

To the Graduate Council:

I am submitting herewith a dissertation written by Irene Elizabeth Paulauskas entitled "A Study of the Photoelectrochemical Properties of KTaO_3 and ZnO in Alkaline Electrolytes." I have examined the final electronic copy of this dissertation for form and content and recommend that it be accepted in partial fulfillment of the requirements for the degree of Doctor of Philosophy, with a major in Materials Science and Engineering.

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A Study of the Photoelectrochemical Properties of KTaO₃ and ZnO in Alkaline Electrolytes

A Dissertation
Presented for the
Doctor of Philosophy
Degree
The University of Tennessee, Knoxville

Irene Elizabeth Paulauskas
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Dedication

I dedicate this work to all of those who have supported me throughout. You will all know how you have helped me: my mum, my dad and Lelyte; my grandparents; Cangurito and The Boiz; Bibina and Mappy; and Dr. R. A. Buchanan.

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Abstract

In this work, single crystals of n-type, semiconducting oxide photoelectrochemical cell photoanodes have been investigated. The central focus of this study was the growth and characterization of n-type Potassium Tantalate (KTaO_3) single crystals as a function of doping elements and doping concentration. The purpose of these investigations was to exploring the use of semiconducting oxides in PEC cells for solar energy applications. The doped tantalate crystals were examined using a variety of electrical, optical, and photoelectrochemical techniques that included: current-voltage, capacitance-voltage, quantum yield, optical transmission, and ellipsometry. Quantum yield measurements were performed in the PEC cell configuration both as a function of illumination wavelength and time. Zinc Oxide (ZnO) was also studied in detail as a PEC Cell photoanode material since it is known to have a higher photo-response and a direct band edge, in contrast to KTaO_3 . The oxides Barium Tantalate (BaTiO_3), and Strontium Tantalate (SrTiO_3) were also examined. Although, doping did not affect the wavelength of the onset of optical absorption in any of the samples, it did affect some of the electrical characteristics as well as the measured photo-response during PEC cell operation.

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1 Introduction

Development of alternative fuels is becoming increasingly important as resources of fossil fuels diminish and respective energy costs increase. Environmental pressures are also driving the need for greener alternative fuels for use in both the home and in industry.

Hydrogen presents one solution in this regard, though existing production techniques can not be considered environmentally friendly given the resultant CO₂ emissions in the case of steam reforming, or continued use of fossil fuels when produced via water electrolysis [1.1]. However, the use of photoelectrochemical (PEC) cells provides an option to produce hydrogen without the environmental consequences [1.1,1.2]. In these cells, the photo-assisted dissociation of water into hydrogen and oxygen is achieved by absorbing optical energy (e.g. sunlight) through one of the cell electrodes. When an alkaline electrolyte is used, this electrode is known as the photoanode. In order for the photoanode to be capable of driving the electrolysis reaction using solar energy (i.e., the reaction: $\text{H}_2\text{O} \xrightarrow{h\nu} \text{H}_2 + \frac{1}{2}\text{O}_2$), it must have very specific properties. Specially, it needs to be a semiconductor with a sufficiently small band gap to absorb photons with sufficient energy for the water dissociation reaction to occur - but also to absorb the maximum possible amount of photons from the solar spectrum (Figure 1.1, please see appendix for all tables and figures). Even though the theoretical energy needed for this reaction is 1.23 eV, a band gap of ~ 2 eV has been established as an optimum target to account for the non-ideal nature of the interfaces and contacts throughout the system (i.e., an increase in the overall resistance of the PEC circuit). Also, the band edges of the photoanode must be appropriate for producing water dissociation - otherwise there will not be an effective driving force for the reaction, and an external bias voltage will be needed. Of course, the photoanode material must also be chemically stable in the PEC cell environment. Although these properties are well defined, finding a semiconductor that meets all of these

essential requirements has proven to be a complex, and presently unresolved, materials challenge. For example, the band gap of classic semiconductors such as CdTe matches the energy of the solar spectrum reasonably well, but these materials lack chemical stability in the electrochemical environment, and they undergo photo-anodic dissolution. One group of materials with the potential for solving this problem is represented by the semiconducting oxides such as KTaO_3 , TiO_2 , SrTiO_3 and ZnO [1,3-5]. Oxides of this type tend to be more chemically stable in the photoelectrochemical cell environment; but they have wide band gaps that do not absorb a large fraction of the solar spectrum. A more in- depth explanation of the PEC cell operation and the approaches taken to overcome the photoanode absorption issue are discussed in section 3.1.

The general objective of this work was to alter beneficially the electronic properties of KTaO_3 single crystals by doping the material during the crystal growth process by using a systematic approach with a variety of dopant elements. The goal of these studies is to “sensitize” KTaO_3 so as to absorb lower energy irradiation, while maintaining the material’s chemical stability during the PEC cell operation. The concept behind using single crystal KTaO_3 as a model material is that it is relatively simple to grow and to dope, and it also tolerates a wide range of compositional variations enabling greater flexibility in terms of altering its electronic properties towards the solar spectrum. In order to achieve this goal, the following investigations have been undertaken:

- Establishing the effectiveness of the crystal-growth method when using single and multiple doping elements as a mean to obtain doped n-type KTaO_3 .
- Studying the electrochemical behavior of the semiconducting n-type KTaO_3 crystals in the presence of a highly basic electrolyte at room temperature.

- Determining the relationship between the doping level and the doping species and the electronic properties, as well as the impact of high doping levels on the stability of crystals in the PEC cell environment.
- Understanding the basic principles that determine the overall photoelectrochemical behavior of doped n-type KTaO_3 as observed at different wavelengths in the PEC cell.
- Comparing the influence of doping on the photoelectrochemical behavior of other semiconducting systems such as the direct band semiconductor, ZnO .

The present manuscript has been divided into 5 chapters, and it is a compilation of journal articles that were written based on the work performed during course of the subject Ph.D. dissertation research. Chapter 1 is the present introduction. Chapter 2 establishes a general overview of the differences of the PEC behavior between 4 different n-type semiconductor oxides KTaO_3 , BaTiO_3 , SrTiO_3 , and ZnO , and how these differences correlate with optical properties such as the indirect (for KTaO_3 , BaTiO_3 , SrTiO_3) or direct (for ZnO) absorption mechanism. Chapters 3 and 4 are a detailed study of the growth of the n-type KTaO_3 single crystals, the PEC cell characterization and its correlation with the semiconducting properties of the crystals. Chapter 5 treats the study of ZnO single crystals doped with various doping elements and their carrier concentrations in the PEC cell environment. This work has either been published, accepted for publication, or submitted for publication in: Thin Solid Films (Chapter 2) [1.6], The Journal of the Electrochemical Society (Chapter 3) [1.7], the Journal of Applied Physics (Chapter 4), and the Journal of Materials Research (Chapter 5).

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Appendix

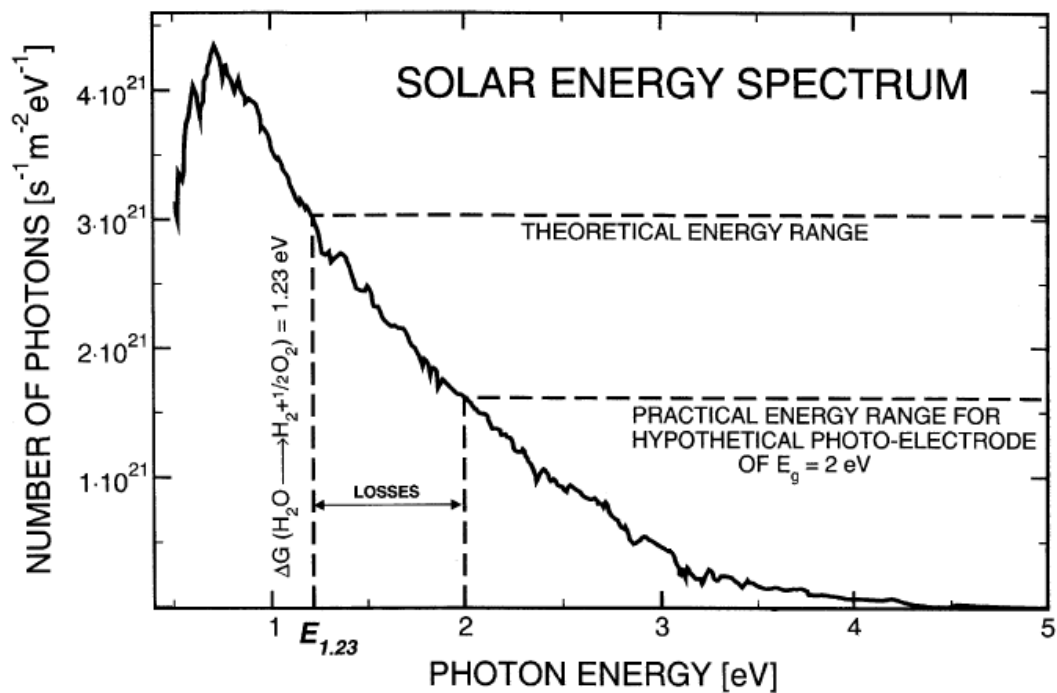


Figure 1.1 Number of photons vs. the photon energy for the Air Mass 1.5 solar spectrum. Edited from reference 1.1.

2 Photoelectrochemical studies of semiconducting photoanodes for hydrogen production via water dissociation

This chapter is a journal article with the same name published in *Thin Solid Films* in 2008 by I. E. Paulauskas, J. E. Katz, G.E. Jellison Jr., N. S. Lewis, and L. A. Boatner:

I. E. Paulauskas, J. E. Katz, G.E. Jellison Jr., N. S. Lewis, and L. A. Boatner, *Thin Solid Films* **516**, 8175 (2008).

My use of "we" in this chapter refers to my co-authors and myself.

Abstract

Single crystals of various n-type semiconducting oxides have been investigated in order to better understand the relationship between their photoelectrochemical behavior and their optical properties. The single crystals used in this study were all n-type and consisted of: KTaO_3 , BaTiO_3 , SrTiO_3 , and ZnO . Current density versus applied potential measurements indicated that all of the crystals exhibited diodic properties when in contact with a highly basic electrolyte (8.5 M NaOH at room temperature). The ZnO electrodes, however, exhibited some degradation after exposure to the operational cell environment. Results indicate that the spectral quantum yield of the crystals is related to the penetration depth of the incident light, meaning that electron-hole pairs formed far from the semiconductor-liquid junction are less likely to be collected than those formed near the surface (*e.g.* inside the depletion regions). Additionally the quantum yield was found to decrease with time. In the case of the KTaO_3 , the decay of the quantum yield was fit to a double exponential, which suggests a complicated process is operative for this material. Ongoing research is directed toward understanding the influence of both temperature variations and the surface/electrolyte interface on the effects observed in the case of KTaO_3 .

2.1 Introduction

Photoelectrochemical (PEC) mechanisms that provide for the “clean” production of hydrogen and oxygen from the electrolysis of water by using solar energy or other sources of optical energy started with the pioneering work on semiconducting n-type TiO_2 and have been intensively studied over the past decades [2.1-2.6]. Currently, the problems with PEC cell photoanodes include finding materials: (a) with band gaps that better match the solar spectrum, (b) whose band edges are located at potentials that allow the direct photo-induced evolution of H_2 and O_2 , and (c) materials that exhibit a high level of chemical stability against photoanodic dissolution. Unfortunately, these fundamental requirements of photoanode stability, band gap, and absolute band edge positions necessary for efficient solar conversion have not yet been resolved; consequently, the application of this process as an efficient and practical method for hydrogen production is presently not possible. Finding a solution to all three of these problems in a single system has proven to be extremely difficult, but resolving these issues is indispensable to making significant advances in this area.

The photoanodes used in this study consisted of the following n-type single crystals: potassium tantalate (KTaO_3), barium titanate (BaTiO_3), strontium titanate (SrTiO_3), and zinc oxide (ZnO). These crystals belong to a more extensive group of materials that have been studied as photoanodes in photoelectrochemical cell systems for hydrogen production [2.5-2.12]. It is known that the wide band gap ($\text{KTaO}_3 = 3.64 \text{ eV}$ [2.13], BaTiO_3 and $\text{SrTiO}_3 \sim 3.3 \text{ eV}$, and $\text{ZnO} = 3.34 \text{ eV}$ [2.14]) of these materials is a major limitation to their use as photoanodes in PEC cells for hydrogen production.

Nevertheless, there is still a lack of in-depth understanding of how the optical properties of these materials affect their overall behavior in the photoelectrochemical systems. Therefore, the present work focuses on how the measured photoresponse and quantum yield correlate with the intrinsic properties of the crystal, including their direct or indirect absorption mechanism and the associated absorption coefficient.

2.2 Experimental

The KTaO_3 single crystals investigated here were grown using a slow cooling method from a non-stoichiometric melt [2.15] with the doping agents added in the initial melt to produce semiconducting, degenerately doped n-type KTaO_3 . Hall Effect measurements showed that the doping concentrations yielded carrier concentrations on the order of 10^{18} - 10^{19} cm^{-3} . Reduced SrTiO_3 crystals were obtained from Commercial Crystal Laboratories, Inc., hydrogen-reduced BaTiO_3 crystals were obtained from Deltronic Crystal Industries; and doped ZnO was obtained from CERMET (doping elements included rare earth metals such as Er). All of the single crystals were n-type semiconductors.

The PEC cell electrodes were fabricated from ~ 1 mm thick samples, using a 600 grit final surface finishing step. Electrical back contacts were fabricated by using pure indium dots to solder a gold wire on to the back of the samples, which had been previously coated with an In-Ga eutectic. At the front contact, the semiconductor is in contact with the electrolyte solution consisting of 8.5 M NaOH (pH = 14.9). Insulating epoxy was used to cover those areas of the electrode that were to be electrically isolated from the electrolyte.

The contacted electrode was placed in an H-shaped cell with a quartz window in the compartment that contained the photoanode electrode. A saturated calomel electrode (SCE) was

used as the reference electrode, and a platinum strip served as the counter electrode. Current density vs applied potential (J-E) measurements were performed under potentiostatic control (PAR Model 2263) both in the dark and under illumination, with the incident illumination provided by a 500 W high-pressure Hg arc lamp. The applied voltage sweep rate was 20 mV/sec. The voltage sweep was cycled in both positive and negative directions in order to examine any hysteresis effects.

Spectral quantum yield (QY) measurements were performed using the system described above, but in this case, the sample was illuminated using monochromatic light with a bandwidth of ~ 5 nm. The current was read using a Keithley 2400 source meter in series with the PEC cell. The illumination intensity was monitored by a split-reference beam that was incident on a Si photodiode which had been previously calibrated using a NIST standard photodiode. In order to reduce stray light effects, a BG-24 filter was placed at the entrance slit of the monochromator. The samples were held at 0 V vs. SCE, and the illuminated region was ~ 2 mm in diameter ($\sim 3.14 \text{ mm}^2$).

Two different types of QY measurements were performed: a spectral QY determination in which the external QY was measured as a function of the wavelength; and a time-resolved QY, where the photocurrent was monitored as a function of time, with a time resolution of ~ 0.5 sec. Absorption coefficient values were determined in previous work (KTaO₃ from reference 2.13, ZnO from reference 2.16, BaTiO₃ and SrTiO₃ from reference 2.17).

2.3 Results

The J-E curves shown in Figure 2.1 (Please see appendix for all figures) show diode-like rectification for all of the electrode samples examined. The KTaO_3 photoanode samples were characterized by consistently lower current densities than the BaTiO_3 and SrTiO_3 electrodes. ZnO electrodes gave the highest photocurrent densities, and these were nearly twice that of the BaTiO_3 and SrTiO_3 electrodes. However, the ZnO electrodes did show visual evidence of increased surface roughness subsequent to the measurements.

The spectral quantum yield results are presented in Figure 2.2, where the solar spectrum is also shown for comparison. The KTaO_3 samples show a significant QY only for those wavelengths less than 350 nm. The QY of KTaO_3 peaks at ~ 250 nm, and has a tail in the region from 300 to 340 nm. The maximum QY varied from 0.15 to 0.30 for different KTaO_3 electrodes. Both the SrTiO_3 and BaTiO_3 electrodes exhibited a relatively flat QY response from 230 to 310 nm - at which point the QY slowly decreased to 0 at a wavelength of ~ 380 nm. The QY for the ZnO electrodes was essentially flat, until a wavelength of ~ 360 nm, where the QY dropped to zero at 400 nm. A small shoulder was observed between 390 and 400 nm. Consistent with the J-E measurements, the ZnO photoanode had the highest QY, followed by SrTiO_3 , BaTiO_3 , and KTaO_3 .

The time-resolved QY for a highly doped KTaO_3 sample, illuminated at a wavelength of 260 nm, is shown in Figure 2.3. A plateau is reached after 4.2 hrs (15×10^3 sec) of exposure to the light, with a drop in the QY of about 7% of the initial value. While the time dependence is not a simple exponential decay, the data can be fitted to:

$$\text{QY} = 0.173 + 0.013 \exp\left(-\frac{t}{240 \text{ sec}}\right) + 0.009 \exp\left(-\frac{t}{3400 \text{ sec}}\right) \quad (2.1)$$

with $R = 0.99$, indicative of two time constants (clearly additional decay states would also fit). BaTiO_3 and SrTiO_3 exhibited a qualitatively similar behavior to that observed for the KTaO_3 electrodes, while the ZnO samples reached an equilibrium current value considerably faster than the other oxides (< 2 s at 260 nm).

2.4 Discussion

The KTaO_3 , SrTiO_3 and BaTiO_3 samples showed similar J-E curves, with an inflection at -1.7 to -1.2 V vs. SCE, attributed mainly due to the presence of oxygen in the electrolyte. The ZnO sample showed a large peak in the current density near -1.6 V vs. SCE for increasing potentials. While the origin is unknown at this time, we suspect that it is due to chemical interactions at the interface between the electrolyte and the ZnO electrode.

The observed photo-response was consistent with the QY behavior as expected. The differences in the photocurrents among the various oxides are ascribed primarily to the band gap energy of the specific material, but differences are also dependent on the optical absorption coefficient (see Figure 2.4). The larger photo-response of the ZnO , compared to the other electrodes, is in part related to its smaller band gap, but also to the flat, relatively high value of the absorption coefficient at energies greater than the band gap. On the other hand, the lower observed photocurrents for the KTaO_3 , BaTiO_3 and SrTiO_3 electrodes are related to both the larger band gap energy and the absorption mechanism, discussed below.

In order to understand the optical response of the PEC cells under illumination, it is necessary to consider the quantum yield measurement results in conjunction with the optical absorption characteristics. The shape of the observed QY curves was consistent with the shape of

the absorption coefficient curves shown in Figure 2.4. From this figure, it is clear that ZnO exhibits a sharp drop in the absorption coefficient near its band gap energy at $\lambda = 370$ nm, while the KTaO₃, BaTiO₃ and SrTiO₃ electrodes show a more gradual drop in the absorption coefficient with increasing wavelength near their respective band gap energies.

Another important consideration is related to the depletion width of the semiconductor-electrolyte junction. Since all of materials used here were heavily doped, the depletion region was relatively small in all cases. For example, the KTaO₃ crystals were degenerately doped with carrier concentrations of $\sim 10^{18}$ resulting in depletion widths of 0.06 to 0.2 μm [2.18]. The indirect optical transition results in a smaller absorption coefficient as well as smaller QYs; as the wavelength is increased toward the band gap energy, the absorption coefficient decreases (i.e., the optical penetration depth increases). KTaO₃ has an indirect edge at 340 nm (3.64 eV), with the first direct edge at 290 nm (4.35 eV) [2.13]. In this wavelength region, electron-hole pairs will be created in the bulk of the material, well beyond the depletion region, requiring transport of the minority carriers by diffusion to reach the depletion region to be separated and subsequently collected. However, defects in the material can result in recombination of many of these minority carriers before charge collection takes place, thereby resulting in a reduced QY.

On the other hand, photons that are absorbed near the surface (as in the case of ZnO for wavelengths shorter than the bandgap) create electron-hole pairs in the depletion region that will be immediately subjected to an accelerating electric field. This will enhance the probability that minority carriers are separated and collected. Intermediate absorption coefficients (e.g., BaTiO₃ and SrTiO₃ in the region 320-380 nm) will result in intermediate values of the QY.

The maximum value of the QY did not reach unity for any of the samples. The maximum QY of the KTaO₃ photoanode at 250 nm was < 0.3 . This indicates that there is some

recombination mechanism that takes place in the near surface region that reduces the generated minority carrier holes. The origin of these defects is not known at this time.

Time-resolved measurements indicate the presence of complex defects acting within the system that change the concentration of the minority carriers. The QY vs. time for KTaO_3 (Figure 2.3) shows a complicated decay scheme requiring at least two exponentials. The fact that the QY decays in this way indicates that the light reduces the collection of minority carrier holes.

2.5 Conclusions

The quantum yield behavior was related to the penetration depth of the incident light. Electron-hole pairs formed deeper in the crystal are less likely to be collected (at least in part) due to the presence of defects, small depletion regions, and short minority carrier diffusion lengths. In the case of KTaO_3 , the drop of the quantum yield as a function of time yielded a decay fit to a double exponential, and was associated with the presence of at least two different types of electrically active defects/traps in the crystals. The KTaO_3 , BaTiO_3 , and SrTiO_3 photoanodes were found to be chemically stable in the PEC cell environment, while the ZnO electrodes were found to undergo some surface alteration during electrochemical testing in the basic electrolyte. Continuing research is concentrating on the nature of the recombination centers in order to better understand their role in the reduction of the charge carriers. Additionally, the effect of significantly lowering the doping concentrations to increase the depletion region width as well as the minority carrier diffusion length is being explored.

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Appendix

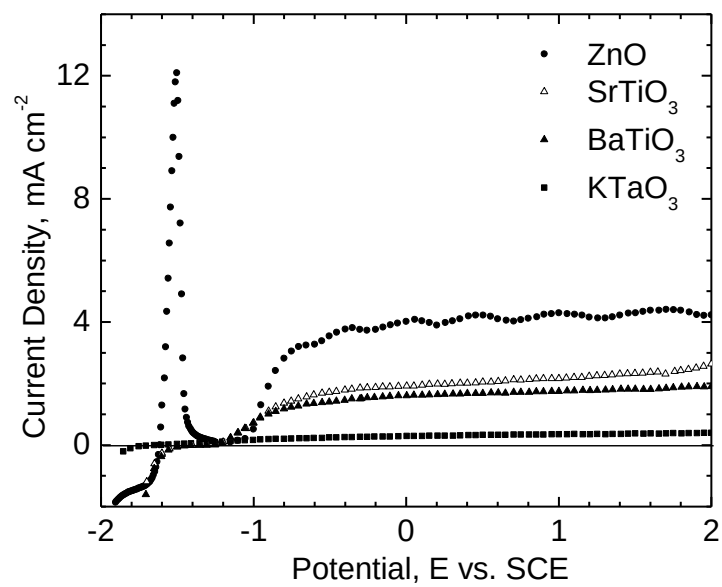


Figure 2.1 Current density vs. applied potential curves for various n-type semiconducting oxides in an electrolyte of 8.5 M NaOH (pH = 14.9) at room temperature.

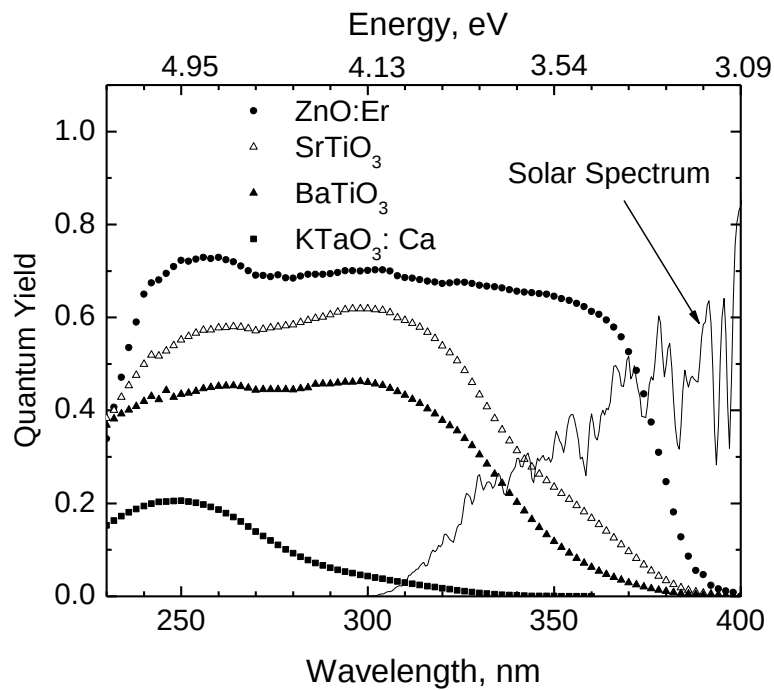


Figure 2.2 Spectral quantum yield of various n-type semiconducting oxides. ZnO and KTaO₃ samples were doped with Er and Ca respectively. Time dwell per data point in the figure is 20 s.

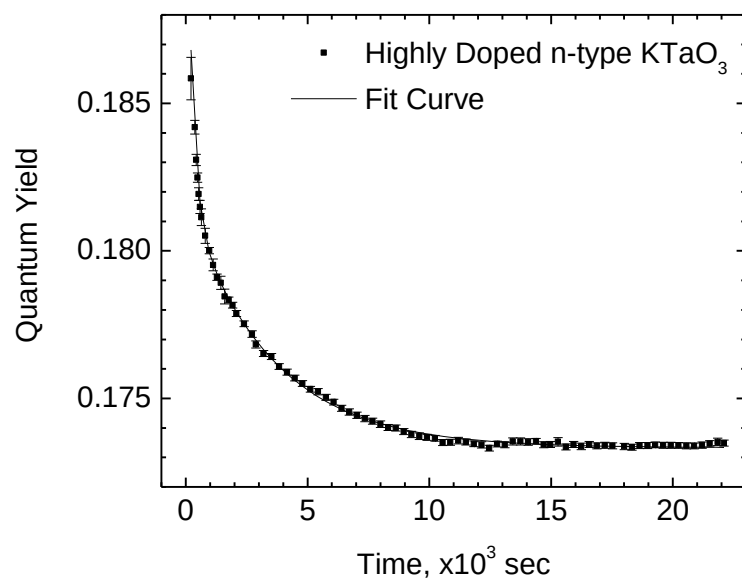


Figure 2.3 Variation of the quantum yield measured at 260 nm as a function of time for a highly doped KTaO_3 electrode.

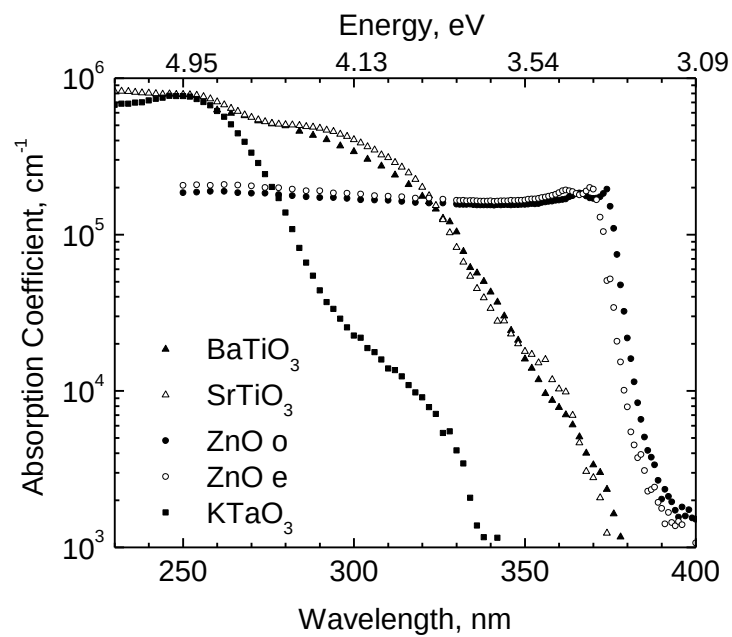


Figure 2.4 Absorption coefficient of various semiconducting oxides. The KTaO₃ data has been re-plotted from Ref. 2.13, the ZnO data from Ref. 2.16, and the SrTiO₃ and BaTiO₃ data from Ref. 2.17.

3 Growth, characterization, and electrochemical properties of doped n-type KTaO_3 photoanodes

This chapter is a journal article with the same name published in the *Journal of the Electrochemical Society* in 2009 by I. E. Paulauskas, J. E. Katz, G.E. Jellison Jr., N. S. Lewis, L. A. Boatner, and G. M. Brown:

I. E. Paulauskas, J. E. Katz, G. E. Jellison Jr., N. S. Lewis, L. A. Boatner and G. M. Brown , *J. Electrochem. Soc.* **156**, B580 (2009).

My use of "we" in this chapter refers to my co-authors and myself.

Abstract

The effects of compositionally induced changes on the semiconducting properties, optical response, chemical stability, and overall performance of KTaO_3 photoanodes in photoelectrochemical (PEC) cells have been investigated. Single crystals of n-type Ca- and Ba-doped KTaO_3 with carrier concentrations ranging from $0.45 - 11.5 \times 10^{19} \text{ cm}^{-3}$ were grown and characterized as photoanodes in basic aqueous electrolytes PEC cells. The photoelectrochemical properties of the crystals, including the photocurrent, photovoltage, and flat-band potential in contact with 8.5 M NaOH(aq) were relatively independent of whether Ca or Ba was used to produce the semiconducting form of KTaO_3 . All of the Ca- or Ba- doped KTaO_3 single-crystal photoanodes were chemically stable in the electrolyte and, based on the open-circuit potential and the band-edge positions, were capable of unassisted photochemical H_2 and O_2 evolution from H_2O . The minority-carrier diffusion lengths values were small and comparable to the depletion region width. Photoanodic currents were only observed for photoanode illumination with light above the band gap (i.e., $\lambda < 340 \text{ nm}$). The maximum external quantum yield occurred at $\lambda = 255 \text{ nm}$ (4.85 eV), and the depletion width plus the minority-carrier diffusion length ranged from 20 to 65 nm for the various KTaO_3 -based photoanode materials.

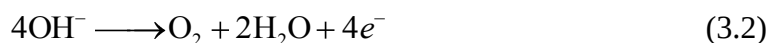
3.1 Introduction

Photoelectrochemical (PEC) cells provide an energy conversion mechanism through which light can be directly converted into a chemical fuel and/or electrical energy. PEC cells that are capable of evolving $\text{H}_2(\text{g})$ from aqueous solutions are of particular interest since they offer a potential method for directly generating hydrogen fuel through the use of solar energy. However, no existing PEC system is presently capable of efficiently converting sunlight to hydrogen gas without an applied bias voltage.

In a typical photoelectrochemical cell, electron-hole pairs are formed in the semiconductor upon the absorption of photons having an energy greater than the band gap of the material. These electron-hole pairs are separated by diffusion gradients and/or by the electric field present at the semiconductor-liquid interface (Figure 3.1, please see appendix for all tables and figures). If the photoanode is in contact with an alkaline electrolyte, the majority-carrier electrons are driven to the back contact, and eventually reduce an acceptor species at a counter-electrode to form hydrogen via the reaction:



The minority-carrier photogenerated holes flow in the opposite direction, and oxidize the donor species at the semiconductor-liquid interface, producing oxygen through the reaction:



These equations combine to give the overall cell reaction:



PEC cells can thus provide a method for the direct conversion of solar energy into hydrogen, producing a fuel that can be stored and transported for subsequent use.

Several fundamental requirements exist, however, in order for any PEC cell to be useful for converting solar energy into chemical fuel or electrical power. First, the photoelectrode must strongly absorb sunlight and efficiently produce electron-hole pairs. Second, these electron-hole pairs must be separated and collected. Finally, the charge carriers must be energetically and kinetically capable of driving the chemical reactions associated with water dissociation, while minimizing deleterious ancillary processes, such as the corrosion of the electrode itself. Appropriate values of the band gap and of the absolute positions of the conduction and valence bands relative to the electrochemical potentials for H_2 and O_2 evolution in water are critical for efficient water dissociation based on PEC cells. The band gap must be sufficiently small (optimally < 2.0 eV) so that a significant portion of the Sun's energy is captured and converted, and additionally, the positions of the bottom of the conduction band, E_{CB} , and the top of the valence band, E_{VB} , must be above and below the positions of the hydrogen and oxygen evolution potentials, respectively. These constraints impose a thermodynamic limit on the minimum band gap of >1.23 eV for a single-photon threshold device [3.1]. Several semiconducting photoanodes, such as SrTiO_3 [3.2], ZrO_2 , Ta_2O_5 and others [3.3], split water efficiently with no applied bias voltage and are photochemically stable, but unfortunately, their large band gaps (3.4-3.7 eV) prohibit significant absorption and conversion of most of the terrestrial solar spectrum.

The factors that control the stability of semiconductor photoanodes are among the least-well-understood aspects of PEC cells. The oxidation of water to O_2 is a four-electron process that proceeds through a series of partial reactions, generally creating highly reactive radical intermediates that are bound to the semiconductor surface. The intermediates must remain on the electrode surface to facilitate the subsequent oxidation steps in the electrolysis reaction, yet

these intermediates may be capable of weakening or breaking bonds associated with the surface atoms of the electrode. The properties essential for good catalytic action can, therefore, also lead to undesired corrosion reactions. All of the presently known photoelectrodes that are both thermodynamically capable of water splitting and kinetically stable under illumination in aqueous solutions, in fact, do not absorb a significant portion of the solar spectrum. In contrast, known materials (such as CdTe or InP) that do absorb sunlight efficiently cannot sustain unassisted photochemically induced water-splitting in a stable fashion [3.4].

At least two approaches have the potential to overcome the limited light absorption of stable, wide band-gap, semiconducting photoanodes. One approach uses dye-sensitization to extend the optical response of nanocrystalline metal oxide photoelectrodes [3.5-3.7]. In these devices, the surface of a mesoporous, wide band-gap semiconductor, such as TiO₂, is coated with a monolayer of sensitizer molecules (generally a Ru-polypyridyl complex). Upon light absorption by the dye, the photogenerated electron is injected into the conduction band of the semiconductor, creating a photocurrent at photon energies significantly below the band gap of the semiconducting metal oxide electrode itself. These systems are capable of absorption of >920 nm photons, with quantum yields approaching unity and solar energy conversion efficiencies reported in excess of 10% [3.6]. This approach, however, has not (to date) been applied successfully to the efficient generation of H₂ and O₂ from water, because the systems only operate efficiently in non-aqueous solvents and with the I₃⁻/I⁻ redox couple as the electron shuttle in the electrolyte.

A second approach is to develop a material that inherently meets the three criteria for efficient unassisted photoelectrochemical solar-energy-based water splitting. Rather than using molecular surface modification, the bulk composition of the material can be altered, as has been

demonstrated in the case of a nickel-doped indium tantalum oxide photoanode, to extend the optical absorption of an otherwise wide-band-gap semiconductor [3.8]. At sufficiently high levels, “dopant” atoms can serve not only to provide charge carriers, but also to potentially alter the intrinsic nature of the material, thereby affecting its crystal and band structure, optical absorption, and electronic properties. Predicting such effects via calculations is not yet possible, and the scope of relevant experimental data is also limited [3.9].

In the present work, we have employed single crystals of KTaO_3 as a model stable semiconducting photoanode system to investigate the effects of compositional variations on the electronic properties of this material and to elucidate its associated performance as a photoanode in a photoelectrochemical cell. Pure KTaO_3 is a highly resistive ($\sim 10^{15}$ ohm-cm), cubic perovskite crystal with a band gap of ~ 3.64 eV [3.10]. When doped with alkaline-earth impurities such as calcium or barium, the resistivity of KTaO_3 can be decreased to ~ 0.05 ohm-cm [3.11]. Although n-type KTaO_3 is known to be a stable material that is capable of unassisted photoelectrochemical water splitting [3.12-3.15], the overall solar energy conversion efficiencies of this system are low, due to the wide band gap and poor absorption of the solar spectrum. In this work, n-type KTaO_3 single crystals have been degenerately doped with Ca or Ba ions with the goal of altering the band structure as a means of “sensitizing” the KTaO_3 response to lower energy irradiation, while maintaining the established chemical stability of KTaO_3 photoanodes during the operation of a PEC cell.

The optical and electrochemical properties [3.12-3.21], band structure [3.10-3.22], and the crystal structure [3.23] of KTaO_3 have previously been studied in detail, both in the presence and absence of dopant atoms. This prior work, however, has not addressed how compositionally induced changes in semiconducting properties (such as the carrier concentration, mobility, and

resistivity) affect the overall performance, optical response, and chemical stability of KTaO_3 photoelectrodes in operating PEC cells. Furthermore, the present work elucidates the positions of the band edges as a function of the dopant species and dopant concentration at the high dopant levels that are employed.

3.2 Experimental Details

3.2.1 Crystal Growth and Sample Preparation

The KTaO_3 single crystals used in the present studies were grown with a variety of dopant impurities by using the technique of solidification from a nonstoichiometric melt [3.24]. In this crystal-growth process, predetermined levels of the impurity were added to a Ta_2O_5 and K_2CO_3 mixture. Extra K_2CO_3 was also added to the growth charge to maintain an excess of K_2O that results from the thermal decomposition of potassium carbonate. The n-type semiconducting KTaO_3 single crystals were grown by adding the alkaline-earth elements Ca or Ba in their carbonate form (CaCO_3 or BaCO_3 respectively) to the $\text{Ta}_2\text{O}_5 + \text{K}_2\text{CO}_3$ mixture.

The crystal-growth charges were placed in Pt crucibles, covered with Pt sheets, and heated in air to 1390 °C. The charges were then held at this temperature for 2 h, cooled at 1 °C per h to 1350 °C, at 0.75 degrees per h to 1300 °C, and finally at 1 degree C per h to 900 °C. At this point the furnace was turned off but the crucibles remained in the furnace until room temperature was reached. The unreacted flux was then dissolved with water. The entire crystal growth process lasted ~21 days.

The crystals showed a well-defined rectangular or square cross section (Figure 3.2). The dark central portion in Figure 3.2 is the heavily doped region (resistivity, $\rho \sim 10^{-1} \Omega\text{-cm}$), and the clear region is the un-doped material ($\rho \sim 10^{15} \Omega\text{-cm}$). This concentration gradient in the dopant

density is commonly reported for KTaO_3 [3.20, 3.25], and is a result of the effect of the segregation coefficient of impurities such as Ca and Ba.

The crystals naturally grew along their (100) faces, as determined by Laue X-ray back reflection analysis. Photoanode samples were cut from the doped (dark) region of the crystal parallel to their longest (100) face, to minimize the effects of dopant concentration gradients [3.26]. The specimens were then lapped and polished to form ~ 1 mm thick plates and were then finished with a 600-grit surface.

Immediately after polishing, ohmic contacts were made to the KTaO_3 plates by soldering a gold wire, using pure In dots, to a region of the crystal that had been coated with an In-Ga eutectic. The contacts were then covered with conducting silver paste. Insulating epoxy was used to cover the back contact surfaces and to define the surface area of the electrode that would be exposed to the electrolyte. Impedance spectra confirmed that the back contacts were ohmic. Exposed electrode areas were determined using Image SXM software by comparing a scanned image of the electrode surface to that of a template of known dimensions.

Companion Hall-effect samples were created on nominally square plates that had areas ranging from 21 mm^2 to 70 mm^2 . Ohmic contacts were made to these plates by coating indium on the four corners of the samples immediately after polishing. Hall-effect measurements were performed using the Van der Pauw configuration [3.27]. The resistivities of the Ca- and Ba-doped samples were between $(0.76 - 3.8) \times 10^{-2} \Omega\text{-cm}$, and the carrier concentrations varied from $(0.4 - 2) \times 10^{19} \text{ cm}^{-3}$, consistent with prior reports of the properties of Ca-doped KTaO_3 [3.20]. The carrier concentration varied by up to a factor of three within samples cut from the same crystal, presumably due to dopant segregation effects. The measured Hall mobilities ranged

from 22 to 28.6 cm² V⁻¹ s⁻¹ and were somewhat lower than those reported previously [3.11], possibly due to the presence of atomic-scale defects in the material.

2.2.2 Electrochemical Methods

The quartz electrochemical cell was H-shaped, with a porous frit separating the two cell compartments. One of the cell chambers had a flat quartz optical window (to transmit light longer than 180 nm) to facilitate UV illumination of the photoanode. Electrochemistry was performed in a 8.5 M NaOH(aq) (pH 14.9) solution at room temperature, with a Pt counter electrode and an aqueous saturated calomel reference electrode (SCE).

3.2.2.1 Electrochemical Impedance Spectroscopy:

Frequency-dependent impedance spectra were collected between 1 and 10⁵ Hz using a Solartron Model 1286 potentiostat and Model-1260 impedance analyzer. The data were collected every 100 mV under reverse bias conditions for dc biases ranging from 0.9 to -0.7 V vs. SCE. The data were fit from 1 to 10⁴ Hz to a three-element equivalent circuit that consisted of a resistor in series with a parallel combination of a capacitor and a resistor. The flat-band potential, E_{fb} , and the carrier concentration, N_D , of the samples were determined by a conventional Mott-Schottky analysis of the impedance data using the equation:

$$\frac{1}{C_{sc}^2} = \frac{2}{q\epsilon_0\epsilon_s N_D A^2} \left(E - E_{fb} - \frac{kT}{q} \right) \quad (3.4)$$

where C_{sc} is the space-charge capacitance (C cm⁻²), E is the potential of the electrode (V), k is Boltzmann's constant, T is the temperature (K), q is the charge on an electron, ϵ_0 is the dielectric constant of vacuum, ϵ_s is the static dielectric constant of KTaO₃ [3.11], and A is the electrode area (cm²). Extrapolation of C_{sc}^{-2} vs. E to the x-intercept yielded $E_{fb} + kT/q$, and the slope yielded the dopant density of the sample. Details regarding this technique can be found elsewhere [3.3,

3.28]. A least-squares linear analysis of the C_{sc}^{-2} vs. E plots gave excellent fits to the data (Figure 3.3). In certain cases, the data at large negative voltages were excluded, due to non linearity. Flat-band potentials were found to be between -1.2 and -1.4 V vs. SCE (Table 3.1), which is comparable to the value reported by Bolts *et al.* of -1.3 V vs. SCE at pH 13 for n-type KTaO_3 [3.29].

3.2.2.2 Current vs. Potential Behavior

Current density vs. potential (J - E) data were obtained by illuminating the samples with a 150 W Xe arc lamp or an Oriel 66902 solar simulator with Air Mass (AM) 1.5 conditions. Data were collected at 50 mV s^{-1} in deoxygenated solutions, both in the dark and under illumination, using a Solartron Model 1287 potentiostat. The J - E data obtained for all of the crystals showed rectification regardless of the type or concentration of the dopant (Figure 3.4). Under simulated AM 1.5 illumination, the Ca- and Ba- doped KTaO_3 samples displayed mutual similar values of the current density at 0 V vs. SCE (Table 3.1).

To determine the open-circuit potential, E_{oc} , measurements were performed at constant photocurrent ($50 \text{ }\mu\text{A}$ at 0 V vs. SCE). This facilitates the comparison of the E_{oc} values between samples under constant injection flux of minority carriers [3.30]. These measurements indicated that for the Ca- and Ba- doped samples, the E_{oc} values were similar (see Table 3.1). The average E_{oc} between these samples was -1.36 V vs SCE with a standard deviation of ± 0.1 V, which is in agreement with previous reports ($E_{oc} = -1.25$ V vs. SCE) [3.14]. In all cases, the E_{oc} values were more negative than the formal potential for the H^+/H_2 redox couple at the pH of concern ($E^{0'}(\text{H}^+/\text{H}_2) = -1.12$ V vs. SCE at pH = 14.9).

3.2.2.3 Quantum Yield

Measurement of the quantum yield (Φ) included a determination of the quantum yield as a function of wavelength as well as a function of time for a given wavelength. The experimental set-up consisted of a Xe arc lamp and a single-pass monochromator set at a 5 nm bandwidth. To reduce stray light in the monochromator resulting from the zeroth order reflection from the grating, a BG-24 filter was placed at the entrance slit of the monochromator. The output beam was focused using a fused silica lens, and the intensity of the beam was continuously monitored by splitting off a portion of the light with a fused silica plate and directing the resulting split portion into a Si photodiode. A second NIST-calibrated Si diode was used to calibrate the illumination intensity incident on the sample. The photocurrent from the KTaO_3 electrodes at each wavelength was measured using a Princeton Applied Research Model 2263 potentiostat/galvanostat.

Samples were held at 0 V vs SCE. Reflection losses due to the quartz window in contact with the electrolyte as well as the reflection from the electrode-electrolyte interface were taken into account. The illumination areas were $\sim 1.7 \text{ mm}^2$ and were significantly smaller than the actual electrode surface.

While all samples were measured using the direct current (dc) method described, we also measured samples 2 and 5 (see Table 3.1) using chopped light, no statistically significant difference between chopped data and the dc data was observed.

External quantum yield (Φ_{ext}) results indicate that the samples were photoactive at wavelengths $< 340 \text{ nm}$ ($E > 3.64 \text{ eV}$), with maximum external quantum yields ranging from 0.18 to 0.4 at 255 nm (Table 3.1). Figure 5 shows the external quantum yield for various samples. The spectral response of all the samples exhibited a characteristic shape consisting of a broad peak (at

255 nm) followed by a tail between 300 and 340 nm. The observed behavior is consistent with the peak in the quantum yield reported previously by Ellis *et al.* at ~254 nm [3.14]. Additionally, Φ_{ext} was found to change within the same sample. Figure 3.6 shows two quantum yield data sets measured from sample 2, the only change in the measurements was the location of the illumination spot. Significant changes in Φ_{ext} only were observed at the lower wavelengths, with the maximum difference observed at the peak of the spectral response.

Time-resolved quantum yield measurements were performed at 260 and 320 nm. At both wavelengths, the decrease in Φ_{ext} from its initial value could be fit using a double exponential, equation 3.5:

$$\Phi_{\text{ext}}(\lambda) = A_0 + A_1 e^{-t/t_1} + A_2 e^{-t/t_2} \quad (3.5)$$

Results for a selected Ca- and a Ba- doped crystal are displayed in Table 3.2. The data for sample 2 at 260 nm has been previously reported in Ref. 3.31, and is used in Table 3.2 for comparison purposes. The time constants indicate for both samples that Φ_{ext} reached equilibrium considerably faster at 320 nm (which is inside the tail region of the Φ_{ext} curve, see Figure 3.5) than at 260 nm (the peak region). Some difficulties were present while measuring sample 5 at 320 nm, since the Φ_{ext} decay time constant approached 10 s, which is close to the time resolution of the system.

Additional time-resolved quantum yield measurements at 260 nm using a deoxygenated 8.5 M NaOH electrolyte at room temperature were performed to better analyze the possibility of oxygen formation at the surface of the KTaO_3 electrode as a function of time. Deoxygenation was achieved by sparging ultra-high-purity He in the electrolyte. This process was initiated 1.5 h before the measurement started and was maintained throughout the measurement. The He

sparging not only helped to keep the electrolyte deoxygenated, but also reduced any mass transfer effects at the photoanode/electrolyte interface. The decreased photocurrent measured at the KTaO_3 electrode was also fit to a double exponential similar to Eq. 3.5, where $A_0 = 2$, $A_1 = 0.08$, $t_1 = 370 \pm 4$, $A_2 = 0.11$, and $t_2 = 5310 \pm 20$ ($R^2 = 0.90$).

3.3 Results and Discussion

3.3.1 J-E Behavior of Doped KTaO_3 :

The observed low photocurrent densities were primarily the result of the small overlap of the KTaO_3 optical absorption range with the lamp's irradiance spectrum (Figures 4 and 5), which has only a small fraction of its total power at wavelengths < 300 nm. *J-E* data under illumination showed an inflection point at -1.4 V vs SCE. This behavior is commonly observed with metal oxide semiconductors. At more positive voltages, the band edges are sufficiently bent to efficiently collect photogenerated carriers. As the potential is scanned into the negative region, the bands are flattened, reducing the collection efficiency of photogenerated charge carriers to zero. However, due to the slow interfacial kinetics and deoxygenated electrolytes, essentially no dark current passes at these potentials, resulting in net zero current. Finally, as the applied potential is made sufficiently negative to overcome the overpotential for the reduction of water, a cathodic current is observed. The hysteresis observed in Figure 3.4 between the reverse and forward scan direction was a function of the scan rate used (50 mV s^{-1}), indicating the presence of a time dependence in the measurements.

3.3.2. Mott-Schottky Analysis

Mott-Schottky analysis of the impedance spectra provided the values of the flat-band potentials of the samples in the dark. Despite the consistency of the measured flat-band potentials, values of N_D varied significantly among the samples, having values in the range of $(0.4 \text{ to } 12) \times 10^{19} \text{ cm}^{-3}$. Self-segregation of dopants during the crystal growth process precluded extremely precise control of the doping levels.

Given the flat-band potential and the dopant density, the potential of the bottom of the conduction band edge is given by:

$$E_{CB} = E_{fb} - \frac{kT}{q} \ln \left(\frac{N_C}{N_D} \right) \quad (3.6)$$

where N_C is the effective density of states in the conduction band. Note that the second term in equation 3.6 is relatively small due to the large values of N_D . The value of N_C is:

$$N_C = 2 \left(\frac{2\pi m_e^* kT}{h^2} \right)^{3/2} = 1.42 \times 10^{19} \text{ cm}^{-3} \text{ at } 298 \text{ K} \quad (3.7)$$

where m_e^* is the effective mass of electrons in the conduction band,¹⁷ and h is Planck's constant.

Given the conduction-band edge and the band gap, the position of the top of the valence band can be readily calculated. The position of the band edges was similar for the various samples (Table 3.1), and in all cases, the $\text{H}_2\text{O}/\text{H}_2$ and O_2/OH^- formal potentials (-1.12 and 0.11 V vs. SCE, respectively, at pH= 14.9) fell within the band gap of the KTaO_3 , indicating that the samples are thermodynamically capable of electrolyzing water with zero applied bias.

As the electrode potential approaches the flat-band potential, the depletion width goes to zero and the differential capacitance of the space-charge region increases so that the depletion region capacitance no longer dominates the total capacitance of the system. Other capacitive

elements, such as that of the double layer, which, in the equivalent circuit, are in series with the space-charge region capacitance, will contribute significantly to the measured capacitance under such conditions. This was commonly observed as a deviation from linearity of the C_{sc}^{-2} vs. E plots at potentials negative of -0.2 V vs. SCE (Figure 3.3). The data at potentials approaching flat-band were thus excluded from the Mott-Schottky analysis.

3.3.3 Quantum Yield

The various samples all exhibited photocurrents over similar ranges of excitation energies, indicating that the replacement of K^+ with varying amounts of the electron donors Ca^{2+} and Ba^{2+} did not measurably sensitize the $KTaO_3$ to longer wavelengths illumination. This insensitivity to doping at these levels may be due to the dopant atoms, despite their high concentration, not forming a significant density of states within the band gap. Alternatively, the newly formed states may lack a sufficiently strong interaction with the band states of intrinsic $KTaO_3$ to absorb visible light.

3.3.4 Optical Measurements and Quantum Yields

Spectroscopic ellipsometry and optical transmission data of both doped and un-doped $KTaO_3$ indicate that the lowest optical gap in $KTaO_3$ is indirect, with an energy of 3.64 eV [3.10]. Three higher energy direct gaps also exist, with energies of 4.35, 4.68, and 5.03 eV, respectively. The data presented in Ref. 3.10 have been re-plotted in Figure 3.7 to emphasize the characteristics of the optical absorption that are important in understanding the photoelectrochemistry of $KTaO_3$. Figure 3.7a depicts the penetration depth of light versus wavelength, where the penetration depth is the inverse of the absorption coefficient, representing the depth at which the light intensity is reduced to $1/e \sim 37\%$ of its incident value. As can be seen

from this plot, light in the 300-340 nm region is preferentially absorbed $\sim 1 \mu\text{m}$ from the surface of the sample.

One consequence of the deeper penetration of light is that the electron-hole pairs are generated far into the crystal and must diffuse to the depletion region near the surface to be collected. This constraint reduces considerably the quantum efficiency for photons at generated at long wavelengths. Using the simple solar cell model [3.32], it can be shown that for crystals exhibiting ideal behavior, the external quantum yield ($\Phi_{\text{ext}}(\lambda)$) is described by:

$$\Phi_{\text{ext}}(\lambda) = \frac{\alpha(\lambda)L}{\alpha(\lambda)L + 1} (1 - R(\lambda)) \quad (3.8)$$

where $\alpha(\lambda)$ is the optical absorption coefficient of the material, L is the minority-carrier diffusion length, and $R(\lambda)$ is the surface reflectance. In deriving equation 3.8, three important assumptions are made:

1. The depletion width (W) is considerably smaller than the penetration depth of light.
2. The cell thickness is large compared to L .
3. L is much larger than W .

Part of the usefulness of equation 3.8 is that it represents a simple way to utilize the experimentally measured values of Φ_{ext} to estimate the minority carrier diffusion length for semiconductors such as single crystal Si [3.33]. However, in cases where semiconductors exhibit a more complex, non-ideal, behavior, such as the degenerate n-type KTaO_3 used in this study, assumptions like those made in deriving equation 3.8 are no longer reasonable, and parameters like W become more important in understanding the photoelectrochemical behavior of these crystals. If we assume that the cell thickness is considerably larger than L , then the internal quantum yield due to the base of the cell, $\Phi_{\text{int,B}}$, is given by:

$$\Phi_{\text{int},B}(\lambda) = \frac{\alpha(\lambda)L}{\alpha(\lambda)L + 1} \exp(-\alpha(\lambda)W) \quad (3.9)$$

Similarly, the internal quantum yield due to the depletion region, $\Phi_{\text{int},DR}$, is given by:

$$\Phi_{\text{int},DR}(\lambda) = 1 - \exp(-\alpha(\lambda)W) \quad (3.10)$$

The total external quantum yield of the system is given by:

$$\Phi_{\text{ext}}(\lambda) = \Phi_{\text{int},B}(\lambda) + \Phi_{\text{int},DR}(\lambda) [1 - R(\lambda)] \quad (3.11)$$

Using equations 3.9 and 3.10, the external quantum yield of the system can be expressed as:

$$\Phi_{\text{ext}}(\lambda) \approx \left[1 - \frac{\exp(-\alpha(\lambda)W)}{\alpha(\lambda)L + 1} \right] (1 - R(\lambda)) \quad (3.12)$$

where the quantum yield is not only linked to the minority carrier diffusion length, but also to the depletion width. Equation 3.12, and the absorption coefficient of KTaO_3 shown in Figure 3.7b, imply that $\Phi_{\text{ext}}(\lambda)$ should decrease monotonically from ~300 nm to 340 nm, in accordance with observations (see Figures 3.5 and 3.6).

Since equation 3.12 is less restrictive than equation 3.8, and still models an ideal system, it is a good starting point for understanding the photoelectrochemical behavior of these degenerately doped semiconductors. Expanding equation 3.12 in a Taylor series and keeping only first-order terms yields:

$$\Phi_{\text{ext}}(\lambda) \approx (W + L)\alpha(\lambda) [1 - R(\lambda)] \quad (3.13)$$

equation 3.13 thus provides an expression that links W and L in a single term. Figure 3.8 shows a plot of Φ_{int} vs $\alpha(\lambda)$ for two representative samples, which according to equation 3.13, should result in a linear dependence with a slope proportional to $W+L$. For all fits, the multiple-correlation coefficient was 0.99.

To obtain approximate values for W , an ideal one-sided abrupt junction was assumed, and was estimated using [3.24]:

$$W = \sqrt{\frac{2\epsilon_s}{qN_D} \left(V_{bi} - \frac{2kT}{q} \right)} \quad (3.14)$$

where V_{bi} is the built-in voltage. Figure 9 shows the depletion-layer width (W) as a function of the carrier concentration, for three different values of the built-in voltage (V_{bi}). For our n-type KTaO_3 samples, W was estimated to range from 20 nm for the crystals with higher carrier concentrations ($\sim 10^{20} \text{ cm}^{-3}$) to 90 nm for the lower-doped crystals ($\sim 4 \times 10^{18} \text{ cm}^{-3}$).

Figure 3.10 shows the calculated slopes (from equation 3.13), expressed in nm, as a function of the carrier concentration for the Ca- and Ba-doped samples. Two points are immediately evident from this plot: 1) no obvious correlation is present between the slope and the carrier concentration, and 2) the slopes (ideally representing $W+L$) have comparable magnitudes to the estimated depletion width. This suggests that L and W have similar values and, consequently, are difficult to quantify individually and/or that additional issues (such as an inhomogeneous surface) make this system more complicated than the ideal case. As a result, the slope may represent all these effects taken together.

The noted differences in the quantum-yield behavior can be at least partially explained by the time-resolved data (Table 3.2). As previously noted in Ref. 3.31, the observation of at least two time constants to define the decay behavior indicates that multiple electrically active defects reduce the quantum yield of the devices. The present study found that this double exponential decay scheme was independent of the wavelength used or the doping specie at these high carrier concentrations. Additionally, the magnitudes of the time constants indicate that when electron-hole pairs are formed near the surface of the crystal ($\lambda = 260 \text{ nm}$ has a penetration depth of ~ 16

nm), the time needed for the charge-collection process to reach equilibrium is much larger than when the electron-hole pairs are primarily formed deeper in the crystal ($\lambda = 320$ nm has a penetration depth of ~ 1100 nm) and away from the depletion region. Additionally, the relative decay of the quantum yield for a given sample was independent of wavelength. For sample 2, at 260 nm the percentage of reduction from the initial external quantum yield (A_0) to its equilibrium value ($A_1 + A_2$) was $12.7 \pm 1.1\%$, while at 320 nm this reduction was $14.4 \pm 0.5\%$. Similarly, the quantum yield decline changes for sample 5 at 260 and 320 nm were $6.1 \pm 0.4\%$ and $8.4 \pm 0.6\%$, respectively.

Due to the large magnitude of the time constants obtained when light was preferentially absorbed at the surface of the electrodes, an additional time-resolved quantum yield curve was measured using a deoxygenated electrolyte in order to estimate the formation rate of O_2 molecules at the surface of the photoanode. The photo-induced current measured from the photoanode as a function of time has been fitted to a double exponential. This curve allowed the calculation of the total charge in Coulombs used by the system, which can then determine the total amount of moles of electrons used per second. Using equations (1), (2) and (3) to calculate the amount of moles of O_2 produced as a function of time, enables the rate of formation of O_2 molecules (assuming a O_2 molecule diameter of 0.29 nm) to be estimated. Knowing that the light spot size is 1.7 mm, in ideal circumstances it can be estimated that about 15% of the spot size could be covered by an O_2 monolayer after one second of illumination, if every electron measured is part of the water dissociation reaction.

These results suggest that at least two processes could be causing the reduction of quantum yield as a function of time. On one hand, there is the possible formation of an oxygen monolayer that could effectively reduce the area for light absorption on the photoanode, which

consequently will reduce the quantum yield; however, this process should equilibrate relatively rapidly since the entire light-spot area should be covered in ~ 7 sec, and no bubbles were observed to form by optical examination of the cell during these measurements. On the other hand, the defects in the material may be susceptible to light-induced changes, whereby the light changes the defect into a recombination center. Obviously, there is a significant dependence on the penetration depth of light, where the light-induced change near the surface is considerably slower than the light-induced change further into the bulk of the material. Furthermore, there are significant sample-to-sample differences, particularly in the concentration of defects that are susceptible to light-induced changes. Another complication is that the quantum yield was never close to 1 for any of the samples studied. As a result, many of the electron-hole pairs created are lost to recombination centers, even for electron-hole pairs collected in the depletion region (for $\lambda = 260$ nm). This may mean that surface recombination plays an important role in determining the ultimate collection efficiency for KTaO_3 photoelectrochemical cells. Clearly, a number of unanswered questions remain regarding the minority-carrier transport and recombination processes in these materials.

3.4 Conclusions

The addition of Ca^{2+} or Ba^{2+} (through the use of CaCO_3 and BaCO_3 , respectively, in the crystal growth process) yielded highly doped n-type KTaO_3 . The conductivities and carrier concentrations of these KTaO_3 samples were greatly increased as a result of doping and the doped crystals were dark blue.

The quantum yield of the n-type KTaO_3 photoanodes did not correlate with the alkaline-earth element (i.e., Ba vs Ca) used for doping. A photoresponse was only observed under UV

irradiation ($\lambda \leq 340$ nm), reaching a maximum response at ~ 255 nm. Since less than 2% of the total radiance from the Sun is below 360 nm, additions of Ca or Ba did not offer an effective practical mechanism for improving the solar response of semiconducting KTaO_3 . All of the heavily doped KTaO_3 photoanodes were found to be chemically stable, and based on these open-circuit potentials and band-edge positions, were thermodynamically capable of unassisted photochemical H_2 and O_2 evolution from H_2O .

Determinations of the minority-carrier diffusion lengths suggest that these values are small and similar to those of the depletion-region width. Both factors will significantly increase the probability for the minority carriers to recombine, consistent with the observed reduction in quantum yield as the light was preferentially absorbed deeper in the crystal.

Time-resolved measurements indicated that, regardless of the penetration depth of the light, the quantum yield decrease was characterized by the presence of at least two time constants, which were associated with at least two types of electrically active defects. Although the reduction of the quantum yield may, in part, be associated with the formation of an oxygen layer at the surface of the semiconductor, it is also possible that the effect of the complex defects present in the semiconductor became significant when electron-hole pairs were formed near the surface of the semiconductor.

Ongoing experimental efforts are focused on finding more effective dopant species (or combinations thereof), exploring the possibility of significantly lowering the doping concentrations to increase the depletion region width as well as the minority carrier diffusion length, and the use of thermochemical reduction treatments as a means of sensitizing KTaO_3 to achieve more efficient photoelectrochemical production of H_2 under terrestrial solar irradiation.

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Appendix

Table 3.1 Summary of photo-physical properties for selected Ca- and Ba-doped KTaO₃ electrodes. The carrier concentrations and flat band potentials were determined using a Mott-Schottky analysis of the impedance spectra.

Sample	Dopant	Carrier Concentration (x 10 ¹⁹ cm ⁻³)	Flat-Band Potential (V vs SCE) ^a	Conduction Band Potential (V vs SCE) ^a	Valence Band Potential (V vs SCE)	Maximum External Quantum Yield ^b	<i>J</i> under AM1.5 illum. (μA/cm ²) ^c	<i>E</i> _{oc} ^d (V vs. SCE)
1	Ca	0.46 ± 0.05	-1.24	-1.63	2.0 ± 0.3	0.30	42.7	-1.26
2		1.32 ± 0.19	-1.31	-1.67	1.9 ± 0.4	0.18	34.6	-1.34
3		4.70 ± 0.60	-1.21	-1.53	2.1 ± 0.4	0.15	19.7	-1.40
4		5.40 ± 0.50	-1.41	-1.73	1.9 ± 0	0.35	54.5	-1.47
5	Ba	0.40 ± 0.08	-1.16	-1.55	2.1 ± 0.3	0.21	44.5	-1.50
6		10.30 ± 2.10	-1.16	-1.46	2.1 ± 0.3	0.40	54.7	-1.28
7		11.50 ± 2.30	-1.28	-1.58	2.0 ± 0.1	0.29	52	-1.22

a) Values ±0.02. b) Values ±0.01. c) Measured at 0 V vs. SCE. d) Current density kept constant at 50 μA cm⁻² by varying the light intensity.

Table 3.2 Exponential decay fitting parameters for the time-resolved quantum yield measurements

Sample	Wavelength (nm)	Penetration Depth ^a (nm)	A_0 ^b	A_1 ^c	t_1 (sec)	A_2 ^c	t_2 (sec)	χ^2 ^d
2	260 ^e	16	0.173	0.013	240 ± 20	0.009	3400 ± 30	0.72
	320	1100	0.017	0.002	18 ± 1	0.0007	160 ± 4	0.27
5	260	16	0.197	0.006	798 ± 95	0.006	5220 ± 300	0.07
	320	1100	0.015	0.001	8 ± 1	-	-	1.35

a) From Ref. 3.10. b) Errors limits < 1%. c) Error limits < 7%. d) The reduced χ^2 is used as the figure of merit of the fit, where $\chi^2 \leq 1$ indicates a good fit. e) From Ref. 3.31

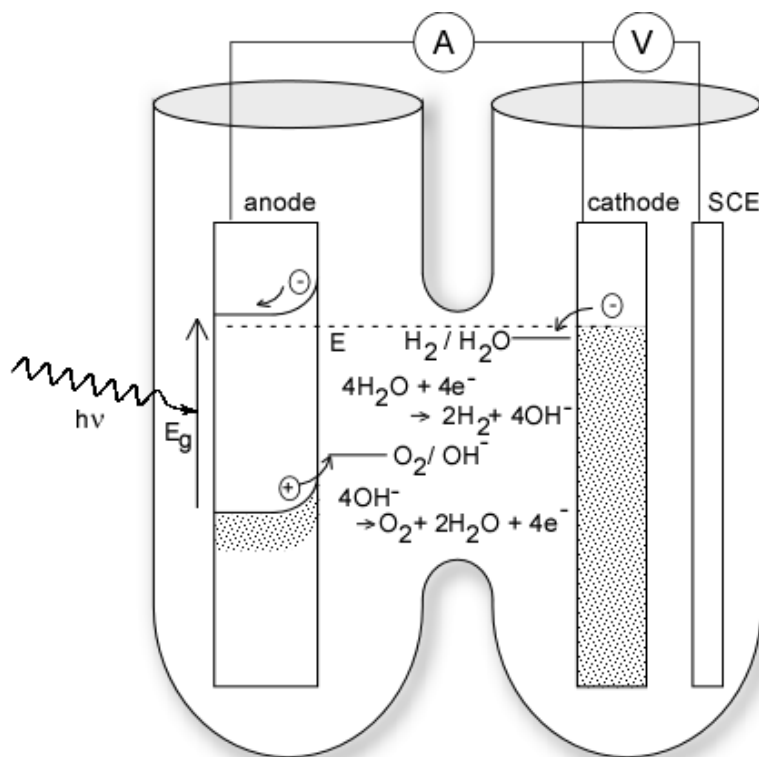


Figure 3.1 Schematic representation of a photoelectrochemical cell using an n-type semiconducting photoanode in an alkaline electrolyte. When light strikes the anode, electron-hole pairs are formed and then separated by the electric field that is present due to the band bending at the surface of the semiconductor. Oxygen is formed at the surface of the semiconductor, while hydrogen is formed at the surface of the cathode, in this case, Pt.

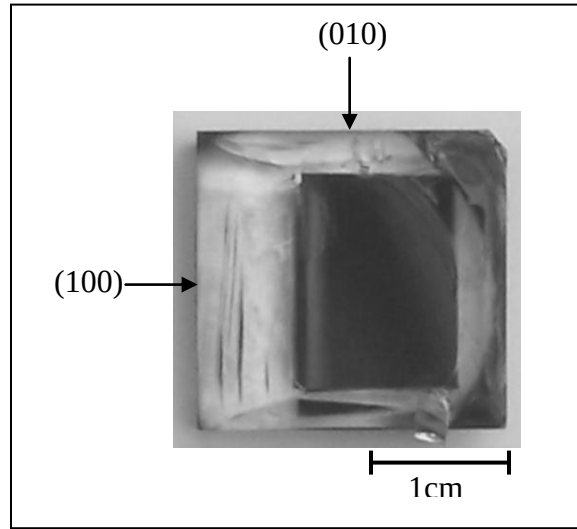


Figure 3.2 As-grown KTaO₃ single crystal. Crystals naturally grew with (100) faces (or equivalent faces), and two important regions could readily be distinguished visually: a dark central region, which is the n-type doped KTaO₃ ($\rho \sim 10^{-2} \Omega\text{-cm}$), and a transparent region of pure and highly resistive KTaO₃ ($\rho \sim 10^{15} \Omega\text{-cm}$).

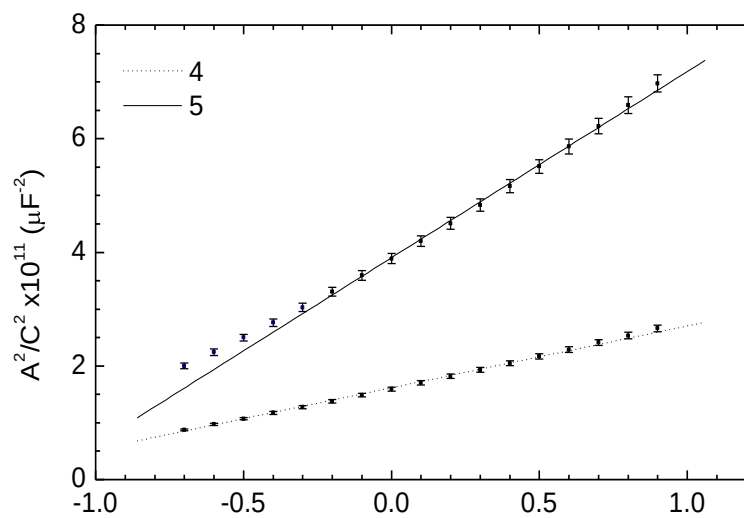


Figure 3.3 Mott-Schottky plots for Ca- (sample 4) and Ba- (sample 5) doped KTaO_3 crystals in a highly alkaline aqueous solution (Details for KTaO_3 samples 4 and 5 can be found in Table 3.1).

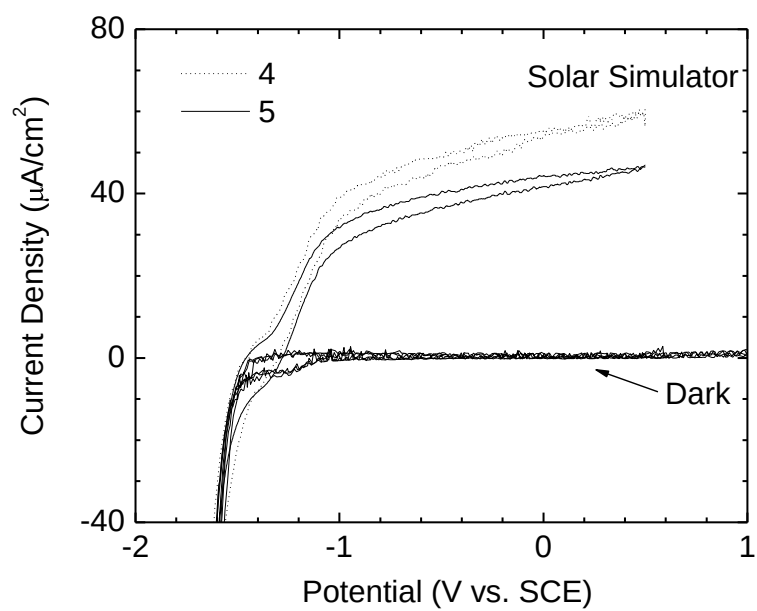


Figure 3.4 Photo-response of selected KTaO_3 samples under AM 1.5 illumination.

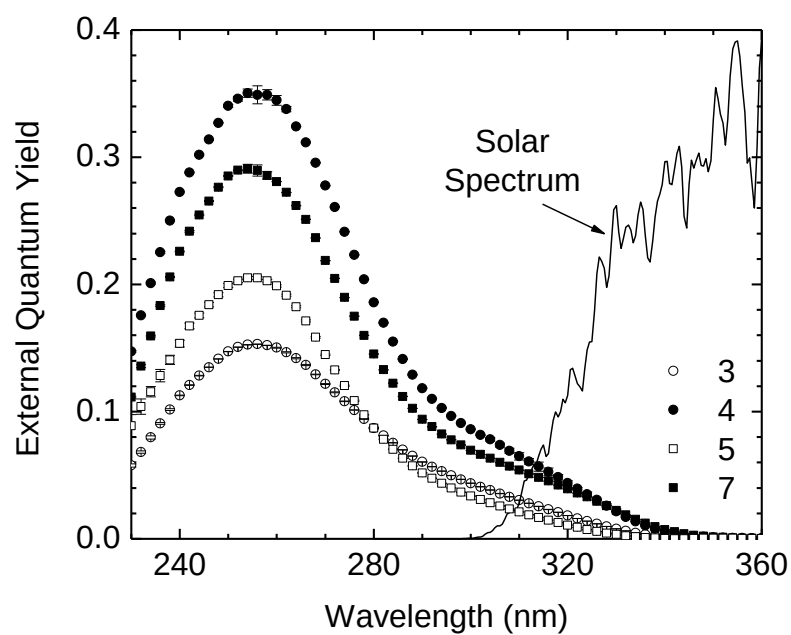


Figure 3.5 Spectral response for various Ca- (circles) and Ba- (squares) doped KTaO₃ samples. The AM 1.5 solar spectrum is also shown (in arbitrary units).

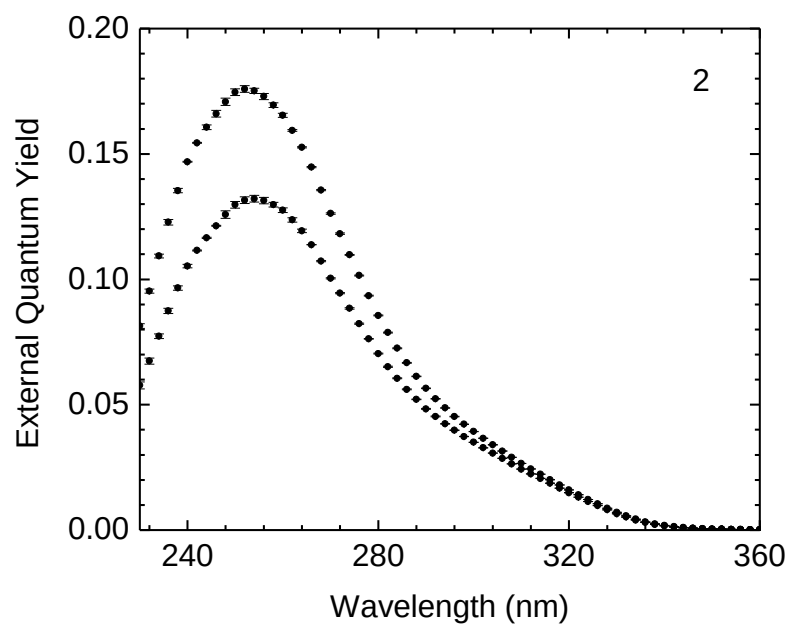


Figure 3.6 Variations of the external quantum yield for sample 2.

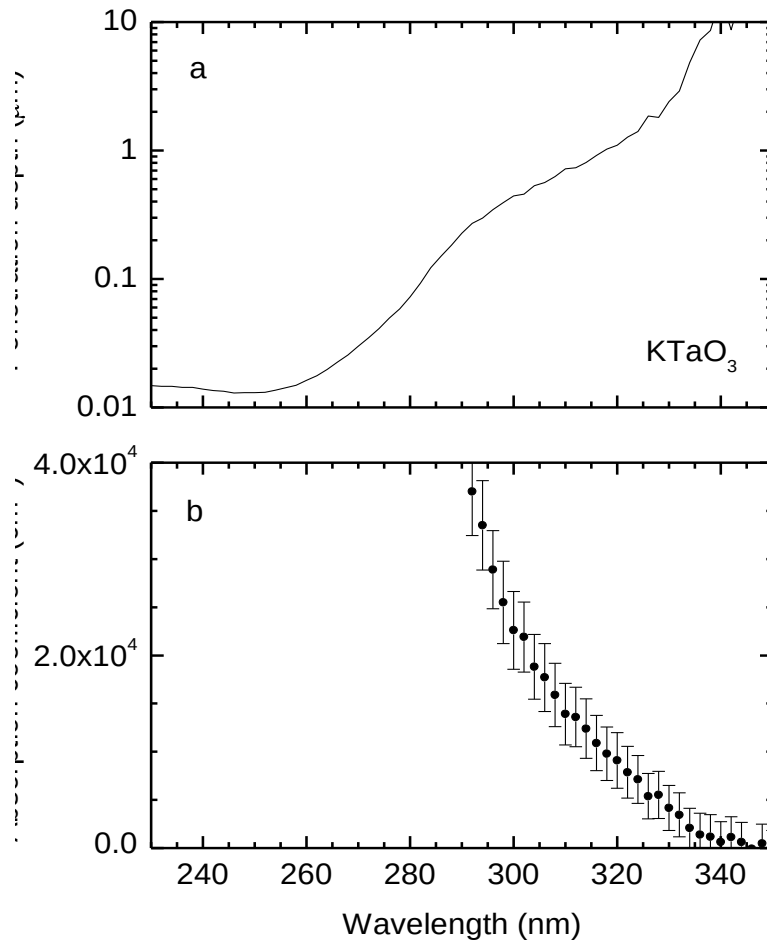


Figure 3.7 The penetration depth of light: (a) taken as the inverse of the absorption coefficient, from Ref. 3.10, (b) The absorption coefficient (including data from Ref. 3.10).

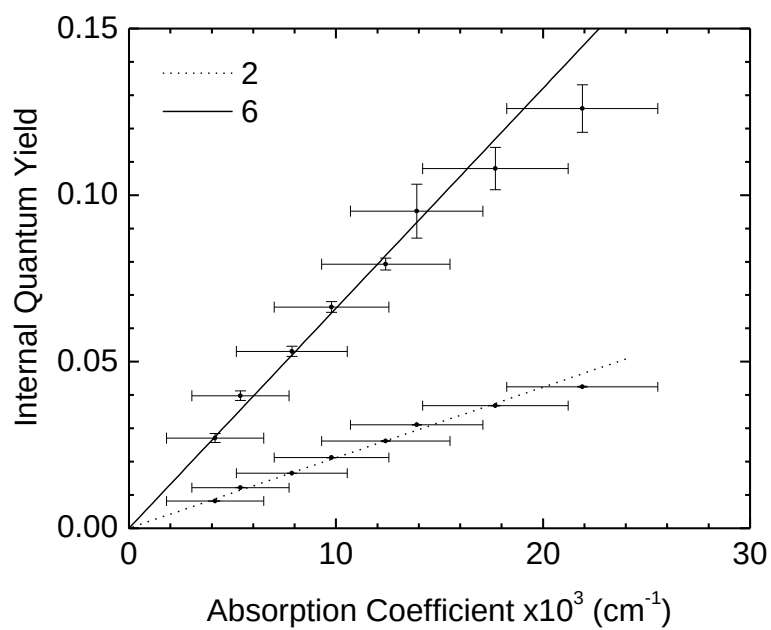


Figure 3.8 Internal quantum yields as a function of the absorption coefficient for representative Ca- (sample 2) and Ba- (sample 6) doped KTaO₃ crystals.

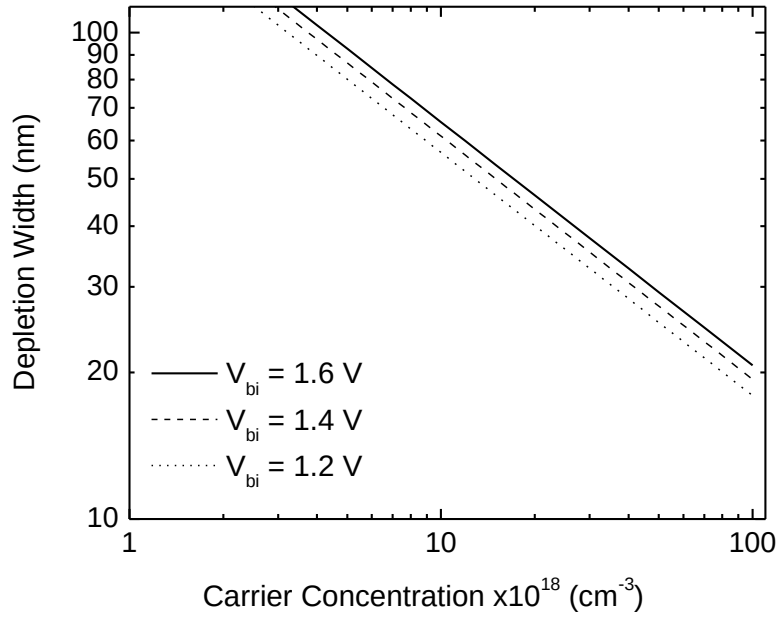


Figure 3.9 Estimated values of the depletion width, W , for the heavily doped KTaO_3 crystals as a function of the carrier concentration at the semiconductor/electrolyte interface. A one-sided “abrupt” junction is assumed.

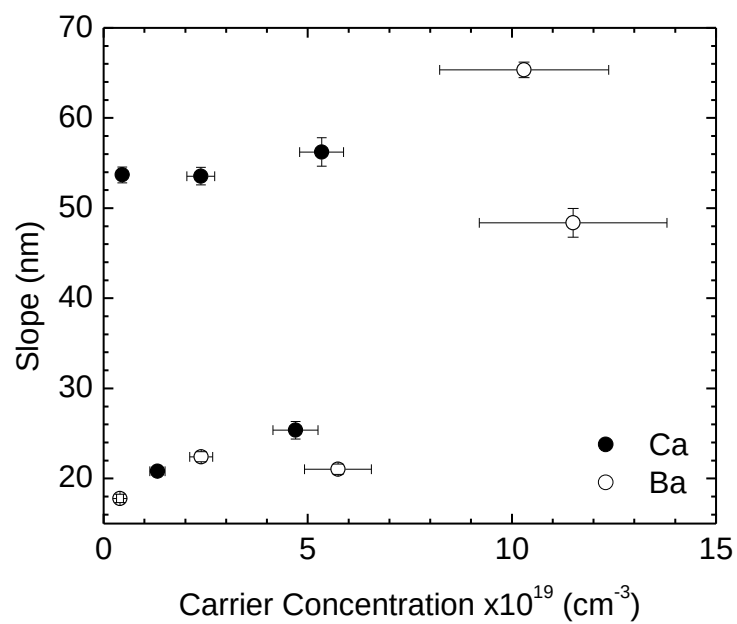


Figure 3.10 “Slope” of equation 3.13 (ideally representing the minority carrier diffusion length + the depletion width) vs. the carrier concentration.

4 Photoelectrochemical properties of n-type KTaO_3 single crystals in alkaline electrolytes

This chapter is a journal article by the same name submitted to the *Journal of Applied Physics* in 2009 by I. E. Paulauskas, G.E. Jellison, and L. A. Boatner.

Abstract

Semiconducting KTaO_3 single crystals were investigated as a model potential photoanode for hydrogen production using photoelectrochemical cells. To modify the electronic properties of KTaO_3 by reducing the bandgap and thereby increasing the absorption of light at longer wavelengths, the crystals were doped during growth. A wide range of dopant elements was employed that consisted primarily of transition metal atoms. Most of the crystals exhibited n-type behavior with carrier concentrations from 4×10^{18} to $2.6 \times 10^{20} \text{ cm}^{-3}$. The position of the band edges indicated that the crystals were thermodynamically capable of water dissociation. External quantum yield (QY) measurements revealed that the samples were photoactive up to a wavelength of $\sim 350 \text{ nm}$. The indirect bandgap and a parameter denoted as E_1 , that is related to the direct band edge of the semiconductor, were found to be the same for all the samples. These results indicate that the various dopants and treatments did not produce changes in the KTaO_3 electronic structure that were sufficient to significantly modify the behavior of KTaO_3 in a PEC cell.

4.1 Introduction

Photoelectrochemical (PEC) cells are devices that offer an environmentally benign, clean mechanism for converting optical energy into chemical energy in the form of hydrogen fuel. A schematic representation of a PEC cell using an n-type semiconducting photoanode is shown in Figure 4.1 (Please see appendix for all tables and figures) [after Ref. 4.1]. In this configuration, electron-hole pairs are formed when light with an energy larger than the bandgap (3.64 eV for KTaO_3 [4.2]) is absorbed at the photoanode. Under ideal conditions, the presence of a depletion layer will separate the charges, and the minority carrier holes will reach the semiconductor/electrolyte interface. When using an alkaline electrolyte, the holes will react with the hydroxyl ions to form oxygen at this surface through the reaction:



Similarly, the electrons from the semiconductor will flow to the cathode (generally made of platinum) and react with the water forming hydrogen at this surface via the reaction:



Combining equations 4.1 and 4.2 gives the following overall reaction:



This implies that PEC cells can be used as an environmentally friendly means of directly producing hydrogen and oxygen through the absorption of solar light. However, various requirements need to be fulfilled for this process to be both thermodynamically possible and efficient in practice. These requirements include the necessity for the bandgap of the photoanode to be sufficiently small to absorb a significant portion of the solar spectrum (ideally a bandgap of < 2 eV). Additionally, the top of the valence band should be more positive than the

electrochemical potential for the oxygen evolution reaction (e.g., 0.11 V vs. SCE in pH = 14.5), and the bottom of the conduction band needs to be more negative than the potential for the hydrogen evolution reaction (e.g., -1.12 V vs. SCE in pH = 14.9) (Figure 4.1). Otherwise there is no driving force for the reactions to occur, and the application of an external bias voltage will be necessary. Additionally, the photoanode material must be chemically stable in order to avoid photoanodic dissolution of this electrode during the PEC cell operation. A more detailed explanation of the PEC cell operating mechanisms can be found elsewhere [4.3-4.5].

Since Fujishima and Honda discovered the potential use of TiO_2 single crystals as photoanodes in PEC cells [4.6], the use of semiconducting oxides as a photoanode material has been extensively studied, since these materials are frequently stable when exposed to the electrolyte during PEC cell operation. However, the poor light absorption of these oxides (resulting from their large bandgaps) is a key problem that is still to be overcome in order for this type of cell to efficiently produce hydrogen from the dissociation of water.

The present work represents the extension of an ongoing effort [4.1] to modify the electronic structure of PEC cell photoanodes by utilizing semiconducting KTaO_3 single-crystal electrodes as a model system – with the goal of achieving the absorption of light at longer wavelengths that ideally closely match the solar spectrum. In this work, a wide range of systematic compositional changes was achieved through the nature of the dopants and the dopant combinations employed during the single crystal growth process. Our previous work [4.1] has shown that the use of Ca- or Ba-, as a single doping element does not significantly modify the range of optical absorption of KTaO_3 - implying that the bandgap was not effectively reduced. In the present study, the elements utilized for the doping of KTaO_3 consisted of the alkaline earths Ca and Ba combined with various other impurities - with an emphasis on the transition metals.

The concept of using transition metals as dopants rests on the known effects that such elements have on the electronic and photo-catalytic properties of semiconductors such as TiO_2 (e.g. by shifting the photo-response towards visible light) [4.7-4.11]. When doping with elements such as Ca and Ba, the change in the conductivity of KTaO_3 is attributed to replacement on the K^+ sites by Ca^{+2} or Ba^{+2} [4.12,4.13], leaving one electron to contribute to the conductivity per potassium site replaced. In the case of the transition metals, the increase in conductivity is associated with the substitution of either (or both) cation sites (K^{+1} and Ta^{+5}) by the impurity atoms. The details regarding specific dopant substitutional sites for some of the metals used in this study (e.g., Yb, Fe, Ni, Mn and Ti) can be found in the literature [4.14-4.17]. It was anticipated that from the approach of systematic doping used here, it should be possible to identify whether specific dopants are advantageous in modifying the KTaO_3 electronic structure and, thereby, sensitize this material towards the range of the solar spectrum.

4.2 Experimental Details

4.2.1 Crystal Growth and Electrode Preparation

The KTaO_3 single crystals used in this study were grown by spontaneous nucleation resulting from the slow cooling of a non-stoichiometric melt [4.14]. The KTaO_3 crystals were grown by combining 20 g and 9.4 g of high-purity Ta_2O_5 and K_2CO_3 powder respectively. An excess of K_2CO_3 is used to compensate for the K_2O produced by thermal decomposition that results in the desired non-stoichiometric melt during the crystal growth process. Doping of the KTaO_3 crystals was achieved by adding the dopant elements to the KTaO_3 crystal-growth mixture noted above. In this study, the dopants consisted of a wide range of elements and combinations of elements that were generally added in the oxide form. A compilation of all of

the doped crystals grown for this study is given in Tables 4.1 through 4.3. These tables have been divided according to the dopant species employed: i.e., for samples doped with Ca with the addition of other elements (Tables 4.1a and 4.1b), samples doped with Ba and other elements (Table 4.2), and the remainder of the samples that are labeled with the generic metallic doping designation, M, (Table 4.3).

Figure 4.2 shows a section of a typical KTaO_3 single crystal grown using the technique outlined above. Here the dark portion of the crystal is doped KTaO_3 , and the clear portion is undoped, insulating KTaO_3 . This is a segregation effect that takes place during the growth process and that begins at a nucleation site with a melt that is rich in the dopant elements, and eventually, when the melt is depleted of the dopant impurities, the undoped section of the crystal begins to grow. These crystals naturally grow with (100) faceting, and the samples used for testing were obtained following the same steps described in detail in reference 4.1. The samples consisted of 1-mm thick, (100)-oriented plates with a 600 grit surface finish. A submicron surface finish was given to the samples used in the Scanning Electron Microscopy (SEM) images.

Electrical contact to the KTaO_3 single-crystal plates used to form the electrodes was achieved by covering one face of the sample with an In-Ga eutectic and then soldering a gold wire using an In dot. Silver paste was used to give the back contact additional mechanical strength, and insulating epoxy was finally used to cover the areas that were not to be exposed to the electrolyte.

4.2.2 Electrochemical Measurements

The electrochemical testing was performed in a 3-electrode cell configuration using an H-shaped cell similar to the schematic shown in figure 4.1. A flat quartz window on the chamber where the KTaO_3 photoanodes were placed was used to achieve homogeneous UV illumination

of the photoanode. A saturated calomel electrode (SCE) was used as the reference electrode, and a platinum sheet was used as the counter electrode. All of the electrochemistry studies were performed at room temperature using 8.5 M NaOH as the electrolyte.

4.2.2.1 Electrochemical Impedance Spectroscopy

Electrochemical impedance spectroscopy was performed to determine the carrier concentration of the KTaO_3 samples using Mott-Schottky analysis as represented by the following equation:

$$\frac{1}{C_{SC}^2} = \frac{2}{q\epsilon_0\epsilon_s N_D A^2} \left(E - E_{fb} - \frac{kT}{q} \right) \quad (4.4)$$

where C_{SC} represents the space charge capacitance, q the charge of the electron, ϵ_0 the dielectric constant of vacuum, ϵ_s the dielectric constant of KTaO_3 [4.12], N_D the carrier concentration, A the area of the electrode exposed to the electrolyte, E the applied potential, E_{fb} the flat band potential, k is Boltzmann's constant, T the temperature in degrees Kelvin, and q is the electron charge. The details of this technique can be found in the literature [4.18].

Impedance data were taken from 1 to 10^4 Hz between -0.7 to 0.7 V vs. SCE using a Princeton Applied Research (PAR) Model 2263 potentiostat/galvanostat. The data was then fit to an equivalent three-element circuit consisting of a resistance followed by a second resistance with a capacitance element connected in parallel.

Additionally, the conduction band energy (E_{CB}) was estimated using:

$$E_{CB} = E_{fb} - \frac{kT}{q} \ln \left(\frac{N_C}{N_D} \right) \quad (4.5)$$

where N_C , the effective density of states in the conduction band, equals $1.42 \times 10^{19} \text{ cm}^{-3}$ at 298 K [4.1].

4.2.2.2 Current Density vs. Potential Curves

Current density vs. applied potential (J-E) curves were measured using a Princeton Applied Research (PAR) Model 2263, with a scan rate of 20 mV/s. The J-E curves for the samples were measured both in the dark and under illumination that was provided by a 500 W Hg arc lamp.

4.2.2.3 Quantum Yield

The QY of the samples was measured using a 75 W Xe arc lamp and a single-pass monochromator with a 5 nm bandwidth. A BG-24 glass filter was placed at the entrance of the monochromator to reduce stray light effects. The photocurrent of the semiconducting photoanode was measured using the PAR 2263. This instrument was also used to maintain the potential of the photoanode at 0 V vs. SCE. A more detailed description of this method can be found in reference 1. Additionally, an electrode consisting of an optically polished surface was held at 0 V vs. SCE for 72 hr during illumination with a 150 W Hg(Xe) arc-lamp to establish the chemical stability of the electrodes during PEC cell operation. A Hitachi S-3400N system was used to obtain SEM images and Energy Dispersive X-ray Spectroscopy (EDS) data.

4.3 Results and Discussion

4.3.1 Carrier Concentration and Conduction Band Energies

From the impedance measurements, it was possible to determine the space charge capacitances of the samples at the various potentials. Based on the Mott-Schottky analysis (equation 4.4), the samples were found to exhibit n-type semiconducting properties. The carrier concentrations varied from 4×10^{18} to $2.6 \times 10^{20} \text{ cm}^{-3}$, and the associated values are shown in

Tables 4.4, 4.5, and 4.6 for selected samples. Sample Ca1 was subsequently heat treated in a CO atmosphere for 9 hrs at 900 °C; this heat-treated sample is referred as Ca1*. Sample numbers followed by a or b refer to samples that come from the same crystal. Changes in the carrier concentration from samples coming from the same crystal are not unexpected due to segregation effects that inherently take place during the melt-growth process and result in an inhomogeneous distribution of the impurities [4.12,4.13,4.19].

Using the E_{fb} calculated from the Mott-Schottky analysis (equation 4.4 and 4.5), E_{CB} was determined as shown in Tables 4.4, 4.5 and 4.6. This value did not change significantly among the different samples, and the average value for all of the samples is -1.49 ± 0.07 V vs. SCE. The E_{CB} were found to be very similar to those reported in reference 1 for the Ca- and Ba- doped KTaO_3 crystals, and are also more negative than -1.12 V vs SCE (the electrochemical potential of the hydrogen evolution reaction - equation 4.2). With a bandgap of 3.64 eV, the valence band energy can be estimated to be approximately 2.15 V vs. SCE, which is more positive than 0.11 V vs. SCE (the oxygen reaction potential at this NaOH concentration – equation 4.1), indicating that, analogous to the Ca- and Ba- doped KTaO_3 , the crystals grown for this study are also thermodynamically capable of water dissociation without an applied external bias. Additionally, due to the magnitudes of N_C and N_D , the conduction band energy and the flat band potential are apparently quite close to each other (equation 4.5).

4.3.2 Current Density vs. Potential

Samples Ca23 and Ca24 (doped with Ca and Li) and samples M10 and M11 (doped with B), did not exhibit a photocurrent when placed in the PEC cell. This result was expected since these crystals were clear - indicating that these dopants did not result in semiconducting KTaO_3 .

The remainder of the doped KTaO_3 electrodes exhibited diode-like behavior in the PEC cell with a photo-response at potentials higher than the flat band value. A set of representative curves both in the dark and under illumination is shown in Figure 4.3 for sample Ba6-b. The inflection point at approximately -1.3 V vs. SCE is a common feature in metal oxide semiconductors [4.20] that has previously been described for n-type KTaO_3 crystals [4.1], and is at least partially related to the reduction of the collection efficiency of the minority carriers when the applied potential is close to the V_{fb} value - due to the decrease of the depletion width and also the slow interfacial kinetics of KTaO_3 for the evolution of oxygen [4.21]. Even at this slow scan rates, a hysteresis is observed in the measurement when the direction of the potential sweep is changed. This time dependence has been associated with the presence of at least two types of electronically active defects affecting the movement of the charges across the crystal [4.1,4.22]. Visual inspection of the electrodes after these curves were measured did not reveal any sign of dissolution or degradation of the surface in the cell environment.

In order to further investigate the stability of these crystals, a sample was held at 0 V vs. SCE while illuminated for 72 hr. SEM images of the sample surface before and after this potential hold can be found in figure 4. In this particular KTaO_3 crystal (similar in composition to Ca3), voids that seemed to have a preferential orientation with respect to the crystal were observed (figure 4.4b), which is in contrast to the smooth surface typical of almost all of the crystals grown for this study (figure 4.4a). Backscatter SEM and EDX atomic ratios indicated that the voids and surrounding areas were homogeneous in composition and consistent with KTaO_3 . The nature of the voids has not been determined at this point. A comparison of the crystal surface before and after the 72 hr potential hold (4.4b and 4.4c respectively) indicates that there was a small increase in surface roughness that could be at least partially associated with the

continuous formation and release of oxygen bubbles throughout the experiment. Additionally, the crystal did not exhibit a measurable change in weight before and after this test indicating that the sample did not undergo any net photoanodic dissolution during the cell operation.

4.3.3 Quantum Yield

Figure 4.5 shows the QY results for selected samples. From this figure, it can be seen that the general shape of the QY curve did not change among the samples regardless of the doping type, and that this shape is consistent with what has been previously reported in the literature, i.e., consisting of a broad peak at a wavelength of ~ 255 nm followed by a slow decrease in the QY. This characteristic QY drop has been attributed to the indirect absorption properties of KTaO_3 [4.22] and the penetration depth of light [4.1]. From this figure it is obvious that photons from the light at > 350 nm (or < 3.54 eV) did not produce any photocurrent. Accordingly, this represents a very poor match to the Air Mass (AM) 1.5 solar spectrum shown in Figure 4.5c.

The maximum QY measured at the peak value changed significantly among samples, as can be seen in the results that are tabulated for all of the samples in Tables 4.4 through 4.6. However, there was not an obvious correlation between the peak value and the carrier concentration (Figure 4.6). Previous work has shown that the magnitude of the QY peak can change considerably just by changing the illumination spot on the same electrode surface [4.1]. This effect can be attributed in part to the high concentration of defects and recombination in the crystal, which are a consequence of the high doping concentrations, and their inhomogeneous distribution within a given crystal. The results presented in this paper represent the highest QY point of the electrode surface. In the crystals used in this study, this effect is expected to be even more important since several different species (with different atomic radius) are being introduced

in the crystal at the same time. Consequently, no simple correlation exists between the maximum QY and N_D .

The thermochemical treatment of sample Ca1 after 9 hrs in a CO atmosphere at 900 °C (Ca1*) significantly increased the QY of the crystal over the entire wavelength range, doubling the QY at the peak (figure 4.5a). Since light between 250 and 270 nm is preferentially absorbed within 30 nm from the surface in KTaO_3 [4.2], these results suggest that the heat treatment has resulted in the annealing of some defects in the crystal - particularly close to the surface. This would drastically reduce the possibility of holes recombining or becoming trapped when trying to reach the surface of the crystal. However, even with this improvement in the QY, when light is absorbed at the outer surface of the crystal (e.g. at the peak of the QY curve), the QY is still significantly less than one, indicating that there are still surface recombination sites present.

The QY curves were used to estimate the values of the bandgap (E_g) and the value labeled as E_1 , which is related to the direct band absorption edge of the semiconductor. These values were calculated as the intercepts on the wavelength axis of the QY curve slopes as shown in Figure 4.7. The results for E_g and E_1 in eV can be found in Tables 4.4 through 4.6. These energies were found to be very consistent among all the samples - showing no change as a function of the doping elements or concentration. The average value of E_g estimated for all of the samples in Table 4.4 was 3.67 eV, and for the samples in Table 4.5 and 4.6 it was 3.69 eV (all values with a standard deviation of ± 0.04 .) Since these values are statistically the same, and this result is in agreement with the E_g for KTaO_3 of 3.64 eV, it is possible to state that the doping did not have any measurable effect on bandgap of the material. Similarly, the average values of E_1 were 4.09 ± 0.06 , 4.11 ± 0.07 , and 4.15 ± 0.08 eV for the samples in Tables 4.4, 4.5, and 4.6 respectively. Although these values are not a direct measure of the direct band gap, they serve as

an estimate of the possible changes of the direct band edge as a function of the doping element. The E_1 energies were also found to be the same within the statistical error, indicating that no measurable changes of the direct band absorption of the crystal were achieved. Consequently, it is possible to state that doping these crystals with a wide range of elements or combinations of elements did not create the desired sought changes in the electronic structure of the KTaO_3 , and that the energy states that were created within the gap were not effective in generating quantifiable differences in the behavior of the crystals in the PEC cells.

4.4 Conclusions

With the exception of the KTaO_3 crystals grown with LiCO_3 or B_2O_3 added to the melt as doping agents, all of the crystals in this study were semiconducting, and they exhibited n-type doping with carrier concentrations varying from 4×10^{18} to $2.6 \times 10^{20} \text{ cm}^{-3}$. The band edges were similar to those previously reported for Ca and Ba singly doped crystals [4.1], indicating that the new, more extensive set of crystals investigated here were also capable of water dissociation without the necessity of applying an external bias voltage. The electrodes were found to be chemically stable in the cell environment.

The maximum QY measured at a wavelength of $\sim 255 \text{ nm}$ varied significantly among the samples. However, this value was not clearly correlated with the carrier concentration of the crystals - probably due to a high concentration of defects that can act as traps or recombination centers. The fact that the QY never reaches the value of 1.0 appears to be related to the presence of surface states that are apparently partially annealed in a reducing CO atmosphere.

The systematic doping of the KTaO_3 single crystals, unfortunately, did not produce an increase in the range of optical absorption of the samples, and all the samples were only

photoactive for wavelengths shorter than 350 nm. Estimates of the bandgap and E_1 (a parameter related to the direct energy gap) are consistent with our observation that variations in the nature of either the doping elements or doping concentrations in the KTaO_3 single crystals did not produce any significant changes in the electronic properties of the crystals as determined from the PEC cell properties.

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Appendix

Table 4.1a Crystal growth compositions for KTaO_3 single crystals doped with CaCO_3 and metallic impurities. The amounts of Ta_2O_5 and K_2CO_3 are 20 g and 9.4 g respectively.

Sample	CaCO_3 (g)	TiO_2 (g)	CuO (g)	Bi_2O_3 (g)	Cr_2O_3 (g)	P_2O_5 (g)	Fe_2O_3 (g)	CdO (g)	Sb_2O_3 (g)	NiO (g)
Ca1	0.008	0.015	-	-	-	-	-	-	-	-
Ca2	0.008	0.050	-	-	0.050	-	-	-	-	-
Ca3	0.008	0.100	-	-	-	0.100	-	-	-	-
Ca4	0.008	0.150	-	-	-	-	0.020	-	-	-
Ca5	0.008	-	0.100	-	-	-	-	0.050	-	-
Ca6	0.008	-	0.100	-	-	-	-	0.200	-	-
Ca7	0.008	-	0.100	0.200	-	-	-	-	-	-
Ca8	0.008	-	0.200	0.100	-	-	-	-	-	-
Ca9	0.008	-	0.100	-	-	-	-	-	0.010	-
Ca10	0.008	-	0.100	-	-	-	-	-	0.030	-
Ca11	0.008	-	0.300	-	-	-	-	-	0.060	-
Ca12	0.08	-	0.300	-	-	-	-	-	0.080	-
Ca13	0.016	0.050	-	-	0.010	-	-	-	-	-
Ca14	0.016	0.100	-	-	0.050	-	-	-	-	-
Ca15	0.016	0.100	-	-	0.100	-	-	-	-	-
Ca16	0.016	-	0.100	0.01	-	-	-	-	-	0.1
Ca17	0.016	-	0.200	-	-	-	-	-	0.01	-

Table 4.1b Crystal growth compositions for KTaO_3 single crystals doped with metallic impurities. The amounts of Ta_2O_5 and K_2CO_3 are 20 g and 9.4 g respectively.

Sample	CaCO_3 (g)	GeO_2 (g)	Ga_2O_3 (g)	V_2O_5 (g)	MnO (g)	LiCO_3 (g)
Ca18	0.008	0.200	-	-	-	-
Ca19	0.008	0.300	-	-	-	-
Ca20	0.008	-	0.100	-	-	-
Ca21	0.008	-	-	0.100	-	-
Ca22	0.008	-	-	-	0.410	-
Ca23	0.008	-	-	-	-	0.050
Ca24	0.008	-	-	-	-	0.200

Table 4.2 Crystal growth compositions for KTaO_3 single crystals doped with BaCO_3 and metallic impurities. The amounts of Ta_2O_5 and K_2CO_3 are 20 g and 9.4g respectively.

Sample	BaCO₃ (g)	AgO (g)	CeO₂ (g)	Yb₂O₃ (g)	NiO (g)	Fe₂O₃ (g)	Cr₂O₃ (g)	Cu₂O (g)	MnO (g)	PrO₂ (g)
Ba1	0.003	0.004	0.006	-	-	-	-	-	-	-
Ba2	0.007	0.050	-	0.050	-	-	-	-	-	-
Ba3	0.010	-	-	0.025	0.05	-	-	-	-	-
Ba4	0.010	-	-	0.025	-	0.05	-	-	-	-
Ba5	0.010	-	-	-	-	0.10	0.10	-	-	-
Ba6	0.010	-	-	0.025	-	-	0.05	-	-	-
Ba7	0.010	-	-	-	0.05	-	0.05	-	-	-
Ba8	0.010	-	-	-	-	0.05	0.05	-	-	-
Ba9	0.010	-	-	-	-	-	0.05	0.05	-	-
Ba10	0.010	-	-	-	-	0.05	-	-	0.01	-
Ba11	0.010	-	-	-	-	-	-	-	-	0.025
Ba12	0.014	0.2	-	-	-	-	-	-	-	-

Table 4.3 Summary of growth compositions for KTaO_3 single crystals doped with metallic impurities. The amounts of Ta_2O_5 and K_2CO_3 are 20 g and 9.4g respectively.

Samples	Yb_2O_3 (g)	AgO (g)	CeO_2 (g)	TiO_2 (g)	CdO (g)	Bi_2O_3 (g)	CuO (g)	B_2O_3 (g)	Cr_2O_3 (g)	TaN (g)
M1	0.094	-	-	-	-	-	-	-	-	-
M2	0.094	0.047	-	-	-	-	-	-	-	-
M3	-	0.047	0.019	-	-	-	-	-	-	-
M4	-	0.0094	0.0094	-	-	-	-	-	-	-
M5	-	-	0.0094	-	-	-	-	-	-	-
M6	-	-	-	0.100	0.100	-	-	-	-	-
M7	-	-	-	-	0.100	-	0.100	-	-	-
M8	-	-	-	-	-	0.100	0.100	-	-	-
M9	-	-	-	-	-	-	0.600	-	-	-
M10	-	-	-	-	-	-	-	0.050	-	-
M11	-	-	-	-	-	-	-	0.200	-	-
M12	-	-	-	-	-	-	-	-	0.050	0.010

Table 4.4 Electrochemical and photoelectrochemical data for selected KTaO_3 single crystal samples doped with Ca and other metallic impurities.

Sample	N_D ($\times 10^{19} \text{ cm}^{-3}$)	E_{CB} (V vs SCE)	Maximum QY	E_1 (eV)	E_g (eV)
Ca1	2.1	-1.44	0.23	4.05	3.72
Ca1*	12	-1.48	0.45	4.12	3.66
Ca2	0.7	-1.58	0.24	3.98	3.66
Ca3	2.1	-1.59	0.19	4.12	3.68
Ca5	0.4	-1.56	0.16	4.17	3.72
Ca6	3.6	-1.41	0.35	4.14	3.68
Ca7	26	-1.61	0.36	4.10	3.70
Ca8-a	5.6	-1.55	0.31	4.13	3.69
Ca8-b	4.0	-1.47	0.41	4.13	3.67
Ca9	0.5	-1.43	0.44	4.08	3.65
Ca10	3.4	-1.41	0.32	4.14	3.68
Ca11	2.5	-1.52	0.30	4.14	3.69
C12	0.5	-1.44	0.20	4.10	3.72
Ca13	0.6	-1.47	0.22	4.03	3.68
Ca14	6.7	-1.50	0.41	4.14	3.69
Ca15	1.4	-1.41	0.24	4.02	3.66
Ca17	0.6	-1.49	0.17	4.10	3.69
Ca18	3.3	-1.44	0.26	4.12	3.65
Ca19	4.0	-1.58	0.31	4.13	3.66
Ca22	9.4	-1.43	0.25	4.08	3.78
Ave. Error	10%	± 0.08	± 0.03	± 0.23	± 0.09

Table 4.5 Electrochemical and photoelectrochemical data for selected KTaO_3 samples doped with Ba and other metallic impurities.

Sample	N_D ($\times 10^{19} \text{ cm}^{-3}$)	E_{CB} (V vs SCE)	Maximum QY	E_1 (eV)	E_g (eV)
Ba2	9.4	-1.48	0.25	4.16	3.65
Ba3	0.6	-1.55	0.29	4.11	3.67
Ba4	1.7	-1.66	0.10	4.11	3.67
Ba6-a	0.7	-1.41	0.23	4.16	3.68
Ba6-b	11	-1.53	0.35	4.18	3.69
Ba7	0.6	-1.44	0.23	4.12	3.65
Ba8	2.9	-1.45	0.18	4.11	3.70
Ba9	10	-1.61	0.28	4.14	3.67
Ba11	1.0	-1.57	0.18	4.08	3.70
Ba12	4.5	-1.49	0.28	4.09	3.68
Ave. Error	10%	± 0.06	± 0.03	± 0.14	± 0.07

Table 4.6 Electrochemical and photoelectrochemical data for selected samples doped with metallic impurities.

Sample	N_D (x 10¹⁹ cm⁻³)	E_{CB} (V vs SCE)	Maximum QY	E₁ (eV)	E_g (eV)
M2	1.8	-1.48	0.16	4.21	3.66
M3	2.2	-1.58	0.16	4.19	3.72
M4	3.8	-1.45	0.13	4.08	3.68
M5	1.2	-1.53	0.10	3.94	3.67
M8-a	2.6	-1.46	0.30	4.20	3.68
M8-b	1.8	-1.42	0.21	4.11	3.71
M9-a	1.5	-1.44	0.31	4.20	3.69
M9-b	1.6	-1.61	0.40	4.17	3.68
M12-a	1.5	-1.47	0.18	4.20	3.74
M12-b	4.2	-1.43	0.23	4.12	3.68
Ave. Error	10%	±0.07	±0.03	±0.18	±0.05

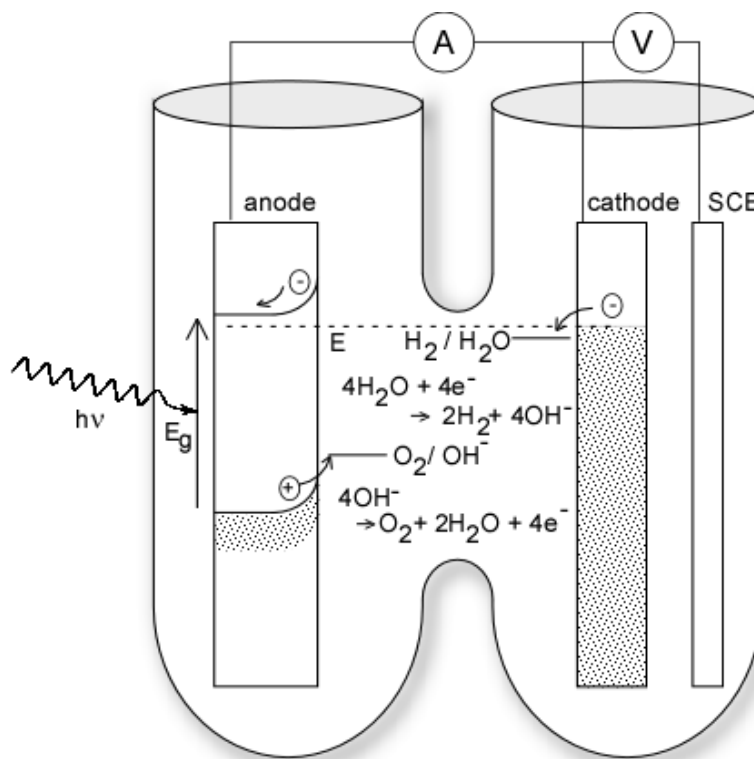


Figure 4.1 Schematic of a photoelectrochemical cell using an n-type photoanode in an alkaline electrolyte. [After reference 4.1.] The various reactions and band-bending effects are indicated. Ideally, when light with an energy larger than the bandgap is absorbed at the photoanode, electron-hole pairs are formed and separated by the electric field present in the depletion region. Holes react at the surface of the photoanode to form O_2 , and the electrons reach the cathode to form H_2 .

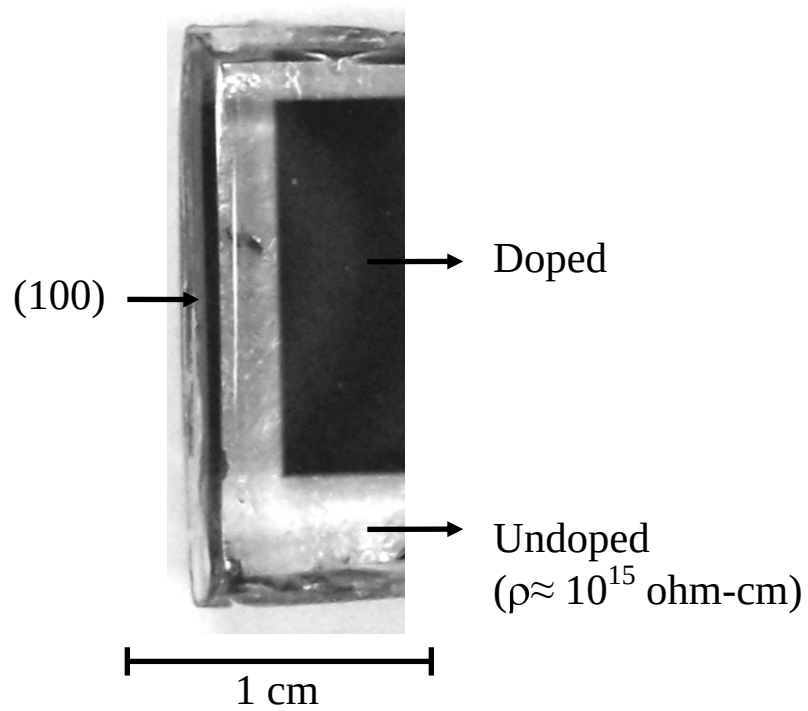


Figure 4.2 Top view of a section of a KTaO₃ single crystal grown from a nonstoichiometric melt. The central dark blue area is the doped semiconducting portion of the crystal, and the outer clear portion is the un-doped, insulating region.

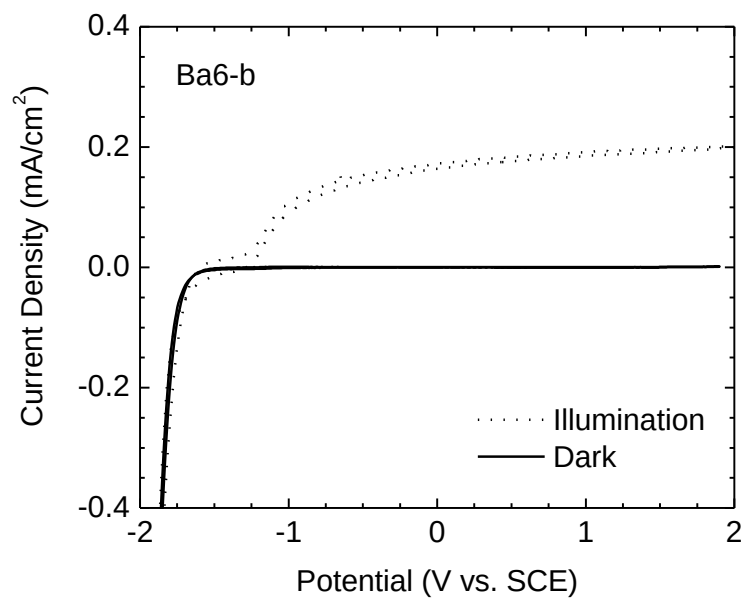


Figure 4.3 Current density vs. applied potential curves in the dark and under illumination for the electrode denoted as sample Ba6-b. All the samples exhibited diode like behavior with a photo-response measured for potentials more positive than the flat-band.

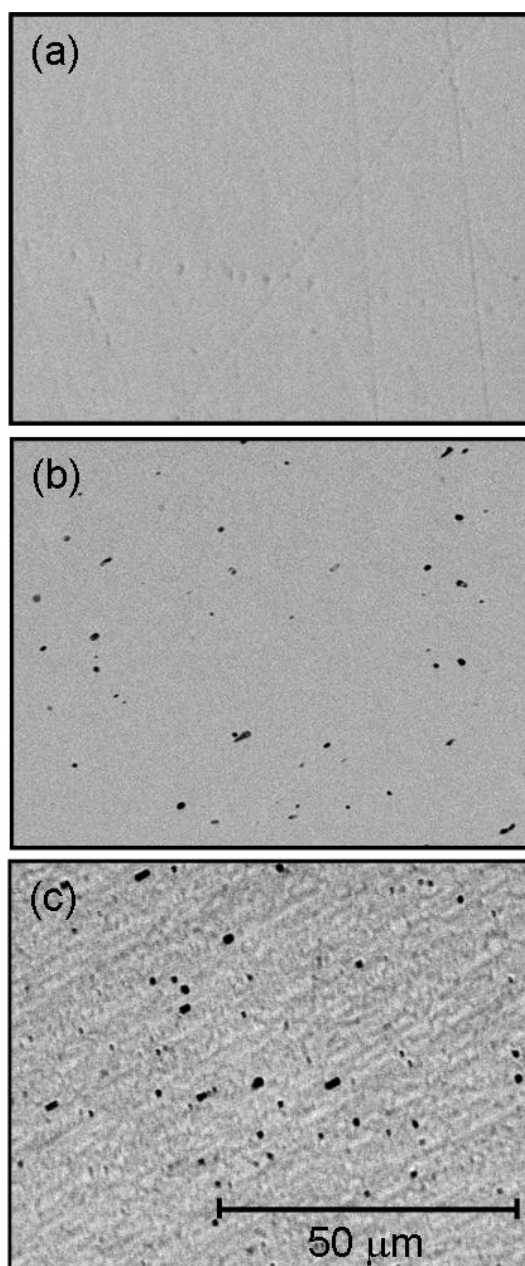


Figure 4.4 Scanning electron microscope images of (a) typical surface of a KTaO₃ crystal grown for this study – linear features on the image are polishing scratches; (b) a typical surface of a crystal with a similar composition to Ca3 indicating that in rare instances voids that seemed to have a preferential orientation with respect to the crystal surface were observed; (c) same surface as (b) after a potential hold at 0 V vs. SCE for 72 hr in the PEC cell under illumination. A small increase in surface roughness was observed after testing; however, there was no measurable change in weight of the sample.

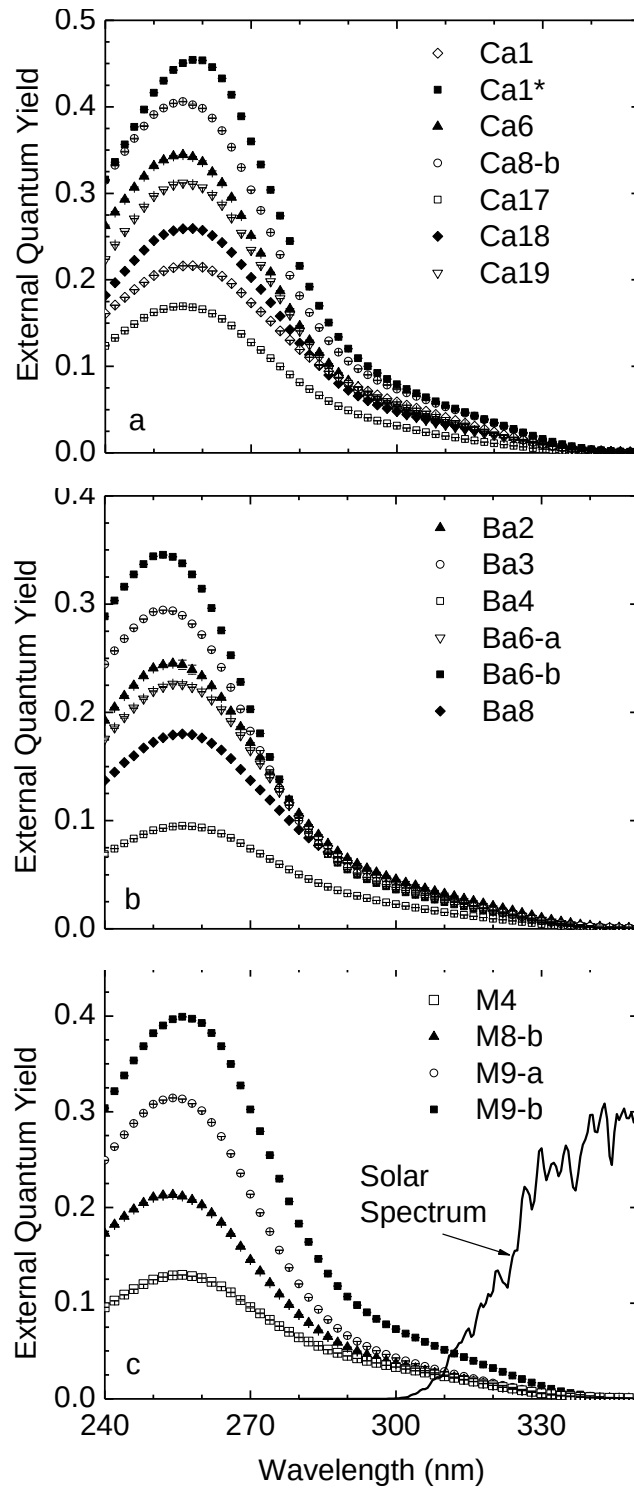


Figure 4.5 External quantum yields for selected KTaO₃ crystals doped with (a) Ca and metallic impurities, (b) Ba and metallic impurities, and (c), only metallic impurities. The range of optical absorption did not change among the samples regardless of the doping nature or its concentration; and it only offers a very small overlap with the AM 1.5 solar spectrum shown in (c).

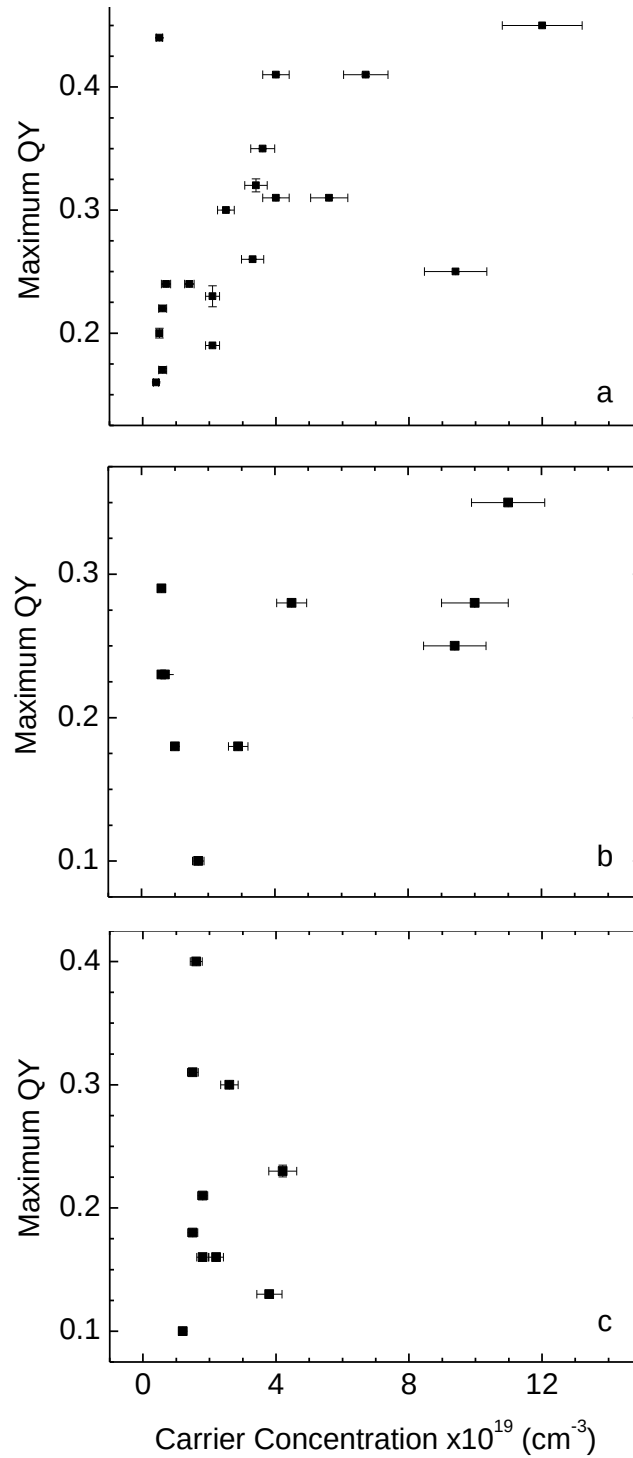


Figure 4.6 Maximum quantum yield as a function of the carrier concentration for KTaO_3 crystals doped with: (a) Ca and metallic impurities, (b) Ba and metallic impurities, and (c) only metallic impurities. The lack of a simple correlation between these two parameters is attributed to a combined effect of the high carrier concentration, inhomogeneous dopant distribution, and a high concentration of defects in the material.

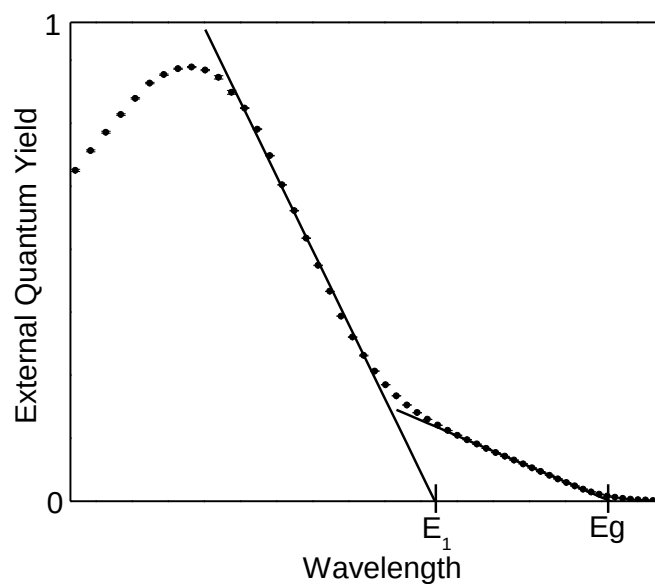


Figure 4.7 Method for making an estimate of the bandgap (E_g) and E_1 (related to the direct band absorption) using the QY curves. These parameters did not change significantly among the crystals; tabulated results for selected samples can be found in Tables 4.4, 4.5, and 4.6.

5 **Photoelectrochemical properties of n-Type ZnO photoanodes**

This chapter is a journal article by the same name submitted to the *Journal of Applied Physics* in 2009 by I. E. Paulauskas, G.E. Jellison, L. A. Boatner, and G. M. Brown.

My use of "we" in this chapter refers to my co-authors and myself.

Abstract

An extensive set of n-type ZnO single crystals, both doped and undoped, has been investigated as a photoelectrochemical cell photoanode material. ZnO photoanodes were characterized by means of potentiostatic cyclic voltage sweeping experiments (both in the dark and under illumination); measurements of the spectral and time dependant photocurrent quantum yield; and determinations of the ZnO absorption coefficient. Current-potential curves exhibited diode-like behavior for all of the crystals. These measurements also revealed the presence of an anodic peak and an accompanying cathodic process at very negative potentials that were independent of the presence of illumination. The features of this peak were found to be dependent on time as well as the NaOH concentration in the electrolyte. Current measurements performed at the peak indicate that charging and discharging effects are apparently taking place at the semiconductor/electrolyte interface. This result is also consistent with significant reactive degradation that is observed on the ZnO photoanode surface after testing. The spectral quantum yield response was found to be strongly dependent on the carrier concentration as well as the penetration depth of light. Although the doping methods employed here were an effective way of increasing the n-type character of the crystals, this excess doping was detrimental to the quantum yield, and it also generated high free carrier absorption at relatively short wavelengths.

5.1 Introduction

The worldwide increasing demand for energy coupled with the ongoing decreasing availability of fossil fuels and the undesirable consequences of their use are driving the need to develop alternative fuels that are both abundant and environmentally safe. Hydrogen is considered to be such a fuel – and one that can be utilized in a wide variety of applications including household energy and transportation.

Currently, the production of hydrogen has primarily been achieved by either the steam reforming of methane, which results in CO₂ emissions, or water electrolysis, which currently requires the combustion of fossil fuels for the generation of electricity [5.1]. Neither method can be considered environmentally friendly. An alternative and more environmentally benign option for hydrogen generation is the use of photoelectrochemical (PEC) cells [5.1,5.2]. These cells enable the clean production of hydrogen and oxygen through the photoassisted dissociation of water. This phenomenon was originally observed by Fujishima and Honda in 1972 when TiO₂ was irradiated with UV light [5.3]. Since that discovery, intensive studies have been conducted using semiconducting n-type oxides such as titanium dioxide (TiO₂), strontium titanate (SrTiO₃), potassium tantalate (KTaO₃) and zinc oxide (ZnO) [5.1,5.4-5.8]. These materials absorb the solar energy or other optical energy sources and drive the water electrolysis reaction ($2\text{H}_2\text{O} \xrightarrow{h\nu} 2\text{H}_2 + \text{O}_2$). However, no PEC system has yet been identified that can efficiently convert sunlight to hydrogen without an applied bias.

The primary problem consists of finding electrode materials with bandgaps that efficiently match the solar spectrum and band edges that allow for the direct photo-induced evolution of hydrogen and oxygen. Finding n-type materials that meet these criteria and that also exhibit the chemical stability required to avoid photoanodic dissolution in the PEC cell

environment represents the fundamental materials challenge that needs to be overcome to achieve a significant advance in this area. The metal oxide semiconductors KTaO_3 , TiO_2 , and SrTiO_3 are all attractive candidates for this application because they have been shown to be stable in the PEC cell electrolyte. However, their bandgaps are too large for efficient solar energy conversion.

While the photoanodic chemical stability of ZnO is not as high as SrTiO_3 , KTaO_3 or TiO_2 , nevertheless, its use as a photoanode material has been investigated in earlier studies due to its relatively high level of photoactivity [5.9,5.10]. In the present study, both doped and undoped ZnO single crystals are used as the photoanode materials in photoelectrochemical cells. With a bandgap of 3.35 eV [5.2], ZnO has direct band absorption, and it is known to exhibit n-type semiconducting characteristics even when up-doped - due to the presence of defects such as Zn on O antisites and oxygen vacancies that are formed during growth [5.11]. It is also known that ZnO undergoes photoanodic dissolution in aqueous electrolytes [5.12,5.13], and has poor absorption of the solar spectrum. The goals of the present work are to attempt to modify the electronic properties of ZnO through the use of various dopant elements and heat treatments in order to achieve better solar energy absorption and potentially improve the ZnO surface stability in an operating PEC cell environment.

5.2 Experimental Procedure

5.2.1 Sample Preparation

All of the ZnO single crystals used in this study were grown from the melt by Cermet, Inc., Atlanta, GA and are described Table 5.1 (Please see appendix for all tables and figures). Samples 1 through 6 were doped by a thermochemical treatment of an un-doped single crystal

plate in a vacuum-sealed quartz ampoule in the presence of the vapor of the dopant metal. The remaining crystals (7 through 10) were doped in the melt during growth under a high oxygen pressure (Details of this melt growth system can be found in Ref. 5.14). The ZnO plates were rectangular in shape with approximate dimensions of $10 \times 5 \times 0.5 \text{ mm}^3$ and were polished with a submicron surface finish.

The electrical contacts to the ZnO photoanodes used in the photoelectrochemical cell characterization studies were formed by coating one side of the plate with an InGa eutectic solution. A gold wire was then attached to the InGa-coated surface by soldering with an indium dot. This contact was then covered with silver paste to increase the mechanical strength of the contact. The area of the plate exposed to the PEC cell electrolyte was controlled by using an insulating epoxy. Contacts to the ZnO plates used in the Hall Effect measurements were made by depositing gold on four corners of the samples.

5.2.2 Electrochemical Measurements

All of the electrochemistry studies were performed using a three-electrode H-shaped cell with a quartz window to permit efficient transmission of the UV portion of the light to the semiconducting photoanodes. A platinum strip served as the counter electrode, and a saturated calomel reference electrode (SCE) was used. The cell measurements were performed using a PAR Model 2263 Potentiostat/Galvanostat. Unless otherwise specified, the electrolyte used was 8.5 M NaOH at room temperature.

5.2.2.1 Current vs. Potential Curves

Several types of current vs. potential curves were measured. With the exception of the scan-rate-dependant curves, the scan rate used for all of the other measurements was 30 mV/s. Cyclic voltammetry was performed in going from the negative towards the positive potential and

starting at the most negative potential value (unless otherwise specified). Current density vs. applied potential (J-E) curves were measured both in the dark and under illumination, with the illumination provided by a collimated 75 W Hg(Xe) arc lamp.

To better understand the nature of the features exhibited by these curves, measurements were also made at various NaOH electrolyte concentrations (i.e., 0.01M, 0.1M, 1M, 3M, 5M, 7M, and 9M) and also by using a de-aerated electrolyte. Additionally, cyclic voltammetry curves were measured at various scan rates (i.e., 1, 5, 10, 20, 50, and 100 mV/s) in both quiet and stirred electrolyte. All of these measurements were performed under dark conditions. In addition to the curves specified above, current vs. applied potential curves were measured at the anodic portion of the curve and by sweeping from positive to negative potentials (also under dark conditions).

5.2.2.2 Quantum Yield

Two different types of quantum yield (QY) measurements were performed - one consisting of measuring the external QY as a function of the wavelength and the other by making measurements as a function of time at a given wavelength. For both types of measurements, the potential in the PEC cell was held at 0 V vs. SCE.

The illumination system consisted of a Xe arc lamp and a single-pass monochromator with a 5 nm bandwidth. A BG-3 glass filter was used on the entrance slit of the monochromator to reduce stray-light effects. The spot size was ~1.5 mm in diameter. For the spectral QY measurements, the dwell time between the points was set to 1 and 100 sec to establish possible time-related effects. The time-dependent QY measurements were performed at 260, 350, and 370 nm. A detailed description of the setup used for both types of QY measurements can be found in reference 15.

Transmission measurements at wavelengths between 350 and 800 nm were performed for some of the ZnO single crystals by using a Perkin Elmer Instruments Lambda 900 Spectrometer. Scanning electron microscope (SEM) images and Energy Dispersive X-ray Spectroscopy (EDS) data were taken using a Hitachi S-3400N system.

5.3 Results and Discussion

5.3.1 Carrier Concentration

Table 5.1 shows the doping concentrations determined from Hall Effect measurements of the various n-type ZnO single crystals. These carrier concentrations indicate that the doping levels are very high - even for the un-doped ZnO, which had a carrier concentration of $\sim 5.5 \times 10^{16} \text{ cm}^{-3}$. Neither the carrier concentration, nor the color of the samples was dramatically affected when the ZnO crystals were thermochemically treated with Cd and Te. In fact, the carrier concentration between the un-doped and the Te doped, and between the Cd and the Te doped crystals were the same within the experimental error. However, the Mg- and Zn-treated crystals did exhibit a change in color (from clear to dark orange), and the carrier concentration increased by more than an order of magnitude. The crystals doped during growth exhibited carrier concentrations in the range of 10^{18} cm^{-3} , which is near degeneracy. The highest carrier concentration was obtained for the Ga+Li doped crystal that had a blue coloration.

5.3.2 Electrochemical Measurements

According to the notation used in this paper, anodic currents are positive, indicating that electrons are collected at the back contact of the semiconducting electrode. The source of these electrons can either be from an oxidation reaction or a photoelectrochemical process. Similarly,

the cathodic currents are set as negative. These are associated with electrons flowing from the semiconducting electrode into the electrolyte, and are related to reduction reactions.

5.3.2.1 Current vs. Potential Behavior

The J-E curves indicated that all of the ZnO crystals exhibited diode-like rectification. Figure 5.1 shows the J-E curves in the dark and under illumination for sample 4. The small photo-response is, in part, attributable to the low intensity of the incident illumination above the ZnO band gap, $E_g = 3.4$ eV (365 nm). In this figure, it can also be seen that, as the potential was made more positive from a starting potential of -2.1 V vs. SCE, an anodic peak with a maximum at approximately -1.5 V vs. SCE was observed - regardless of the presence of light. Similarly, when the voltage sweeping direction was reversed, a cathodic peak was observed at approximately -1.72 V vs. SCE.

Visual inspection of the electrode during the measurements indicated the formation of a surface product during the cathodic peak currents (indicated as “region D” in Figure 5.1). This product started to dissolve as the anodic peak currents were initiated (region F), and it appeared to be completely dissolved when the maximum peak current was reached. Additionally, bubbles were formed at the electrode surface when the sweeping potential was ≤ 2 V vs. SCE (region E).

Changes in the direction of the cyclic sweep did not generate behavioral differences in the observed features. Additionally, the peaks were not affected by the presence of oxygen in the electrolyte. However, when the cyclic voltammetry sweep was limited to potentials between ~ -1.6 and 1 V vs. SCE, which omits the cathodic peak in the curve, neither the anodic nor the cathodic peaks were observed (Figure 5.2). Furthermore, a voltage sweep from -1.5 to -2.1 V also showed no cathodic peak.

The presence of these peaks, as well as the increase in the surface roughness of the ZnO electrodes after the cyclic voltammetry scans, indicated that chemical reactions at the ZnO-electrolyte interface had taken place that were responsible for the dissolution of the ZnO electrode into the electrolyte. The absence of the anodic peak in the scan between -1.6 and 1 V vs. SCE, shows that this peak is related to the oxidation of the surface product generated during the cathodic peak.

The effect of the NaOH concentration on the J-E behavior of the samples can be seen in Figure 5.3. The peak current was found to increase with increasing NaOH concentration. The “flat” cathodic currents are a consequence of the low conductivity of the electrolyte when the concentration was 0.01 M and 0.1 M NaOH. Additionally, the peak potential was found to become more negative as the NaOH concentration increased with a slope of approximately 120 mV per decade between 0.01 M and 5 M NaOH (Figure 4). This indicates that 2 electrons are involved in the chemical reaction taking place in the anodic peak. An equilibrium and/or saturation value appears to be reached at sufficiently high NaOH concentrations (≥ 7 M NaOH).

The scan-rate dependence of the cyclic voltammetry curves measured in a quiescent and a stirred electrolyte indicated that the currents increased with the scan rate (Figure 5.5). This tendency is expected when a diffusion layer is involved in the charge or mass transfer process, and it can be understood in terms of the time spent at each potential of the scan and the time available for the formation of a diffusion layer. This effect became more noticeable via the overall increase in the current that was measured when the electrolyte was stirred (Figure 5.5b) - as opposed to when it was quiescent (Figure 5.5a). The peak of the current densities in quiescent conditions as a function of the square root of the scan rate is shown in Figure 5.6. The least-squares fits are also shown ($R^2 = 0.98$ for both fits). This linearity suggests that the reactions

taking place at the electrode surface are subject to a diffusion-controlled process where the anodic currents are very likely being limited by the inward flow of water and/or hydroxyl ions (OH^-) and the outward flow of the reacting species from the electrode through the layer of the electrochemically generated species.

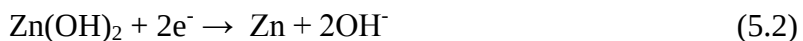
The nature of the cathodic currents was studied by holding a ZnO electrode at the cathodic peak potential for 17 hrs. The surface product obtained was metallic gray, and an X-ray diffraction examination indicated that it was Zn metal with minor traces of ZnO (Figure 5.7). Figures 5.8, 5.9, and 5.10 show the SEM images of the structures obtained at the surface of the electrode. Figure 5.8 shows the beginning stages of the Zn metallic growth after only 1 min of reaction time (the brighter the area in the image, the higher the Zn concentration with respect to oxygen.) However, it was not possible to estimate the Zn/O ratios by EDS due to the high magnification needed to observe the surface details. Figure 5.9a shows a low magnification view of the general surface after a 17 hr reaction time. The structure of the altered surface layer consists of a series of “star-shaped” crystals that are loosely bound together. Other structures indicating the dendritic growth of the crystals were also observed (see Figure 5.9b). EDS results indicated that these crystals consisted primarily of Zn metal with traces of oxygen. Table 5.2 shows the atomic percent (at%) compositions estimated by EDS analysis of the structures indicated in Figure 5.10. These results show that in some of the structures found on the altered ZnO electrode surface, non-stoichiometric oxygen was also present.

Based on these findings it is possible to correlate the regions A, B, C, D, E, and F of the J-E curve indicated in Figure 1 with the particular processes taking at the ZnO electrode. In regions A and B, the potential is 0 V vs. SCE in the dark and under illumination (with an energy larger than the band gap) respectively. The semiconductor is in reversed bias conditions and away

from the flat-band potential, V_{fb} , which is located at approximately -0.9 V vs. SCE in this electrolyte [5.16]. The behavior of the J-E curve in this region is determined by the presence of a depletion region. In the near total absence of minority carriers (in the dark), the saturation current (due to holes) and the injection current (due to electrons) are equal - and consequently no net current is measured. However, when the electrode is illuminated, the concentration of minority carriers will increase markedly, and the depletion region will facilitate their collection at the surface of the semiconductor. Consequently, an increase in photocurrent is measured that is directly related to the illumination intensity. The photoelectrochemical behavior of ZnO in this region will be discussed in more detail in Section 5.3.2.2.

As the potential becomes more negative and approaches V_{fb} , the bias generating the depletion width is reduced. Consequently, the photocurrent starts to decrease as the injection current increases until it becomes zero (region C) at V_{fb} .

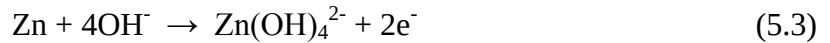
While the electrolyte conducts holes easily, it does not conduct electrons well. As the potential becomes more negative than V_{fb} , very little current is observed until the cathodic peak near -1.72 V vs. SCE is reached (region D). As previously noted, these currents are related to the reduction of Zn^{+2} to $Zn^0(s)$ at the semiconductor-electrolyte interface. Studies by M. Cai et al have observed a similar peak in the electrochemical behavior of Zn metal in alkaline solutions [5.17]. Accordingly, it is possible to establish that the cathodic currents are the result of either or both of the following two reactions:



As the potentials are swept in a more negative direction, these reactions stop occurring, and the fast increase in the cathodic currents in region E can be, in part, attributed to the

dissolution of the semiconductor with the formation of hydrogen that is expected from the high negative potentials - and that is also consistent with the bubbles observed during the measurements. From Figure 5.3, it can be seen that when the NaOH concentration in the electrolyte is between 1 and 9 M, the slopes of the cathodic current do not change. The activation energy required for this reaction, as estimated from these slopes, is approximately 0.1 eV.

When the direction of the potential sweep is changed and the potentials are made more positive, the cathodic currents are followed by region F that includes the anodic peak. From an inspection of the semiconductor during the cyclic sweeping, it is known that Zn metal is present at the surface of the electrode when the anodic currents start to rise - indicating that the source of the anodic current in region F is associated with the re-oxidation of Zn. M. Cai et al. have attributed the increase in the anodic current in Zn electrodes to the formation of the zincate ions by means of the overall reaction [5.17, 5.18]:



It is suggested that this is a “step reaction” involving the formation of various zincate complex ions such as $\text{Zn}(\text{OH})^-$ and $\text{Zn}(\text{OH})_3^-$. In pure Zn electrodes, the reaction is expected to be limited by the inward flux of OH^- into the reaction site. However, in our ZnO crystals, the reaction may also be limited by the availability of Zn metal at the interface. This may account for the overlapping of the curves at 1, 5, and 10 mV/s in Figure 5.5b. Additionally, as the potentials are made more positive than the peak value, the zincate ions can apparently become saturated and precipitate at the interface as a very loose $\text{ZnO}_{1-x}(\text{OH})_{2x}$ adsorbed species. This may account for the presence of oxidized Zn that forms as indicated by the EDS data. However, the surface interactions between the ZnO crystal and the electrolyte at such negative potentials may well be

more complicated than this, and further study is necessary to fully understand the surface kinetics reactions involved as a result of these applied potentials.

5.3.2.2 Quantum Yield

The ZnO (QY) results are presented in figure 5.11. The shape of the QY curve is consistent with the results of previous work [5.15], and it is related to the absorption coefficient and, hence, the penetration depth of light in ZnO. The drop in the QY near the band edge energy was not as sharp as expected for a direct band semiconductor due to the ± 5 nm bandwidth of the monochromator. The feature observed immediately before this drop is an effect of the exciton absorption just below the band edge [5.19]. Additionally, Figure 5.11 shows that the optical excitation range remained unchanged - indicating that significant energy states in the band gap were not formed regardless of the doping type or concentration.

The height of the QY curve was found to decrease as the carrier concentration increased. Figure 5.11a shows that the highest QY was observed for the un-doped crystal (sample 1), followed by samples 2 and 3 that had statistically identical carrier concentration values. Samples 5 and 6 were both heat treated with Zn metal vapor for 30 min, and a slightly higher carrier concentration was obtained when the temperature was held 50 °C higher (sample 6). This change in carrier concentration was sufficient to produce a drop of ~20% in the QY. The lowest QY of the thermochemically treated samples was obtained for sample 4, which suggests that the introduction of the magnesium impurity results in additional recombination centers.

From the group of ZnO samples doped during growth, samples 7, 8, and 9 exhibited a similar QY (Figure 5.11b) - consistent with the fact that the measured carrier concentrations are statistically the same. The lowest measured QY was found for sample 10, which exhibited the highest overall carrier concentration.

Time-dependant measurements of the QY indicated that the ZnO photoanodes exhibited a very small time dependence as compared to that observed for degenerate KTaO₃ in the same type of photoelectrochemical cell environment [5.15,5.20]. The longest relaxation time in the QY occurred at a wavelength of 260 nm, where it required ~30 sec to equilibrate. However, the total changes in the QY values were less than 2% for all of the wavelengths tested.

5.3.3 Optical Measurements and Quantum Yield

To better understand the photoelectrochemical behavior, a study was made of the correlation of the ZnO and cell properties with the optical absorption characteristics. Figure 5.12 shows the penetration depth of light (ordinary polarization) in ZnO as a function of the wavelength in the UV region. Since all of the crystals were oriented with the c-axis perpendicular to the surface, the ordinary optical functions are used. This data is calculated as the inverse of the absorption coefficient (α) measured in reference 5.19. As can be seen in the figure, there is a linear increase in the penetration depth between 260 and 340 nm, where the 340-350 nm wavelength light is absorbed ~10 nm deeper than the 260 nm light. These differences are important since the electron-hole pairs formed within the depletion width have a much higher probability of being collected than those formed deeper in the material so that they then have to undergo diffusion in order to reach the depletion width.

The depletion width for the ZnO electrodes was estimated using an ideal one-sided abrupt junction approximation represented by equation [5.21]:

$$W = \sqrt{\frac{2\epsilon_s}{qN} \left(V_{bi} - \frac{2kT}{q} \right)} \quad (5.4)$$

where ϵ_s represents the static dielectric constant (7.61 from Ref. 22), q the electron charge, N the carrier concentration, k Boltzman's constant, and T the temperature in Kelvin. Figure 5.13

shows the ideal depletion widths for three built-in voltages (V_{bi}) as a function of the carrier concentration.

Comparing the values of W and the penetration depth of light is useful in understanding the decay of the QY observed between 260 and 350 nm. From Figure 5.12 it is observed that at 260 nm, the light is preferentially absorbed at 54 nm from the surface of ZnO. At this wavelength, the ideal W for the un-doped crystal (sample 1) is ~ 110 nm, indicating that the electron-hole pairs are ideally being formed within the depletion width and consequently the QY is at its highest value. As the wavelength increases, the penetration depth of the light also increases, which causes the electron-hole pairs to be formed deeper in the crystal - thus decreasing the quantum yield. The consistent decay of the QY with the penetration depth of light at this larger depletion width suggests that a considerable number of defects in the crystal and/or surface states are present thereby preventing the holes from being collected at the surface of the material. This is not unexpected due to the high carrier concentration that is present for even a “non-doped” ZnO single crystal. Similarly, for those samples exhibiting medium values of QY (e.g. sample 7), the ideal depletion width is on the order of 28 nm – a value that is already much smaller than the penetration depth of light in that wavelength range. Electron-hole pairs are then preferentially being formed beyond the depletion width, and the holes need to diffuse to the depletion width. This is a more inefficient process that significantly increases the probability of the holes recombining. Consequently, the overall QY decreases when compared to the lower doped crystals. A similar trend is observed for sample 10, which has the highest overall carrier concentration that reduces its ideal depletion width even further (~ 10 nm), and hence, it has the smallest measured QY.

In reference 5.20, it is shown that the external QY of a semiconductor can be modeled by:

$$QY(\lambda) \approx \left[1 - \frac{\exp(-\alpha(\lambda)W)}{\alpha(\lambda)L + 1} \right] (1 - R(\lambda)) \quad (5.5)$$

where W is the depletion width, L is the minority carrier diffusion length, $\alpha(\lambda)$ is the absorption coefficient and $R(\lambda)$ is the surface reflectance. The derivation of this equation starts with the fundamental base and depletion width photocurrent estimations that is used for solar cells [5.23] and that already assumes ideal mobility and uniformity of the doping distribution in the crystals as well as no recombination of charges in the depletion region. The main assumption used in the derivation of equation 5.5 is that the total thickness of the cell (in our case the thickness of the crystal) is much larger than minority carrier diffusion length. This equation represents a good approximation to the QY behavior of ideal crystals in the PEC cell, and it was used to estimate the minority carrier diffusion length in our ZnO crystals.

Figure 5.14 shows the estimated L for samples 2 and 7 as a function of the wavelength using the QY results shown in Figure 5.11. Overall, the minority carrier diffusion lengths for sample 2 were larger than those of sample 7, which is expected due to its lower carrier concentration. This higher value of L is also partially responsible (in addition to W) for the higher QY measured for this sample. This trend was observed for most of the ZnO crystals; with the exception of samples 1 and 3, for which there were significant error bars. The decrease of L as a function of the wavelength is probably a consequence of the increase in the penetration depth of light in the crystals. Since these crystals are degenerately doped, at any given point, both W and L are dependent on the local characteristics of the crystal that can affect both the mobility of the charges as well as the electric field distribution within the crystal (particularly at these high doping concentrations.) Also, from the results of the cyclic voltammetry sweeps, it is expected that the electrode surface will partially consist of adsorbed species formed by the

interactions of the OH^- ions with the surface Zn. The total effect of these surface products on the QY is not presently understood, but it will affect the behavior of the charge transfer at the interface - which will, in turn, significantly alter the behavior of the crystals from the ideal assumptions made in the derivation of equation 5.5.

The effect of the high carrier concentration can also be observed in Figure 5.15 where ellipsometry and optical transmission data were used to calculate the absorption coefficient of ZnO for samples 7 to 10. The ellipsometry data (upper curve from 250 to 400 nm) was re-plotted from Ref. 5.19 for use in this figure, since doping does not appreciably affect the optical properties above the band edge. However, the transmission data (lower part of the curve between 400 and 800 nm) was found to change significantly as a function of the carrier concentration. The absorption coefficient of the un-doped crystal decreases as a function of wavelength in this range. On the other hand, the absorption coefficient of samples 7, 8, and 9 (which have equivalent carrier concentrations) seems to reach higher and similar values at the longer wavelengths. The absorption coefficient of sample 10 (the most heavily doped) is the highest through the entire wavelength range. This behavior in the absorption is caused by free carrier absorption; however at these short wavelengths, it was not possible to establish the origin of the free carrier absorption (acoustic phonons, optical phonons and/or ionized impurities), and the error limits on the measurements preclude the drawing of any further conclusions. Sharp lines exhibited by samples 1, 8, and 9 between 480 and 560 nm are apparently indicators of impurity bands.

5.4 Conclusions

The J-E curves show that the ZnO crystals exhibit diode-like behavior and are photoresponsive at biases that are more positive than the flat band potential. These curves also showed the presence of a cathodic and an anodic peak at potentials ≤ -1.1 V vs. SCE. These peaks are associated with a diffusion-controlled process where two electrons are involved in the dissolution and re-oxidation of Zn at the electrode-electrolyte interface, respectively. High cathodic currents for potentials ≤ 2 V vs. SCE are partially attributed to the dissolution of the anode during the formation of hydrogen. No dependence of the chemical stability of the ZnO electrodes on any of the dopants utilized here was observed.

Measurements of the QY at 0 V vs. SCE showed no change on the optical absorption range. For a given sample, the decrease in QY observed between 260 and 350 nm was found to be an effect of the increase in the penetration depth of light. Furthermore, the magnitude of the QY was also correlated with the carrier concentration. At a given wavelength, higher carrier concentrations were linked to lower QY values since the increase in carrier concentration reduces W . As W decreases, there are more and more photons that will be absorbed beyond W and that then have to diffuse to reach W , which is a significantly more inefficient process. Additionally, the higher carrier concentrations (total difference of 2 orders of magnitude from the lowest doped to the highest doped) indicate that there will be more defects present in the crystal structure that will reduce the minority carrier lifetime and further reduce the QY.

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Appendix

Table 5.1. ZnO single crystals description

Sample	Doping			Color	Carrier Concentration ($\times 10^{17} \text{ cm}^{-3}$)
	Doping Element	Temperature ($^{\circ}\text{C}$)	Time (hr)		
1	None			Clear	0.55 ± 0.01
2	Te	1100	4	Clear	0.72 ± 0.21
3	Cd	1100	4	Clear	0.80 ± 0.01
4	Mg	1150	18	Dark Orange	14 ± 1
5	Zn	1100	0.5	Dark Orange	11 ± 1
6	Zn	1150	0.5	Dark Orange	15 ± 1
7	Gd	Doping elements directly added to the melt		Light Green	10 ± 4
8	In + Li			Light Blue	11 ± 5
9	Er			Light Green	14 ± 4
10	Ga + Li			Blue	67 ± 4

Table 5.2. Atomic percent composition estimated by energy dispersive X-ray spectroscopy from Figure 5.10.

	Zn	O
a	60	40
b	68	32
c	79	21

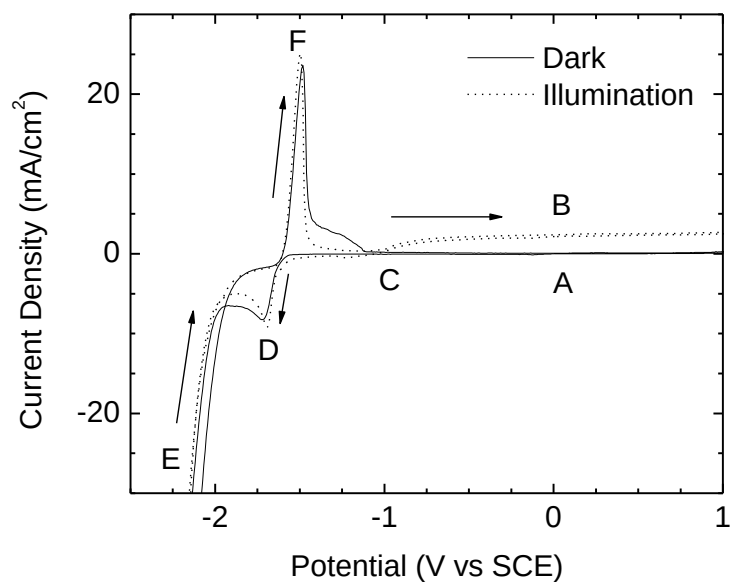


Figure 5.1 Current density vs. applied potential curves for ZnO single crystal electrode sample No. 4 in the dark and under illumination illustrating the various regions of the cyclic voltage sweep curves. Arrows are used to emphasize the direction of the cyclic potential sweep.

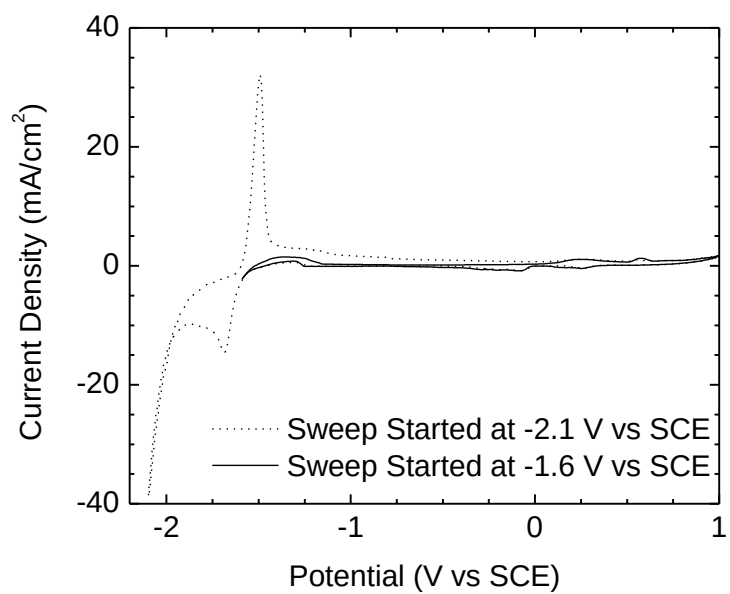


Figure 5.2 Current density vs. applied potential curves for ZnO single crystal electrode sample 4. Both curves were measured in dark conditions.

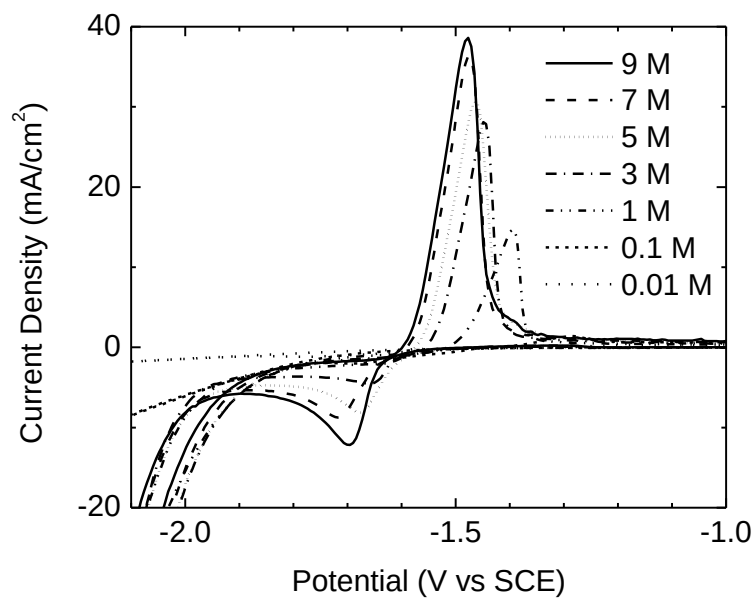


Figure 5.3 Changes in the current vs. applied potential behavior of ZnO single crystal electrode sample 4 as a function of the NaOH concentration in the electrolyte.

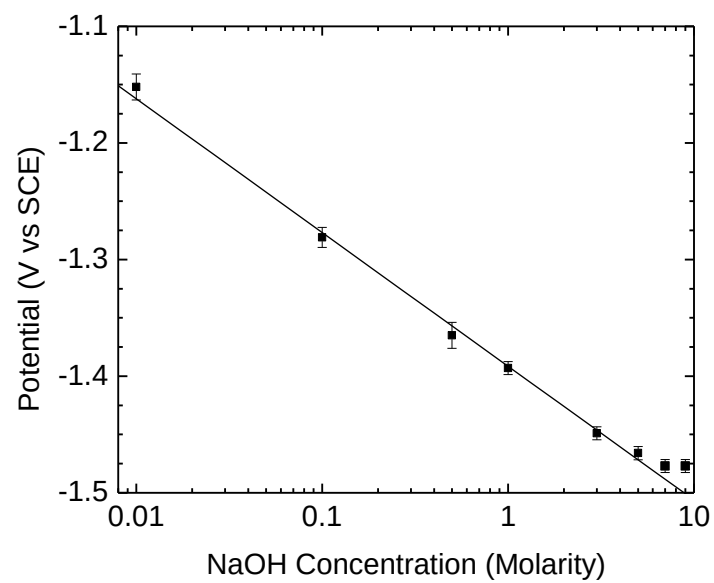


Figure 5.4 Peak potential as a function of the NaOH concentration in the electrolyte for ZnO electrode sample 4.

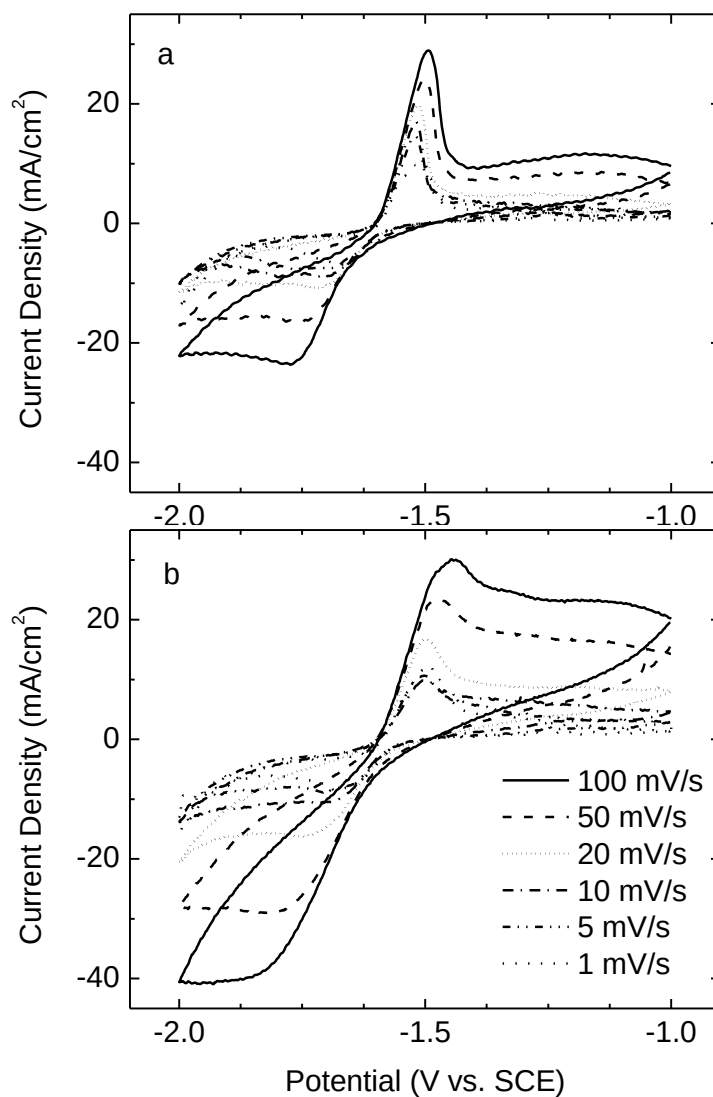


Figure 5.5 Current vs. applied potential curves for ZnO electrode sample 4 at various scan rates in a quiet (a) and stirred (b) electrolyte.

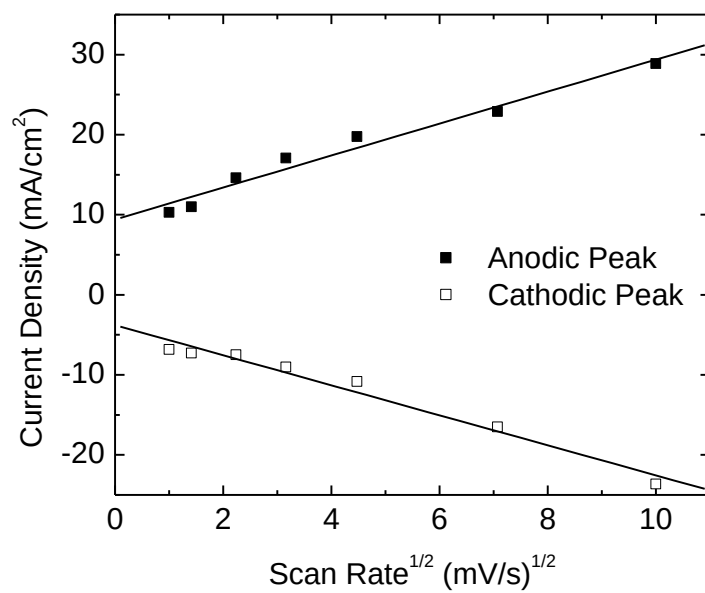


Figure 5.6 Anodic and cathodic peak current densities from Fig. 5a as a function of the square root of the scan rate. Least squares fits are also shown.

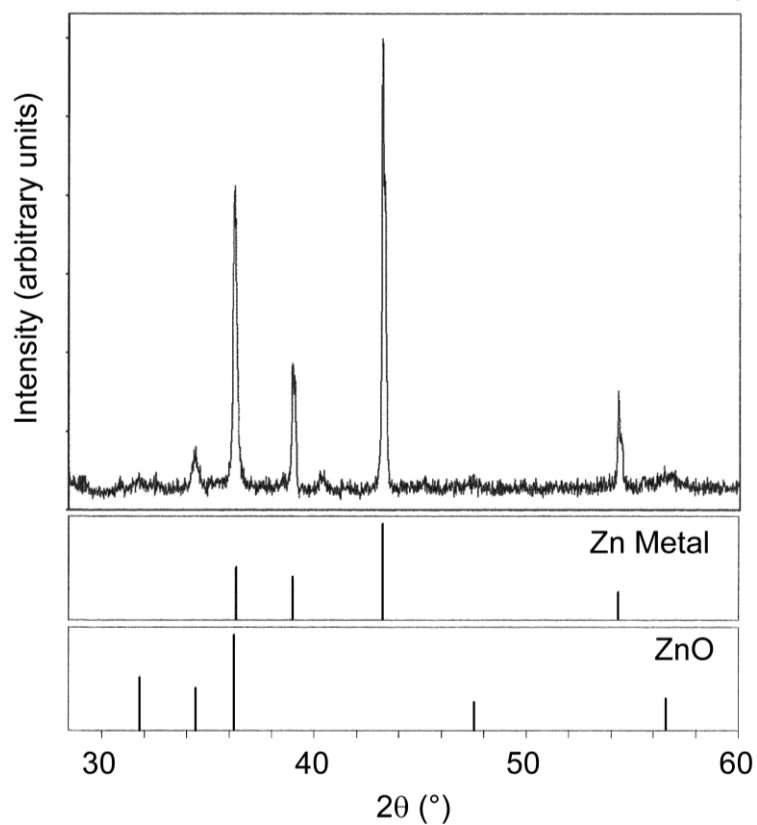


Figure 5.7 X-Ray diffraction pattern of the altered surface product generated during the reduction reaction of a ZnO single crystal PEC cell electrode showing the formation of metallic zinc on the photoanode surface. Weak x-ray diffraction peaks from ZnO are also present.

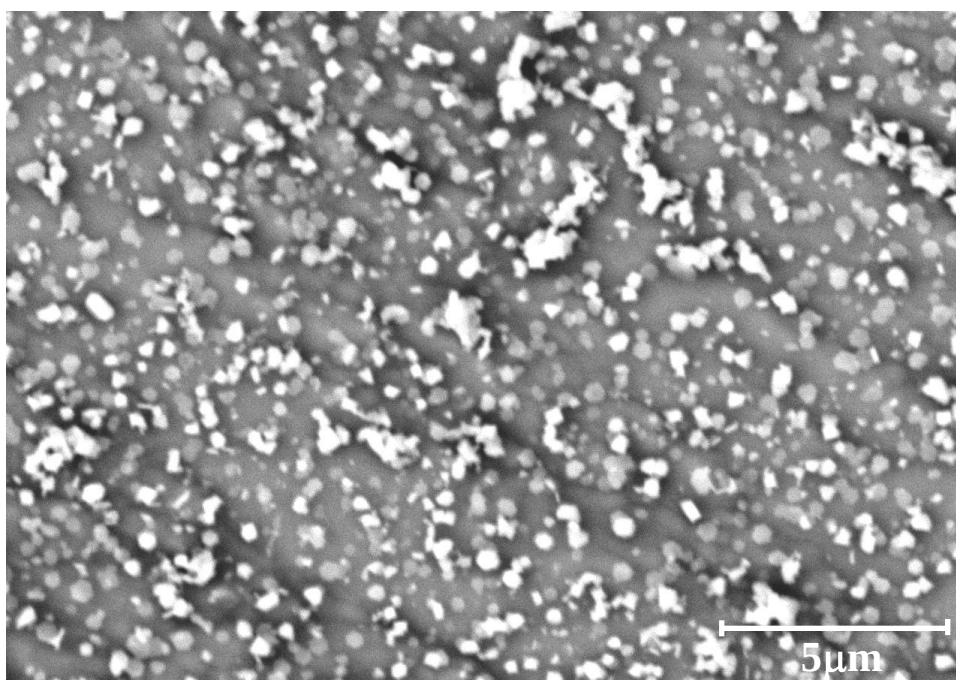


Figure 5.8 Early onset growth of metallic zinc on the single crystal ZnO electrode surface. The cell operation/ reduction time was 1 min.

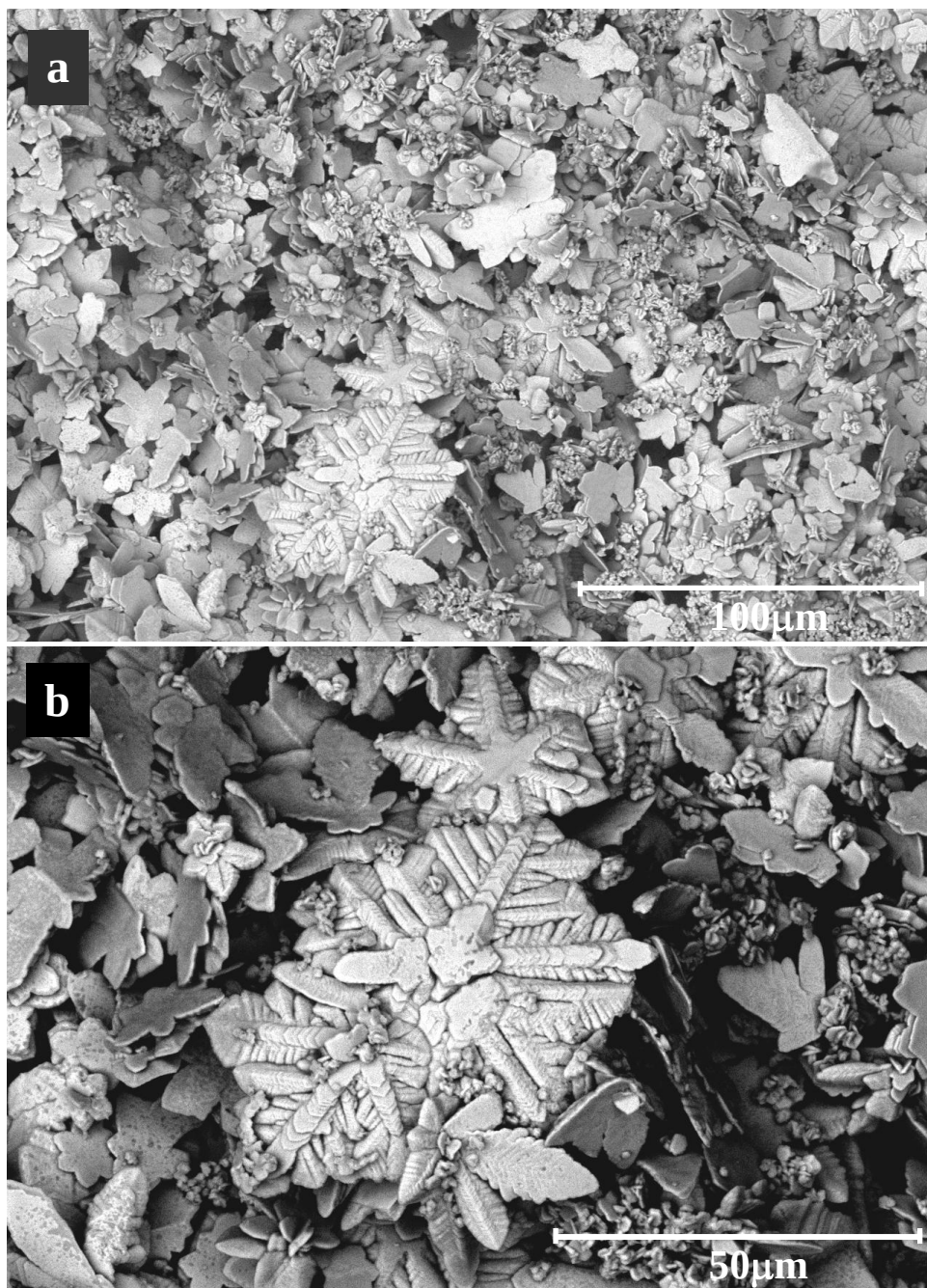


Figure 5.9 Metallic Zn crystals formed at the surface of a ZnO single crystal photoanode. a) overall low magnification view, b) detailed view of the dendritic growth morphology.

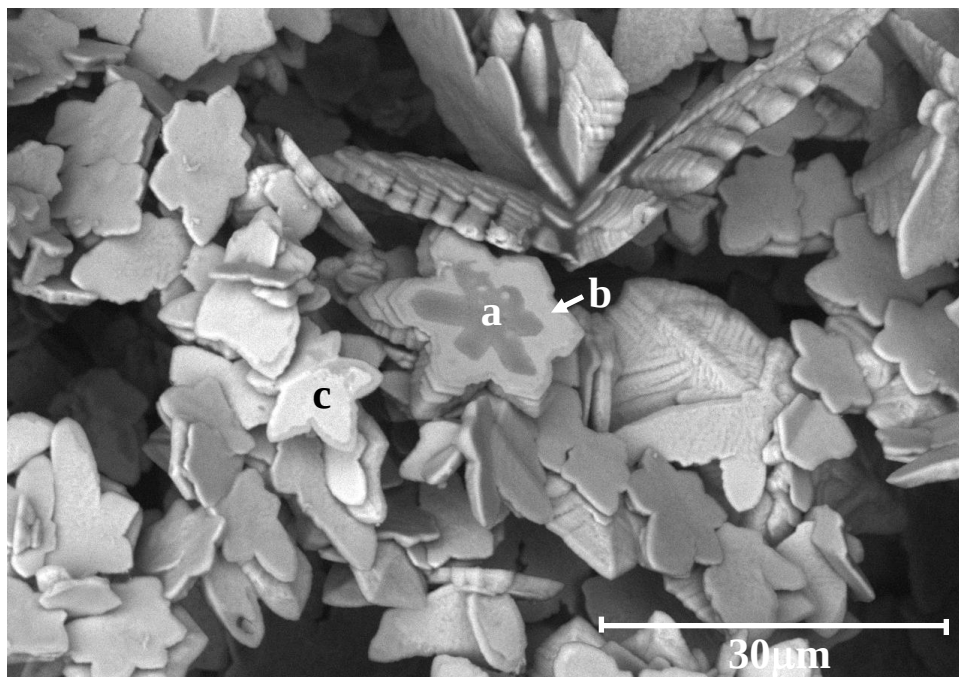


Figure 5.10 Crystal structures formed at the surface of a ZnO electrode after electrochemical reduction under PEC cell operation for 17 hrs. The darker regions indicate a higher oxygen concentration. The compositional results of an EDS analysis of the indicated regions a, b, and c is shown in Table 5.2.

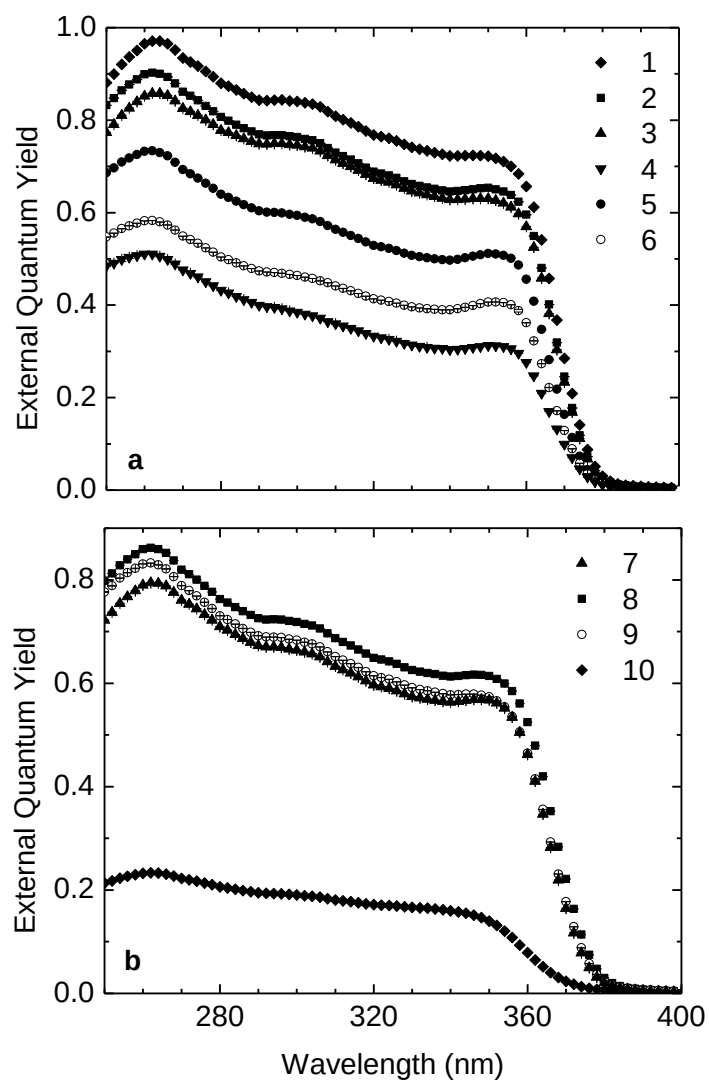


Figure 5.11 Spectral photocurrent quantum yield of the various single crystal ZnO semiconducting photoanodes for: (a) the thermochemically doped (1-6) samples and (b) the samples (7-9) doped in the melt during growth.

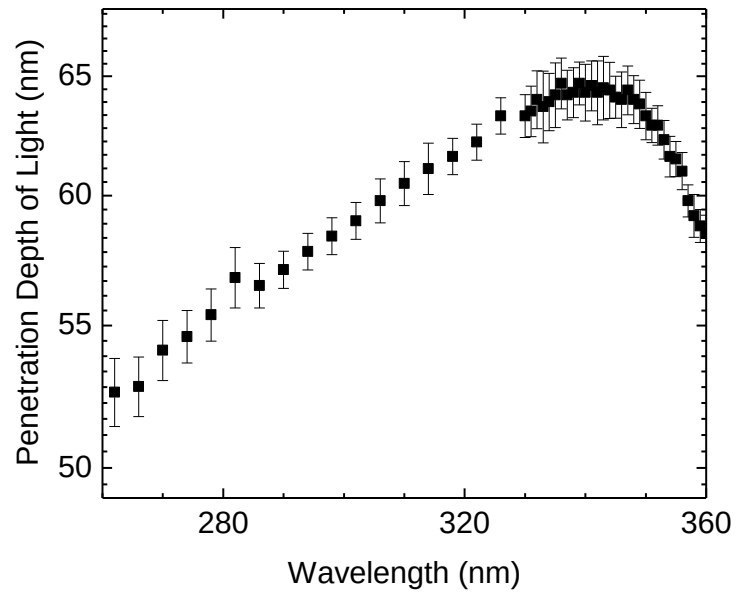


Figure 5.12 Penetration depth of light as a function of the wavelength for ZnO. Data re-plotted from Ref. 5.19

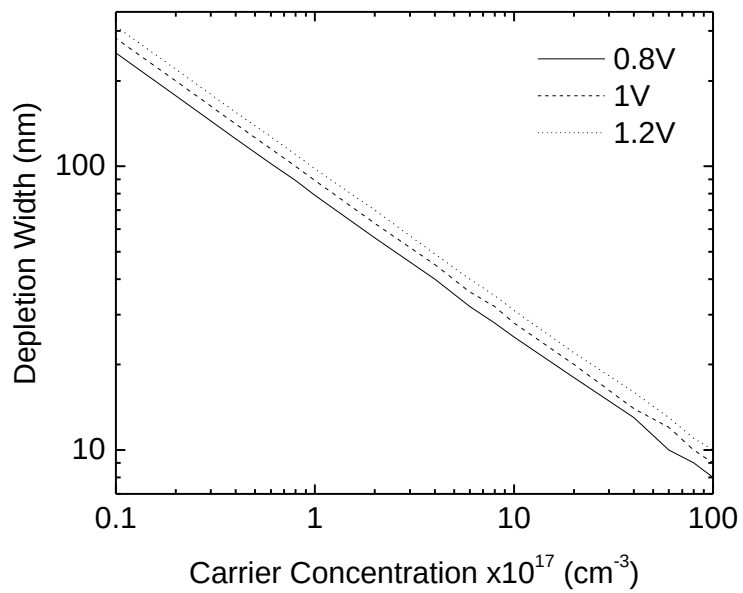


Figure 5.13 Estimated depletion widths for ZnO single crystals as a function of the carrier concentration at the semiconductor/electrolyte interface for three different built-in potentials (V vs SCE)

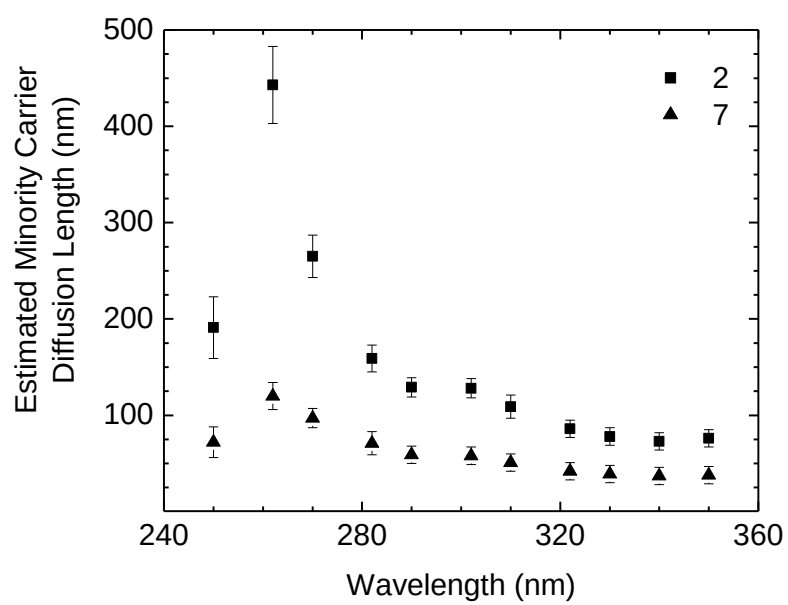


Figure 5.14 Minority carrier diffusion lengths for ZnO single crystal PEC cell electrodes 2 and 7, estimated using Equation 5.5.

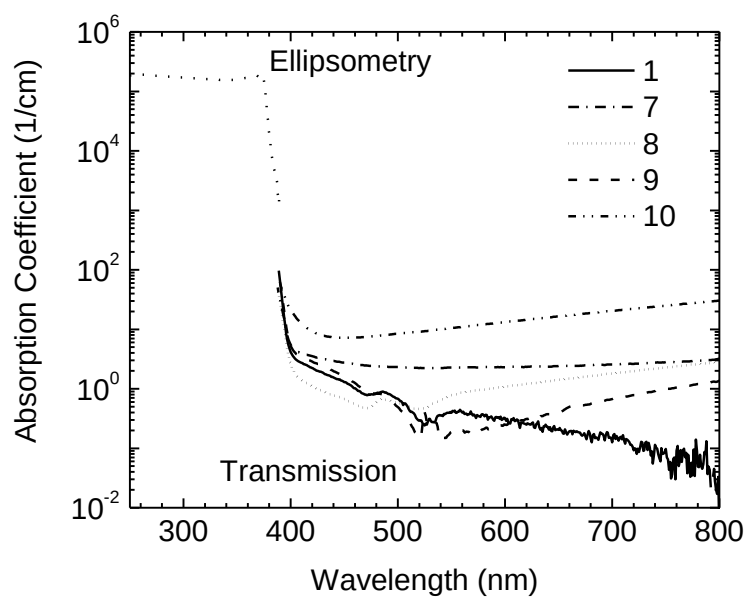


Figure 5.15 Absorption coefficient as a function of wavelength for the indicated doped and undoped ZnO single crystals.

Vita

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