Fall 12-15-2011

# Photocatalytic Activity of Zinc Oxide Thin Films Prepared by DC Sputter Deposition and Thermal Oxidation

Robert Louder
*Coastal Carolina University*

## Recommended Citation

Louder, Robert, "Photocatalytic Activity of Zinc Oxide Thin Films Prepared by DC Sputter Deposition and Thermal Oxidation" (2011). *Honors Theses*. 105.
https://digitalcommons.coastal.edu/honors-theses/105

# PHOTOCATALYTIC ACTIVITY OF ZINC OXIDE THIN FILMS PREPARED BY DC SPUTTER DEPOSITION AND THERMAL OXIDATION

2011

BY

ROBERT LOUDER

APPLIED PHYSICS

Submitted in Partial Fulfillment of the
Requirements for the Degree of Bachelor of Science
In the Honors Program at
Coastal Carolina University

DECEMBER 2011

# Abstract

Zinc oxide (ZnO) is a wide-bandgap semiconductor with a broad range of applications, such as photocatalysis. The photocatalytic properties of ZnO result from the highly oxidizing holes and reducing electrons that are induced on the ZnO surface by ultraviolet (UV) light. The efficiency of electron-hole pair formation is therefore critical for photocatalysis, and thus the optical quality of the films in the UV region is of critical importance. ZnO thin films have been fabricated using DC sputter deposition of Zn-metal films followed by thermal oxidation at different temperatures (300, 600, and 900°C). Characterization of the optical properties of the resulting ZnO thin films through photoluminescence indicates that increasing oxidation temperature leads to reduced UV excitonic emission. The photocatalytic activities of the films were also characterized by measuring the efficiency of degradation of Rhodamine B dye in solution. The photocatalytic efficiency of the film annealed at a temperature of 300°C was higher compared to those of the films annealed at temperatures of 600°C and 900°C. The increased photocatalytic efficiency is attributed to the increased optical quality of the films that results from lower oxidation temperatures.

# 1 Introduction

Zinc oxide (ZnO) is a highly useful and practical wide bandgap semiconducting material with a broad range of applications, including self-cleaning and anti-fogging surfaces, sterilization, gas sensing, energy production, and environmental purification. Some of these applications use the photocatalytic properties of ZnO that result from the highly oxidizing photogenerated holes on the ZnO surface induced by exposure to ultraviolet (UV) light. ZnO can thus be used to photocatalyze the oxidation of various organic chemicals in applications such as environmental remediation and self-cleaning surfaces. For such applications, ZnO thin films are preferable to nanoparticles or colloidal suspensions because of they are reusable and relatively easy to recover from the environment in which they are used. ZnO films are also transparent, and have potential for use in transparent self-cleaning surfaces.

We have recently developed a technique to fabricate ZnO thin films by thermally oxidizing Zn-metal thin films that have been physically deposited on various surfaces using sputter deposition. Characterization of the morphological and photophysical properties of the thin films shows that increasing oxidation temperature leads to greater strain between crystal grains and the incorporation of significant defects, which results in reduced optical quality. Therefore, films fabricated at higher oxidation temperatures should exhibit reduced photocatalytic activity.

In this study, we have characterized the photocatalytic activities of ZnO thin films fabricated with oxidation temperatures of 300°C, 600°C, and 900°C by measuring the efficiency of photocatalytic degradation of Rhodamine B dye in solution. This progression of analysis reveals correlations between the fabrication conditions, the resulting optical quality properties, and the photocatalytic activities of the ZnO thin films. These results can be applied in the optimization of ZnO thin films fabricated for use in photocatalytic applications.

# 2 Theory

## 2.1 Semiconductor theory

The electrical conductivity of a material is dictated by the presence (or absence) of free electrons in the highest energy orbitals of the atoms that make up the material, as the electrons are the charge carriers that propagate, or conduct, electricity to through a material. Conductivity is often modeled by the band theory of solids, illustrated in Figure 1, which plots the possible energies of electrons in the outermost orbitals of the atoms in a solid material. The electrons that occupy the outermost electron shell of an atom are called valence electrons, and the energy of the shell that they occupy is called the valence band. Higher in energy than the valence band is the conduction band. Electrons that are present in the conduction band have a high enough energy to overcome binding to any individual atom and are free to move throughout the atomic lattice of the solid material, thereby conducting electricity.

The energy difference between the conduction band and valence band of a material is called the band gap. Insulators have a large band gap, so virtually all of their outermost electrons reside in the valence band and are unable to conduct electricity. In conductors, however, there is virtually no band gap and the valence band and conduction band overlap, so some or all of the valence electrons are free to move about the atomic lattice in the conduction band, allowing the material to conduct electricity.

Semiconductors are unique materials with electrical conductivities between that of conductors and insulators [1]. The intermediate conductivity is attributed to the intermediate size of the band gap, which is large enough so that the a semiconductor does not normally conduct electricity, but small enough so that thermal or other external energy applied to the material can promote valence electrons into the conduction band, allowing the material to conduct electricity. The amount of external energy required to excite electrons into the conduction band is the band gap energy, and is specific to the semiconductor material. The excited electrons that are promoted to the conduction band leave behind vacancies in the valence band called holes and can be modeled as positive charges that that can also propagate charge through the material [1]. Whether electrons or holes are the main charge carriers dictates whether the material is *n*-type or *p*-type, respectively.

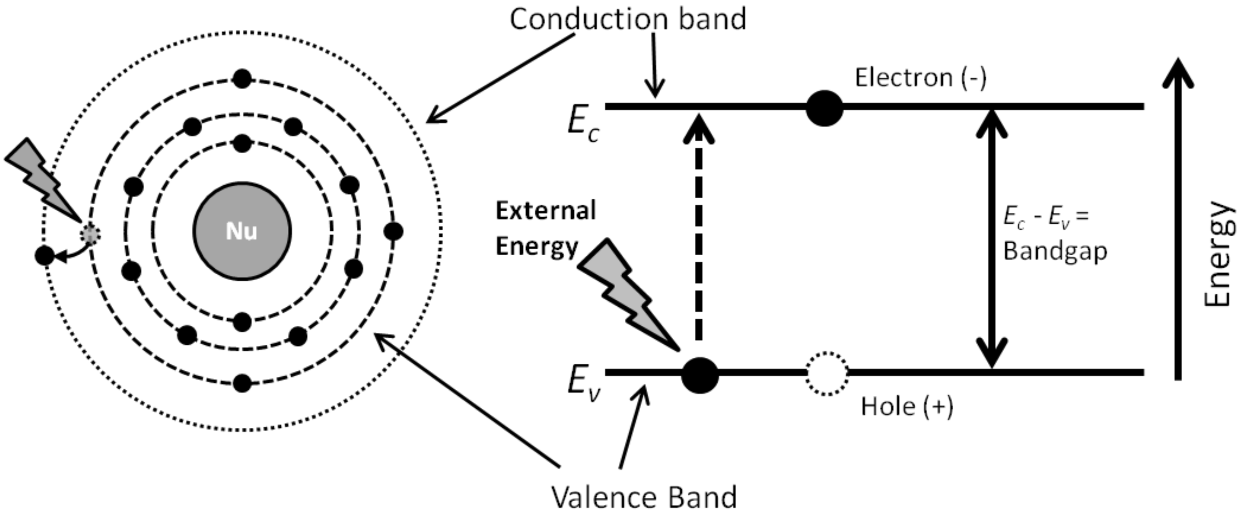

**Figure 1. Schematic representation of semiconductor band theory.** A generalized semiconductor atom is represented on the left, with the electrons, represented as black dots, orbiting the nucleus (Nu) in their respective orbital shells, represented by dashed lines. A close-up of the energy band structure of the conduction and valence bands is shown to the right.

Semiconductors have been fundamental in the development of modern electronics. A few different materials are commonly used in semiconductor materials that are commercially manufactured for electronics, including silicon and gallium arsenide, though a myriad of other materials are continually being researched and developed for practical use in a variety of applications. The precise electronic properties of each semiconducting material vary, and different materials may thereby be optimal for certain applications.

## 2.2 Photocatalysis

One specific property exhibited by some semiconductors is the ability to use light energy to catalyze oxidation-reduction reactions [2, 3]. Those semiconductors that exhibit photocatalytic activity share the ability to generate electron-hole pairs on their surface a due to the absorption of light energy [4]. Because semiconductors each have unique band gaps, the energy, and therefore wavelength, of light needed to generate the electron-hole pair depends on the specific semiconducting material.

The photogenerated holes on the semiconductor's surface have a high oxidation potential while the photogenerated electrons have a high reduction potential [4, 5]. Several types of aqueous reactions catalyzed by electron-hole pairs lead to the formation of the hydroxyl radicals and reactive oxygen species that are directly responsible for the oxidative degradation of organic compounds. One of these reactions involves the oxidation of water ( ) by a hole ( ) into hydrogen ion ( ) and hydroxyl radical ( ):

Another reaction involves the reduction of molecular oxygen ( ) into a superoxide radical ( ) by a photogenerated electron ( ):

The superoxide radical can then be further reduced by another electron and pair with two ions to form hydrogen peroxide ( ):

The hydrogen peroxide can then be reduced by an electron to form hydroxyl radicals:

By these reactions, either the electrons or the holes of the photogenerated electron-hole pairs can produce hydroxyl and superoxide radicals that can subsequently degrade organic compounds [4, 5]. It has also been proposed that the electrons or holes themselves may be responsible for at least some of the degradation of organics. Most likely, however, a large combination of chemical reactions involving various intermediates ultimately leads to the degradation of the organic compounds, which complicates the mathematical descriptions of the rates at which the overall degradation occurs [5].

Simplified mathematical descriptions of the degradation reactions have been used to experimentally quantify and compare photocatalytic activities. For most purposes, especially when the concentration of the contaminant is less than 10 ppm, the reaction can be considered first order, meaning that the rate of change in concentration of the contaminant, —, follows the general relationship

where is the concentration at any given time during the reaction, and is the rate constant [5]. This equation has been modified for solid photocatalysts to account for the surface area of the photocatalyst and the intensity of the incident light, such that

where is the intensity of light used and is the total surface area of the photocatalyst [4]. The solution to this differential equation is

where is the initial concentration of contaminant. The above equation demonstrates how the concentration of the contaminant changes over time. In order to make the concentration-time relationship linear, the equation can be rewritten as the integrated rate law,

Zero- and half-order rate laws have also been used to describe the photocatalyst degradation reactions. The differential and integrated forms of the zero-order rate law are

respectively. The differential and integrated forms of the half-order rate law are

## 2.3 Applications of photocatalysts

Semiconductors with photocatalytic activity have found use in many applications, including the photodegradation of environmental pollutants in water and air [6, 7]. Many environmental pollutants are organic in nature, and many proposed methods of environmental decontamination involve oxidation of the organic pollutants [8]. However, using semiconductor photocatalysts to oxidize and remove such pollutants from the local environment has many advantages over alternative methods [7]. Many of the semiconductor photocatalysts are themselves nontoxic and do not present additional harm to the environment in which they are used, contrary to most other methods of decontamination. Furthermore, the semiconductor photocatalysts do not need to be re-activated after undergoing photoinduced oxidation and reduction reactions. Conversely, activated carbon, a popular choice for water purification, requires expensive and potentially polluting reactivation [9].

Another traditional means of decontamination involves microorganisms, such as bacteria, that biologically degrade toxic organics [9]. However, these processes occur at a much slower rate compared to photocatalytic oxidation by semiconductors, and are inefficient at concentrations below ppm levels, while semiconductor photocatalysts can oxidize pollutants present in the ppb range. Additionally, many pollutants can also be toxic to the microorganisms themselves, while the semiconductor photocatalysts degrade most organic pollutants non-selectively [5].

Another application of photocatalysts is in the photo-cleansing of surfaces. Colloidal suspensions of photocatalyst nanoparticles have been used in paints and other surface treatments to create self-cleaning and self-sterilizing surfaces [6, 10]. Similarly, photocatalyst thin films can be used in transparent surfaces to create self-cleaning windows or fingerprint-resistant touch screens, for example [11].

Many applications of decontamination using semiconductor photocatalysts involve the sun as a practical source of UV illumination, although only ~2-3% of solar radiation is high enough in energy to induce semiconductor-catalyzed oxidation [12, 13]. Accordingly, the photodegradation efficiencies of the semiconductor photocatalysts designed for these uses need to be optimized in order to be of practical use.

It is believed that the specific photocatalytic activity of a semiconductor photocatalyst is dictated mainly by the efficiency of electron-hole pair formation in response to UV illumination [4, 5]. Thus, the optical quality of the semiconductor material in the UV region is of critical importance in optimizing its photocatalytic activity. The optical quality of the material is in turn mainly dependent on its nano-scale structure, which is greatly affected by the specific method used to fabricate the material. Because the methods and materials available for the fabrication of semiconductor photocatalysts vary greatly, there is a large range in the optical quality of the resulting materials and a need exists for optimizing fabrication conditions and materials for optimal photocatalytic activity in specific applications [6].

The optical quality of a semiconductor material can be characterized by measuring the photoluminescence (PL) excitation under illumination from varying wavelengths of light. When the semiconductor is illuminated with light, the binding energy between the formed electron-hole pair is emitted as light.  The wavelength of light that produces the highest PL excitation corresponds to the energy of the bound electron-hole pairs, or excitons, formed in the semiconductor, which is roughly equal to the material's bandgap energy. The overall intensity of PL at this wavelength is dependent on the efficiency of electron-hole pair formation at is a measure of the relative optical quality of the material.

## 2.4 Previous studies investigating semiconductor photocatalysts.

As previously mentioned, a myriad of options exist for fabricating metal-oxide nanostructures, each unique method of fabrication produces nanostructures with unique photocatalytic abilities. Accordingly, there is great interest in finding those preparation methods that optimize semiconductor photocatalytic efficiency and the photocatalytic properties of semiconductor nanostructures prepared by various methods have been intensively researched.

The photocatalytic properties of $TiO_2$ nanostructures have been investigated far more extensively than other metal-oxide semiconductors. This is most likely because $TiO_2$ was used in the studies by Fujishima et al that initially discovered photocatalytic ability of semiconductor materials [2, 3]. In these studies, $TiO_2$ and Pt photoelectrodes were used to investigate the nature of photoinduced electrolysis of water by the metal electrodes in the absence of an external voltage.

Since these initial studies, the research into semiconductor photocatalysis has expanded enormously, and other materials such as zinc oxide (ZnO) have recently gained attention [14-17]. ZnO is considered a good semiconductor photocatalyst, though it has not been studied as extensively as some other semiconductor photocatalysts, such as $TiO_2$, mostly due to historical reasons [15, 17]. ZnO is nontoxic, physically stable, and chemically inert, with the exception of photo-induced oxidation. ZnO has a band gap of 3.3 eV, which results in a relatively high oxidizing power that is strong enough to completely oxidize most organic compounds to $CO_2$, $H_2O$, and inorganic ions [14, 16].

Many studies have used ZnO nanoparticles in the form of colloidal suspensions. However, as Fujishima et al. point out, the nanofilm form of these semiconductors is preferable to particles for use in fluid decontamination because the nanoparticles need to eventually be collected and removed from the fluid [4, 17]. Additionally, the films are transparent and also have potential for use in applications such as self-cleaning windows and display screens [11]. The methods available for creating semiconductor thin films vary far more than those available for nanoparticle synthesis. Therefore, the photocatalytic activities of the films are more inconsistent and the task of finding the optimal conditions for photocatalytic oxidation requires more extensive research.

Two general approaches have been used to characterize photocatalytic activity [5]. The first approach measures the rate of the final stage of the overall degradation reaction by monitoring $CO_2$ formation during the reaction. However, monitoring the evolution of $CO_2$ in contaminated media does not specifically provide information on the degradation of the contaminant, as the rate of $CO_2$ formation is significantly affected by intermediates formed during the degradation process. The second characterization approach is concerned with the initial stage of the degradation processes and measures the change in concentration of the reacted organic substrate. For this approach, an organic dye such as rhodamine B is often used to simulate a contaminant because the change in concentration of the dye in solution can be easily detected through spectrophotometry, and calculating the rate of degradation of the dye is relatively straightforward [12, 18] .

# 3 Methodology

Zn-metal thin films were grown on a UV-transparent sapphire substrate using a DC sputter deposition system and subsequently oxidized at annealing temperatures of 300°C, 600°C, and 900°C in a bench top furnace. The structure and morphology of the films was then characterized through atomic force microscopy. The optical properties of the films were also characterized by measuring PL excitation at 1.5-3.5 eV.

Following morphological and optical characterization, the photocatalytic activities of the films were characterized by measuring the degradation of Rhodamine B dye (rhoB) in solution. RhoB was used to simulate an organic environmental contaminant that could be removed by a photocatalytic semiconductor because its concentration in solution can be accurately and straightforwardly measured spectrophotometrically. Oxidized rhoB products do not absorb visible light, so the concentration and the resulting absorbance of the rhoB solutions decrease as the rhoB is oxidized by the ZnO photocatalysts. The overall photocatalytic activities of the materials therefore correlate to the rate of change in the concentration of the rhoB solutions as measured by UV-Vis spectrophotometry.

The UV-Vis spectrophotometer was first calibrated in order to determine the relationship between absorbance measurements and rhoB concentrations. This was accomplished by measuring the absorbance of known concentrations of rhoB and constructing a calibration curve from the resulting measurements (Fig. 2). The concentrations in the rest of the experiment were then calculated from the absorbance measurements using the equation of the calibration curve. Another important result of the calibration curve analysis is the determination of the linear range of the absorbance-concentration relationship. According the calibration for rhoB, this range occurs between 1-8 ppm rhoB, so an initial concentration of 8 ppm rhoB in solution was used for the photodegradation experiments accordingly.

Each ZnO thin film was incubated in an 8 ppm rhoB solution while irradiated with UV light at a constant power density of about 80 μW/cm. The absorbance of the solution was taken after 10, 20, 30, 45, 60, 90, 120, 150 and 180 minutes of UV irradiation at the peak absorbance wavelength (553 nm) for maximum sensitivity, and the corresponding rhoB concentration was calculated using the equation of the rhoB calibration curve. The change in concentration of rhoB in solution over time was plotted in order to compare the photocatalytic activities of the films qualitatively. In order to account for differences in the surface areas of the films in plotting the change in rhoB concentration over time, the total change in concentration of rhoB at each time interval was divided by the specific surface area of the film and plotted against the time of UV irradiation.

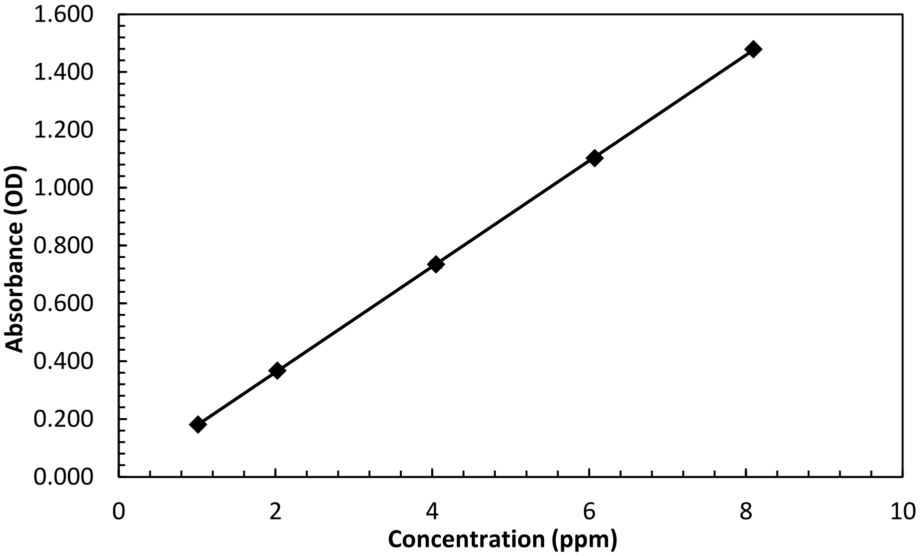

**Figure 2. RhoB calibration curve for 1-8 ppm linear concentration range.**

In order to determine the order of the overall degradation reaction, the data was also plotted according to the integrated rate laws for half- and first-order reactions (the original plot of the change in rhoB concentration over time follows the integrated rate law for the zero-order reaction). According to the half-order rate law, ——— was calculated and plotted against UV irradiation time. Assuming first order kinetics, the log of the ratio divided by the surface area of each film, or — , was also plotted against irradiation time. The equations of the best linear fit for among the different order rate laws was then used to calculate the photocatalytic-rate constant, *k*, which was used to compare the photocatalytic activities of the films quantitatively. While the light intensity is a factor in calculating the rate constant, the same light intensity was used for each experiment and its effect on the rate of each reaction can be negated.

## 4 Results and Discussion

Topographical atomic force microscopy scans of the ZnO thin film surfaces, shown in Figure 3, reveal a significant difference in grain size between the films fabricated at different oxidation temperatures. Specifically, the films oxidized at 300°C are characterized by smaller crystal grains that are more evenly distributed (Fig. 3a) compared to the large and uneven crystals observed in the films oxidized at 600°C (Fig. 3b) and 900°C (data not shown). The films oxidized at 600°C and 900°C exhibit very similar topography when visually compared to each other.

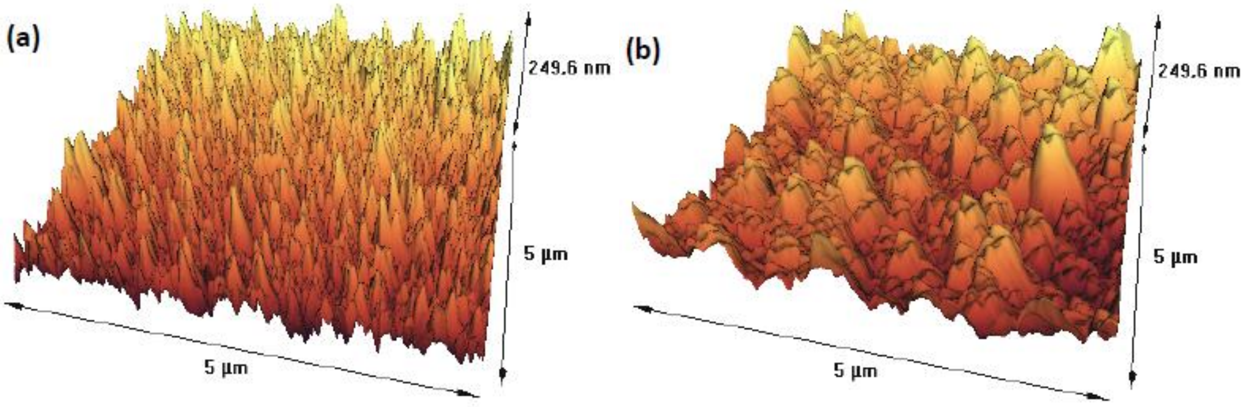

**Figure 3. 3D topographical atomic force microscope scans of the (a) 300°C-oxidized and (b) 600°C-oxidized films.**

The PL spectra of the films fabricated at different oxidation temperatures are superimposed in Figure 4. The peak PL excitonic emission of all films occurs at 3.3 eV, which is in agreement with the expected bandgap energy of ZnO. The excitonic emission of the films at this energy decreases with increasing annealing temperature, with a ~60% reduction in peak height occurring between the 300°C-oxidized and 600°C-oxidized films, and a ~90% reduction in peak height occurring between the 600°C-oxidized and 900°C-oxidized films. The PL results indicate that that increasing oxidation temperature leads to reduced optical quality. Together, these results may suggest that reduced optical quality in Zn films oxidized at higher temperatures is attributed to greater strain between the crystal grains and the incorporation of significant defects.

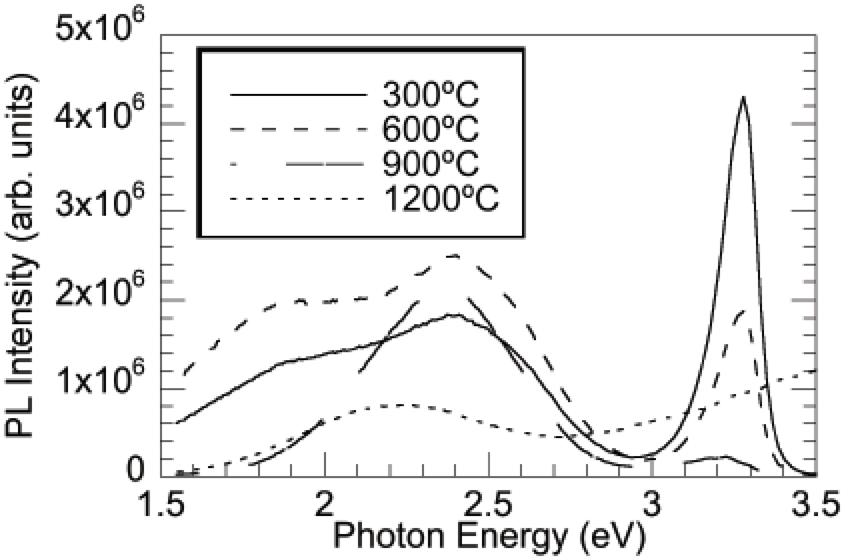

**Figure 4. Representative PL spectra of the films fabricated at various oxidation temperatures.**

The photocatalytic efficiency of the 300°C-oxidized film was also higher compared to those of the 600°C-oxidized and 900°C-oxidized films (Fig. 5), further supporting the trend observed in the PL-determined optical quality of the various films. Since PL excitation is directly correlated to electron-hole pair formation on the semiconductor surface, the films with higher optical quality have higher rates of electron-hole pair formation. Furthermore, the oxidation and reduction reactions that lead to the degradation of rhoB and other organic compounds by the semiconductor photocatalysts are dependent on the availability of electrons and holes on the surface of the semiconductor, so the optical quality of the films is the most important factor in the photocatalyzed degradation by the semiconductor. The effective surface area on the nano-scale may also affect the photocatalytic activities of the films, though the precise extent of its significance is difficult to determine [18]. However, because the 300°C-oxidized films have smaller grain sizes, their surface area is effectively larger than the films oxidized at higher temperatures, resulting in higher rates of contact with molecules in solution and ultimately leading to higher reaction rates.

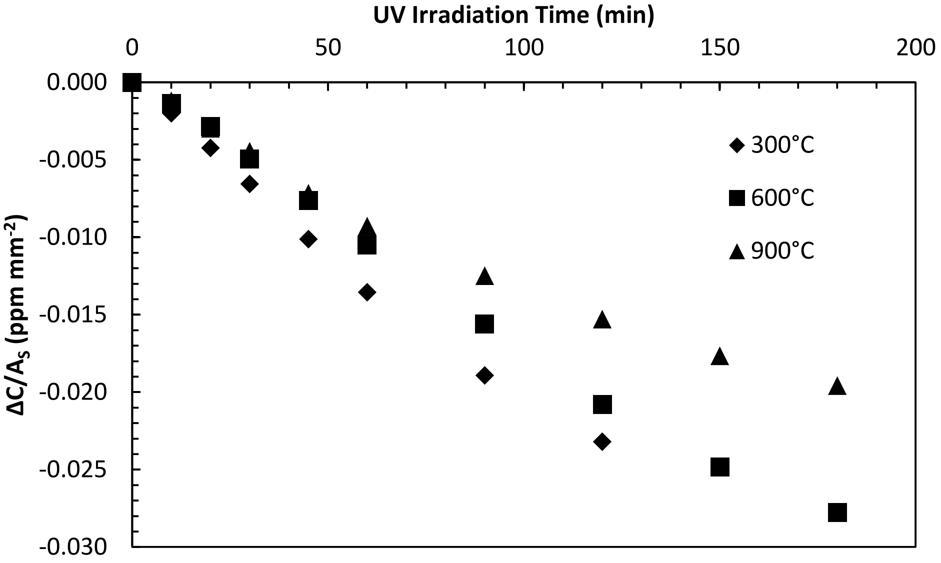

**Figure 5. Change in rhoB concentration in solution over UV irradiation time with films fabricated at different oxidation temperatures.** *Change in concentration is normalized for the surface area of each film.

The half-order rate law proved to be the a better approximation to the overall reaction than the more commonly applied first-order rate law, indicated by the higher coefficient of determination ( ) values for the linear fits to the integrated half-order plots (Fig. 6). The orders of the individual reactions that ultimately lead to the degradation of organic compounds such as rhoB by semiconductor photocatalysts vary between zero and one depending on the reaction. When these reactions are coupled, the order of the overall reaction is somewhere between zero and one, and so the best approximation is most likely to be the half-order rate law.

However, the order of the overall reaction is determined by which reaction types predominate at any given moment, which itself is dependent on a multitude of factors. One factor that determines the predominant reaction that is taking place at any given moment is the concentration of the various molecules involved in the degradation reactions, which is varies significantly over time. The order of the overall reaction can thus change over the course of the photocatalysis experiment due to decreasing concentration of rhoB or increasing concentrations of free radicals and peroxides in solution. The change in overall reaction order is apparent in the semi-log plot representing the first-order rate law, which is linear during the initial ~60 minutes of irradiation time (Fig. 7), and significantly non-linear thereafter.

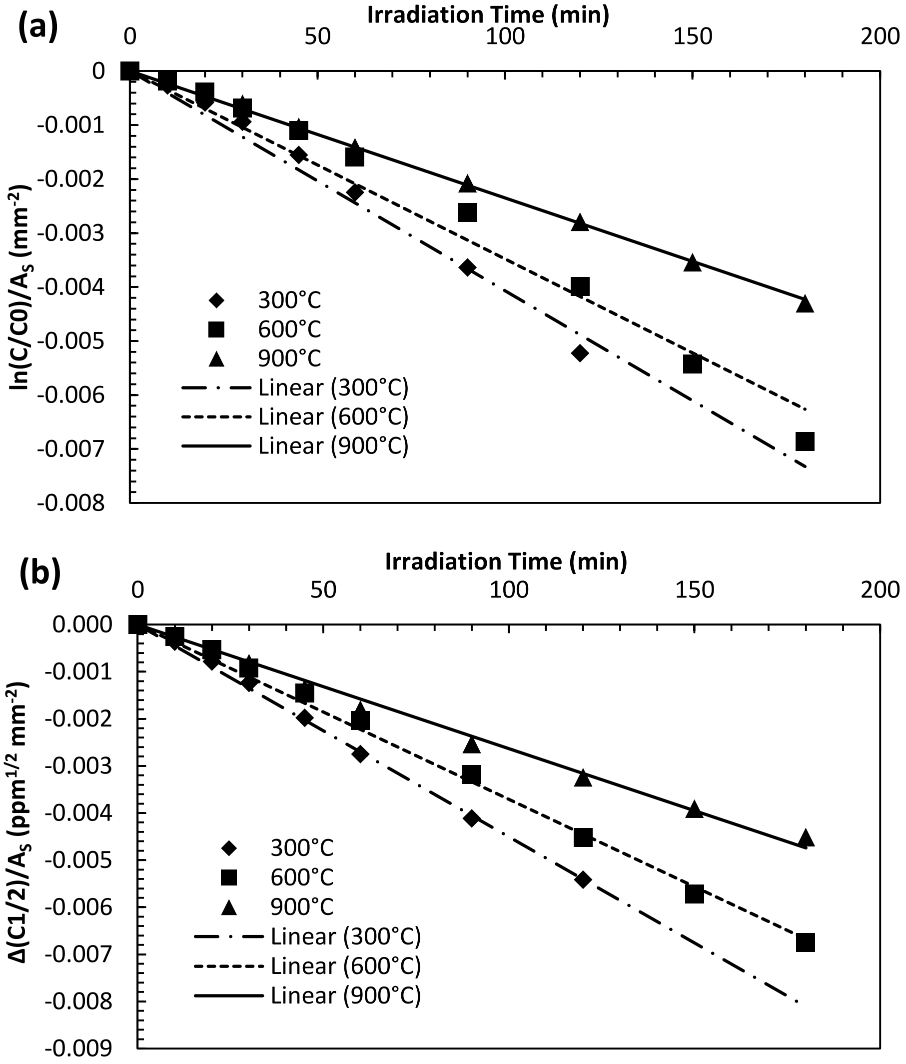

**Figure 6. Change in rhoB concentration in solution over UV irradiation time with films fabricated at different oxidation temperatures, plotted according to the integrated rate laws for (a) first-order and (b) half-order reactions.** *Change in concentration is normalized for the surface area of each film.

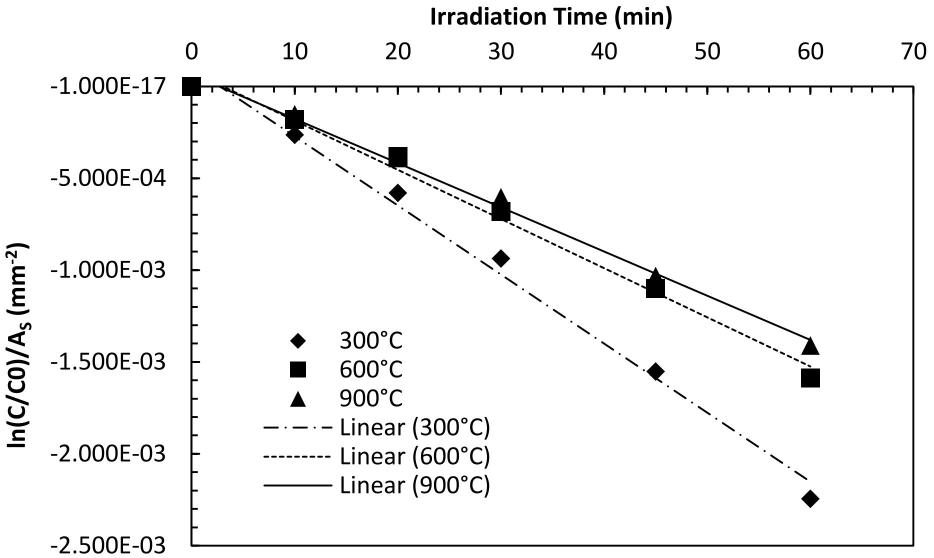

**Figure 7. Change in rhoB concentration in solution over first 60 minutes of UV irradiation time with films fabricated at different oxidation temperatures, plotted according to the integrated rate laws for first-order reactions.** *Change in concentration is normalized for the surface area of each film.

For reasons of simplicity and uniformity between studies, the first order rate law has commonly been applied to quantify the photocatalytic activities of the semiconductor photocatalysts. However, because the half-order rate law seems to be a better and more logical approximation, the photocatalytic activities were calculated in this study using half-order formulas. The photocatalytic activities of the films, reported in Table 1, show that the activity of the 600°C-oxidized films was reduced by ~20% compared to the 300°C-oxidized films, and that of the 900°C-oxidized films by ~30% compared to the 600°C-oxidized films. Interestingly, this is the same proportion in reduction as the reduction in peak PL excitation, providing concrete support for the strong correlation between photocatalytic activity, optical quality, and physical morphology of the films, which are all dependent on the oxidation temperature used during fabrication.

| Film oxidation temperature (°C) | Photocatalytic activity ( ) |
|---|---|
| 300 | |
| 600 | |
| 900 | |

**Table 1. Photocatalytic activities of films oxidized at various temperatures**

# 5 Conclusion

The experiments carried out in this study represent logical advances in semiconductor photocatalyst characterization from what has previously been investigated and reported in the literature. For one, the ZnO thin films used in these experiments were prepared by a method for which the effects on photocatalytic activity have not yet been analyzed. Furthermore, the analysis of the effect of the annealing temperature used in the thin film preparation presented here has not previously been investigated. This progression of analysis reveals a strong correlation between the fabrication conditions, resulting morphologies and optical properties, and corresponding photocatalytic activities of the ZnO thin films.

# 6 References

[1] Ives MB, Luo JL, Rodda JR (2001) Passivity of Metals and Semiconductors, The Electrochemical Society Inc.

[2] Fujishima A, Honda K (1972) Electrochemical photolysis of water at a semiconductor electrode. *Nature* 238:37–38.

[3] Fujishima A, Kobayakawa K, Honda K (1975) Hydrogen production under sunlight with an electrochemical photocell. *J. Electrochem. Soc.* 122:1487–1489.

[4] Fujishima A, Rao TN, Tryk DA (2000) Titanium dioxide photocatalysis. *Journal of Photochemistry and Photobiology C: Photochemistry Reviews 1* 1-21.

[5] Carp O, Huisman CL, Reller A (2004) Photoinduced reactivity of titanium dioxide. *Progress in Solid State Chemistry* 32:33-177.

[6] Fujishima A, Zhang X (2006) Titanium dioxide photocatalysis: present situation and future approaches. *C. R. Chimie* 9:750-760.

[7] Anpo M (2000) Utilization of TiO2 photocatalysts in green chemistry. *Pure and Applied Chemistry* 72:1265-1270

[8] Oppenlander T (2003) Photochemical Purification of Water and Air. Wiley-VCH, Weinheim.

[9] Juan KD (1984) The fundamental and practice for the removal of phenolic compounds in wastewater. *Industrial Pollut. Prevention Control* 3:88

[10] Banerjee S, Gopal J, Muraleedharan P, Tyagi AK, Raj B (2006) Physics and chemistry of photocatalytic titanium dioxide: Visualization of bactericidal activity using atomic force microscopy. *Current Science* 90:1378-1383.

[11] Watanabe T, Nakajima A, Wang R, Minabe M, Koizumi S, Fujishima A, Hashimoto K (1999) Photocatalytic activity and photoinduced hydrophilicity of titanium dioxide coated glass. *Thin Solid Films* 351:260-263.

[12] Gustavsson AK, Schuler E (2010) Solar photocatalytic degradation of rhodamine B by $TiO_2$ nanoparticle composites [Master's Thesis].

[13] Sakthivel S, Kisch H (2003) Daylight photocatalysis by carbon-modified titanium dioxide. *Angew. Chem. Int. Ed.* 42:4908-4911.

[14] Nishio J, Tokumura M, Znad HT, Kawase Y (2006) Photocatalytic decolorization of azo-dye with zinc oxide powder in an external UV light irradiation slurry photoreactor. *J. Hazardous Materials* B138:106-115.

[15] Qamar M, Muneer M (2009) A comparative photocatalytic activity of titanium dioxide and zinc oxide by investigating the degradation of vanillin. *Desalination* 249:535–540.

[16] Anandana S, Ohashib N, Miyauchia M (2010) ZnO-based visible-light photocatalyst: Band-gap engineering and multi-electron reduction by co-catalyst. *Applied Catalysis B: Environmental* 100:502-509.

[17] S. Chakrabarti, B.K. Dutta, Photocatalytic degradation of model textiledyes in wastewater using ZnO as semiconductor catalyst, J. Hazard. Mater.B112 (2004) 269–278.

[18] Xioahong W, Zhaohua J, Huiling L, Shigang X, Xinhuo H. Photo-catalytic activity of titanium dioxide thin films prepared by micro-plasma oxidation method. *Thin Solid Films* 441:130-134.