

Characterizing Optical Signatures of TiO_2 Amorphous Precursors

Patrick Berry
Advisor: Dr. Janet Tate

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

Bachelor of Physics

Department of Physics
Oregon State University
May 10, 2019

Table of Contents:

1	Introduction.....	5
	1.1 Optical Properties of Thin-Film Semiconductors.....	7
	1.2 Band Gap and Tauc Analysis.....	8
2	Methods and Materials.....	10
	2.1 Grating Spectrometer.....	10
	2.2 Scout.....	12
	2.3 Samples	12
3	Results and Discussion.....	14
	3.1 Substrate.....	14
	3.2 Amorphous Samples.....	15
	3.3 Crystalline Samples.....	19
4	Conclusion	23
5	References.....	24

Abstract:

TiO₂ typically crystallizes into three polymorphs: brookite, rutile, and anatase. The phase selection problem in TiO₂ is the lack of understanding what conditions cause amorphous TiO₂ to crystallize into one of its three polymorphs during an annealing process. It has been recently shown that phase selection in TiO₂ is highly dependent on thin-film, amorphous precursor thickness and oxygen content. This is contrary to the previous thought that amorphous precursors are indistinguishable, as indicated by common identification techniques like X-ray diffraction and Raman spectroscopy. By way of simple transmission and reflection spectroscopy, this paper expands on this idea by searching for optical signatures present in amorphous TiO₂ that indicate what phase will be “selected” during an annealing process. Absorption spectra in range of 300-1000 nm distinguishes the anatase precursor from the other precursors, with the anatase precursor having an absorption coefficient of approximately $6.2 \times 10^3 \text{ cm}^{-1}$, while the brookite and rutile precursors show approximately $3.3 \times 10^4 \text{ cm}^{-1}$. Furthermore, the behavior of the transmission spectra in the long wavelength range can be linked to oxygen content, confirming the hypothesis that oxygen content plays a major role in phase selection. Tauc analysis performed on absorption spectra in range on 200-350 nm did not sufficiently differentiate the precursors from one another. However, Tauc analysis performed on crystalline samples showed consistent differences, indicating that transmission and reflection spectroscopy may be a viable method of polymorph identification. This paper further explores the phase selection problem by investigating optical properties that can be used to predict what polymorph amorphous TiO₂ will crystalize into during an annealing process.

1 Introduction:

Titanium dioxide (TiO_2) is a naturally occurring, wide-gap, semiconducting oxide of titanium. Its applications are numerous and include use as a color pigment, an ingredient in sunscreen, as coating for dielectric mirrors, as well as a photocatalyst that exhibits superhydrophilicity that allow the manufacture of self-cleaning glass and anti-fog coatings [1]. TiO_2 generally crystallizes into three distinct crystal phases, called “polymorphs: brookite, rutile and anatase, with each having a unique band gap, refractive index and extinction coefficient. These properties have been successfully characterized in rutile, but there is still disagreement and mystery with regard to these properties in the cases of brookite and anatase. This is because, despite the widespread study of TiO_2 and its applications, there exist many hurdles in identifying and characterizing the optical and semiconducting properties of the three crystal phases [2].

The first hurdle in characterizing these properties is that there is not a consensus on how to determine the band gap of these polymorphs from optical data alone. The assumption of an indirect or direct band gap transition can drastically affect the band gap value extrapolated from a given dataset. In his Ph.D. thesis, performing a meta-analysis of 129 reported theoretical or experimental band gaps of the three crystal phases, Haggerty not only showed inconsistencies in the assumptions made by researchers, but that *consistent* assumptions still led to inconsistent band gap values for the three crystal phases. In other words, it is unsurprising, given a single data set, that the assumption of direct or indirect band gap transition type will result in differing band gap values, but it is surprising that making the same assumption of transition type will still give inconsistent values across multiple datasets [2].

The second hurdle is related to identifying crystal phases. While there are many methods of identifying these crystal phases, none of them is cost efficient or time efficient. These methods include synchrotron X-ray diffraction, micro-Raman spectroscopy, high resolution transmission electron microscopy, and energy dispersive X-ray spectroscopy [3].

Third, the synthesis route for brookite has been historically either overly complicated at best, or unknown at worst, and involved templated substrates, or stabilizing sodium ions [3]. The lack of understanding around the conditions that are favorable for growth of brookite has likely been compounded by the high cost of identification, which inhibits the fine tuning of the trial and error process needed to determine growth conditions. There are few reports of pure brookite thin films, and those that exist do not have good optical characterization [4].

Professor Janet Tate's group at Oregon State University has been studying thin-film TiO_2 . Specifically, they have been studying what variables cause an amorphous precursor of TiO_2 to crystallize into a particular polymorph after an annealing process, otherwise known as the phase selection problem. Amorphous precursor TiO_2 with no discernible, consistent crystal structure in any direction, once it is annealed, can crystallize into a recognizable structure or a mixture of recognizable structures. They have found that phase selection is highly dependent on film thickness and deposition conditions, and less so on the annealing conditions and substrate type [3]. They have been able to develop reproducible deposition recipes for all three crystal phases of TiO_2 , including brookite. This is exciting because it enables the synthesis of large amounts of each polymorph, which in turn allows for the direct comparison of each polymorph's optical and electronic properties. Also, the fact that which crystal phase an amorphous sample "selects" during an annealing process is highly dependent on that sample's deposition conditions indicates that there may be physical observables present in the amorphous precursor that can be used to predict what crystal structure will grow in the annealing process.

The goal of the work reported in this thesis is to address following questions: (i) Can UV-Vis-NIR spectroscopy, measure optical properties such as refractive index and absorption to a degree of uniqueness for each crystal structure that a thin-film sample of unknown TiO_2 crystal structure can be identified? (ii) Are any of those signatures present in the amorphous precursor form? This is an important research question because, if it is indeed possible, spectroscopy may be a valid, cheap, and simple way to identify the polymorph of TiO_2 , and perhaps more important, identify which precursors will become which polymorph. At present, the amorphous precursors are not distinguishable using Raman spectroscopy or X-ray diffraction, although the crystalline forms are distinguishable.

The crystal phase an amorphous sample "selects" during an annealing process is highly dependent on that sample's deposition conditions, namely film thickness and oxygen pressure. This indicates that there may be physical observables present in the amorphous precursor that can indicate what crystal structure will grow in the annealing process. This thesis hopes to address following question: Using only UV-Vis-NIR spectroscopy, beyond thickness, are there artifacts in the transmission and reflection spectra, refractive index, or absorption of amorphous thin-film TiO_2 sample that indicate what crystal structure it will later form in an annealing process? The answer to this question will contribute to our understanding of the phase selection.

1.1 Optical Properties of Thin-Film Semiconductors:

Optical properties of interest present in thin films are their complex refractive indices and absorption coefficients. This information can be obtained through transmission and reflection spectroscopy. From that information, properties such as film thickness, and band gap can be extracted.

The complex refractive index of an absorbing material is given by

$$n(\lambda) = n_r + i\kappa, \quad (1)$$

where the real part of the refractive index can be approximated by the Sellmeier equation,

$$n_r^2(\lambda) = 1 + \sum_i \frac{B_i \lambda^2}{\lambda^2 - C_i}, \quad (2)$$

and the complex part of the refractive index is

$$\kappa = \frac{\alpha \lambda}{4\pi} \quad (3)$$

where α is absorption. Assuming normal incidence, transmission (T_1) and reflection (R_1) at the film-glass interface are then [5]

$$T_1 = \frac{4n_{film}n_{substrate}}{(n_{film} + n_{substrate})^2},$$
$$R_1 = \left| \frac{n_{film} - n_{substrate}}{n_{film} + n_{substrate}} \right|^2. \quad (4)$$

From total transmission (T) and reflection (R), which accounts for all three interfaces, a films thickness (d) can then be determined by analyzing the location of interference fringes in the transmission and reflection spectra. These interference fringes, however, prevent any meaningful understanding of the film's absorption coefficient α . These fringes can be removed by a process that results in what we call the reflection- corrected transmission (T_c) [6]:

$$T_c = \frac{T}{1 - R}. \quad (5)$$

By properly accounting for the the effect of interference, the corrected transmission gives the ratio of transmitted (I_t) to incident (I_0) light, and is a first order approximation of Beer's Law where

$$\frac{T}{1 - R} \cong e^{-\alpha d}. \quad (6)$$

It follows that, given thickness d , absorption can be found by:

$$\alpha \cong -\frac{\ln\left(\frac{T}{1 - R}\right)}{d}. \quad (7)$$

1.2 Band Gap and Tauc Analysis:

The band gap of materials in thin-film form is evidenced by a region of the transmission spectrum with high absorption, leading to little or no light transmission at those wavelengths. Quantifying the band gap, i.e. the onset of high absorption can be done by performing Tauc analysis. Tauc analysis linearizes an absorption spectrum and plots it on an energy scale. Extrapolating the linear region to its intercept on the energy axis then gives a band gap value. The process of linearizing absorption data is given by $(\alpha E)^n$, where n is equal to 2, or $\frac{1}{2}$, and E is energy, typically given in electron-volts. Setting n equal to 2 assumes a material with a direct band gap transition type, while setting n equal to $\frac{1}{2}$ assumes an indirect band gap transition type. For TiO_2 , some reported direct gaps for brookite, rutile, and anatase are 3.56 eV, 3.37 eV, and 3.53 respectively. Indirect gaps: 3.13 eV, 3.20 eV, and 3.01 eV [7]. An example of a Tauc plot is given in Fig. 1. For an amorphous sample where crystal momentum is not a well-defined quantity, the concept of "direct" loses meaning, and optical spectra are often analyzed as indirect band gap spectra. However, we use both analyses because they are so prevalent in the literature.

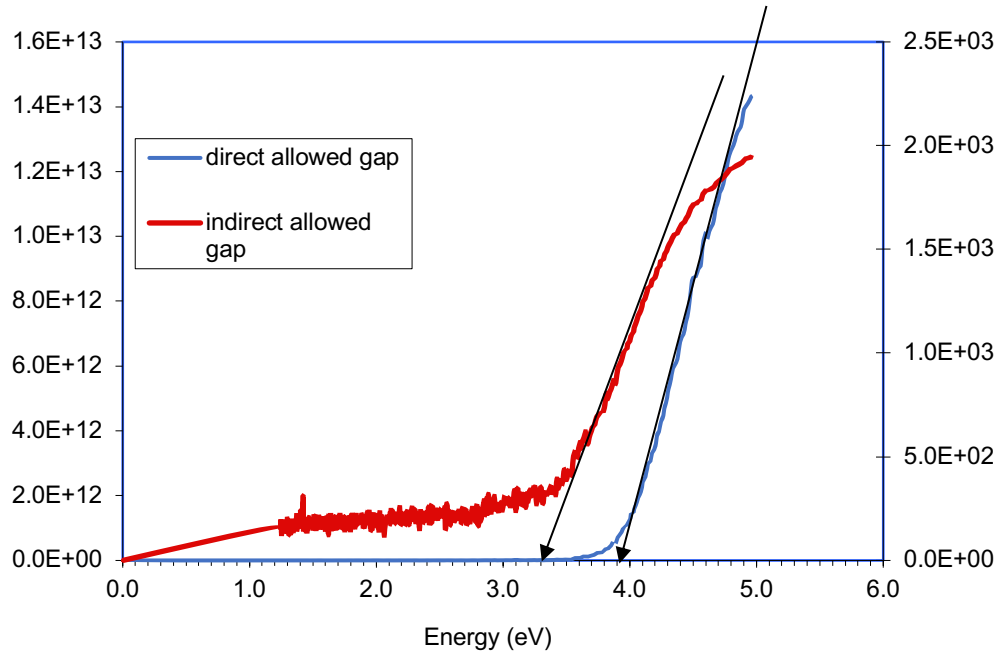


Fig. 1: Example of Tauc analysis process. The blue curve is assumes a direct band gap transition type, and its values are given on the left vertical axis. The red curve assumes an indirect band gap tranistion type and its values are given on the right vertical axis. Extrapolation of the linearized regions of the curves to the energy axis show band gaps of 3.3 and 3.9 eV for indirect and direct types respectively.

2 Methods and Materials:

2.1 Grating Spectrometer:

All transmission and reflection spectra were collected by a grating spectrometer (GS) as seen in Fig. 2.1 The GS filters light produced by a Xenon lamp into a single wavelength by way of monochromator outfitted with 0.25 micron grating. The filtered light is then collimated and focused onto the sample. Passing through, or reflecting off the TiO_2 sample, the resulting light is then measured by a silicon detector. This process is repeated as the monochromator filters the xenon lamp light in increments of 1 nm, from 200-1000 nm. Before measuring the transmission or reflection of a sample, raw lamp and ambient light spectra were measured such that the transmission and reflection spectra are calculated from the power P measured in various beams by:

$$T = \frac{P_t - P_{\text{ambient}}}{P_{\text{lamp}} - P_{\text{ambient}}}$$

$$R = \frac{P_t - P_{\text{ambient}}}{P_{\text{lamp}} - P_{\text{ambient}}}.$$

(8)

This procedure, as well as the equipment design can be seen in Fig. 2.1. An example plot of transmission, reflection, and corrected transmission (eq. 5) is given in Fig. 2.2.

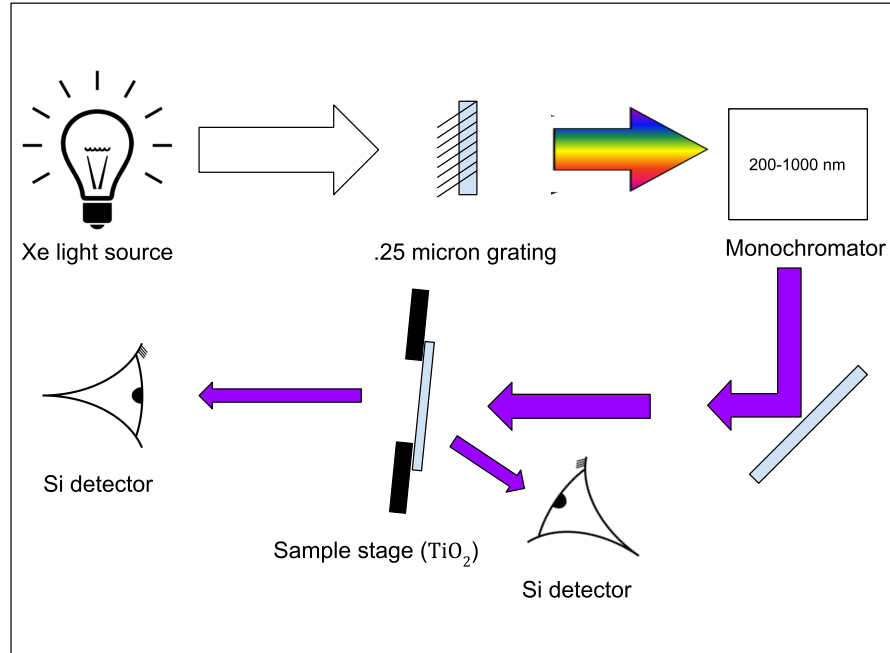


Figure 2.1: Schematic of GS, shown collecting T and R . Collection of T_{lamp} requires the sample stage be empty, and collection of T_{dark} requires the sample stage be blocked.

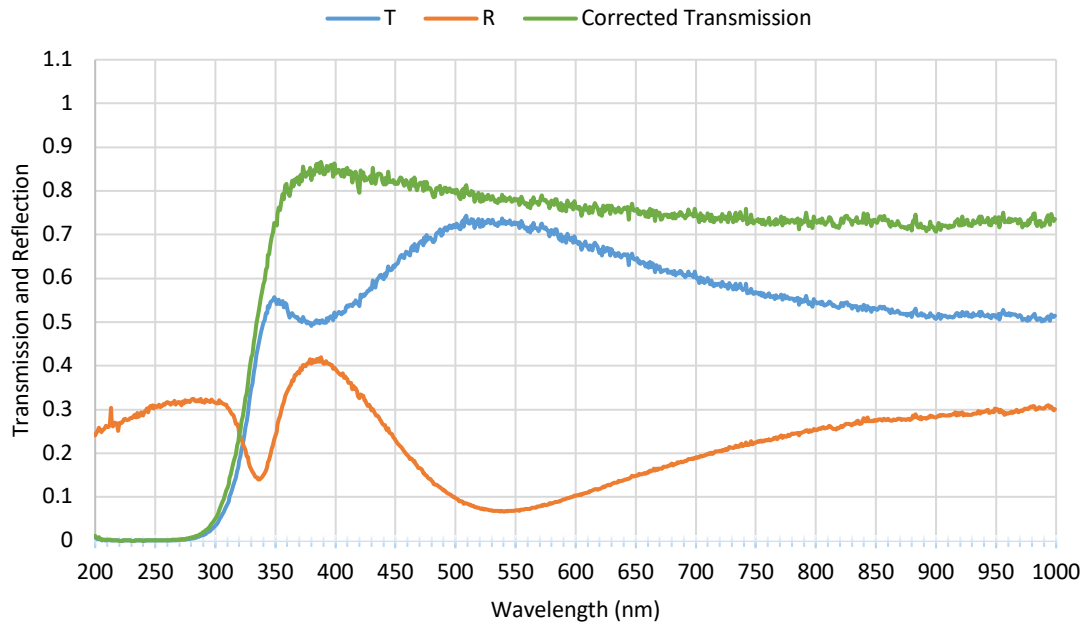
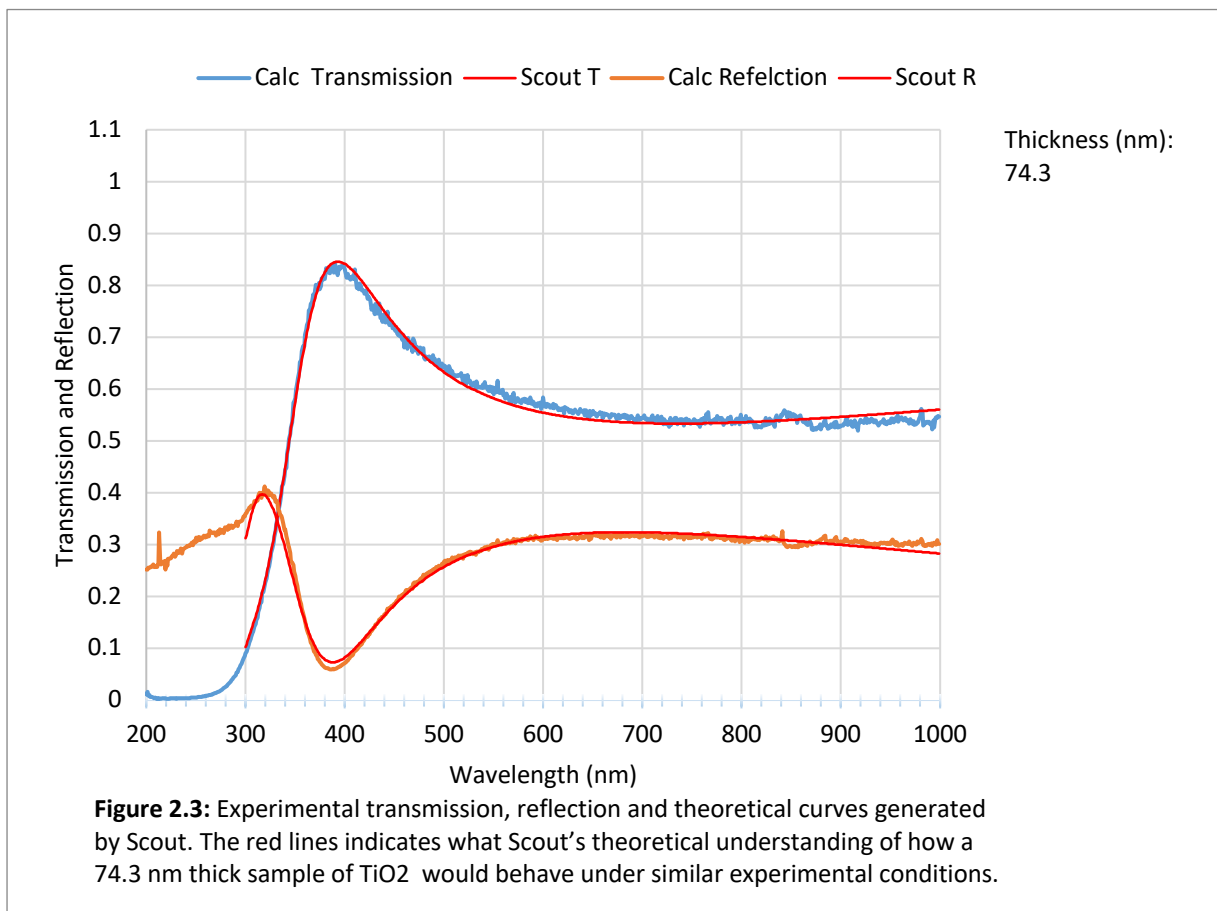


Figure 2.2: T (blue), R (orange) and $\text{Corrected } T$ (green) for an amorphous sample. In the high energy region, at about 350 nm, Corrected T decreases sharply as wavelength decreases, indicating the band gap. In the low energy region the corrected transmission shows an absorption of about 25%. The local maxima in T and corresponding minima in R , i.e. interference fringes, are used to determine film thickness.

2.2 Scout:

Scout is commercially available software program used for the analysis of optical spectra developed by W. Theiss. We use its optical modeling capability. Scout takes into account the known properties of the materials and produces a theoretical curve that yields the unknown properties. For example, the TiO_2 samples being measured are deposited on 1 mm thick glass slides produced by Eagle Glass; the properties of these slides--index of refraction, thickness, absorption, etc.--are known, allowing Scout to model these slides with the presence of TiO_2 . The resulting theoretical curve produces useful properties such as film thickness. An example of Scout-generated theoretical curves fit to experimentally collected data can be seen in Fig 2.3.



2.3 Samples:

All samples are generated by Okan Agirseven, a graduate student in Prof. Tate's lab. Amorphous samples are generated by sputtering titanium from a titanium metal target onto a glass substrate in an Ar-O_2 atmosphere. The Ti is oxidized at the substrate; the extent of

oxidation is determined by the oxygen partial pressure. Samples are then cleaved into two portions, one of which is then annealed while the other remains in an amorphous form, allowing for a side-by-side comparison of the crystallized sample and its amorphous precursor. Crystalline structures of the annealed samples are identified by Agirseven by Raman spectroscopy.

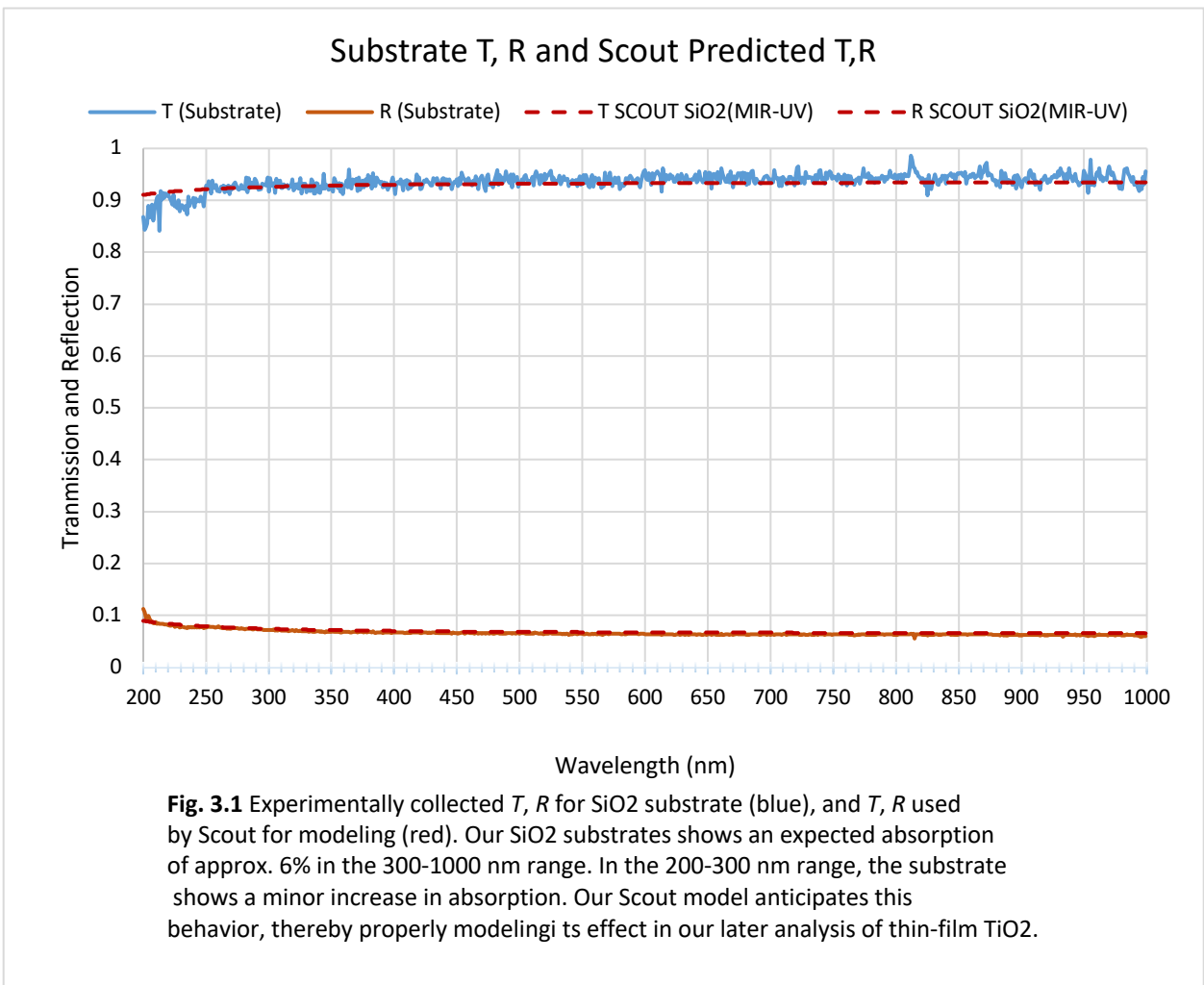
Table 1 gives a list of samples measured, their dominant phase fractions, partial oxygen pressure during deposition, and approximate thicknesses. Thickness were determined by Scout or independently by Agirseven. It should be noted that the phase fractions listed are only valid for the annealed samples, however, it is useful to consider the properties of their amorphous precursors with this information. Literature surrounding TiO_2 polymorphs typically assigns a color scheme that helps differentiate data from the three polymorphs: blue for brookite, red for rutile, and green for anatase. This convention is reflected in Table 1, and through the rest of this report.

Sample No.	Dominant Polymorph (%)	Partial O ₂ Pressure (%)	Deposition Time (min)	Approximate Thickness (nm)
002	Brookite (99B, 1R)	2.86	15	26
025	Brookite (99B, 1R)	2.86	17	36
029	Brookite (99B, 1R)	2.86	17	34
049	Brookite (93B, 7R)	2.86	20	50
030	Rutile (22B, 78R)	2.86	34	71
039	Rutile (15B, 85R)	2.86	52	103
040	Anatase (100A)	2.86	17	30
043	Anatase (100A)	2.86	17	31
044	Anatase (100A)	2.86	80	33
050	Anatase (95A, 5B)	2.86	20	51
Table 1: List of samples measured, their dominant phase fractions, partial oxygen pressures during deposition, deposition times, and approximate thicknesses.				

3 Results & Discussion:

3.1 Substrate:

First, transmission and reflection spectroscopy was performed on the SiO_2 substrate. This was done to determine the wavelength ranges where absorption may be attributable to the substrate as opposed to our thin-film TiO_2 . It was also done to ensure that Scout could accurately model our substrate and thereby not confuse the optical behavior of our thin-film TiO_2 with that of the substrate. Fig. 3.1 is shows T and R of the substrate with a Scout generated fit to the data.



The absorption of the substrate is negligible in the 200-350 nm range, where the largest changes occur in TiO_2 . This is important because it means large changes in absorption are entirely attributable to TiO_2 and we do not have to carefully model the substrate to extract

information about TiO_2 . Some glass substrates, treated with additives to control softening, have strong absorption close to where TiO_2 does so it is very important to check literature reports of thin-film TiO_2 absorption to ensure that the substrate has been properly modeled.

3.2 Amorphous Samples:

Films consisting of amorphous precursor to the three TiO_2 polymorphs of interest were then measured and characterized by Scout and Tauc analysis. Fig. 3.2 shows a compilation of corrected transmissions (eq. 5) as a function of wavelength for 9 amorphous samples.

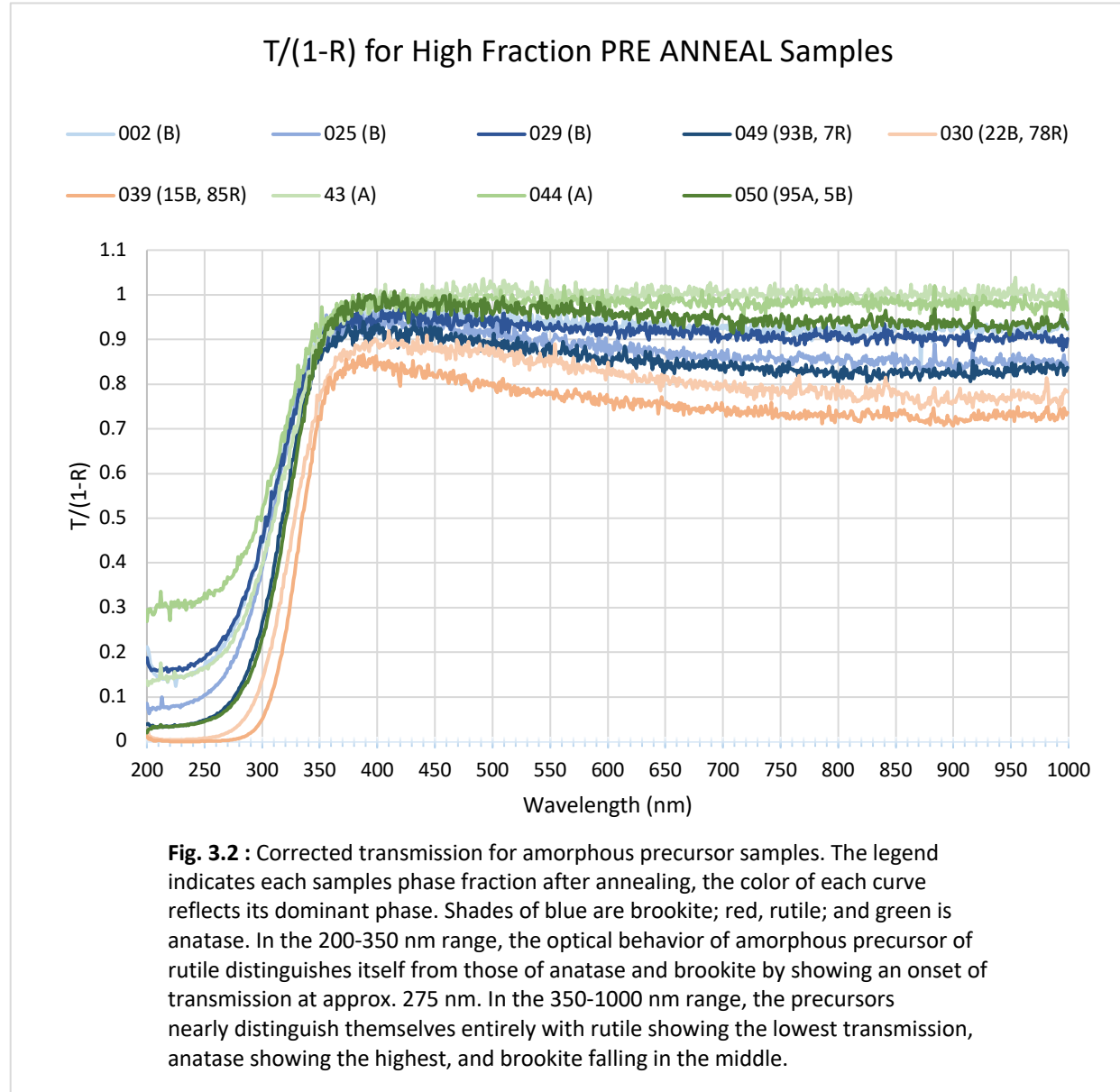


Fig. 3.2 shows evidence that each amorphous precursor exhibits behavior unique enough to further justify investigating precursor-specific optical signatures. Our group's previous research has shown that the formation of anatase is correlated with highly oxygenated amorphous precursors, while rutile grows from oxygen deficient films. These relationships present themselves in Fig. 3.2. Evidence of relative oxygen content can best be seen in the 400-1000 nm range where the transmission of each precursor nearly distinguishes itself from the others. Anatase's amorphous precursor shows high, constant transmission that resembles the optical behavior of fully oxygenated, crystalline TiO_2 , while rutile shows a lower transmission that decreases with wavelength, resembling the transmission spectrum expected from a metal. Transmission alone cannot be used to explain any differences amorphous precursors, as transmission scales with both absorption and film thickness (eq. 6), and the effect of film thickness is not immediately apparent in Fig 3.2. Fig.3.2 further confirms the amorphous precursors relationship oxygen content, however further analysis is needed to identify precursor-specific optical signatures.

Figure 3.3 shows absorption of each sample as a function of wavelength, calculated from eq. 7, using the thicknesses given in Table 1. This was done to investigate whether or not the apparent differences in transmission spectra seen in Fig. 3.2 can be uniquely attributable to differences in the absorption coefficients of the amorphous precursors. Unlike transmission, the absorption coefficient of a material should not be affected by thickness.

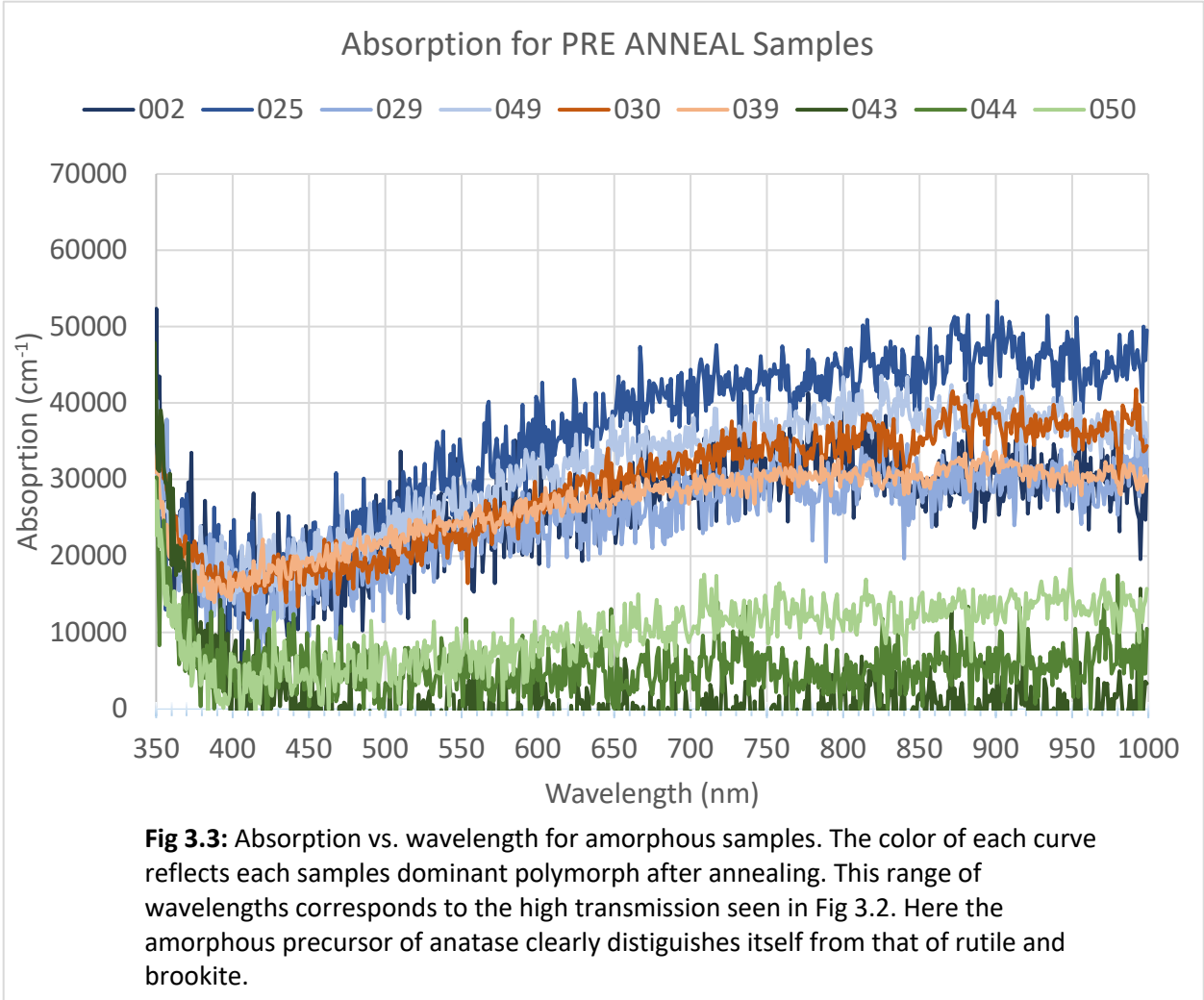


Fig. 3.3 clearly shows the absorption spectra of the anatase amorphous precursor differentiating itself from those of brookite and rutile. In the higher wavelength range (>650 nm), the anatase precursor shows an absorption of $0\text{--}10000\text{ cm}^{-1}$, while the brookite and rutile precursors show absorption of $25000\text{--}45000\text{ cm}^{-1}$. This means that the distinctive, comparatively high transmission of the anatase precursors seen in Fig. 3.2 can be attributed to a unique absorption coefficient and are not attributable the small thickness of the samples. Because the absorption spectra of the brookite and rutile precursors are functionally indistinguishable, it also means that the apparent differences of transmission between the rutile and brookite precursors are likely due to a difference in thickness, and not due to a difference in absorption coefficients. By showing an optical signature of the anatase precursor in the form of low absorption, these results suggest that the amorphous precursors of brookite, rutile, and anatase may have unique optical characteristics that distinguish one from the others.

Tauc analysis was also performed on the transmission spectra in order to determine if each precursor had any unique direct or indirect band transitions. Table 2 is a table Tauc analysis results, as well a column that specifies absorption at 850 nm. The value of 850 nm was chosen arbitrarily in an attempt to quantify the results presented in Fig 3.3. The table also contains average values for each method of analysis, for each precursor.

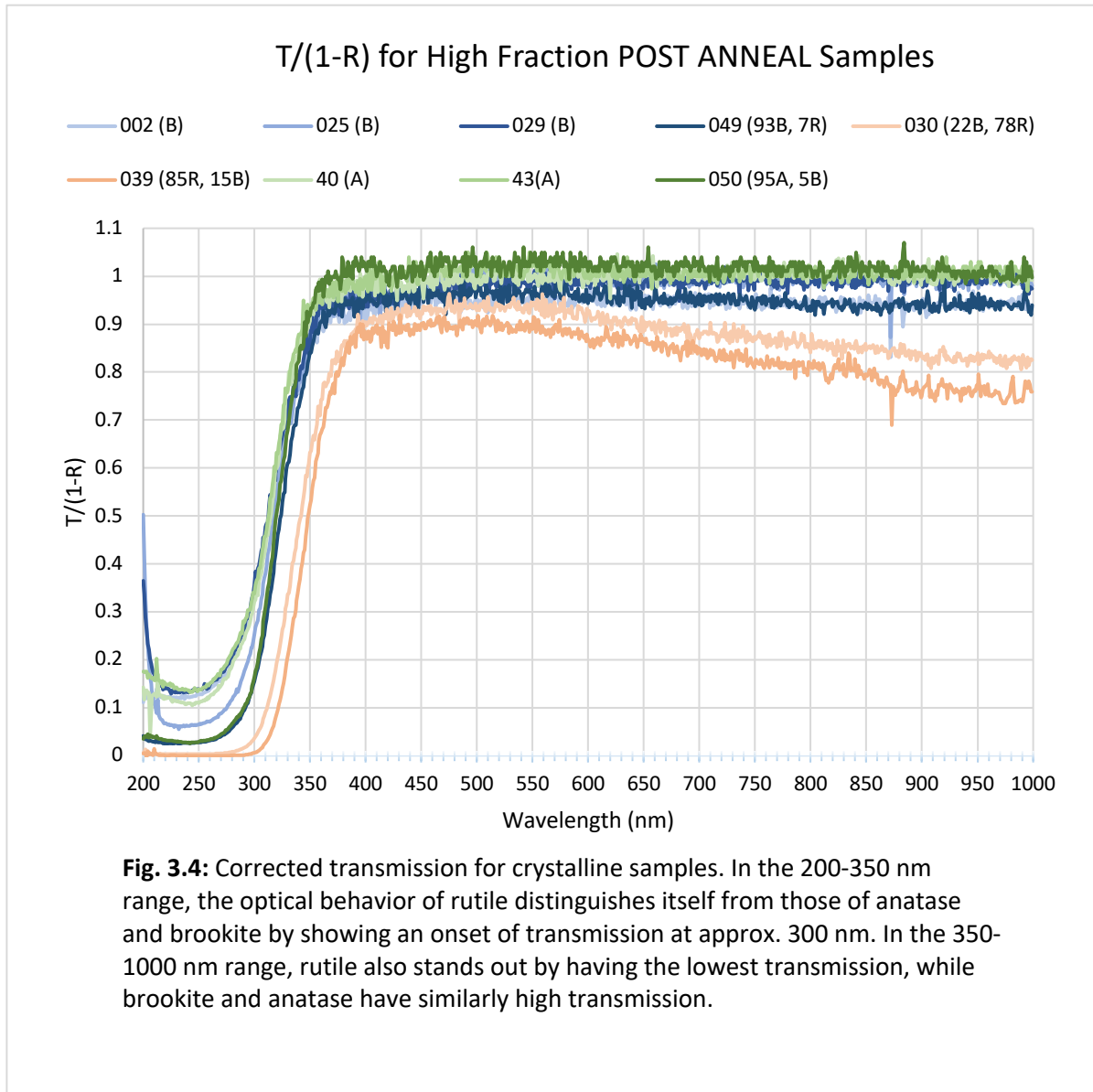
Sample No.	Dominant Precursor (%)	Tauc Indirect (eV)	Tauc Direct (eV)	Absorption at 850 nm (cm ⁻¹)
002	Brookite (99B, 1R)	3.30	4.05	2.85 x 10 ⁴
025	Brookite (99B, 1R)	3.30	4.12	4.37 x 10 ⁴
029	Brookite (99B, 1R)	3.25	4.00	2.89 x 10 ⁴
049	Brookite (93B, 7R)	3.30	4.10	3.79 x 10 ⁴
	Brookite Average	3.29	4.06	3.47 x 10⁴
030	Rutile (22B, 78R)	3.30	4.10	3.48 x 10 ⁴
039	Rutile (15B, 85R)	3.30	4.10	3.02 x 10 ⁴
	Rutile Average	3.30	4.10	3.25 x 10⁴
043	Anatase (100A)	3.25	3.80	1.45 x 10 ³
044	Anatase (100A)	3.30	3.80	4.33 x 10 ³
050	Anatase (95A, 5B)	3.30	3.90	1.29 x 10 ⁴
	Anatase Average	3.28	3.83	6.22 x 10³

Table 2: Table of Tauc analysis results for amorphous precursors, absorption at 850 nm, and their average values for each precursor.

Neither the direct nor indirect Tauc analysis results seem to show significant differences between the amorphous precursors. The direct Tauc analysis seems to show a slightly greater difference between the precursors but performing this type of analysis on amorphous materials is illogical because amorphous materials have no discernible crystal structure in any direction, and assuming a direct analysis may yield results that do not have any physical meaning. Quantifying the absorption in the region of low absorption shows that the anatase precursor has an absorption an order of magnitude lower than those of brookite and rutile, confirming the trend seen in Fig. 3.3.

3.3 Crystalline Samples:

The annealed portions of the samples were also measured by the same procedures. This was done for a number of reasons. Beyond yielding insights into polymorph growth, and beyond simply measuring their optical properties, this was done to determine if transmission and reflection spectroscopy is a viable method of identifying the TiO_2 polymorphs. It is important to note that the annealed portions of the samples are the one that actually consist of the polymorphs used to identify the amorphous precursors is the earlier discussion. The following discussion will refer to fully crystalline samples. Fig. 3.4 shows a compilation of corrected transmissions (eq. 5) as a function of wavelength for 9 crystalline samples.



When compared to the transmission spectra of the amorphous precursors seen in Fig. 3.2, the transmission spectra of the crystalline samples all show a net increase in transmission, particularly in the high wavelength region. As a result, the transmission spectra of brookite is harder to distinguish from anatase, but rutile stands out as least transmitting film over the entire wavelength range. We believe that this net increase in transmission seen in the crystalline samples is due to further oxygenation of the samples during the annealing process. We believe that each amorphous precursor is indiscriminately oxygenated in the annealing process, thereby decreasing free carrier density and decreasing absorption.

Fig 3.5 shows absorption of each sample as a function of wavelength, calculated from eq. 7, using the thicknesses given in Table 1.

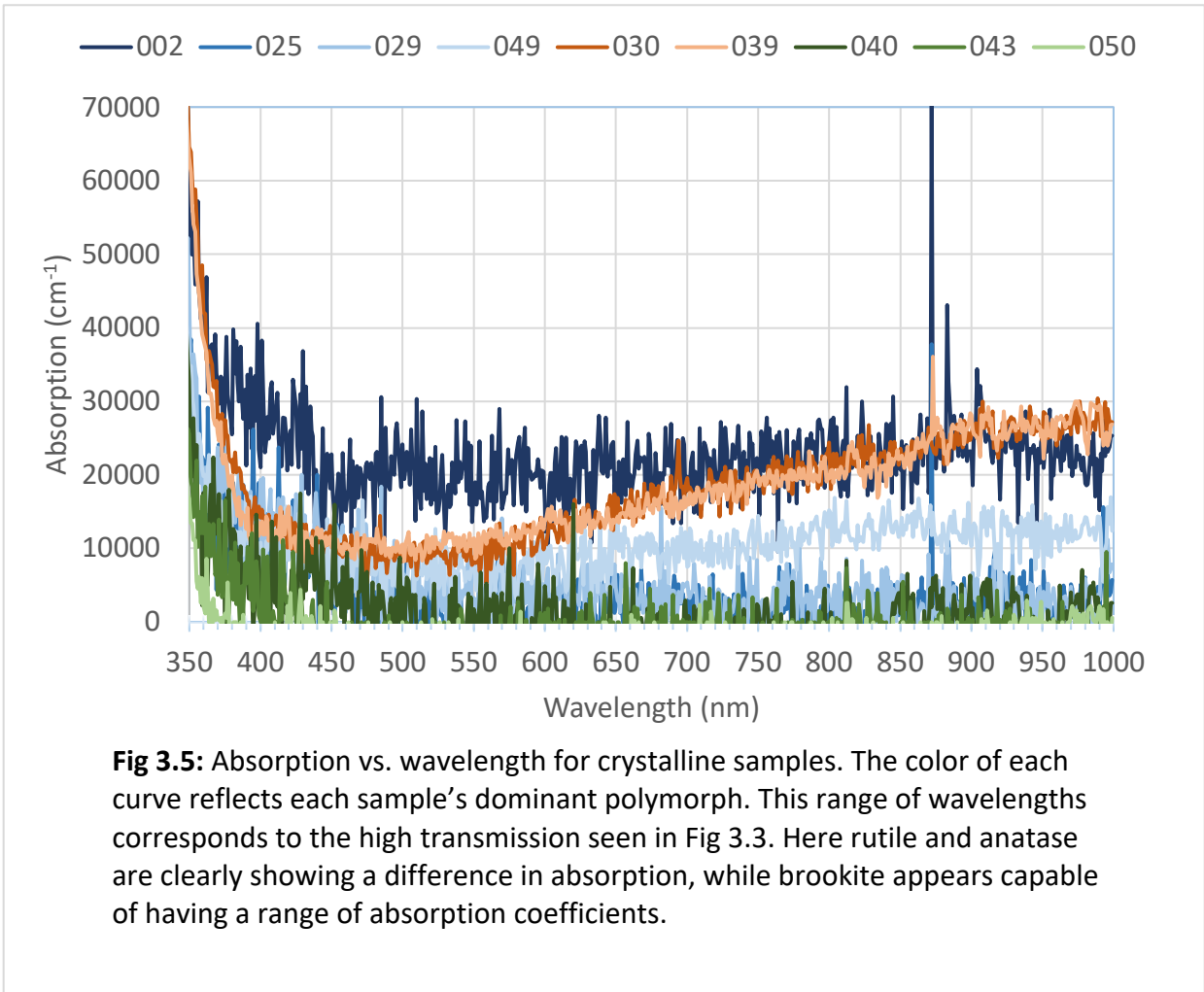


Fig. 3.5 very clearly shows anatase and rutile having measurably different absorption coefficients, with anatase showing almost no absorption at all, and rutile showing about 10000-30000 cm^{-1} . This is not surprising, as polymorphs of the same chemical formula are expected to oftentimes have unique properties, but what is surprising is that brookite seems capable of having a range of absorption coefficients. Fig. 3.5 shows brookite samples that have absorptions similar to anatase, similar to rutile, and also some that lie in between. If we are to assume that absorption is proportional to free carrier density, which is inversely proportional to oxygen content, then these results show that rutile growth favors less oxygenation, while anatase favors maximal oxygenation, and brookite growth can occur at differing levels of oxygenation.

Table 3 is a table Tauc analysis results, as well a column that specifies absorption at 850 nm. The table also contains average values for each method of analysis, for each polymorph.

Sample No.	Dominant Polymorph (%)	Tauc Indirect (eV)	Tauc Direct (eV)	Absorption at 850 nm (cm^{-1})
002	Brookite (99B, 1R)	3.3	3.9	2.22×10^4
025	Brookite (99B, 1R)	3.4	4.0	2.25×10^3
029	Brookite (99B, 1R)	3.3	4.0	2.89×10^3
049	Brookite (93B, 7R)	3.4	4.0	1.28×10^4
	Brookite Average	3.35	4.0	1.02×10^4
030	Rutile (22B, 78R)	3.2	3.9	2.28×10^4
039	Rutile (15B, 85R)	3.3	3.8	2.23×10^4
	Rutile Average	3.25	3.85	2.25×10^4
040	Anatase (100A)	3.5	3.9	3.34×10^3
043	Anatase (100A)	3.5	3.9	0
050	Anatase (95A, 5B)	3.5	3.9	0
	Anatase Average	3.5	3.9	N/A
Table 3: Table of Tauc analysis results for polymorph, absorption at 850 nm, and their average values for each polymorph.				

Table 3. shows that neither the indirect or direct gaps measured agree very well with the literature values given in the introduction. This is not of great concern as it is also known that Tauc analysis is an imperfect procedure, and it often yields a variety of results that should be theoretically equal, or it is outright misused [2]. However, Table 2 does show that Tauc analysis performed with a consistent procedure on absorption data extracted from transmission and reflection spectroscopy can yield results that differentiate the polymorphs from one another. This shows that simple transmission and reflection spectroscopy can possibly be a viable method of identifying the polymorphs of TiO_2 .

4 Conclusion:

An understanding of the phase selection problem in TiO_2 would benefit science and industry by allowing for the control of phase selection. TiO_2 has already proven itself to be a handy material as an ingredient in sunscreen, a diametric coating, etc. Controlling phase selection would allow for the finer tuning of TiO_2 's already useful properties. As such, were measured amorphous precursors to TiO_2 's three polymorphs by transmission and reflection spectroscopy in an attempt to further address the phase selection problem. From transmission and reflection data, absorption was extracted and compared. The absorption spectra of the anatase precursor distinguished itself from those brookite and rutile. Tauc analysis was also performed on each absorption spectrum, but the differences between the precursors seemed to minute to make any claims.

Taken as a whole, it is difficult to determine whether the results present clear optical signatures that differentiate the precursors from one another, or whether these results just simply reflect the differences we already knew about before the experiment, namely thickness and oxygen content. The fact that the anatase precursor has measurably smaller absorption in the near infrared region hints at the idea that these optical signatures may exist, but more data, and further analysis would be needed to find them.

For the crystalline samples, the methods of this experiment seem to be sufficient enough to identify TiO_2 polymorphs, albeit with some improvements. Improving these methods would require a greater certainty in film thickness, as a greater certainty of film thickness would give more precise absorption spectra of thin-film samples, which would in turn increase the accuracy and certainty of Tauc analysis. These improvements are not insurmountable, which is encouraging because transmission and reflection spectroscopy is a far cheaper more time efficient process than other methods of identification such as synchrotron X-ray diffraction, micro-Raman spectroscopy, high resolution transmission electron microscopy, and energy dispersive X-ray spectroscopy.

Further work would first need to utilize samples of a singular polymorph. Only 60% of the samples considered in this report were singular in phase, and we did not have any pure rutile samples. Secondly, these pure phase samples would need to be numerous, and deposited for the widest possible range of thicknesses. This would allow a single polymorphs precursor to be compared at different thicknesses, and it would allow the three precursors to be compared at the same thickness. Beyond that, investigation of the optical properties of mixed phase samples then be possible and could like explain some of the results presented in this report.

5 References:

- [1] K. Nakata, A. Fujishima, "TiO₂ Photocatalysis: Design and Applications", Journal of Photochemistry and Photobiology C: Photochemistry Reviews Volume 13, Issue 3, (2012)
- [2] Haggerty, J. Amorphous TiO₂: A Thin Film Synthesis Route to Stabilization of Metastable TiO₂ Brookite. PhD Thesis (Oregon State University, 2018).
- [3] Haggerty, J. E. S. *et al.* High-fraction brookite films from amorphous precursors. *Scientific Reports* **7**, (2017).
- [4] Alotaibi, A. M., Sathasivam, S., Williamson, B. A., Kafizas, A., Sotelo-Vazquez, C., Taylor, A., Parkin, I. P. Chemical Vapor Deposition of Photocatalytically Active Pure Brookite TiO₂ Thin-Films. *Chemistry of Materials*. **30**, 1353 (2018).
- [5] E. Hecht, *Optics*, 132, (Pearson Education Inc, 2017).
- [6] D.H McIntyre, Thin Film Interference, (Oregon State University, 2010)
<http://physics.oregonstate.edu/~tatej/TateLabWiki/doku.php?id=mustread:start>
- [7] Reyes-Coronado, D., Rodriguez-Gattorno, G., Espinosa-Pesqueira, M. E., Cab, C., Coss, R. D., Oskam, G. (2008). Phase-Pure TiO₂ nanoparticles: anatase, brookite and rutile *Nanotechnology*, **19**(14), 145605.
- [8] Lance, R. Optical Analysis of Titania: Band Gaps of Brookite, Rutile and Anatase. Undergraduate Thesis, Oregon State University (2018).
- [9] Tucker, D. A. Optical Characterization of Transparent Conductive Thin Films. Undergraduate Thesis, Oregon State University (2018).