Characterizing Titania Polymorphs Synthesized From Sputtered Amorphous Precursor Films

By: David T Rivella Jr

Department of Physics

Oregon State University

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Advisor: Janet Tate

Table of Contents

Table of Figures

TiO$_2$ is a material that can form with several different structural polymorphs. Since each polymorph has different physical characteristics and properties the ability to create each one with high purity is important for application purposes. In this work, a protocol to create amorphous TiO$_2$ thin films using RF sputtering was found. These amorphous films were then annealed to create three different polymorphs: anatase, rutile, and brookite. It was found that rutile formed in samples that were around 60nm thick, while thinner samples preferred mixes of anatase and brookite. An attempt to determine the extent of the influence of the partial pressure of oxygen was in determining which polymorph formed was due to made. When compared to samples made via pulsed laser deposition, the sputtered samples showed similar trends, and it appears that the two methods are very comparable.

1. Introduction

TiO$_2$ is a widely studied material with many different uses. It has applications as a white pigment for paints, toothpaste, food coloring, cosmetics, and other commercial goods, as well as being used as photocatalytic and photovoltaic purposes[1],[2]. Part of what makes TiO$_2$ useful is that it comes in several different polymorphs, which means that there are several different crystal structures that can be formed that are all stoichiometrically TiO$_2$. There has been a lot of research to find out how to make different polymorphs, as well as how to modify the polymorphs in order to better suit the application (such as engineering oxygen vacancies[3], doping[4], or by mixing different polymorphs together at specific ratios[5]). The most commonly used polymorphs are currently rutile, the ground state, and anatase, a metastable state. These are two of the three naturally occurring crystal structures, and can be reliably made with high purity. The third naturally occurring polymorph of TiO$_2$ is brookite. These three crystal structures are depicted in Figure 1. Although mostly pure rutile and anatase can be produced, a method for high purity production of brookite has proved difficult, as the mechanism and selection process for which polymorph will grow is still largely unknown[6]. Since each different structure has different physical characteristics (most notably band gap and index of refraction[7]), each one can be better suited for different applications. This desire to synthesize specific polymorphs has led us to investigate under what parameters each structure forms.

An investigation into TiO$_2$ polymorph synthesis was performed by our group in the past and found that the polymorph grown showed a clear dependence on the sample thickness, with anatase favoring thicker samples (showing up at samples with greater 45nm thickness), high fractions of anatase favoring thinner samples(<45nm), and a small thickness range where high percentages of brookite formed (between 37-65nm)[6]. In this previous study, amorphous TiO$_2$ was grown using pulsed laser deposition. Amorphous samples were used because the amorphous state is the highest energy state so in order to get metastable states it would be lowering the energy and entropy of the system, thus working with nature.
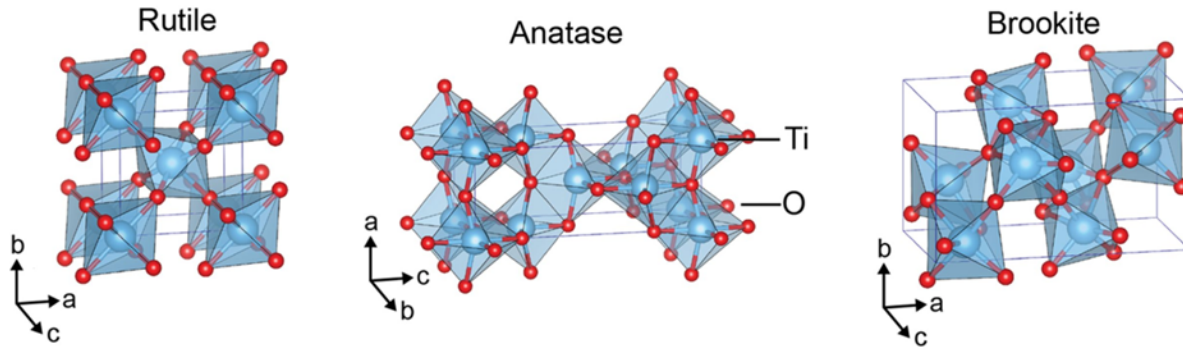
Figure 2: The crystal structure of rutile, anatase, and brookite polymorphs[6]

For this new study, RF sputtering was used instead of pulsed laser deposition. Sputtering was chosen because the two systems have many similarities to them, but also key differences. They are both highly energetic processes that work by ejecting material from target that then is deposited onto the substrate. There are, however, important differences between the two processes. A side by side picture of how each one works can be seen in Figure 2. Pulsed laser deposition works by hitting the target with a pulsed high energy laser. This converts the target into a complex plasma which deposits onto the substrate. The complex plasma consists of three main parts, ions, neutrals, and clusters. The ionized particles can make up between 10% - 70% of the plasma, depending on the energy density and wavelength of the laser, and can have a total energy between 0-2000eV, with an average energy between 100eV and 400eV. The neutral particles have make up 30% -90% of the plasma, depending largely on how ionizable the material is, and have an average energy of around 10eV. Another major part of the plasma plume is the large clusters of material that get ejected from the target. These clusters can range from nanometer size to micron size, and generally travel an order of magnitude slower than the ionized and neutral particles (with speed being measured in cm/s). These clusters are generally uniformly distributed in where they are deposited based on the thickness of the sample. So thicker locations on the sample tend to have more clusters[8]. One of the main determinants of the thickness of the sample is the shape of the plume and the location of the substrate in correlation to that. In general the shape of the plume resembles a tear drop shape with varying thicknesses, and it generally deposits in material in a conical manner. Towards the center there will be a lot of material, and towards the edges there is less material, causing a large conical thickness gradient[8],[9].

Sputtering works by introducing a (inert) gas into the vacuum chamber as well as electrons. The electrons present in the system collide with the gas, knocking off another electron and making a gas ion. A dc voltage is applied between the target and substrate which causes the ion to collide with the target. Some of the momentum of that ion transfers to the target and ejects some material[10]. Generally speaking the gas particles need to have a minimum kinetic energy of 25eV in order to eject material from the target[10],[11], and the ejected material will have an average kinetic around 10-25eV[11]. And since the gas ions fill the entire chamber they can bombard the target from every direction, meaning material is ejected from the target in every direction and fills the entire chamber. This makes for a uniform thickness in the deposited samples. One potential drawback to sputtering is that, although it might be less energetic than pulsed laser deposition, it is still a highly energetic process. The issue with this is that a higher kinetic energy means that the atoms have a higher mobility once they are deposited, and higher mobility means an increase crystallinity in the sample[12]. This means that sputtering often

produces crystalline samples, while amorphous samples are desired. Fortunately there have been several instances where people have grown amorphous TiO_2 using sputtering[13],[14],[15],[16], and their work was used as a base reference for determining parameters used in this study while exploring what parameters were necessary to form amorphous TiO_2.

The main reason for switching to the sputtering is because it is a readily available technique in commercial settings and much more common than PLD. It is therefore important to compare between the sputtered and the pulsed laser deposited samples to see if the results obtained via PLD transfer to sputtered samples. Since thickness was determined to be an important factor for which structure forms the thickness gradient present in pulsed laser deposition is not ideal. Sputtering makes uniform thickness samples so it can allow a better investigation into the thickness importance. Another reason for using sputtering is because by having good control on the thickness we can investigate other parameters. Reports show that rutile tends to form at lower oxygen partial pressures, and anatase forms at higher partial pressures of oxygen[17],[18], showing that partial pressure of oxygen, pO_2 has an influence in determining the polymorph and is another parameter that should be studied.
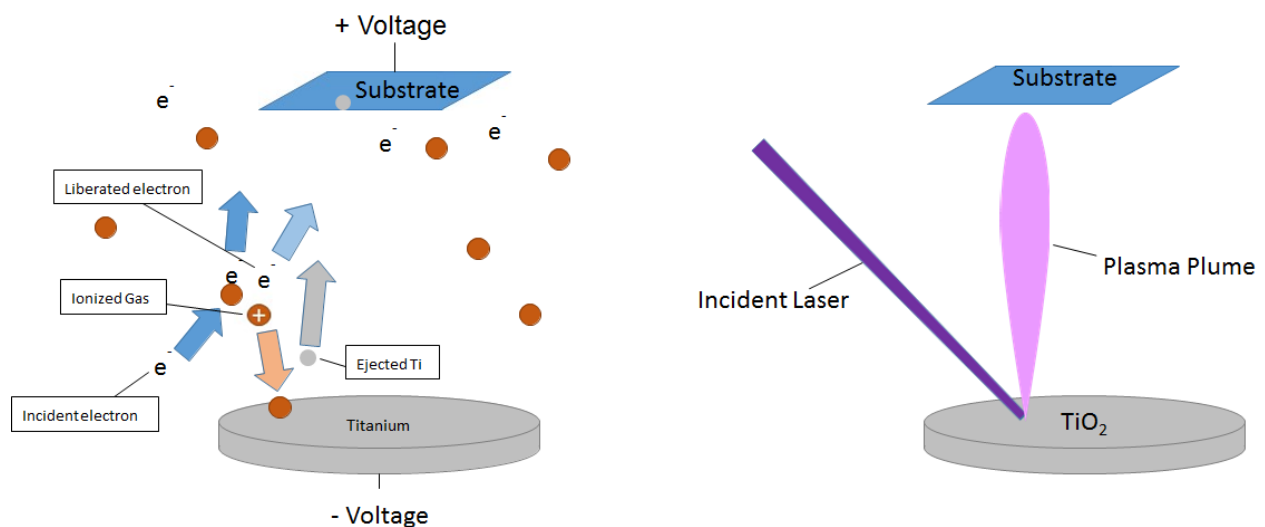
Figure 3: Sputtering Configuration (Left) and Pulsed Laser Deposition (Right)

2. Experiment

2.1 Substrate Preparation

The TiO_2 films were grown via RF sputtering on amorphous SiO_2 and single crystal Si <100> substrates. The SiO_2 substrates were cleaned for two minutes with Liquinox brand liquid soap soap at a ratio of 1:10 soap to de-ionized (di) water and then rinsed with di-water for two minutes. Afterwards they were ultrasonicated for 5 minutes in acetone (99.5%) and then 5 minutes in isopropanol (99.9%) before being blow dried with N_2 gas. They were then further dried in an oven at 120°C for 10 minutes. In order to better preserve the smooth surface, the Si substrates were not cleaned with soap, but they were

ultrasonicated for 5 minutes in acetone and 5 minutes in methanol (99.8%) before being blow dried with N_2 gas and heated at 120°C for 10 minutes. In order to limit contamination the samples were always cleaned within two hours before being transported to the clean room, where the sputtering system was. The substrates were transported in closed plastic sample holders with one substrate per holder and the holders all contained in a closed plastic bag.

2.2 Sputtering Parameters

Once the substrates were clean, the films were then grown via RF sputtering of a titanium metal target in an argon/oxygen atmosphere. The base pressure of this system sits between low 10^{-7} to mid 10^{-8} torr, and the atmosphere during deposition is controlled with two different gas inputs. One input is pure argon, while the other input can be switched between pure oxygen or a 90:10 argon/oxygen mix. The second input (O_2 or Ar/O_2) shared a hose that led into the chamber, so when switching between the two, the system was purged for 45 minutes in order to clear the hose. A rough schematic of the chamber and gas inputs can be seen in figure 3. When not switching gas inputs, the chamber was purged for 15 minutes using a flow rate of 10 sccm for each gas input prior to each deposition in order to reduce contaminants. Prior to the deposition the Ti target was presputtered for 10 minutes with just argon and then for 5 more minutes with argon and oxygen flows using the same parameters used for the deposition.
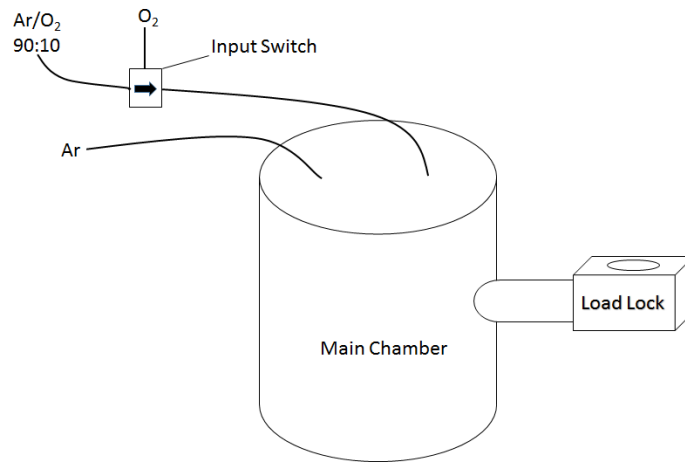

Figure 4: Gas Input Diagram

For this experiment, the RF power was always set to 100W, the processing pressure was always set to 2.5mTorr, the sample was located approximately 2.5 cm from the target, and the target was spinning at a rate of approximately 33rpm. The argon flow was present for every deposition and for samples with a pO_2 below 10% the argon/oxygen mix was used. For samples at or above 10% pO_2 the pure oxygen gas input was used. For this experiment pO_2 is measured in flow rate (sccm), so for example a pO_2 of 10% means that the argon flow was 9 sccm and the oxygen flow was 1 sccm. The majority of the samples for this experiment were made with 1% or 5% pO_2, however a 10% and a 20% sample were made in order to compare them to samples made via pulsed laser deposition. More 10% and 20% pO_2 samples were planned, but time did not permit for them. The deposition durations chosen were 7.5, 10, 15, and 30 minutes, where the growth rate for the films was approximately 2nm/minutes for the parameters

chosen (giving goal thicknesses of 15, 20, 30, and 60 nm). The chosen combinations of pO_2 and deposition times can be seen in Table 1.

	pO₂ (%)			
	1	5	10	20
7.5	x	x		
10		x		
15	x	x		
30	x	x	x	x

Time (min) — row labels for 7.5, 10, 15, 30.

Table 1: deposition times and pO₂ values chosen

2.3 Annealing

Once the films were deposited, the samples were cleaved in half, and half of each sample was annealed using an AET Thermal RX thermal annealer. The anneal procedure started with a 10 minutes purge of N_2. After that the sample was heated up to 340°C over a period of 375 seconds. This was immediately followed by a 180 second ramp up to 400°C degrees. The temperature was held at 400°C for three minutes before the system was allowed to cool down to room temperature. The cooling down was not controlled and occurred at the natural rate of the system. A plot of this can be seen in Figure 3, where the cooling down is assumed linear for plotting purposes.
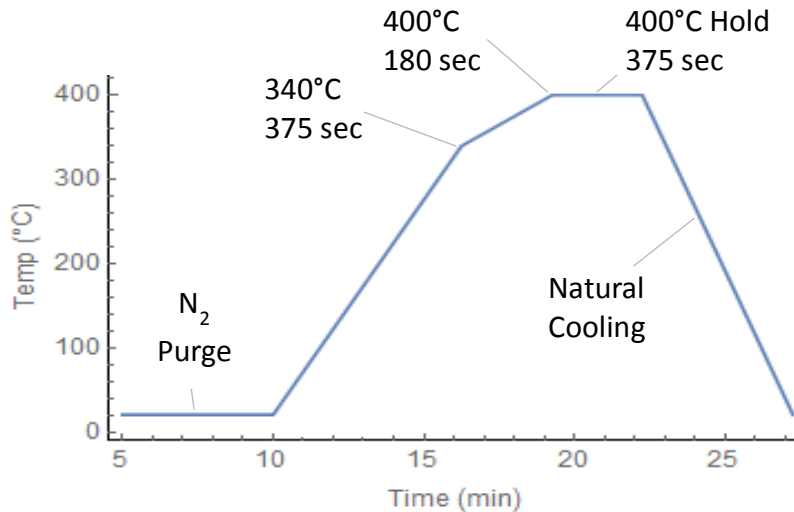
Figure 5: Annealing Temp vs Time

2.4 Characterization

Several methods were used to analyze the samples, both pre- and post-anneal. The primary investigation was done with Raman spectroscopy, using a Horiba Jobin-Yvon LabRam800 spectrometer with a 532nm laser of approximately 1µm. The data was analyzed using the LabSpec 5.0 software suite where background subtraction and Guassian peak fitting was done so that the data could be compared to a reference spectrum in order to tell which structure was present. For this investigation

the sample was put under a microscope and different polymorphs could be seen by their different colors (some appearing darker or lighter) and their morphology (describe shapes and growth habit). Raman spectroscopy was done on each different section of the film to identify the polymorphs present and then the entire sample would be viewed in order to determine the relative percentages of each polymorph in the sample.

Some samples wouldn't produce a clear enough Raman signal in order to identify which structures were present. These samples were analyzed using grazing incidence x-ray diffraction (GIXRD). This was done on a Rigaku IV X-ray diffractometer with Cu k-α radiation with λ = 1.5406 Å. The scan was between 10° and 70° as a 2θ grazing incidence scan with an incident angle of approximately 0.6°. Once the data was collected the substrate signal and noise would be eliminated using the software PDXL so that polymorph phases could be identified. One drawback to the XRD is that it can identify which structures are present, but is not reliable at estimating composition ratios. However, the phases could be compared to unidentified phase ratios determined in Raman in order to say what each phase percentage is.

The thickness for each sample was determined optically in a homegrown system that uses a deuterium light source. The transmission and reflection of light between λ=195nm and λ=1118nm. For each sample transmission would be recorded without anything between the source and detector, with a something blocking the light beam, and with the sample in the beams path so that the light goes through the sample. Reflection was taken with a mirror, with something blocking the path, and off of the sample. This would provide a transmission and reflection reference as well as a transmission and reflection for the sample, which allows for the change caused by the sample to be found. An example of this data (from sample #2) can be found in Figure 5. Once collected the data was put into an analysis software, Scout, that used curve fitting in order to fit a model of the sample on a fixed substrate to the data in order to optimize the thickness parameter in the model.
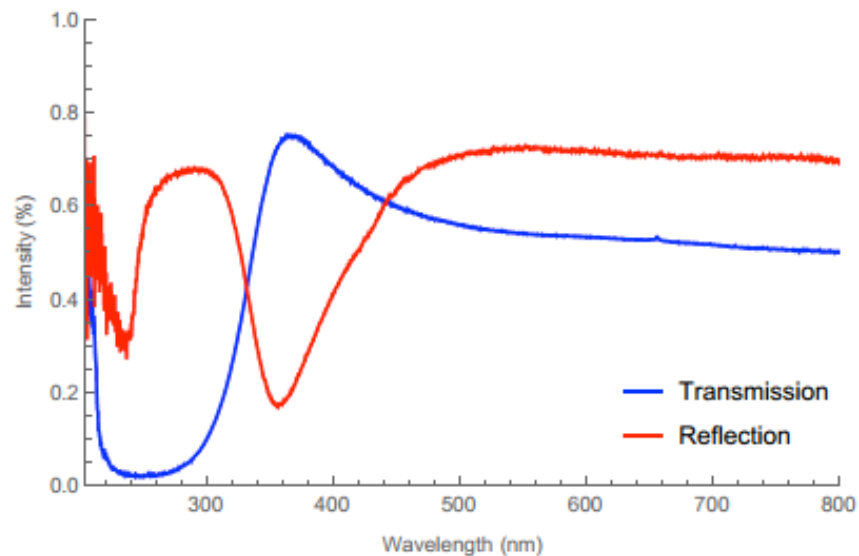

Figure 6: Example Transmission and Reflection Data

Atomic force microscopy (AFM) was also performed on a pre-annealed sputtered sample and a pre-annealed sample made by pulsed laser deposition. The scans were done on an MFP-3D in attractive

mode over a 10μm x 10μm section. The scans were then uploaded into the accompanying MFP-3D software which ran statistical analysis on the scans, specifically looking at roughness values.

3. Results

Using the thickness measurements at several points around the samples it was found that the samples grew at a rate of about 2nm/min. The estimated and actual thicknesses can be found in table 2, where N/A entries mean that a sample wasn't made for that goal and each goal follows the 2nm/min assumption. By taking multiple measurements across the sample it was also found that all the samples had a thickness variance of ±3nm or less.

Goal (nm)	Actual 5%pO_2 (nm)	Actual 1%pO_2 (nm)
60	61	60
30	26	27
30	22	N/A
30	28	N/A
20	19	N/A
15	18	17

Table 2: Goal Thicknesses and Actual Thicknesses

This shows that while the samples do have uniform thickness, there isn't a guaranteed same thickness across multiple of the same run. For most cases the thickness difference is small (1-2nm), but occasionally outliers do happen, as the 22nm sample shows.

A result of the Raman and grazing incidence x-ray diffraction can be found in Table 3, where a blue highlight means a SiO_2 substrate, a green highlight means a Si<100> substrate, the highlighted number is the reference sample number, and next to each number is the composition in the form of rutile/anatase/brookite. All of the compositions that just say how many phases there are indicate samples on which Raman spectroscopy was inconclusive, and which were unable to the analyzed using GIXRD. Unfortunately the XRD required maintenance before all the samples could be run. One thing to note about the Raman process is that sometimes the sample would be photoactive under Raman spectroscopy. What this means is that when looking at the sample after performing a Raman scan the sample would show a visibly brighter patch around where the Raman measurement took place. An example of this can be seen in Figure 5. This seemed to be randomly distributed among the samples, and doesn't follow any trend, but the samples that showed high photoactivity were more likely to produce noisy Raman signals. Literature suggests that photoactivity in TiO_2 can be attributed to oxygen vacancies, so this tells us that some samples may have a noticeable oxygen deficiency[19][20].

Time (min)	pO2 (%)							
	1		5		10		20	
7.5	17	2 phases	3	1/19/80				
	21	1 phase						
10			18	2 phases				
			22	1 phase				
15	7	1 phase	2	1/0/99				
	9	1 phase	4	1/85/15				
			11	40/0/60				
			12	1 phase				
			20	1 phase				
30	8	1 phase	1	100/0/0	5	100/0/0	6	100/0/0
	10	1 phase	23	85/15/0				

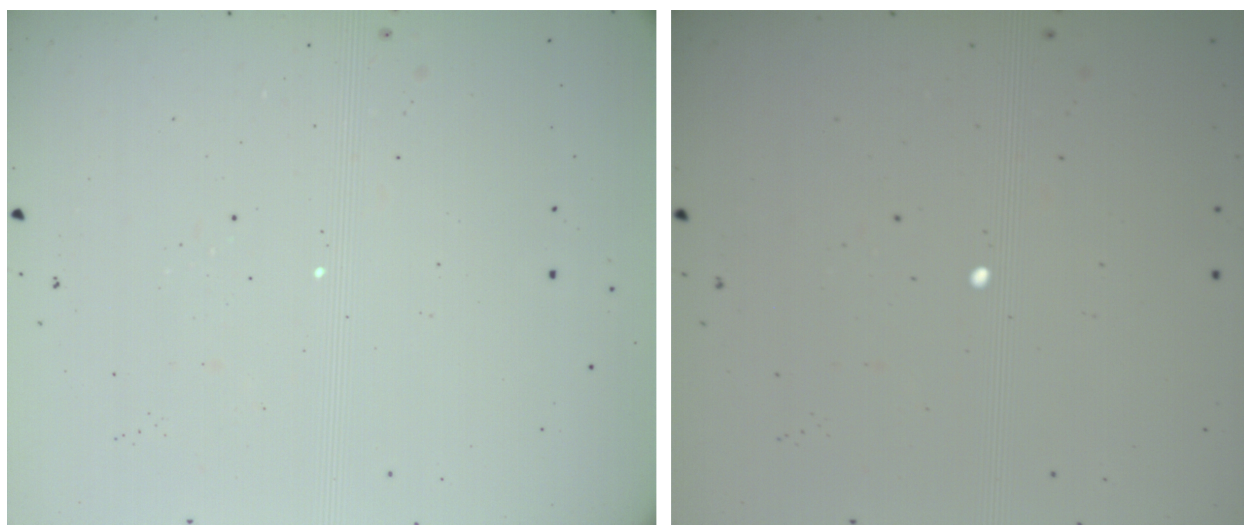Table 3: Sample Compositions

Figure 7: Laser Indicating Location of Raman Scan (Left) and Residual Photoactivity After Scan (RIght)

In order to interpret these data, a plotting program was written in Mathematica. This program is a form of plotting known as parallel coordinates, and it rescales a column of data to be between zero and one and plots a line for each row, with each row representing a different sample. This allows for multiple different parameters to be plotted on independent axes but still allows for tracking of each individual sample by following a specific line. For this program, each line is colored according to a heatmap that can look at any column of data for the coloring. Figure 4 shows all the samples that we have identified phase fractions for being color coded based on the thickness of the sample.
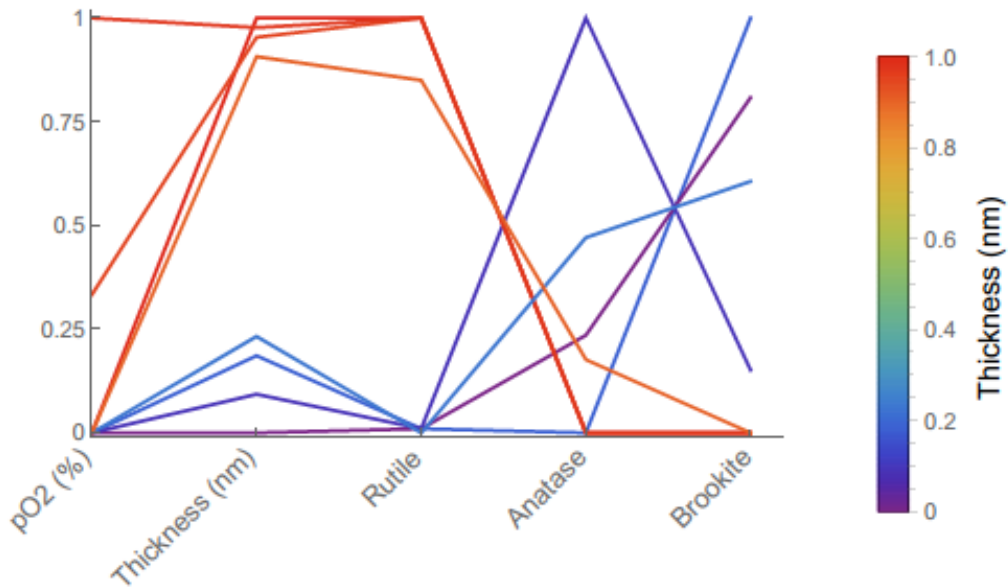
Figure 8: Phase Fractions Parallel Coordinates Plot

These data show that the rutile phase only forms for the thicker samples, while anatase and brookite prefer the thinner samples. This matches well with the pulsed laser deposition results. These data also show that rutile formed for all pO_2 values. Although this seems in contradiction with the literature, the highest pO_2 used in this experiment was 20%, or 0.5mTorr this is still a smaller pressure than described in the papers[17],[18].

Unfortunately due to the missing data no pO_2 claims can be made about anatase and brookite. It is able to say that the claim that the thinnest samples will favor anatase may not be correct, as the pulsed laser deposition experiment suggested.

The AFM work, shows that the sample made from the sputtering system is much smoother than the sample made via pulsed laser deposition. For example, the amplitude maps of ~30nm sputtered and pld samples can be seen in figure 5. Gwyddion calculated an rms roughness of 0.603 nm for the sputtered sample and 1.29 nm for the pulsed laser deposition sample, showing the sputtered being noticeably smoother.
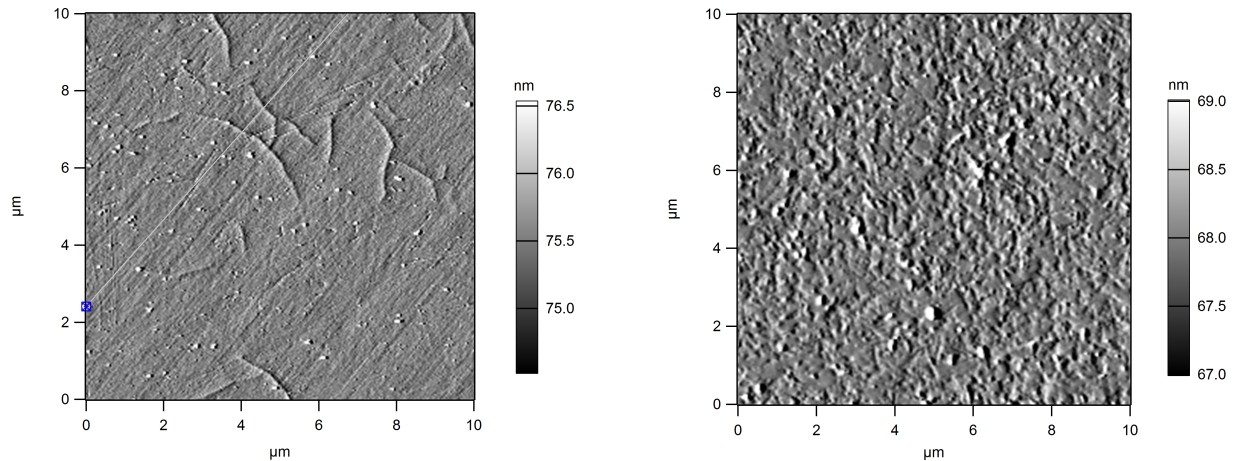
Figure 9: AFM Scans of Amorphous Sputtered (left) and Amorphous PLD (right) Samples

4. Comparison Between Sputtering Results and Pulse Laser Deposition Results

The primary difference between the sputtering and pulsed laser deposition samples is the thickness gradient. The sputtered samples showed a uniform thickness with at most a ±3nm difference. This variation also appeared to be consistent across all samples. On the pulsed laser samples there is a thickness gradient of about 30%[6], which corresponds to a difference in thickness of 6-22nm depending on the sample. The sputtering samples also appear to be much smoother than the pulsed laser samples. These two features are expected based on the difference in how the systems work. In sputtering, a thin layer of material is deposited everywhere within the vacuum chamber, while in pulsed laser deposition systems, the deposition is based on the location and geometry of the plasma plume. This is the main reason for the low thickness gradient in the sputtered samples and the large thickness gradient in the samples made with pulsed laser deposition. The roughness has to do with ejected material from the target. In pulsed laser deposition, the plasma plume contains clusters, while the sputtering is just small amounts of atoms being released, without these clusters. This is why the pulsed laser samples are so much rougher than the sputtered samples[8].

In terms of results, both systems showed that rutile prefers thicker samples, although the specified thickness as to where the large fractions of rutile show up are noticeably different among the two systems. In the pulsed laser deposition samples rutile appeared around 50 nm and became the dominant phase around 75nm[6] while the sputtering shows pure rutile samples around 60 nm. The sputtering system also doesn't show thickness correlation on the thinner samples to say that thinner samples prefer anatase, as was suggested by the pulsed laser deposition experiments.

When a pO_2 study was done using pulsed laser depositions the results were as seen in Figure 6, where each box is a represented by the composition of that sample, with red being for rutile, blue being for brookite, and green being for anatase. For a comparison, the 0.1mTorr corresponds closely to the 5% pO_2 and the 0.5mTorr corresponds to the 20% pO_2.

Figure 10: Sputtering pO₂ study (top) and PLD pO₂ study (bottom)

This pulsed laser deposition study shows that at low pO₂ values rutile forms for much thinner samples. It doesn't agree with the samples smaller than 30nm, though, since the sputtering results showed that those were still all or mostly rutile. Other differences show up in how brookite can be seen at thicknesses above 30nm, which was not seen in the sputtering samples. Overall the pulsed laser deposition results show anatase at small thickness, brookite in the middle, and then rutile in the biggest while the sputtering didn't see a strong enough trend to say that thinner samples favored anatase over brookite.

5. Conclusion

Amorphous TiO₂ was successfully deposited onto SiO₂ and Si<100> using RF sputtering. These samples are very uniformly thick, with a thickness variation of ±3nm, and with the parameters used grow at a rate of about 2nm/min. These samples are both more uniform in terms of thickness and less rough than similar samples made via pulsed laser deposition. A post-anneal analysis showed that all three polymorphs of TiO₂ were created, as desired. This analysis also showed that the thicker samples (around 60nm) formed almost pure rutile samples (in some cases actually pure rutile samples), and this didn't seem to depend on the pO₂ present, although all pO₂ values were within the range that rutile is expected to grow. The thinner samples showed both brookite and anatase polymorphs at various concentrations, but a correlation between thickness composition was not identified. Overall the general thickness to composition plot is very similar to the thickness study performed via pulsed laser deposition, but disagree as to where the thicknesses are. The pulsed laser deposition pO₂ study is in general agreement with composition vs thickness vs pO₂ though. Unfortunately, though, a thorough pO₂ investigation could not be performed using sputtering due to machine failure. Future work should be done in order to fully map out the pO₂ influence on polymorph synthesis. The overall conclusion of this

study shows that sputtering offers a more uniformly thick sample, and therefore more parameter control, than the pulse laser deposition method and that preliminary results show that the two systems seem to agree with one another in terms of pO_2 and thickness outcomes.

6. Future Work

More work is planned to continue this study in the future. One aspect of it will be to create more samples with 10% and 20% pO_2, as there are only one for each of those oxygen partial pressures. Also, x-ray diffraction should be performed on all of the samples that were inconclusive under Raman. This was planned for this study, but machine failure halted that progress. Once the machine is fixed this can be completed. Another step that should be done is to create samples with larger total partial pressures of oxygen to see if they follow a similar trend to the samples made via pulsed laser deposition. This wasn't done in this study since the vacuum chamber in which samples are made can not exceed a pO_2 of 20%. With the current synthesis protocol (that uses 2.5mTorr total working pressure) this allows for a maximum of 0.5mTorr pO_2 of oxygen. In order to create higher pressure pO_2 samples the total working pressure of the deposition will have to be changed. There is a potential that the samples won't be amorphous at the higher pressure, and if this is the case then a new protocol using the other control parameters (power, substrate to target distance) might have to be changed as well.

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Appendix: Parallel Coordinates Code With Example Output

*****KNOWN ISSUES*****

1)   If a column of data does not have any cells that are strictly numbers the rescaling function will and plot will produce errors for that column, but the code should still work (and just ignore that column)
        If a column has exactly one cell that is strictly a number it will rescale the entire column to that value and all lines will pass through that point. Oddly enough the filler lines that span gaps will still function correctly as if the lines hadn't passed through that point which means the code acknowledges that the data doesn't have a value there, despite the fact that it's plotting a value
        If a column as two or more cells that are strictly numers then this error won't occur

2)   If the column that you chose to scale your colors off of has a missing value the code won't know what color to assign that line.
        Temp(?) Solution Turn that line black
****

MultiplotV4 will import an excel sheet and plot it so that each column is normalized and each row is connected with a line.

MultiplotV4 will skip any empty cells and draw lines to the two points around the empty line.
For example, if there's data such as {1, ,3} (where the data for 2 doesn't exist) the plot will draw a line from 1 to 3

MultiPlotV4 can draw circles at the two points adjacent to a gap in data in order to signify that it is discontinuous data

If there is a column of data that has all the same value MultiplotV4 will do one of two things.
        If the absolute value of the column is between 0 and 1 it will assign that column to be the absolute value of what it was.
        If the absolute value of the column is larger than one then it will assign the column to be 0.5

Note MultiplotV4 is recommended over V3. MultiplotV4 can do the same thing as V3 but chooses line colors for missing sections based on index numbers instead of coordinate values. This is better since if repeating coordinate values existed V3 wouldn't know what color to chose to for that line. V4 also has a protocol for when all values of a column of data are the same, which would produce an error in V3

Plot with Gaps

Note "Plot with Gaps" needs to be run in order to run the rest of the program later on

Works by turning all values that aren't strictly numbers into "Null" inputs before rescaling each column to sit between 0 and 1 and plotting the data. "Null" inputs are ignored in the plotting by default

```
(*Imports the data*)
data = Import["T:\\Physics\\Tate Group\\Share\\Rivella,
    David 2017-current\\Mathematica\\Plotter\\test3.xlsx"]
```

```
{{{Index, Num 1, Num 2, Num 3, Num 4, Num 5, Num 6, Num 7, Num 8},
  {1., 8., 96., 91., 51., 56., 32., 0.2, 97.}, {2., 8., 88., , , 65., 55., 0.2, 19.},
  {3., 8., 59., 59., 32., 76., 57., 0.2, 41.}, {4., 8., 44., , , , 94., 0.2, 94.},
  {5., 8., 16., 1., 22., 41., 7., 0.2, 38.}, {6., 8., 73., 88., , 61., 88., 0.2, 23.},
  {7., 8., 37., 100., 89., 76., 4., 0.2, 26.},
  {, 8., 33., 84., 0., 75., 17., 0.2, 45.}, {9., 8., 4., 29., 33., 18., 36., 0.2, 14.},
  {10., 8., 66., 71., 0., 12., 43., 0.2, 95.}}}
```

```
(*Gets rid of first set (top row in excel)
 and reduces the amount of subsets
 (takes the set of {sets of sets} and reduces it to a set of sets)*)
cleanedData = data[[1, 2 ;; -1]]
```

```
{{1., 8., 96., 91., 51., 56., 32., 0.2, 97.}, {2., 8., 88., , , 65., 55., 0.2, 19.},
 {3., 8., 59., 59., 32., 76., 57., 0.2, 41.}, {4., 8., 44., , , , 94., 0.2, 94.},
 {5., 8., 16., 1., 22., 41., 7., 0.2, 38.}, {6., 8., 73., 88., , 61., 88., 0.2, 23.},
 {7., 8., 37., 100., 89., 76., 4., 0.2, 26.}, {, 8., 33., 84., 0., 75., 17., 0.2, 45.},
 {9., 8., 4., 29., 33., 18., 36., 0.2, 14.}, {10., 8., 66., 71., 0., 12., 43., 0.2, 95.}}
```

```
(*Checks for cells without strictly numbers*)
numTest = Table[
  Array[
    NumericQ[cleanedData[[n, #]]]
      &, Length[cleanedData[[n, All]]]],
  {n, Length[cleanedData[[All, 1]]]}]
```

```
{{True, True, True, True, True, True, True, True, True},
 {True, True, True, False, False, True, True, True, True},
 {True, True, True, True, True, True, True, True, True},
 {True, True, True, False, False, False, True, True, True},
 {True, True, True, True, True, True, True, True, True},
 {True, True, True, True, False, True, True, True, True},
 {True, True, True, True, True, True, True, True, True},
 {False, True, True, True, True, True, True, True, True},
 {True, True, True, True, True, True, True, True, True},
 {True, True, True, True, True, True, True, True, True}}
```

```
(*makes a list of all cells without strictly numbers*)
nulls = Position[numTest, False]
```

```
{{2, 4}, {2, 5}, {4, 4}, {4, 5}, {4, 6}, {6, 5}, {8, 1}}
```

```
(*replces without strictly numbers with Null*)
nullData = ReplacePart[cleanedData, nulls → Null]
```

```
{{1., 8., 96., 91., 51., 56., 32., 0.2, 97.},
 {2., 8., 88., Null, Null, 65., 55., 0.2, 19.},
 {3., 8., 59., 59., 32., 76., 57., 0.2, 41.},
 {4., 8., 44., Null, Null, Null, 94., 0.2, 94.},
 {5., 8., 16., 1., 22., 41., 7., 0.2, 38.}, {6., 8., 73., 88., Null, 61., 88., 0.2, 23.},
 {7., 8., 37., 100., 89., 76., 4., 0.2, 26.},
 {Null, 8., 33., 84., 0., 75., 17., 0.2, 45.},
 {9., 8., 4., 29., 33., 18., 36., 0.2, 14.}, {10., 8., 66., 71., 0., 12., 43., 0.2, 95.}}
```

Page 19 of 25

```
(*Rescales each number based on its
 columns data so that the column is between 0 and 1
 Uses the same math as the "Rescale" function. The "Rescale"
 function uses the Max and Min operations, which can't handle "Nulls"
 y and x coorespond to column and row number,
respectively. To visualize these number you can use the "Grid" function*)
rescale[y_, x_] :=
 Part[
  nullData[[y, x]] /
    (TakeLargest[nullData[[All, x]], 1] - TakeSmallest[nullData[[All, x]], 1]) -
   TakeSmallest[nullData[[All, x]], 1] /
    (TakeLargest[nullData[[All, x]], 1] - TakeSmallest[nullData[[All, x]], 1]), 1]

(*Rescales each column to be between 0 and 1 by using the previously defined
 "rescale" function *Note* not to be confused with the "Rescale" function*)
(*If the column of data is all the same number one of two things happens:
      -if the absolute value of the number is
    between 0 and 1 it returns the absolute value of the number
       -if the absolute value of the number is not
    between 0 and 1 it returns 0.5*)
normData = Table[
  Array[
   If[
     TakeLargest[nullData[[All, #]], 1] == TakeSmallest[nullData[[All, #]], 1]
       && Abs[Part[TakeLargest[nullData[[All, #]], 1], 1]] ≤ 1,
     Abs[Part[TakeLargest[nullData[[All, #]], 1], 1]],
     If[TakeLargest[nullData[[All, #]], 1] ==
       TakeSmallest[nullData[[All, #]], 1], 0.5, rescale[n, #]]]
    &, Length[nullData[[1, All]]]],
   {n, Length[nullData[[All, 1]]]}]
{{0., 0.5, 1., 0.909091, 0.573034, 0.6875, 0.311111, 0.2, 1.},
 {0.111111, 0.5, 0.913043, -0.010101 + 0.010101 Null,
  0. + 0.011236 Null, 0.828125, 0.566667, 0.2, 0.060241},
 {0.222222, 0.5, 0.597826, 0.585859, 0.359551, 1., 0.588889, 0.2, 0.325301},
 {0.333333, 0.5, 0.434783, -0.010101 + 0.010101 Null,
  0. + 0.011236 Null, -0.1875 + 0.015625 Null, 1., 0.2, 0.963855},
 {0.444444, 0.5, 0.130435, 0., 0.247191, 0.453125, 0.0333333, 0.2, 0.289157},
 {0.555556, 0.5, 0.75, 0.878788, 0. + 0.011236 Null, 0.765625, 0.933333,
  0.2, 0.108434}, {0.666667, 0.5, 0.358696, 1., 1., 1., 0., 0.2, 0.144578},
 {-0.111111 + 0.111111 Null, 0.5, 0.315217, 0.838384, 0., 0.984375, 0.144444, 0.2,
  0.373494}, {0.888889, 0.5, 0., 0.282828, 0.370787, 0.09375, 0.355556, 0.2, 0.},
 {1., 0.5, 0.673913, 0.707071, 0., 0., 0.433333, 0.2, 0.975904}}
```

```
(*Grabs the first set (top row in excel)*)
labels = data[[1, 1]]
```

{Index, Num 1, Num 2, Num 3, Num 4, Num 5, Num 6, Num 7, Num 8}

```
(*Forms the x-axis labels based on the "labels" set*)
center = Row[{#, Invisible[#]}, ""] &;
xticks =
 Table[{n, center@Rotate[Style[ToString[labels[[n]]], FontSize → 12], 45 Degree]},
   {n, Length[labels]}]
```

{{1, $\underset{Index}{}$ }, {2, $\underset{Num\ 1}{}$ }, {3, $\underset{Num\ 2}{}$ }, {4, $\underset{Num\ 3}{}$ },

 {5, $\underset{Num\ 4}{}$ }, {6, $\underset{Num\ 5}{}$ }, {7, $\underset{Num\ 6}{}$ }, {8, $\underset{Num\ 7}{}$ }, {9, $\underset{Num\ 8}{}$ }}

```
(*Which column the coloring is based off of*)
refColumn = 3;

(*Determines the colors of the lines based on the selected colomn,
for example: cleanData[[n,1]] uses the first data column*)
plotColors = Table[
  If[NumericQ[normData[[n, refColumn]]] == True, ColorData["Rainbow"] /@
    Range[normData[[n, refColumn]], normData[[n, refColumn]]], Black],
  {n, Length[cleanedData[[All, 1]]]}]]
```
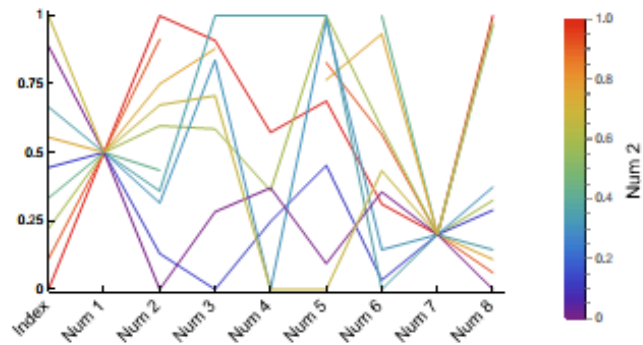
{{■}, {■}, {■}, {■}, {■}, {■}, {■}, {■}, {■}, {■}}

Page 21 of 25

```
dataPlot =
 ListLinePlot[normData, (*PlotMarkers→{Graphics[{Disk[{0,0}]}],0.025},*)
  PlotRange → {{1, Length[data[[1, 1]]] + 0.2}, {-.01, 1.02}},
  Frame → {{True, False}, {True, False}},
  FrameTicks → {{{0, 0.25, 0.5, 0.75, 1}, {None}}, {xticks, {None}}},
  PlotStyle → plotColors,
  PlotLegends → BarLegend[{"Rainbow", {0, 1}},
   LegendLabel → Placed[center@Rotate[labels[[refColumn]], 90 Degree], Right]]]
```

Plot with gaps filled in

Works by deleting all Null inputs that sit at the beginning or end of a row. It then looks for the points adjacent (before and after) where the remaining Nulls are, filtering for midpoints, and making lists of the endpoint pairs. It then finds the appropriate color each pair and creates lines and dots to put onto the graph

note Some functions produce error codes but still work. This is because it's writing to a list and appending to it at the same time. Since it can't write to a list index that doesn't exist an error is given, but since it's also appending to it the code works.

```
(*checks for and deletes empty cells at the beginning or end of a row,
these empty cells interfere with line drawing, uses the index numbers*)
endNulls = Array[
    If[nulls[[#, 2]] == 1 || nulls[[#, 2]] == Length[normData[[1, All]]],
        endNulls[[#]] = "Voided", endNulls[[#]] = nulls[[#]]] &, Length[nulls]];
endNullsDel = DeleteCases[endNulls, "Voided"]
```

```
{{2, 4}, {2, 5}, {4, 4}, {4, 5}, {4, 6}, {6, 5}}
```

```
(*grabs all the cells before and after the empty cells and assigns*)
adjacentNullPoints =
    Flatten[Array[{List[endNullsDel[[#, 1]], endNullsDel[[#, 2]] - 1], List[
        endNullsDel[[#, 1]], endNullsDel[[#, 2]] + 1]} &, Length[endNullsDel]], 1];
(*Sorts the grabbed cells into increasing order*)
sortedNullAdjacents = Sort[adjacentNullPoints]
```

```
{{2, 3}, {2, 4}, {2, 5}, {2, 6}, {4, 3},
 {4, 4}, {4, 5}, {4, 5}, {4, 6}, {4, 7}, {6, 4}, {6, 6}}
```

```
(*deletes and points that aren't endpoints by
 deleting all adjacent points that are also null points*)
sortedNullAdjacentsDel =
 DeleteCases[sortedNullAdjacents, Alternatives @@ endNullsDel]
```

```
{{2, 3}, {2, 6}, {4, 3}, {4, 7}, {6, 4}, {6, 6}}
```

```
(*groups every other point together to give two endpoints to a line*)
start = sortedNullAdjacentsDel[[1 ;; -1 ;; 2]];
finish = sortedNullAdjacentsDel[[2 ;; -1 ;; 2]];
linePoints = Array[
  List[start[[#]], finish[[#]]] &, Length[start]]
```

```
{{{2, 3}, {2, 6}}, {{4, 3}, {4, 7}}, {{6, 4}, {6, 6}}}
```

```
(*maps the endpoints onto the normalized data*)
linePairs =
 Array[
  List[
    List[linePoints[[#, 1, 2]],
      normData[[linePoints[[#, 1, 1]], linePoints[[#, 1, 2]]]]],
    List[linePoints[[#, 2, 2]], normData[[linePoints[[#, 2, 1]],
      linePoints[[#, 2, 2]]]]]]
    &, Length[linePoints]]
```

```
{{{3, 0.913043}, {6, 0.828125}},
 {{3, 0.434783}, {7, 1.}}, {{4, 0.878788}, {6, 0.765625}}}
```

```
(*Indexes and then deletes all line pairs that have a null in the first
 or second point. These occur if the first or last datapoint for a row
 is missing as well as ones immediately following or preceding it*)
nullLines1 = Array[
    If[NumericQ[linePairs[[#, 1, 1]]] == False, voidedLinePairs[[#]] = #, "GoodLine"]
      &, Length[linePairs]];
nullLines2 = Array[
    If[NumericQ[linePairs[[#, 2, 2]]] == False, voidedLinePairs[[#]] = #, "GoodLine"]
      &, Length[linePairs]];
nullLinesDel = DeleteCases[nullLines2, "GoodLine"];
linePairsDel = Delete[linePairs, List /@ nullLinesDel]
```

```
{{{3, 0.913043}, {6, 0.828125}},
 {{3, 0.434783}, {7, 1.}}, {{4, 0.878788}, {6, 0.765625}}}
```

```
lineColors = Delete[
  Flatten[Array[plotColors[[linePoints[[#, 1, 1]]]] &, Length[linePoints]], 1],
  List /@ nullLinesDel]
```

{■, ■, ■}

```
lines = Array[Graphics[{lineColors[[#]], Thick, Dashed, Line[linePairsDel[[#]]]}] &,
  Length[linePairsDel]]
```

{-----------------------, _____ , ----------------------}

```
Show[
 dataPlot (*the original plot (with gaps)*),

 ListPlot[linePairs, PlotStyle → lineColors,
  PlotMarkers → {Graphics[{Circle[{0, 0}]}], 0.03}]
  (*add dots before and after a gap in data*),


 lines (*adds the lines between the gaps in data*)]
```

Page 25 of 25