



Growth and Re-Crystallization of Titanium Dioxide and its Uses in Dye-Sensitized Solar Cells.

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Program Information:
National Science Foundation
Grant #0852057

Research Experience for Undergraduates
Summer 2009

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Abstract

Solar cells have long been the energy of the future, but there exist two major obstacles: cost and efficiency. With the emergence of Dye-sensitized solar cells and other low cost methods for producing solar cells, a more efficient way to produce these low cost materials was needed. By maximizing the grain growth of titania using in-situ TEM heating the conductive properties of titania, become much more efficient and viable for solar cell and other uses. The titania is deposited onto molybdenum grids in its amorphous stage using RF sputtering. The samples are heated to temperatures ranging from 200-400°C, and the nucleation and crystallization is observed in the TEM. Although an optimal temperature was not conclusively determined, a solid method of analysis was determined. Using classical phase change kinetics and simple image analysis to find the crystalline volume fraction we were able to produce an analysis of the density and percentage of the sample that was crystallized. From that, the average grain size of each sample was calculated. Further investigation is needed to determine what temperature produces the best grains and how this can be applied for use in low cost solar cells.

Introduction

Titanium Dioxide has long been used in many common applications such as paint, sunscreen, other pigments, and more recently as a photo-catalyst. Titanium Dioxide, also known as titania, is a very good candidate for low cost solar cells, particularly in its Anatase form. Due to its low production cost, it would significantly reduce the cost of the solar cells on the market. In order to maximize its conductivity, a large grain size is preferable due to the reduced number of boundaries present. In order to observe the crystallization, in-situ heating was used in the TEM, and the images from the TEM gave us the data needed for the analysis. This method allows real-time observation of the crystallization, allowing for better data collection and analysis. The objectives for this project include attempting deposition of our own samples, in order to reduce waiting time for samples deposited elsewhere, obtaining data from the TEM using various temperatures, and verifying that the phase of the sample is the Anatase phase, using electron diffraction. Once these are accomplished, the final objectives will be to analyze the data to determine crystalline volume fraction and grain density, and then finally determine the average grain size.

Broader Impact

Although the research done for this project did not involve any immediate applications, there are future areas of research that show significant promise for future applications. One of the most interesting areas of future research is in dye-sensitized solar cells. One of the major problems with current solar cells is the cost of producing a cell with an acceptable efficiency.⁽⁴⁾ By using titania instead of silicon, the cost of production can be significantly reduced. This will lead to cheaper cells, which in turn will lead to a wider availability of energy. By determining the best way to produce pure and large crystals we will be able to further reduce costs while maximizing efficiency.

Procedure

Sample Preparation

The samples all need to be mounted on TEM grids in order to observe them in the TEM. These grids are approximately 3mm in diameter and only about 100um thick. The grids we use are made of Molybdenum with a thin carbon or silicon coating. The titanium dioxide sample is deposited onto these grids using a variety of procedures. The methods we attempted here at SDSMT included vacuum evaporation and a form of deposition using an ion beam miller. For the evaporation method, we tried a variety of procedures. The most successful attempt utilized a tungsten boat covered with a molybdenum boat with a small hole drilled over the sample. The TEM grids were suspended about 5cm above that. The boat was resistively heated with a 20 A current until it was white hot. The heating lasted for forty-five minutes and gave us varying thicknesses of deposition, for unknown reasons. This method was met with limited success and never produced evenly distributed grids, though it was superior to other attempts with no molybdenum boat cover. The grids we ended up using the most came from *South Dakota State*, where they used a RF sputterer to produce 100um thick evenly distributed samples on the grids.

TEM operation & Grid heating

The main method used for collecting data was through direct observation in the TEM. The TEM used in our lab is a Hitachi H7000-FA TEM, operated at 125 KV. The sample is inserted into the TEM using the Gatan Model 628 single-tilt heating holder, and the chamber is then pumped down to about 10^{-3} Pa. Once the sample is in vacuum, the TEM filament is heated and the sample is inserted into the beam path. There is a phosphorescent screen for direct observation, or a CCD camera that take high-resolution images.

For our data collection, we set up the camera to take series of images at set time intervals using the program iTEM. This allowed us to have evenly spaced pictures over a long period to watch the crystallization of the sample occur. In general, we used a standard magnification of 20,000X to obtain clear and focused pictures. Any closer than that did not reveal any more detail. There were very fine controls for manipulating the sample holder, making it simple to move the sample around and view different section of material. The titanium dioxide required heats between 200°

C and 600° C to crystallize into its Anatase phase. Lower temperatures produce no change, and higher temperatures produce the rutile phase of crystallization, which is not as useful for conductive properties.

A heating sample holder was required to allow us to heat the sample in the TEM. The sample needed to be heated slowly and in stages to make sure it was heated uniformly and that the region of interest stayed in focus and in the center of the screen. This typically involved 100-degree increments up until the final temperature was achieved. The picture series then began and continued until the entire sample changed from amorphous to Anatase. The temperature range that the data was collected in varied from 240° C to 350° C. This range produced the best crystallization time for collecting data, any lower and crystallization did not occur, and any higher made the sample crystallize in less than a minute and in many cases less than 30 seconds which is not enough time to align and image everything properly.

Beam Temperature Measurement

One of the first problems encountered when trying to collect data was the effect of the beam on the sample. It appeared that the electron beam heated the sample up enough to cause only local crystallization and not throughout the whole sample. A series of experiments were conducted to try to quantify and measure this effect. The sample holder used had a thermocouple off to one side of the grid in order to measure the temperature of the grid. The problem with this sensor is that the beam shines on such a small portion of the sample, that the heat did not conduct all the way back to the sensor. In order to figure out how much the beam affected the sample, a low magnification setting of 200x was used to illuminate the entire sample at once. This was done on various samples and the average heating was calculated from that and will be taken into account for data analysis.

Crystallization Verification

One of the key factors to the usefulness of the titanium dioxide samples is the current phase it is in. The amorphous and rutile phases are not useful for solar cells or any other photo conducting processes. This is due to a larger band gap and a lower effective electron mass. Since only the Anatase phase is useful, it is important to verify that the sample is indeed in the right phase. We can quickly rule out the amorphous phase by direct TEM observation of the sample. It is easy to see which parts of the sample are crystallized and which parts are still in the amorphous phase. While it is possible to tell the Anatase and rutile phases apart in this same way, there is a much more reliable and effective method: diffraction patterns and Kikuchi lines. By using Convergent Beam Electron Diffraction (CBED), it is possible to map out the different zones of the individual crystals and identify which phase that crystal is in.

Experiment/Results

Through the *in situ* heating of the titanium dioxide, the various samples were crystallized and a large amount of data was collected. The samples were heated for the various times and temperatures listed in table 1 below. All of the samples were prepared at South Dakota State University, using an RF sputtering technique at room temperature with an Argon flow of 20sccm, to a thickness of 100nm on a molybdenum grid with a carbon or silicon support film.

Deposition of Samples

Our own attempts at preparing samples were met with very limited success. Using a Molybdenum boat with a small hole in it to cover all but the sample TiO_2 seemed to give us the best results. This method covered the tungsten element almost completely so that there was much less contamination while still allowing the titania through. The filament was heated using a variable current, which we set to 20A and let run for about 45 minutes. The deposition occurred in a bell jar evaporator at 10^{-4} torr. After cooling everything down, the sample was observed under the TEM. This observation showed that although some titania was deposited, it was not evenly distributed and there was still a high amount of contamination. Attempts to re-crystallize the sample did not work, even at temperatures that would crystallize a normal sample in under a

minute. Since preparing our own grids was not very feasible, we instead used the uniform and reasonably reliable ones made at South Dakota State.

Data Collection

Table 1 lists of all the samples that data was collected on and the parameters of the data collection. For each sample, data was collected at an evenly spaced time intervals over the entirety of the heating process. In general, this time step was between three and five seconds. At each of these intervals, a picture was taken with Olympus SIS Veleta 14-bit, 4-megapixel CCD side-mount camera in the TEM. This picture shows a small, but representative fraction of the sample, which is then used to ultimately determine the average grain size, of the sample.

Table 1- TiO₂ sample collection specifications

Sample Designation	Magnification	Heating Time (seconds)	Temperature (°C)	Notes/support film
A7*	20,000x	~1400	240	Beam area only/C
A8*	20,000x	~600	275	Beam area only/C
B6**	12,000x	~1800	300	Beam area only/C
C7	20,000x	~300	325	Si
C8	20,000x	~300	300	Si
C10	20,000x	~7200	260	Beam area only/Si

* Sample was reheated to 300° C to finish crystallization

** Sample was reheated at 350° C to finish crystallization

The first step in the analysis process is determination of the crystalline volume fraction. This is done by taking a series of around ten evenly spaced pictures from the data set and separating the amorphous part from the crystallized part. To do this, we used the picture editing software, Gimp, to color the amorphous parts blue and the crystallized parts red. Once the set of pictures was made up of only those two colors, they were transferred into the Digital Micrograph program, where we used a script to take the picture and give us back the percentage of the picture, which was red (crystallized). It is then possible to take this set of data and graph it to see how quickly the sample crystallizes. This growth can be modeled by using equation (1) below, which was obtained from previous research in this field⁽³⁾

$$X_c(t) = 1 - \exp\{-[(t-t_0)/t_c]^3\} \quad (1)$$

Where X_c is the fraction of the sample that is crystallized, t_0 is the initial time and t_c is the characteristic crystallization time.

The next part of the analysis is the counting of the grains that appear in each picture. This was manually done by pure observation of the pictures. From the number of grains it was easy to determine the grain density at each point since the area of the picture is known. From this data, it is possible to calculate an average grain size. Although this is not part of what was done in this project it will be an important part in future analysis and is worth mentioning.

Beam Heating Measurement

One of the first obstacles that needed to be overcome was the problem of beam heating in the TEM. This heating caused only localized areas of the sample to crystallize while heating. By using some previous crystallized samples, some partially crystallized samples, and some completely amorphous samples, a range of temperature differences was found to be caused by the TEM beam itself. Since the heating element and sensor are off to one side of the heating holder, the very fine and focused beam did not register on the overall temperature.

This was first discovered when heating at a low temperature and then attempting to look at other areas of the sample. It was discovered that only the area that was illuminated by the beam during heating, crystallized, leading us to believe that the beam was heating up that area of the sample beyond the temperature of the rest of the sample. Since there was no way to have the holder register that localized heat change, a method for determining the change in temperature was needed. By expanding the beam in low magnification mode, we were able to spread the beam evenly over the entire sample so that it was now heated everywhere instead of just in a localized area. In table 2 below, the different samples and temperature differences are noted.

Table 2- Beam Heating Measurements

Sample	Magnification	Voltage (KV)	Initial Temp (°C)	Final Temp (°C)	Change (°C)
090604B10	100x	100	18.62	24.9	6.28
090604B10	100x	125	18.8	27.4	8.6
090604A10	100x	125	21	28.5	7.5
090604A10	100x	100	20.5	25.5	5
A8	200x	100	20.03	26.25	6.22
A8	200x	125	20.85	28	7.15

This gives an average temperature change of 5.83 °C for 100KV and 7.75 °C for 125KV. All the samples crystallized during research were done at 125KV so we can assume the temperature was at least seven degrees higher.

This test is not very conclusive since it modifies several things as compared to the normal crystallization process. First, the beam is much less concentrated in this test, in order to get the whole sample to heat up instead of just the one area. Also in low magnification mode, some of the lenses are moved around so the beam is not going through as many lenses to get to the sample. However, both these factors would lessen the heating, so we can assume that the beam heating is probably $>8^{\circ}\text{C}$. This difference can be very significant when the heating temperature is close to the crystallization threshold.

Phase Verification

The final part of the experimental procedure was to attempt to verify that the crystals are in the right phase by looking at the different crystalline zone axes. By using Convergent Beam Electron Diffraction (CBED) in the TEM, we are able to find specific patterns that give information on the zone and phase of the crystal being diffracted. In normal diffraction mode, the TEM sends out a parallel beam of electrons that diffract through the entire region that is being viewed. In CBED however, the beam is focused down to a single crystal at one point so that the only diffraction seen is from the one point on the one crystal. This allows the phase and zone of the crystal to be recognized and characterized.

This is one of the most accurate ways to determine what phase the crystal is in, however it is only for the particular crystals you observe, and not generally true for the whole sample. To get a

better idea of the entire sample, random crystals must be observed throughout the sample and if a certain phase is repeated throughout, it can be reasonably assured that the phase is consistent throughout the sample.

In order to find the correct zones of the crystal, careful use of Kikuchi lines is used to follow the patterns back to the axes of the crystal. These Kikuchi lines are patterns of intersecting lines that form patterns in such a way that they lead back to the zones of the crystal. Once a primary zone is found, the diffraction pattern shows heavy symmetry and the spacing of the diffraction pattern and the pattern itself can be used to identify both what zone is being observed, and what phase the crystal is in.

Although the analysis of the CBED patterns was not part of the project, several promising pictures were taken that should provide the necessary data to identify the phase of the crystallized sample.

Discussion

The actual analysis of the data collected was not done during the time spent researching. This will be done later; however, there were many things learned that would need to be applied in the future. The discovery of the beam heating, as shown in Figure 1, was perhaps the biggest setback in the project, for the simple reason that it called into question all data previously collected. However, upon further observation, the beam heating seems to only affect the temperature and the shape and size of the crystals did not seem to be affected when compared to other areas of the sample. Therefore, other than a temperature correction, no other changes were needed.

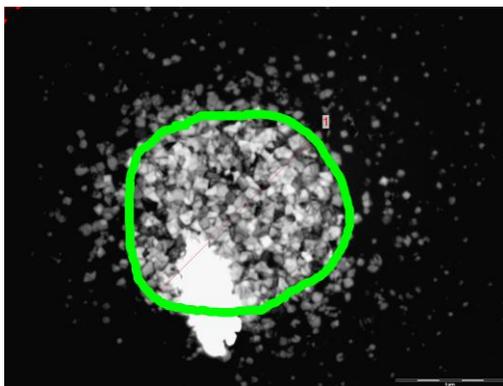


Figure 1: Visual of beam heating, only the area around the beam is crystallized (beam area shown approximately in green), while the outsides of the sample are still mostly in amorphous form

Enough data was collected to perform multiple analyses and hopefully reach a conclusion about the size of grains as related to temperature. In addition, another thing to look at is the size of the grains from the RF sputtered samples as compared to samples prepared through other methods. If the method of growth affects the grain sizes then that could lead to a completely new area of research.

The actual crystallization of the films gave varying results when comparing temperature to time of crystallization. Although the higher temperatures usually crystallized faster, there were some cases where it took a long time for the sample to crystallize even at a high temperature. One factor that had an effect on the time was the starting condition of the sample. As seen in Figure 2, the very “clean” looking samples generally took longer to crystallize, while the “dirty” ones crystallized much faster.

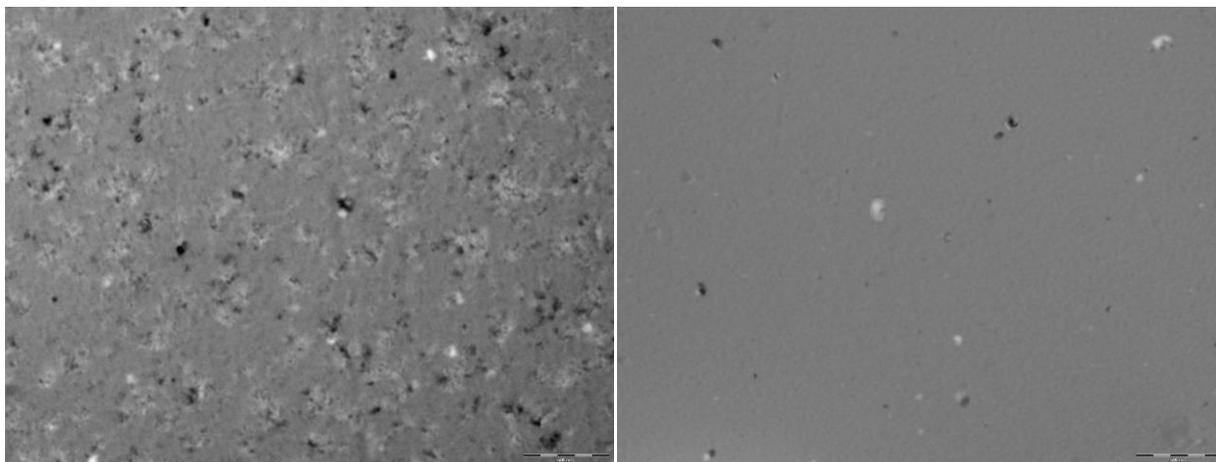


Figure 2: (Left) “Dirty” sample that seems to have black spots everywhere, may be small crystals or chunks of material from the sputtering process. (Right) “Clean” sample has a very even spread of amorphous material. (Crystals in the clean photo were not there at start, but rather formed during the first few minutes of heating)

There are many variables present when trying to crystallize these samples, and these are just a few of the major ones. The data collected throughout the research was taken in order to control these variables as well as provide solid data for analysis in the future. With the crystallized samples, a conclusion should be found and the research can then continue into other areas such as effect of deposition method on crystallization or even further down the road, applications to use in dye-sensitized solar cells.

Conclusions

Titanium dioxide has had many uses in the past and continues to have a wide variety of applications even as technology advances. With the onset of dye-sensitized solar cells, the application of the crystallization of titania has greatly increased and warrants further research. The research done on the re-crystallization of titania should continue and the analysis should be completed in order to maximize the grain size and discover the best size for future use. It is worth noting that the effect of the beam should be taken into account and more research conducted in that area to determine the precise effect of the beam heating on the crystallization to further verify that there are no unexpected effects. Once that is completed research should focus on using optimized crystals in solar cells to maximize efficiency and cost effectiveness.

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Acknowledgments

Support for this program provided by NSF is greatly appreciated. Also thanks to, Dr. Alfred Boysen and Dr. Michael West for their support and direction throughout the REU program. Lastly, thanks to Dr. Phil Ahrenkiel for his guidance and help with my research as well as the training on the TEM and other equipment he provided.