RESISTIVITY MEASUREMENTS WITH HYSTERESIS IN CRYSTALLINE THIN FILMS OF VANADIUM DIOXIDE BY FOUR-POINT PROBE

by

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DEPARTMENT APPROVAL

of a senior thesis submitted by

Arthur William Brown

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

Date	Richard Vanfleet, Advisor
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ABSTRACT

RESISTIVITY MEASUREMENTS WITH HYSTERESIS IN CRYSTALLINE THIN FILMS OF VANADIUM DIOXIDE BY FOUR-POINT PROBE

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Resistance of crystalline thin films of vanadium dioxide with varying grain sizes were measured using a tungsten carbide tipped four-point probe and computer data collection. Resistivity was obtained through a conversion factor dependent on sample geometry. Temperature was measured concurrently, and was slowly varied within a range from 295 K to 360 K. As temperature is increased, a metal-to-insulator transition (MIT) was observed near 340 K. Hysteresis is observed upon cooling where the reverse transition occurs at a lower temperature. The upper (heating) transition temperature decreases as the grain size gets smaller and smaller grains were seen to have a wider hysteresis gap.

ACKNOWLEDGMENTS

I would like to thank Robert Davis and Richard Vanfleet for there continual guidance and patience in guiding my research, and for teaching me so much through both their time and examples. They are remarkable people. I would also like to thank Felipe Rivera, for his knowledge and help in the experimental setup, and his help in compiling this thesis, Michael Rawlins, for making good samples, Brendan Turner, for providing examples of needed code and being a friend who brings humor into the everyday, Jeff Farrer, who gave excellent advice on many occasions, and Gavin Giraud, for his encouragement. Most of all, I wish to thank my wife, Sierra Rachel Brown, and my two boys, Hyrum Eliott Brown and Wesley Allen Brown, for being patient and loving, and providing unmeasureable joy in my life, without which none of this would been possible.

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Chapter 1

Introduction

1.1 Vanadium Dioxide

Vanadium, a metal used as a carbide stabilizer in forming steels [1], can be made into continuous crystalline thin films with various oxide stoichiometries through the process of solid-phase crystallization by thermal annealing. Different temperatures and durations for the anneals can produce different grain sizes in the films, from 10 nanometers up to a few hundred nanometers, at which point the films become discontinuous. For example, a 50 nanometer film of amorphous vanadium annealed at 400 Celsius for 10 minutes will generate 50 to 70 nanometer grains in a crystalline film [2]. Varying the oxygen pressure in an argon environment during the anneal will actually change the stoichiometry of V_XO_X [2]. Of particular interest is Vanadium dioxide (VO_2).

VO_2 has been shown to undergo a phase change in resistivity, in other words a "metal-to-insulator transition" (MIT), initiated by change in temperature [3–5]. This transition occurs when the VO_2 films are heated to approximately 340 K, and is of a magnitude of 10^4 or 10^5 [6]. Because the transition temperature is relatively close to

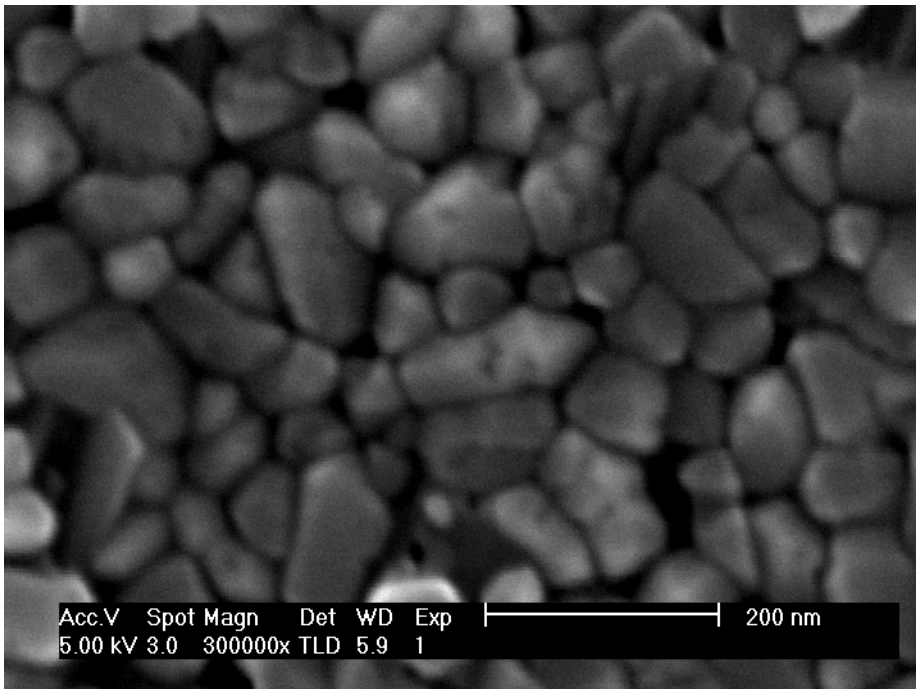

Figure 1.1 SEM image of a sample of vanadium dioxide (VO_2), which was annealed at 400 Celsius for 12 hours (V50_08). The grain sizes are within the range of 50 to 100 nm, and the crystalline film is largely continuous. Image Credit Felipe Rivera.

room temperature, it has potential value in technology development through energy effective real world applications.

Because the MIT is large in magnitude, VO_2 has been proposed for use in switching devices [6], and also thermochromic glazing of windows with anti-reflection coatings [7]. In the heat of the summer, near infra-red light can be virtually blocked from entering a window, reducing the use of air conditioning. A home with VO_2 glazed widows can save 30 percent of its energy consumption [7].

The transition temperature can also be manipulated with the application of an electric field to the VO_2 [8]. Increasing the electric field will lower the transition temperature [8]. Hysteresis has been observed in crystalline VO_2. Bulk samples show little hysteresis, but smaller grain samples show an increased resistivity. An increase has been observed when crystal size diminishes [9].

1.2 Four-Point Probe Resistivity Measurements

To measure resistivity of a flat sample, it is convenient to use four small probes in contact with the sample, linearly aligned and with equal spacing between them. Tungsten carbide is often used for the tips to prevent breaking and loss of contact with the sample.

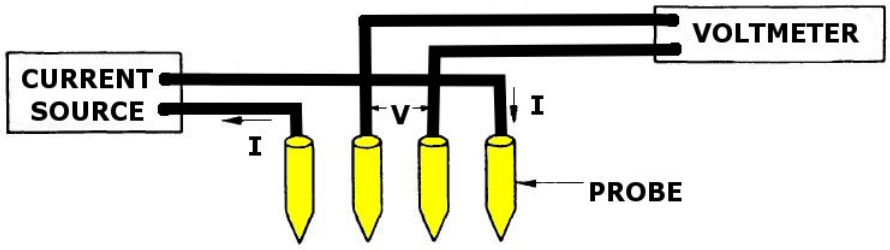

Figure 1.2 Current flows through the outer probes while voltage is measured on the inner probes [10].

Current is sent through the outer probe while the voltage difference between the inner probes is measured. If the voltage measurement can be performed without drawing current and the sample is semi-infinite, then, assuming a spherical distribution of current, resistance is given by

$$R = \int_s^{2s} \frac{\rho}{2\pi x^2}\, dx = \frac{\rho}{4\pi s} \tag{1.1}$$

which, assuming R=V/2I because of probe configuration, gives a bulk resistivity of

$$\rho = 2\pi s(\frac{V}{I}) \tag{1.2}$$

where s is the spacing between probes, V is the voltage difference measured between the inner probes, and I is the current flowing through the outer probes [10].

For thin film resistivity measurements, spherical distribution can be replaced with

cylindrical distribution, and resistance becomes

$$R = \int_s^{2s} \frac{\rho}{2\pi x t}\, dx = \frac{\rho}{2\pi t} \ln 2 \tag{1.3}$$

which changes resistivity to

$$\rho = (\frac{\pi}{\ln 2})(\frac{V}{I})(t) \tag{1.4}$$

For extremely narrow thin film samples, a linear current distribution can assumed [11]. For thin film samples that are not large enough to assume an ideal cylindrical distribution, but not narrow enough to assume linearity, a further correction factor, c, must be multiplied to ρ.

$$\rho = (\frac{\pi}{\ln 2})(\frac{V}{I})(t)c \tag{1.5}$$

Conducting and non-conducting boundaries must be treated differently [10]. Valdes provides graphs displaying the correction factors in various cases (see Fig. 1.5), and Smits provides tables for reference [10, 12].

In order to prevent surface leakage that would distort the resistance measurements, the measured sample must be flat [10]. Orientation imaging microscopy on the films has shown that the VO_2 crystals lie with their 001 axis completely in the x-y plane [2], which implies that the samples are relatively flat and will not distort resistance measurements through surface leakage.

1.3 Sheet Resistivity

Sheet resistance is commonly used when referring to the resistance of thin films. Because thickness of a sample is not always known, it is helpful to define a method for quantifying resistances of arbitrarily thin films. The units of sheet resistance are Ω/square, which does not require film thickness.

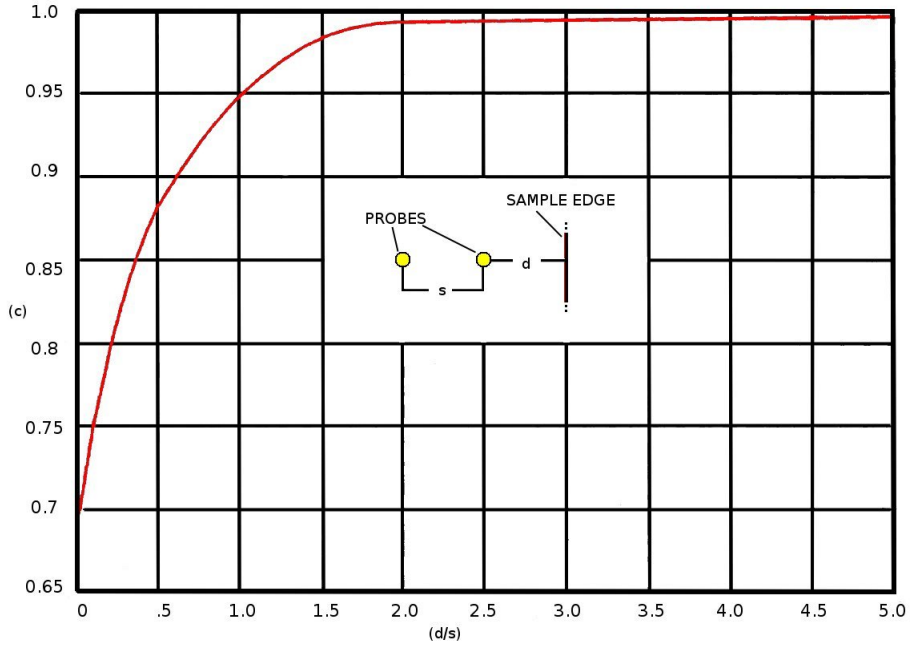

Figure 1.3 Correction factor for a non-conducting boundary perpendicular to a four point probe. When the ratio of l to s exceeds five, no correction factor is necessary [10].

If a thin film sample were cut into a perfect square, and resistance was efficiently measured from one complete boundary to the opposing boundary, length and width would be equal. The resulting equation becomes

$$R_{sheet} = \rho\frac{l}{wt} = \frac{\rho}{t} = \frac{\pi}{\ln 2}(\frac{V}{I})c \tag{1.6}$$

where c is the additional correction factor required for non-ideal samples. Because of the simple nature of the calculation, using sheet resistance to quantify thin films by four-point probe measurements is standard.

Chapter 2

Experimental Methods

2.1 Heating Apparatus

Amorphous vanadium on a silicon dioxide wafer was cleaved into small pieces, annealed separately at a predetermined oxygen pressure in different temperatures to form VO_2 crystalline films, and mounted onto SEM stubs with carbon paint.[1] They were then examined in the SEM to determine grain size. A few of the samples were exposed to irregularities in the annealing process, and were seen to be discontinuous in their crystal structure. Such films were not used in this experiment. The stubs were then place into the top of a 5cm X 5cm X 2cm aluminum block, which had been machined to allow a heating rod to be inserted through its core. A vairiac was attached to the heating rod, and voltage was slowly increased or decreased by hand to raise or lower the temperature of the block (see Fig. 2.2). The block was set on top of a larger metal plate that acted as a heat sink to stabilize the temperature change.

[1] Thanks to Felipe Rivera and Michael Rawlins for annealing a significant number of VO_2 samples.

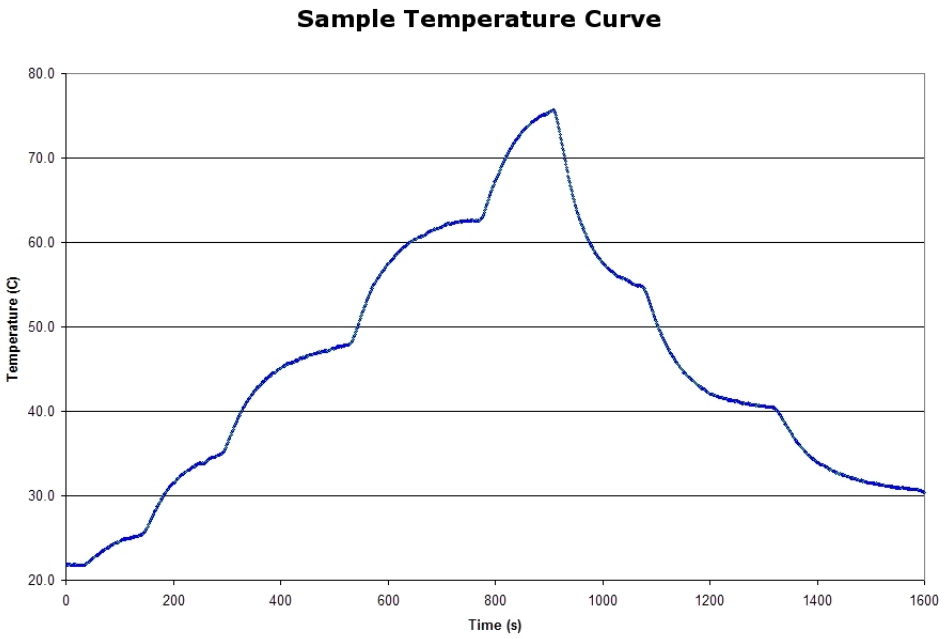

Figure 2.1 Temperature was controlled by hand, using a variac and heating rod. In order to gather as many data points as reasonably possible, the voltage was shifted multiple times in smaller increments up and down.

2.2 Temperature Measurements

A thermocouple was attached to a micro-manipulator, and was put in contact with the surface of the SEM stubs, abutting the VO_2 films. For a few configuration runs, another thermocouple was placed on the surface of the actual VO_2 film, and no difference was observed between the two thermocouples while heating and cooling. The second thermocouple was removed to prevent interference with resistivity measurements. The thermocouple was plugged into a National Instruments Data Acquisition Board, through which temperature data was recorded with a Labview VI. A cover was placed over the entire apparatus to reduce air currents that might destabilize the temperature measurements. Data was accurate to the second decimal place.

2.3 Four-Point Probe and Multimeter

A Signatone tungsten carbide four-point probe with tip spacing of 62.5 mills was used to provide the collinear points of contact with the VO_2 films. A HP-3478A multimeter, with General Purpose Interface Bus (GPIB) capability, was used in conjunction with a Labview VI to digitally record resistance measurements.

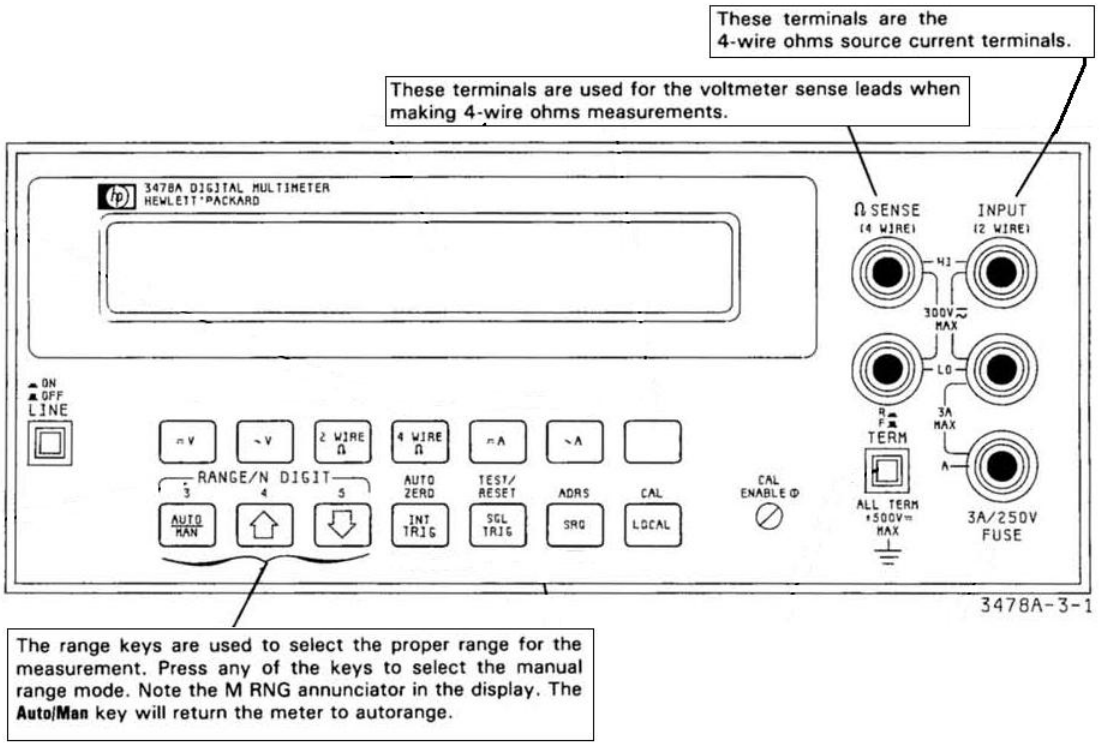

Figure 2.2 The 4-wire function is used to generate resistance measurements. The outer probes are plugged into the current terminals, and the inner probes are plugged into the voltage terminals. Taken from the Hewlett-Packard HP-3478A Digital Multimeter Service Manual.

Each sample was also measured with a micrometer to determine width and length, and was assumed to be rectangular despite minor flaws in the cleaved edges. The film thickness was 50nm for all measured VO_2 samples. Correction factors were determined using this geometry. The resistance obtained from Labview was combined

with the geometry-based correction factors and the film thickness to obtain resistivity and sheet resistance.

To test the accuracy of the setup, two thin films of zinc oxide were tested for resistivity. A 3640$\mathring{A}$ film was tested at 100mA, and showed .295 V across the center probes. This gave 13.30 Ohms/square sheet resistivity, and 4.864*10^{-4} Ohms/cm, compared to the expected values of 13.06 Ohms/square and 4.575*10^{-4} Ohms/cm. Also, a 3730$\mathring{A}$ film was tested at 100mA, and showed .474 V across the center probes. This gave 21.47 Ohms/square sheet resistivity, and 8.008*10^{-4} Ohms/cm, compared to the expected values of 21.02 Ohms/square and 7.829*10^{-4} Ohms/cm. This was deemed sufficiently accurate.

2.4 Hysteresis

The transition temperature was defined as the mid-point in the phase change from cold to hot. It was identified by inspecting the resistivity curve and finding the middle temperature value between the point where the slope begins a to accelerate away from a constant line, and the point where the slope becomes constant again. Hysteresis was determined by finding the resistivity at that transition temperature, and then finding the other temperature where the same resistivity was observed. The difference between those two temperatures was defined to be the hysteresis gap.

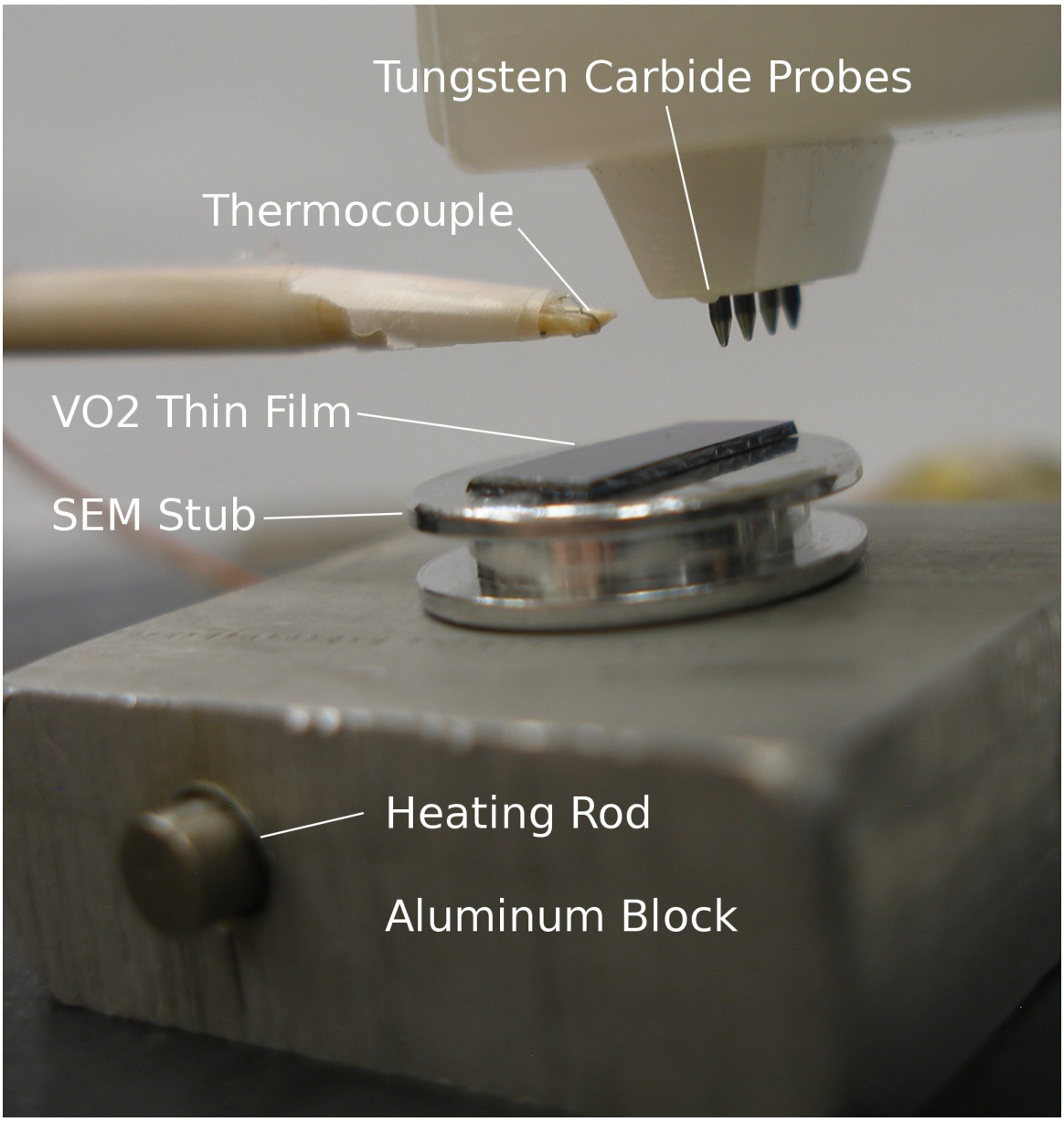

Figure 2.3 Both the thermocouple and the four point probe could be lowered until brought into contact with the VO_2 films. The aluminum block acted as a placement station, that could be slid out from underneath the probes to allow removal of the SEM stub. A small wooden dowel was attached to a micromanipulator to hold the thermocouple.

Chapter 3

Results and Conclusions

3.1 Geometry Dependent Hysteresis

Hysteresis was seen the resistivity of all of the films, including a control film of amorphous vanadium. Smaller grains show smaller hysteresis, while larger grains seem to have a wider hysteresis gap.

In Figure 3.1, a similar constant slope exists outside of the phase change for all of the samples. The only significant change in these regions lies in resistivity. The largest grain sample was seen to have the greatest hysteresis, while smaller grains had less.A film of 15nm average grains showed a 4.2K wide gap, while a film of 85nm average grains showed a 9.5K gap.

While it has been previously observed that hysteresis of films with grains larger than 100 nm will diminish relative to increase in grain size, we also observed that grains smaller than 100nm will lose hysteresis relative to a decrease in grain size. The 15nm grain sample particularly showed excessive decrease in not only hysteresis but also resistivity. Also, its phase change was of a magnitude less than 10, which, compared to the other samples showing 10^3, was very small. Nothing in the range

of 10^4 or 10^5 was observed, probably because the film grains were smaller than those used in previous work. With so many more grain boundaries, the lower resistance may not be possible. The particles may change their resistance significantly, but the number of boundaries does not change, and may have significant impact on the resistance.

Transition temperature was also observed to shift with grain size. Smaller grains transitioned at cooler temperatures, while the larger grains followed previously observed trends. The 85nm film transitioned almost exactly at 340K. This may imply that the larger grains require more energy to overcome the energy barrier and undergo the phase change.

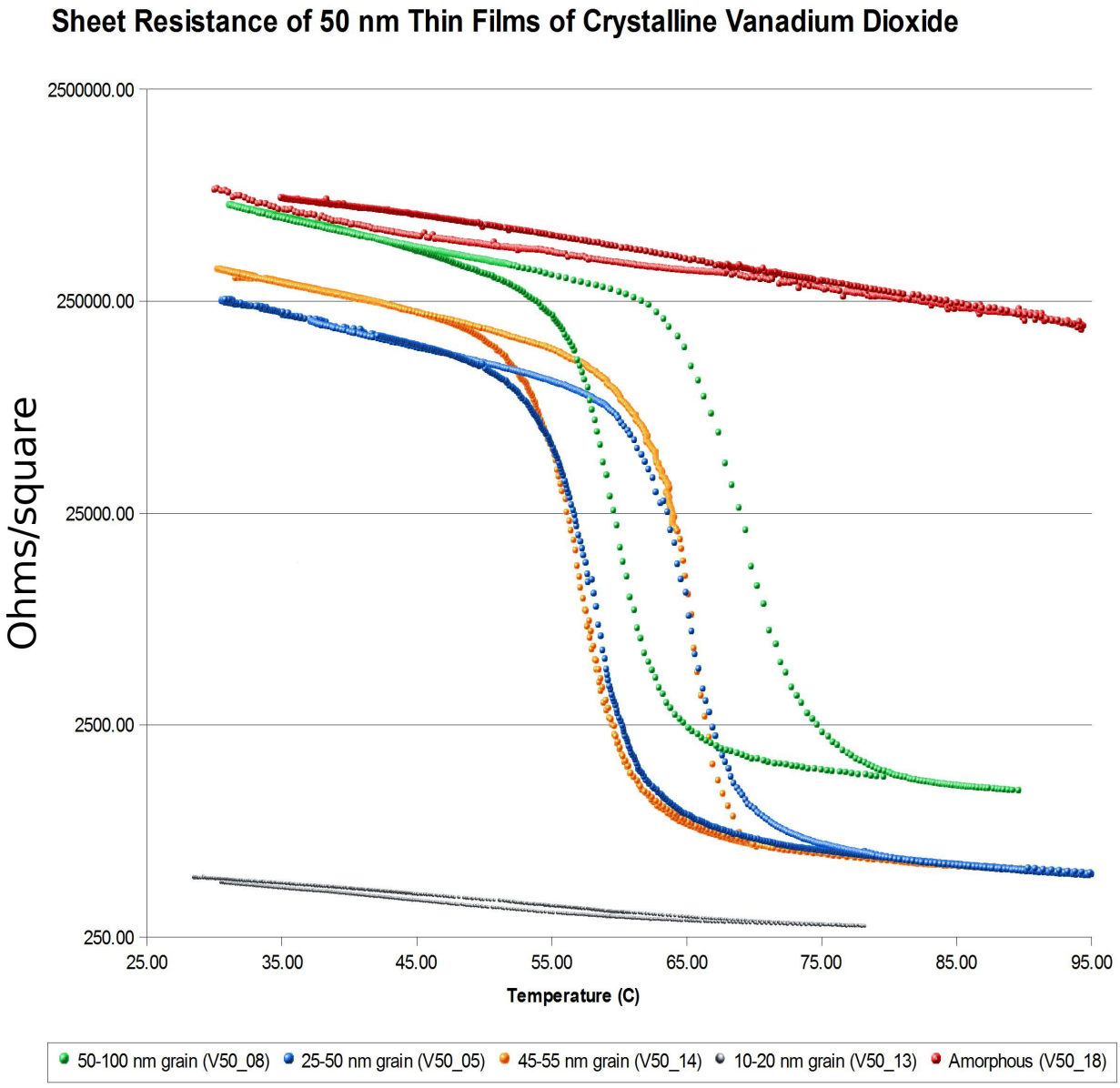

Figure 3.1 50 nm thick VO_2 films show varying hysteresis depending on grain size.

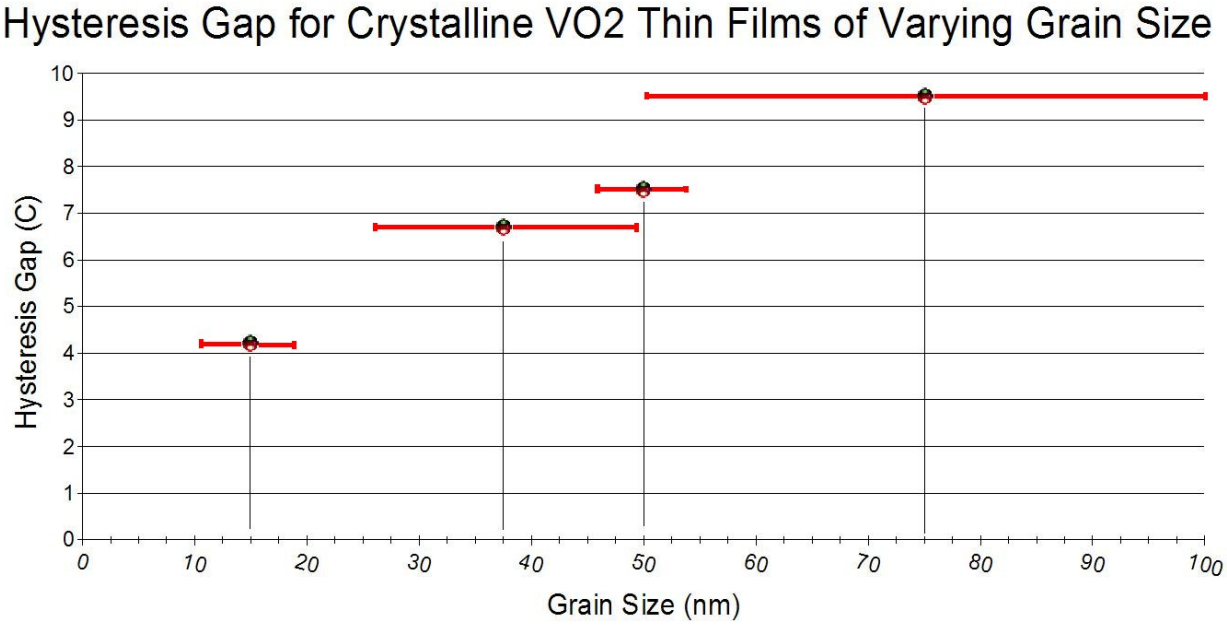

Figure 3.2 Hysteresis of VO_2 thin films was observed to decrease with smaller grain sizes. The hysteresis was measured at the transition temperature by finding the alternate temperature

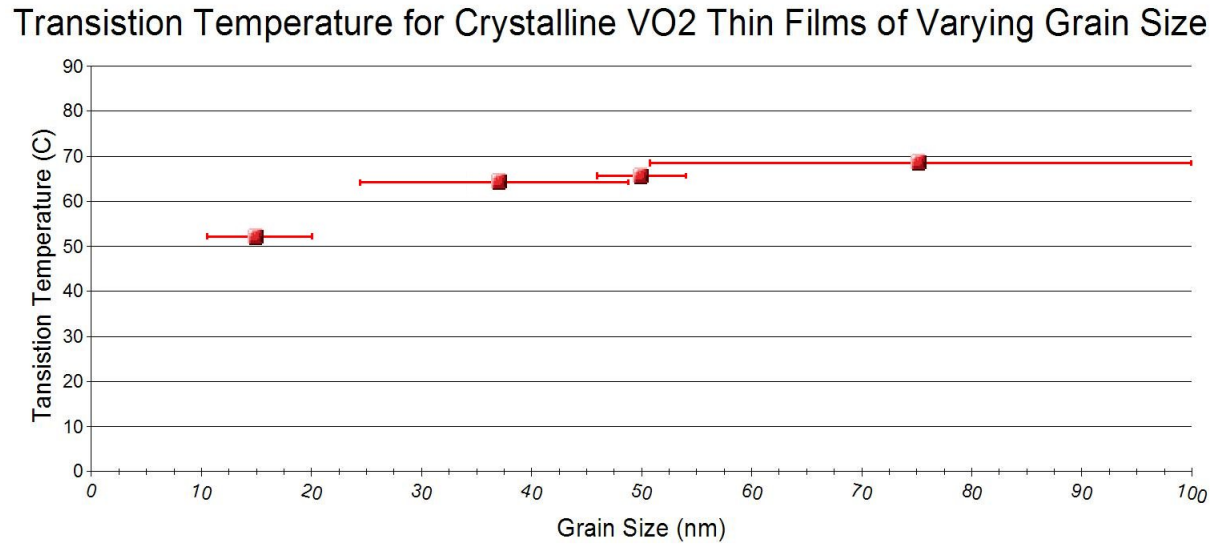

Figure 3.3 Transition temperature of VO_2 thin films was observed to decrease with smaller grain sizes.

3.2 Future Work

Confirming the results of the 15nm sample is necessary. Because it was dramatically different from the others, it needs to be shown that equipment error did not play a role in the data. Also, the amorphous film should be looked at again to verify that the observed hysteresis was not an error.

Testing more samples of different sizes and actually finding the critical grain size at which hysteresis is no longer observed is the next important element in understanding the nature of VO_2. It is possible that grain sizes that are closer to the critical size may exhibit an even stronger hysteresis than those observed in this thesis. Also, grains not in contact with one another, but within a few nanometers of each other should be observed and manipulated to show if on a local scale, some grains can maintain the metal phase, while others can maintain the insulator phase. I believe this is very possible, but it should physically be shown. Actual application of the VO_2 phase change to fields other than those mentioned previously may depend on this knowledge.

A suggested improvement in the experiment that will provide greater accuracy would be to test films with a larger surface area, and to ramp the temperature at an even slower rate than was used. Using a film sample with dimensions greater than 15*s by 15*s would mean that the correction factor would simply be $\pi/ln2$, and rough cleaved edges would not influence the data at all. Due to a lost vanadium sputtering target, supply was limited and we only tested smaller samples.

If cleanser data could be obtained, it may be beneficial to take the second derivative of the resistivity curve to more accurately find the transition temperature. The beginning and end of the phase change would be seen as a discontinuity in the second derivative. The midpoint temperature value between these two points would be the

transition temperature.

It would be beneficial to observe the phase change of VO_2 in a constant temperature, induced by a voltage change. If there is a significant hysteresis gap between raising and lowering voltages, it would be more convenient for actual application of the VO_2 phase change to future technology.

3.3 Applications

The possible uses of the phase change in vanadium dioxide extend into various fields, some of which have been mentioned previously. Because of the hysteresis, there is a sizeable temperature range where a state of low resistance and a state of high resistance can co-exist. If these states could be switched electrically, as suggested, then these two states could be used to store information as a memory element. Non-volatile RAM, such as flash memory, or non-magnetic hard drives, both with high data density, might be possible.

Another possible application of VO_2 lies in the field of security. A thin film of amorphous vanadium could be laser annealed in micron-sized sections, each for a specific time to generate a certain grain size. This film would be mounted on a car key or an identification card, which could then be quickly heated and cooled by a device that could determine the amount of hysteresis in resistance in each of the sections. The data would then be matched to predetermined numbers to give clearance. It would be difficult to provide a counterfeit in this system, because this hysteresis property of VO_2 is unique, laser annealing technology is limited, and there are relatively few experts in this field.

Bibliography

[1] Los Alamos National Laboratory, "Vanadium," http://periodic.lanl.gov/elements/23.html (Accessed 1 August 2008).

[2] F. Rivera, Masters thesis, Brigham Young University, 2008.

[3] F. J. Morin,"Oxides Which Show a Metal-to-Insulator Transition at the Neel Temperature," Phys. Rev. Lett.**3** (1959) 3436.

[4] D. P. Partlow, S. R.Gurkovich, K. C. Radford, and L. J. Denes: "Switchable vanadium oxide films by a sol-gel process," J. Appl. Phys. **70** (1991) 443.

[5] M. Borek, F Qain, V. Nagabushnam, and R. K. Singh: "Pulsed laser deposition of oriented VO thin films on R-cut sapphire substrates" Appl. Phys. Lett. **63** (1993) 3288.

[6] Y. Muraoka and Z. Hiroi:"Metalinsulator transition of VO thin films grown on TiO (001) and (110) substrates" Appl. Phys. Lett. **80** (2002) 583.

[7] Moon-Hee Lee and Jun-Seok Cho: "Better thermochromic glazing of windows with an anti-reflection coating" Thin Solid Films **365** (2000) 5-6.

[8] P. P. Boriskov, A. A. Velichko, A. L. Pergament, G. B. Stefanovich, and D. G. Stefanovich: "The Effect of Electric Field on MetalInsulator Phase Transition in Vanadium Dioxide" Tech. Phys. Lett. **28** (2002) 5:406408.

[9] R. Lopez, T. E. Haynes, and L. A. Boatner, L. C. Feldman and R. F. Haglund, Jr.: "Size effects in the structural phase transition of VO2 nanoparticles" Phys. rev. B, Condensed matter and materials physics **65** (2002) 22:224113.

[10] L. B. Valdes: "Resistivity Measurements on Germanium for Transistors," Proceedings of the IRE **42** (1954) 2:420

[11] U. C. Berkeley: "Four-Point Probe Manual" http://microlab.berkeley.edu/ee143/Four-Point_Probe/ (Accessed 1 August 2008)

[12] F. M. Smits: "Measurement of Sheet Resistivities with a Four-Point Probe" Bell Syst. Tech. J. **37** (1958) 711718, http://www.four-point-probes.com/smits.pdf (Accessed 1 August 2008)

Appendix A

LabView Code

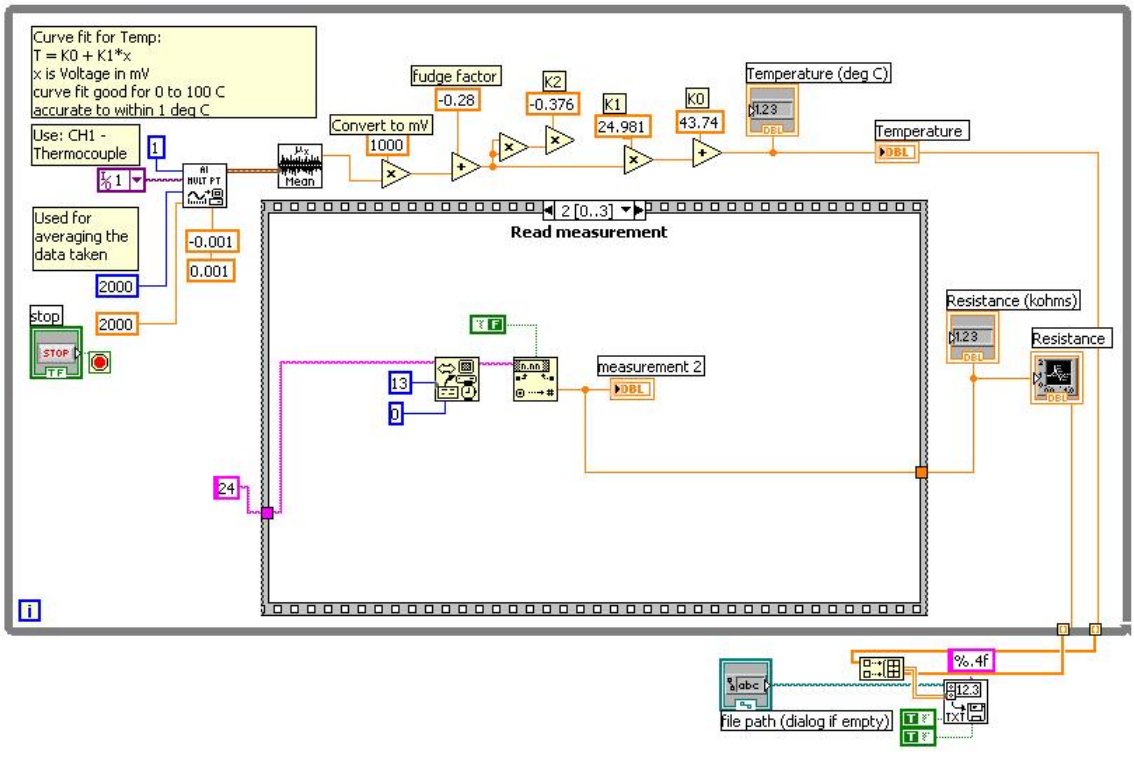

Figure A.1 The Labview VI incorporated data from both a thermocouple through DAQ board and a multimeter through a GPIB card in the CPU. Data was averaged to reduce noise.

Appendix B

Sample Geometry

B.1 Film Surface Dimensions

Crystal sizes on the different films were estimated through SEM images. The width and length of the film was determined with a micrometer. All of the films were 50 nm thick before annealing, and were assumed to have kept that thickness.

Sample Name	Width (mm)	Length (mm)
V50_05	5.01	10.75
V50_08	9.34	4.35
V50_11	9.73	4.38
V50_12	8.52	4.76
V50_13	8.04	4.90
V50_14	6.68	4.68
V50_15	5.34	3.83

Figure B.1 Sample dimensions after cleavage, measured with a micrometer.

B.2 SEM Images

Grain size was determined by choosing various locations on the sample to view with the SEM, and visually estimating the dimensions of clear grains. Some grains were elongated, but representative grains that were essentially equifacial were used to classify the films. The following images were provided by Felipe Rivera Brigham Young University.

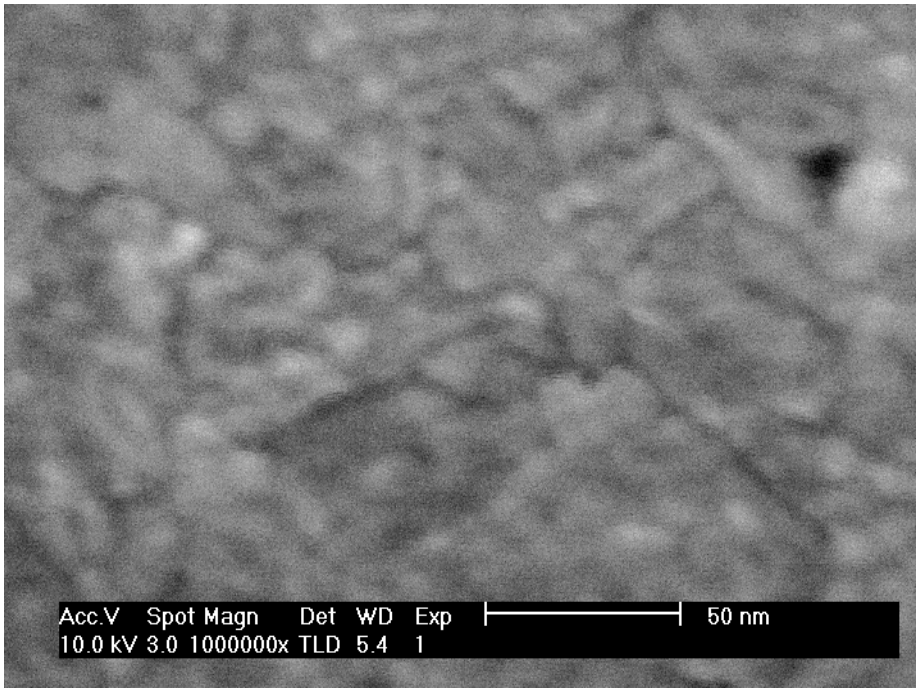

Figure B.2 SEM image of 10-20 nm grains of VO_2 (V50_13). Grains on this film are realtively homogenous, without much elongation or irregularity.

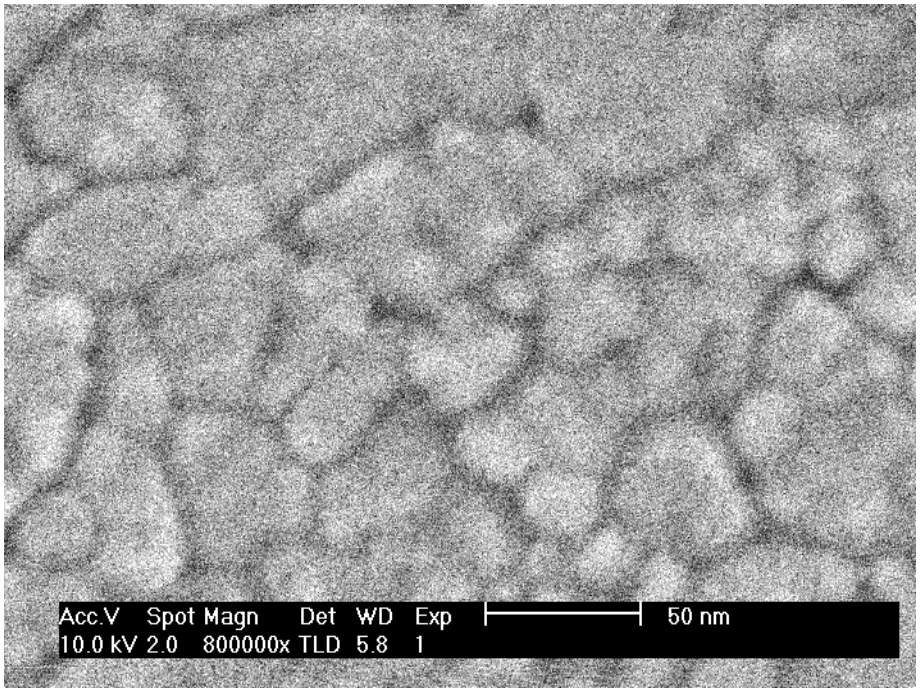

Figure B.3 SEM image of 20-50 nm grains of VO_2 (V50_05). Again, this film is fairly homogenous, without much elongation or irregularity.

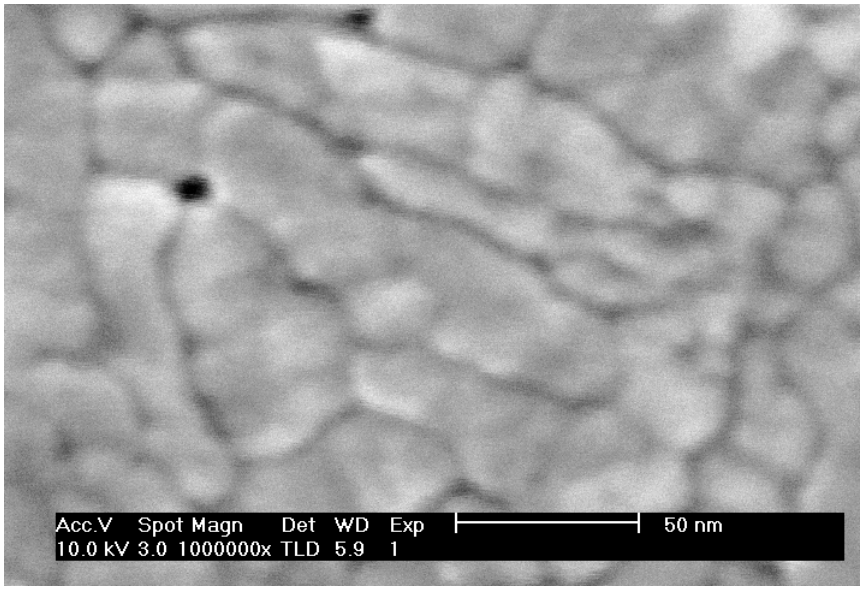

Figure B.4 SEM image of 45-55 nm grains of VO_2 (V50_14). This film is less homogenous than the other films, but the same method was used here. Dimensions of average size particles were visually estimated.