Optical Analysis of Titania: Band Gaps of Brookite, Rutile and Anatase

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A thesis presented in the partial fulfillment of the requirements for the degree of

Bachelors of Physics

Department of Physics
Oregon State University
May 5, 2018
Contents

1 Introduction .................................................. 2

2 Optical Phenomena of Thin Films ......................... 3
   2.1 The Index of Refraction ........................................ 3
   2.2 Absorption ...................................................... 4
   2.3 The Band Gap .................................................. 5

3 Methods ....................................................... 6
   3.1 The Grating Spectrometer ...................................... 6
   3.2 SCOUT for Optical Modeling .................................. 9

4 Results and Discussion ..................................... 12
   4.1 Band Gap Dependence on Thickness ......................... 14

5 Conclusion .................................................. 15

6 Appendix .................................................... 16
   6.1 Grating spectrometer settings .................................. 16
   6.2 Filtering 2nd Order Light ..................................... 16
   6.3 Band gap of the substrate ..................................... 17

7 Using SCOUT ................................................ 17
   7.1 User configurations ............................................ 17
   7.2 The Layer Stack ............................................... 18
   7.3 Materials ...................................................... 18

8 Acknowledgments ............................................ 18
List of Figures

1 Indirect and direct band gaps ................................................. 5
2 The grating spectrometer. ....................................................... 7
3 TiO$_2$ Raw Film Spectra .................................................. 7
4 Transmission, reflection, and corrected transmission spectra. ........ 8
5 High-energy region of raw spectra ........................................... 9
6 Screenshot of the SCOUT interface ......................................... 10
7 Refractive index model constructed in SCOUT. .......................... 11
8 Density of states in the OJL band gap model. ............................. 11
9 High-fraction brookite film on SiO$_2$ ....................................... 12
10 High-fraction anatase film on SiO$_2$ ....................................... 13
11 High-fraction rutile film on SiO$_2$ ......................................... 13
12 Gap energy vs. Thickness for many polyphase TiO$_2$ films. The phase plots (Rutile, Brookite, Anatase) show how much of each phase is present in each film. .......................................................... 14
13 Measurements taken on film 056-1. There is an inverse relationship between the gap energy and film thickness—an artifact of the analysis. ................. 15
14 SnCaSe measurement. $T$, $R$, and $T/(1-R)$ with and without a color filter. . 17
List of Tables

1 Literature on the band gaps of rutile, anatase, and brookite. . . . . . . . . 2
2 Band gaps and thicknesses of high-fraction films of anatase, rutile and brookite. 12
3 Grating Spectrometer Settings . . . . . . . . . . . . . . . . . . . . . . . . . 16
Abstract

The optical transition in high-fraction polymorphs of titania (TiO$_2$) were investigated to determine the band gap behavior of the most common polymorphs—brookite, rutile, and anatase—the values of which are varied in the literature. The direct optical band gaps of brookite, rutile, and anatase, were determined to be 3.37(7)eV, 3.41(11)eV and 3.59(2)eV respectively.

TiO$_2$ was grown in-house via pulsed-laser deposition onto fused silica. The reflection and transmission spectra of high-phase fraction brookite, rutile and anatase, were measured with a grating spectrometer. Optical analysis software, SCOUT, was implemented with dielectric function models to perform a parameter fitting on transmission and reflection spectra, produced by the optical models, to the experimental data. From the parameter fitting, the optical absorption and index of refraction were extracted. The index of refraction was approximately 2.5 at 500 nm. A relationship in the high-phase brookite film showed a relationship between the thickness and band gap. Initially this appears to be a quantum well effect. However, the relationship is in face determined to be a consequence of our calculations favoring band gap fitting at low thicknesses—leading to an artificial trend.


1 Introduction

TiO$_2$ is used abundantly in industry for paint pigmentation, as a photocatalyst, in dye-synthesized solar cells, as a UV-protectant and more [1][2][3][4]. TiO$_2$ is a wide band gap semiconductor, with three common polymorphs; rutile, anatase and brookite. The ground state, rutile, is easy to make and the most common found in industry, while brookite is the least. As a result, rutile has been studied extensively, and its band gap energy is the most well-known band gap of 3.0 eV. The band gaps of brookite and anatase are not known to the same degree of precision as rutile—anatase has been reported to have a band gap of about 3.2 eV, and brookite has been reported to have a band gap anywhere between 3 eV to 3.6 eV. There is a lack of consistency in the literature values of the band gaps of TiO$_2$’s polymorphs as shown in Table 1. TiO$_2$ is usually assumed to be a direct band gap semiconductor, so many labs measure for the direct band gap (labeled D). Often the indirect gap is measured as well (labeled I).

<table>
<thead>
<tr>
<th>Ref/Year</th>
<th>Rutile (eV)</th>
<th>Anatase (eV)</th>
<th>Brookite (eV)</th>
<th>TiO$_2$ (B) (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>[3],2008</td>
<td>3.01(I)-3.37(D)</td>
<td>3.20(I)-3.53(D)</td>
<td>3.13(ID)-3.56(D)</td>
<td></td>
</tr>
<tr>
<td>[4],2018</td>
<td>3.45 (D)</td>
<td>3.2</td>
<td>3.45 (D)</td>
<td>3.0-3.2</td>
</tr>
<tr>
<td>[5],2014</td>
<td>3.2</td>
<td>3.2 (I)</td>
<td>3.03,3.05,3.13 (I)</td>
<td></td>
</tr>
<tr>
<td>[6],2012</td>
<td>3.0 (I)</td>
<td>3.2 (D)</td>
<td>3.2 (D)</td>
<td>3.29 (D)</td>
</tr>
<tr>
<td>[7],2014</td>
<td>3.03</td>
<td>3.03</td>
<td>3.20</td>
<td></td>
</tr>
<tr>
<td>[8],2013</td>
<td>3.20</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Table 1: Literature on the band gaps of rutile, anatase, and brookite.

The goal of this thesis is to provide measurements for the band gap of high-fraction brookite, anatase, and rutile films. TiO$_2$ films of high-phase brookite, rutile, and anatase were grown and characterized. The films are deposited in a an amorphous phase using pulse-laser deposition, then annealed at 400$^\circ$ C. Most of our films are annealed into some combination of the three polymorphs. It is not understood yet how to make TiO$_2$ consistently choose the brookite phase, although ways to make pure-phase TiO$_2$ nanoparticles from amorphous TiO$_2$ and other techniques for growing high-fraction brookite films are in development [3][4]. We have produced several films of high-phase brookite, anatase and rutile in thin film form, and transmission and reflection spectra are measured using a grating spectrometer. The direct band gap of the high-phase films were then calculated using an optical analysis software.

The band gaps of brookite, anatase, and rutile films are characterized using optical spectrometry. Transmission and reflection data are taken between λ = 200 → 2000 nm via grating spectrometer. Rudimentary calculations are performed using the Sellmeier equation to model the refractive index and standardized thin film analysis. A method developed for calculating the band gap developed by linearization of the absorption curve, colloquially called Tauc analysis, is used to measure the band gap [10]. Tauc analysis provides us with a way to measure the spectra for a direct or indirect band gap by linearizing the absorption curve two different ways.
Another way we measure the band gap is by using an optical analysis software called SCOUT. SCOUT provides a model constructed by [12] for incorporating direct band gap transitions in the dielectric function models of our film. The direct gap model in SCOUT is used to efficiently measure the spectra of many TiO$_2$ films. SCOUT calculates the theoretical transmission and reflection spectra from modeling a film with a dielectric function model on a substrate of our choice, then fits the theoretical spectra to the experimental data by adjusting parameters in the dielectric function model. This is a powerful method for film characterization, and is capable of distinguishing the band gaps of rutile, brookite and anatase.

2 Optical Phenomena of Thin Films

Our lab grows TiO$_2$ phases in thin film form. To determine the optical properties, the transmission and reflection spectra are measured using a grating spectrometer. The spectra are then analyzed for absorption, refractive index and thickness. The films contain two major features that help in the determination of the thickness and band gap: interference fringes and strong absorption at the band gap. The interference fringes are a product of the interference of internal reflections happening inside the film. The periodicity and size of the fringes in the transmission and reflection spectra let us determine the thickness $d$ of the film. Once the thickness is known, the absorption can be determined by removing the fringes from the transmission spectra, then applying Beer’s law and solving for the absorption $\alpha(\lambda)$.

2.1 The Index of Refraction

The index of refraction $\tilde{n}(\lambda)$ of a material contains all the optical quantities we might want to study. In the spectral region accessible by our grating spectrometer, the real part of the index of refraction is approximated by the Sellmeier equation (equation 1).

$$n^2(\lambda) = 1 + \sum_{i=1}^{N} \frac{A_i \lambda}{\lambda_i^2 - \lambda^2}$$  \hspace{1cm} (1)

The Sellmeier equation is expanded to the first order for approximating the index of refraction of an unknown material. To compute the index of refraction of a thin film on a substrate, the transmission and reflection coefficients are computed from the Sellmeier equation and a preliminary guess for film thickness. The absorption is calculated from the corrected transmission, then related to the extinction coefficient $\kappa$ by $\alpha = 4\pi\kappa/\lambda$. Theoretical transmission and reflection coefficients are computed from the index of refraction of substrate and film by the definitions of transmittance and reflectance. In practice, the angle of incidence is $\theta_i = 5.5^\circ$. This is a sufficiently small angle to assume $\cos \theta_i \approx \cos \theta_t \approx 1$. The transmission and reflection coefficients

$$R = \frac{I_r}{I_0} = \left| \frac{\tilde{n}_{film} - \tilde{n}_{substrate}}{\tilde{n}_{film} + \tilde{n}_{substrate}} \right|^2$$  \hspace{1cm} (2)

$$T = \frac{I_t \cos \theta_t}{I_0 \cos \theta_i} = \left| \frac{\tilde{n}_{film}}{\tilde{n}_{film} + \tilde{n}_{substrate}} \right|^2$$  \hspace{1cm} (3)
Where the index of refraction is the complex function:

\[ \tilde{n}(\lambda) = n_r + i\kappa \]  

(4)

In practice, an optimization algorithm changes parameters \( A_i \) and \( \lambda_0i \) in the Sellmeier equation as well as thickness \( d \) to minimize the difference between theoretical transmittance and reflectance to the experimental data. The model fits the data in the low absorption region, where only fringes are present. Completion of the fit yields the real part of the index of refraction \( n_r \) and the thickness \( d \). Once the absorption is determined, the wave vector \( \kappa \) is simulated from the absorption by the relationship:

\[ \kappa = \frac{\alpha\lambda}{4\pi} \]  

(5)

Which completes the dielectric function \( \tilde{n}(\lambda) \) for our material.

### 2.2 Absorption

Calculation of the band gap starts by measuring the absorption of a film. We first assume the normalized intensity of reflection \( R \), transmission \( T \) and absorption \( A \) add up to 1.

\[ T + R + A = 1 \]  

(6)

This is an assumption that works well for determining the absorption from bulk materials, but the transmission and reflection data in films contain interference “fringes” that don’t permit us to treat the absorption this way. We define the ‘corrected transmission’, \( T_c \), to be the transmitted intensity of light when there are no interference fringes. It is shown by McIntyre [13] that by dividing the transmission by 1 minus the reflection, removes the fringes from the spectra (for low absorption regions).

\[ T_c = \frac{T}{1 - R} \]  

(7)

The corrected transmission will correctly remove the fringes from the film. The absorption is defined by the change in intensity per unit length. For an absorption \( \alpha(\lambda) \) and film thickness \( d \), the transmitted intensity for a film with no interference effects would be \( I_t(\lambda) \) in accordance with Beer’s Law.

\[ I_t = I_0 e^{-\alpha d} \]  

(8)

We can treat the corrected transmission as the transmission of light through our film with the interference fringes removed (as it if were a bulk sample). The corrected transmission is then the ratio between the throughput intensity and the incident intensity.

\[ \frac{I_t}{I_0} = \frac{T}{1 - R} = e^{-\alpha d} \]  

(9)

If the sample thickness is known (from analysis of the fringes), then absorption \( \alpha \) can be solved for by
\[ \alpha = \ln \left( \frac{1 - R}{T} \right) \]  

The absorption \( \alpha(\lambda) \) contains all the relevant information for analyzing the band gap. Computing the band gap can be done by linearizing the absorption and checking for the onset of strong absorption (Tauc method) or by fitting a parameter model to the relevant spectra.

### 2.3 The Band Gap

The band gap is indicated by the region of strong absorption. One way to calculate the band gap is using a method of analysis proposed by Tauc, Grigorovici, Vancu [10] which involves linearizing the absorption—this is called the Tauc method. In the Tauc method, the density of states is assumed to be parabolic, so that it can be linearized by a square-root function. When the conduction band is directly above the valence band, the transition is called a direct gap. If the conduction band is offset in momentum space with respect to the valence band, the transition is called an indirect gap. Both gap types are shown in Figure 1. The absorption is linearized by the function \((\alpha E)^n\), where \(n = 2\) for direct gap materials and \(n = 1/2\) for indirect gap materials. The absorption \(\alpha\) is multiplied by the energy \(E\) to make the quantity dimensionless.

![Figure 1: Indirect and direct band gaps](image)

Each polymorph of TiO\(_2\) that we find in our films has a different band gap, and each band structure has indirect and direct transitions. Since all three phases show up in most of our films—optical data is taken on regions where all three phases are present and multiple kinds of transitions are taking place in each spectrum. We attempt to calculate the band gap by assuming that the film has only a direct transition and only an indirect transition—which means that both Tauc linearizations of absorption are used in band gap calculations. The idealized representations of the density of states used in the Tauc method loosely match real absorption in experiment. Due to the complexity of features such as tail states, we use optical modeling software for computations. The optical models in SCOUT can fit the experimental data by changing the parameters of a direct gap model and the index of refraction. Performing measurements this way let the model adjust the dispersion relation and the band gap simultaneously to obtain the best possible fit.
3 Methods

The thin films are measured optically by analyzing the transmission and reflection spectra of the film in ultra-violet (\(\lambda = 250\) nm) visible and near infrared regions (\(\lambda = 2000\) nm). The transmission and reflection spectra contain interference fringes, which are analyzed to measure the thickness of the film and dispersion relation of the material. The absorption and band gap of the film are analyzed by computing the corrected transmission spectra, which contains information about the absorption of the film. The spectra are measured using a grating spectrometer, then analyzed with optical modeling software.

3.1 The Grating Spectrometer

The grating spectrometer (Figure 2) is used to measure the transmission and reflection spectra of our samples. With all the available settings (listed in the appendix), the grating spectrometer has a range of \(\lambda = 175\) nm to \(\lambda = 1998\) nm. This is made possible by two lamps, four gratings, six color filters, and two detectors for measuring various ranges of wavelengths. Table 2 in the appendix contains the working ranges of each component. It is important that the temperature of the lamp (Xe or W) does not change throughout the measurement, so lamps are given sufficient time to reach a steady state temperature and intensity. The calculated reflection and transmission data contain artificial noise if a steady intensity has not been achieved. An ozone eater is secured to the lamp to remove the ozone, protecting the experimentalist from exposure. The lamp light enters a double monochromator fitted with the correct diffraction gratings to isolate a particular wavelength. The gratings are optimized to strongly reflect particular wavelengths. The 0.25 micron grating is optimized to select 250 nm, the 0.50 micron to select 500 nm light etc. The ‘single wavelength’ light leaves the monochromator, is collimated then focused into the detector. When measuring a typical spectrum, the power is measured at a single wavelength, then the monochromator scrolls to the next wavelength. This is done in increments of 1 nm until the whole spectrum is measured.

The raw lamp spectrum is measured first. The raw lamp spectrum is the transmitted intensity directly from the monochromators, with no film in place. The background spectrum is measured by the detector when the beam is blocked. Next the sample is placed in the beam’s path to measure the reflection and transmission intensities. The sample is placed at an angle so that when the reflection intensity is measured, the detector is not placed in the optical path. The angle of incidence is kept very small \(\theta_i < 6^\circ\) so that we can use the small angle approximation \(\sin \theta \approx \theta\) for computing the transmission and reflection. The raw transmission is collected by passing the beam through the sample, and the raw reflection is collected from the reflected light. Figure 3 shows the set of raw data collected from a TiO\(_2\) sample with a Xe lamp source. Notice that the largest spectra is the lamp spectra (blue), which contains the total intensity at each wavelength. The raw transmission and reflection spectra (grey and yellow respectively) are lower. On this scale, the dark spectrum (orange) appears to be zero.

The spectra gathered from measuring the reflected and transmitted beam intensities are raw spectra. The actual reflection and transmission spectra are computed by subtracting the background (dark) spectrum then dividing by the lamp spectrum. The resulting spectra are
Figure 2: The grating spectrometer.

Figure 3: TiO$_2$ Raw Film Spectra
heretofore referred to as transmission and reflection, and they will be used in the analysis.

Once the raw data are collected, the transmission ($T$) and reflection ($R$) spectra are calculated by first subtracting the dark spectrum, then dividing by the lamp reference spectrum. This will yield the actual percent intensity (between 0 and 1) of reflection and transmission for all wavelengths measured. The reflection and transmission are calculated by:

$$R = \frac{I_r - I_{dark}}{I_{lamp} - I_{dark}}$$  \hspace{1cm} (11)

$$T = \frac{I_t - I_{dark}}{I_{lamp} - I_{dark}}$$  \hspace{1cm} (12)

The spectra shown in figure 4 are the reflection and transmission spectra calculated from the raw data. The gray curve is the corrected transmission $T/(1 - R)$. The corrected transmission is the transmission of the sample with the fringes removed. This is useful for calculating the band gap using Tauc analysis, for which you need the corrected transmission (equation 9).

Figure 4: Transmission, reflection, and corrected transmission spectra.

The data for TiO$_2$ film 072-4 was taken in the 250 to 999 nm range. The transmission and reflection curves (blue and orange) contain fringes in the region of low absorption (above $\lambda = 350$ nm). We can see in the transmission and corrected transmission the data drops to zero around $\lambda = 350$ nm. The band gap is seen where the absorption begins to set in around 360 nm.
Figure 5 shows the intensities of the raw data in the high-energy region. The background intensity (Raw Dark) is about $10^{-12}$ W through the whole range. Raw data collected with an intensity less than $10^{-11}$ W are unlikely to yield physical information because the intensity is comparable to the background level. Spectra taken in the ultraviolet region of our lamp in Figure 5 show the absolute minimum of resolvable intensity starts around 175 nm or 7 eV. At this energy, the effect of the lamp warming causes the reflection spectra to be larger than the intensity of the lamp—which is a nonphysical result. This is cured by letting the lamp warm up for a longer time. The optimal time to take data is at least an hour after the lamp has been turned on.

### 3.2 SCOUT for Optical Modeling

An optical modeling software called SCOUT is used to calculate the index of refraction, thickness and the band gap. SCOUT computes the transmission and reflection spectra from a user-defined layer stack (Figure 6). The layer stack for measurements has a thin film on a substrate. Each layer is given properties based on the material that constitutes it. The material which is being studied is given a model for the index of refraction—in this case the Sellmeier model. The model usually contains information about dispersion and absorption, features which are captured in the Sellmeier equation OJL interband transition model (discussed later).

Figure 6 shows a screenshot of the SCOUT interface just after a fit has been performed on a TiO$_2$ film on a 1 mm glass SiO$_2$ substrate. Theoretical (blue) and experimental (red)
transmission and reflection spectra are on the right—a preliminary glance tells us this is a good fit. The center displays the current layer stack: TiO$_2$ on SiO$_2$, and the left side displays the sample name, measured thickness, fit deviation, fit rating, and values of all the fit parameters used in the measurement. The fit rating says this measurement is “Acceptable”, but the user must judge for themselves whether or not the fit parameters are physically reliable. For TiO$_2$, we expect our band gap to be between 3.1 eV and 3.7 eV (25,000 cm$^{-1}$ and 30,000 cm$^{-1}$).

Figure 6: Screenshot of the SCOUT interface

To measure a thin film on glass, a substrate and thin film are defined in the layer stack, with air in the half spaces on either side. The user defines the substrate (usually amorphous glass), and the layer is given the properties of that material which are defined in the SCOUT database or added by the user. The layer has some unknown thickness, index of refraction, and absorption. These properties are given models with unknown parameters. The Sellmeier equation is used to model the index of refraction, and the absorption is modeled by the OJL band gap model. From the model for index of refraction, transmission and reflection spectra are produced and compared to experimental data. The experimentalist gives SCOUT the power to manipulate the model parameters (Sellmeier coefficients, band gap strength etc.). In a optimization routine, SCOUT will change the model parameters to produce reflection and transmission spectra that match up to experiment. For our measurements, SCOUT is given the Sellmeier coefficients and parameters to the OJL band gap model. A typical model of index of refraction is shown in Figure 7. The black and red lines are the real and complex parts of the index of refraction respectively.

SCOUT can handle any number of layers, as well as the coherence of each layer. The plane wave will retain its phase in layers that are coherent, and lose its phase in layers that are incoherent. If the film is thin with respect to the coherence length of the light, then the layer should be made coherent so that the light retains its phase through that layer. This is a useful feature in SCOUT because only thin layers are coherent. The thin film layers are
generally about 50-300 nm thick, while the substrates are generally 1 mm thick. As a result, the plane wave will retain its phase through the film and not the substrate.

The O'Leary, Johnson, Lim (OJL) interband transition model (Figure 8), simulates direct band gap absorption with tail states. The model has four parameters: gap energy, strength, gamma, and decay. The gap energy expresses the width of the band gap, the gap strength determines how sharp the gap onset is, the gamma parameter expresses the sub-gap absorption which could come from tail states or general disorder, and the decay expresses how much the absorption decays after the gap in the high-frequency range.

The OJL model is similar to the Tauc model in that it assumes a parabolic density of states—but it also contains a decaying exponential in the gap region. This is useful for modeling tail states and line broadening in experimental data. OJL is used in tandem with the Sellmeier equation to produce the complete index of refraction model used in the measurement. The parameters of the OJL model and coefficients in the Sellmeier equation become the “fit parameters” SCOUT uses to perform measurements.
4 Results and Discussion

Each TiO$_2$ polymorph of interest (Brookite, Anatase and Rutile) has been created in a high-phase fraction thin film form. Several regions of interest on each film were measured and calculated for thickness, absorption and band gap behavior. The amorphous precursors were created under specific conditions using pulse-laser deposition, then annealed at 400° C to crystallization. The films were then measured using the grating spectrometer in the UV-Vis region and calculations were performed in SCOUT.

<table>
<thead>
<tr>
<th>Film No.</th>
<th>Phase Composition</th>
<th>No.</th>
<th>Thickness (nm)</th>
<th>$E_{\text{gap}}$ (eV, D)</th>
</tr>
</thead>
<tbody>
<tr>
<td>079</td>
<td>Anatase (100%)</td>
<td>2</td>
<td>75.1</td>
<td>3.58</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>70.2</td>
<td>3.61</td>
</tr>
<tr>
<td>080</td>
<td>Rutile (100%)</td>
<td>2</td>
<td>52.0</td>
<td>3.33</td>
</tr>
<tr>
<td></td>
<td></td>
<td>5</td>
<td>31.8</td>
<td>3.49</td>
</tr>
<tr>
<td>056</td>
<td>Brookite (88%)</td>
<td>(multiple)</td>
<td>55(6)</td>
<td>3.37(7)</td>
</tr>
</tbody>
</table>

Table 2: Band gaps and thicknesses of high-fraction films of anatase, rutile and brookite.

Table 2 lists the band gaps of anatase, rutile and brookite. The band gaps of anatase and brookite are close to those found in literature: anatase has a band gap of about 3.6 eV, and brookite a band gap of 3.4 eV, which is confirmed by Alotaibi. Rutile was measured to have a larger band gap (3.3 – 3.5 eV) than is usually found in the literature. One spectrum (reflection, transmission and corrected transmission) are plotted against wavelength for one measurement on each film shown in the table in Figures 9, 10, and 11.

Figure 9: High-fraction brookite film on SiO$_2$

All three high-fraction films exhibit features common of TiO$_2$ spectra. In the visual and near infrared regions we see fringe behavior onset in the reflection and transmission spectra.
These are removed in the corrected transmission—as it is approximately equal to unity in the visual to near infrared regions for all films. In the ultraviolet region, photons have enough energy to excite the electrons across the band gap—which causes strong absorption, at which point the transmission goes to zero. The strong absorption also causes the reflectivity increase to about 0.35 in each film.

Figure 12 contains four plots with data from TiO$_2$ polyphase films. The top left plot shows the distribution of all the measurements taken. In the “All Films” figure, an ‘x’ indicates one measurement. All four plots contain the same films, but the size of the markers
Figure 12: Gap energy vs. Thickness for many polyphase TiO$_2$ films. The phase plots (Rutile, Brookite, Anatase) show how much of each phase is present in each film.

in the Rutile, Anatase and Brookite plots indicate the respective amount of Rutile, Anatase and Brookite in each film. There is no obvious trend in the anatase phase, but the brookite tends to favor thicknesses below 80nm, and rutile favors higher thicknesses—although trace amounts are present in many films. This is consistent with an observation in the literature which points out that the brookite favors this same thickness region [1].

4.1 Band Gap Dependence on Thickness

The data in Figure 12 shows a subtle relationship between the film thickness and the size of the band gap. In the high-fraction brookite films and anatase films, it appears as though the band gap is getting larger as the film thickness decreases. Figure 13 contains the 23 measurements taken on film 056. If we look at the measurements performed on this film, which is primarily brookite, there is a linear relationship between the band gap and film thickness. I will argue that this feature is an artifact caused by how our films are measured.

The feature that most significantly affects the measurement in the UV region is the band gap—where the transmission undergoes strong absorption. The visible region of the spectra is mostly affected by the thickness $d$—which contributes to the number and frequency of fringes. For any given film, SCOUT will try to fit the fringe region as well as the band gap region. SCOUT will often have to sacrifice precision in the UV region (where the gap is) for precision in the visible region (which is dominated by fringes). This is standard because our models
do not match the behavior of TiO$_2$ perfectly.

When the film becomes very thin, the number of fringes in the region of measurement decreases to nearly zero. When this is the case, SCOUT will sacrifice additional precision in the thickness of the film, in order to make the UV region (and therefore band gap) fit better. Changing the thickness of a very thin film does not significantly affect the fit in the visible range but changing the band gap significantly affects the fit in the ultraviolet range. Consequently, for very thin films, the band gap is measured with increasing flexibility—which causes an artificial relationship between the band gap and thickness to emerge. In figure 12, there is no relationship between band gap and thickness in the rutile or anatase phases, and the relationship across multiple brookite films is less certain.

5 Conclusion

Our lab produced high phase fraction rutile, brookite and anatase from amorphous precursors. The transmission and reflection spectra were measured using a grating spectrometer. The data were then characterized in SCOUT, which used models for the index of refraction and band gap to produce theoretical data then perform a minimization routine to change the model parameters to fit the theoretical to the experimental spectra. The spectra of our high phase fraction films were measured and the optical parameters were calculated in SCOUT, yielding the values in table 2. A trend emerged in our analysis of the high phase fraction brookite film, but it was argued that the relationship is an artifact of the analysis. In future work, we will determine a more accurate model for TiO$_2$, and compare the calculations of the band gap for various optical models that were not used in our analysis.
6 Appendix

6.1 Grating spectrometer settings

Table 3 lists the grating spectrometer settings available and the wavelengths they can be safely be used at to obtain correct data. In a typical measurement of a TiO$_2$ film, the grating spectrometer is set to measure from 250 nm to 1000 nm in 1 nm increments with the 0.25 micron grating, Xe lamp, silicon detector, and no filter. This allows the user to take data of a large enough region for fitting in SCOUT, while preventing the need to switching filters or gratings. The 0.25 grating is strongly reflective in the UV region, making the band

<table>
<thead>
<tr>
<th>Setting</th>
<th>Value</th>
<th>Range $\lambda$ (nm)</th>
</tr>
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<tbody>
<tr>
<td>Lamp</td>
<td>Xenon (Xe)</td>
<td>175→1750</td>
</tr>
<tr>
<td></td>
<td>Tungsten (W)</td>
<td>250→1998</td>
</tr>
<tr>
<td>Color Filter</td>
<td>None</td>
<td>200→400</td>
</tr>
<tr>
<td></td>
<td>345 nm</td>
<td>400→650</td>
</tr>
<tr>
<td></td>
<td>651 nm</td>
<td>650→1220</td>
</tr>
<tr>
<td></td>
<td>1200 nm</td>
<td>1220→2000</td>
</tr>
<tr>
<td>Grating (suggested)</td>
<td>0.25 micron</td>
<td>200→1000</td>
</tr>
<tr>
<td></td>
<td>0.50 micron</td>
<td>200→1500</td>
</tr>
<tr>
<td></td>
<td>1.0 micron</td>
<td>500→2000</td>
</tr>
<tr>
<td></td>
<td>2.0 micron</td>
<td>1000→2000</td>
</tr>
<tr>
<td>Detector</td>
<td>Silicon (Si)</td>
<td>200→1120</td>
</tr>
<tr>
<td></td>
<td>Indium-Gallium-Arsenic (InGaAs)</td>
<td>200→2000</td>
</tr>
</tbody>
</table>

Table 3: Grating Spectrometer Settings

6.2 Filtering 2nd Order Light

When measuring a sample, the correct color filter must be used to ensure the second-order light is blocked. This only applies for regions of the film 2nd order light is not absorbed by the band gap. For example, TiO$_2$’s largest band gap is about 3.2 eV, so the user needs to start using the color filter at 860 nm. At that point, not all the 380 nm light will be absorbed by the band gap, and the intensity from that light will be measured. For measuring a TiO$_2$ film up to 1000 nm, the second-order light is dim enough that there is not a big impact. But if we look at a SnCaSe sample which has a lower band gap, we can see clearly how the intensity from second-order light affects the near infrared measurement.

Figure 10 shows the transmission and reflection spectra of a SnCaSe film which has been measured with and without a color filter. The spectra labeled “filter” were taken correctly by inserting a color filter to stop second order light. The spectra R, T, and T/(1-R) has been taken without a filter. The band gap of the SnCaSe film stops absorbing at about 800 nm. We can see that the second order light (which has different interference fringes) skews the spectra above 1600 nm (see the red dashed line). The effect is strong above 1700 nm, when more second-order light is showing through.
6.3 Band gap of the substrate

Our films were grown on was either fused silica, soda-lime silicate (SLS), Eagle Corning XG (EXG) glass, or a silicon wafer. Glass has a band gap of about 9 eV, well above TiO$_2$, but some of our substrates have a band gap similar to TiO$_2$’s band gap of about 3.5-3.8 eV depending on the polymorph. EXG has a band gap of about 5.8 eV (EXG optical properties) and SLS has a band gap of about 5 eV. If the band gap of the substrate is too close or smaller than the film, the calculated absorption might end up being that of the substrate. The correct substrate needs to be chosen when performing the analysis in SCOUT. SCOUT contains the optical properties of many common materials, and new material properties can be added to the SCOUT database.

7 Using SCOUT

7.1 User configurations

All the films were measured using an optical fitting software SCOUT produced and distributed by Wolfgang Thiess. In order to measure the optical properties of a film in SCOUT, SCOUT needs to be configured to fit the transmission and reflection spectra. A configuration can be created and saved for a later time. Configurations can be loaded by clicking File → Open. A window opens up for the user to navigate to a configuration to load. Configurations can be saved by clicking File → SaveAs then selecting the folder and naming the new configuration.
7.2 The Layer Stack

To customize the configuration for measuring the properties of thin films, a new layer stack should be created with at least two layers: a thin film and thick layer, where the thin film is arranged above the thick layer. A half-space of air or vacuum is added on either side to simulate the atmosphere. Something to notice is that the thin film is labeled as “coherent” and the thick layer is “incoherent”, which is the only real difference between these two objects. A simple layer gives the user the option to have coherence or not. The material of the substrate can be chosen by drag-and-dropping a material from the materials database listed on the right of the layer stack. If the film has a known dielectric function, it can be chosen from the materials database, otherwise they will create a new material with some susceptibilities.

7.3 Materials

A new material can be created and added to the “materials” menu. A new material will have properties that are called “susceptibilities” in SCOUT. The built-in susceptibilities include features to model simple index of refraction, oscillators, interband transitions, and more. For a semiconductor, we can add two susceptibilities to model it accurately: a Sellmeier index of refraction, and a band gap. The real part of the index of refraction is added by creating a new “index of refraction” susceptibility, then entering the Sellmeier equation into the real part of the susceptibility. The band gap model we generally choose is the OJL2 band gap model. This was proposed in a paper by O’Leary, Johnson and Kim. It models a direct band gap with some effects from tail states. This does a good job of simulating the band gap of a semiconductor, while modeling flaws in materials by an exponentially decaying density of states. The susceptibilities contain parameters that can be adjusted to change features in the material. In the OJL2 model, the Gap Energy parameter changes the energy of the band gap.

8 Acknowledgments

I would like to thank my research advisor Dr. Janet Tate who taught me about the physics of thin films and gave me tutoring in technical writing and professional development. I would like to thank James Haggerty, James May, Okan Agirseven, and Bethany Matthews for giving me insight into materials physics, trusting me with their films, and supporting my endeavors. I would like to thank Dr. McIntyre for letting me use his lab for film characterization. I acknowledge support from the Dr. Russ and Dolores Gorman Faculty Scholar fund.
References


