CHARACTERIZATION OF CRYSTALLINE VANADIUM DIOXIDE BY TRANSMISSION ELECTRON MICROSCOPY

by

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This thesis has been reviewed by the research advisor, research coordinator, and department chair and has been found to be satisfactory.

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ABSTRACT

CHARACTERIZATION OF CRYSTALLINE VANADIUM DIOXIDE BY TRANSMISSION ELECTRON MICROSCOPY

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Vanadium dioxide undergoes a phase transition from semiconductor to metal near 68°C, and consequently has many potential optical and electronic applications. The phase change is a structural change between two crystalline phases. Initially amorphous films of vanadium dioxide (VO_2) were annealed to achieve crystallization. These thermally annealed thin films of vanadium dioxide were then characterized through use of Transmission Electron Microscopy (TEM). TEM imaging was used to determine if crystallinity had been achieved at various temperatures. Samples annealed at temperatures as low as 400°C were shown to exhibit crystal formation. The crystal grain size and surface morphology were seen to vary significantly with changing annealing temperature and time. Different crystal sizes are shown to result in different electrical properties [4]. The transition between the two crystal phases has also been observed in electron diffraction patterns of the annealed samples. By heating

the samples in the TEM and analyzing changes in electron diffraction patterns, we have begun to characterize the transition temperature for different particle sizes.

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Chapter 1

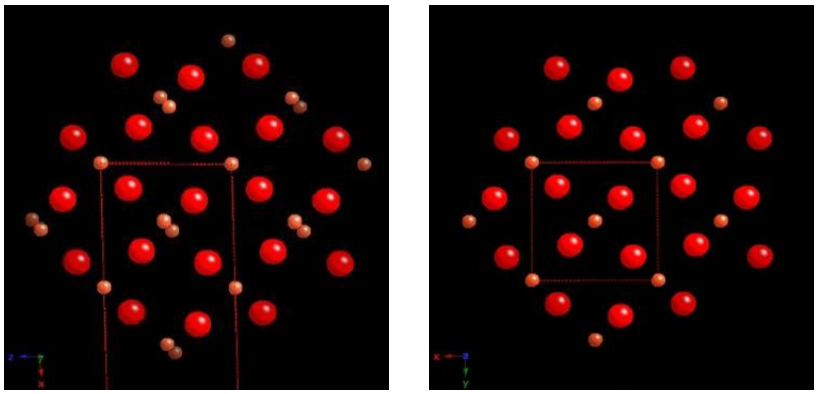
Introduction

1.1 Vanadium Dioxide

Vanadium dioxide (VO_2) has been studied by many researchers because of a remarkable phase transition it undergoes near 68°C. As the temperature increases, crystalline VO_2 is observed to change very quickly from a tetragonal crystal structure to a monoclinic crystal structure. This transition occurs on the order of femtoseconds [1].

The most significant change in this transition occurs when the misaligned vanadium atoms in the tetragonal state align in the monoclinic state. This results in a halving of the unit cell. To see the difference between these two states, see Figure 1.1.

One of the many interesting results of this transition is vanadium dioxide's transition from semiconductor to metal. At temperatures near room temperature, vanadium dioxide is in the tetragonal phase and is observed to behave like a semiconductor. It exhibits relatively high resistivity. As temperature increases, however, crystalline vanadium dioxide experiences an abrupt transition from the tetragonal, semiconductor phase to a monoclinic, metal phase, wherein the resistivity drops several orders



(a) (b)

Figure 1.1 (a) Crystalline VO_2 in the tetragonal (cool) phase. (b) Crystalline VO_2 in the monoclinic (hot) phase. Note how the size of the unit cell changes during the phase transition.

in magnitude.

As a consequence of this transition, vanadium dioxide has many potential electric and optical applications. It is known to exhibit thermochromism, which is defined as a temperature-dependent color change. It has already found many optical uses, such as a coating for "smart windows" that let light in but keep heat out [2], and as an ultraviolet modulator and polarizer [3]. It has also been used for optical and holographic storage, fiber-optical switching devices, laser scanners, missile training systems, and ultrafast optical switching [4].

Because of the phase transition, it has also been suggested that research be done to see if VO_2 would serve as a useful memory storage device that could be electrically or optically switched to represent 0's and 1's. Because of its very fast transition, this could prove to be increasingly useful as computer speeds accelerate.

1.2 Transmission Electron Microscopy

Transmission electron microscopy (TEM) utilizes a beam of very energetic electrons. These electrons pass through the sample, whether it be a crystal, a powder, or a biological specimen. The interaction of the electrons with the sample is magnified and detected on a phosphorescent screen near the base of the microscope. For an observable amount of electrons to pass through the sample, it must be very thin. Consequently, a large amount of time is spent polishing and thinning the samples compared to the amount of time spent actually viewing the samples in the microscope. The images, however, can be viewed at very high resolution, up to the point where the observer can detect individual atoms. This high resolution allows us to view crystallization that we could not observe using other methods. An example of both crystalline and amorphous material is shown in Figure 1.2.

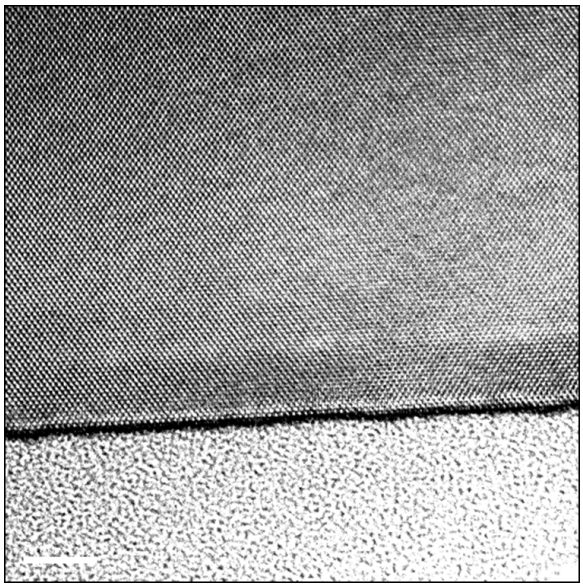


Figure 1.2 A high resolution cross-section TEM image of crystalline silicon and amorphous silicon dioxide. The top portion of the image represents a crystal, with the atoms arranged in lines. The lower portion represents an amorphous layer, with the atoms arranged haphazardly.

In addition to producing high resolution images, another benefit of TEM is that we can switch to diffraction mode to observe the diffraction patterns of different crystal structures. This proved to be useful in our research because the phase transition of VO_2 is due to a change in crystal structure. In the right orientation, we are able to view these phase transitions as changes in diffraction patterns in the transmission electron microscope.

This was useful because we have a heating stage for the TEM. This stage allows us to insert a sample into the microscope, and then control the temperature of the sample by driving a current through the stage and measuring the temperature with a thermocouple. By doing this, we were able to drive the thermal phase transition and observe changes in the images produced in the TEM.

Chapter 2

Methods

2.1 Samples Studied

The University of Central Florida provided the samples used for this study. Silicon wafers were thermally annealed to provide a layer of silicon dioxide (SiO_2). These wafers were then placed in a chamber containing oxygen gas. Vanadium was sputtered onto these wafers until the desired thickness (≈50 nm) of amorphous vanadium dioxide was obtained. A cross-section of the resulting wafer is depicted in Figure 2.1.

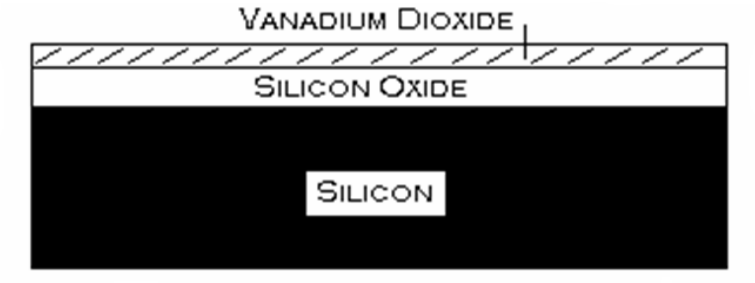


Figure 2.1 A cross section view of the samples used in this study.

Amorphous vanadium dioxide exhibits similar properties to crystalline vanadium dioxide. For example, as temperature increases, the resistance of the sample decreases.

Figure 2.2 shows resistance of a sample of amorphous vanadium dioxide as a function of temperature. However, the magnitude of the resistance change is much smaller than the change in crystalline silicon, which undergoes a resistance change of a several orders of magnitude. To compare this against crystalline VO_2, see Figure 3.1.

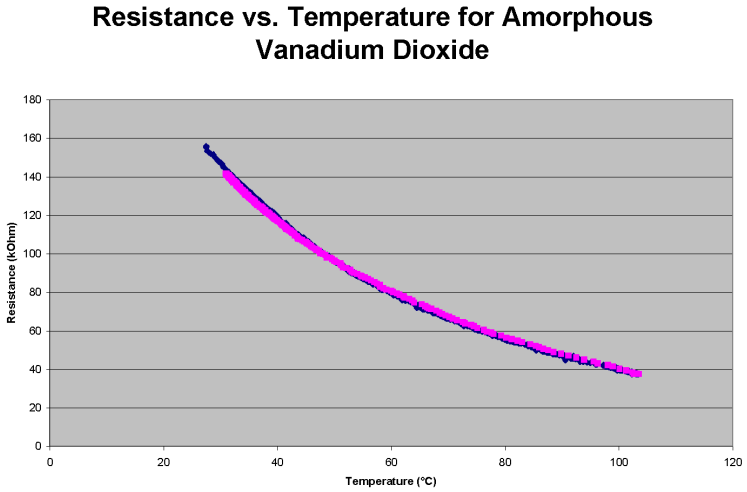


Figure 2.2 Resistance as a function of temperature for an amorphous vanadium dioxide film.

At Brigham Young University, these samples were annealed at various temperatures ranging from 300°C to 1000°C under an argon flow to prevent them from oxidizing further. This study focused on four particularly interesting samples, prepared under the following conditions:

- Annealed at 400°C for seventeen hours,
- Annealed at 450°C for seventeen hours,
- Annealed at 450°C for twenty minutes,
- Annealed at 1000°C for twenty minutes.

These samples are interesting because they span the range of observed results. The sample annealed at 400°C for seventeen hours exhibited small crystal formation in an

essentially continuous film. This also represents the lowest temperature at which we have observed crystal formation. The sample annealed at 450°C for twenty minutes exhibited polycrystalline growth throughout the sample, which has not been observed using other characterization methods. The sample annealed at 450°C for seventeen hours resulted in a film of many larger, contiguous particles. Finally, the sample annealed at 1000°C for twenty minutes resulted in the largest crystal formation we have observed, with large isolated particles available for diffraction analysis.

2.2 TEM Sample Preparation

In order to prepare the samples for TEM analysis, they must be thinned and polished until they are very thin. A target thickness for a TEM sample is usually less than 50 nm. This thinning is accomplished by mounting a small portion of the sample onto a tripod (an example is shown in Figure 2.3) and polishing it at an angle on diamond lapping films.

Two types of samples are usually prepared. The first is a plan view. This is prepared by polishing nearly parallel to the surface of interest. When finished, the images produced are oriented as if you were looking directly down onto the sample surface as it was prepared. See Figure 3.3(b) for an example of a plan view.

The second type of sample that is usually prepared is a cross section. Preparing this type of sample requires that you take a piece of your sample and glue the surface of interest to another piece of material. This other material could be more of your sample or a piece of silicon. The result is a "sandwich" of the surface being studied. The sample is then prepared by polishing perpendicular to the surface of interest until the desired thickness is achieved. The result is a cross section of the sample being studied so that you can observe different layers instead of just the surface of

Figure 2.3 An example of a tripod used for TEM sample preparation.

the sample. See Figure 3.2 for an example of a cross section.

2.3 TEM Analysis Methods

There are three types of TEM images that we used to analyze the samples we had prepared: bright field images, diffraction patterns, and dark field images.

Bright field images are produced by the transmitted beam passing directly through the sample. Some of the electrons passing through the sample interact with it and are scattered, or diffracted. In a bright field image, all diffracted beams are blocked through use of an aperture. Areas of the sample that are thicker or contain heavier atoms will appear darker than other areas because they scatter more of the transmitted beam. This imaging method allows us to view crystallinity and provides a good general image for TEM analysis because of its high contrast. Most of the TEM

images presented in this study are bright field images, unless otherwise specified.

Diffraction patterns are related to the crystal lattice being observed. As the transmitted beam passes through the sample, the diffracted beams are collected and form multiple spots. These spots each correspond to a different crystal plane, and the spacing between the spots is inversely related to the distance between atomic planes. In this sense, a diffraction pattern can be thought of as a Fourier transform of the crystal lattice being observed. This gives us information about the crystal structure of the material being studied and its orientation. This analysis method is used in Figure 3.8.

Dark field images correspond to a specific diffraction peak in the diffraction pattern. The direct beam is blocked after passing through the sample and one of the diffracted beams is collected to form an image. The parts of the image that will appear brighter are those parts of the sample whose crystal planes contribute to that particular diffraction peak. This method can be used to study only those areas of the sample that are in a particular crystal orientation. This analysis method is used in Figure 3.5

2.4 Other Characterization Methods

Several other methods are also being used by other members of the VO_2 group to characterize VO_2 crystallization, none of which deliver a complete understanding of the process without the others. These include scanning electron microscopy (SEM), orientation imaging microscopy (OIM), and electrical measurements.

2.4.1 Scanning Electron Microscopy

Scanning electron microscopy (SEM) is an imaging method that relies on the use of an electron beam to produce surface images. A focused beam of electrons is scanned across the sample. Secondary electrons, which are generated in the top surface layers of the sample being analyzed, are detected and correlated with probe position to deliver a mock three-dimensional image of the surface being studied. Figure 3.7(a) is an example of the kind of image that can be obtained using scanning electron microscopy.

2.4.2 Orientation Imaging Microscopy

Backscattered electrons from the electron beam of the SEM can also be detected to give information regarding the crystal structure of the sample. This kind of microscopy is called orientation imaging microscopy (OIM). As more energetic electrons interact deeper into the surface of the sample, they are backscattered along its crystal planes. Capturing these backscattered electrons reveals several lines, called Kikuchi lines, which reveal detailed information about the crystal structure and orientation of the sample being analyzed. For an example of these lines, see Figure 3.7(b).

A serious disadvantage of SEM analysis is that particles smaller than about 50 nm cannot be easily viewed in a surface image, and crystals smaller than this size do not give very good OIM images, since most of the electrons travel deeper than the crystals themselves. We have found than several samples that give no indication of crystallinity using SEM methods can be clearly seen to be crystalline using TEM imaging. An advantage that SEM has is that sample preparation requires much less preparation time than TEM samples, so many more samples can be observed quickly.

2.4.3 Electrical Measurements

The most interesting result of VO_2's phase transition is its change from semiconductor to metal. As mentioned, crystalline VO_2 changes from a semiconductor to a metal when heated beyond its transition temperature. When cooling, it changes back to a semiconductor at a slightly lower temperature. This kind of "memory-dependence" is called hysteresis, and can be viewed in Figure 3.4, where the resistance as a function of temperature is shown while heating and cooling. The magnitude of this hysteresis (or how wide the gap is) appears to depend, at least in part, on particle size [5]. This transition is very fast, but the temperature at which it occurs appears to vary depending on particle size.

To make resistance measurements, two small gold wires were attached to the vanadium dioxide film. By running a known voltage through another known resistor in series with the film and measuring the voltage drop across the known resistor, members of the VO_2 group were able to calculate the resistance of the film. The sample was then placed on a controlled heating stage and resistance measurements were made as a function of temperature. Resistance measurements presented in this study are the work of Felipe Rivera and Michael Clemens.

Chapter 3

Data

3.1 Sample annealed at 400°C for 17 Hours

The lowest temperature at which we have observed crystal formation is the sample that was annealed at 400°C for seventeen hours. SEM imaging and OIM were unable to detect any sign of crystallinity, due to what we found to be the small size of the crystals formed. Electric measurements, however, indicated that there must have been some sort of crystalline formation. These measurement indicated temperature-dependent changes in resistance that were far greater than the magnitude of changes observed in amorphous vanadium dioxide. See Figure 3.1 for a plot of resistance as a function of temperature on this sample.

The transition temperature for this sample was observed to be about 50-55°C, which is much lower than the reported transition temperature for crystalline VO_2 in the bulk. Analysis of the graph also reveals that the transition does not occur rapidly, as would be expected for a single particle. The gradual slope of the graph in Figure 3.1 is indicative of many different particles undergoing a phase transition *at different temperatures*. We have observed that smaller particles undergo the phase transition

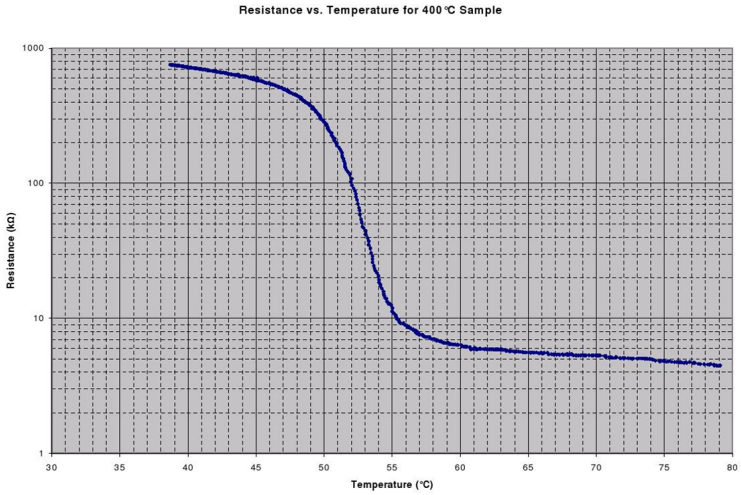
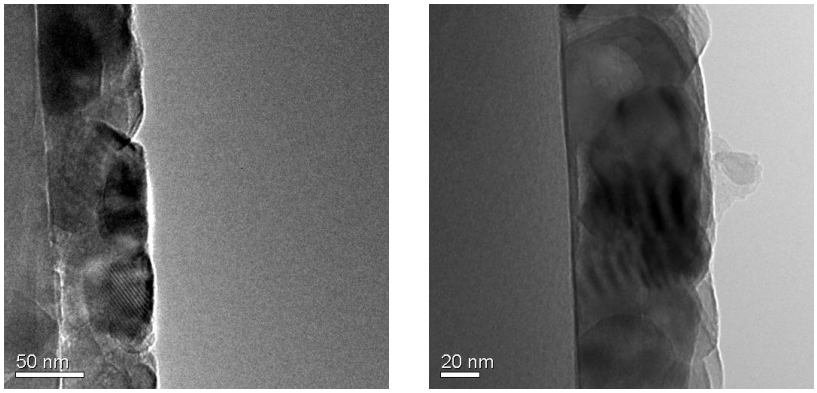


Figure 3.1 A plot of resistance of VO_2 annealed at 400° for 17 hours as a function of temperature. The phase transition seems to occur near 45-55°C.

at a lower temperature. Consequently, a wide range of transition temperatures ought to be indicative of a wide range of particle sizes. If all of the crystals were exactly the same size, we would expect the transition to be visible on this graph as a vertical line as all of the particles changed from a semiconductor to a metal.

Once we had prepared a TEM sample for study, we observed that some crystallization had taken place in this sample. Figure 3.2 displays two images of a cross section of this sample. Close examination will reveal some alternating dark and light lines across some of the sample. These fringes are called Moiré fringes, and are the result of two diffraction gratings being superimposed at different angles. In this case, the "diffraction gratings" are the crystals in this sample. The fringes are indicative of two crystals on top of each other, which diffract the electrons coming through. The resulting interference pattern is visible as these periodic fringes.

The crystals formed seem to be around 30-50 nm, but did not seem to separate into completely isolated particles. Instead, the crystals are spread throughout the relatively smooth film. This smoothness, coupled with the size of the crystals, is one



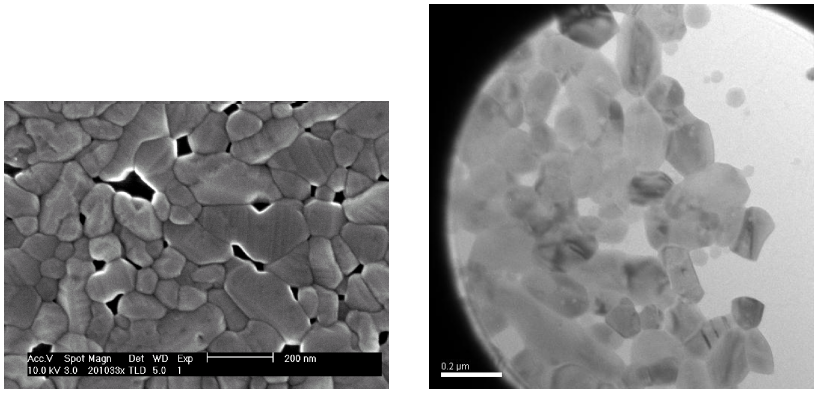
(a) (b)

Figure 3.2 (a),(b) TEM images of a cross section of VO_2 annealed at 400°C for 17 hours.

reason why SEM and OIM analysis failed to identify this sample as crystalline. This sample is a good example of how different characterization methods are necessary to fully understand the samples. Since SEM and OIM analysis did not reveal any changes in the sample, we required electrical measurements and TEM imaging to identify the crystal formation in this sample. The temperature at which the resistance changes and the magnitude of the hysteresis are both results of the nature of the crystals formed. These small, but continuous crystals seem to have resulted in a transition temperature (45-55°C) that is much lower than the transition temperature in the bulk (68°C).

3.2 Sample Annealed at 450°C for 17 Hours

The sample that was annealed at 450°C for seventeen hours exhibited formation of larger crystals. This sample formed a mass of contiguous crystals, exhibited as an SEM image in Figure 3.3(a). Since these crystals form a semicontinuous layer, we were able to obtain resistance measurements for the surface of this sample. A plot of resistance of this sample as a function of temperature is shown in Figure 3.4.



(a) (b)

Figure 3.3 (a) An SEM image of VO_2 annealed at 450°C for 17 hours. (b) A TEM image of a plan view of the same sample.

When viewed as a plan view sample in the TEM, we confirmed the size of the particles and were able to notice some small bubbles inside several of the crystals. We believe that these bubbles are deposits of argon left over from the annealing process. However, we have not yet been able to confirm this theory in the TEM. We were also able to view crystal orientations in a dark field image. This means that the beam was centered on a specific off-center diffraction peak, and only crystals lining up with this orientation would be visible in the image.

Using this technique, we heated a sample in the TEM. This was accomplished through use of a temperature-controlled heating stage driven by a current source

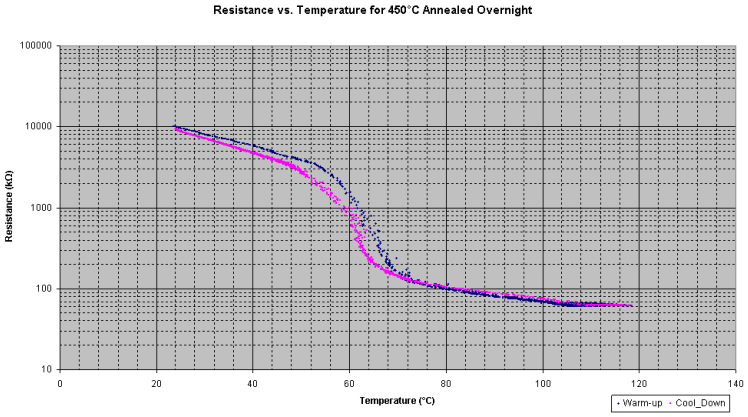


Figure 3.4 A plot of resistance of VO_2 annealed at 450° for 17 hours as a function of temperature. The two curves represent heating and cooling of the sample.

and measured with a thermocouple. This allowed us to control and measure the temperature of the vanadium dioxide *inside* the TEM. This method was devised so that we could observe the structural changes associated with the phase transition.

By capturing an off-center diffraction peak and forming a dark field image, we were able to observe the phase transition as atoms in the vanadium dioxide shifted and changed the diffraction condition of the crystals. Figure 3.5 shows the changes in dark field images as this sample cooled. Using this method, we observed the phase transition for particles of different sizes. Figure 3.5 illustrates how different particles experienced the transition at different temperatures. The larger particle circled in Figure 3.5(a) changed between 67-75°C. The smaller particle circled in Figure 3.5(c), however, did not undergo a change until somewhere between 44-60°C.

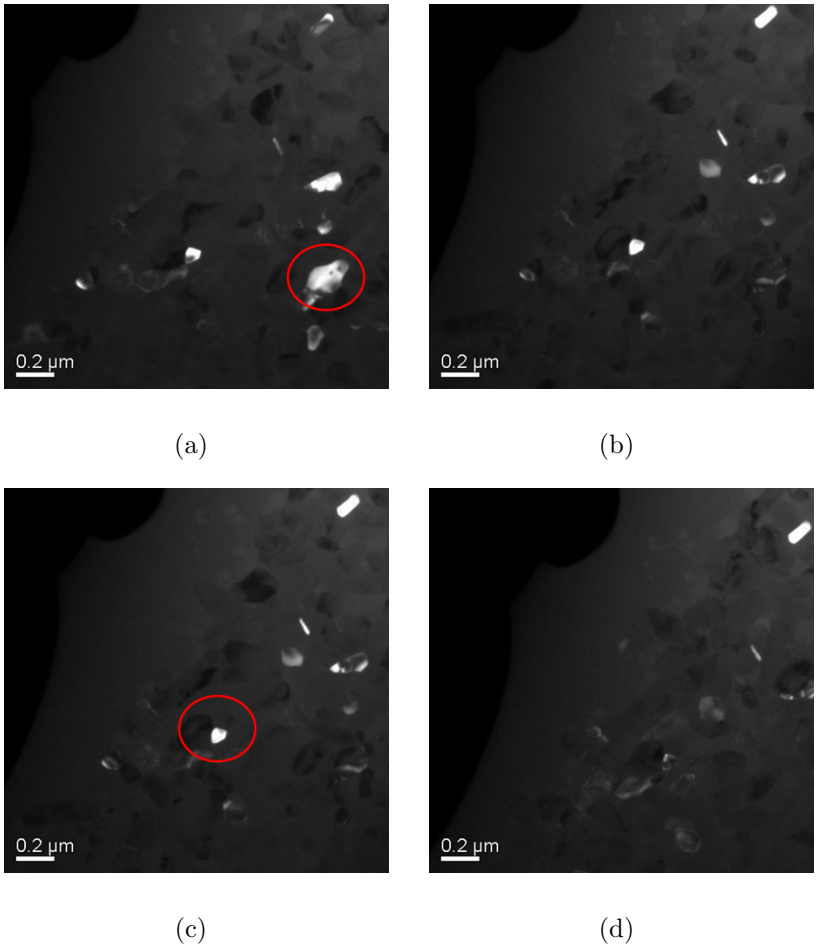
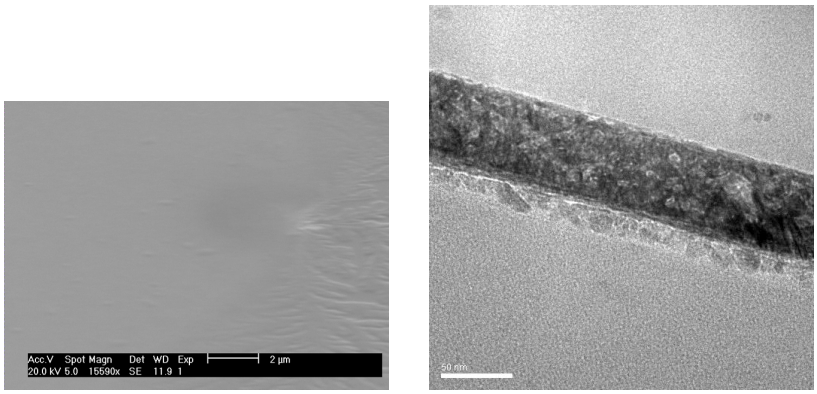


Figure 3.5 Dark field images of a TEM plan view of VO_2 annealed at 450°C for 17 hours, sample temperature (a) 75°C, (b) 67°C, (c) 60°C, (d) 44°C.

3.3 Sample Annealed at 450°C for 20 Minutes

The sample that was annealed at 450°C for twenty minutes is another excellent example of crystal formation that was not visible using SEM or OIM imaging. The SEM image visible in Figure 3.6(a) is completely smooth and shows no signs of crystal formation. The OIM results were similar. However, Figure 3.6(b), a cross-section view of the sample in the TEM, reveals that the entire sample was polycrystalline. In this case, the crystals that were formed were extremely small, and we would expect

any electrical measurements to indicate a very low transition temperature. At this point, however, no electrical measurements have been made on this sample.

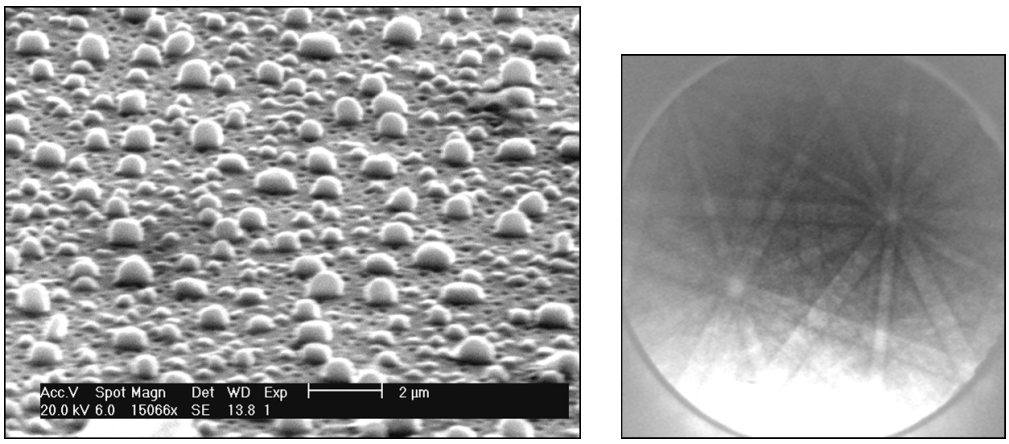


(a) (b)

Figure 3.6 (a) An SEM image of VO_2 annealed at 450°C overnight. No crystals are visible here. (b) A TEM image of a cross section of the same sample. We can see here that crystallization has clearly taken place.

3.4 Sample Annealed at 1000°C for 20 Minutes

The hottest temperature at which any samples were annealed was 1000°C. At this temperature, we observed the vanadium film condensing into very large particles (about 0.5-1.0 μm). However, instead of forming a mass of contiguous crystals like the sample annealed at 450°C, this sample resulted in large, isolated crystals. SEM and OIM images of these particles are shown in Figure 3.7. The OIM image clearly shows the Kikuchi lines mentioned earlier.



(a) (b)

Figure 3.7 (a) An SEM image of VO_2 annealed at 1000°C for 20 minutes. (b) An OIM image of a particle on the same sample, clearly displaying Kikuchi lines indicative of crystallinity.

The size of the particles in this sample made it an excellent candidate for further analysis using electron diffraction patterns. Placing these in the TEM using the heating stage mentioned earlier, we were able to control the temperature of the particles. Since the particles formed were large and monocrystalline, it was easy to obtain a coherent electron diffraction pattern such as those in Figure 3.8.

The phase transition, as mentioned earlier, results in a halving of the unit cell.

When this occurs, the distance between diffraction peaks in the diffraction pattern (which has units nm^{-1}) *doubles* and we see an entire row of peaks in the diffraction pattern disappear, as shown in Figure 3.8.

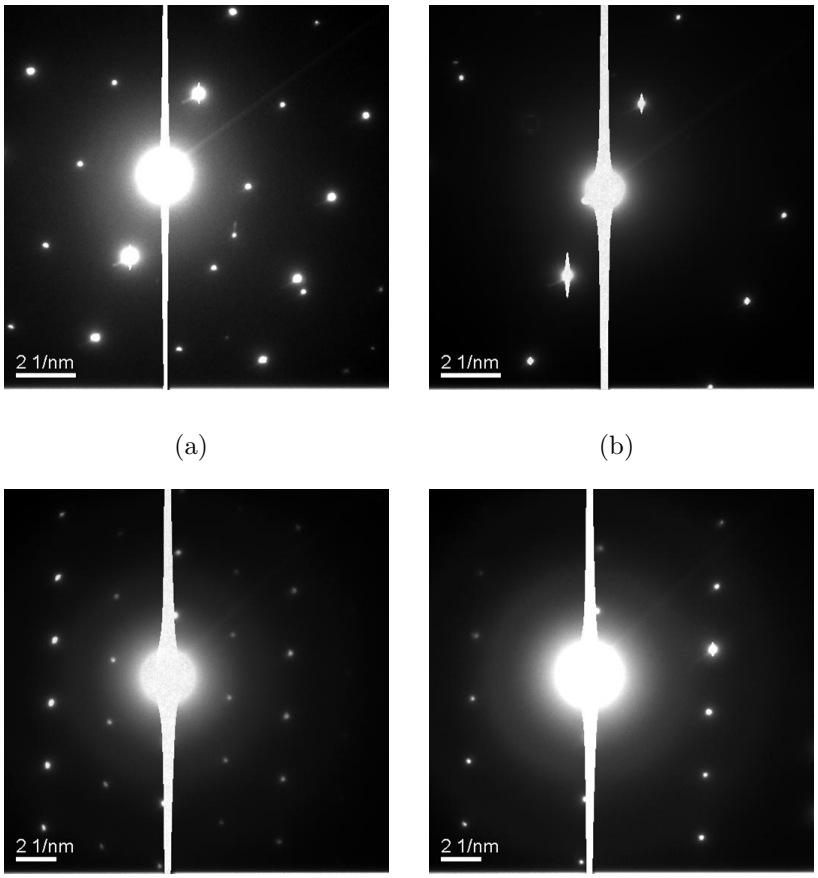


Figure 3.8 (a) Diffraction pattern of a large VO_2 crystal at room temperature. (b) Diffraction pattern of the same crystal at 70°C. (c),(d) Similar results on a different particle at the same temperatures.

This result is extremely important because we were able to confirm the structural phase transition of vanadium dioxide, rather than relying on secondary data such as changes in resistance to determine whether or not the phase transition had occurred. This method, coupled with dark field imaging, can be very powerful because it al-

lows us to isolate single particles and observe their specific transition temperatures. Further work should be done in this area to determine exactly what dependence the transition temperature has on particle size.

Chapter 4

Conclusions

Our results confirm the findings of previous researchers that VO_2 particle size increases and crystallinity improves when annealing time increases [5]. While very small polycrystalline particles were formed on the sample annealed at 450°C for twenty minutes, larger monocrystalline particles were observed on the sample annealed at the same temperature overnight. We have also confirmed that particle size increases as annealing temperature increases. We have observed that small crystals are formed at temperatures as low as 400°C, while larger crystals are formed at 1000°C even when annealed for a much shorter time. These results are not new, but confirm previous work.

TEM analysis has permitted us to identify evidence of crystallinity in samples annealed at lower temperatures that could not be observed using other observation methods. We identified crystals formation in a sample annealed at 400° for 17 hours, which showed no evidence of crystallinity using SEM or OIM.

Our study of the structural phase transition of our samples in the TEM using the heating stage has confirmed the composition of our sample. By observing this transition and comparing against theoretical diffraction patterns we have confirmed

that the substance that we are dealing with really is vanadium dioxide, as opposed to a different oxide such as vanadium pentoxide (V_2O_5). This enables us to proceed with further experiments without worrying that we may be dealing a different material.

Perhaps the most important result of this study is the observation of the structural phase transition in the TEM using diffraction patterns. Rather than using indirect methods to observe the phase transition, such as changes in optical index or resistivity, we are able to observe the actual structural transition by observing the changes in the diffraction pattern of individual crystals in the TEM as the sample temperature is controlled using our heating stage. This will enable further work to be done on individual particles of different sizes to identify how particle size affects the transition temperature on the nanoscale.

We have demonstrated that the transition temperature for the phase transition of vanadium dioxide is dependent upon particle size. While the phase transition is reported to be around 68°C in the bulk, we were able to identify transitions occurring at temperatures as low as 50-55°C in the sample annealed at 400°C. This transition temperature was identified by members of the group using electrical measurements to characterize the sample. The crystals in this samples were approximately 50 nm or less in size, and this small size led to a decrease in transition temperature for the phase transition from semiconductor to metal. The sample annealed at 450°C overnight exhibited a transition temperature as low as 55-65°C. This is not surprising, since the crystals in this sample were significantly larger than those in the 400°C sample.

These transition temperatures necessarily span a wide range of temperatures because of the variance in particle sizes in any particular sample. We have not observed a uniform particle size in any of these samples, nor should we expect to. However, TEM analysis has permitted us to view the phase transition for individual particles. It has confirmed that smaller particles do, indeed, have a lower transition temperature.

Further research should be done to identify exactly how the transition temperature depends on particle size by observing many crystals of differing sizes and driving the transition thermally. By analyzing the diffraction patterns and dark field images in the TEM, further research will be able to identify and better understand the particle size-dependence of the transition temperature.

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