasma would supply sufficiently energetic electrons to initiate reaction. Even though higher powers may supply more electrons of higher energy, they simply are not needed to decompose iron carbonyl. Higher power levels may have other effects, however, such as increased ion bombardment of the growing film surface or promotion of other gas phase reactions.

The effect of RF frequency can be seen from Fig. 21. Unlike RF power, RF frequency affected film density under some deposition conditions. The data of Fig. 21 are therefore plotted in terms of mass deposition rate.

3.3 Deposition Mechanisms and Kinetics

The use of atmospheric pressure CVD to make iron oxide thin films from iron carbonyl has drawn attention to the specific reaction mechanism by at least two authors. MacChesney proposed that gas phase iron carbonyl adsorbs on a heated solid surface, where it decomposes (11). In the presence of oxygen gas, the iron readily oxidizes to hematite. In this mechanism, the rate limiting step is thought to be the decomposition of the adsorbed carbonyl. This is
Fig. 21. Deposition rate dependence on plasma frequency. Power level was 10 W RF power, deposition temperature was 250°C and \( \text{O}_2/\text{Fe(CO)}_5 \) was 1.
because the activation energy for decomposition (20 Kcal/mole) is greater than the adsorption energy, $-\Delta H_{\text{ads}}$ (5 Kcal/mole). On the other hand, CO, which is present as a decomposition product, adsorbs very strongly ($-\Delta H_{\text{ads}} = 22$ Kcal/mole). Thus, large concentrations of CO would inhibit CVD iron oxide deposition, by preferentially occupying surface sites.

Another theory was proposed later by Mason (10). Mason suggested a homogeneous mechanism whereby Fe(CO)$_5$ molecules in the gas phase undergo nucleation to form a smoke particle. This particle continues to grow via a rate limiting heterogeneous mechanism. The smoke particle finally reaches the heated CVD surface, where it undergoes pyrolysis and subsequent oxidation. Mason presents evidence which suggests the smoke consists of lower carbonyls.

It is doubtful that the rate limiting step in plasma deposition is either of the two limiting steps proposed in the aforementioned theories. As stated earlier, the energy of electrons in the glow discharge is more than sufficient to decompose the iron carbonyl in the gas phase. Even without oxygen, and at room temperature, iron carbonyl readily decomposes in the glow discharge. Once decomposed, gas phase iron or iron oxide particles should readily deposit on nearby surfaces. This alone accounts for the lower activation
energy for plasma enhanced deposition. Mason obtained qualitative agreement between his nucleation theory and his observed reaction order of iron carbonyl concentration. Thus, one would expect that plasma deposition would have a reaction rate dependence on iron carbonyl concentration different from that seen for deposition without a plasma. Diagnostic work is therefore necessary to interpret the kinetic results presented up to this point.

3.4 Analysis of the Plasma Deposition Process

Analysis of a plasma deposition process requires a non-intrusive method. In order to be sure the actual process is being observed, one must use a technique that does not disturb the glow discharge. On the other hand, direct sampling of atomic and molecular species from the plasma is extremely difficult. Any charged particles may collide with a sampling orifice and become neutralized. Free radicals or metastables are likely to change form before direct analysis takes place. And in plasma deposition, the species of primary interest, the products, are likely to deposit out of the gas phase as a solid before being sampled. Thus, a low concentration will be present in the gas phase, and may not be detected by analytical techniques.
All analysis methods currently used for plasma deposition suffer from these shortcomings. Mass spectrometry requires direct sampling from the plasma. Optical emission spectroscopy (OES) is non-intrusive and does not require direct sampling, but the primary species of interest, the products which will form the solid film, are hard to detect, due to low gas phase concentration. When the film material is not transparent, experiments are often ruined by "dirty windows": the film material deposits on the view port preventing observation of the discharge.

Nevertheless, both of these methods have been used for plasma diagnostics. Catherine, Turban and Grolleau used mass spectrometry to analyze a silane plasma and were able to devise a sampling system that allowed some unstable products to be sampled (76,77). Kampas and Griffith used optical emission spectroscopy to identify gas phase atomic and molecular species in a silane glow discharge used for deposition of amorphous silicon solar cells (78,79). Yokoyama and others investigated a silicon nitride system using OES to obtain information on film growth mechanisms (80).
3.5 Optical Emission Spectroscopy for Analysis of Plasmas

Identification of gas phase atomic species is relatively straightforward. Atoms, when activated by impact with an electron, achieve an excited electronic energy state. After a short period of time, the excited atom drops to a lower energy state, emitting a photon of a characteristic wavelength. This wavelength is called an atomic line. It is because atomic transitions result in the emission of discrete energies at well catalogued wavelengths that identification of atomic species is possible.

Identification of molecular species is not so straightforward. Because of vibrational and rotational modes of energy dissipation, molecular species emit photons in large groups of wavelengths, or bands. For many systems, these bands are not well characterized and the relative intensities of different bands within a system is a strong function of the method of excitation. For identification of gas phase molecules, one must identify several bands from a single system to confirm identification.

Once peaks are identified, their intensity can be used to ascertain information on the relative concentration of the species.
The term "actinometry" has been coined to describe this technique (82). This technique has been reviewed and described in a number of publications, so only a brief description will be given here (83,84).

The intensity of photon emission from a gas phase species can be described as:

\[ I_x = k_x n_x \eta_x e \]  

[11]

for a particular emission line. In this equation, \( I_x \) is the photon intensity for species \( x \) at the particular wavelength, \( k_x \) is a proportionality constant, \( n_x \) is the gas phase concentration of species \( x \), \( \eta_x \) is the excitation efficiency of the discharge, and \( e \) the electron concentration. If another gas is present in the discharge at a known concentration and if excitation from the ground to the emitting state is the primary excitation process, Eqn. [11] can be applied to both to obtain this expression:

\[ \frac{n_x}{n_y} = \frac{I_x}{I_y} \left[ \frac{k_x \eta_x e}{k_y \eta_y e} \right] \]  

[12]

If the factor in brackets is constant for changes in deposition conditions, then Eqn. [12] can be used to determine the change in
concentration of species x relative to the concentration of species y, merely by measuring the ratio of peak intensity for those species. Thus, plasma power, pressure, feed concentration or any other parameter can be varied by the experimenter, and the particular effect on the gas phase concentration of any atomic or molecular species can be determined.

The question then becomes, when is the bracketed factor in Eqn. [12] constant? Only when the excited states responsible for emission are "close" in energy (82-84). This is because the distribution function of electrons in the plasma may change in unpredictable ways with changes in plasma conditions. Only nearly adjacent energy levels are sure to have similar concentrations when these changes take place. Just how close the energies of the excited atomic or molecular states must be is unclear. Coburn suggests that they be within 1-2 eV of each other (83), but d'Agostino et al. have recently conducted experiments which suggest that energy levels as far apart as 8.2 and 19.8 eV may behave similarly to variations in plasma conditions (84).

Using OES for analysis of the Fe(CO)$_5$-O$_2$ system immediately suggests a number of problems. Iron oxide is certainly not transparent and even a few tens of nm will absorb most light above 560 nm. Thus, arranging for a view port may be a problem. More
critically, actinometry of the species of interest, i.e. FeO and Fe emissions, may be impossible due to the low excitation energies of these species: 1.3 and 2.2 eV, respectively. None of the noble gases have emitting energy states at these low energy levels. Finally, all experimental data suggest that Fe(CO)$_5$ deposits readily in an oxygen plasma. Therefore, gas phase concentrations of FeO and Fe are almost certain to be small. This will result in low intensities.

The problem of dirty windows was easily solved by building a viewport into the base of the reactor, shown in Fig. 6a. The viewport consisted of a 5 inch by 1 inch diameter sleeve upon which a stainless steel flange holding a quartz window was mounted. Since the iron carbonyl was introduced into the reactor far downstream, and the oxygen upstream, any particles likely to deposit were swept away from the viewport.

The problem of finding an actinometer gas was more formidable. Nitrogen was finally chosen. Though N$_2$ is a reactive gas, it is not likely to undergo substantial change under the conditions used in this study. Iron nitride is a known compound, but it is unstable and decomposes at 200°C. It is also unlikely that such a compound would form in a strongly oxidizing atmosphere such as that used in
this work. Moreover, no measurable amount of nitrogen was ever found in any film by the analyses used in Chapter 4. Nitrogen has a relatively low energy excited state (7.32 eV) and has many peaks of high intensity throughout the spectrum. In order to make certain a known concentration of N₂ was present, a mixture containing 5% N₂ in O₂ was prepared. For any flow rate, it was therefore easy to calculate the exact concentration of N₂ in the reaction mixture.

3.6 Optical Emission Spectroscopy Results

The spectrum obtained from the O₂, N₂, Fe(CO)₅ plasma at 50 W is shown in Fig. 22. Figure 22a shows the near infra-red portion of the spectrum from 700 to 900 nm in an expanded version. Table 1 indicates the actual band systems and transitions noted in the two figures.

As Fig. 22 indicates, CO and N₂ dominate the spectrum. Of course the concentration of CO in the plasma is substantial. Each Fe(CO)₅ molecule donates 5 CO to the plasma upon decomposition. Under the conditions used in this study, 20-60% of the discharge gas will be CO. Of course some CO will oxidize to CO₂, but work by Brown
Fig. 22. Typical optical emission spectrum. See Table 1 for meaning of peak designations. Plasma conditions are 50 W RF at 13.6 MHz, 10 sccm $O_2$ and 4 sccm $Fe(CO)_5$. 
Fig. 22a. Near infrared portion of optical emission spectrum from 22.
<table>
<thead>
<tr>
<th>Peak Species</th>
<th>Emission System</th>
<th>Energy Above Ground State (eV)</th>
<th>Transition</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>N₂</td>
<td>2nd Positive</td>
<td>11.1</td>
<td>C₃πᵤ → B₃π₉</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>1st Positive</td>
<td>7.32</td>
<td>B₃π₉ → A3Σ⁺</td>
<td>86</td>
</tr>
<tr>
<td>N₂⁺</td>
<td>Meinel's Auroral</td>
<td>A²πᵤ → X²Σ⁺</td>
<td></td>
<td>86</td>
</tr>
<tr>
<td>CO</td>
<td>3rd Positive</td>
<td>10.4</td>
<td>b³Σ → a³π</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>Angstrom</td>
<td>10.8</td>
<td>B'Σ → A'π</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>Triplet</td>
<td>7.52</td>
<td>d³Δ → a³π</td>
<td>86</td>
</tr>
<tr>
<td></td>
<td>Asundi</td>
<td>6.87</td>
<td>a¹³Σ⁺ → a³π</td>
<td>86</td>
</tr>
<tr>
<td>O(I)</td>
<td>Triplet*</td>
<td>9.15</td>
<td>3s⁵S⁰ → 3p⁵P</td>
<td>89</td>
</tr>
<tr>
<td></td>
<td>Quintuplet*</td>
<td>11.0</td>
<td>3p³P → 3s¹³D⁰</td>
<td>89</td>
</tr>
<tr>
<td>FeO</td>
<td>IR System</td>
<td>1.30</td>
<td>D⁵π → X⁵Σ⁺</td>
<td>90</td>
</tr>
<tr>
<td>Ar(I)</td>
<td>Singlet*</td>
<td>11.55</td>
<td>4s[1 1/2] → 4d[2 1/2]</td>
<td>89</td>
</tr>
<tr>
<td>Fe(I)</td>
<td>Singlet*</td>
<td>2.18</td>
<td>a⁵P → z⁵P⁰</td>
<td>89</td>
</tr>
</tbody>
</table>

Table 1. Emission systems noted in plasma. (*) indicates atomic lines.
indicates that this reaction will not go to completion under the conditions used here (85). Fortunately, CO emission in an electrical discharge is well characterized. By comparing the spectrum in Fig. 22 with one obtained for a pure CO discharge and by consulting published data (86,87), the identifications listed in the spectra and Table 1 were made. All 4 CO systems have been known to occur in electrical discharges. The Third Positive and Angstrom systems are characterized by sharp, single headed bands degraded to shorter wavelengths. The CO Triplet system is characterized by broad, triple headed bands, extending from 400-540 nm. The longer wavelength bands noted in the literature (540-646 nm) were not observed. The Asundi bands have a much more complex structure, containing multiple heads. Only the most intense bands at wavelengths greater than 700 nm appeared, with heads at 721 and 731 nm.

The nitrogen peaks were very intense even though nitrogen gas content in the plasma was less than 5%. The First and Second positive systems are well characterized and often occur as impurities in a glow discharge apparatus (86). Meinel's Auroral system (783, 787 nm) also typically appears in low pressure electrical discharges.

Atomic oxygen emission was observed at two wavelengths, 777 and
798-799 nm (88,89). Both are closely-spaced multiplets, but with the monochrometer used here, the individual heads were not distinguished.

All FeO and Fe emissions were at much lower intensity, probably due to the relatively low concentration of these particles in the gas phase. For this reason, only those peaks in the range 700-900 nm could be observed, away from the high intensity CO and N₂ bands blanketing the rest of the spectrum. (See Fig. 22a.)

The only iron atomic line observed under usual conditions was at 869 nm. This line is usually the most intense line in any iron spectrum (86,89). Two other iron lines were seen under conditions of high plasma power and high iron carbonyl concentration, at 833 and 839 nm. These lines had much lower emission intensity, but are also commonly seen in emission spectra.

In contrast to all other species found in the glow discharge, the FeO system is not well characterized. This is not difficult to understand. Few reliable and sustainable sources of FeO exist. FeO is easily dissociated. The spectrum is extremely complex, with broad, many headed bands of low intensity (90). Theoretical interpretation of FeO molecular spectra has been made only recently, and its ground and excited electronic states proposed (90-93).
Current opinion holds that the ground state is probably $^5\Delta$, but the $^5\Sigma$ ground state proposed by West and Broida has not been completely ruled out (90,91). In the symbolism for molecular spectroscopy, the capitol Greek letter indicates the quantum number for angular momentum for that orbital ($\Sigma=0$, $\pi=1$, and $\Delta=2$.) and the left superscript is the spin multiplicity. (Each unpaired electron adds $1/2$ to $S$, where $2S+1 =$ spin multiplicity.) The $^+$ superscript for the $^5\Sigma^+$ state designation indicates positive symmetry with regard to reflection through the axis of symmetry.

The only bands observed for FeO are in the 700-900 nm range, where CO and $N_2$ emissions do not interfere. The bands are of relatively low intensity, but most of the heads reported by West in this range are present (Fig. 22a). The energy of the emitting $D^5\pi$ state listed in Table 1 is that proposed by West for transition to the $X^5\Sigma^+$ ground state. (D and X are the state designations used by West for the first excited state and the ground state, respectively (90).)

For the lower $^5\Delta$ state, this value would be approximately 0.5 eV greater. Nevertheless, the energy required to promote FeO to this excited state is extremely low relative to that for the lowest energy excited state for nitrogen (7.3 eV).

Plasma conditions were varied in order to ascertain the effects of
Fig. 23. Variation of emission intensity ratio with Fe(CO)$_5$ mole fraction. Ratio taken is N$_2$ 2$^{nd}$ positive peak intensity at 333 nm with N$_2$ 1$^{st}$ positive intensity at 679 nm. Plasma conditions were O$_2$ flow rate = 10 sccm, 13.6 MHz at RF power = 50 watts.
those variations on the relative concentrations of species identified in the plasma. The parameters of most interest in this study were the iron carbonyl feed content and plasma power, due to their marked effect on film properties. (Those properties will be discussed in later sections.) But before relative concentrations were calculated, work was done to determine if by varying these parameters the plasma would be affected in ways which would make actinometry impossible.

Nitrogen emits from two distinct transitions. Equations [10] and [11] should apply equally well, however. For nitrogen, the First Positive system (emitting state 7.32 eV above ground) is much lower in energy than the Second Positive system (11.1 eV). According to Eqn. 11, $I_x/I_y$ will remain constant with changes in plasma conditions if the change in electron energy levels in the plasma is proportional at both energies. If this is the case, then the energy requirements for the actinometer gas are relaxed somewhat. Figure 23 compares the ratio of the First Positive (679 nm) and Second Positive (337 nm) systems of $N_2$ with variation of mole fraction iron carbonyl. It is clear that the ratio remains constant over the range of variation used in this work. This is also the case for variations in plasma power. Figure 24 indicates how this ratio changes with response to power. Once again the ratio of $N_2$ peaks of
Fig. 24. Variation of emission intensity ratio with reactor power. See Fig. 23 for ratio meaning. RF power was 50 W, and frequency was 13.6 MHz, using an $O_2/Fe(\text{CO})_5$ ratio of 10.
very different energies remains constant over the entire range, indicating proportional changes in electron populations at those two energy levels.

The effect of power on individual peak intensities was investigated next. Figure 25 shows this relationship for the O(I) line at 777 nm, and the N$_2$ bandhead at 679 nm. Both emission intensities increase with increasing power. The ratios of the two intensities are calculated and displayed in Fig. 26. If Eqn. [11] holds in this case, then this ratio should be proportional to atomic oxygen concentration in the reaction mixture. This is certainly a reasonable result. Work by Bell and Kwong on production of atomic oxygen in an RF glow discharge showed a similar power dependence (94).

Similar analysis is used in Figs. 27 and 28. Figure 27 shows the emission intensities of the nitrogen band at 679 nm, and the Fe(I) line at 869 nm for a Fe(CO)$_5$ flow rate of 1 sccm. Both emissions increase in a similar, monotonic fashion. The ratios of the peaks are indicated in Fig. 28 for both the 1 sccm data of Fig. 27 plus data for a 4 sccm Fe(CO)$_5$ flow rate. These results indicate that the ratio of the two emissions changes relatively little with increases in plasma power. This is not an unreasonable result if
Fig. 25. Emission intensity for peaks at 679 nm ($N_2$) and 777 nm ($O$). Deposition conditions were $O_2/Fe(CO)_5 = 10, 13.6$ MHz RF.
Fig. 26. Ratio of emission intensities displayed in Fig. 25.
Fig. 27. Emission intensity for peaks at 679 nm (N₂) and 869 nm (Fe). Plasma conditions were O₂/Fe(CO)₅ = 10, 13.6 MHz.
Fig. 28. Ratio of emission intensities displayed in Fig. 27. Plasma frequency was 13.6 MHz and oxygen flow rate was constant at 10 sccm. Iron carbonyl flow rate was 1 sccm (*) and 4 sccm (+).
the deposition rate dependence on power shown in Fig. 20 is considered. Since the iron carbonyl bond strengths are relatively weak, even the low energy electrons present in a 10 watt power plasma would easily decompose the material. Thus, Fe gas phase concentrations should not show a power dependence. The concentration dependence of Fe(I) on iron carbonyl feed fraction will be discussed below.

Figures 29-32 summarize the results obtained for the four reactive species identified in the glow discharge. In all cases, N\textsubscript{2} First Positive system peaks are used as the actinometer. Data for CO in Fig. 29 show an unexpected power dependence. If Fe(CO)\textsubscript{5} decomposition is not limited by the electron energies present in the plasma at low powers, why would CO concentration increase with increasing power, while Fe concentration remains constant? The dependence becomes more pronounced at higher iron carbonyl feed content. It may be that high plasma powers inhibit the side reaction of CO oxidation to CO\textsubscript{2} or actually dissociate CO\textsubscript{2} that is formed, thus allowing a larger CO concentration in the plasma. Another explanation is that emitting Fe atoms are the result of FeO dissociation in the gas phase, rather than direct dissociation of Fe(CO)\textsubscript{5}. By this scheme, CO groups would be removed from the
Fig. 29. Variation of CO content of plasma with Fe(CO)$_5$ mole fraction. Plasma frequency was 13.6 MHz, and O$_2$ flow rate was 10 sccm. RF power levels were 50 W (+) and 10 W (*).
Fe(CO)$_5$ in a stepwise fashion, each carbonyl group being progressively more difficult to remove. As higher plasma power levels are used, more and more CO is produced in the gas phase. On the other hand, reaction of Fe(CO)$_x$ with O may be independent of $x$, and plasma power level as well. Thus, CO and Fe would not show proportional gas phase concentrations.

The data of Fig. 30 for oxygen atom concentration show an interesting feature. At an iron carbonyl feed content of about 10%, O atom concentration reaches a sharp peak, particularly at 50 watts power. These data are completely reproducible and this trend held at other plasma power levels as well. The reason for this effect remains unclear, however.

Oxygen atoms in the plasma can come from three sources: O$_2$, FeO, and CO. It is possible that some O atoms are produced from reaction of O$_2$ with Fe(CO)$_x$, or that iron carbonyl acts as a catalyst for O atom production at low Fe(CO)$_5$ concentrations. At higher iron carbonyl concentrations, however, the catalytic effect would be masked by removal of O atoms by iron carbonyl oxidation. Further, as the feed content of Fe(CO)$_5$ increases, that of O$_2$ decreases. It is interesting to note that 9% is also the Fe(CO)$_5$ feed content at
Fig. 30. Oxygen atom content of plasma dependence on Fe(CO)$_5$ mole fraction. Plasma frequency was 13.6 MHz and O$_2$ flow rate was 10 sccm. Plasma power levels were 25 W (*), 50 W (+) and 100 W (o).
the which deposition rate dependence on iron carbonyl no longer fits Eqn. [9]. (See Fig. 17.)

The data for iron atoms in Fig. 31 indicate very little power dependence as expected. This agrees well with the data in Fig. 28, and also with the lack of dependence of deposition rate on power. The S-shape of the curves is interesting, particularly the apparent saturation effect at iron carbonyl concentrations greater than about 20%. This corresponds to the same shape as that in Fig. 29 for CO content of the plasma. This may be an indication of a lower iron carbonyl decomposition rate. Even without a dependence on power, perhaps the higher overall flow rate under these conditions (4 sccm Fe(CO)$_5$, 10 sccm O$_2$) results in a shorter residence time, and lower conversion. If Fe atoms are the result of the dissociation of FeO rather than Fe(CO)$_5$, residence time effects may also limit the production of atomic Fe.

Iron oxide formation in the gas phase is evidenced by the appearance of molecular FeO peaks (Fig. 22a), and the variation of FeO with plasma power and composition is shown in Fig. 32. As expected, FeO increases with increasing iron carbonyl in the plasma feed. The increase appears to be essentially constant, and independent of power. This is different for the cases of CO and
Fig. 31. Dependence of atomic iron in plasma on Fe(CO)$_5$ mole fraction. Plasma frequency was 13.6 MHz and O$_2$ flow rate was 10 sccm. Plasma power levels were 25 W (•), 50 W (+) and 100 W (o).
Fig. 32. FeO concentration in plasma variation with Fe(CO)_5 mole fraction. Plasma frequency was 13.6 MHz and O_2 flow rate was 10 sccm. Plasma power levels were 25 W (*), 50 W (+) and 100 W (o).
Fe(I) shown earlier, and suggests that FeO production is independent of Fe content of the plasma. It is possible that FeO is being formed in the gas phase rather quickly, but that a certain portion of that FeO is continually dissociated due to high energy electrons in the plasma. The dissociation energy of FeO is 4.2 eV (95). Unfortunately, it is not possible to determine the absolute ratio of Fe to FeO in the plasma using optical emission spectroscopy alone. Optical emission data can only convey the relative concentration of an individual species in the plasma, since the proportionality constants of Eqn. [12] cannot be determined without information relating emission intensity to absolute concentration. In Fig. 33, that relative concentration is plotted vs. iron carbonyl feed fraction. It is important to remember that the FeO/Fe ratio is only in relative units. However, it is interesting that the ratio decreases drastically in the range from 0 to .15 mole fraction iron carbonyl. This is also the range in which the oxygen atom concentration increases through a maximum, then decreases, as well as the range noted for the unusual transition for iron oxide deposition rate. (See Figs. 30 and 17, respectively.) This suggests that oxygen atoms are intimately involved in the deposition mechanism at low concentrations of iron carbonyl, but at higher iron carbonyl concentrations, iron atoms are formed in the plasma in excess of the number of O atoms.
Fig. 33. Concentration ratio of FeO/Fe variation with Fe(CO)$_5$ mole fraction in feed. Plasma power was 50 W at 13.6 MHz and O$_2$ flow rate was 10 sccm.
Chapter 4

Film Composition

Thin films produced by plasma deposition frequently have compositions unobtainable by other deposition methods. The electronic properties of materials are frequently dominated by chemical composition, particularly when impurities are present. Therefore, it is important to determine the exact chemical constitution of the films produced in this study.

4.1 Elemental Analysis

Bulk analysis, described in Sec. 2.4, was first utilized to determine film stoichiometry. The technique used for iron analysis was capable of a high degree of accuracy for the films of the thickness and iron composition produced here. Unfortunately, because of the small quantity of carbon present in the films, and limitations on the oxidation method of analysis, carbon analysis was
frequently impossible. Carbon is determined from gas chromatography analysis of the exit gas from the oxidation furnace. Since carbon dioxide is always present in this gas stream, more than 25 μg carbon must be present in the sample to be confident of results. For a 1 μm film, analysis of carbon contents less than 3 atomic percent was not reliable. Both the parallel plate reactor and the tubular reactor were used to produce films for elemental analysis. For the conditions used in this study, equivalent deposition conditions produced films of identical elemental composition. Thus, reactor temperature, flow rate and power appeared to have a greater effect on film composition than reactor configuration.

Figure 34 shows the effect of feed gas composition on the composition of the deposited film. Since these data were taken at a total pressure of 200 mtorr, a partial pressure of oxygen at 100 mtorr would correspond to a 1:1 mixture of O₂ and Fe(CO)₅. The trends shown here are not unreasonable. At zero partial pressure oxygen, films consist mainly of iron with small amounts of oxygen and carbon. As oxygen feed content increases, oxygen incorporation in the film increases drastically. For example, at P₀₂ = 50 mtorr, a film composition corresponding to a FeO stoichiometry is seen. Whether this film contains both Fe and Fe₂O₃ or is composed of FeO, wustite, is unclear. This question will be discussed in Sec. 5.2.
Fig. 34. Variation of film composition with oxygen content of plasma. Films were made at 250° C, 13.65 MHz and 10 W RF. Total pressure was 200 mtorr.
when x-ray diffraction results are presented. Further increases in oxygen feed content lead to greater incorporation of oxygen in the film, up to about 60 mtorr, after which stoichiometry changes little. However, at an iron atom content of 34%, only 51% oxygen would be expected for a Fe$_2$O$_3$ stoichiometry. Of course some oxygen may be associated with carbon in the film, but as P$_{O_2}$ increases from 60 to 100 mtorr, C content decreases, while O content increases. Clearly, some oxygen is incorporated into the film in unexpected ways.

Carbon contents above the detection limit (3 atom % for a 1 μm film) were noted in many films. The film produced at 0 mtorr O$_2$ in Fig. 34 has approximately equal amounts of C and O. Incorporation of carbon as CO in the films is not unexpected. As was clear in Sec. 3.6, CO content of the plasma is very high, particularly at low O$_2$ feed contents. CO adsorbs on polycrystalline thin film iron surfaces with a heat of adsorption ($\Delta H_{ads}$) of 32-46 Kcal/g-mole (96). Other possibilities for carbon incorporation are the formation of iron carbides and incorporation of carbon suboxides.

As the partial pressure of oxygen increases, carbon content decreases somewhat. This may be due to oxidation of carbon on the film surface and subsequent desorption to the gas phase. There may
also be competition from oxygen molecules and atoms for surface sites at higher $P_{O_2}$, and thus less film coverage of CO during deposition.

Deposition temperature also had an influence on film composition, as noted in Fig. 35. At room temperature, the C content was substantial, over 15%. This value decreased rapidly with increasing temperature until about 150$^\circ$ C. Lower temperature films probably contained carbonates (2). The exact nature of the carbonates is unknown, since $Fe_2(CO_3)_3$ is not a known compound, but the ease with which these films were etched with HCl suggests their presence. Carbonates would probably decompose at temperatures of 150$^\circ$-200$^\circ$ C, therefore decreasing carbon content.

While carbon content decreased with temperature from 30$^\circ$-150$^\circ$ C, oxygen content increased. This might be expected if the increase led to the value of stoichiometric $Fe_2O_3$, but oxygen content is clearly in excess of this value.

Going to still higher temperatures, Fig. 36 indicates that this excess oxygen content disappears at 300$^\circ$ C, and at higher temperatures very near $Fe_2O_3$ stoichiometry exists. Carbon content likewise changes little, being in the 3-4% range for all films, very
Fig. 35. Film composition variation with deposition temperature. 10 W RF power at 13.6 MHz and $O_2/Fe(CO)_5 = 1$. 
Fig. 36. Film composition variation with deposition temperature. 50 W RF power at 4 MHz and \( \frac{O_2}{Fe(CO)_5} = 10 \).
near the detection limit. These samples were all made at 50W RF and 4 MHz. An $O_2/Fe(CO)_5$ ratio of 10 was used.

4.2 Spectroscopic Analysis

Elemental analysis of thin films conveys important information concerning stoichiometry, but gives little information concerning the types of compounds present and variations in a film's composition profile. Moreover, the data for carbon content is of questionable accuracy. In order to provide this information, some of the films were analyzed by Auger electron spectroscopy (AES), electron spectroscopy for chemical analysis (ESCA or XPS) and secondary ion mass spectrometry (SIMS). Auger samples were produced using both the parallel plate reactor and the tubular reactor. Samples for ESCA and SIMS were all deposited in the parallel plate plasma reactor.

Detailed descriptions of these techniques, their theory and their usage can be found in the literature (96-99). In AES a beam of energetic electrons strikes the surface atoms of a material. Some of those atoms eject core electrons. The electron vacancies thus created are filled by deexcitation of other electrons from outer
orbitals. That energy of deexcitation can be transferred to still another electron in the atom. If this final electron is ejected from the solid into the vacuum, it is an Auger electron and is of an energy characteristic of the atom from which it was ejected. By analyzing the distribution of electron energies from a material, the elemental composition can be identified. AES can also be coupled with a sputtering system. If a material is sampled at regular intervals during the sputtering process, a composition depth profile can be constructed.

In ESCA, x-rays are used to eject electrons from atoms in a material. These electrons are often bonding electrons, and the energies of the electrons are characteristic of the type of compound from which the electron was ejected. Thus both elemental identification and molecular bonding information are obtained. Finally, SIMS analysis uses high energy argon ions to eject atoms, molecules and ions from a material. These species are subsequently analyzed by a mass spectrometer.

Figures 37a-d show Auger spectra for different samples. Samples a, b and c were deposited by plasma deposition using 13.6 MHz RF at 10 watts power. Deposition temperatures were $400^\circ$, $250^\circ$ and $500^\circ$ C, respectively. Samples a and c were produced using an $O_2/Fe(CO)_5$
Fig. 37. AES spectra for three films deposited at 10 W RF, 13.6 MHz: a. deposited at 400°C and O$_2$/Fe(CO)$_5$ = 10. b. deposited at 250°C and O$_2$/Fe(CO)$_5$ = 1. c. deposited at 500°C and O$_2$/Fe(CO)$_5$ = 10. d. same film as c. spectrum taken after surface layers removed by sputtering.
ratio of 10. For sample b, this ratio was 1. Samples show peaks characteristic of carbon (271 eV), oxygen (510 eV) and iron (594, 648 and 704 eV). But the sample shown in Fig. 37a indicates a much lower carbon content than that for Fig. 37b. This is due to the higher deposition temperature (400° C) for Fig. 37a than for Fig. 37b (250° C). The trend shown here is consistent with that for carbon content found by elemental analysis. Much of this carbon is due to surface impurities and background gases in the Auger vacuum chamber which are adsorbed on the solid during analysis. This is seen more clearly in Figs. 37c-d. In Fig. 37c, a spectrum close to Fig. 37a is noted, with apparently a similar carbon content. But upon sputtering through the film surface to a depth of 5 nm, most of that carbon disappears, Fig. 37d.

Figures 38a-d show composition profiles for four samples. Samples a, b and d were deposited by plasma deposition using 13.6 MHz RF at 10 watts power. Deposition temperatures were 400°, 250° and 500° C, respectively. Sample c was produced by indirect plasma deposition at 500° C, using the feed content described in Sec. 2.2. Feed gas ratios (O₂/Fe(CO)₅) for samples a, b and d were 10, 1 and 10, respectively. Comparison of Figs. 38a and b, which correspond to Figs. 37a and b, indicates that in both samples most carbon is found
Fig. 38. Composition profiles determined by AES. 38a and b correspond to 37a and b. Figure 38c made by indirect plasma deposition at $500^\circ$ C, and d corresponds to 37c, d.
at the surface. But the carbon found in Fig. 38b shows a surface concentration of over 30%, and extends 60 nm into the film (assuming a sputtering rate of 30 nm/min). From that point, the carbon is at a level such that it may merely have been adsorbed from background gases. Detection of carbon contents above 1% should easily be determined even with background CO present. Thus, the Auger spectra for the low temperature films do not support the 3-4% carbon contents seen from elemental analysis. On the other hand, the large oxygen excess seen from elemental analysis of 250°C films is consistent with Fig. 38b. Figures 38 a and c both correspond to films formed at 500°C, and show close to Fe₂O₃ stoichiometries. However, Fig. 38c was made by the indirect plasma deposition method discussed earlier. The main difference between the films seems to be oxygen content. The indirect plasma film has a slight oxygen excess compared to Fe₂O₃ stoichiometry. However, the surface of the plasma film has an oxygen excess, and an iron deficiency. This is probably due to exposure of the film to the plasma. During deposition, the plasma would contain activated CO groups which would compete with oxygen for surface adsorption sites. After deposition, the plasma film surface was bombarded with oxygen ions for approximately one minute. (See Experimental Procedures, Sec. 2.2.) Also, the plasma film seems to have a sharper film/substrate
interface. This may be due to the difference in film pretreatment. While an oxygen plasma was used to clean the surface for the plasma film, the substrate for the indirect plasma film was exposed only to the oxygen discharge downstream. The oxygen plasma may have sputtered away some of the surface oxide, resulting in a smoother surface. Both films show little or no carbon.

ESCA was used to determine the types of compounds present in a film deposited at 250°C, using an $O_2/Fe(CO)_5$ ratio of 1 and 10 W RF at 13.6 MHz. The spectrum for this experiment is shown as Fig. 39a. As usual, iron, carbon and oxygen are present. Figures 39b and c show a more detailed view at the energies appropriate to the 1s electron of carbon and the $2p_{1/2}$ and $2p_{3/2}$ electrons of iron, respectively. The large carbon peak centered at 285 is characteristic of surface hydrocarbon contamination. But the smaller peak at 288 is at an energy characteristic of a metal carbonyl. Such binding energy may occur as a result of incomplete carbonyl dissociation during deposition, or more probably, CO trapped in the film during deposition. The two iron peaks in Fig. 39c may be due to either FeO or $Fe_2O_3$; the two are not readily distinguished. It is clear, however, that no unoxidized iron is present in the film.
Fig. 39a. ESCA spectra of film plasma deposited at 250° C, 10 W RF at 13.65 MHz and $O_2/Fe(CO)_5 = 1$. b, c indicate expanded regions.
SIMS was also used to analyze this particular film. Values for m/e of 56, 28, 16 and 12 were found and monitored throughout. The resulting profile can be seen in Fig. 40. These data are not normalized, and can only be considered relative for each individual m/e value. The profile for m/e = 56 is doubtless due to the iron in the film, and 16 the oxygen. The m/e = 12 profile is carbon, and may be due to hydrocarbon surface contamination. The unexpected value at m/e = 28 may be due to CO. Clearly, there is more of this substance at the film’s surface, but extends well into the film. While this may account for the small amount of carbon in the film, it is certainly not conclusive. One possibility is that the carbon in the film tends to segregate at the surface.
Fig. 40. SIMS profile for plasma deposited film described in Fig. 39.
Chapter 5

Film Structure

The structure of thin film photoanodes is nearly as important as composition in determining their electronic and photoelectrochemical properties. Optimal properties would be found in perfectly epitaxial layers, while a highly polycrystalline or an amorphous film would perform in an inferior manner. Moreover, the properties of the different crystalline forms of iron oxide are known to differ greatly. Structural properties were investigated using density measurements, x-ray diffraction and scanning electron microscopy.

5.1 Film Density

The density of deposited films was easily determined by the techniques indicated in Sec. 2.3. Density was found to vary in response to some deposition conditions. For example, Fig. 41 shows this variation with changes in O₂ feed content for a total
Fig. 41. Variation of film density with oxygen content of plasma during deposition at 250° C. RF power was 10 watts at 13.6 MHz. Total pressure was 200 mtorr.
deposition pressure of 200 mtorr, at 250° C. These data are in clear agreement with those of Fig. 35, which shows the variation of film composition with oxygen feed. At the point of no oxygen addition, films consist mainly of iron under these conditions. And indeed, the density of pure, single crystal iron is 7.9 g/cm³ (100). The measured density of 6.0 g/cm³ for the plasma deposited film may be due to structural imperfection and/or the incorporation of carbon and oxygen in the films. As oxygen content increases in the films (with increasing O₂ partial pressure) density decreases rapidly. The densities of the bulk iron oxides range from 4.2 to 5.2 g/cm³ depending on the specific crystalline type. But at 250° C, most film densities were approximately 3 g/cm³. These low values may be due to a high degree of structural disarray, porosity or incorporation of trapped gases in the film structure (which is indicated in Figs. 35-37 and Fig. 38d). Densities approaching the theoretical value were only found at higher temperatures. Figure 42 shows how film density gradually approaches the theoretical value of 5.2 g/cm³ as deposition temperature increases. Thus, at 450–500° C, a high degree of structural perfection may be present. Note also that under these conditions, a near perfect stoichiometry for Fe₂O₃ is always found (Fig. 36).
Fig. 42. Film density dependence on deposition temperature for films made at 50 watts RF at 4 MHz and $O_2/Fe(CO)_5 = 10$. 
5.2 X-Ray Diffraction Results

X-ray diffraction was used to help evaluate the crystallinity of the films, and to determine the exact crystalline form. Indeed it was found that a number of crystal forms could be produced by varying deposition conditions. Published X-ray diffraction data for $\alpha$-$\text{Fe}_2\text{O}_3$, $\text{Fe}_3\text{O}_4$, and $\gamma$-$\text{Fe}_2\text{O}_3$ are found in Table 2, 3 and 4, respectively.

Figure 43 shows x-ray diffraction results for three plasma deposited films produced under different oxygen partial pressures. With no oxygen addition, only diffraction of the $\alpha$ phase of iron is seen in the films, with a sharp peak at a 2$\theta$ value of 48°. This is consistent with results indicated previously. When oxygen is added at a ratio of $O_2/\text{Fe(CO)}_5 = 0.5$, the peak at 48° disappears entirely, and very broad peaks centered at 30, 35 and 43 degrees are noted. These three peaks correspond to interplanar lattice spacings found in both $\text{Fe}_3\text{O}_4$ and $\gamma$-$\text{Fe}_2\text{O}_3$. These two crystalline forms have similar spinel-like structures with similar lattice spacings. Thus, their diffraction patterns vary by 2$\theta$ differences of about 0.5° or less,
Table 2. X-Ray Diffraction Data for α-Fe$_2$O$_3$ (17).

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<tr>
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<td>.963</td>
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</tr>
<tr>
<td>111.5</td>
<td>.932</td>
<td>4</td>
<td>840</td>
</tr>
</tbody>
</table>
Fig. 43. X-ray diffraction results for films deposited at 10 W RF, 13.6 MHz and 250° C. Diffraction varied with feed gas ratio as indicated.
and are not readily distinguished. However, the rather broad peaks found here may be due to a mixture of the two phases. Broad peaks can also be the result of very small crystallites (101).

Once the ratio of $O_2/Fe(CO)_5$ reaches 1.0, these same peaks become larger and sharper. At the 2θ values of 30, 35 and 43 degrees, the relative intensities are approximately 30, 100 and 20, respectively. This is in good agreement with the data of Tables 3 and 4 for both $Fe_3O_4$ and $γ-Fe_2O_3$. Thus, the structure is that of randomly oriented crystallites, but whether these crystallites are $Fe_3O_4$ or $γ-Fe_2O_3$, or a mixture of both is unclear. The composition data of Chapter 4 suggest a preponderance of $Fe_2O_3$, however.

The small peak at 42° is unexpected. The only structure which shows diffraction at this value of 2θ is wustite ($FeO$) (17). According to published data, 41.9° is the highest intensity peak for wustite (17). Wustite is unstable at temperatures below 570° C, at which point it decomposes into $Fe_3O_4$ and Fe (16). Wustite can be preserved by quenching, but this particular film was deposited at only 250° C. Unfortunately, the presence of this peak suggests that $FeO$ may be present in other films as well, and this may complicate interpretation of the composition data presented earlier.
Higher deposition temperatures, when combined with a higher gas phase concentration of oxygen, always result in the $\alpha-\text{Fe}_2\text{O}_3$ crystalline form. Figure 44 shows x-ray diffraction data for two films deposited with an $O_2/\text{Fe(CO)}_5$ ratio of 10 at 300° and 350° C. Both higher deposition temperature and higher oxygen content were necessary to produce the $\alpha$ crystal form. For the 350° film in Fig. 44, the peaks at the approximate 2θ values of 33, 36, 39, and 41 at approximate relative intensities of 20, 13, 30 and 100 are somewhat different from the powder diffraction file values of 30, 2, 50 and 100 (Table 2). This difference may be due to preferred orientation of the crystallites in the film (101).

Variation of other deposition conditions resulted in even more drastic deviations from published intensity values. In Fig. 45, x-ray diffraction data are shown for films deposited at three different temperatures on glass substrates. These films were made using 4 MHz RF at 50 W power, and an $O_2/\text{Fe(CO)}_5$ ratio of 10. The 350° C film showed diffraction at 2θ values of 33, 36, 41, 50, 54, 58, 62.5 and 64. The relative intensities were 100, 50, 25, 30, 45, 10, 20, and 10, respectively. These are reasonably close to the published values for randomly oriented polycrystalline samples, Table 2. As deposition temperature increased, however, the peaks at
Fig. 44. Change of x-ray diffraction of films deposited on glass with deposition temperature variation. Deposition conditions were 50 W RF power at 4 MHz, with $O_2/Fe(CO)_5 = 10$. 
Fig. 45. X-ray diffraction variation with temperature for films deposited on glass at 4 MHz, 50 W RF with $O_2/Fe(CO)_5 = 10$. 
33, 50 and 54° decreased drastically, with a corresponding increase in intensity at 2θ = 64° and 39°. These changes in intensity are probably due to preferential ordering of crystallites in the growing film. At very low deposition temperatures, atoms and molecules which reach the surface of the growing film lack sufficient energy to migrate across the film surface. These particles are thus frozen at the positions of impact, and cannot assume ordered locations. The result is an amorphous structure. At higher deposition temperatures, atoms can migrate across the surface of the film, increasing the likelihood that crystallites of appropriate ordering for the material at hand will form. But at moderate deposition temperatures, this surface migration may be over a limited distance and small crystallites of differing orientation will result. If substrate temperature is increased to further enhance surface migration, crystallites can become larger, and crystallites of a particular orientation will possess more favorable, or lower energy, positions for particle incorporation. Indeed, highly ordered and even single crystal structures are possible at high deposition temperatures (74).

Other deposition variables affect film structure. For example, Fig. 46 shows diffraction results for three films made at different RF power levels, 400° C. An O₂/Fe(CO)₅ ratio of 10 was used here as
Fig. 46. X-ray diffraction variation with RF power at 4 MHz. Films were deposited on glass at 400° C with $O_2/Fe(CO)_5 = 10$. 
well. The film made at 10 watts appears to have a structure close to that for randomly oriented crystallites. Both films made at higher power levels differ from this condition, with the 50 watt film showing the fewest diffraction peaks. These results suggest that RF power level may have an effect on crystallite orientation as well. This is to be expected in plasma deposition. In the plasma environment, the growing film is continuously exposed to ion and electron bombardment. As deposition power increases, the plasma potential increases as well, leading to higher energy electron and ion bombardment. This bombardment transfers energy to atoms on the film's surface, increasing the surface mobility of those atoms. Thus, higher power levels should lead to increases in atom migration and thus larger, more oriented crystallites. On the other hand, very high power levels may so increase ion bombardment that radiation damage occurs.

In the course of this work, films were deposited on various substrates. For most analytical work, glass substrates were used. Iron substrates were used for photoanode production. Interestingly, film structure varied with the substrate used. Figure 47 shows diffraction patterns for films deposited on three substrates at 500°C, 10 W RF at 13.6 MHz, and an \( \text{O}_2/\text{Fe(CO)}_5 \) ratio of 10. All three films vary significantly from the powder diffraction patterns, but
Fig. 47. Change in X-ray diffraction properties for films deposited on the indicated substrates. All depositions at 500°C, 10 W RF at 13.65 MHz with $O_2/Fe(\text{CO})_5 = 10$. 
differences from each other are significant as well. The film on glass had the highest intensity diffraction peaks, while the film on the silicon substrate had the lowest. Crystallite orientation on all films was different. Different substrates resulting in different film structure is not unexpected. When plasma deposition is initiated, atoms or molecules in the gas phase must adsorb on the substrate surface. This will happen at particular nucleation sites which possess a structure favorable for condensation and nucleation. Naturally, the surface of iron, silicon and glass will be very different. It is therefore expected that nucleation site energy and location will differ as well.

5.3 Scanning Electron Microscopy Results

It is important to note that iron oxide can exist as a mixture of phases (16,17). In some cases, a surface layer of one phase can overlie a bulk phase of another (73). X-ray diffraction may only detect the major phase in these thin film structures. The technique is limited by the number of crystallites present in the film which diffract the incident x-ray beam. Therefore, scanning electron microscopy (SEM) was used to investigate film morphology. If a surface layer were present, such a layer might be detected by SEM.
Figures 48a–d show plasma films deposited on silicon at four different temperatures. All these films were deposited at 50 watts RF power at 4 MHz and an O₂ flow rate of 10 sccm, Fe(CO)₅ at 1 sccm. The film deposited at 500° C, Fig. 48a, clearly shows the largest and most highly oriented crystallites. Films deposited at 350–450° C, Figs. 48b–d, show an increasing degree of crystallinity with increasing temperature. This agrees well with the x-ray diffraction data presented earlier.

Plasma power level had a substantial effect as well. In Figs. 49a, b and c films which were plasma deposited at 10, 25 and 50 watts on silicon substrates at 500° C are shown. An O₂/Fe(CO)₅ ratio of 10 was used to deposit the plasma films. Figure 49d is a film produced by indirect plasma deposition at 500° C, included for comparison. Of the plasma deposited films, the one produced at 50 watts (Fig. 49c) seems to have the most regularity. This micrograph shows highly oriented crystallites of close to uniform size. The lower power films in Figs. 49a and b seem to be highly crystalline, but do not have the regularity in structure noted for the 50 watt film. These data indicate that higher plasma powers aid the formation of highly ordered structures, and agree well with the analysis presented in the previous section. Therefore, it is
Fig. 48. Scanning electron micrographs of films plasma deposited on single crystal silicon for four different deposition temperatures, a-d: 500°, 450°, 400°, and 350° C, respectively. Power was 50 W at 4 MHz, and O₂/Fe(CO)₅ = 10.
Fig. 49. Scanning electron micrograph for films deposited on single crystal silicon for three different RF power levels, a-c (10, 25 and 50 watts, respectively) and by indirect plasma deposition, d. e and f are profiles of c and d, respectively. Deposition temperature was 500°C, RF frequency 4 MHz and $O_2/Fe(CO)_5 = 10$. 
surprising that the indirect plasma film, Fig. 49d, possess such a regular structure, with such large crystallites. Perhaps oxygen atoms which reach the surface of the growing film from the ionization chamber impart a significant amount of energy to the surface, thus aiding the formation of the large crystallites. The lack of ion bombardment with the indirect plasma may also allow the larger crystals to form. Figures 49e and f show profiles of the same films noted in Figs. 49a and d, respectively. With both films, it is clear that individual crystallites extend the entire thickness of the film, indicating a columnar growth pattern.

Comparison of films deposited on different substrates is made in Fig. 50a–c. These films were all made at 50 watts, 500° C. Figure 50c is the same as that in Fig. 49c, but films in Figs. 50a and b were deposited on iron and glass, respectively. Clearly, use of the silicon substrate leads to the most highly ordered film, but the crystallites for the film on the iron substrate are larger than those on the glass. On the other hand, more than one crystallite orientation may be present in the films deposited on iron and glass substrates. This would be consistent with x-ray diffraction data, which showed diffraction at a number of different values of 2 for the glass and iron substrate samples, but only diffraction at 33.2° for the film on silicon.
Fig. 50. SEMs of films deposited on three different substrates at 500° C, 50 W RF at 4 MHz, $O_2/Fe(CO)_5 = 10$. Substrates: a. Silicon. b. Iron foil. c. Glass.
Of course only iron substrates can be used for photoanodes. Therefore, scanning electron micrographs were taken of the different types of photoanodes used in this study. Figure 51a–d shows iron oxide films produced by 4 different techniques, all at 500° C: plasma deposition, thermal oxidation at $P_{O_2} = 1$ atm., indirect plasma deposition, and gas phase deposition with no plasma at all (CVD). The difference between the films is striking. The plasma film, Fig. 51a, has moderately sized crystallites, about 0.1–0.2 μm across, and an acicular shape in an orientation perpendicular to the substrate. In contrast, the thermal film, Fig. 51b, has much smaller crystallites with no particular orientation. Both films were reasonably uniform across the surface, and porosity appears to be low. In contrast, the two films deposited without a plasma show very long acicular crystallites, and much higher porosity. The two non-plasma deposited films have a similar appearance, but the indirect plasma film in Fig. 51c has somewhat larger crystallites than the CVD film, Fig. 51d. These large crystallites may be absent in the plasma deposited film due to ion bombardment during film growth.
Fig. 51. SEMs of different types of iron oxide thin films on iron substrates, all made at 500°C. a. Plasma deposition at 50 W RF power, 4 MHz and \( \frac{O_2}{Fe(CO)_5} = 10 \). b. Thermally grown. c. Indirect plasma deposition. d. Deposited from the gas phase in plasma reactor without using a plasma.
Chapter 6

Optical Properties

The optical properties of a material are important in determining its efficiency as a liquid junction solar cell. The two most critical properties are reflectance and absorptance. Reflected light and that transmitted through the material are not utilized. Only light that is absorbed is available for conversion to chemical or electrical energy. Thus it is important that a thin film photoanode have low reflectance and high absorptance.

Reflectance data are shown in Fig. 52. It is clear that the film deposited on quartz (curve 1) was much more reflective than the films on iron substrates (curves 2, 3). Also, the thermally grown film (curve 2) displayed a higher reflectance than the plasma deposited film on iron (curve 3). The two reflectance curves for films on iron substrates have similar shapes, which are very different from the reflectance curve for iron oxide deposited on quartz. This may be due in part to interference effects, which are
Fig. 52. Reflectance spectra of three iron oxide thin films. 1. Plasma deposited on quartz. 2. Thermally grown on iron foil. 3. Plasma deposited on iron foil. Both plasma films were deposited at 500 °C, 10 W RF power at 13.6 MHz and \( \frac{O_2}{Fe(CO)_5} = 10 \).
functions of film structure, film thickness and substrate refractive index. The thickness of the two plasma deposited films was identical, but films deposited on iron were found to have a more crystalline structure than films deposited on amorphous substrates. The lower reflectance for the plasma deposited film compared to the thermally grown film may have been due to the larger, more developed crystallites in the plasma film. (See Sec. 5.3.)

The refractive index for any material at a single wavelength can be calculated from Fresnel's formula (100):

\[ n = \frac{(1+R^{1/2})}{(1-R^{1/2})} \]  

[13]

where \( n \) is the refractive index of the film material and \( R \) is the total reflectance. The literature value for refractive index at the standard lithium wavelength (670.8 nm) is 2.94–3.09 (100). This agrees well with the value calculated for the plasma deposited film on quartz by Eqn. [13] (\( R = 0.27, n = 2.92 \)), but is substantially greater than that noted for the other two films.

The difference in reflectance may be due to differences in film structure. From the micrographs in Sec. 5.3, it is clear that the films deposited on iron and glass possess very different structures. The film on the iron substrate has large, acicular
crystallites which form a much rougher surface than that seen for the plasma film deposited on glass. The thermally grown film has larger crystallites as well, but not as large as those of the plasma deposited film. It is therefore likely that the difference in reflectance for the three films is due to differences in structure for those films.

Film transmittance was considered next. Figure 53 shows the optical density of three films of different thicknesses deposited on quartz. The optical density is defined as

\[ D = -\log(T) \]

where \( T \) is the fraction of light transmitted through the film, and \( D \) the film's optical density. \( D \) is also called the absorbance of the film. Figure 53 indicates optical density local maxima at 210 and 400 nm. The peak at 210 nm may indicate an optical transition, but the 400 nm peak corresponds to the sharp reflectance increase in the range 350-420 nm. The region 420-600 nm shows a gradual decrease in optical density, which is similar to that seen for CVD Fe₂O₃ (9, 101). Part of this decrease corresponds to the 2.2 eV indirect electronic transition noted by several authors (16,30,31). The shorter wavelength portion of this decrease in optical density (420-560 nm) may be due to another reported transition at 3.2 eV.
Fig. 53. Optical density spectra of three films plasma deposited on quartz of the indicated thickness. Films were deposited under conditions identical to those in Fig. 52.
But because of the reflectance peak at 420 nm, the transition appears to occur at a lower energy.

Reflectance and transmittance data can be used to determine optical absorptance, or the fraction of incident light absorbed by the film.

\[ R + T + A = 1 \]  \[ \text{(15)} \]

In this expression, \( A \) is the optical absorptance, \( R \) reflectance and \( T \) transmittance. Absorptance for the plasma deposited film is indicated in Fig. 54. As expected, optical absorptance drops off drastically at approximately 560 nm (2.2 eV), which is the published bandgap energy for \( \alpha-\text{Fe}_2\text{O}_3 \) (30, 31). Figure 54 shows that the 90 nm film of \( \text{Fe}_2\text{O}_3 \) absorbs over 75% of incident light at wavelengths below 400 nm, and greater than 60% in the range 400-520 nm.

Clearly, plasma deposited \( \text{Fe}_2\text{O}_3 \) thin films absorb very strongly in this portion of the visible spectrum, which is typical of iron oxide produced by other means (9). Since 90 nm is a relatively thin film, it should be easy to deposit thicker films which absorb nearly all incident light.

The Lambert law relates light absorbance to film thickness.
Fig. 54. Calculated optical absorptance spectrum of plasma deposited iron oxide on quartz using the data of Figs. 52, 53.
Here, $A$ is the absorbance as before, $\alpha$ the linear absorption coefficient and $x$ is the film thickness. As expected, Eqn. [16] indicates that thicker films absorb more light, thus transmitting less. In order to predict the most appropriate thickness for an iron oxide photoanode, the data of Fig. 54 were replotted in terms of absorption depth, or $\alpha^{-1}$. This quantity indicates the thickness of film required to absorb $1-1/e$ or 63% of incident radiation. Optical absorption depth vs. wavelength is shown in Fig. 55. This graph shows clearly that nearly all light is absorbed in the near surface region of the film, even at near bandgap energies. Thus, iron oxide photoanodes probably will not be limited by light absorption: even the thinnest photoanodes should absorb sufficient light to efficiently convert sunlight to electrical or chemical energy.
Fig. 55. Calculated absorption depth of plasma deposited iron oxide using the data of Figs. 52, 53.
Chapter 7

Electrical Properties of Films

The electrical properties of materials used for liquid junction solar cells ultimately determine their energy conversion efficiency. The electrical properties considered in this study are conductivity and carrier concentration. By relating changes in electrical properties to variations in deposition conditions, it may be possible to optimize the plasma deposition process for production of thin film photoanodes. For example, it has been determined that very high resistivities result in poor photoanodes due to ohmic loss through the semiconductor bulk (52). Conversely, very low resistivity due to high carrier concentration results in depletion regions too thin to absorb a great deal of light. The relationship between depletion region thickness, $W$, and carrier concentration, $N$, is:

$$W = \left(\frac{2e \varepsilon \varepsilon_0 / eN}{s} \right)^{1/2} \left(V - V_{fb}\right)^{1/2}$$

[17]
where \( \varepsilon_s \) is the dielectric constant of the semiconductor, \( \varepsilon_0 \) is the permittivity of free space, \( e \) the electronic charge, \( V \) the photoanode potential and \( V_{fb} \) the flatband potential (102).

Iron oxide resistivity can be varied by reduction or impurity incorporation as discussed in Sec. 1.3. It was hoped that variation of \( O_2/Fe(CO)_5 \) feed ratio during plasma deposition would have a similar result. Figure 56 shows the results of this attempt, for films deposited at \( 250^\circ \) C on glass substrates with a total operating pressure of 200 mtorr. The films were 1-2 \( \mu \)m thick. Resistivity was measured using the four-point probe, as described in Sec. 2.7. Current-voltage characteristics were linear over the range 5-20 nA. These currents resulted in voltage drops of about 1-20 volts.

Clearly, resistivity changes drastically for small changes in oxygen feed content. These data agree well with composition data presented in Chapter 4. At 0 partial pressure \( O_2 \) (no \( O_2 \) added during deposition) films possessing metal-like conductivity are deposited: these films are 80\% iron. But just as small increases in oxygen feed content result in large increases in film oxygen content (Fig. 34), resistivity increases sharply as well. The film produced at \( P_{O_2} = 54 \) mtorr had a resistivity of \( 1.8 \times 10^2 \) ohm-cm. Composition
Fig. 56. Electrical resistivity of films plasma deposited on glass at different plasma oxygen contents. Deposition conditions were 250°C, 13.6 MHz at 10 W RF power. Total pressure was 200 mtorr.
data presented in Sec. 4.1 indicated that this film contained equal amounts of iron and oxygen, but x-ray diffraction results for this film, Sec. 5.2, indicated only the presence of Fe$_3$O$_4$ and/or γ-Fe$_2$O$_3$. The resistivity of Fe$_3$O$_4$ is approximately $4 \times 10^{-3}$ ohm-cm (16). The higher resistivity noted here may be the result of high porosity, as suggested by the density data of Sec. 5.1. Increasing plasma oxygen content further increased film porosity, and may have acted to oxidize Fe$_3$O$_4$ to γ-Fe$_2$O$_3$. The resistivity of γ-Fe$_2$O$_3$ is not accurately known, but is probably 2-3 orders of magnitude higher than that for Fe$_3$O$_4$ (54). Unfortunately, the resistivity variation over 10 orders of magnitude in Fig. 56 indicates that precise control of resistivity may be difficult by varying oxygen feed content.

When the iron oxide films were tested as photoanodes, it was found that only those films deposited at O$_2$ to Fe(CO)$_5$ feed ratios of approximately 6 or greater displayed any photocurrent at all. The highest photocurrents were obtained from photoanodes deposited with an O$_2$/Fe(CO)$_5$ feed ratio of 10. Therefore, all further electrical measurements were directed toward determining the properties of films deposited with this feed ratio.
As previously indicated, the carrier concentration is particularly significant since it determines the space charge region thickness and the depth available for light absorption in the semiconductor surface. Carrier concentration is usually determined from impedance measurements of the photoelectrochemical cell by plotting $1/C^2$ vs. voltage, thereby generating a Mott-Schottky plot (103).

Experimental difficulties in performing capacitance measurements of solid/liquid interfaces have been previously discussed (31). Most of these difficulties involve complex interactions between the semiconductor and the electrolyte. For instance, specific ion adsorption on the semiconductor surface and variation of the Helmholtz layer capacitance with voltage have been suggested as causes of non-linear Mott-Schottky plots and non-Nernstian electrode behavior (31). The presence of surface states and electrode surface treatments also have a strong influence on Mott-Schottky plot linearity (104, 105). Further, the difficulty of interpreting non-linear Schottky-Mott plots has been addressed (31,106,107). Therefore, a technique capable of measuring semiconductor electrode carrier concentrations without the use of an electrolyte was utilized to determine carrier concentrations.
7.1 Capacitance-Voltage Technique

Impedance measurements in photoelectrochemical cells are used to ascertain the thickness of the semiconductor space charge or depletion region. In n-type semiconductors, this region is initially formed by the net flow of electrons from the semiconductor into the electrolyte. However, a depletion region can also be formed merely by applying an electric field across a semiconductor. If a dielectric layer is present on the semiconductor surface, high electric fields can be applied without initiating current flow. This latter structure is called a Metal/Insulator/Semiconductor (MIS) capacitor, and is the basis of many solid state devices.

Capacitance-voltage measurements of the MIS structure represent a well-established diagnostic technique utilized in the fabrication of integrated circuits. The usual goal of MIS measurements is the determination of dielectric properties such as dielectric constant and electronic charge levels in the film. In these investigations, the electrical properties of the semiconductor (usually silicon) are well-known. However, as will be indicated below, electrical properties of the semiconductor can also be obtained. A number of
reviews discuss the capacitance-voltage technique in detail (108, 109) so only a brief description will be given here.

The total capacitance of the MIS structure is given by the series capacitance of the insulator and the semiconductor:

\[ C = \frac{1}{C_I} + \frac{1}{C_{sc}} \]  

[18]

Here \( C \) is the total capacitance, \( C_I \) that of the insulator, and \( C_{sc} \) the semiconductor space charge capacitance. If a positive potential is applied to a dielectric layer above an n-type semiconductor, majority carriers (electrons) accumulate at or near the semiconductor/insulator interface, giving essentially zero depletion width. In this case, \( 1/C_{sc} \) would be negligible compared to \( 1/C_I \) and the total capacitance is the insulator capacitance.

As the voltage becomes negative, electrons are driven away from the dielectric/semiconductor interface, and a depletion region is formed. This depletion or space charge region presents an additional capacitance in series with the dielectric capacitance (Fig. 57). As the negative potential is increased, more electrons are repelled from the semiconductor surface, and the depletion region widens, thereby increasing the space charge capacitance, and reducing the overall capacitance due to the series combination given
Fig. 57. Theoretical capacitance-voltage plot of an MIS structure. Inset indicates the origin of the two series capacitances for this structure.
in Eqn. [18]. When sufficiently negative voltages are applied so that minority carriers (holes for an n-type semiconductor) are attracted to the surface, the space charge region has reached its maximum value, and the capacitance remains nearly constant with further increases in potential. Of course, the maximum width of the depletion region is dependent upon the doping level and the dielectric constant of the semiconductor.

The maximum and minimum capacitance values can be used to calculate the charge carrier concentration, $N$, in the semiconductor (109, 110).

$$N = \frac{2C_s^2 (INV)}{\varepsilon_a s_o (C_{\text{max}}/C_{\text{min}} - 1)^2}$$

where

$$s_{(INV)} = ((\sigma^2 + V')^{1/2} - \sigma)^2$$

$$\sigma = 1/C_I (\varepsilon N/2s_s s_o)^{1/2}$$

$$V' = V - V_{fb}$$

In these equations, $\varepsilon_I$ and $\varepsilon_s$ are the dielectric constants of the
insulator and the semiconductor, respectively, \( e \) is the electronic charge, \( \varepsilon_0 \) the permittivity of free space, and \( \varphi_s \) is the semiconductor surface potential. The surface potential can be estimated by the method of Goetzberger and Nicollian (110). \( V_{fb} \), the flatband potential, can be estimated by Heiman's method (111).

The slope of the central portion (depletion region) of the curve is also related to the carrier density by the expression (108):

\[ \frac{dC}{dV} = \frac{C^3}{s_o \epsilon N} \]

which upon integration becomes:

\[ \frac{1}{C^2} = \frac{2}{s_o \varepsilon_0 \epsilon N (V-V_o)} + \frac{1}{C_i^2} \]

It is important to note that Eqn. [20] was obtained in a depletion approximation. However, as long as the space charge layer is greater than twice the extrinsic Debye length, \( \lambda \), where

\[ \lambda = \left( \frac{2kT}{e^2 N} \right)^{1/2} \]

Eqns. [20] and [21] represent good approximations (112). In the present case, \( 2\lambda \) is approximately 20% of the depletion layer thickness at inversion. In Eqn. [21], \( k \) is the Boltzmann constant,
T is temperature and $V_o$ is a constant which accounts for interface and/or insulator charges. Naturally, this expression is similar to the usual Mott-Schottky relation, but $V_o$ is not related to the electrolyte dependent flatband potential.

The capacitance-voltage technique is strictly applicable only to single crystals and epitaxial layers (109). The films produced here were polycrystalline, and the possibility that the films were conduction network limited in their electrical behavior cannot be ignored. Grain boundaries may also distort local electric fields, leading to erroneous results. Structural data presented in Chapter 5 suggested that many films consisted of large, oriented crystallites. If individual crystallites extended the entire thickness of the film, as the SEM profiles presented earlier indicated, the film may act as a single crystal material.

The results of CV and other electrical measurements for selected Fe$_2$O$_3$ samples are summarized in Table 5. The dielectric constant of the iron oxide films varied from 56-113, with higher values corresponding to higher RF power levels for deposition. Values reported in the literature for bulk iron oxide range from 80 to 120 for the α crystal form (31, 48), and approximately 10 for the γ form (113).
<table>
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<tr>
<th>Power (W)</th>
<th>Temperature (°C)</th>
<th>Thickness (µm)</th>
<th>Electron Concentration (cm³)</th>
<th>Dielectric Constant (at 1 MHz)</th>
<th>Resistivity (Ohm·cm)</th>
<th>Electron Mobility (cm²/V·s)</th>
<th>Depletion Layer Thickness (µm)</th>
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<td>113</td>
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<tr>
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<td>1.9</td>
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<tr>
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<td>0.050</td>
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<tr>
<td>25</td>
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<tr>
<td>350</td>
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<td>$6.1 \times 10^{16}$</td>
<td>60</td>
<td>$3.4 \times 10^3$</td>
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Table 5. Deposition Conditions and Electrical Properties of Plasma Deposited Iron Oxide Thin Films. Electron concentrations were determined from application of Eqn. [21].
Iron oxide film resistivity varied over two orders of magnitude, depending upon deposition conditions.

Relative capacitance \( \left( \frac{C}{C_1} \right) \) data from two \( \text{Fe}_2\text{O}_3 \) films of thickness 1.7 \( \mu \text{m} \) (sample 1) and 2.4 \( \mu \text{m} \) (sample 2) are shown in Fig. 58. Note that positive bias voltage refers to that voltage applied to the dielectric of the MIS structure. It is clear that sample 1 shows a nearly theoretical shape, when compared to Fig. 57. Using Eqn. [19], the carrier concentration for sample 1 is \( 5.3 \times 10^{15} \text{ cm}^{-3} \). On the other hand, sample 2 shows somewhat unusual behavior, in that a very large potential (9 volts) is required to bias the sample into inversion. Such behavior is probably due to the rather thick insulator deposited on this film, and the high dielectric constant iron oxide film. The carrier concentration for this second sample is \( 1.3 \times 10^{16} \text{ cm}^{-3} \).

According to Eqn. [21], a plot of \( 1/C^2 \) vs. bias voltage should yield a straight line. Such a plot is shown in Fig. 59. Note, however, in this case voltage is referenced to that applied to the film substrate, rather than the aluminum contact atop the dielectric. In agreement with Eqn. [21], both samples 1 and 2 clearly yield a straight line on this plot, with carrier concentrations of \( 6.5 \times 10^{15} \) and \( 1.7 \times 10^{16} \text{ cm}^{-3} \), respectively.
Fig. 58. Variation of relative capacitance with DC voltage for the MIS structure shown in Fig. 57. The SiO<sub>2</sub> thicknesses are 64 nm for sample #1 (1.7 μm Fe<sub>2</sub>O<sub>3</sub>) and 125 nm for sample #2 (1.9 μm Fe<sub>2</sub>O<sub>3</sub>). See Table 5 for additional information on these samples.
Fig. 59. Analysis of capacitance-voltage data according to Eqn. [21], for the samples of Fig. 58. The slopes of the lines are related to the carrier concentration. Resulting values of the carrier concentration are given in Table 5.
These values are in good agreement with results calculated earlier from Eqn. [19].

For comparison purposes, a number of iron oxide samples were studied using the Mott-Schottky technique. In nearly all cases, the resulting plots were non-linear, and the results were difficult to reproduce. For the sample deposited at 500°C and 50 W, a linear Mott-Schottky plot was obtained, but the carrier concentration from this plot was $7 \times 10^{18} \text{ cm}^{-3}$, an unexpectedly high value. The reasons for this discrepancy are not clear. The Mott-Schottky plot measurements were all made using the impedance bridge at 1 KHz, while the C-V plots were performed at 1 MHz. However, variations in the dielectric constant of the various $\text{Fe}_2\text{O}_3$ films investigated were insignificant for these two frequencies. Further, the discrepancy does not appear to be due to Helmholtz layer capacitance as such a series capacitance would result in a decrease in the total capacitance. On the other hand, surface states are known to act as an impedance in parallel to the depletion layer capacitance (104). This may lead to the higher capacitance values observed here. Indeed, semiconductor-solution interactions are known to lead to the formation of surface states for $\text{Fe}_2\text{O}_3$ as well as other materials (115-117).
As observed in Table 5, carrier concentrations for iron oxide films vary over two orders of magnitude, yet no consistent trends appear as to the effects of film deposition conditions upon this property.

Electron mobilities of the plasma-deposited films were calculated from the equation:

\[ \mu = \frac{1}{N\rho} \]  

where \( \mu \) is the electron mobility, and \( \rho \) is the resistivity of the film. These values are also given in Table 5. Electron mobility changed only slightly with changes in deposition conditions in the range noted here. Hole mobilities were not determined. Other investigators have noted that hole mobilities of iron oxide tended to be about 1-2 orders of magnitude lower than electron mobilities, however (27-29). Electron mobilities for iron oxide are extremely low compared to the mobilities found for other semiconductors. Silicon, for example, has an electron mobility of 1900 cm\(^2\)/V-s (100). The low mobilities do not appear to be the result of structural defects, as the electron mobility values in Table 5 are comparable to those for single crystal iron oxide (48). Indeed, the electron mobility of iron oxide is known to vary from \( 10^{-1} \) to \( 10^{-5} \)
em\textsuperscript{2/V-s} \hspace{1em} (28,48). This suggests that the capacitance-voltage technique can be successfully utilized to determine the electrical characteristics of the thin films produced in this study. Unfortunately, the low mobilities of the iron oxide films may degrade their photoelectrochemical properties. Photogenerated electrons and holes must flow through the film to the counter electrode and the photoanode surface, respectively.

Equation [17] was utilized to calculate the depletion region thickness at 0.5 volt bias for these samples. This thickness varied from 230 to 1600 nm. This is greater than the optical absorption depth at most wavelengths. (See Sec. 6.1.) Therefore, it is unlikely that the solar energy conversion efficiency of these films will be limited by a thin depletion region.
Chapter 8

Photoelectrochemical Properties

8.1 Introduction

The photoelectrochemical properties of plasma deposited iron oxide thin films were measured directly using the equipment and procedures indicated in Sec. 2.9. Photoanode potential and incident radiation wavelength were used as independent variables in all tests, with the generated current being the dependent variable. The amount of product gas produced (hydrogen) was not measured directly. Thus, it was assumed that all current produced in the cell resulted in the electrolysis of water to hydrogen and oxygen, or 100% Faradaic efficiency. Previous work has shown that this assumption is reasonable (118).

With any solar energy conversion device, efficiency is of paramount concern. For photoelectrolysis, calculation of efficiency is a more complex procedure than with a conventional photovoltaic
device. This is because more energy input terms (incident radiation and external cell bias voltage) and output terms (hydrogen gas and electrical power) must be considered. In addition, different authors account for these terms in somewhat different manners. Should the energy output value of the hydrogen produced be considered the thermodynamic value or that which would result from its use in another process (i.e., direct combustion or a non-ideal fuel cell)? Should the overall efficiency be calculated relative to the thermodynamic potential, or the potential obtained when the overvoltage of the best available metal electrode is taken into consideration? Unfortunately, these questions have not been adequately considered in the literature. In most cases, only the quantum efficiency under particular operating conditions (i.e. anode potential) is reported. The quantum efficiency refers to the proportion of photons which result in charge transfer to the electrolyte and is calculated by this expression:

\[ \eta = \frac{I_{ph}}{I_{hv}} \]  

[24]

where \( \eta \) is the quantum efficiency, \( I_{ph} \) is the measured photocurrent, or the current under illumination minus that obtained in the dark, and \( I_{hv} \) is the photon flux at a particular photon energy, \( hv \). Correction for reflection using Fresnel's formula, Eqn. [13], was
made for all quantum efficiency calculations presented here. In all cases, $\eta$ is a strong function of wavelength and anode potential. Indeed, most photoelectrodes have very low quantum efficiencies when no external bias is present (35-42). Though quantum efficiency may be useful as an indicator of the properties of a particular photoanode material, it gives little information concerning overall energy conversion efficiency. Quantum efficiency data for photoanodes produced in this study will be presented throughout this chapter, and specific energy conversion efficiency information will be presented in Sec. 8.6.

Throughout this chapter, comparison of plasma deposited films will be made with other types of iron oxide photoanodes described in the literature. Quantum efficiency calculations allow this comparison to be made. However, it is also important to perform measurements against a photoanode reference. The reference chosen for this purpose was thermally oxidized iron foil. This is because the properties of thermally oxidized iron are well known: several reports of the photoelectrochemical properties of this material have appeared in the literature (53-55, 57-58). Also, thermally oxidized iron oxide appears to have properties similar to bulk polycrystalline iron oxide photoanodes (119). All thermally oxidized films were made by oxidation in a quartz tubular furnace at
500° C with O₂ at one atmosphere flowing at a rate of 10 sccm. Oxidation times were varied up to one hour, but films oxidized for 30 minutes were found to produce the highest photocurrents. The thermal films referred to hereafter were produced in this manner. As indicated in Sec. 2.2, thermally grown iron oxide films are a complex structure consisting of a thin outer layer of α-Fe₂O₃, and a thicker Fe₃O₄ inner layer. The outer layer would be responsible for photoelectrochemical activity. Using the data of Hussey et al. this outer α-Fe₂O₃ layer would be approximately 0.2 µm thick under the oxidation conditions used here (oxygen at 1 atm., 30 minutes oxidation time at 500° C) (4).

8.2 Current-Voltage Characteristics

All photoanodes were tested by measuring electrolysis current as a function of applied voltage, both with and without illumination. This is a particularly useful measurement, because it indicates how large an external bias, if any, is required to drive the electrolysis reaction. Results are reported relative to a reference electrode so that cathodic overpotential effects do not interfere with measurements of photoanode properties. The results of such a
test are presented in Fig. 60 for one photoanode under polychromatic light. This photoanode was made by plasma deposition at 50 W, 4 MHz RF. Deposition temperature was 500°C, and an O₂/Fe(CO)₅ ratio of 10 was used. The film was 0.26 μm thick. Unfortunately, no current is seen until an anode potential of approximately -0.5 volts vs. a saturated calomel electrode (SCE) is reached. In 1 M NaOH, the equilibrium hydrogen potential is -1.06 volts vs. SCE. Therefore, -0.5 volts vs. SCE would correspond to a bias voltage of approximately 0.56 volts relative to the equilibrium hydrogen potential. However, this is substantially lower than the thermodynamic requirement of 1.23 volts for electrolysis.

Application of greater bias results in ever increasing current density, until current passes even in the dark, at approximately 0.8 volts vs. SCE. An increase in photocurrent with voltage is expected for several reasons: 1) Increased bias results in greater band bending at the semiconductor surface, thus increasing the electron-hole pair separation energy. 2) Increased bias extends the width of the depletion region in the semiconductor surface. 3) Increased bias provides additional energy to overcome ohmic losses in solution and the semiconductor bulk. Dark current is generally thought to be due to tunneling of holes through the depletion region when electric fields are sufficiently high (14).
Fig. 60. Current-voltage characteristics of a plasma deposited iron oxide thin film photoanode. Deposition conditions were 500 °C at 50 W RF power, 4 MHz and $O_2/Fe(CO)_5 = 10$. The film was 0.26 μm thick. Scale below shows relationship between reference electrode (SCE) and equilibrium redox potentials.
Electron-hole pair separation comes about by an avalanche process in the dark at high bias.

By subtracting dark current from light current, one arrives at a photocurrent, or the amount of additional current due to irradiation of the photoanode surface. Figure 61 shows this quantity for the data in Fig. 60, compared to similar data taken for an iron oxide film produced by thermal oxidation at 500°C and P_{O2} = 1 atm. for 30 minutes. Using photocurrent, one arrives at a point of saturation, after which additional voltage does not result in increased photocurrent. This value is typically 0.6 to 0.9 volts vs. SCE. Saturation is reached when the applied bias is sufficient to extend the depletion region to its maximum value, and/or when the electric field at the surface is at its maximum value.

It is not surprising that an external bias is required to electrolyze water. The previously reported flatband potentials of iron oxide photoanodes are -0.6 to -0.8 volts vs. SCE in 1 M NaOH (31,48). The flatband potential is the most negative electron energy value possible for a photoanode. Thus, an external bias will always be required to electrolyze water for a photoanode with this flatband potential. Plasma deposited iron oxide films apparently have a flatband potential near that of the iron oxide photoanodes.
Fig. 61. Photocurrent-voltage characteristics of a plasma deposited photoanode compared to a thermally grown thin film photoanode. The plasma film corresponds to that in Fig. 60. The thermal film was produced by oxidation at 500°C for 30 minutes in 1 atm O₂.
While it is not surprising that a small bias is required to initiate photoelectrolysis, it is unfortunate and unexpected that photocurrent is such a small value at low biases, and only reaches the saturation value at bias voltages greater than 1.5 volts. This is not true of all systems. For example TiO$_2$ has a flatband potential of approximately 0.5 volts lower than Fe$_2$O$_3$, but reaches 90% saturation photocurrent with only about 0.5 volts bias (74). Single crystal and pressed pellets of Fe$_2$O$_3$ sometimes have higher photocurrents at low bias (48,49). Iron oxide thin films made by thermal oxidation and CVD have low photoresponse at low bias (3,14).

Because a number of materials used as photoanodes have shown this unfortunate behavior, the problem of low photocurrent at low bias has been addressed by various investigators. Reichman used a computer model to determine the effect of space charge recombination on photoanode current-voltage characteristics (120). The model showed that space charge region recombination can be a significant loss mechanism at low voltages, but decreases with higher voltage. This is due to minority carrier accumulation in the depletion region, which is highest at low bias.
Surface recombination may also degrade photocurrent at low bias voltages. Results presented in Chapter 7 strongly suggest the presence of surface states at the film/electrolyte interface. Such surface states are prime candidates for recombination (122). According to the optical properties presented in Chapter 6, most electron-hole pairs are produced near the film surface. At low bias, band bending at the surface will be small, and electrons may accumulate here. Holes may then recombine with the electrons via surface states.

The data presented thus far do not yield all the information on the energetics of the photoanode. Using monochromatic light, specific wavelengths can be selected to determine how wavelength variation affects photoresponse. Also, monochromatic light allows the calculation of quantum efficiency by Eqn. [24].

Figure 62 shows these results for the photoanode tested in the previous two figures. All three wavelengths used showed a photoresponse. However, only 363 and 437 nm are within the solar spectrum. Quantum efficiency values are rather low, but increase with anode potential. Even at very high bias, however, quantum efficiency is still less than 50%. Other materials, such as TiO₂, can have quantum efficiencies as high as 90% (74). Lower quantum efficiencies are typical for bulk polycrystalline and single crystal
Fig. 62. Photocurrent-voltage properties of a plasma deposited photoanode using monochromatic light of the indicated wavelength. Anode is the same as that in Fig. 60.
Fe₂O₃, however and specific comparisons will be made in Sec. 8.3.

8.3 Current-Wavelength Characteristics

Determination of the complete spectral response of a photoanode was made by scanning across the spectrum of the mercury arc lamp with the photoanode at a fixed potential. In this way, a continuous determination of quantum efficiency vs. wavelength was made. This information was then used to determine the bandgap and solar energy conversion potential for a photoanode.

Current-wavelength data at three anode potentials is presented in Fig. 63 for another plasma deposited photoanode. This anode was deposited at 500°C at 13.6 MHz, 10 W RF. An O₂/Fe(CO)₅ ratio of 10 was used here as well. The thickness of this film was 0.52 μm. As expected, quantum efficiencies are higher for higher anode potentials. Also, quantum efficiency drops off as wavelength approaches 560 nm (2.2 eV), which is the reported bandgap for bulk iron oxide (35,49). Unfortunately, this quantum efficiency decrease is gradual, over a large portion of the spectrum. This is unfortunate, as the longer wavelength region, 350-600 nm is the portion available from sunlight. The quantum efficiency response in
Fig. 63. Quantum efficiency of plasma deposited photoanode across the solar spectrum for three anodic potentials. Anode was made by deposition at 500 °C, 10 W RF power at 13.6 MHz and O$_2$/Fe(CO)$_5$ = 10. The film was 0.52 μm thick.
this region is probably due to the nature of the 2.2 eV electronic transition. Since this is an indirect transition, less absorption will take place at near-bandgap energies.

Current-wavelength response at lower anode potentials differs somewhat. Quantum efficiency peaks at about 360 nm, falling off at both shorter and longer wavelengths. Also, long wavelength response is particularly poor. The lower quantum efficiency at short wavelength may be due to the smaller electric fields at the semiconductor surface for the lower bias voltages. High energy photons will deliver their energy to electron/hole pairs at the surface. Energy greater than bandgap energy will be transferred to the electron. That energy is available for overcoming the potential energy barrier for electron/hole recombination at the semiconductor surface. Moreover, shorter wavelength light is absorbed nearer the solid-liquid interface. (See Chapter 5.) In the absence of strong band bending, electron/hole recombination is more likely with short wavelength illumination.

Poor response at long wavelengths with low anode potential may be the result of the thinner depletion region. (See Eqn. [17].) Only that light which is absorbed in the depletion region is likely to result in electron/hole pair separation. Thus, a thinner depletion region would allow for less light absorption in that region, and
less charge transfer to the electrolyte.

The quantum efficiencies seen here are surprisingly low. Materials other than iron oxide have higher quantum efficiencies. TiO$_2$, for example, has quantum efficiencies which approach 100% (74). Bulk iron oxide also has low quantum efficiency. Quinn et al. reported that single crystal iron oxide had a peak quantum efficiency of about 40%, but this result was not corrected for reflection (48). (Loss from reflection is about 20%). Kennedy and Frese have reported quantum efficiencies greater than 50% using pressed pellets of Fe$_2$O$_3$ (49). Quantum efficiencies of thermally oxidized or CVD Fe$_2$O$_3$ thin films have not been reported in the literature. Low quantum efficiency may be due to one of the recombination processes indicated in Sec. 8.2. Another possibility may be related to the electronic transitions involved in this process. According to the optical data in Chapter 6, over 70% of incident light is absorbed within a 90 nm film for visible wavelengths less than 500 nm. Yet quantum efficiencies are well under 50%. Thus, a large portion of light is absorbed by the iron oxide, but does not result in charge transfer to the solution. According to Kennedy and Frese, two distinct electronic transitions are involved: one at 1.8 eV, the other at 2.2 eV (31). Unfortunately, only the 2.2 eV transition results in charge transfer.
to the solution. According to this view, the 2.2 eV transition involves electron transfer from $O^{2-}$ to $Fe^{3+}$. The hole on the oxygen ion is then transferred to the electrolyte, and the electron is free to conduct current through the semiconductor. On the other hand, the 1.8 eV electronic transition is thought to involve electron transfer from one iron ion to another:

$$2Fe^{3+} \rightarrow Fe^{2+} (Fe^{3+} + e^-) + Fe^{4+} (Fe^{3+} + h^+)$$

[25]

In this case, the hole is at an energy level inappropriate for charge transfer to the solution, and charge trapping or recombination results. Thus, only a portion of absorbed light results in solution electrolysis.

Comparison of the current wavelength properties of this last plasma deposited photoanode and the thermally grown film indicated earlier is illustrated in Fig. 64. Correction for reflection was made, using the optical data in Chapter 6 for each type of film, and Eqn. [6]. As before, the plasma deposited photoanode has greater photoresponse. Interestingly, both short and long wavelength response are poor for the thermally grown film. Since the films are at identical potentials, the reasons cited previously for low anode potential response cannot apply. Structural differences between the films may be pertinent. In Sec. 5.3, micrographs of both films were
Fig. 64. Spectral response of a plasma deposited photoanode compared to a thermally grown film. Both anodes were at a potential of 0.6 V vs SCE. The plasma film is the same anode as that in Fig. 63, and the thermal film is that noted in Fig. 61.
presented. The thermal film consisted of smaller, more disordered crystallites. Such a structure may have inferior electrical properties, and charge trapping or electron/hole recombination could be significant. This problem may be particularly severe at the film surface, resulting in poorer short wavelength response. Poor long wavelength response may be due to either the thickness of the film (Thickness of the thermally grown films could not be accurately determined, but was approximately 0.2 μm. See Sec. 8.2.) or the film's structure. Films oxidized for longer times (up to 1 hour) did not show improved long wavelength performance. This difference in photoresponse for different film types will be discussed further in the next section.

8.4 Optimization of Photoelectrochemical Properties

Preceding sections indicated that changes in deposition conditions have large effects on the properties of the deposited films. Therefore, an attempt was made to optimize the properties of thin film photoanodes by judicious manipulation of those parameters. Parameters which were found to effect the properties of films were reactant feed composition, film thickness, deposition temperature, and RF power level. A total plasma pressure of 200 mtorr was used
for all depositions.

Reactant feed composition had a surprisingly large effect on photoelectrochemical properties of films. Figure 65 illustrates this effect for films deposited at 350°C and 50 W RF power. Here, photocurrent refers to saturation photocurrent for each anode, using polychromatic light. Oxygen to iron carbonyl feed ratios less than 5 produced anodes which showed no photoresponse at all. Increasing that ratio to 6 resulted in working photoanodes. Photoanodic behavior improved with increasing $O_2/Fe(CO)_5$ ratio, until a value of about 10 was reached. Therefore, the oxygen to iron carbonyl feed ratio was kept at 10 for photoanode production in the remainder of this study.

That feed content affects photoanode behavior is expected, but not to this large extent. The electrical data presented in Chapter 7 indicated that resistivity increases with increasing oxygen feed content. But this effect appeared to saturate at approximately equimolar mixtures of $O_2$ and $Fe(CO)_5$. Likewise, the data presented on film chemical composition in Chapter 4 revealed little compositional difference between films deposited at $O_2/Fe(CO)_5$ ratios of 1 and 10. Nevertheless, film chemical composition may have been affected over a wider range of feed contents to an extent
Fig. 65. Saturation photocurrent of plasma deposited photoanodes vs. the ratio of oxygen to iron carbonyl used for their deposition. These films were made at 350°C, 50 W RF power at 4 MHz, $O_2/Fe(CO)_5 = 10$. 

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too small to be detected by the methods discussed in Chapter 4. It must be realized that small deviations from stoichiometry could greatly change the photoelectrochemical properties of the films. Indeed, Shinar et al. showed that adding only 0.01% $\text{Fe}_3\text{O}_4$ to pressed pellets of $\alpha$-$\text{Fe}_2\text{O}_3$ drastically changed the photoresponse of these photoanodes (52). The actinometry data presented in Chapter 3 clearly indicated that the plasma concentration of CO, O atoms, Fe atoms and FeO all changed with feed content over this range. This may have resulted in small changes in film composition. For example, the ratio of FeO to Fe in the plasma decreased drastically at approximately 0 to 0.15 mole fraction iron carbonyl. (See Fig. 33.) This is an $\text{O}_2/\text{Fe( CO)}_5$ ratio of about 5.7. If this additional gas phase iron condensed on the film surface, three things may have happen: 1) It may have become part of the film, resulting in metallic iron in the iron oxide film. 2) It may have oxidized at the surface. 3) It may have adsorbed CO molecules from the gas phase. Either 1) or 3) would have affected the electrical and photoelectrochemical properties of the film. Metallic iron would be capable of donating electrons to the $\text{Fe}_2\text{O}_3$ lattice, thus increasing conductivity. But large changes in conductivity were not observed in this range of feed contents. On the other hand, the presence of metallic iron would aid the incorporation of CO into the growing
film, perhaps several CO molecules per Fe atom (96). The spectral data of Chapter 3 showed large amounts of CO in the plasma during deposition. Figure 29 shows how CO concentration increases with increasing iron carbonyl feed contents. Once part of the film, CO may form carbon suboxide. Carbon suboxide is known to be a semiconductor, though its type has not been determined (121). It is known to have a bandgap of 1.8 eV. If p-type, it may donate holes to the lattice which may recombine with electrons in the semiconductor bulk or depletion region. Carbon impurities, in many molecular forms, may act as trapping sites for charge carriers (123). Interestingly, oxygen can sometimes mitigate the adverse effects of carbon impurities (124). Thus, the effect of feed gas content on film photoelectrochemical properties may be due to the CO content of the plasma gas during deposition.

The effect of film thickness had a much greater effect on photoanode performance than might be expected. Figure 66 shows current-voltage curves for 5 photoanodes of different thicknesses. These films were all deposited at 500°C, 50 W RF power at 4 MHz, using an O₂/Fe(CO)₅ feed ratio of 10. In general, the thin films (< 0.5 µm) had superior performance. This would suggest that films thicker than 0.5 µm were thicker than the maximum space charge layer thickness of the film. Any additional thickness would act as a
Fig. 66. Photocurrent-voltage characteristics of films of different thicknesses. These films were deposited at 500°C, 50 W RF power at 4 MHz, with O₂/Fe(CO)₅ = 10.
resistor in series with the photoanode, thus reducing the photoelectrolysis current. But from the data presented in Chapter 7, this is not the case. The maximum depletion region thickness for films deposited under these conditions would be about 1 μm. Apparently, then, these films perform better when the total thickness is significantly less than what would be the maximum depletion region thickness.

This may indicate that depletion layer recombination is indeed a serious problem. If most light is absorbed near the surface of the film (as the data of Fig. 55 indicates) then a thicker depletion region would not enhance the photoresponse. On the other hand, a thicker depletion region would add distance through which electrons must travel to complete the circuit. This extra distance would provide the opportunity for electron-hole pair recombination, since close to intrinsic conditions exist in the depletion region (i.e., equal numbers of electrons and holes).

Deposition temperature also affected photoanode performance, as Fig. 67 illustrates. Here, films were deposited at 50 watts RF power. The film deposited at 500°C clearly had superior performance, and this performance deteriorated with decreasing deposition temperature. This result is certainly reasonable when compared to the structural data of Chapter 5. At the highest
Fig. 67. Effect of deposition temperature on photocurrent-voltage characteristics of plasma deposited films. These films were made at 50 W RF power, 4 MHz, and $O_2/Fe(CO)_5 = 10$. Thicknesses of the films made at 500°, 450°, 400°, and 350° C were 0.26, 0.4, 0.36 and 0.46 μm, respectively.
temperatures, films with larger, more oriented crystallites are produced. These larger crystallites result in superior photoelectrochemical properties. This is probably due to improved electron conduction through the semiconductor. Table 5, Chapter 7 indicates that electron mobility increases with increasing temperature. This suggests that current losses through electron trapping or recombination is a less significant problem at higher deposition temperatures.

Improvement of photoelectrochemical properties with increasing deposition temperature may also be due to chemical effects. Incorporation of carbon in the films almost certainly occurred, though it was difficult to detect using the analytical techniques mentioned in Chapter 4. The trends of the data, though, indicated that increasing deposition temperature reduced the carbon content of the films. As mentioned previously, carbon may adversely affect the electrical properties of the film.

Plasma power level also had an effect on the photoelectrochemical properties of the films. Figure 68 is a current-wavelength plot of three films plasma deposited at 500°C using 13.6 MHz RF, but at the power levels indicated. An O₂/Fe(CO)₅ ratio of 10 was used to produce these films as well. Across the spectrum, the 10 watt film
Fig. 68. Effect of RF power level on the spectral response of plasma deposited photoanodes. All films were deposited at 500°C, 13.6 MHz and O₂/Fe(CO)₅ = 10. Films made at 10 W, 25 W, and 50 W were 0.52, 0.51 and 0.43 μm thick, respectively.
has superior quantum efficiencies, though the difference is not
great. This result qualitatively agrees with data obtained for
plasma deposited TiO₂ (74). Actinometry results also indicate that
plasma gas CO contents are higher at higher RF power levels. (See
Fig. 29.) As noted previously, high plasma CO content is correlated
with degraded photoelectrochemical properties. On the other hand,
the structural and electrical properties of the films seem to
improve with increasing RF power from 10 to 50 watts. Since changes
in quantum efficiency are small, competing effects may be involved.

In Figs. 61 and 64, the photoresponse of a plasma deposited film
was compared to that for an iron oxide film made by thermal
oxidation of iron. It was clear that the plasma film outperformed
the thermal film. Other iron oxide films were made by different
deposition techniques for comparison and to ascertain possible
reasons for the superior performance of the plasma films. Films
were made by the indirect plasma deposition technique described in
Sec. 2.2. Films were also made by a chemical vapor deposition
technique (CVD): deposition was accomplished by flowing reactant
gases through the deposition chamber at the usual flow rates without
any plasma at all. The same substrates were used as before (iron
and glass), and substrate temperature was 500°C. Deposition rate
was approximately half that seen when a plasma was used.
All deposited films outperformed the thermally grown film previously described. Figure 69 illustrates the current-wavelength properties at 0.6 volts vs. SCE for all four types of films considered. The best plasma deposited film was considerably more efficient at both short and long wavelengths than films made by any other technique. Indeed, the indirect plasma film had performance very similar to that seen for the film deposited without a plasma. These differences may be related to film structure. The surfaces of the four photoanodes of Fig. 69 were shown in micrographs previously, Fig. 51a–d. The indirect plasma film seemed to have more in common with the CVD film in terms of structure. The short and long wavelength response of both films was in fact comparable.

Two differences were noted between the plasma deposited films and the CVD films. The CVD films had resistivities almost an order of magnitude higher than the plasma deposited films ($2 \times 10^5$ ohm-cm). This may indicate smaller carrier concentrations, or more current degradation via defects. Smaller carrier concentrations would lead to a thicker depletion region for a given anode potential. More space charge region recombination would result. Structurally, the CVD films consisted of long, whisker-like crystallites. Conversely, the plasma films contained a more regular, less porous structure. The difference in performance may be related to these features. The
Fig. 69. Spectral response of four types of iron oxide thin film photoanodes: (o) Plasma deposited at 500° C, 10 W RF power at 13.6 MHz and O_2/Fe(CO)_5 = 10. The film was 0.52 μm thick. (x) CVD at 500° C, O_2/Fe(CO)_5 = 10. This film was 0.23 μm thick. (*) Indirect plasma at 500° C. Film thickness was 0.58 μm. (+) Thermally grown.
long, whisker-like crystallites in the CVD and indirect plasma films were not present in the plasma film, due to constant ion bombardment on the film surface during deposition. This ion bombardment may stabilize the surface toward the formation of surface states, hence limiting surface recombination. At longer wavelengths, the more regular crystallite structure may have aided photon absorption, resulting in higher quantum efficiency.

High porosity generally aids interfacial chemical reactions by providing additional surface area for charge transfer. In photoelectrolysis, however, this is not the case. Only illuminated surface area aids photoelectrochemical charge transfer. On the other hand, porosity may degrade photocell performance by exposing the metal substrate to the electrolyte (42). This exposure may drain off current from the desired reaction, or may damage the anode through corrosion. High porosity would also be troublesome if the grain boundaries in the film were exposed to the electrolyte. Indeed, high porosity also results in more grain boundaries and possible trapping or recombination sites (42). Considering the structures in Fig. 51, then, it should come as no surprise that the plasma film is a superior photoanode.

The superior photoresponse of the plasma film may also be related to film chemical composition. All three types of films had
identical stoichiometries according to elemental analysis. But the Auger profiles in Fig. 38 point out the difference in surface structure. The plasma film had an oxygen excess at the surface, while the indirect plasma film showed no such surface feature. Perhaps this excess oxygen served to stabilize unsatisfied iron bonds at the surface, ultimately reducing the density of surface sites which form upon exposure to atmosphere or the electrolyte of the photoelectrochemical cell.

Iron oxide CVD photoanodes made by Hardee and Bard were reported to be quite smooth (47). However, these films were sintered at 1200\degree C. Apparently, the deposition temperatures used here were not sufficient to produce this type of structure. On the other hand, the plasma film has a much smoother appearance even when deposited at only 500\degree C. This is probably due to ion bombardment of the film's surface during deposition.

The difference between the deposited films and the thermally grown film may also be related to structure. From the micrographs of Fig. 51, it is clear that the thermally grown film consisted of small, disordered crystallites. The reflectance data in Fig. 52 are consistent with this observation, since smaller crystals would tend to be more reflective at longer wavelengths. Such a film may have
degraded electron transport properties due to this structure. Smaller crystallites would possess more grain boundaries, which may serve as recombination sites for electron/hole pairs.

Another possibility may be related to carrier concentrations in the thermal films. Wilhelm et al. found that thermally oxidized iron oxide films had carrier concentrations approximately 1 to 2 orders of magnitude larger than those reported in Chapter 7 (54). This value of carrier concentration would reduce the space charge region thickness to less than 100 nm. This is of the same order as the optical absorption depth. It is possible, then, that thermally oxidized films are limited by too thin a depletion region at longer wavelengths. This would explain the particularly poor long wavelength quantum efficiency for the thermally oxidized film.

8.5 Backside Illumination Effects

Surface recombination was mentioned as a likely candidate for the low quantum efficiencies found with plasma deposited iron oxide photoanodes. Therefore, an experiment was undertaken to determine the relative significance of surface recombination for these films. Surface recombination is likely because most light is absorbed very
near the semiconductor-electrolyte interface. If surface states are present at mid-bandgap energy levels, electrons and holes may recombine there. If the electron/hole pairs were somehow generated elsewhere in the film, away from the surface, surface recombination would be less of a problem.

Figure 70 illustrates one possibility. This technique was used originally by Mollers in an investigation of TiO$_2$ photoanodes (108). If the iron oxide film were deposited on a transparent, conductive substrate, SnO$_2$ for example, the film could be illuminated from the back side. It is unlikely that similar surface states would be present at the SnO$_2$/Fe$_2$O$_3$ interface. Electron/hole recombination would not take place, and higher quantum efficiencies would result.

A film was deposited on SnO$_2$ covered glass as described in Sec. 2.8. The film was made under the usual conditions (500$^\circ$C, 10 W RF, 200 mtorr and O$_2$/Fe(CO)$_5$ = 10). The thickness of the film was 0.76 μm. The resulting spectral response seen with this film is illustrated in Fig. 71. It is clear that backside illumination yields stronger photoresponse over part of the spectrum. Short wavelength response increases rapidly from 335 to 360 nm for backside illumination. But SnO$_2$ is a semiconductor, with a bandgap
Fig. 70. Diagram showing the theoretical result of illuminating a film through both front and back surfaces.
Fig. 71. Spectral response of plasma deposited thin film to illumination from the front and back sides. Deposition conditions were 500°C, 10 W RF power at 13.6 MHz and \( \frac{O_2}{Fe(CO)_{5}} = 10 \). The film was 0.76 \( \mu \text{m} \) thick.
of 3.5 eV (350 nm) (35). This is the absorption edge of SnO₂, and this portion of the spectrum is not reaching the iron oxide film. From 360 to 450 nm, backside illumination gives photoresponse up to 3 times greater than illumination from the front. Apparently, surface recombination is particularly significant in this region. But for longer wavelength light, > 500 nm, illumination from both front and back give approximately the same result. This is the region where absorption depth begins to increase. (See Fig. 55.) This light is absorbed further from the surface, so surface recombination is not a significant problem here. Therefore, for wavelengths less than 500 nm, surface recombination is an important factor limiting the quantum efficiency of iron oxide thin film photoanodes. The significance of surface recombination has not been mentioned in the literature for iron oxide photoanodes, but is known to be a significant factor limiting the quantum efficiency of other photoanodes under short wavelength illumination (74,125).

Surface treatment was investigated as a means to improve quantum efficiency. Treatment of the photoanode surface may poison the anode toward surface recombination. Kennedy and Frese found that dipping poor photoanodes in KI improved their performance, but that the best photoanodes were not improved (50). Williams found that chlorine treatments improved the properties of TiO₂ photoanodes.
(74). In this work, four surface treatments were investigated:

Photoanodes were dipped in KI, NaBr and NaCl solutions (all 1 M). In addition, one anode was etched in HCl (10%) for 30 seconds to remove surface layers. None of these treatments showed a significant improvement in quantum efficiency. The film which was exposed to NaBr was seriously damaged. Sodium citrate (1 M) was used as an electrolyte for comparison with NaOH. The sodium citrate solution did not show a substantial improvement in photocurrent over NaOH. An onset potential of approximately 0.1 volt lower than that noted for 1 M NaOH was observed. A lower onset potential is expected due to a shift in redox couple potential with changing pH. Sodium citrate displays a pH of 9 at 1 M concentration. The Nernst equation predicts a change in flatband potential of 0.3 volts, however (for 0.059V/pH change).

8.6 Efficiency for Photoelectrochemical Energy Conversion

Calculation of efficiency for a liquid junction solar cell is not as straightforward as that for a conventional photovoltaic device. This is due to the multiple energy inputs and outputs, as well as the method used to determine the energy content of those inputs and outputs. As mentioned in Sec. 7.1, data are usually presented in
terms of quantum efficiency. But quantum efficiency only indicates the fraction of photons converted into electrons, and does not directly consider external bias on the system.

No universally accepted energy balance around an photoelectrochemical cell exists. Parkinson, Eror and Scaif have all proposed complete energy balance methods of considering solar conversion efficiency (126, 127 and 41 respectively). Parkinson's method can be expressed as:

\[ a = \frac{(E-V_B)I(V_B)/P_{hv}}{100} \]  \[26\]

where \( a \) is the energy conversion efficiency in percent, \( E \) the energy equivalent of hydrogen produced (1.23 volts), \( V_B \) the bias voltage, \( I \) the current in amps between the photoelectrode and the counter electrode in the external circuit and \( P_{hv} \), the light flux power at a particular wavelength. Moreover,

\[ \frac{I}{P_{hv}} = \eta/hv \]  \[27\]

where \( \eta \) is the quantum efficiency as before and \( hv \) the photon energy in electron volts. Equation [26] then becomes:

\[ a = \left[ \frac{(1.23 - V_B)\eta/hv}{100} \right] \]  \[28\]
This efficiency calculation method includes external bias effects and can be integrated across the solar spectrum to estimate the total solar power output if complete efficiency-wavelength data were obtained. On the other hand, no inefficiencies involved with the end use of hydrogen gas are considered.

Quantum efficiency-voltage data taken using monochromatic light at three wavelengths is presented in Fig. 72. This photoanode, which was deposited at 500°C, 10 W RF power, 13.6 MHz, $O_2/Fe(CO)_5 = 10$, and pressure = 200 mtorr, showed performance superior to all others produced in this study. The thickness of this film was 0.52 µm. The voltage in this case is bias voltage, rather than anode potential. Thus, these data can be used directly with Eqn. [27] to calculate an overall energy conversion efficiency.

The results of this calculation are displayed in Fig. 73. As expected, efficiencies are much lower than the quantum efficiencies seen in Fig. 72. Indeed, efficiencies are much less than those seen for other types of photovoltaic devices. It is also unfortunate that the longest wavelength curve (426 nm) is also the wavelength of lowest efficiency, since most of the solar spectrum is in this region.
Fig. 72. Quantum efficiency at the indicated wavelength and bias voltage. Film was deposited at 500°C, 10 W RF power at 13.6 MHz and $O_2/Fe(CO)_5 = 10$. The film was 0.52 μm thick.
Fig. 73. Photoconversion efficiency and bias voltage for light at the indicated wavelength. Same anode as in Fig. 72.
It is interesting that an optimum operating voltage is apparent in this data. This is due to competing effects. At low bias voltage, the net energy yield factor, \((1.23 - V_B)\), is high, but quantum efficiency is low. As voltage increases, quantum efficiency increases, but \((1.23 - V_B)\) decreases. The optimum operating voltage is about 0.7-0.8 volts.

At 0.75 volts, the photoanode is contributing approximately 0.5 V to photodecomposition. This is a surprisingly low value, especially considering that the bandgap energy of iron oxide is 2.2 eV. Only a portion of this energy seems to be available for photodecomposition. Of course some energy will be needed to provide band bending at the semiconductor surface for efficient charge transfer. But the greatest loss is probably due to differences in energy levels between the \(\text{Fe}_2\text{O}_3\) valence band and the \(\text{O}_2/\text{H}_2\text{O}\) redox energy level in solution. According to Kennedy and Frese, this energy difference is about 1 volt for bulk polycrystalline iron oxide (31). The energy level of the valence band at the surface is fixed by the properties of the semiconductor and the type of electrolyte used. If plasma deposited iron oxide films have similar properties, then only 1.2 volts would be left for photodecomposition of water. However, no current at all is seen until a bias voltage of 0.5 volts is present, and of that about 0.4 volts is required for
band bending. The difference in energy level between the Fermi energy and the conduction band energy (perhaps 0.2 V) also must be considered, since the Fermi energy, not the conduction band energy, is the electron energy level for charge transfer from the metal counterelectrode. It is therefore reasonable that such bias levels are necessary to initiate photoelectrolysis. It is unfortunate, however, that quantum efficiencies at these bias levels are rather low.

A complete energy conversion efficiency can be determined by integrating the single wavelength efficiencies calculated by Eqn. [28] over the complete visible spectrum. Such a calculation would consist of this expression:

\[ \varepsilon' = \frac{\int P(\lambda) \varepsilon(\lambda) \, d\lambda}{\int P(\lambda) \, d\lambda} \]  

[29]

where \( P(\lambda) \) is solar power at a particular wavelength, \( \lambda \), in \( \text{mW/cm}^2/\mu\text{m} \) from Fig. 4, and \( \varepsilon' \) is the total solar conversion efficiency. Data used for this calculation are displayed in Fig. 74, in the form of a solar efficiency-wavelength plot for the photoanode being discussed at 0.8 volts bias. Using Simpson's rule for a numerical integration of Eqn. [29] and integrating from 300 to
Fig. 74. Photoconversion efficiency across the visible spectrum at 0.8 volts bias. Same anode as in Fig. 72.
700 nm, a solar power production of 3.16 W/m$^2$ was determined. (This is the numerator of Eqn. [29].) This results in a total solar energy conversion efficiency of 0.6%. (The calculated solar power, the denominator of Eqn. [28], was 524 W/m$^2$). Clearly, this is not an optimistic result.

As indicated earlier, efficiency calculations of this sort are generally missing from the literature. The only efficiency calculations for iron oxide found were for a p/n cell, using Fe$_2$O$_3$ for both photoelectrodes. An efficiency of 0.05% was calculated here, a figure considerably lower than the 0.6% obtained in this work (34). It must be remembered, however, that comparison of a Schottky cell with a p/n cell is somewhat misleading. Each type of cell has its own advantages and inefficiencies. (See Sec. 1.4.)
Chapter 9

Conclusions

9.1 Film Deposition

Iron oxide films were deposited under a variety of conditions. Films were made at temperatures ranging from ambient to 500°C, and 10-50 W RF power and 4 and 13.6 MHz. Various ratios of $O_2/Fe(CO)_5$ were used. Deposition rate varied with changes in all deposition parameters, from 60 to 200 nm/minute. OES was used to investigate deposition chemistry. Gas phase species identified in the plasma included Fe, FeO, CO and oxygen atoms. It is likely that iron carbonyl decomposed in the glow discharge, and iron atoms oxidized before condensation occurred on the substrate surface.
9.2 Film Composition

Films were composed mainly of oxygen and iron, with small fractions of carbon (0-20%). At temperatures above 350°C, films had stoichiometries corresponding to Fe₂O₃, with a trace amount of carbon possible.

9.3 Film Structure

Thin film density ranged from 2.5 to 5 g/cm³, depending on deposition conditions. Various phases were identified: α-Fe, Fe₃O₄, FeO, Fe₂O₃ (both α and γ). Crystallite size and orientation varied with deposition conditions and substrate material.

9.4 Optical Properties

Films deposited on quartz had optical properties similar to those reported for bulk iron oxide. Films deposited on iron foil were
less reflective than those deposited on quartz. A thermally grown film was more reflective than the deposited film. The optical absorption depth for wavelengths less than 500 nm was 50 to 100 nm.

9.5 Electrical Properties

Film resistivity varied over 10 orders of magnitude, depending on the amount of $O_2$ used during reaction. High frequency C-V measurements allowed calculation of carrier concentration and electron mobility. Carrier concentrations were approximately $10^{16}/cm^3$ for films which showed photoelectrochemical activity. This would result in a depletion layer thickness of about 1000 nm at 0.5 volts bias.

9.6 Photoelectrochemical Properties

The photoelectrochemical properties of plasma deposited iron oxide thin films were similar to those found for bulk polycrystalline and single crystal iron oxide. A photocurrent onset potential of about -0.5 volts vs. SCE was noted in 1 M NaOH. Photocurrents were low at
low bias. Quantum efficiency was approximately 45% for the best anode at 0.6 V vs. SCE for wavelengths less than 300 nm. The best photoanodes were produced by plasma deposition at 500°C, 10 W RF power at 13.6 MHz and a feed gas content of 10:1 O₂ to Fe(CO)₅. Films 0.5 μm thick performed best. Plasma deposited films were superior to films produced by the following alternatives: thermal oxidation, chemical vapor deposition without a plasma, and indirect plasma deposition. Using Parkinson's technique for calculating solar conversion efficiency a theoretical solar energy conversion efficiency of 0.6% was obtained. Films were also deposited on transparent substrates. Illumination from the backside resulted in higher quantum efficiencies than by front side illumination. Both surface recombination and space charge region recombination may be responsible for the low efficiencies seen for iron oxide. Electronic transitions which utilize photons but do not contribute to photocurrent may also limit efficiency.

9.7 Recommendations

Plasma deposition is a useful technique for making thin film photoanodes. Thin films of stoichiometric iron oxide can be made.
possessing a high degree of crystallinity and electrical properties very near those of single crystal iron oxide. The flexibility of plasma deposition makes it possible to optimize the properties of the photoanode. Iron oxide is not the best material for a thin film photoanode, however. Quantum efficiencies are low compared to other materials, and the flatband potential is not appropriate to the redox couples involved in photoelectrolysis.
Chapter 10

References


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Appendix

List of Symbols

- \( A \) Absorptance
- \( A \) Substrate area, cm\(^2\)
- \( C_i \) Insulator capacitance, pF/cm\(^2\)
- \( D \) Optical density
- \( e \) Electronic charge, C
- \( e \) Electron concentration, cm\(^{-3}\)
- \( I_{hv} \) Photon flux, mA/cm\(^2\)
- \( I_{ph} \) Photocurrent, mA/cm\(^2\)
- \( I_x \) Emission intensity
- \( k \) Boltzmann's constant
- \( k_x \) Proportionality constant
- \( n \) Refractive index
- \( n_x \) Gas phase concentration of emitting species, cm\(^3\)
- \( P_{hv} \) Light power flux, W/cm\(^2\)
- \( R \) Reflectance
- \( R \) Deposition rate, mm/min
- \( R' \) Deposition rate, mg/min/cm\(^2\)
T Transmittance
T Temperature, °K
t Deposition time, minutes
t_f Film thickness, nm
V_{fb} Flatband potential, volts
W Depletion layer thickness, nm
w Film weight, mg
X Mole fraction iron carbonyl
x Film thickness, cm
α Linear absorption coefficient, cm⁻¹
ε Energy conversion efficiency
ε' Total solar conversion efficiency
ε_I Insulator dielectric constant
ε₀ Permittivity of free space
ε_s Iron oxide semiconductor dielectric constant
η Quantum efficiency
η_x Glow discharge excitation efficiency
λ Debye length, nm
λ Photon wavelength, nm
μ Electron mobility, cm²/V·s
ρ Resistivity, ohm·cm
ψ_s Semiconductor surface potential, volts
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