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SENSITIZED PHOTOELECTROLYSIS OF WATER WITH SUNLIGHT

Final Report for June 1, 1977—December 31, 1978

By
Amal K. Ghosh
H. Paul Maruska

December 1978

Work Performed Under Contract No. EG-77-C-02-4271

Exxon Research & Engineering Company
Government Research Laboratories
Linden, New Jersey

U.S. Department of Energy

Solar Energy

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ABSTRACT

A study was made of solar driven water photoelectrolysis cells employing semiconductor electrodes. An extensive review of the literature was undertaken, and the three major problem areas for these devices were identified: corrosion, poor sunlight absorption, and external bias requirement. Although many semiconductors had been tested, none had proven free of all three defects. Two approaches were thus followed for the experimental studies: impurity sensitization of wide band gap stable oxides, and heterostructure formation between unstable sunlight absorbers and corrosion resistant oxides. Water decomposition was achieved with visible light excitation of Cr-doped TiO_2 . Transport properties were studied for TiO_2 and SrTiO_3 electrodes doped with V, Cr, Mn, Fe, Co and Ni. The correlation between bias requirement and electron affinity of oxides was identified. Performance of heterostructure electrodes was shown to be limited either by pin hole problems or by potential barriers between the valence bands.

1. INTRODUCTION

There have been a considerable number of studies in the last few years aimed at decomposing water to produce the valuable chemical specie hydrogen, with the energy for the process supplied by sunlight. Since water is transparent to the solar spectrum, it has been necessary to identify materials that are capable of absorbing the incident solar radiation and transferring the energy to the water in order to effect decomposition. Investigations have now been made of more than 50 different organic and inorganic materials which have appeared promising for use as sunlight absorbers in water photoelectrolysis cells. An important class of materials that have received widespread attention for this process are solid-state semiconductor electrodes. Such materials can be considered to be catalysts, because they do not undergo any chemical changes during this process, but rather present a surface at which the solar energy can drive the water-splitting reactions. Thus, they only serve to increase the rate of the reaction.

All of the semiconductor materials that have been tested in various laboratories suffer from one or more of three problems, viz., (1) corrosion, (2) poor sunlight absorption, (3) external bias requirement. These problems have limited conversion efficiencies for water photoelectrolysis cells to 1% or less. The major problem plaguing most semiconductors when they are illuminated in an aqueous environment is corrosion. For such materials, it has been concluded that it is thermodynamically more favorable to decompose the electrode than to decompose H_2O . In fact, the only semiconductors which have proven to be stable in this environment are several wide band gap oxides, most notably TiO_2 , $SrTiO_3$, $BaTiO_3$, and WO_3 .

However, these oxides exhibit a second problem, because all of them have band gaps greater than 3 eV and can only absorb light of wavelengths shorter than 400 nm. Thus, under the best of circumstances, they absorb less than 10% of the incident solar radiant energy. Finally, there are also several other stable oxide materials with smaller band gaps, such as Fe_2O_3 , HgTa_2O_7 and HgNb_2O_7 , which are good sunlight absorbers, but suffer from a third problem. These oxides have large electron affinities, so that their conduction bands are located at potentials significantly more positive than the potential of the hydrogen redox reaction. Consequently, a large electrical bias energy must be supplied externally, in addition to the optical energy, in order to run the water splitting reaction with these electrodes. This external bias is a waste of energy, and in cases where the electrical bias exceeds 1.2V, the efficiency of the photoelectrolysis cell is by definition zero, since 1.2V will already decompose water at non-illuminated metal electrodes.

Clearly, some new approaches to this problem are required. The goal of the present study has been to identify new combinations of materials which are suitable for use as sunlight absorbing electrodes in water decomposition cells. It is required that in addition to being sensitive to a large proportion of the incident solar radiation, such materials also remain stable during operation and function with a minimum of external bias. The specific research objectives have been:

- (1) to identify combinations of known stable oxide semiconductor hosts with novel transition metal oxide substituents which give superior performance (improved sunlight absorption and minimum bias requirements) as electrodes in photoelectrolysis cells;

- (2) to investigate various combinations of cladded structures (heterostructures) which show promise as photosensitive electrodes, in terms of stability against photocorrosion and degree of conversion of water to hydrogen.

Our statement of work for this project has comprised the following tasks:

Task A. Literature Review.

Task B. Preparation, Testing and Evaluation of Doped Electrodes.

Task C. Preparation, Testing and Evaluation of Heterostructure Electrodes.

Task D. Preparation of Reports.

It was judged that the best way to tackle the problems inherent in water photoelectrolysis cells would be to start with the materials which have already been shown to give the best response, and to alter the properties of these materials in particular ways designed to improve their response. The two materials which have shown the best characteristics as photoelectrolysis electrodes are TiO_2 and SrTiO_3 . They are both stable, and require little or no biasing to generate hydrogen. Copious amounts of hydrogen and oxygen can be generated from water when these materials are illuminated with a strong uv source, such as Mercury Lamp, but not from a weak uv source like sunlight. The best sunlight conversion efficiency that we have measured is 1.3% for TiO_2 , and 0.25% for SrTiO_3 (1). No other semiconductor has proven even this good. Our aim, therefore, is to extend the absorption of TiO_2 and SrTiO_3 into the visible portion of the spectrum, the region of strongest solar insulation, by adding transition metal oxide substituents and by forming heterostructures with good sunlight absorbers.

This report has been divided into three major sections, covering a review of the literature, impurity sensitization techniques, and hetero-structure devices. Each section is self-contained and has been prepared with its own set of references and figures. A summary of the work is given as a final section.

Reference

1. Amal K. Ghosh and H. Paul Maruska, J. Electrochem. Soc., 124, 1516 (1977).

2. LITERATURE REVIEW: PHOTOCATALYTIC DECOMPOSITION OF
WATER AT SEMICONDUCTOR ELECTRODES

A paper reviewing all of the work which has been done on water photoelectrolysis, from 1839 up through 1977, has been prepared. The literature on photoelectrolysis was thoroughly searched (by computer) and 119 references are included with the manuscript. Critical interpretations of the important concepts of this area of investigation are given in the paper. The currently available theory of semiconductor-liquid junctions is described. Techniques for improving the response of cells are discussed, and the expected maximum sunlight conversion efficiency (of sunlight to hydrogen) for this system is calculated.

This complete review of water photoelectrolysis has provided us with a strong background of the field. It has been used as a basis for the experimental portions of our investigations. This section of the work has been published in the Journal of Solar Energy, Volume 20, pages 443-458 (1978).

2. PHOTOCATALYTIC DECOMPOSITION OF WATER AT SEMICONDUCTOR ELECTRODES

2.1 Introduction

The current energy crises has created a tremendous interest in discovering new sources of fuel to increase our dwindling resources. In the following article, we shall review one aspect of this search, concentrating on the specific chemical reaction which involves the sensitized photodecomposition of water to form oxygen and hydrogen, an extremely important fuel:

The system employs an abundant raw material (water) and produces a fuel (hydrogen) which may be readily stored and shipped. This fuel can be used not only to provide heat for environmental control and cooking, but also to conveniently produce electrical power efficiently, cleanly, and cheaply, in a fuel cell or engine generator. In addition, the hydrogen can be used as the basic raw material for producing other clean fuels and valuable chemicals from various sources such as coal and shale.

In 1974, Paleocrassas (1) wrote a review article on "Photocatalytic Hydrogen Production." Since that time there has been a tremendous explosion of information and work on this subject. The present article will attempt to avoid overlapping with the earlier report. The discussion will

be limited to the photosensitized oxidation of water at semiconductor electrodes. Therefore it will not include photoelectrochemical solar cells or photogalvanic devices (where no net chemical products are created but power is drawn from the cell in the external circuit).

2. The Decomposition of Water

The outstanding natural example of the sensitized photodecomposition of water is photosynthesis. The sensitizer in this case, chlorophyll, absorbs sunlight and catalyzes the decomposition of water. The oxygen from the decomposition is released to the atmosphere while the hydrogen is used to reduce carbon dioxide to carbohydrates. The efficiency of photosynthesis, however, is quite low (highest about 1%) and produce a fuel (carbohydrates) most suitable for use only as food.

The direct formation of hydrogen by photolysis of water has been investigated by many workers. The energy required to photoexcite water directly to the triplet state (which in turn will decompose to hydrogen and oxygen) has been found to be in the region of 190-310 nm (6.5-4.0 eV).⁽²⁻⁷⁾ Unfortunately, this is well outside most of the solar energy spectrum available on earth (350-1100 nm or 3.5-1.1 eV). However, water may be decomposed to hydrogen and oxygen electrochemically (heterogeneously) with a potential difference of only about 1.23 volts. This potential difference is equivalent to a 1000 nm photon.⁽¹⁾ Therefore, if light of this wavelength could be used effectively in an electrochemical cell, it should be theoretically possible to decompose a molecule of water using just two of these photons. Actually, in any practical electrolysis cell, there are over-potentials and other losses, which will be discussed in more detail later.

The high energy required for direct photolysis is the result of the formation of radical intermediates such as H and OH. It is necessary to pass over a high potential barrier, but the energy difference between the initial (H_2O) and final (H_2 , O_2) states is only 1.23 eV. This is obviously an excellent situation for catalysis. Conventional electrolysis is a catalytic process involving adsorption of the ionic species OH^- and H^+ on metallic electrodes, but the high cost of electricity makes this process unsuitable for the large-scale generation of hydrogen. However, if sunlight could be used to provide the energy for the electrolysis, then an economically feasible system could result. One way that such a system could be arranged in a straightforward manner would be by connecting currently available photovoltaic solar arrays to existing electrolysis units, but the cost of electricity from silicon solar cells is even more prohibitive than from other sources. What is needed to accomplish photoelectrolysis in a simple, inexpensive manner is an electrode material which can directly absorb the incident sunlight and utilize this energy to drive the water splitting reaction. One excellent possibility appears to be a photosensitive semiconductor electrode.

3. Semiconductor Electrodes

Photoelectrochemical effects at semiconductor surfaces have been known for a long time. Indeed, the first description of a photocurrent due to illumination of a semiconductor electrode (AgCl) with sunlight was given by Becquerel in 1839 ⁽⁸⁾, although little further work was done on this topic for the next hundred years. Then in 1955, Brattain and Garrett ⁽⁹⁾ made a classical investigation of the effects of light on Germanium in

contact with an electrolyte, while in 1960 Richard Williams ⁽¹⁰⁾ studied this process with a number of compound semiconductors, viz., CdS, CdSe, CuI, ZnO, ZnS, ZnTe, and GaAs. A number of other investigations with various materials followed ⁽¹¹⁻¹⁷⁾. Many of the fundamental theories of semiconductor electrodes in contact with solutions were formulated by Gerischer in several publications ⁽¹⁸⁻²⁰⁾ between 1960 and 1970.

Basically, a semiconductor may exhibit conductivity which is either n-type (mobile electrons in the conduction band) or p-type (mobile holes in the valence band). These mobile charge carriers in the semiconductor electrode (electrons or holes) were shown to interact with various redox couples in the solutions. A semiconductor does not have a continuum of electronic energy states (it has a band gap), and therefore a semiconductor electrode differs from a metal because in a semiconductor there are only certain particular energy levels - the valence band, the conduction band, (plus any surface states) - which can interact with ionic species in the electrolyte. In the dark, oxidation of ions in the solution can occur under conditions of anodic (positive) bias via the conduction band in n-type materials and via the valence band in p-type materials. Reduction proceeds with cathodic (negative) bias again via the conduction band in n-type materials and via the valence band in p-type materials.

To a first approximation, oxidation currents for anodically biased n-type semiconductor electrodes are not seen unless the potential of the redox couple in the solution is at least as negative* as the potential of the conduction band at the interface, and conversely, reduction currents for cathodically biased p-type semiconductor electrodes only exist if the potential

*Negative potentials indicate energy levels closer to vacuum level.

of the redox couple in the solution is at least as positive as the potential of the valence band at the interface. For redox couples located at energies within the region of the forbidden energy gap for either type of semiconductor, and for redox couples anodic of the conduction band for an n-type electrode or cathodic of the valence band for a p-type electrode, no electrochemical reaction should occur and no currents should flow. Since the actual states of any redox couple are distributed in energy, there is no sharp cutoff of the reactions at the band edge energy, but rather an exponential decrease in current as that energy level is passed. This system is the analogue of a metal-semiconductor Schottky barrier junction.

There is generally a space charge region at the semiconductor-electrolyte interface, due to differences in the electrochemical potential of the two regions, and consequently the bands in the semiconductor are usually bent upward in n-type materials (electron depletion region formed) and downward in p-type materials (hole depletion region formed). The band bending is increased by anodic bias for n-type materials or cathodic bias for p-type materials, and eventually a potential for the electrode can be reached at which carriers will tunnel. For example, with an n-type material, tunnelling can occur from a redox level located anodic of the conduction band at the interface (located at an energy level between the valence and conduction bands), through the triangular potential barrier in the semiconductor depletion region, to states lying at lower energies (more anodic potentials) in the conduction band in the interior of the semiconductor. This situation is shown schematically in Figure 1. This case is analogous to reverse bias breakdown (by the Zener mechanism) in a solid-state device. So the semiconductor-liquid electrolyte junction

is the difference in electron affinity of the semiconductor and the electrochemical potential of the ionic species in the solution, in the same way that the work function of a metal will determine if a metal-semiconductor contact is ohmic or rectifying.

The semiconductor-solution interface is considered to be composed of three capacitances in series: the semiconductor space charge region, the Helmholtz layer (adsorbed ions) in the solution, and the solution diffuse double layer (Guoy layer). At high ionic concentrations in the solution the capacitance of the diffuse double layer can be neglected. The capacitance of the Helmholtz layer, C_H , is expected to be much larger than that of semiconductor space charge layer, C_{SC} , and therefore the Mott-Schottley relationship gives

$$\frac{1}{C_{SC}^2} = \frac{2}{q\epsilon\epsilon_o n_o} \left(V - V_{fb} - \frac{kT}{q} \right) \quad (2)$$

where: q = electronic charge

ϵ = semiconductor dielectric constant

$\epsilon_o = 8.85 \times 10^{-14}$ coul/V-cm

n_o = carrier concentration

V = applied voltage

V_{fb} = potential at which the semiconductor bands are flat

Studies (16, 17) have shown that this relationship is indeed satisfied for most of the systems tested, and from the straight line obtained on C_{SC}^{-2} vs. V plots, n_o and V_{fb} have been determined for a number of materials.

4. Semiconductor Electrodes Under Illumination

When light is applied to a semiconductor-liquid electrolyte system, it becomes possible to obtain a photovoltage and a photocurrent, in analogy to a solid state photovoltaic device. For example, in the case of an n-type material in contact with a solution, the illumination creates excess electrons in the conduction band and excess holes in the valence band, so that the quasifermi levels for electrons and holes are shifted according to:

$$\Delta E_{Fn} = kT \ln \frac{n_o + n^*}{n_o} \quad (3)$$

$$\Delta E_{Fp} = kT \ln \frac{p_o + p^*}{p_o} \quad (4)$$

where n_o , p_o are the equilibrium carrier concentrations in the dark ($n_o \gg p_o$) and n^* , p^* are the excess carriers from the illumination. Since in an n-type material p_o is very small, ΔE_{Fp} will be very large. On the other hand, n^* may not even be as large as n_o if the light is not very intense, thus changes in ΔE_{Fn} will be small. It is clear that the major effect will involve the minority carriers (holes). It is then possible for oxidation processes which were forbidden in the dark to occur via the optically generated minority carriers in the valence band, and this effect has been observed many times. The rate of the electrochemical reaction is determined by the kinetics of the optically generated minority carriers. A sketch of the type of I-V characteristics which is encountered for semiconductor-liquid junctions is shown in Figure 2, both in the dark and under illumination.

Thus, by 1970 a considerable amount of study had been given to the properties of semiconductors in contact with electrolytic solutions, and theories had been formulated explaining many of the results. However, although this topic had been a fruitful area for research, it had not developed much practical significance (outside of providing some etching techniques). There was a critical problem encountered with all of the materials tested: corrosion (10, 20). In some cases the semiconductors corroded spontaneously in the dark (forming essentially a battery), while in most cases corrosion did not occur unless the electrode was illuminated. Instead of oxidizing reduced species in the aqueous electrolyte, holes in the n-type semiconductor valence band were found to oxidize the electrode itself. Holes in such an n-type semiconductor represent broken bonds, while electrons in a p-type semiconductor are excess bonds, so that in either case accumulation of the photogenerated carriers at the surface can lead to a rupturing of the lattice. For example, with n-type CdS the reaction with light is

The two electrons can reduce Cd^{++} at a counter-electrode. The coating of elemental sulfur covers the surface in a few minutes and the reaction ceases.

Of course, if an electrode would remain stable under illumination, then it could be used to generate useful chemical products in a solution, while itself only acting as a photocatalyst. As we mentioned earlier, one of the most useful chemical reactions is the electrolysis of water. This

reaction requires the application of at least 1.23 V between two electrodes, although overvoltage problems actually require that 1.6-1.8 V be applied to drive significant currents. The hydrogen produced in this process is a very valuable chemical, even more so today with the shortages of natural gas and oil. If sunlight could be used to drive the water electrolysis reaction this would be an extremely important way to achieve energy independence, since both sunlight and water are abundant, inexhaustible resources.

Now, it is certainly possible to power a conventional water electrolysis unit with electricity derived from single crystal silicon photovoltaic devices exposed to sunlight. This has recently been demonstrated using a solar array panel from the Mariner 4 spacecraft ⁽²¹⁾, but the authors admitted that hydrogen produced by this technique would be very expensive due to the very high cost of silicon solar cells. But in 1972, Fujishima and Honda ⁽²²⁾ showed that it is possible to use the semiconductor TiO_2 (rutile) in contact with water to generate both hydrogen and oxygen under illumination, and claimed that the material suffered no degradation. This report soon created great new interest in the field of semiconductor-electrolyte interfaces.

5. Water Photoelectrolysis at TiO_2 Electrodes

The water photoelectrolysis cell demonstrated by Fujishima and Honda was a major breakthrough because for the first time a semiconductor electrode was found which remained stable in an aqueous solution under illumination. In their cell, oxygen was evolved at the anode (TiO_2) and hydrogen at the cathode (Pt), and the following reactions in their acidic electrolyte were postulated:

They estimated a quantum yield of 10% when the TiO_2 was irradiated with a 500 W Xenon Lamp. After operation, no titanium was detected in the solution. Wrighton and coworkers ⁽²³⁾ confirmed that illuminated TiO_2 is indeed stable in solution. The identity of the gases evolved at the TiO_2 electrode in their experiment was determined by irradiation of the TiO_2 in a 1 M NaOH $\text{D}_2^{18}\text{O}/\text{D}_2^{16}\text{O}$ (1/4) solution. One expects that from such a solution the ratio of $^{16}\text{O}_2$ to $^{16}\text{O}^{18}\text{O}$ should be 2:1, and indeed this was found, suggesting that the reaction is not simply photorelease of oxygen from TiO_2 ⁽²³⁾. This conclusion was further substantiated by these workers through careful weighings of their samples, which indicated no weight changes even after more moles of O_2 were generated than the moles of TiO_2 present as the electrode.

There was a report by Harris and Wilson ⁽²⁴⁾ that aging effects, such as losses in quantum efficiency and changes in surface morphology, were encountered with illuminated TiO_2 anodes operated in 1.0 N H_2SO_4 . However, the Handbook of Chemistry and Physics lists TiO_2 as soluble in H_2SO_4 ⁽²⁵⁾ even in the dark, and experiments we have performed in our laboratory on very thin films of TiO_2 confirm that there is some solubility in sulfuric acid. Most experiments on photoelectrolysis with TiO_2 have

in fact been carried out in strongly basic solution, such as the previously discussed tests of Wrighton, et al. In an alkali solution, again neglecting mechanistic details, the oxygen and hydrogen reactions in a photoelectrolysis cell are:

A representative I-V characteristic found in our laboratory for TiO_2 in 5 M KOH solution, in the dark and illuminated with a 200 W mercury lamp, is shown in Figure 3. Notice that although intense illumination shifts the potential for oxygen generation from anodic values (equilibrium potential for the OH^-/O_2 couple = + 0.16 V vs. SCE) to - 1.03 V vs. SCE, the potential for hydrogen generation at the dark Pt counterelectrode is - 1.07 V vs. SCE, and therefore the cell will not operate spontaneously. Various investigations have established that an anodic bias is always required for water decomposition with illuminated TiO_2 . The minimum bias is 0.15-0.25 V (23, 26) and this can be supplied by a battery, but a number of articles (27-31) have reported supplying the bias chemically, by placing the TiO_2 electrode in the basic solution while using an acidic solution for the Pt counterelectrode (and a salt bridge connecting the solutions). A difference in pH of 13 between the solutions will supply a bias of 0.78 V, and vigorous generation of gases has been seen when such TiO_2 cells are illuminated.

It has been determined that photoelectrolysis of water proceeds spontaneously (no bias required) in cells where the TiO_2 anode is replaced with a related compound, SrTiO_3 (32-34). SrTiO_3 is also quite stable under illumination. Again for this material, Wrighton and coworkers (33) determined the stability by weighing samples and labeling the water with ^{18}O , as described earlier.

6. Bias Requirements for TiO_2 and SrTiO_3 Electrodes

The necessity for a bias voltage (or a differential cell) for TiO_2 but not for SrTiO_3 in a photoelectrolysis cell has been the subject of some study, in our laboratory and elsewhere ⁽³²⁾. A clear picture of the relations of the energy bands in these semiconductors to the redox levels in the solution should explain this situation. In solid-state semiconductor measurements the energy bands are positioned relative to vacuum; while the presence of a liquid electrolyte necessitates a different reference, namely, the saturated calomel electrode, SCE. As a guide, one may recall that SCE is at +0.24 V from the normal hydrogen electrode NHE, while NHE is about 4.5 eV below vacuum, so that SCE is 4.74 V below vacuum. By convention in electrochemistry, negative potentials are plotted upward on a diagram.

We set up a number of cells using various TiO_2 and SrTiO_3 samples, and we measured open circuit photovoltage, capacitance vs. voltages and current vs. potential. The absolute magnitude of the open circuit photovoltage was found to be as high as 0.72 V for TiO_2 and 0.94 V for SrTiO_3 . The dark fermi level for these semiconductors in contact with a pH = 14 solution was at -0.31 V vs. SCE for TiO_2 and -0.28 V vs. SCE for SrTiO_3 . When flooded with the entire output of the 200 W Hg lamp, the potential of the TiO_2 electrode became -1.03 V while that of the SrTiO_3 electrode became -1.22 V vs. SCE.

The flat-band potential is the potential at which there is no excess charge in the semiconductor in the region of the semiconductor-solution interface, i.e., the condition where there is no band-bending in

the semiconductor. Obviously, the flat-band potential can be determined by the potential of the fermi level under intense illumination. Thus V_{FB} (flat-band potential) must be at least -1.03 V for TiO_2 .

A large number of capacitance-voltage (C-V) measurements were made to help us to determine the flat-band potential V_{FB} of TiO_2 and of $SrTiO_3$ in a solution. From the $1/C^2$ vs. V plots, we determined $V_{FB} = -1.03$ V at pH = 14 for TiO_2 samples, in accordance with the published value (35, 36). In all cases, V_{FB} changed with pH by the factor 0.059 pH. Carrier concentrations determined from the C-V data were consistently in the 10^{20} cm^{-3} range.

From a carrier concentration of 10^{20} cm^{-3} , one can calculate a barrier width of about 10^{-6} cm. However, assuming the mobility of TiO_2 is of the order of unity (37), then the carrier concentration determined by the C-V data appears too large for our measured sample resistivity of 1 Ω -cm. On the other hand, if we take $\mu = 0.1$ and $\rho = 0.5 \text{ } \Omega$ -cm, then indeed it is consistent to have 10^{20} carriers/ cm^3 .

Our current-potential measurements were made for a number of TiO_2 and $SrTiO_3$ samples by using a standard three electrode system. In a 5 M KOH solution with pH = 14, the H_2/H_2O redox couple is located at -1.07 V vs. SCE and the O_2/OH^- couple is at +0.16 V. When TiO_2 cells were scanned in the dark, cathodic reducing currents flowed at potentials negative of the hydrogen couple, but only negligible anodic oxidizing currents were found, as shown in Figure 3. When the samples were illuminated with the Hg lamp, little change ($\sim 10\%$ increase) was noted in the cathodic currents, but major increases in anodic currents were encountered, again illustrated in Figure 3. On the scale used, the dark current and the

reducing current are too small to show in the potential range covered, while an anodic photo-current of up to 50 mA/cm^2 was measured. When such a large current flows, hydrogen generation is so rapid that the Pt counterelectrode literally foams. The situation in the potential range of -0.9 to -1.4 V is shown in greater detail in Figure 4. Anodic currents begin to flow upon illumination with TiO_2 electrodes at precisely -1.03 V . However, with SrTiO_3 , the anodic current commences flowing at -1.23 V .

The foregoing measurements show clearly why TiO_2 cells require a small bias, while SrTiO_3 cells can photoelectrolyze water without any bias. In order for a cell to operate spontaneously without any applied bias, it is necessary that with the application of light, the potential for the evolution of oxygen become more negative than the potential for the evolution of hydrogen. For TiO_2 , this clearly does not happen, while for SrTiO_3 it does (Figure 4). Notice that even though a SrTiO_3 cell can operate spontaneously, the application of a small bias will greatly increase the current and therefore improve the cell efficiency. Thus, the effect of an 0.15 V bias on a TiO_2 cell is to move the potential for oxygen evolution just to the negative side of the potential for hydrogen evolution.

The above results allow us to construct the energy-band diagrams for TiO_2 and SrTiO_3 , in the dark and in the light, shown in Figure 5. All potentials are referred to SCE. These diagrams were constructed for a solution with $\text{pH} = 14$, but changing the pH only serves to move the positions of the energy levels in tandem relative to SCE, without otherwise altering their relative placements. Of course, changing the pH of the solution will alter its resistivity and therefore can affect the magnitude

of the photocurrent. With the application of light to TiO_2 , the electron fermi level E_{Fn} rises according to Equation 3, but not high enough to allow the electrons, which must then pass through the external circuit to the Pt, to transfer to the $\text{H}_2/\text{H}_2\text{O}$ level in the solution. The hole fermi level E_{Fp} drops according to Equation 4 sufficiently far down to allow holes to transfer to the O_2/OH^- level, allowing evolution of oxygen. However, if dissolved oxygen is present in the solution, electrons from the Pt are able to transfer to the O_2/OH^- level, reducing O_2 instead of H^+ and completing a photogalvanic cell (31, 38). With a small negative bias applied to the Pt in a cell with no dissolved oxygen, though, the electrons acquire enough energy to become capable of reducing hydrogen.

As illustrated in Figure 5 for SrTiO_3 , on the other hand, E_{Fn} becomes more negative than $\text{H}_2/\text{H}_2\text{O}$ upon illumination, and the cell operates spontaneously. As Mavroides and Tchernev first pointed out (31), it is necessary to consider the electron affinity as well as band gap of a material when selecting semiconductors for use as photosensitive electrodes. The electron affinity will determine the position of the conduction and valance bands with respect to the $\text{H}_2/\text{H}_2\text{O}$ and O_2/OH^- redox levels, and therefore decide if the cell will require a bias. The electron affinity of SrTiO_3 is less than that of TiO_2 , and therefore SrTiO_3 cells can operate without a bias. The band gap on the other hand, determines what percentage of the available solar spectrum can be utilized by the device. In this respect, neither TiO_2 nor SrTiO_3 are very good photocatalysts for use in sunlight, because with band gaps of, respectively, 3.0 and 3.2 eV, these materials are transparent to more than 90% of the solar irradiation available on earth.

It should now be clear from Figure 5 that the photo-voltage that can be measured in the external circuit only indicates the change in position of the electron fermi level upon illumination, while the total photopotential available for electrolyzing water is the difference between the electron and hole fermi levels. In analogy with a solid state photovoltaic device, one may consider the O_2/OH^- redox couple to be a contact to the valence band while the H_2/H_2O redox couple acts as a contact to the conduction band. Therefore the maximum photovoltage one can obtain from this device is the potential difference between the O_2/OH^- and H_2/H_2O redox levels, namely, 1.23 V, and consequently for direct comparison with solid state photovoltaic devices, one should calculate the power available from a photoelectrolysis cell as the product of this photovoltage, 1.23 V, and the photocurrent.

7. Energy Balance for Photoelectrolysis

Nozik has considered the energy balance in a photoelectrolysis cell in detail (28, 39). For a Schottky barrier device with an inert counterelectrode as shown in Figure 6

$$E_g + V_A = V_B + (E_c - E_f) + \frac{\Delta G}{nF} + \eta_a + \eta_c + iR + V_H \quad (12)$$

Here, E_g is the semiconductor band gap, V_A is any applied external bias, V_B is the band bending at the semiconductor surface, E_c is the conduction band energy, E_f is the fermi level, $\Delta G/nF$ is the free energy change per electron for the chemical reaction, η_a and η_c are the respective overpotentials at the anode and cathode, iR is the Ohmic loss, and V_H is the potential drop across the Helmholtz layer in the electrolyte. The band

bending potential V_B supplies the energy for separating the optically generated hole-electron pairs. Even though the open circuit photovoltage which is measured in the external circuit is determined by the band bending, it should be stressed that the band bending potential does not always contribute to the chemical energy stored in the system. The potential for water electrolysis is not simply supplied by the sum of the band bending plus the external applied bias, as some have claimed (29, 40), and, indeed, the total energy output (stored chemical energy plus electrical energy) is not only as great as the band bending, as others have asserted recently (41). In fact, only if a load resistance is placed in the external circuit, between the active-and counter-electrodes, will the band bending determine the electrical energy available from the cell. Such a situation applies for an electrochemical photocell, like the $\text{CdS}/\text{Na}_2\text{S-S}$ cell, where the same redox couple (i.e., S^{-2}/S) undergoes reactions at both electrodes and no net chemical products are formed (42-45).

However, when the function of the cell is water electrolysis, two redox couples ($\text{H}_2/\text{H}_2\text{O}$ and O_2/OH^-) are involved and the two electrodes are short circuited. The net voltage drop experienced by an electron as it passes through the entire circuit consists of first, an optical excitation from the valence to the conduction band, next, a drop of V_B as it moves to the interior of the crystal, followed by an essentially iso-energetic transfer to the counter-electrode, where it should react with H_2O to form H_2 . This electron is stored with the hydrogen; it does not complete the circuit (back to the valence band) until the time that it is allowed to recombine with oxygen formed at the anode. This oxygen, of course, was formed when an OH^- ion donated an electron to the valence band. However, if the case

of a semiconductor such as TiO_2 , the electron that is transferred from the conduction band to the Pt electrode lacks sufficient energy to react with the water to produce H_2 . This is analogous to having a series resistance in the circuit, and now the band bending photovoltage must supply energy to the electron to overcome the resistance. With TiO_2 this is still not enough, and a further external bias voltage must also be supplied. But for materials which have their flat band potential far above the hydrogen level (such as GaP), neither the band bending voltage nor an external bias are required.

As further proof of this concept, consider that the open-circuit photovoltages reported for TiO_2 cells are in the range of 0.5-0.7 V (22, 26, 27, 46) and yet with an additional bias of only 0.2 V, water electrolysis results (23, 26). And SrTiO_3 cells with similar open-circuit voltages and no bias requirement are also able to decompose water. The apparent conceptual difficulty is resolved by realizing that only the majority carrier electrons, and not the minority carrier holes, are available for measurement in the external circuit, and so the energy stored in the holes is not considered. Incidentally, if the solution were replaced by a metal to form a normal Schottky barrier, then the hole from the valence band of the semiconductor would simply dissipate its energy as a number of phonons (heat) when it rises up to the fermi level in the metal. In a photoelectrolysis system, this energy can be stored as a chemical product.

Nozik has further proposed that enhanced efficiencies for photoelectrolysis can be achieved if both the anode and the cathode electrodes are optically active semiconductors. Now instead of collecting the majority carrier electrons at the ohmic back contact of the n-type anode material and transferring them through the external circuit to the counterelectrode, the electrons that contribute to the reduction process

are optically generated minority carriers created in a p-type cathode material. The majority electrons from the n-type material and the majority holes from the p-type material constitute a recombination current in the external circuit. In general, the energy balance is

$$E_g(n) + E_g(p) = V_B(n) - V_B(p) - \Delta E_f(n) + \Delta E_f(p) + \Delta G/nF + \eta_a(n) + \eta_c(p) + iR + V_H(n) + V_H(p).$$

As Nozik pointed out, the maximum energy separation that can occur between the two types of minority carriers, and hence, the maximum energy available for doing chemical work, depends on the electron affinities of the two materials. Consider Figure 7, in which for convenience the term $E_c - E_f$ has been neglected, and no external bias is applied. Now in the case where both the n- and the p-type members are the same material (Figure 7a), the energy separation between the minority carriers can be as large as the band gap (if losses such as over-potentials are negligible). However, in the extreme (if unrealizable) case where two materials have equal band gaps and the flat band potential is the same for the two materials, as in Figure 7b, then the energy available for chemical work will be twice the band gap. This energy is not dependent on the intensity of the illumination of the cell; however, as illustrated in Figure 7c, if a conventional p-n junction device were to be used to drive two external inert (Pt) electrodes to accomplish electrolysis, then the intensity of illumination becomes very important. This feature arises because with the p-n junction device, when the minority carriers cross the junction region and are ultimately collected they actually become majority carriers, and as such are applied to the external platinum electrodes. These collected

carriers suffer energy degradations while traversing the band bending regions on the sides of the junction on which they are in the majority: this loss in energy is exactly the same as the one suffered by the electrons collected from the n-type anode (Figure 6), when they are applied through the external circuit to the inert cathode, as described above. What we have here is an apparent advantage for the photoelectrolysis cell concept: with these cells it is possible to utilize highly energetic minority carriers to drive chemical reactions. And this is accomplished without resorting to the extreme light intensities that would be necessary to obtain an open-circuit voltage equal to the band gap in a conventional p-n junction device, according to

$$V_{oc} = \frac{nkT}{q} \ln bL, \quad (14)$$

where L is the light intensity and b is a constant.

However, caution must be exercised before we conclude that the p-n photoelectrolysis cell leads to higher efficiency. In order for the device to operate, both electrodes must be illuminated. If the two electrodes are the same material, then they will have to be illuminated separately, doubling the area and hence halving the current density. It is important to count the number of photons required for the process. Assuredly, at very low (and therefore impractical) light levels, the voltage from an all solid state device will be negligible, while every photon can generate chemical products in a photoelectrolysis cell. But at sunlight intensities, a silicon solid state device can develop an open circuit voltage of about half the band gap, so that under these conditions a photoelectrolysis cell using silicon and requiring twice the area fails to give an advantage. Note that one might use two semiconductor electrodes with different band gaps placed so as to intercept the light in series

and therefore not require doubling the area. In this case it may be possible to achieve an improvement, but if one of the electrodes has a very wide band gap (such as TiO_2) then the cell current will be limited by the carrier generation rate in that material.

There have been several investigations of cells having both the anode and cathode electrodes as illuminated semiconductors. In all reports, n-TiO_2 was used as the anode and p-GaP was used as the cathode (39, 47-49), although, in addition, n-SrTiO_3 and p-CdTe have also been evaluated (48). When the cathode is illuminated p-GaP , then an illuminated n-TiO_2 anode will allow spontaneous water decomposition (no external bias required) (39). But the reported efficiency of 0.25% in simulated sunlight for this type of device remains low, due to the poor sunlight response of TiO_2 .

Unfortunately, Nozik's energy balance Equation 13 does not allow us to specify the materials we need for an efficient photoelectrolysis cell, because the overpotential terms η_a and η_c are a priori unknown parameters. There are a number of possible causes for overpotentials at electrode; an interesting discussion of this problem has been given recently by Bockris (50). It appears that the major contribution to the overpotential on the TiO_2 anode evolving oxygen under illumination is simply due to the fact that the O_2/OH^- energy level lies quite high above the valence band of the TiO_2 . In this case, if $V_b = 0.7$ and $\Delta E_f \approx 0.1$, then the hole and electron generated by the light will be about 2.2 V apart at the interfaces with the solution. Since C-V measurements (35) have indicated that the $\text{H}_2/\text{H}_2\text{O}$ level is located at approximately V_{fb} for

TiO₂, then the O₂/OH⁻ level is 1.7 V above the valence band. So while this may be considered to be an overpotential, the loss of 1.7 V involved here is independent of the rate of the reaction, and so it does not conform to the Butler-Volmer Equation, as discussed by Bockris (51):

$$J = (\text{const}) [e^{-\alpha nF/RT} - e^{(1 - \alpha)nF/RT}] \quad (15)$$

That is, overpotential is the energy (eV) by which an electron in an electrode material has to be excited above the energy it possessed at thermodynamic reversibility to cause a specific emission rate to an ionic acceptor in the solution (50). It appears that while the loss of 1.7 V may be fundamental to the TiO₂-water system because of the relative placements of the energy levels, in principle, at least, such large "overpotentials" should not be necessary with other materials. However, all oxygen electrodes exhibit overpotentials at significant currents, usually about 0.4-0.5 eV (52). On the other hand, the overpotential for hydrogen evolution on platinum is negligible, and therefore we may use Equation 12 to estimate, the minimum band gap necessary for a Schottky barrier type of photoelectrolysis cell as

$$E_g = 0.3 + 0.1 + 1.23 + 0.5 + 0 + 0.05 + 0.05 = 2.23 \text{ V.} \quad (16)$$

Here we have taken the remaining band bending to be 0.3 V with illumination. Of course, as noted earlier, the energy bands of the semiconductor and the redox levels in the solution must be properly aligned (i.e., correct electron affinity for the semiconductor) in addition to the requirement for a proper band gap energy for the photosensitive electrode.

8. Theory of the Semiconductor-Electrolyte Interface as a Schottky Barrier

a. Wavelength Dependence of the Photocurrent

We have noted a number of times now that the semiconductor-electrolyte interface is considered to behave in a manner analogous to a metal-semiconductor Schottky barrier. This view is taken because the solution is much more conducting than the solid phase, and therefore, essentially all of the depletion region falls within the semiconductor. It should therefore be possible to derive an expression relating the magnitude of the response of a cell to the wavelength of the incident light, and this has been done recently by Ghosh and Maruska (26) for TiO_2 . Briefly, consider a semiconductor electrode of thickness ℓ , with a depletion region of width ℓ_b and a minority carrier (hole) diffusion length L . The number of photogenerated carriers within dx at a distance x from the solution-semiconductor interface is proportional to

$$\phi N_x \exp(-\alpha x) dx \quad (17)$$

where ϕ is the quantum efficiency, N is the number of incident photons, and α is the absorption constant for photons of this wavelength. There are two components to the hole current, one generated in the barrier region and one due to diffusion from the bulk, so that

$$p = \phi N \int_0^{\ell_b} \alpha \exp(-\alpha x) dx + \phi N \int_{\ell_b}^{\ell} \alpha \exp(-\alpha x) \exp[-(x-\ell_b)/L] dx \quad (18)$$

and therefore

$$J = qNG \left[[1 - \exp(-\alpha \ell_b)] + \frac{\alpha}{\alpha + \beta} \exp(\beta \ell_b) \{ (\exp-(\alpha + \beta) \ell_b) - (\exp-(\alpha + \beta) \ell) \} \right] \quad (19)$$

Here J is the photocurrent/cm², $\beta = 1/L$, and G is a factor related to the photoconductive gain in the barrier region as well as to the process governing the transport of the holes across the interface.

Using the absorption spectrum for TiO₂ available in the literature (53) to relate α to λ (the wavelength of incident monochromatic light), Ghosh and Maruska (26) determined that there is a good fit of their experimental data with the relationship given in Equation 19, as shown in Figure 8. They determined that barrier widths were of the order of 10⁻⁶ cm, and hole diffusion lengths were of the order of several microns. Significantly, longer diffusion lengths were found for Al-doped TiO₂ (4.5 microns) than for undoped TiO₂ (1.2 microns). Since in either case the hole diffusion length is much greater than the barrier width, then the photoconductive gain is approximately unity for short wavelength light absorbed entirely within the barrier region. For light with $340 < \lambda < 420$ nm, a larger proportion of carriers are collected in Al-doped TiO₂ due to the improved diffusion from the bulk. In sunlight with a measured intensity of 105 mW/cm², the conversion efficiency (defined as the ratio of the energy stored in the hydrogen produced to the energy of the incident sunlight) was found to be as high as 1.3% for Al-doped TiO₂ cells. A sunlight conversion efficiency of 0.4% had been reported earlier (54) for undoped TiO₂, and a value of 0.6% was published more recently (55). Another report (56) of 0.8% efficiency is questionable because of the low incident solar power (40 mW/cm²) which was assumed (not measured). It may not be possible to use concentrators to increase the cell current, because the photocurrent appears to saturate at high intensities (57).

At shorter wavelengths below about 350 nm, the quantum efficiency has been shown to be constant (23, 26). This constant value is significantly larger for Al-doped TiO_2 samples than for undoped samples (26). It is possible that there are major differences occurring from sample to sample between the bulk values of hole lifetime and mobility and the barrier region values of these quantities. This could explain the differences in the value of G. However, it appears more likely that the rate limiting step is the process of hole transfer to the electrolyte, and this process appears to require the presence of surface states to allow isoenergetic transfer (58). Following the discussion of Boddy (17), one may consider the following sequence of steps for oxygen formation at the surface of TiO_2 :

where --- O^- is a surface oxygen ion and p^+ is a hole. Then

where $[-\text{V}]$ is an oxygen vacancy. Next

and

This reaction sequence does not indicate an actual corrosion of the semiconductor because only the initial oxygen comes from the structure, with subsequent oxygen coming from the water in a repeated cycle. A discussion of the surface reaction along similar lines has been given by Gissler, et al. (59). Now if Al^{3+} replaces Ti^{4+} at some surface sites in Al-doped TiO_2 , this alteration may increase the probability of Equation 21. Since Al^{3+} introduces one more electron than Ti^{4+} , the structure may relax more readily by creating an oxygen vacancy to compensate for the extra charge. Augustynski, et al. have now also reported improved response for TiO_2 doped with 6% Al_2O_3 (60).

b. Voltage Dependence of the Photocurrent

The derivation given above can be extended to show the dependence of the photocurrent on the voltage across the depletion region. Basically, the connection is made by giving the relationship between the width of the barrier region, ℓ_b , and the voltage, V:

$$\ell_b = \left(\frac{2\epsilon\epsilon_0}{qNd} \right)^{1/2} V^{1/2} \quad (24)$$

This has been done, for example, by Bulter and Ginley (61) who obtained

$$J = q \Phi_0 \left\{ 1 - \frac{\exp [-\alpha W_0 (V - V_{fb})^{1/2}]}{1 + \alpha L_p} \right\} \quad (25)$$

where $W_0 = (2\epsilon\epsilon_0/qNd)^{1/2}$. Also, Laser and Bard (62-64) used a more exact computer simulation technique to generate these characteristics. In general, agreement with experimental results is excellent at higher voltages (greater than a few tenths of volt), but deviations are found at small voltages. Wilson has proposed (65) that this difficulty is encountered because one of the boundary conditions usually taken is that $p = 0$ at $x = \ell_b$, which neglects surface recombination. He has instead used the boundary condition,

$$- D \frac{dp}{dx} = S p \text{ at } x = l_b \quad (26)$$

where S is directly related by terms involving the voltage to the sum of the surface recombination velocity and the surface charge transfer reaction velocity. He determined that surface recombination is only important at small values of the voltage, near V_{fb} . Laser and Bard pointed out also that at potentials close to flat band, the photogenerated electrons will not be effectively driven away from the surface, and so a back reaction involving electrons from the conduction band reducing O_2 back to OH^- can occur ⁽⁶⁴⁾. However, since TiO_2 must be operated at some small anodic bias because of problems with the hydrogen reaction, these difficulties are not encountered in operating cells, and in fact, 100% quantum efficiencies have been achieved.

9. Increasing the Sunlight Response

We have shown now that the theory of semiconductor-solution photo-electrolysis cells has been fairly well developed, except (especially) for the detailed mechanisms of charge transfer across the interface. However, no practical devices have yet been achieved. All electrode materials which have been tested so far suffer from either or both of the following problems:

1. The semiconductor corrodes under illumination.
2. The semiconductor is a poor absorber of sunlight.

A number of approaches are being pursued to overcome these difficulties. These include (a) new small band gap semiconductors, (b) dye sensitization, (c) heterostructure formation, and (d) impurity sensitization.

a. New Small Band Gap Semiconductors

Many new materials are currently being prepared and tested in various laboratories. For example, there are other titanates such as $SrTiO_3$ ⁽³²⁻³⁴⁾, $BaTiO_3$ ⁽⁶⁶⁻⁶⁸⁾, and $CaTiO_3$. Unfortunately, even though these materials are stable, they have band gaps even wider than that of

TiO_2 , SnO_2 (69, 70), KTaO_3 (71) and SiC (72) also possess very large band gaps. WO_3 (73-75) with a band gap of 2.7 eV shows promise, but very little current is generated with photons of energy less than 3 eV, and 100% quantum efficiency is not reached until 275 nm. Apparently this problem is the result of an indirect band gap (74). There are also some stability problems with WO_3 (but it may be stable in certain electrolytes), and in addition it requires a large bias because it has too large an electron affinity. Fe_2O_3 (76-78) also has a smaller band gap, 2.2 eV, and from that standpoint would be ideal. But high efficiencies have not been reported with Fe_2O_3 , again due to an indirect band gap (slowly increasing absorption constant) and large electron affinity (77). However, Fe_2O_3 appears to be completely stable, and in fact, it is the only semiconductor with absorption at 550 nm, the peak of the solar spectrum, which exhibits stability. Further work is needed with this material to overcome its defective properties. It is possible to synthesize a number of compounds of the iron oxide-titanium oxide system (iron titanates), but these materials do not show as good a response as either Fe_2O_3 or TiO_2 (79). YFeO_3 has a band gap of 2.6 eV, larger than Fe_2O_3 , but it requires less bias (80).

There have recently appeared three publications describing photo-electrochemistry at a large number of oxide semiconductors. Clechet, et al. (81) studied the oxides of titanium, niobium, tantalum, and zirconium, all of which have very large band gaps and therefore poor sunlight absorption. Kohl, Frank and Bard (82) synthesized and tested TiO_2 , Fe_2O_3 , V_2O_5 , WO_3 , PbO , Bi_2O_3 , CuO , Cr_2O_3 , CoO , CdO , MnO_2 , and SrO in polycrystalline form. All of these materials except for TiO_2 , Fe_2O_3 , and WO_3 showed either poor photocurrents or corrosion (or both). Kung, et al. (40) tested TiO_2 , SrTiO_3 , BaTiO_3 , Fe_2O_3 , CdO , CdFe_2O_4 , WO_3 , $\text{PbFe}_{12}\text{O}_{19}$, $\text{Pb}_4\text{Ti}_3\text{WO}_{13}$, HgTa_2O_7 , and HgNb_2O_7 and reported that these

were all stable, at least in certain ranges of pH. The band gaps of the cadmium, lead and mercury compounds were determined to be in the range of 1.8 - 2.4 eV, and a photo-response with $\text{H}_{82}\text{Ta}_{207}$ was found at wavelengths as long as 650 nm. However, a disturbing trend was discovered: with these particular semiconductors, the smaller the band gap, the larger was the electron affinity, and therefore, the larger was the required bias voltage. There is another survey ⁽⁷²⁾, though, which indicated that there exist a number of smaller band gap materials such as GaAs, GaP, CdSe and CdS which have much smaller electron affinities and hence should not require external bias voltages. The ability of a semiconductor to photoelectrolyze water without an applied bias has been correlated with the electronegatives of the constituent atoms by Butler and Ginley ⁽⁸³⁾.

The more common n-type semiconductors such as CdS, CdSe, GaAs, and Si have been known to be unstable for a long time. As we discussed briefly before, some of these, such as CdS, can be stabilized effectively with proper solutions containing the anion, such as S^{-2}/S , but then no water photolysis results ⁽⁴²⁻⁴⁵⁾. Rather, the sulfur/sulfide couple undergoes the reduction and oxidation, and power can be drawn from the external circuit. This type of cell is outside the scope of this paper. There have been a couple of recent papers describing illuminated Si electrodes ^(84, 85) and CdS electrodes ⁽⁸⁶⁾ where no stabilizing agents were introduced into the water. Two recent review articles have appeared by Gerischer ⁽⁸⁷⁾ and by Williams ⁽⁸⁸⁾ which discuss the corrosion problems suffered by most smaller band gap materials.

A listing of various materials which have been used in photo-electrolysis cells is given in Table I. When values of the flatband potential listed in this chart are positive versus hydrogen, then they indicate the approximate external bias required (negative values indicate spontaneous operation).

b. Dye Sensitization

A large number of dyes are capable of absorbing incident visible light and transferring the excited state to the substrate material. Materials like the silver halides, ZnO and TiO_2 have band gaps of 3 eV and larger and thus intrinsically respond only to uv excitation, but in their normal use for imaging processes, they can be made to respond to sunlight by dye sensitization. For example, a variety of cyanine dyes are known to photosensitize TiO_2 for the photographic process ⁽⁸⁹⁾. With an n-type substrate material such as TiO_2 and the generally p-type dyes, a heterojunction will form. On absorption of photons of visible light by the dye, electron-hole pairs are formed and can be separated at the junction, so that the electrons move into the TiO_2 while the holes are injected into the solution. In general, in a heterojunction, the smaller of the two energy gaps determines the voltage output that can be achieved from the photocell ⁽⁹⁰⁾. Thus, if the dye has a band gap of 2 eV, the voltage differences between the n and p regions should be about 2 V, and this should be sufficient to electrolyze water.

In our laboratory we have studied a number of cyanine, merocyanine, rhodamine, styryl and phenothiazine dyes in our cells. Two techniques were used for depositing the dye on the surface of the TiO_2 wafers: Vacuum deposition and solution dipping. For vacuum deposition the dye was heated in a vacuum system so a thin film 1000Å thick deposited on the TiO_2 by sublimation. For solution dipping, the dye was dissolved in a suitable solvent and the TiO_2 wafer was then dipped into the solution, withdrawn and allowed to dry. No difference in performance could be attributed to the number of coatings of dye used. All cells contained neutral (pH = 7) 0.1 M KCl solution.

Sensitization was determined by measuring a photocurrent in response to visible light, and a number of the dyes were found to respond to the illumination. Peak sensitization wavelengths were found in the range of 450 to 550 nm, in the visible portion of the spectrum. The highest quantum efficiency measured was about 0.7% at 510 nm with several merocyanine dyes, while a cyanine dye showed a peak sensitization at 550 nm with a quantum efficiency of 0.1%. The rhodamine, styryl and phenothiazine dyes which were tested showed very little or no sensitizing effects on TiO_2 in our photoelectrolysis cells, although some of them are known to be strong sensitizers for photographic (non-aqueous) processes ⁽⁹¹⁾. These dyes may have been desorbed from the TiO_2 surface during rinsing or while in the electrolyte solution. Tsubomura, et al. ⁽⁹²⁾ reported studying dyes such as Rhodamine B, Rose Bengal, Eosin Yellow, and Acridine Orange adsorbed on TiO_2 and ZnO substrates. They measured quantum efficiencies of 0.1-1.0%. A number of other dyes have also been tested using these substrates ⁽⁹³⁻⁹⁸⁾.

The major problem with the dyes studied is the rapid degradation of response. It was found in our studies that the region of the dye-coated electrodes which had been illuminated showed severe bleaching, so that the normal blue color of the TiO_2 rather than the red color of the dye became visible. Current deterioration in all of the dyes was quite rapid, and usually the current dropped by an order of magnitude in a matter of minutes. It is likely that during operation, oxidation of the dye, rather than oxidation of the water, is taking place at the illuminated anode. Even if the process were capable of producing oxygen, it is most likely that this oxygen would then rapidly react with the dye molecules and destroy them. Tsubomura, et al. ⁽⁹²⁾ found that the decay in photocurrent could be restrained by adding the "super-sensitizer" hydroquinone. However, in this situation they did not report the observation of any oxygen evolution, and neither has any other paper. If no oxygen is evolved

from the solution, then some other specie must be undergoing oxidation. In this case it must be the super-sensitizer.

Thus, it has been shown that the organic dyes tested thus far exhibit the same instability problems that are found with most smaller band gap semiconductors. Possibly this system can be used as an electrochemical photocell, where the oxidized super-sensitizer migrates to the counter-electrode to be reduced.

c. Heterostructure Formation

This method of sensitization is an attempt to combine the corrosion resistance of several wide band gap semiconductors with the good sunlight absorbing characteristics of smaller band gap materials. This type of heterostructure device is used with the stable wide band gap semiconductor, which is transparent to most of the incident solar spectrum, in contact with the solution. The optical generation of hole-electron pairs is then expected to occur in the shielded small band gap material, so that subsequent carrier transport through the wide band gap material is essential for the device to operate. There have been attempts to form heterostructure devices by depositing TiO_2 on GaAs, GaP, CdS, CdSe and Si (99-102). A similar approach involved coating GaAs with molybdenum oxide (103). Studies have also been made on structures where a thin metal film, such as gold, was used to protect small band gap semiconductors from corrosion (104-106). Of course, a film of metal sharply reduces the light transmission to the substrate.

Let us first discuss the metal coatings. If the metal film is thick enough to be continuous (free of cracks and pinholes), then the device acts simply as if it were a conventional metal-semiconductor Schottky barrier in series with an electrolysis cell (104). The maximum voltage

available from this device is just the band bending at the metal-semiconductor junction, and this voltage is typically not large enough to decompose water. The energy difference between the optically created hole in the semiconductor valence band and the fermi level in the metal film is dissipated as phonons, instead of contributing to the generation of chemical products. This device would work if it were possible to find some metal which would make contact to the semiconductor at the level of the valence band, so that the energy of the holes would not be dissipated. It has been possible to actually decompose water with an illuminated n-GaP/Au electrode where the gold film was not continuous (105). Here the solution came into contact with the semiconductor through the cracks in the metal film, and it was claimed that corrosion was contained because the gallium hydroxide was held within the cracks instead of peeling away and exposing more GaP surface to corrosion. These heterostructures showed response to visible light up to 550 nm, with a quantum efficiency of 11% at 420 nm and an estimated sunlight conversion efficiency of 1-2%. However, there remains the question of long term stability of these devices, and this problem will require further study.

Overcoatings with wide band gap semiconductors have so far not given very encouraging results. Tomkiewicz and Woodall (102) have studied devices made from n-type GaAs and GaAlAs coated with SnO_2 , Nb_2O_5 , Al_2O_3 , TiO_2 , or Si_3N_4 . As far as they could determine, the films did not suffer from pinholes, yet localized corrosion occurred anyway. They postulated diffusion of some species in the electrolyte through the intact films to the surface of the substrate semiconductor, and they felt that this problem could not be overcome by better sample preparation. Furthermore, they determined that the entire photocurrent was generated in the film and not in the substrate. Perhaps rather than having ions from the

electrolyte diffusing through the film to cause corrosion, photogenerated holes in the film diffuse inward, instead of to the surface, and oxidize the substrate material.

Kohl, Frank, and Bard ⁽¹⁰¹⁾ used chemical vapor deposition to coat n-type TiO_2 onto n-Si, p-Si, n-GaAs, p-GaAs, n-GaP, n-InP, and n-CdS. First of all, crack- and pinhole-free films were not obtained on CdS, GaAs or GaP by this method, and the usual photocorrosion problems were observed. The TiO_2 films deteriorated and eventually fell off. Durable, crack- and hole-free films of TiO_2 were deposited on n-Si and n-InP. The action spectra for n-InP/ TiO_2 and n-Si/ TiO_2 were the same as that found for TiO_2 ; i.e., photoeffects were only found with light of $\lambda < 400 \text{ nm}$. Similar results were seen for p-type substrates. They concluded that they were not able to inject holes from the small band gap substrate into the TiO_2 , which was hydrogen reduced after deposition and therefore n-type.

It can be seen that the major problem involved here is hole transport. If two n-type materials with different band gaps, but with each having the fermi level close to the conduction band edge, are joined to form a heterojunction, then there will result a barrier in the valence band. And this barrier will prevent the flow of holes from the smaller band gap material to the larger one. It would be possible to extract the holes by tunneling if the outer large band gap film is very thin, but films thin enough to allow tunneling are unlikely to be coherent. The structure which deserves more study is an $n^+ - n$ device in which the fermi levels have been properly adjusted so as to avoid any barrier in the valence band.

d. Impurity Sensitization

An interesting approach for extending the response of a wide band gap material such as TiO_2 to visible light is impurity doping. The excitation of the impurity into the TiO_2 bands can result in free electron and hole formation. This is described by the following equations and Figure 9.

Impurity Sensitization

Figure 9(a) shows an electron excited from the impurity level to the conduction band. The ground state level of the ionized impurity level may shift. The hole in the ground state level can ionize by heat or light and result in a free carrier. Figure 9(b) is similar to Case (a) with the exception that the impurity level is roughly midway between bandgap and it does not shift after ionization.

Figure 9(c) shows the case where the catalyst material is doped with two impurities. Optical excitation in these levels gives rise to free electrons and free holes. Obviously the cases described need roughly two photons for excitation. The photons may be of the same energies or one may be much larger than the other.

It has been demonstrated that the transitions described above are possible in solids and in particular in the titanates. (107-112) There are many reports which describe the locations and position of impurity levels (such as Fe, Co, Cr, Mn, V, Ni) relative to the bandgap in rutile and similar materials of interest. (107-111) The transition in some cases is strong and comparable in strength to bandgap excitation. (113, 114)

Ghosh and Maruska (26) have shown that water photoelectrolysis can actually be accomplished using visible light on a Cr-doped TiO_2 electrode. Their cell required a minimum bias of 0.6 V and generated a current of 0.35 mA/cm². All uv light from the Hg lamp source which could have provided band to band transitions was removed with an appropriate filter. Hydrogen and oxygen were collected at the electrodes, and the $\text{TiO}_2\text{:Cr}$ remained stable under extended illumination. Further work is in progress to find other dopants which can give stronger absorptions.

Morisaki et al., (115) have also reported photocurrents due to visible light excitation of TiO_2 , and their action spectrum showed a peak response around 800 nm. However, this photocurrent was cathodic, occurring only when the TiO_2 electrode was held at potentials more negative than the $\text{H}_2/\text{H}_2\text{O}$ level. They ascribed this response to excitation of surface states, but it should be noted that reduced TiO_2 shows optical absorption around 1 micron due to defect states (oxygen vacancies or Ti^{3+}). (116) Thus this effect could also have been a case of impurity sensitization.

10. Outlook

Assuming that we wish to use solar energy to obtain hydrogen from water by electrolysis, then the critical question is whether it is possible to find a photosensitive electrode material which will have an efficiency comparable to silicon solid state devices and yet be less expensive. It must be remembered that 4 silicon photovoltaic cells connected in series will be necessary to generate the same voltage for electrolysis as can be achieved by one photoelectrolysis electrode with a 2.2 eV band gap. By counting the number of AM1 sunlight photons which can be absorbed by a material with a 2.2 eV band gap (assumed to be direct so that the absorption constant increases rapidly with wavelength after the absorption edge), we can calculate a maximum photocurrent of 11 mA/cm² (117). The total available solar power at

AM1 is 100 mA/cm^2 , so that the maximum sunlight conversion efficiency for a photoelectrolysis cell may be calculated as

$$\eta = \frac{1.47I}{P_L} = 16\% \quad (31)$$

where 1.47 is obtained from the heat content per mole of hydrogen. If it would be necessary to supply a bias, for example, of 0.4 V, then the maximum efficiency would be 12%. This value compares very well to silicon, especially since only 1/4 of the area is required. Furthermore, even if silicon cells had an efficiency of 20%, a conventional electrolysis unit of 70% efficiency used in conjunction with the silicon devices would give an overall efficiency of 14%. Therefore, we do not concur with the recent conclusion of Manassen et al. (118) that technological prospects of photoelectrochemical decomposition of water is dim; at this time, we do not see a fundamental reason that high efficiencies for this process cannot be attained. But the materials problems remain formidable.

And furthermore, perhaps some attention should be given to driving chemical reactions other than water electrolysis in these solar powered cells. There are numerous organic as well as inorganic reactions that can be run at an illuminated electrode which could produce fuels. Some redox couples have already been tested (58, 119) and current multiplicated (due to combined oxidation and reduction at the same electrode) has been observed. (119) It is certainly possible that the corrosion problems exhibited by so many of the small band gap semiconductors will be relieved in a non-aqueous electrolyte.

11. Summary

Although semiconductor electrodes have been studied for a long time, the problem of photocorrosion made them of limited use in practical devices. The discovery that TiO_2 is stable in an illuminated electrochemical cell brought a great new interest to this topic. The photoelectrolysis of water

to provide the useful fuel hydrogen was shown to be possible using a TiO_2 anode. However, the efficiency of hydrogen production in sunlight has been low because TiO_2 is a poor absorber of visible light. A number of techniques for improving the response are now being tried. A number of new semiconductors with smaller band gaps, such as Fe_2O_3 , WO_3 , and p-GaP are being studied. Dye sensitization has only received limited attention, but decomposition problems have again occurred. Formation of heterostructures between stable wide band gap materials and corrosion-prone small band gap semiconductors needs further work, as does the area of increasing the visible light response through impurity doping.

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Table I

Semiconductors Tested as Electrodes for Photodecomposition of Water

Material	Bandgap E_g	Flatband Potential vs. Hydrogen	Highest Q.E. of Carrier Generation(%)	Remarks	Reference
TiO_2	3.0	0.05	100	Stable	22-24, 26-31, 36, 40, 82
$SrTiO_3$	3.2	-0.2	100	Stable	32-34, 40
$BaTiO_3$	3.3	0.1	30	Stable	66-68, 40
$KTaO_3$	3.5	-0.2	6	Stable	71
$FeTiO_3$	2.2	1.1	15	Leaching of Fe atoms noted	79
$Pb(La)TiO_3$	3.0	-	-	Too resistive	66
$Pb(La,Zr)TiO_3$	2.9	-	High?	Too resistive	66
Fe_2TiO_4	2.1	1.2	15	Leaching of Fe atoms noted	79
Fe_2TiO_5	2.2	1.5	15	Stable	79
$BaTi_{1-x}Fe_xO_{3-x}$	2.8	-	-	Photoresponse quenched	68
Fe_2O_3	2.2	0.7	40	Stable at pH >6	76-77, 82
Cu_2O	2.2	-	-	Corrodes	88
CuO	1.7	1.0	-	Corrodes	82
WO_3	2.7	0.5	100	Stable at low pH	73, 74, 75, 40
ZnO	3.2	0	-	Corrodes	14, 19
SnO_2	3.5	0.5	100	Stable	69, 70
SiC	3.0	-1.3	-	Corrodes	72
V_2O_5	2.75	1.2	-	Corrodes	82
PbO	2.8	0.45	-	Corrodes	82
Bi_2O_3	2.8	0.7	-	Corrodes	82
$YFeO_3$	2.6	0.5	1	Stable	80

Table I (Continued)

Material	Bandgap E _g	Flatband Potential vs. Hydrogen	Highest Q.E. of Carrier Generation(%)	Remarks	Reference
Cr_2O_3	1.4	-	-	Corrodes, poor response	82
CoO	0.5	0.8	-	Corrodes, poor response	82
CdO	2.3	-	-	No response	82,40
MnO_2	0.3	-	-	No response	82
SrO	5.7	-	-	No response	82
Si	1.1	-0.7	-	Corrodes	84,85
InP	1.3	-0.2	-	Corrodes	101
GaAs	1.4	-0.5	-	Corrodes	101
GaP	2.2	-1.0	-	n-type corrodes, p-type stable	39
CdS	2.4	-0.5	-	Corrodes	86,88
CdSe	1.7	-0.2	-	Corrodes	88
ZnSe	2.6	-	-	Corrodes	88
CdFe_2O_4	2.3	0.8	-	Poor response but stable	40
$\text{PbFe}_{12}\text{O}_{19}$	2.3	1.0	-	Stable at high pH	40
$\text{Pb}_4\text{Ti}_3\text{WO}_{13}$	2.4	0.4	-	Stable at high pH	40
$\text{Hg}_2\text{Ta}_2\text{O}_7$	1.8	1.2	-	Stable	40
$\text{Hg}_2\text{Nb}_2\text{O}_7$	1.8	1.1	-	Stable	40
ZrO_2	5.0	-1.0	-	Stable	81
Ta_2O_5	4.0	-0.4	-	Stable	81
Nb_2O_5	3.4	0	-	Stable	81

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- Figure 7. Energy relationships in devices using both n- and p-type materials.
- Figure 8. Best fit of experimental quantum efficiency data for undoped and Al-doped TiO_2 to the theoretically developed response curves based on diffusion length and barrier width (Ref. 26).
- Figure 9. Possible absorption processes due to dopant impurities in a material such as TiO_2 ,

Figure 1. A Semiconductor electrode in contact with a solution containing a redox couple R/O .

Figure 2. Current-voltage characteristics of an n-type semiconductor electrode, in the dark and under illumination.

Figure 3. Typical current-voltage characteristics for an n-type TiO₂ electrode in 5M KOH, both in the dark and illuminated.

Figure 4. Details of the current-voltage characteristics of illuminated TiO₂ and SrTiO₃ electrodes in the potential region of the H₂/H₂O redox couple (5M KOH solution).

Figure 5. Energy level diagrams for TiO₂ and SrTiO₃ photoelectrolysis cells in the dark and under illumination.

Figure 6. Energy relationships for an illuminated semiconductor electrode in contact with a solution.

Figure 7. Energy relationships in devices using both n- and p-type materials.

Figure 6. Best fit of experimental quantum efficiency data for undoped and Al-doped TiO_2 to the theoretically developed response curves based on diffusion length and barrier width (Ref. 26).

Figure 9. Possible absorption processes due to dopant impurities in a material such as TiO_2 ,

3. PREPARATION, TESTING AND EVALUATION OF DOPED ELECTRODES

3.1. Introduction

TiO_2 and SrTiO_3 have not proved useful in practical water photo-electrolysis cells because they can only absorb a very limited portion ($\lambda < 400\text{nm}$) of the solar spectrum. However, these two materials have been shown to be highly efficient at converting ultraviolet light to chemical energy (1). It should be possible to improve the situation for these wide band gap semiconductors by incorporating substituant atoms into the lattice which can absorb visible light. In effect, this requires introducing either deep donor or deep acceptor levels into these wide band gap semiconductors, levels that are located at least 0.5 eV from the band edges. Such impurity levels would then be able to absorb light of wavelengths as long as 500 nm, and thus the electrodes should respond to about 30% of the incident solar radiation.

It is known that visible light absorption can be induced in the titanates by the introduction of transition metal impurities. For example, Faughnan (2) has reported very high oscillator strengths f for optical transitions in the visible portion of the spectrum with a number of transition metals incorporated in SrTiO_3 . He measured $f(\text{Fe})=0.4$, $f(\text{Ni})=0.25$ and $f(\text{Mo})=0.1$, while the strength of the intrinsic band-to-band absorption in SrTiO_3 is 0.2. Since the optical absorption constant α is directly proportional to f , it should be possible to obtain significant visible light absorption in TiO_2 and SrTiO_3 doped with various transition metals. The specific transition metals that we have chosen for study are V, Cr, Mn, Fe, Co and Ni. We also used Al since our earlier study (1) had shown that this dopant leads to an increased minority carrier diffusion length in TiO_2 .

It is interesting to note that adding dopants to wide band gap semiconductors such as TiO_2 and SrTiO_3 may have the beneficial effect of increasing the visible light response without also increasing the electron affinity (and hence, the bias requirements). This effect will be discussed in more detail later.

3.2. Experimental

All of these samples were single crystals grown by the flame fusion technique, purchased from NL Industries. The dopants were added to the starting TiO_2 or SrTiO_3 powder in the form of their oxides. Concentrations of dopants were specified in the range of 0.05-0.5 wt.%. At high dopant concentrations the crystals were found to be badly cracked, so higher impurity levels are not possible (for crystals grown in this manner). Slices 1 mm thick were cut from these crystals with a diamond saw. These slices were individually heated in an rf furnace in flowing hydrogen (1 l/min) for one hour at either 600°C for TiO_2 or 950°C for SrTiO_3 , to make them conducting. The samples were then polished with alumina paste only on the back side, to facilitate contacting them with indium. Previous experience has shown that polishing the front surface (the one which contacts the electrolyte) diminishes the photoresponse. A copper wire was bonded to the indium contact of each slice, and then the entire electrode, except for the front surface, was coated with epoxy.

Cells consisted of a pyrex dish filled with 5M KOH electrolyte, an appropriate holder for the doped TiO_2 electrode, a platinum-black counter electrode, and a reference saturated calomel electrode. The solution was thoroughly purged with flowing nitrogen during operation.

Samples were illuminated with either of two light sources, a Schoeffel 200 W Mercury Lamp, or a Bausch and Lomb 150 W Xenon Lamp outfitted with a grating monochromator. Special filters, designed for use with the Mercury Lamp, allowed an unambiguous differentiation between photocurrents due to band-to-band (intrinsic) absorption and impurity absorption. These filters were 4 mm thick polished slabs of undoped TiO_2 and SrTiO_3 . When the appropriate filter was placed between the light source and any undoped electrode, no photocurrents were measured, proving that the filter was capable of removing all photons with energy equal to or greater than the band gap. Therefore, when photocurrents were observed from doped electrodes when the filter was in place, we were confident that they resulted only from excitation of the dopants.

Photocurrents were measured with a Kiethley 610C electrometer. Bias voltages were supplied from a Hewlett-Packard 6216A power supply. Data was recorded on a Hewlett-Packard 7004B X-Y recorder. Electrochemical measurements were performed with a combination of Princeton Applied Research 173 potentiostat and 175 signal programmer.

3.3. Results and Discussion

3.3.1a. Visible light response of doped electrodes

The addition of transition metal dopants did indeed provide visible light absorption in TiO_2 and SrTiO_3 crystals. Crystals of undoped TiO_2 and SrTiO_3 in the fully oxidized state are transparent, while the doped samples were dark brown in color. The optical absorption spectra of undoped and Cr-doped TiO_2 are compared in Figure 1. For another example, the optical absorption spectrum of Mn-doped TiO_2 is shown in Figure 2. The structureless

absorption spectra of the dopants extend from the intrinsic absorption edge of TiO_2 at 415 nm, across the entire visible spectrum, although with monotonically decreasing intensity. The absorption spectra due to V, Fe, Co and Ni impurities were equivalent in shape and intensity to the Cr and Mn spectra. Al doping did not affect the absorption spectrum.

When undoped titanate wafers are reduced in hydrogen, they become blue-black in color, although this absorption in the red will not give any photocurrent. In a similar manner, the doped wafers all became black after the hydrogen heat treatment, so that it was not possible to measure the absorptions due to impurities after reduction. It is certainly possible that the absorptions of the dopants will be different for crystals in the oxidized and in the reduced states, as we shall discuss subsequently.

Significantly, though, photocurrents were found as a result of visible light excitation for some of the dopants, viz., Cr, Mn and Fe. The action spectra in the visible region for Cr and Mn in TiO_2 are shown in Figure 3. The photocurrents at wavelengths greater than 415 nm have the same structureless, monotonically decreasing shape as the absorption spectra measured for the fully oxidized samples. The visible light responses of Mn and Cr in SrTiO_3 were found to be quite equivalent to those shown in Figure 3 (with a shift in absorption edge wavelength, of course).

The photocurrent generated when visible light was used on Cr-doped TiO_2 proved large enough to allow the observation of the generation of hydrogen and oxygen. The filter described in the experimental section was used to select the visible component of the 200 W Mercury light spectrum, and the observed photocurrents were 0.3 mA/cm^2 with Cr-doped TiO_2 and 0.06 mA/cm^2

with Mn-doped TiO_2 . Only about $2\mu \text{ A/cm}^2$ was generated with Fe-doped TiO_2 . No photocurrents were found with V, Ni- or Co-doped TiO_2 samples using visible light excitation. The fact that hydrogen and oxygen generation was observed with visible light excitation of Cr-doped TiO_2 shows conclusively that the hole and the electron, produced in this material by the light, are mobile and are transported to the surfaces as required. The current-voltage characteristics for a representative Cr-doped TiO_2 electrode are shown in Figure 4. Again, similar properties were found for Cr and Mn in SrTiO_3 .

There is an interesting difference in the response times observed for those dopants which showed photocurrents with visible light (Cr, Mn and Fe). With Cr-doped TiO_2 , the rise time is much less than 1/4 sec (instrument limited), as shown in Figure 5, while with Mn-doped TiO_2 , the rise time is 70 sec, as shown in Figure 6. The response of Fe-doped TiO_2 is also slow (approximately 1 min.). Very slow response times are characteristic of deep traps; after the traps are filled, the full photocurrent is achieved. When the light is turned off, the deep traps are slowly thermally emptied, resulting in currents long after cessation of excitation. Notice in Figure 6 that there is an initial jump in photocurrent, both when the light is turned on and when it is turned off. This rise time, which is less than 50 msec, (again instrument limited), may be the minority carrier lifetime. These results suggest that the excited states for Mn and Fe may lie below the conduction band, accounting for the poor photocurrents seen with these dopants.

3.3.2 UV Light Response of Doped Electrodes

The addition of dopant impurities to the titanates was found to have major effects on the uv response of such electrodes. Action spectra for undoped, Al-doped, and Cr-doped TiO_2 electrodes are shown in Figure 7. The spectrum of $\text{TiO}_2\text{:V}$ is shown in Figure 8, that of $\text{SrTiO}_3\text{:Cr}$ in Figure 9, $\text{SrTiO}_3\text{:Mn}$ in Figure 10, and $\text{SrTiO}_3\text{:Fe}$ in Figure 11. Although the action spectra of all TiO_2 samples became flat at wavelengths shorter than 340 nm, some were already flat at 380 nm. SrTiO_3 spectra became flat below 320 nm. This difference is attributed to variations in minority carrier diffusion length. The influence of minority carrier diffusion length on device performance can be described as follows. The photoelectrode is considered to behave in an analagous fashion to a metal-semiconductor Schottky barrier, with a barrier region (electric field region) in the vicinity of the surface, and a bulk (field free) region. Electron-hole pairs are separated by the field in the barrier region, and with the n-type titanates the holes are driven to the interface with the solution where they can oxidize water, while the electrons are collected at the back contact and applied to the counter-electrode, where they produce hydrogen. Thus, the photocurrent will have two components, one due to carriers generated by light absorbed in the barrier, which are immediately separated, and the other due to carriers generated by light absorbed in the bulk, which must diffuse to the barrier region to be separated. Long wavelength light (in the case of TiO_2 , light with wavelengths around 400 nm, while with SrTiO_3 , light with wavelengths around 385 nm) will penetrate deep into the sample bulk, because the absorption constant for such light is low. Carriers produced by this light must diffuse to the barrier. The fraction of these carriers that

does not recombine and thus is collected will depend on the minority carrier lifetime, and hence on the diffusion length. In this way, it is possible to obtain the minority carrier diffusion length by studying the long wavelength response of the cells.

Let us calculate the photocurrent that will flow in a photo-electrolysis cell. Consider monochromatic incident light with N photons/cm², for which the material absorption constant is α , and where Q is the number of carrier pairs produced for each absorbed photon. Then the number of photogenerated carriers produced within dx at a distance x from the solution-semiconductor interface is proportional to

$$QN\alpha \exp(-\alpha x) dx \quad (1)$$

The carriers produced in the bulk, at a distance x from the surface, will have a fraction proportional to

$$\exp(-(x-l_b)/L) \quad (2)$$

diffuse to the edge of the barrier region, where l_b is the width of the barrier region and L is the diffusion length. The others will recombine and be lost; it is assumed here that recombination in the barrier region may be neglected. Then the total number of holes contributing to the current is given by

$$p = QN \int_0^{l_b} \alpha \exp(-\alpha x) dx + QN \int_{l_b}^{\ell} \alpha \exp(-\alpha x) \exp[-(x-l_b)/L] dx, \quad (3)$$

where ℓ is the thickness of the semiconductor. The first term accounts for carriers generated in the barrier region, and the second term is for carriers from the bulk. Therefore, the total photocurrent is given by

$$J = qNG \left[[1 - \exp(-\alpha l_b)] + \frac{\alpha}{\alpha + \beta} \exp(\beta l_b) \{ (\exp(-(\alpha + \beta) l_b) - (\exp(-(\alpha + \beta) l)) \} \right]. \quad (4)$$

Here J is the photocurrent/cm², and $\beta = 1/L$. G is a factor related to the quantum efficiency Q , the photoconductive gain in the barrier region, and to the process governing the transport of holes across the interface.

By using the known absorption spectra of TiO₂ (3) and SrTiO₃ (4), we have been able to calculate from equation (4) the action spectra for photoelectrodes having various diffusion lengths from 0.1 to 10 microns (assuming $l_b = 1000$ Å). These curves are compared with our experimental data for TiO₂ in Figure 12. It can be seen that Al doping, while providing no increase in visible light absorption, gives the longest minority carrier diffusion length of 8 microns. Typically, undoped TiO₂ (not shown) has $L = 1$ micron. On the other hand, Cr-doping, which provides the best visible light response, lowers the diffusion length to 0.2 micron. The dopants Mn and Fe give values of 1-2 microns. The calculated diffusion lengths for all of the dopants in both TiO₂ and SrTiO₃ are given in Table 1.

Notice that in Figure 12, all the responses have been normalized so that $J/qNG = 80\%$. However, the maximum value of this efficiency factor actually varies widely for the different dopants, as shown in Figure 13, and in just the same way as the diffusion lengths varied. Therefore, although Cr is the most effective dopant for extending the response into the visible portion of the spectrum, it also induces the largest reduction in the uv response. Al doping, while not contributing to the visible light response, is most instrumental in improving the uv response. We have reported earlier (1) that we have measured conversion efficiencies of 1.3% (light of hydrogen) in actual 100 mW sunlight with Al-doped TiO₂ electrodes. Again, results with SrTiO₃ are comparable.

One might consider using both Al and Cr as dopants in the same crystal. We have tried this, as shown in Figures 12 and 13, and the results are intermediate. Perhaps further work along the lines of dopant combinations could lead to maximum values of uv and visible response in the same electrode.

3.3.3 Photoconductive Gain in the Electrodes

At this point, it is instructive to question whether there is a correlation between the maximum collection efficiency in the short wavelength region and the diffusion length. Specifically, let us consider the results with TiO_2 . For $\lambda < 340 \text{ nm}$, all of the light will be absorbed within the barrier region, because then $\alpha > 10^5 \text{ cm}^{-1}$. Under these circumstances, we may calculate the photocurrent as follows:

$$J = q\phi \frac{\tau}{T_b} \quad (5)$$

where ϕ is the carrier generation rate, τ is the lifetime, and T_b is the time required to transit the barrier region under the influence of the electric field. This is just the standard definition of photoconductive gain. Now, if the potential across the barrier region is V and the carrier mobility is μ , then

$$T_b = \ell_b^2 / V\mu. \quad (6)$$

Thus,

$$J = q\phi\tau \frac{V\mu}{\ell_b^2} \quad (7)$$

But the lifetime τ is related to the diffusion constant D by

$$\tau = L^2/D, \quad (8)$$

and

$$D = \mu kT/q, \quad (9)$$

so that

$$\tau = qL^2/\mu kT. \quad (10)$$

Substituting,

$$J = \frac{q\phi qL^2 V\mu}{\mu kT \ell_b^2} \quad (11)$$

and rearranging

$$J = \left(\frac{qV}{kT}\right) \left(\frac{L}{\ell_b}\right)^2 q\phi. \quad (12)$$

Under the conditions at which the cells are operated, $qV/kT \approx 40$, so that the gain is less than unity only if $L < \ell_b/6$. This means that if $L = 1$ micron, which is typical for most samples, then $\ell_b > 6$ microns, which is much larger than expected. Both from capacitance measurements and from curve-fitting to equation (4), we have concluded that ℓ_b is of the order of 0.1 micron. There appear to be two possible explanations for the fact that various samples show different collection efficiencies, although our calculations indicate that the photoconductive gain should be unity for all devices. First, the lifetime (and hence the diffusion length) may be different in the barrier than in the bulk. The fermi level lies much farther below the conduction band in the barrier region than in the bulk, and this can uncover recombination centers introduced by the dopants. Such recombination centers will reduce the lifetime.

Another possibility is that the dopants are responsible for introducing surface recombination sites which compete with the charge transfer reaction to the solution. If indeed the lifetime is different in the barrier due to recombination centers, so that $L < \ell_b/6$, then increasing V should increase the collection efficiency, according to equation (12). Therefore, we have measured the dependence of collection efficiency on applied bias for TiO_2 samples doped with Cr, Mn, and Al, as shown in Figure 14. With Al dopant, saturation is reached after 0.4V, while with Cr dopant saturation is still not seen even at 1.2V, which gives support to our explanation.

3.3.4 Photoresponse of Semi-Insulating $\text{TiO}_2\text{:Cr}$

Studies of electrochromic (5) and photochromic (2) processes in titanates have shown that the oxidation state of the dopant is quite important in determining the strength of the light absorption due to that dopant. For example, it was shown that Ni^{2+} results in a "clear" crystal of SrTiO_3 with no visible light absorption, while Ni^{3+} , the oxidized state, gives a brown coloration. All of our tests on doped titanates had involved reduced and therefore highly conducting samples. A test was made with an oxidized crystal of chromium-doped TiO_2 . A slice 200 microns thick was cut from a boule, and the resistivity was measured to be $3 \times 10^7 \Omega\text{-cm}$. This resistivity is considerably lower than that found for "undoped" TiO_2 , which is normally about $10^{12} \Omega\text{-cm}$, but it is not unexpected because if a dopant has a lower oxidation state than +4 in TiO_2 (Cr is +3), then oxygen vacancies will form to afford charge compensation. If the electrons from the donors (oxygen vacancies) are shallow and are thermally promoted into the conduction band, then the resistivity will be reduced.

The photoresponse of semi-insulating $\text{TiO}_2\text{:Cr}$ is compared with the spectrum of reduced $\text{TiO}_2\text{:Cr}$ in Figure 15. There is considerably more response at long wavelengths in the insulating sample, as we might expect from the discussion above. Thus, for example, the strength of response at 400 nm has decreased to only 1/2 of the maximum in the semi-insulating TiO_2Cr , while it decreases to only 1//10 of the maximum in the conducting material. On the other hand, though, the maximum response in the semi-insulating sample is only 1/100 that found for conducting crystals. It would be very advantageous to find a way, perhaps by adding other dopants, to retain in conducting TiO_2 the same oxidation state of Cr which occurs in the semi-insulating case. The difference in response between conducting and insulating titanates will be more fully discussed in Section 4.

3.3.5 Electron Affinity and the External Bias Requirement

An alternative to the use of dopants for extending the response of various wide band gap oxide semiconductors such as TiO_2 into the visible portion of the spectrum would be to choose other oxides with smaller band gaps. There are a number of other elements that form oxides with smaller band gaps, such as Fe, Pb or Hg. We must restrict ourselves to oxides because other anions (i.e., S, Se, Te, As, P) form semiconductors which corrode in photoelectrolysis cells. Of course, we are not considering oxides which show metallic conductivity. In Table II, we present a list of 20 oxides which have already been tested in photoelectrolysis cells, along with their band gaps and the minimum bias requirement for cell operation. This bias corresponds to the difference between the flat band potential of the semiconductor and the potential of the $\text{H}_2\text{O}/\text{H}_2$ redox level; a negative value indicates that the flat band potential lies above $\text{H}_2\text{O}/\text{H}_2$ and no bias is required. It is readily apparent from this table that the sum of the band gap + the minimum external bias = 3.2 eV

(within 10%) for all of these materials. Recall that the standard potential of the H^+/H_2 redox level is located 4.5eV below the vacuum level. Thus, we may conclude that the valence band for any of these oxides is composed mainly of oxygen 2p states and lies roughly 7.5eV below the vacuum level at $pH = 0$. In other words, the removal of an electron to vacuum from the valence band of these semiconductor oxides in contact with water at $pH = 0$ requires about 170,000 cal. (Changing the pH of the solution does not alter the basic argument because the potentials of all of the levels shift by the factor $-.059 \text{ pH}$.) We should note that oxides of group I elements of the form M_2O may not follow this rule because of cation shielding (twice as many cations as oxygen), as evidenced by Cu_2O (6). But certainly all the oxides of the alkali metals are water soluble and thus of no interest. Furthermore, Cu_2O is p-type (thus it acts as a cathode), and is known to corrode (7). Also Ag_2O is known to decompose spontaneously when exposed to light (8). Au_2O is not only unstable, it is unrealistically expensive.

Now here is the problem with oxide semiconductors as seen from the table. First, since the OH^-/O_2 level is located only 5.7eV below vacuum, we always appear to be faced with an "over voltage" of 1.8V, which is energy entirely lost. That is, the optically generated holes are produced with 1.8eV more energy than required to oxidize OH^- . And second, if the band gap is decreased by changing cations, so that more solar energy is absorbed, then the bias requirement appears to always increase. Changing cations essentially serves only to alter the location of the conduction band. When $V_b > 1.2V$, the efficiency is by definition 0, and one might as well take the apparatus indoors and perform conventional electrolysis. The table indicates that there is a trade off between solar absorption and bias

requirement. Approximately 1.8eV is lost as a combination of photons which are not absorbed and in extra energy required from an external source.

If indeed certain oxides are the only semiconductors that will remain stable in water photoelectrolysis cells, and if the valence bands of the stable oxides all lie 7.5eV below vacuum, then one possible solution to the problem would be to develop a technique for altering the electron affinities of the oxides. Of course, if such a technique were uncovered, it certainly must not render the oxides less stable or lead to a suppression of hydrogen and oxygen generation. Basically, then, we would want an oxide semiconductor with a small enough band gap to be a good absorber of sunlight, and for which we have decreased the electron affinity sufficiently to allow hydrogen generation without the need for an external bias.

However, some wide band gap oxides such as SrTiO_3 already have a small electron affinity and require no bias for operation in photoelectrolysis cells. We have now demonstrated that the inclusion of dopants, especially chromium, allows the absorption of visible light by SrTiO_3 and TiO_2 (it has the same effect as reducing the band gap would). But now we have generated positive holes at a potential closer to the OH^-/O_2 level, because the impurity states are located above the valence band, while still producing the electrons in a conduction band situated appropriately for hydrogen reduction. Thus impurity doping appears to be a way of overcoming the problem of maintaining a proper electron affinity (to keep the external bias at a minimum) while increasing visible light absorption in wide band gap oxides such as SrTiO_3 . The process is illustrated in Figure 16, wherein the energy levels are compared for a doped wide band gap oxide and a smaller band gap oxide.

3.4 Conclusion

We have demonstrated in this study that the properties of TiO_2 and SrTiO_3 photoelectrodes can be markedly altered by the introduction of transition metal and aluminum dopants. Even though the magnitude and shape of the visible portions of the absorption curves found for the dopants V, Cr, Mn, Fe, Co, and Ni are similar, the optical transitions involved in these absorption spectra must be substantially different. One might speculate that since the absorption spectra are similar, the absorption is not specific to the individual dopants but rather a manifestation of disorder in the lattice introduced by the dopants. The absorption in the visible would then be a tailing of the band gap absorption, caused by localized electric fields at the impurities, which result in band bending on a small scale. Such band bending can allow virtual transitions at less than band gap energies to be followed by quantum mechanical tunnelling to conduction band states at lower energies a short distance away (the Franz-Keldysh Effect) (9). But this explanation is inconsistent with the photocurrent data, which showed steadily decreasing photocurrents with dopants chosen across the fourth row of the periodic table. If the Franz-Keldysh Effect were responsible for the visible light absorptions, then equal photocurrents should be encountered for all dopants. The absorptions for Fe, Co, and Ni, which result in little or no photocurrents, may involve d-d transitions localized at the impurity atom, resulting in no free carriers. The Mn absorption involves a deep level, since the response time is very slow. The best visible light photocurrents were observed with Cr, so this absorption must involve efficient transitions which result in free carriers. But conversely, the Cr centers also provide efficient recombination levels which reduce the uv response. The response of V is

anomalous, in that the diffusion length is lowered, while visible light response is not gained. The dopants with low visible light response do not affect the uv response, as one might expect. Further work is needed to ascertain if certain combinations of dopants can be found which will allow us to tailor an electrode to our specifications of good visible and uv response, as well as long term stability and operation without a bias. Our initial results have shown that combining Al and Cr dopants leads to improvements in both the responses, but so far, these improvements have not been great enough to allow us to assemble a practical device. However, it is significant that the photoelectrolysis of water has been accomplished using only visible light on a cell with a stable semiconductor anode, Cr-doped TiO₂.

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Table 1

MINORITY CARRIER DIFFUSION LENGTH IN TiO_2
AND SrTiO_3 DOPED WITH THE TRANSITION METALS

Transition metal dopant	V	Cr	Mn	Fe	Co	Ni	(Al)	
Diffusion length in TiO_2	0.1	0.2	1	2	2	2	8	Microns
Diffusion length in SrTiO_3	-	0.1	0.2	1	-	-	-	Microns

TABLE II

Band gap and minimum bias requirement for oxide anodes in water photo-electrolysis cells.

<u>Material</u>	<u>E_g (eV)</u>	<u>qV_b^* (eV)</u>	<u>$E_g + qV_b$ (eV)</u>	<u>Reference</u>
Ta ₂ O ₅	4.0	-0.4	3.6	10
SnO ₂	3.5	0	3.5	11
KTaO ₃	3.5	-0.2	3.3	12
Nb ₂ O ₅	3.4	0	3.4	10
BaTiO ₃	3.3	-0.1	3.2	11
SrTiO ₃	3.2	-0.2	3.0	13,14
ZnO	3.2	0	3.2	15
TiO ₂	3.0	+0.1	3.1	13,16,17
PbO	2.8	+0.4	3.2	18
Bi ₂ O ₃	2.8	+0.7	3.5	18
WO ₃	2.7	+0.5	3.2	18
YFeO ₃	2.6	+0.5	3.1	19
Pb ₂ Ti ₃ WO ₁₃	2.4	+0.4	2.8	11
CdFe ₂ O ₄	2.3	+0.8	3.1	11
PbFe ₁₂ O ₁₉	2.3	+1.0	3.3	11
Fe ₂ O ₃	2.2	+0.7	2.9	18
FeTiO ₃	2.2	+1.1	3.3	20
Fe ₂ TiO ₄	2.1	+1.2	3.3	20
Hg ₂ Ta ₂ O ₇	1.8	+1.2	3.0	20
Hg ₂ Nb ₂ O ₇	1.8	+1.1	2.9	11

*Flat band potential vs H₂/H₂O at pH = 14.

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- Figure 13. Measured quantum efficiency of TiO_2 electrodes with various dopants.
- Figure 14. Dependence of the quantum efficiency on applied bias for TiO_2 electrodes with various dopants.
- Figure 15. Comparison of the photoresponse spectra of semi-insulating and hydrogen-reduced $\text{TiO}_2\text{:Cr}$ photoelectrodes.
- Figure 16. Comparison of the location of relevant energy levels for a small band gap oxide (such as Fe_2O_3) and doped SrTiO_3 , when illuminated with visible light.

FIGURE 1

OPTICAL ABSORPTION OF UNDOPED
AND Cr-DOPED TiO_2

Figure 2. Optical absorption of Mn-doped TiO_2 .

FIGURE 3

PHOTOCURRENTS WITH Cr-DOPED TiO_2 AND Mn-DOPED TiO_2
IN THE VISIBLE PORTION OF THE SPECTRUM

FIGURE 4

CURRENT-VOLTAGE CHARACTERISTICS
OF A Cr-DOPED TiO_2 CELL

Figure 5. Response of Cr-doped TiO_2 illuminated with visible light.

Figure 6. Response of Mn-doped TiO₂ illuminated with visible light.

FIGURE 7

QUANTUM EFFICIENCY OF TiO_2 ELECTRODES
IN A DIFFERENTIAL CELL WITH $\Delta\text{pH}=13$

Figure 8. Photoresponse spectrum of vanadium-doped TiO_2 .

Figure 9. Photoreponse spectrum of chromium-doped SrTiO₃.

Figure 10. Photoresponse spectrum of manganese-doped SrTiO₃.

Figure 11. Photoresponse spectrum of iron-doped SrTiO₃.

Figure 12. Theoretical action spectra for TiO_2 Schottky barrier devices compared with experimental results found for various dopants.

Figure 13. Measured quantum efficiency of TiO₂ electrodes with various dopants.

Figure 14. Dependence of the quantum efficiency on applied bias for TiO_2 electrodes with various dopants.

Figure 15. Comparison of the photoresponse spectra of semi-insulating and hydrogen-reduced $\text{TiO}_2:\text{Cr}$ photoelectrodes.

FIGURE 16

COMPARISON OF THE LOCATIONS OF RELEVANT
ENERGY LEVELS FOR A SMALL BAND GAP OXIDE
(SUCH AS Fe_2O_3) AND DOPED SrTiO_3 , WHEN
ILLUMINATED WITH VISIBLE LIGHT

4. PREPARATION, TESTING AND EVALUATION OF HETEROSTRUCTURE ELECTRODES

4.1 Introduction

We discussed above the difficulties that are encountered with water photoelectrolysis electrodes. It is now well known that all semiconductor materials which have been evaluated in various studies as potential candidates for photoelectrolysis electrodes suffer from one or more of the following problems:

- Poor sunlight absorption
- Corrosion
- External bias requirement

TiO₂ and SrTiO₃ electrodes do not undergo corrosion, but they are not good absorbers of sunlight. Our attempts to sensitize TiO₂ to visible light with transition element dopants have thus far not met with great enough success, because the dopants we have used have not provided strong enough absorptions, due to solubility constraints. Thus no single material is available at this time which can perform satisfactorily in a cell. It appears that a good way to tackle the problem of finding a suitable electrode would be to form composite structures which can combine the useful features of various materials. Such heterostructures must be chosen so as to overcome the defective properties of the individual members.

Heterostructure electrodes consist of a composite of two materials which have been selected to give good sunlight absorption while providing stability against corrosion. The basic criterion for formulating a heterostructure electrode is to start with a material which possesses good sunlight absorption characteristics. Obviously, if the available solar energy is not absorbed, there can be no photocurrent. Therefore, one member of

any heterostructure should have a small enough band gap to absorb a significant portion of the incident solar flux. However, the band gap cannot be too small. We have shown (1) that even though the thermodynamic equilibrium potential for the water splitting reaction is 1.2V, considerations of loss mechanisms such as band-bending, series resistance, and electrode surface over-voltages will require that a semiconductor have a band gap of about 2eV, in order that the optically generated holes and electrons have sufficient energy for the process. Therefore, we have concentrated our efforts on heterostructures involving CdS, CdSe, and ZnTe. The second member of each of the heterostructures was chosen to guard against corrosion, and candidates included SrTiO_3 , TiO_2 , SnO_2 , and Al_2O_3 .

There have been two major reports in the literature on the formation of heterostructure electrodes consisting of small band gap sunlight absorbers plus wide band gap stabilizers. Kohl, Frank and Bard (2) used chemical vapor deposition to form thin films of n-type TiO_2 on n-Si, p-Si, n-GaAs, p-GaAs, n-GaP, n-InP, and n-CdS. For the n-n heterostructures, durable crack and hole-free coats of TiO_2 were only formed on Si and InP, while the structures based on GaAs, GaP, and CdS were not coherent. The n-Si/n- TiO_2 and n-InP/n- TiO_2 heterostructures only showed a wavelength response attributable to the TiO_2 portion of the composite. The authors concluded that holes generated in the Si or InP were not injected into the TiO_2 due to a barrier in the valence bands. Crack and hole-free composites of p-Si/n- TiO_2 and p-GaAs/n- TiO_2 were also formed by Kohl et al. (2), while the other heterostructures involving p-GaP/n- TiO_2 were not coherent. Once again, with the coherent samples, only a response due to the TiO_2 was observed. This again indicated a barrier in the valence band.

On the other hand, samples that showed holes and cracks in the TiO_2 film exhibited photocurrent responses characteristic of the small band gap member. But this current was found to be the result of corrosion processes. After some time, the TiO_2 films floated off from the substrates, and the photocurrents decayed as the corrosion proceeded. Thus, the solution had entered the cracks and pin holes and came into contact with the small band gap member.

Another report on heterostructures has been given by Tomkiewicz and Woodall (3). These workers sputtered TiO_2 , Al_2O_3 and Si_3N_4 onto GaAs and GaAlAs, and also deposited SnO_2 and Nb_2O_5 onto GaAs. They found that corrosion was not eliminated, although their films of the wide band gap materials appeared to be pin hole free. Again, significant photocurrents were only found when light was used which had a short enough wavelength to excite the TiO_2 layers. Therefore, hole transport from the small band gap materials through the TiO_2 to the solution was not found. The authors maintained that these results did not preclude the possibility of finding a pair of semiconductors with proper band matching that would allow minority carrier transport through the outer film.

We have sketched simplified band diagrams for representative heterostructures, and these are presented in Figure 1. The first diagram, (a), illustrates the case where both the small and the wide band gap semiconductors are highly conducting n-type materials. All of the heterostructures described in the literature involved highly conducting materials (2,3). Here a discontinuity in the valence bands is encountered, and there is a high barrier to hold flow from the small to the large band gap material. There can be no current flow in this situation, even though charges are created by light absorbed in the inner semiconductor.

It should be possible to overcome this problem by changing the energetic location of the fermi level in the large band gap material, as illustrated in Figure 1b. When the large band gap material is made sufficiently insulating, then the fermi levels can line up so as to give a barrier in the conduction bands. This barrier does not pose a problem because electrons are transported away from it, to the rear metal contact. Of course, there is a price to pay, because now the electrons collected from the inner material at the metal contact will have energies significantly lower than H^+/H_2 redox potential in the water. It will therefore be necessary to supply an external bias to bring the electrons up to the level of the hydrogen reaction. But this can easily be done. It is only necessary to use an illuminated p-type semiconductor for the cathode, as has been described by Nozik (4) and by Bockris (5). For example, p-type GaP and p-type CdTe have been shown to be stable cathodes in photoelectrolysis cells. The limiting factor that has caused low efficiencies in all such p-n photoelectrolysis cells has been the poor performance of the illuminated anode, and not the cathode. If a heterostructure anode can give a good response, there will be no problem in finding a suitable semiconductor cathode to add bias to the cell.

For laboratory purposes, the bias can be supplied by an external battery, leading to the band diagram depicted in Figure 1c. Here we expect that the insulating wide band gap semiconductor will be the most resistive element in the circuit, so that the entire supplied potential will be dropped across it. The band bending afforded by the bias can aid in charge separation.

We have divided our experiments on heterostructure electrodes into two areas. In the first set of experiments, we used very thin single crystal wafers of the wide band gap semiconductors SrTiO_3 and TiO_2 as the corrosion inhibitors. We were completely confident that these crystals contained no pinholes. The smaller band gap semiconductors CdS and CdSe were vacuum evaporated onto these crystals. In the second series of experiments, the stable wide band gap materials TiO_2 , SnO_2 , Al_2O_3 and Fe_2O_3 were deposited by various techniques onto the surfaces of single crystals of CdS , CdSe , ZnTe and Si .

4.2 Experimental Techniques

4.2.1 Evaporation of CdS and CdSe onto Single Crystals of SrTiO_3 and TiO_2

To avoid any problem with pin holes in the wide band gap member of the heterostructure, we used SrTiO_3 in the form of thin single crystal wafers. These wafers were sawed and polished to a final thickness of 75 microns. We noted that 75 microns may prove too thick to allow the magnitude of current flow that would be required in high efficiency devices, but it was very inconvenient at this stage to handle thinner specimens. However, we judged that if some small stable current flow could be obtained from these devices, then there would be enough interest in the structures to warrant a larger engineering effort to obtain thinner wafers.

Our electrode design is shown in Figure 2. We started with glass slides, 1" x 1 1/2" x .05", which served as mechanical supports. We had 3 mm holes drilled through the center of these slides. Polished single crystal wafers of SrTiO_3 , 3 mils in thickness, were epoxied to each glass

slide, directly over the hole. The CdS films were then evaporated onto the SrTiO_3 , followed by an indium ohmic contact. After a wire was secured to the indium, the entire back of the electrode was encapsulated with epoxy. Thus, when a finished electrode was immersed in the solution, the liquid only came into contact with the SrTiO_3 . Since these wafers were single crystals, there was no possibility of solution leaking through pin holes to contact the CdS.

It was necessary for us to spend some time developing experimental techniques for the deposition of CdS films. A Veeco Model 776 high vacuum evaporation system was acquired for this purpose. It was necessary to modify the system to suit our needs. We learned that the substrate temperature is quite critical for the formation of good CdS films. It was necessary to use a special shielded evaporation boat, sketched in Figure 3. The shields on the boat help to reduce the amount of heat that the substrate receives from the heated boat. We wanted to be able to control the temperature of the substrate with a variable heater, rather than have uncontrolled heating from the boat. We used a boat current of 180-220 amperes, and this high current requirement necessitated the fabrication of new bus bars for the apparatus. We selected $1/4'' \times 3/4''$ cross section copper bars. These bars were electroplated with nickel and then gold, because of problems with copper sulfide formation during depositions. The copper sulfide flaked off during cleanup and contaminated the seals on the main vacuum valve.

The deposition system is shown in Figure 4. The substrates were positioned 5" above the evaporation boat, on a stainless steel plate. A shutter rode in tracks directly below the plate and controlled the deposition.

A resistive substrate heater was positioned directly on top on one of the substrates, while the other one was not purposely heated. Thermocouples were held in contact with the backs of the substrates. The front (deposition) sides of the substrates were determined to be 30°C hotter than the backs. This is because the front sides also get heated by the evaporation boat.

Much trouble was encountered in depositing the CdS films. In many of the evaporations, we determined that the substrates were heated too high to allow a film to form. On the other hand, when the substrates were too cold, the deposit was very dark brownish black, almost metallic in appearance. Such deposits were too rich in excess cadmium.

The following table lists the deposition parameters for evaporation in which no film was formed on the heated substrate.

Run #12

Substrates: conducting glass

Starting Pressure: 2×10^{-7} torr

Chimney Height: 4"

(1) Degassing of boat to remove air trapped in CdS powder

(a) at 25 amps for 5 min

(b) at 45 amps for 8 min

(c) at 80 amps for 7 min

(d) at 130 amps for 7 min

(e) at 150 amps for 8 min

(2) Deposition cycle

<u>time, min</u>	<u>I, amp</u>	<u>r, Å/sec</u>	<u>thick, μ</u>	<u>p, torr</u>	<u>T(substrate), °C</u>
0	180	60	0	3×10^{-6}	175
7	180	50	-	-	-
12	180	45	3.9	-	-
16	190	50	5.0	2×10^{-6}	175

NOTE: The lower substrate surface, onto which we tried to evaporate, was at about 205°C. This temperature is too high, and the CdS failed to stick.

The problem was solved by moving the substrates 1 1/2" higher above the boat, and designing proper shielding for the boat to prevent it from heating the substrates so much. Here is a deposition which resulted in a good looking, orange film of CdS:

Run #33

Substrates: conducting glass

Starting Pressure: 1×10^{-7} torr

Chimney Height: 5 1/2"

(1) Degassing of boat to remove air trapped in CdS powder

(a) at 100A for 30 min

(b) at 140A for 25 min

(2) Deposition cycle

<u>time, min</u>	<u>I, amp</u>	<u>r, Å/sec</u>	<u>thick, μ</u>	<u>p, torr</u>	<u>T(substrate), °C</u>
0	200	65	0	1×10^{-5}	100
10	202	60	3.2	2×10^{-6}	110
20	200	50	5.1	-	107
30	200	50	8.0	2.5×10^{-6}	107
40	200	40	10.0	1.9×10^{-6}	108

NOTE: It was the heated substrate that had a good appearance. The unheated one was a very dark brown. These two deposits are illustrated in Figure 5.

The good sample from this run was tested in a photoelectrolysis cell. The action spectrum is shown in Figure 6. This is the spectrum expected for CdS. Subsequently, CdS films, as well as CdSe films, were routinely deposited onto SrTiO_3 and TiO_2 substrates.

4.2.2 Deposition of Stable Wide Band Gap Materials Onto Single Crystal Sunlight Absorbers.

These depositions were made by vacuum evaporation, rf sputtering and chemical spraying techniques. The procedures are discussed along with each of these heterostructures in the subsequent sections.

4.3 Experimental Results

4.3.1 Properties of Insulating SrTiO₃

A. Conductivity

It was necessary initially to study the properties of the SrTiO₃ substrate crystals, before heterostructure preparation, to allow meaningful comparisons of electrode characteristics. For example, the current-voltage characteristics of one of these wafers, prepared with a silver contact on each side, is shown in Figure 7. The calculated resistivity of this sample was $1.5 \times 10^{12} \Omega\text{-cm}$. Using this result, we may estimate the carrier concentration as:

$$n = (\rho e \mu)^{-1} = 5 \times 10^6 \text{ cm}^{-3},$$

assuming $\mu = 1 \text{ cm}^2/\text{V-sec}$. Using this result, the position of the fermi level may be estimated from:

$$n = N_c e^{-(E_c - E_f)/kT}$$

Taking $N_c = 10^{20} \text{ cm}^{-3}$, then E_f lies 0.8 eV below the conduction band.

We may now estimate how the bands in CdS and SrTiO₃ may be expected to align at the heterojunction. The electron affinity of CdS is 4.5 eV (6) and the electron affinity of SrTiO₃ is 3.7 eV (7), while the band gaps are, respectively, 2.4 and 3.2 eV. Therefore, both materials should have their valence bands situated 6.9 eV below vacuum level. Then, if the CdS is quite conducting, so that its fermi level is located close to the conduction band, there should not be any barrier between the valence bands, and the heterojunction should look approximately as follows:

If this is the case, then a small bias which makes the SrTiO_3 negative with respect to the CdS will allow the collection of photogenerated holes from the CdS.

B. Photoresponse

A photoelectrolysis cell was set up, consisting of an unilluminated Pt electrode, a 5M KOH solution, and an insulating SrTiO_3 crystal with a Ag back contact. The photoresponse spectrum of this type of cell is shown in Figure 8. Here also is presented a typical action spectrum for highly conducting ($\rho < 1 \Omega\text{-cm}$) SrTiO_3 . The difference between the two spectra is quite unmistakable. Although both curves rise comparably at longer wavelengths, from 430 to 385 nm, the response of the insulating material then drops abruptly, while that of the conducting material exhibits a peak with a half-width of only about 20 nm. It is notable that both of the cells had quantum efficiencies of 1% at 387 nm. This fact appears to indicate that the response of the insulating electrode is only the normal response expected at longer wavelengths, and not some new effect at wavelengths below the absorption edge, such as an excitonic effect.

The peak shown in Figure 8 can be observed in the photovoltaic mode, i.e., with no applied bias. This fact indicates that there must be band bending at the $i\text{-SrTiO}_3/\text{solution}$ interface. The direction of the current indicates that holes are transported to the interface, so the

SrTiO₃ bands must be bent upward. It is interesting to note that there actually is considerable band-bending for the insulating SrTiO₃ electrodes. A particular sample measured in the dark had $V_{oc} = .02V$, $I_{sc} = 1.65 \times 10^{-10}$ amp/cm², and when illuminated with a 150 watt Xenon lamp had $V_{oc} = .42V$, $I_{sc} = 7.3 \times 10^{-7}$ amp/cm². Thus a band-bending of at least 0.4 eV is present.

C. Photoresponse With Bias

We then subjected our cell to a series of positive and negative biases. The polarity of the bias indicates the voltage applied to the silver contact on the SrTiO₃, versus the platinum counter electrode. It is assumed that essentially all of the potential is dropped across the SrTiO₃ because it is much more resistive than any other element in the circuit. Then, Figure 9 shows action spectra at +1.5 and -1.5 V. The spectra are very similar; the negative one had a somewhat larger current. As expected, the direction of photocurrent flow reversed for negative polarity (not indicated in Figure).

As the bias was increased, the photocurrents became larger. In addition, the positive bias spectrum shifted to shorter wavelengths and broadened. This effect becomes quite noticeable at +120 V, as shown in Figure 10, and continues at +400 V, as in Figure 11. Interestingly, at this large bias voltage, the quantum efficiency approaches 100%, although the short wavelength response is still missing.

But with a bias of +800 V, almost the entire spectral response has returned, as shown in Figure 12. The negative bias (-800 V) response has also broadened now. Furthermore, the quantum efficiency with either polarity now exceeds 100%, indicating the onset of secondary photoconductivity. That is to say, with positive bias, electrons must now be injected from

the solution into the conduction band of the SrTiO_3 . Ordinarily, at the low biases of about 1 volt usually applied, the contacts are blocking (i.e., the solution/semiconductor interface is blocking to electrons) and the photoconductive gain cannot exceed unity. At the very high bias level, holes must be trapped and photogenerated electrons must traverse the circuit more than once. In fact, with a bias of -800 V, an electron makes seven passes through the crystal before recombining (or before the hole is extracted at the silver contact). We should note at this point that the photocurrent was much larger than the dark current; the dark current was 50 nA while the negative photocurrent was 7 μA at 385 nm.

D. Intensity Dependence of Photoresponse

The intensity dependence of the peak was measured and it is shown in Figure 13. The magnitude of the photocurrent is linear with light intensity, at least at these low light levels. The peak shifts to somewhat longer wavelengths: 7 nm with a two order of magnitude decrease in light intensity. At the levels of light we have been using, the photoconductivity is definitely not saturated.

4.3.2 Mechanisms of Photoconductivity in Insulating SrTiO_3

We felt it was important to obtain a much clearer understanding of the mechanism for the loss of the short wavelength response in insulating SrTiO_3 . That is, we should know why this uv response is missing, because this may indicate the presence of processes which could kill the response from the CdS, when CdS/SrTiO_3 heterojunctions are formed. The following are five possible mechanisms which might account for the difference in the uv response between insulating and conducting samples:

- (1) surface recombination
- (2) hydrogen reduction process
- (3) large series resistance
- (4) space charges
- (5) fermi level effects on recombination centers

A number of experiments were performed to differentiate between these effects.

A. Surface Recombination

It is well known that surface recombination is often invoked as an explanation for decreases in the short wavelength response of numerous photoconductors. The effect can only be seen for very highly absorbed light which creates carriers right at the surface. We therefore measured the optical absorption of our SrTiO_3 crystals. At 385 nm, where the peak photoresponse occurs, α is about 100 cm^{-1} . Thus, the penetration depth of the light will be 100 microns, while the samples are only 75 microns thick. Clearly, this loss of response is a volume and not a surface effect. Further evidence that the effect is not due to damage in layers near the surface is presented in Figure 14, which shows the photoresponse of a crystal which had been annealed in air at 800°C for 20 hours. The response is unchanged and still only consists of a peak.

B. Hydrogen Incorporation

All of the conducting samples used earlier in this study were made conducting by heating them in flowing hydrogen. This process introduces oxygen vacancies (and/or titanium interstitials) which act as donors. One might speculate that the hydrogen enters the titanate lattice and affects the spectral response, perhaps by tying up dangling bonds. To check this, we rendered some samples conducting by heating them in vacuum. They

were held at 950°C for 4 hours in a pressure of 5×10^{-6} torr. The current-voltage characteristic is shown in Figure 15. The sample is strongly rectifying, giving large currents in the forward bias direction (i.e., when the polarity of the metal contact to the SrTiO_3 is negative, so that the hydrogen reduction reaction in the solution occurs at the SrTiO_3 surface). This same rectifying behavior was observed with hydrogen-reduced crystals. The resistivity is $2.5 \times 10^5 \Omega\text{-cm}$, so this material may be termed "semi-insulating". Interestingly, the full spectral response was found to be restored, as shown in Figure 16. Therefore, hydrogen is not responsible for the effect.

C. Series Resistance

It seems possible that the loss of short wavelength response may be due to a large series resistance, as follows. First of all, it is clear that in the case of an open circuit with infinite series resistance, no current will flow. The question then is whether the bulk resistance of the insulating SrTiO_3 is great enough to reduce the current below measurable levels. Then, when violet light, which is weakly absorbed, is shined on the sample, the conductivity of the entire bulk is increased and a measurable current can flow. But with uv light, which is only absorbed in the front portion of the sample, the bulk resistance in the unilluminated portion blocks current flow. If this were true, then it should be possible to widen the peak (i.e., obtain photocurrents at shorter wavelengths) by taking a spectrum with monochromatic light while simultaneously flooding the sample with weakly absorbed light. We used a tungsten lamp to provide the flooding light, since the output of such a lamp is decreasing sharply in the region from 450 to 350 nm. In fact, if the spectral output of the tungsten lamp is integrated with the absorption

spectrum of SrTiO_3 , a function similar to our photocurrents, such as shown in Figure 8, obtained. Therefore, this lamp serves to increase the conductivity of the entire sample. And yet, a narrow peak in the monochromatic response was still obtained, as shown in Figure 17. The peaks with and without the "white light" flooding have almost the same half-width: 20 and 17 nm, respectively. In fact, the increase in the width occurs at longer wavelengths. The effect of flooding with a more intense source of "white light" is shown in Figure 18. The current due to the "white light" here was an order of magnitude larger than the peak current due to the monochromatic light. And yet, the width of the peak failed to increase, while the magnitude of the peak actually decreased.

Another argument against series resistance can be made from the I-V characteristics, such as in Figure 7. Even with small biases, dark currents can be measured. Thus, comparable light currents would be able to pass through the material if series resistance were the only parameter controlling the magnitude of the current.

Another test was performed on a SrTiO_3 sample where the solution was replaced with two semi-transparent silver contacts, one on the front and one on the back. Now the "white light" was focused on one side while the monochromatic light was incident from the other side. The response was identical with Figure 14. Thus the peak cannot be due to series resistance, as follows. One might suspect that short wavelength response is lost when the penetration depth of the incident monochromatic light becomes too short to illuminate the entire thickness of the sample, leaving a high resistance region of the back contact. Since the samples are 75 microns thick, this could occur for light where the absorption constant $\alpha > 133 \text{ cm}^{-1}$. But if this were true, then shining light onto the back contact should restore the response, which it did not.

D. Space Charge

The argument against space charge blockage is similar to the one about series resistance. In this case, one might consider that if light is absorbed close to the surface, only one carrier type will diffuse (or drift - we do not know at this time if the samples are fully depleted) into the bulk, where it could become trapped. This trapped charge would repel further carriers. However, if weakly absorbed light is incident, carriers of both sign will be equally generated throughout the material, so that it will remain entirely compensated. But if this were the case, then there should also be trouble passing dark currents, and "white light" flooding would alleviate the problem, as we discussed above.

E. Fermi Level Position

At this time, we are inclined to believe that the problem is created by deep lying centers, which change from traps to recombination levels as the fermi level shifts. In highly conducting samples, the fermi level is located about 0.1 eV below the conduction band, while in the insulating samples, it is 0.8 eV below. The occupation of any levels lying in this region will change from filled to empty as the fermi level moves. The occupancy can also be changed by applying an external bias or by moving the quasi-fermi levels apart with "white light" illumination (see above). We are planning further studies to prove this more conclusively.

4.3.3 Photoelectrolysis Cells with Heterostructure Electrodes

A. CdS/SrTiO₃ Electrodes

A series of CdS/SrTiO₃ heterostructure electrodes were fabricated. In all cases, these consisted of a polycrystalline film of CdS on

a single crystal wafer of SrTiO_3 . The SrTiO_3 wafers were 75 microns thick, and the CdS films were usually 4-5 microns thick, although some were thinner. A silver contact was applied to the CdS layer to form a back electrode, and the SrTiO_3 was in contact with the solution. Platinum formed the counter-electrode. Thus, a cell consisted of silver, CdS, SrTiO_3 , solution, platinum. External leads were connected to the silver and the platinum, and polarities refer to the silver.

Photocurrents were measured due to visible light excitation in cells made with heterostructure electrodes from only one of the depositions. This deposition was made with the highest temperature of the CdS boat, 220°C. The photoresponse spectra are shown in Figures 19 and 20, where external biases of +1.5 and +20 V, respectively, were applied. As far as we know, this is the first time that visible light response has been obtained from this type of electrode structure. We are certain that the current was not due to the solution leaking through pin holes to the CdS, because the SrTiO_3 was a single crystal. Apparently, we may have succeeded in injected holes from CdS into SrTiO_3 .

It should be noted that the long wavelength response was not flat, but instead had a broad, shallow peak around 500 nm. There was also considerable added response in the region of 400 nm, when compared to plain SrTiO_3 . The response dropped off to zero below 370 nm, in accordance with the properties of insulating SrTiO_3 that we described earlier.

A current-voltage characteristic for the heterostructure cell is shown in Figure 21. The resistivity decreased by two orders of magnitude when the cell was illuminated by a microscope light, which had an intensity of roughly three suns. There was a greater increase in conductivity in the forward bias (silver negative) than in the reverse bias direction.

Many other depositions did not provide CdS/SrTiO₃ electrodes with visible light response. Some of the SrTiO₃ single-crystal substrates were insulating, while others were partially reduced in vacuum (950°C for 3 hours). During the evaporations of CdS, the substrates were kept at temperatures from 50 to 150°C. However, in no other case was any visible light response from the CdS detected, and thus it was not possible to reproduce the one result of a visible light response with CdS on insulating SrTiO₃. A typical spectral response for a 4 micron CdS film deposited on semi-insulating SrTiO₃ is shown in Figure 22. The small photocurrents found at visible wavelengths are entirely due to the SrTiO₃ crystal. This same response was found after the CdS film was etched away in hydrochloric acid. The small visible light response must be due to impurities, such as chromium, in the SrTiO₃. At this time, we are unable to explain why visible light response was found with only one particular CdS/SrTiO₃ electrode. The deposition parameters for the CdS may be critical.

It is likely that for the vacuum reduced substrates, which have a resistivity of $10^6 \Omega\text{-cm}$, the fermi level lies too close to the conduction band, and thus a barrier exists between the valence bands. In fact, the fermi level can be calculated to lie 0.4 eV below the conduction band for these substrates, which then results in a valence band barrier, according to the model discussed previously.

The insulating SrTiO₃ samples also continued to present a barrier to the transport of holes from the CdS to the solution. They actually may not have been sufficiently insulating, especially since they showed open-circuit photovoltages of 0.4 V. However, it does not appear

to be a simple matter to increase the resistivity of the SrTiO_3 . Annealing samples in air for 24 hours at 950°C did not increase the resistivity. The resistivity in this range is probably determined by impurities, rather than oxygen vacancies. Furthermore, increasing the resistivity, and thus bringing the fermi level further below the conduction band, may further exacerbate the problems with the short wavelength response in the SrTiO_3 . As we mentioned before, if this lack of short wavelength response is, in fact, due to the uncovering of recombination centers, then hole transport through the material may be further impeded by uncovering more centers.

We also were able to provide some slightly hydrogen reduced SrTiO_3 substrates. We accomplished this slight decrease in resistivity to $10^9 \Omega\text{-cm}$ by annealing the samples in hydrogen for 1 hour at 550°C . Heterostructure electrodes were formed by evaporating CdS onto these substrates, but the cells showed action spectra characteristic only of the SrTiO_3 crystals.

B. CdSe/ SrTiO_3 Electrodes

CdSe films were vacuum evaporated onto thin single crystal SrTiO_3 substrates, using the same apparatus as we described earlier for CdS. Substrate temperatures were varied between 50 and 100°C . Both insulating and semi-insulating SrTiO_3 samples, 75 microns in thickness, were used. In no case was any response found at visible wavelengths. Only the short wavelength responses characteristic of the various SrTiO_3 substrates were seen. Theoretically, it is less likely that CdSe would work, because the smaller band gap (1.7 eV) of this material indicates that the valence band should lie higher in energy than the valence band of SrTiO_3 , unless the SrTiO_3 is fully intrinsic, (i.e., $\rho \approx 10^{30} \Omega\text{-cm}$).

C. Monocrystal CdS/Al₂O₃ Electrodes

For these experiments, we started with single crystal slices of CdS. The crystals were first mechanically polished with diamond paste down to 0.25 micron grit size, and then etched in bromine-methanol solution (one drop of Br per 10 cm³ of methanol). The surfaces were then mirror smooth. Aluminum was evaporated in a vacuum system to give a thickness of 50 Å. Such films of Al are semi-transparent. The Al was next exposed to air, which partially oxidizes it. Then each electrode was suspended in a saturated NaCl solution, in such a way that only the aluminized surface was in contact with the liquid. A current was passed through each cell in the dark. These currents decayed rapidly at constant voltage, indicating the growth of passive, insulating films. We do not know at this time if such films were actually Al₂O₃, but a sufficient number of coulombs were passed through the cells to fully oxidize all of the Al to the +3 state.

The electrodes were then exposed to light. The action spectra thus obtained were the ones expected for CdS, as shown in Figure 23. The photocurrent generated with a microscope light decayed with time, as shown in Figure 24. After an exposure to 480 nm monochromatic light, some corrosion was already noticeable, as can be seen in Figure 25. This figure also shows the massive corrosion that was found after extended exposure to the microscope light (intensity of about 3 suns). This is not a satisfactory technique for protecting the surface of illuminated CdS liquid junctions.

D. Monocrystal ZnTe/TiO₂ Electrodes

ZnTe is a p-type semiconductor with a 2.1 eV band gap which could provide a possible photoelectrolysis cathode. Richard Williams showed some years ago (8) that ZnTe will spontaneously corrode in the dark in an aqueous environment. The thermodynamically favored reaction is

rather than

If reaction 2 were favorable, then ZnTe would be stable in the dark, because in this p-type material there are no electrons available in the conduction band to neutralize the 2h^{+} . However, reaction 1 proceeds readily because holes are available in the valence band to neutralize the 2e^{-} . Incidentally, CdS is stable in the dark because there are no holes available in that n-type material to satisfy a reaction of the first type. With illumination, the holes become available.

If ZnTe were overcoated with a corrosion resistant material such as TiO₂, it might remain stable. A single crystal wafer of ZnTe was mechanically polished with diamond paste down to 0.25 micron grit size, and then polished chemically with bromine in methanol. The surface was then mirror smooth. A 50 angstrom thick film of TiO₂ was then sputtered onto the ZnTe. The surface of the crystal was scrupulously cleaned and degreased before the deposition. A titanium dioxide sputtering target was used and the crystal was kept at ambient temperature in the machine.

The surface of this heterostructure was featureless at 100X magnification, as shown in Figure 26a. However, when the electrode was exposed to a 5M KOH solution, a large current of several milliamperes flowed in the dark, and there were no observable photoeffects. Corrosion is evident in Figure 26b, and on one area of the sample, the entire TiO_2 film came off the substrate, as shown in Figure 26c. Therefore, this technique did not relieve the corrosion problem in ZnTe.

E. n-Si/ SnO_2 Electrode

Although the band gap of silicon is only 1.1 eV and therefore too small to allow this material itself to drive the water splitting reaction, it should be possible to use it in conjunction with a second illuminated electrode to give a p-n photoelectrolysis cell. In fact, the two electrodes could be n- and p-type Si, if corrosion can be avoided. In order to protect the surface of a Si sample, it was sprayed with a 1000 Å thick film of SnO_2 . SnO_2 has been shown to be stable in photoelectrolysis cells (9). The SnO_2 was formed by a standard spraying technique using a tin chloride solution (10). The SnO_2 film gave the sample a blue color. The Si surface was carefully cleaned before the deposition. The silicon substrate was n-type with a resistivity of 1 Ω -cm.

The crystal was mounted in a cell using a 5M KOH solution and negligible current ($< \text{nA/cm}^2$) flowed in the dark. The action spectrum is presented in Figure 27. The only response must be due to the SnO_2 film, since SnO_2 has a band gap of 3.5 eV. No measureable photo-current was collected from the Si.

F. p-Si/SnO₂ Electrode

The processing of this crystal was the same as for the n-type Si. The action spectrum was also exactly the same. The polarity of the current was the same in both cases. The polarity would have reversed if the p-Si had been contributing a current. Only the photocurrent generated in the SnO₂ film was collected.

G. CdS/polycrystalline-TiO₂ Electrode

This electrode was prepared by evaporating a thin film of titanium onto a crystal of CdS and then oxidizing it. The surface of the CdS crystal was cleaned and polished as described earlier. Titanium powder was placed in a 1-7/8" x 3/16" tantalum boat in a vacuum evaporation system. A current of 70 amps through this boat melted the titanium ($T_m = 1668^\circ\text{C}$) and gave a deposition rate of 1 Å/sec. A film 100 Å thick was deposited. The crystal was then mounted in a cell containing a 5M KOH solution so that only the titanium film contacted the solution. In the dark, +5V was applied to the cell until the initial current decreased by two orders of magnitude. Our experience in the past with sheets of titanium metal has shown that this technique will grow a good film of TiO₂.

An action spectrum was then taken, and it proved to be quite similar in shape to the one for CdS/Al₂O₃ shown in Figure 23. The magnitude of the photocurrent in the plateau region was only 1/4 as great as the current in Figure 23, indicating that the TiO₂ layer was inhibiting some of the minority carrier flow. (All of the CdS crystals had the same magnitude of photoresponse before processing.) The crystal was illuminated with monochromatic 480 nm light for 1 hour, and there was no decrease in photocurrent nor any signs of corrosion after this period. However, when the electrode

was exposed to "white light" with an intensity of about 1 sun, corrosion became quite apparent. Thus this heterostructure appears to offer relief from corrosion at low light intensity, but not at sunlight intensity.

H. CdSe/polycrystalline TiO₂ Electrode

Using the technique for evaporating Ti that we described above, we also coated a cleaned and polished CdSe electrode with this metal. The CdSe crystal was prepared in the manner described for CdS in Section C. The Ti film was then oxidized in a cell in the dark, with an applied bias of +5V. After the bias was removed, an action spectrum was run, as shown in Figure 28. Photocurrents were found at wavelengths up to 725 nm, which is the band gap of CdSe. The cell was then exposed to 480 nm light for 1 hour, during which time the photocurrent remained constant. No evidence for corrosion was found. However, as in the previous case, we observed corrosion problems at sunlight intensities.

I. CdS/monocrystalline TiO₂ Electrode

CdS was vacuum evaporated onto a single crystal wafer of insulating TiO₂. The evaporation parameters developed for depositing CdS onto SrTiO₃ were used. The undoped TiO₂ was cut and polished in the same manner as the SrTiO₃, and had a resistivity of 10¹¹ Ω-cm. The action spectrum in this cell is shown in Figure 28. This spectrum is characteristic of TiO₂, but any current at visible light wavelengths due to absorption in the CdS is absent. The cell dark current was 5 x 10⁻¹² amp, and thus if there was any photocurrent generated from the CdS film, the magnitude of such currents would have been below the picoamp range, beyond the limit of our instruments. Interestingly, there was no loss of uv response for the

insulating TiO_2 , in contrast to our earlier results with SrTiO_3 . This anomaly remains unexplained at this time. A narrow peak in the response of insulating TiO_2 electrodes has also been reported by Wilson (11).

J. CdS/monocrystalline TiO_2 :Cr Electrode

This electrode was prepared in the same manner as the one above. The TiO_2 crystal was doped with 0.1 wt% Cr and had a resistivity of $10^8 \Omega\text{-cm}$. Once again, the spectral response was found to be characteristic only of the TiO_2 :Cr. There was a visible light response, but it was only due to the Cr dopant. There was no evidence for hole transport from the CdS valence band through the TiO_2 via the Cr acceptor centers.

K. CdS/ Fe_2O_3 Electrodes

The single crystals of CdS were prepared by the method described in Section C above. The Fe_2O_3 films were deposited by rf sputtering from an iron oxide source. Film thicknesses were 30, 70 and 150 angstroms. These electrodes all showed photocurrents characteristic of the CdS substrates (see, for example, Figure 23). Each one of them corroded when they were exposed to "white light" of solar intensities. Thus pin hole problems persisted.

L. CdSe/ Fe_2O_3 Electrodes

The single crystals of CdSe were prepared by the method described in Section C above. Fe_2O_3 films of 50 and 100A thickness were deposited onto the CdSe substrates by rf sputtering. Both of these electrodes exhibited photocurrent spectra in illuminated cells that were characteristic of CdSe (see, for example, Figure 28). Corrosion was once again encountered when the cells were illuminated with "white light" of solar intensity. Pin holes continued to remain a problem. The decay of current with time is shown in Figure 30.

M. CdS/SnO₂ Electrode

The surface preparation of single crystal CdS was described in C above, and the spraying of SnO₂ was described in E. The photocurrent spectrum showed response only from the SnO₂.

N. CdSe/SnO₂ Electrode

The surface preparation of single crystal CdSe was described in C above, and the spraying of SnO₂ was described in E. The photocurrent spectrum for this cell showed response only from the SnO₂.

O. CdS/Al₂O₃ Electrodes

The preparation of single crystal CdS substrates was described above. The Al₂O₃ films, 25, 50 and 100 angstroms thick, were deposited by rf sputtering from an aluminum oxide source. The photocurrents in the cells were characteristic of CdS, but reduced by 2-3 orders of magnitude from the photocurrents observed with uncladded CdS. Illumination of the cells with "white light" of sunlight intensity produced some corrosion effects. These were manifested as isolated yellow dots on the surface, which were likely to be elemental sulphur deposits. The photocurrents were in the microampere range, indicating that currents were only carried through pin holes. The current levels decreased slowly during illumination of the cells, and this observation can be taken as evidence that corrosion processes were proceeding.

4.4 Conclusions

In this part of the study, we have tested a large number of heterostructure electrodes for use in water photoelectrolysis cells. The main emphasis was placed on electrodes consisting of a stable single crystal wide band gap semiconductor onto which a corrosion-prone sunlight

absorber was evaporated. The stable single crystals were wafers of TiO_2 and SrTiO_3 , while CdS and CdSe were used as sunlight absorbers. Since the single crystals were placed in contact with the solution, corrosion problems were eliminated. However, we showed that the position of the fermi level in the wide band gap corrosion inhibiting member of the heterostructure is the critical parameter for determining the magnitude of the photocurrent. If the position of the fermi level in this wide band gap member is such that a potential barrier develops between the valence bands, then minority carrier flow from the sunlight absorber through the wide band gap semiconductor to the solution will be inhibited. Our experiments have shown that it will be necessary to study wide band gap materials with work functions even larger than those that we obtained with either TiO_2 or SrTiO_3 , if a corrosion inhibitor is to be found which will be capable of sustaining a significant flow of minority carriers (i.e., holes).

The other series of electrodes that we studied consisted of single crystal sunlight absorbers (CdS, CdSe, ZnTe and Si) which were overcoated by various techniques with stable wide band gap oxides (TiO_2 , Al_2O_3 , Fe_2O_3 and SnO_2). Although careful preparation techniques were used for obtaining clean, optically smooth surfaces on the crystals, many of the samples exhibited pin hole problems in the corrosion-inhibiting films. These pin holes continued to lead to degradations in device performance, especially at high light intensities. On the other hand, when the stable oxide films were free from pin holes, then we found minority carrier transport was inhibited by potential barriers between the valence bands. This result is the same as the one we obtained when we started with single crystal wafers of the stable oxides.

Therefore the problems that we have identified for all of the cells that were tested can be divided into two groups:

- (i) minority carrier transport inhibited by potential barrier between the valence bands
- (ii) degradation of performance due to pin holes.

We suggest that other systems of materials should be studied which may prove more compatible.

4.5 References

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Figure 27. Photocurrent spectrum of an n-Si/SnO₂ electrode.

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Figure 29. Photocurrent spectrum of heterostructure electrode consisting of CdS evaporated onto single crystal TiO₂.

Figure 30. Photocurrent decay for the CdSe/Fe₂O₃ electrode, cell exposed to incandescent lamp from microscope lamp.

Figure 1. Band diagrams for heterojunction electrodes: (a) both semiconductors n-type, (b) wide band gap material insulating, and (c) wide band gap material insulating, external bias applied.

FIGURE 2
PROFILE OF A HETEROSTRUCTURE ELECTRODE

FIGURE 3
SHIELDED EVAPORATION BOAT

FIGURE 4
CADMIUM SULFIDE VACUUM EVAPORATION SYSTEM

Figure 5. Cadmium sulfide films deposited onto glass slides. The heated slide #2 has the **lighter** colored film. The light circular area on #2 was exposed to illumination in a cell.

FIGURE 6

ACTION SPECTRUM OF EVAPORATED CdS FILM

Figure 7. Current-voltage characteristic of insulating SrTiO_3 crystal (75μ thick) with two silver contacts.

Figure 8. Comparison of photoresponse spectra of insulating and hydrogen reduced SrTiO_3 crystals in photoelectrolysis cells.

Figure 9. Photoresponse spectra for insulating SrTiO_3 with applied biases of ± 1.5 volts.

Figure 10. Photoresponse spectra for insulating SrTiO₃ with applied biases of ±120 volts.

Figure 11. Photoresponse spectra for insulating SrTiO₃ with applied biases of ± 400 volts.

Figure 12. Photoreponse spectra for insulating SrTiO_3 with applied biases of ± 800 volts.

Figure 13. Effect of light intensity on the photoresponse spectrum of insulating SrTiO_3 .

Figure 14. Photoreponse spectrum of insulating SrTiO₃ crystal which had been annealed in air at 800°C for 20 hours.

Figure 15. Current-voltage characteristic of vacuum-reduced SrTiO_3 .

Figure 16. Photoresponse spectrum of vacuum

Figure 17. Photoresponse spectrum of insulating SrTiO_3 , taken while sample is simultaneously flooded with "white light", from an incandescent lamp. No external bias constant, photon flux of $5 \times 10^{14}/\text{sec.}$

18. Photocurrent spectrum of insulating SrTiO_3 with and without a "white light" bias; (a) monochromatic light only, (b) additional microscope light focused on sample.

Figure 19. Photoresponse spectrum of Ag/CdS/SrTiO₃/solution/Pt cell with an applied bias of +1.5 volts.

Figure 19. Photoreponse spectrum of Ag/CdS/SrTiO₃/solution/Pt cell with an applied bias of +20 volts.

Figure 21. Current-voltage characteristics of a Ag/CdS/SrTiO₃/solution/Pt cell, in the dark and under illumination from a microscope light (approximately 3 suns intensity).

22. PHOTOCURRENT SPECTRUM OF CdS/SEMI-INSULATING SrTiO₃ ELECTRODE

23. PHOTOCURRENT SPECTRUM OF CdS/Al₂O₃ ELECTRODE

24. PHOTOCURRENT DECAY FOR THE $\text{CdS}/\text{Al}_2\text{O}_3$ ELECTRODE.
CELL EXPOSED TO INCANDESCENT LAMP.

(c)

(b)

(a)

100 μ

25. CdS/ Al_2O_3 electrode; (a) as prepared, (b) exposed to 480 nm light, (c) exposed to microscope light (~ 3 suns).

(a)

(b)

100 μ

(c)

26. ZnTe/TiO₂ electrode; (a) as prepared, (b), (c) after placing it in a 5M KOH solution in the dark.

27. PHOTOCURRENT SPECTRUM OF AN n-Si/SnO₂ ELECTRODE

28. PHOTOCURRENT SPECTRUM OF A CdSe/TiO₂ ELECTRODE

FIGURE 29

PHOTOCURRENT SPECTRUM OF A HETEROSTRUCTURE ELECTRODE
CONSISTING OF CdS EVAPORATED ONTO SINGLE CRYSTAL TiO_2 .

DEVICE AREA = 1 mm^2 . RESISTIVITY OF $\text{TiO}_2 = 10^{-4} \text{ CM}$.

FIGURE 30

PHOTOCURRENT DECAY FOR THE CdSe/Fe₂O₃
ELECTRODE, CELL EXPOSED TO INCANDESCENT
LIGHT FROM MICROSCOPE LAMP

5. SUMMARY AND SUGGESTIONS

This study has been concerned with identifying techniques for improving the solar conversion efficiency of water photoelectrolysis cells. A detailed search of the available literature on this topic was undertaken, in order to bring into proper perspective the progress and problems that have developed with these cells. Based on this search, a review article was written which included our interpretations and evaluations of the previous work. In general, it was found that although many investigations of solar driven water photoelectrolysis had already been undertaken, no high efficiency cells had yet been reported. All cells suffered from one or more of the following problems:

- corrosion
- poor sunlight absorption
- large external bias requirement

We concluded that we were essentially faced with a formidable materials problem, because no suitable semiconductor electrode material had yet been developed for the process. More than forty different semiconductors have been tested as photosensitive electrodes. All except for several oxides undergo severe corrosion in illuminated cells. The two most successful candidates have been TiO_2 and SrTiO_3 , and most of the research had been concentrated on these materials. But although they remain quite stable in contact with an alkaline aqueous solution, they are poor sunlight absorbers, and hence devices based upon these semiconductors have yielded power efficiencies of not much more than 1%. Other stable oxides with superior sunlight absorption properties have been identified, but cells based upon these materials were all found to require unacceptably large external biases in addition to the solar energy input before hydrogen generation was observed.

In consideration of these findings from past investigations, we decided upon two courses of action designed to improve the response of water photoelectrolysis cells. The two techniques that we studied were impurity sensitization of stable wide band gap oxides, and heterostructures formed between good sunlight absorbers and stable wide band gap oxides.

For the impurity sensitization studies, we introduced the transition metal dopants V, Cr, Mn, Fe, Co and Ni into TiO_2 and SrTiO_3 . Photocurrents were found in response to visible light excitation in cells having TiO_2 or SrTiO_3 electrodes doped with either Cr, Mn or Fe. For the first time, hydrogen and oxygen were generated in a stable photoelectrolysis cell illuminated only with visible light, employing a Cr-doped TiO_2 anode. The minority carrier diffusion lengths in TiO_2 and SrTiO_3 were shown to be determined by the dopants. The longest diffusion length was found for samples doped with Al (10 microns), while Cr doping induced the shortest diffusion length. We suggest that combinations of dopants may be found which will give a strong response to visible light along with a high value of diffusion length. We also showed that all of the oxide materials that have been studied in photoelectrolysis have the valence band situated 7.5 eV below vacuum when in contact with water at pH=0. This leads to an overvoltage of 1.8 V for oxygen generation, and the unfortunate requirement of a large external bias for hydrogen generation with any oxide having a band gap of less than 2 eV. We suggest that impurity doping may be able to provide visible light response (equivalent to decreasing the band gap) while not increasing the electron affinity. (An increase in electron affinity results in an increase in bias requirements). As an alternative, we suggest studies of specific adsorbant species which could decrease the electron affinity (drive the flat band potential more negative) for small band gap oxides which are good sunlight absorbers.

For the second phase of the work, we studied a series of heterostructure electrodes. These electrodes were composites consisting of a good sunlight absorber (CdS, CdSe, ZnTe, Si) and a stable oxide (TiO_2 , SrTiO_3 , SnO_2 , Al_2O_3 , Fe_2O_3), with the stable material in contact with the solution. For the first set of electrodes, we used thin single crystal wafers of SrTiO_3 and TiO_2 as substrates. Obviously these substrates were free of pin holes, and films of CdS and CdSe were vacuum evaporated onto them. Our analysis showed that the position of the fermi level in the oxide was critical for allowing hole transport from the sunlight absorbing member of the heterostructure through the stable transparent cladding material to the solution. Consequently, we used semi-insulating ($\rho = 10^7 \Omega\text{-cm}$) and insulating ($\rho = 10^{12} \Omega\text{-cm}$) samples of TiO_2 and SrTiO_3 as substrates, because the position of the fermi levels for these particular doping concentrations were calculated to reduce the possibility of barriers between the valence bands. However, our experimental results indicated that the work functions of the samples that we used were still not great enough to preclude the formation of such barriers between the valence bands. Although we were not able to produce more insulating samples of these materials, we suggest that developing a method of further increasing the resistivity of TiO_2 or SrTiO_3 (and hence, increasing their work functions) should relieve the barrier problems.

For the second set of heterostructure electrodes, we deposited the stable oxides TiO_2 , SnO_2 , Al_2O_3 and Fe_2O_3 onto single crystals of CdS, CdSe and ZnTe. Although scrupulous care was taken in preparing the surfaces of the crystals, pin hole problems led to degradation in the performance of these electrodes, unless the deposited films were quite thick. Electrodes with thick films of oxides suffered from the minority carrier transport problems outlined

above. Therefore we suggest that the only way that these heterostructure electrodes can be expected to result in significant stable photocurrents in response to visible light would be to develop a technique for depositing continuous, pin hole free, thin (< 20 angstrom) oxide films.