THE NANO-COMPOSE NATURE OF VANADIUM
OXIDE THIN FILMS FOR USE IN INFRARED MICROBOLOMETERS

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ABSTRACT

The current generation of portable, un-cooled infrared imaging devices utilizes thin-film materials with large thermal coefficients of resistivity. Incoming photons are absorbed by the material, converted into heat, and result in a decrease in the resistivity of the thermal sensing layer. Vanadium oxide thin films are used in the majority of these devices as they typically have very large thermal coefficients of resistivity with low noise characteristics.

In the work reported here, reactive pulsed DC sputtering was used to grow a systematic series of vanadium oxide thin films with resistivity ranging from $1 \times 10^{-3}$ to $6.8 \times 10^4$ Ohm cm and TCR varying from 0 to 4% K$^{-1}$. Throughout the parameter space studied, a transition from amorphous to nano-crystalline growth was observed. Films in the range of interest for a microbolometer, i.e. $1 \times 10^{-3}$ to 10 Ohm cm, contain the face-centered cubic (FCC) VO$_x$ ($0.8 < x < 1.3$) phase. Films with larger resistivity were found to be amorphous. Stoichiometry measurements via Rutherford backscattering spectroscopy place many of the nano-crystalline films outside of the FCC VO$_x$ phase field according to the bulk phase diagram. Electron diffraction in the transmission electron microscope confirmed the presence of a secondary oxygen-rich amorphous vanadium oxide phase. The oxygen-rich amorphous phase explains the discrepancy between the observed oxygen content, which is outside of the FCC VO$_x$ phase field, and the presence of FCC VO$_x$, which is limited to a maximum oxygen content of $x = 1.3$.

The resulting microstructure can be described as a nano-composite material composed of a low resistivity crystalline phase embedded in a high resistivity amorphous matrix. A mechanism has been proposed wherein the nano-composite structure of the films results from film growth in alternating oxygen deficient and oxygen rich regions in the chamber. While in the oxygen deficient region the nano-crystalline phase grows preferentially, and while in the oxygen-rich region the amorphous phase grows preferentially. The resulting microstructure is a mixture of the amorphous and nano-crystalline phases, both of which can be controlled by altering the
sputtering geometry. A general mixing rule was used to simulate the observed transport. The resulting electrical properties vary from equivalent circuits of resistors in parallel to resistors in series. The observed data can only be represented by a structure between the two extreme cases, suggesting that neither a percolative network nor isolated grains are desired for application in microbolometers. This work also suggests that the use of vanadium oxide is not specifically necessary, and nanocomposites of other conductors and insulators could result in materials with large negative thermal coefficients of resistivity suitable for use in un-cooled infrared microbolometers.
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<td>Equation 21</td>
<td>125</td>
</tr>
<tr>
<td>Equation 22</td>
<td>141</td>
</tr>
<tr>
<td>Equation 23</td>
<td>141</td>
</tr>
</tbody>
</table>
ACKNOWLEDGEMENTS

This dissertation would not have been possible without the support and guidance of the Penn State IR MURI group. I would like to personally acknowledge Nik Podraza, Raja Srowthi, Prof. Jackson, Prof. Horn, and Prof. Trolier-McKinstry for useful discussions throughout my stay at Penn State.

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Chapter 1

Introduction

In the 1980’s Honeywell developed an ion beam deposition method capable of producing vanadium oxide films with properties suitable for use in un-cooled infrared detectors[1]. The Honeywell technology is currently being used by a number of camera and bolometer manufacturers, and vanadium oxide based systems now make up ~70% of the un-cooled infrared detection market[2].

Ion beam deposition is the dominant method for producing microbolometer-quality VO_x for use in infrared imaging devices; however, the structure and chemistry of vanadium oxide thin films produced by this technique are not well understood. Despite its near 30 year history, and the fact that most manufacturers use the same method, the microstructure and chemistry of this particular type of vanadium oxide thin film have not been cohesively described in the literature. Cole, the author of the patent for the Honeywell ion beam deposition method, describes films composed of mixed vanadium oxides[3], and claims the patented process is capable of producing VO_x with x varying from 1 to 2.5, which conveniently covers much of the V-O phase diagram[1, 4]. The films as described in the patent are amorphous and range from a few hundred to 1500 Å in thickness. This ion beam process is touted as allowing for the deposition of non-stoichiometric vanadium oxide with TCRs ranging from 0.5 to 3%/K and as high as 5%/K[1]. Elsewhere Cole describes the films as mixed oxides, specifically pointing to the compounds, or perhaps compositions of, VO_2, V_2O_3, and V_2O_5, with typical TCR values near -2 %/K and sheet resistivity between 1 and 100 kOhm/square[5-6]. Woods, while working at
Honeywell, describes the temperature sensitive resistor material as being a 1000 Å polycrystalline semiconductor film, with a TCR of ~2%/C [7]. The same technology, licensed by Hughes, resulted in vanadium oxide thin films on the order of 500 Å, described as polycrystalline, with TCRs in the range of 1.5 to 2.1 %/K and sheet resistivity near 22 kOhm/square[8]. Table 1-1 highlights the electrical properties of interest and the vague microstructural descriptions attributed to vanadium oxide thin films either used in microbolometer devices or desired descriptions in patent applications.

Table 1-1 Properties and microstructure of VOx thin films used in microbolometers

<table>
<thead>
<tr>
<th>Author</th>
<th>Microstructure</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>Cole</td>
<td>Mixed vanadium oxides</td>
<td>[5]</td>
</tr>
<tr>
<td>Cole</td>
<td>A mixture of the phases or compositions of VO_{2}, V_2O_3, V_2O_5</td>
<td>[3]</td>
</tr>
<tr>
<td>Wood</td>
<td>Polycrystalline semiconductor</td>
<td>[7]</td>
</tr>
<tr>
<td>Radford</td>
<td>Polycrystalline</td>
<td>[8]</td>
</tr>
<tr>
<td>Cole</td>
<td>Amorphous, non-stoichiometric vanadium oxide</td>
<td>[1]</td>
</tr>
</tbody>
</table>

It is clear that previous descriptions of the microstructure from the literature are conflicting (amorphous vs. polycrystalline) and there are no specific accounts of stoichiometry, yet the papers previously mentioned likely all describe very similar material, as the films that were studied were either made at Honeywell or made using the technology licensed from Honeywell.

It is also clear from the relevant literature [1, 3, 5-7, 9-11], that there is no scientific understanding relating the structure and properties of thin-film vanadium oxide as used in microbolometers. The Honeywell solution was adequate for the device demands throughout the 90’s and 2000s. Times have changed and the demands have increased. Devices are now resolution limited [2]. Unfortunately all current manufacturers of vanadium-oxide based infrared detectors use the Honeywell method or a closely derived counterpart. In other words, at the time of this writing, the companies that make this material have not reported on the
structure or how that structure influences its sensing behavior. As a result, the Honeywell process is no longer sufficient because the demands it once met have changed.

The lack of a cohesive description of the microstructures of films with properties in the range of interest for microbolometers raises some important questions:

- Can films with properties useful for microbolometers be described by a generalized microstructural description?
- What aspects of the microstructure or chemistry impact the relevant material properties?
- Can knowledge of the microstructure provide useful input to future material processing?

It is the goal of this work to explore the structure-property-processing relationships in pulsed direct current (DC) sputtered vanadium oxide thin films. Pulsed DC sputtering offers a convenient deposition method, and though it is not the ion beam sputtering technique referred to as the Honeywell process above, there are remarkable similarities in the structures of the materials resulting from each technique. As will be discussed in detail later in the text, the microstructure of the material is not as indefinable as the existing literature suggests.

Chapter 2 contains the relevant background for this work, starting with an introduction to microbolometers, the type of microelectronic devices that are used in vanadium oxide based infrared detectors. The background continues with relevant past attempts at depositing microbolometer-quality vanadium oxide, including a section specifically concerning the Honeywell process. Based on the structural results to be discussed in Chapter 4, the background continues with a discussion of both the face-centered cubic (FCC) vanadium “monoxide” phase and some of the amorphous vanadium oxide phases, because the FCC VO, phase and
amorphous vanadium oxide are the structural constituents of both pulsed DC and ion beam sputtered VO$_x$, as will be discussed later.

Chapter 3 contains introductions to the processing and analytical methods used in this work. Relevant literature on reactive sputtering is briefly reviewed in the section on pulsed DC sputtering.

The results of this work start in earnest with Chapter 4, which describes the microstructural analysis of this family of materials and the effects of various sputtering parameters on the resultant structure and charge transport properties. The composite microstructural description established in Chapter 4 is carried through into Chapter 5 which describes the evolution of the microstructure as a function of film thickness. The existence of a thickness-dependant structure provided a means to understand the relationship between the composite structure and the electrical properties. This structure-property relationship is discussed in Chapter 5 in terms of resistivity mixing rules, providing a theoretical framework for understanding the resulting transport properties. The mixing rules also allow for some cursory exploration of the independent influences of the constituent phase properties on the composite resistivity and TCR behavior.

Because it is necessary to understand how a given processing route results in a given microstructure, in Chapter 6 a proposed mechanism for the formation of the nano-composite microstructure is described. As will be discussed, it is proposed that a non-homogeneous sputtering atmosphere leads to the growth of nano-composite microstructures from a single reactive target.

As will be shown in Chapter 4, vanadium oxide thin films deposited at room temperature have a voided, columnar structure regardless of their crystallinity. It will be shown
in Chapter 7 that the addition of an RF bias at the substrate alleviates this deficiency, resulting in both a denser microstructure and nano-crystals replete with planar defects. The resulting microstructure closely resembles that observed in ion beam deposited materials.
Chapter 2

Background

There are two main methods used to create night-vision devices. The first method is light amplification, and it requires that the scene being imaged is already illuminated by ambient light such as starlight or moonlight. This method is limited as ambient light is not always available, and other environmental realities such as fog or smoke can easily attenuate the reflected signal to the point that it cannot be detected. The other method is infrared imaging which uses the infrared radiation being emitted or reflected from features of interest in the field of view [11]. Infrared imaging has the advantages that no external radiation source is required and infrared radiation is capable of transmitting through the aforementioned smoke, fog, etc. Imaging with infrared radiation can be accomplished using devices built on several different detection schemes, including pyroelectric methods, thermopile methods, and resistive bolometer methods [10]. The technique of interest in this work uses the resistive bolometer method. The focus of this work concerns the active sensing material that is deposited onto these devices to allow incident infrared radiation to be detected.

2.1 Infrared microbolometers

An Infrared microbolometer is a micro-machined device composed of a free-standing, thermally isolated pixel suspended above readout integrated circuitry (ROIC) via narrow electrically conductive legs, as shown in Figure 2-1. The free-standing design provides the pixel
sufficient thermal isolation from its surroundings so that incident radiation can create a temperature increase in the pixel, while the narrow conductive legs allow sufficient thermal conductance so that the pixel can cool in time to be used at a sufficient frame-rate. The delicate heat-load balance in these micro-machined devices allows them to operate in an un-cooled manner, extending their usefulness to portable applications.

Figure 2-1 Microbolometer pixel structure

The microbolometer pixel is comprised of various thin-film materials engineered to provide mechanical support, infrared absorption, stress balance, detectibility, and thermal conductance. Figure 2-2 shows a cross-sectional diagram of a typical microbolometer stack structure, in which the portion of the stack that becomes the free-standing pixel is located directly above the sacrificial layer. The resulting floating pixel is typically a sandwich structure beginning with Si$_x$N$_y$, which will become the underside of the pixel, VO$_x$ as the active layer, which is capped with SiO$_2$ and finally Si$_x$N$_y$ [1]. During further processing, metal contacts are added in order to interrogate the resistivity of the active layer. Below the sacrificial layer, an infrared reflecting layer can be added in order to reflect unabsorbed radiation back through the microbolometer stack to increase infrared absorption. This reflective layer is paired with a very precise pixel-substrate separation distance to create a ¼ wavelength cavity [12].
2.1.1 Detection mechanism in infrared microbolometers

The free-standing pixel absorbs infrared radiation through the generation of phonons, resulting in a temperature change of the stack, which in turn causes a change in the resistivity of the active layer material. The use of Si$_x$N$_y$ above and below the VO$_x$ helps increase the infrared absorption as the VO$_x$ does not necessarily absorb well in the infrared regions of interest. As the goal is to detect a change in the temperature of the pixel, the first desirable material property is a high thermal coefficient of resistivity (TCR), i.e. a small change in the temperature of the material results in a large change in the resistivity of the material. The TCR is defined by Equation 1.

$$TCCR(\alpha) = \frac{1}{\rho} \frac{d\rho}{dT}$$  \hspace{1cm} \text{Equation 1}

The resistivity change caused by the increase in the temperature of the active layer can be detected by either measuring the change in current through a biased pixel or by measuring the change in bias across a pixel with constant current running through it [10-11]. For some materials, including vanadium oxide, the constant bias or current methods result in considerable self-heating, and the measurement signal is pulsed to mitigate this effect [13-14]. Surprisingly,
the temperature increase due to the pulsed bias, which is around 1 K, is much greater than the temperature increase due to the absorbed photons, which is around 4 mK [13].

Individual microbolometer devices can then be integrated into arrays and, with the appropriate optics, used to form images.

2.1.2 Microbolometer figures of merit

In order to compare the effectiveness of different microbolometer designs, several figures of merit have been established. In any infrared detection device, the ability of the device to convert incident radiation into useful signal is of primary interest, and the figure of merit that describes this relationship is the responsivity ($\Re$) [10], shown by Equation 2.

$$\Re = \frac{\eta \beta i_b \alpha R}{G}$$  

Equation 2

In Equation 2, $\eta$ is the emissivity, $\beta$ is the fill factor, i.e. the areal fraction of the focal plane array covered by active material, $i_b$ is the bias current, $R$ is the resistance, $\alpha$ is the TCR, and $G$ is the thermal conductance of the Si$_x$N$_y$ legs that support the free-standing pixel. As shown in Equation 2, the responsivity is directly proportional to the TCR and the pixel resistance. TCR is the only variable in Equation 2 that can be freely altered to increase responsivity because thermal conductance is essentially predetermined by the geometry of the pixel, and both bias current and pixel resistance are limited by the underlying readout circuitry. The readout circuitry is designed in such a way that the signal voltage should fall within a specified range, resulting in a limitation on the total resistance of the active layer. The total resistance of the stack structure should be around 100 k$\Omega$[15].
The noise equivalent power (NEP) of a microbolometer is defined by Equation 3 [10].

High responsivity is required in order to lower the noise equivalent temperature difference (NETD) of the device. The NETD is the temperature difference of a pixel that results in a difference in the resulting signal with the same intensity as the rms noise of the device[10]. An active layer with a higher responsivity is one means to overcome the NETD limitation, creating a larger signal for a given temperature change. Unfortunately the TCR and room temperature resistivity are related, and the general rule of thumb is a 1% increase in TCR (%/K) for every order of magnitude increase in resistance [3].

\[
NEP = g \sqrt{\frac{k_b T_b^2}{c} \left( 1 + \frac{2}{\alpha^2 T_b \Delta T_b} \right)}
\]

Equation 3

\[
NEP = \frac{A\varepsilon T}{4\pi dL} NETD
\]

Equation 4

2.1.3 Current implementation of microbolometer devices

In the mid to late 1980’s there were several large pushes by government entities, specifically the night vision electro-optics directorate (NVEOD) and DARPA, to develop uncooled night-vision capabilities for the US military [9]. Out of the major contenders only Honeywell and Texas Instruments (TI) were funded for the development of high-density arrays. By 1991 Honeywell had produced a vanadium oxide microbolometer array with 240 x 336 elements, and TI had produced a barium strontium titanate (BST) based pyroelectric device with 80,000 elements [9]. Around the year 2000, military financial support for BST-based device research dried up or was funneled into VO\textsubscript{x} based microbolometer research. As a result, VO\textsubscript{x} based microbolometers now comprise ~70% of the uncooled infrared imaging market [2].
Table 2-1, taken from a review of state-of-the-art infrared imaging research [2], shows modern manufacturers of focal plane arrays, the type of bolometer used, the size of the array, the size of the elements in the array, and the NETD in units of milliKelvin using f/1 optics and a frequency of 20-60 Hz. Many un-cooled detectors are now resolution limited [2], and the demand for smaller pixels results in less area capable of absorbing photons and a corresponding decrease in the responsivity. Therefore, increases in active layer responsivity without large increases in pixel resistance are required.

<table>
<thead>
<tr>
<th>Company</th>
<th>Bolometer Type</th>
<th>Array format</th>
<th>Pixel pitch (μm)</th>
<th>Detector NETD (mK)</th>
</tr>
</thead>
<tbody>
<tr>
<td>FLIR (USA)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>160 × 120 – 640 × 480</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td>L-3 (USA)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240</td>
<td>37.5</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>α-Si bolometer</td>
<td>160 × 120 – 640 × 480</td>
<td>30</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>α-Si / α-SiGe</td>
<td>320 × 240 – 1024 × 768</td>
<td>R&amp;D: 17</td>
<td>30 – 50</td>
</tr>
<tr>
<td>BAE (USA)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240 – 640 × 480</td>
<td>28</td>
<td>30 – 50</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>160 × 120 – 640 × 480</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>1024 × 768</td>
<td>R&amp;D: 17</td>
<td></td>
</tr>
<tr>
<td>DRS (USA)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240</td>
<td>25</td>
<td>35</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>640 × 480</td>
<td>R&amp;D: 17</td>
<td></td>
</tr>
<tr>
<td>Raytheon (USA)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240 – 640 × 480</td>
<td>25</td>
<td>30 – 40</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240 – 640 × 480</td>
<td>17</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>640 × 480, 1027 × 768</td>
<td>R&amp;D: 17</td>
<td></td>
</tr>
<tr>
<td>ULIS (France)</td>
<td>α-Si bolometer</td>
<td>160 × 120 – 640 × 480</td>
<td>25 – 50</td>
<td>35 – 80</td>
</tr>
<tr>
<td></td>
<td>α-Si bolometer</td>
<td>1024 × 768</td>
<td>R&amp;D: 17</td>
<td></td>
</tr>
<tr>
<td>Mitsubishi</td>
<td>Si diode bolometer</td>
<td>320 × 240 – 640 × 480</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>(Japan)</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>SCD (Israel)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>384 × 288</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td></td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>640 × 480</td>
<td>25</td>
<td>50</td>
</tr>
<tr>
<td>NEC (Japan)</td>
<td>VO&lt;sub&gt;x&lt;/sub&gt; bolometer</td>
<td>320 × 240</td>
<td>23.5</td>
<td>75</td>
</tr>
</tbody>
</table>

2.2 Thin-film vanadium oxide

Thin-film vanadium oxide has been produced by many techniques including: direct current sputtering [16], reactive RF sputtering [17], ion beam sputtering [1, 7, 13-14, 18-23], chemical vapor deposition [24], pulsed laser deposition [25-26], molecular beam expitaxy, and atomic layer deposition [27]. Table 2-2 shows a sample of the various techniques used to
deposit vanadium oxide and the phases that were identified in the resulting material. Despite
the many potential methods for film deposition, reactive sputtering processes are very
common, and commercial fabrication of vanadium oxide based microbolometers is currently
performed using a reactive ion beam sputtering process [1].

Table 2-2 Typical processing parameters for thin film vanadium oxide

<table>
<thead>
<tr>
<th>Author</th>
<th>Method</th>
<th>Power</th>
<th>(\text{PO}_2) range</th>
<th>Total pressure</th>
<th>Substrate temperature</th>
<th>Phases identified</th>
</tr>
</thead>
<tbody>
<tr>
<td>Griffiths[17]</td>
<td>RF – reactive</td>
<td>350 W</td>
<td>0.5 to 2.0 mTorr</td>
<td>7.5 mTorr</td>
<td>250 to 450 °C</td>
<td>VO(<em>2), VO(</em>{13}), mixed, amorphous</td>
</tr>
<tr>
<td>Kusano[16]</td>
<td>DC – reactive</td>
<td>Variable</td>
<td>0.6 mTorr</td>
<td>2.0 mTorr</td>
<td>250 to 550 °C</td>
<td>VO(<em>2), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
<tr>
<td>Miyazaki[28]</td>
<td>RF – reactive magnetron</td>
<td>100 W</td>
<td>0 to 10 %</td>
<td>7.5 mTorr</td>
<td>400 °C</td>
<td>VO(<em>2), VO(</em>{13}), V(_4)O(_9), amorphous</td>
</tr>
<tr>
<td>Chung[29]</td>
<td>DC – magnetron</td>
<td>400 W</td>
<td>0 to 9 %</td>
<td>7.5 mTorr</td>
<td>25 °C</td>
<td>VO(<em>2), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
<tr>
<td>Duchene[30]</td>
<td>RF and DC – reactive</td>
<td>50 W</td>
<td>0 to 20 %</td>
<td>2 to 3 mTorr</td>
<td>250 to 450 °C</td>
<td>VO(<em>2), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
<tr>
<td>Kwan[31]</td>
<td>RF – reactive</td>
<td>350 W</td>
<td>0.7 to 2.5 mTorr</td>
<td>7.5 mTorr</td>
<td>325 to 430 °C</td>
<td>VO(<em>2), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
<tr>
<td>Jerominek[32]</td>
<td>DC – magnetron</td>
<td>200 W</td>
<td>0.6 mTorr</td>
<td>1 %</td>
<td>20 mTorr</td>
<td>450 °C</td>
</tr>
<tr>
<td>Rozgonyi[33]</td>
<td>DC – reactive</td>
<td>4.5 kV</td>
<td>1 %</td>
<td>X</td>
<td>400 °C</td>
<td>VO(<em>2), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
<tr>
<td>Hansen[34]</td>
<td>RF – reactive</td>
<td>300 W</td>
<td>0.6 mTorr</td>
<td>10 mTorr</td>
<td>&lt; 100 °C</td>
<td>VO(<em>2), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
<tr>
<td>Wang[35]</td>
<td>RF – reactive magnetron</td>
<td>120 W</td>
<td>0 to 6 %</td>
<td>7.5 mTorr</td>
<td>420 to 480 °C</td>
<td>VO(<em>2)(B), VO(</em>{13}), VO(_9), amorphous</td>
</tr>
</tbody>
</table>

2.2.1 Processing of vanadium oxide for microbolometers

Much of the early literature concerning thin film vanadium oxide is directed towards
producing crystalline VO\(_2\)[18-21, 25, 30-31, 36] because the metal-to-insulator transition is
located at the moderate temperature of 68 °C[37], making it convenient for switching
applications in non-extreme environments[32]. The metal-to-insulator transition is located
perilously close to the operating temperature of microbolometers; however, designs exist that
exploit the extremely large TCR in the metal-to-insulator transition region due to the increase in
responsivity [38]. Operation in the metal-to-insulator transition region requires the use of a heater/cooler, and for that reason thin film VO$_2$ is not typically used for microbolometer applications. It has been suggested that a composition near that of VO$_2$ is desirable, though not necessarily the equilibrium phase[23, 39]. There is a growing population of reports concerned specifically with the application of vanadium oxide thin films for use in microbolometer applications, though only a few of these reports actually contain information about commercially manufactured microbolometer VO$_x$[40-41].

Not all deposition methods are equally viable for depositing the sensing layer of a microbolometer because the current fabrication methods are monolithic, meaning the entire microbolometer bridge structure is formed directly on top of the readout circuitry. As a result the vanadium oxide deposition process must be performed below ~400 °C [3, 22].

Since the development of the Honeywell microbolometer design and ion-beam sputtering process[1], many attempts have been made to find alternative methods for depositing high TCR vanadium oxide thin films. Wang et al. deposited VO$_2$(B), a metastable polymorph, using ion beam sputtering and offering a maximum TCR of -2.6 %/deg C with a sheet resistance of 35 kOhm/square. Annealing the same material in flowing Ar at 400 °C resulted in a decrease in resistivity and TCR, with an eventual transformation to the stable rutile VO$_2$ polymorph[22]. Ion beam sputtering at a higher voltage (900 V) [23] resulted in as-deposited x-ray amorphous films with sheet resistivity around 1 kΩ/square which crystallized to mixed vanadium oxides upon annealing in Ar:O mixtures, and resulted in an increase in the sheet resistance to 50 kΩ/square with a TCR of -2.1 %/K. While neither stoichiometry nor quantitative phase analysis was performed, the authors proposed that post-deposition annealing benefits the resulting films by increasing the oxygen concentration. This is likely true as ion beam
sputtered films made with low oxygen content or high power[23] are too conductive for this application. Annealing of DC-sputtered films resulted in increases in both TCR and resistivity as well[29].

Tungsten has been added to VO$_2$ via reactive pulsed laser deposition, and resulted in a decrease of the metal-to-insulator transition temperature [25], while the addition of tungsten via DC sputtering appears to have increased both TCR and resistivity [42]. Utilizing a large experimental matrix, Wu determined that film TCR is influenced by the following parameters in order of impact: sputtering target bias, substrate temperature, and composition of the sputtering gas [43], though chamber specific effects such as sputtering geometry and gas delivery also have large effects, making these observations less universally applicable.

Other methods such as ion beam enhanced deposition[44] followed by annealing, or annealing of layered V$_2$O$_5$/V/V$_2$O$_5$[45] resulted in potentially useful materials. In several other cases[3, 23, 29, 44-46] annealing was useful in improving electrical properties and stability, and may be a required step in order to stabilize the VO$_x$ prior to vacuum sealing during camera construction[3]. Clearly there is no single way to create material with the desired properties; however, it is evident that single-phase or single-crystal vanadium oxides are not desirable for use in all microbolometers. Many of the works cited above discuss the broad and ambiguous term “mixed oxides” to describe the resulting material. This term could equally mean multiple crystalline phases, multiple cation valence states, multiple polymorphs of the same stoichiometry, or regions of non-homogeneity whilst maintaining the same structure. To make matters more complicated there are claims that the ideal stoichiometry is sub-stoichiometric VO$_2$[23].
2.2.2 Ion beam sputtering of vanadium oxide and the Honeywell process

As described in Chapter 1, the key aspect of the Honeywell ion beam method is the use of a tightly controlled feedback loop on the oxygen flow rate. The PO$_2$ of the chamber is monitored by a residual gas analyzer (RGA) and the mass flow of the oxygen is adjusted to keep the PO$_2$ constant throughout the deposition. By using the RGA, the actual PO$_2$ in the chamber is controlled, as opposed to the mass flow of the gas. The mass flow and the PO$_2$ are by no means the same thing, and actually have a non-linear relationship[47]. Per the patent, the O$_2$ flow is increased in 0.1 sccm intervals until the RGA measures a ten-fold increase in the PO$_2$. The O$_2$ flow is then reduced to roughly the halfway point of the previous interval. Because this is a reactive process, it is subject to a phenomenon termed “poisoning,” which is simply the oxidation of the sputtering target. This oxidation causes a sudden decrease in the sputtering rate due to the stronger bonds in the oxide phases compared to the metallic phase[48-49].

From the above description it appears the set-point for film deposition is maintained on the steep portion of the “poisoning” curve, shown as the line from “A” to “B” in Figure 2-3. This is a difficult position to maintain[48-49], which explains the use of the RGA feedback loop. It is also evident that variability in the PO$_2$ results in a drastic shift on the target oxidation curve, potentially leading to a very different film. Why this particular part of the curve is used in this patent is not specifically stated; however, considering the state the target must be in at this PO$_2$ is potentially instructive. Figure 2-4 shows the fraction of both the target and the substrate that are covered with compound (reacted) material as a function of the flow of reactive gas. If we assume that the Honeywell process does operate on the A->B portion of Figure 2-3, then the target and substrate have a 40 to 100% percent compound coverage according to Figure 2-4. As a 100% coverage is easy to achieve with an oxidized target we can assume that was not the goal.
It appears that the “Honeywell” process keeps the target in a partially oxidized state, potentially with 50% of the target being oxidized. This sputtering process more closely resembles co-sputtering from a vanadium oxide target and a vanadium metal target at the same time, and likely contributes to the unique properties achieved in these films.

Figure 2-3 Relationship between PO\textsubscript{2} and reactive gas flow in a reactive sputtering process. From reference [50].

Figure 2-4 Fractions of the target (\(\theta_t\)) and substrate (\(\theta_c\)) covered with compound instead of metal as a function of reactive gas flow. Note that the theory does not predict a hysteresis in the reactive process, which would show up in the grey area in the figure. Figure taken from reference [50].
Woods reported the logarithmic relationship between the room temperature resistivity ($\rho_{300K}$) and the TCR of ion beam sputtered vanadium oxide[7]. The data from reference [7] has been plotted in Figure 2-5 on a Log(resistivity) scale, which makes the Logarithmic relationship between TCR and $\rho_{300K}$ very apparent. Plotted along with the Woods data is vanadium oxide data from reference [8] which was also deposited via the Honeywell ion beam sputtering technique. It is apparent from the plot in Figure 2-5 that a TCR near -2.0 % K$^{-1}$ can be accomplished at a resistivity$_{300K}$ of 0.1 Ohm cm. It is also apparent that use of the ion beam sputtering technique does not guarantee deposition of the same material from system to system.

Figure 2-5 The relationship between TCR and room temperature resistivity of ion beam sputtered vanadium oxide. Both sets of data were produced using the Honeywell patented process. The data in the figure was taken from references [7-8]
2.3 Vanadium oxide phases of interest for this work

The vanadium-oxygen phase diagram[4], shown in Figure 2-6, is replete with many distinct stable phases, many of which exhibit large thermal coefficients of resistivity. Starting on the metal side with increasing oxygen the phases are: $V_2O[51]$, $VO_x$ (where $0.8<x<1.3$), $V_2O_3[52]$, the homologous series of phases called the Magnelli phases designated by $V_nO_{2n-1}$, $VO_2[53]$, and finally $V_2O_3[54]$, the amorphous counterpart of which has also been largely studied[55-56]. Between $V_2O_3$ and $VO_2$ the phases, denoted by the formula $V_nO_{2n-1}$, exhibit metal-to-insulator transitions, whereby the electrical conductivity of each phase increases several orders of magnitude with increasing temperature due to structural phase transformations[57].

![Vanadium-Oxygen phase diagram](image)

Figure 2-6 Vanadium-Oxygen phase diagram, taken from reference [4].

Table 2-3 depicts some of the common vanadium oxide phases along with their room temperature resistivity values, temperature coefficients of resistivity in the semiconducting and metallic phases, crystal structures, and densities. It is evident from Table 2-3 that vanadium oxide was chosen for use in microbolomter applications because of the high TCR values
observed in the pure crystalline phases. The downside to using a pure crystalline phase; however, is the existence of metal-to-insulator transitions which pose a challenge to readout schemes that rely on a predictable and manageable range of resistivity values, and the inherent dangers in using a material that undergoes a structural rearrangement every time it is cycled through the MIT.

Table 2-3 Crystalline vanadium oxide phases and some of their properties

<table>
<thead>
<tr>
<th>Phase</th>
<th>Crystal Structure</th>
<th>Density at 300 K</th>
<th>Resistivity at 300 K</th>
<th>TCR of semiconducting phase</th>
<th>TCR of metal phase</th>
</tr>
</thead>
<tbody>
<tr>
<td>VO&lt;sub&gt;x&lt;/sub&gt; [58]</td>
<td>Face centered cubic</td>
<td>5.76 g/cc</td>
<td>0.0067 Ω cm</td>
<td>-0.69% K&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>-0.039% K&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;3&lt;/sub&gt; [59]</td>
<td>Monoclinic/corundum</td>
<td>4.87 g/cc</td>
<td>0.005 Ω cm</td>
<td>-12.5% K&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>0.14% K&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>VO&lt;sub&gt;2&lt;/sub&gt; [60]</td>
<td>Monoclinic/rutile</td>
<td>4.34 g/cc</td>
<td>16 Ω cm</td>
<td>-4.5% K&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>-0.06 % K&lt;sup&gt;-1&lt;/sup&gt;</td>
</tr>
<tr>
<td>V&lt;sub&gt;2&lt;/sub&gt;O&lt;sub&gt;5&lt;/sub&gt; [55]</td>
<td>Orthorhombic</td>
<td>3.35 g/cc</td>
<td>630 Ω cm</td>
<td>-2.7% K&lt;sup&gt;-1&lt;/sup&gt;</td>
<td>N/A</td>
</tr>
</tbody>
</table>

Not all of the vanadium oxide phases are relevant to this work. The only crystalline phase observed in both industrial [41] and as-deposited films from this work was the FCC VO<sub>x</sub> phase, while various amorphous vanadium oxides were observed in many of the films deposited herein. The nature of FCC VO<sub>x</sub> and amorphous vanadium oxide will be discussed in more detail below.

2.3.1 FCC vanadium monoxide (VO<sub>x</sub>)

Vanadium monoxide (VO<sub>x</sub>) is a rocksalt-structured crystal composed of two interpenetrating sublattices; one occupied by metal ions and the other by oxygen anions. The crystal can accommodate a large degree of non-stoichiometry, ranging in oxygen concentration from ~0.8 < x < 1.3 at high temperature[51, 58]. This same stability range has been observed in bulk[58] as well as epitaxial thin film geometries[61], though it is uncertain as to whether or not stoichiometries outside this range were attempted in epitaxial form. The gross non-
stoichiometry is accommodated by large concentrations of vacancies on both sublattices. At x=1 there are approximately 15% vacancies on each sublattice[58].

The largest single source of data on FCC VO$_x$ comes from Banus et al. who prepared fifty ingots of VO$_x$ via arc melting and single crystal VO$_{1.29}$ via an arc-Czochralski growth technique[58]. The goal of the work was to provide a consistently measured set of samples that spanned the whole stability range of the monoxide phases TiO$_x$ and VO$_x$, as previous partial collections of data resulted in confusing interpretations, such as the falsely reported metal-to-insulator transition[59] that was later assumed to result from V$_2$O$_3$ contamination[51]. Oxygen content, resistivity as a function of temperature, lattice parameter, vacancy concentrations, density, Seebeck coefficient as a function of temperature, and magnetic susceptibility as a function of temperature were measured for all single-phase samples, though samples outside the stability range were also made[58]. It was found that density decreased and the lattice parameter increased with increased oxygen concentration, as shown in Figure 2-7.

![Figure 2-7 Density (d) and lattice parameter (a$_0$) of FCC VO$_x$ as a function of ‘x.’ From reference [58].](image-url)
The same trend in lattice parameter was found in a series of annealed mixtures of V metal and V$_2$O$_3$[62], and again in samples created by sintering of mixtures of VH$_{1.5}$ and V$_2$O$_3$[63]. Unlike TiO, increasing oxygen concentration results in an expansion of the lattice parameter, as the smaller ionic radius of V$^{2+}$, compared to Ti$^{2+}$, makes the crystal more susceptible to O$^{2-}$ / O$^{2-}$ repulsion[64]. Application of high pressure, thereby decreasing the concentration of atomic vacancies while causing the lattice parameter to increase[65]. The spontaneous incorporation of vacancies at ambient conditions results in a decrease in the energy of the crystal which is greater than the energy lost to the Madelung potential offered by a fully occupied lattice[64].

The “sub-oxide” phases between V and VO are structurally related, and can be viewed as either tetragonal or distorted tetragonal structures wherein the oxygen and vanadium ions occupy separate octrahedral site sub-lattices [51, 66-67]. Introduction of oxygen to the BCC vanadium metal lattice results in an elongation of the unit cell along the corresponding axes. Between metallic V and VO is a phase identified as V$_2$O[66], which can be described as either a tetragonally distorted oxide phase with ordered oxygen vacancies, or as a distorted BCC metal lattice[68], as shown in Figure 2-8.

![Figure 2-8 Comparison of the crystal structures of B.C.C. V metal, tetrahedral V$_2$O and F.C.C. VO$_x$. The VO$_x$ model does not contain the full unit cell and displayed atoms make it falsely appear to have the same stoichiometry of the V$_2$O structure. All structures are drawn to the same scale. The introduction of oxygen atoms along the sides of the structure causes an elongation in one direction (V$_2$O) and then both directions of the structure (VO$_x$).](image-url)
Below a stoichiometry of \( x = 1 \), point defects aggregate into planar arrangements in the form of \( \{111\} \) sheets of oxygen vacancies\(^{[67]} \). The presence of the vacancy sheets results in displacement of V sites resulting in a decrease in the V-V separation. Above a stoichiometry of \( x = 1 \), the dominant defect structure is interstitial vanadium ions tetrahedrally “coordinated” with four metal vacancies\(^{[69]} \). The tetrahedrally coordinated interstitial is the same structure observed in the ordered, high oxygen content phase. The metal interstitial/vacancy tetrahedron is accompanied by V-site displacements, resulting in an increase in the V-V separation.

The concentration of vanadium interstitials has been found to increase with increasing oxygen content\(^{[69]} \). A composition-dependent variation in diffuse electron scattering suggests the defects are spatially correlated\(^{[68]} \) and closely related to the ordered phase (VO\(_{1.2-1.3}\))\(^{[70]} \). The inter-defect distance, however, is different between the ordered and disordered VO\(_x\) phases, with the ordered phase having a longer vector between defect clusters\(^{[69]} \).

Electron diffraction studies suggest the charge state of the vanadium ions in VO\(_x\) is between V\(^0\) and V\(^{1+}\), suggesting the bonding is somewhere between ionic and covalent\(^{[69]} \). Using Pauling’s empirical relationship between electronegativities, \( \chi \) in Equation 5, with \( \chi_V = 1.63 \) and \( \chi_O = 3.44 \), the V-O bond is 56% ionic, and partial ionization of the vanadium atom is expected.

\[
\% \text{ ionic character} = 100 \times \{1 - e^{-1/4(X_A-X_B)^2}\}
\]

Equation 5

The electronic properties of vanadium monoxide are unpredictable based on interpretations relying solely on either crystal field theory (CFT) or tight-binding band theory because the 3d electrons present on the vanadium cation sites are capable of being either localized (CFT) or delocalized (tight-binding)\(^{[65]} \).
Delocalization can occur through several different mechanisms; V-V interaction due to the octahedral sharing of edges or faces, the mixing of high-valence 3d orbitals with neighboring oxygen 2p and 2s orbitals creating cation-anion-cation interactions, and the distortion of octahedral sites due to a high-valence (small) cation, more suited to a tetrahedral site, forming a shorter anion-cation bond [65].

Goodenough postulated a relationship between the ability of electrons to delocalize and the degree to which nearest neighbor cation d-orbitals overlap [71]. The generalized form of this empirical relationship is given by Equation 6 [65].

\[
R_c(M^{m+}) = R_o(z) - \rho_1 m - \rho_2 S_i (S_i + 1) - \rho_3 (Z - Z^{IV})
\]

Equation 6

- \(m\) = cation valence
- \(R_o(z)\) = cation separation
- \(\rho_1, \rho_2, \rho_3\) = empirical coefficients
- \(S_i\) = total 3d electron spin parallel to nearest neighbor electron in question
- \(Z^{IV}\) = atomic number of titanium (for vanadium case)
- \(Z\) = atomic number of vanadium

For the case of V-V separation distances Equation 6 becomes Equation 7 [65] through the input of Goodenough’s semiempirical values for \(R_o\) and \(\rho_i\).

\[
R_c(M^{m+}) = R_o(z) - \rho_1 m - \rho_2 S_i (S_i + 1) - \rho_3 (Z - Z^{IV})
\]

Equation 7

The resulting critical separations are dependent on the vanadium valence and are 2.92 Å for \(V^{2+}\) and \(V^{5+}\) or 2.94 Å for \(V^{3+}\) or \(V^{4+}\) [65].

There an electronic structure with the existence of a gap in the itinerant bands created by V-V orbital overlap due to a non-zero \(U\) value in the crystal[64], as illustrated in Figure 2-9. The \(U\) value is the energy difference between a cation in a \(m+\) state and an \(m+1\) state, while the transfer energy \((b)\) is related to the amount of interaction between the electrons on neighboring atoms. As can be seen in Figure 2-9, the greater the interaction between the neighboring
cation’s electrons, the greater propensity there is for a gapless density of states. In an ideal VO_x crystal, i.e. one without any vacancies, there would be an energy gap in the density of states between a lower band consisting in states of primarily O 2p character and an upper band consisting of states with primarily V 3d character with the Fermi level residing within this gap, this correlates to b < b_g in Figure 2-9, and is shown schematically in Figure 2-10.

![Figure 2-9 Pseudo-particle energy versus transfer energy from reference [64].](image)

The large concentration of defects inherent in this material results in an increased density of defect states in the gap region. Trap states associated with both cation and anion vacancies lie in the vicinity of the gap and overlap in energy, essentially eliminating the bandgap. Cation vacancies result in two trapped holes on the cation site. The two trapped holes create trap states located in the t_2^* band above the Fermi energy.

At x < 1, the cation vacancies are outnumbered by anion vacancies and the resulting hole trap states are annihilated by neighboring anion vacancies (actually by the electrons necessarily trapped at those sites). As a result the band tails above the Fermi level are reduced; however, the second trapped hole state remains in the band. At x > 1, the cation vacancies dominate and the second trapped hole state remains in the band above the Fermi level.
Figure 2-10 Goodenough’s proposed density of states for VO$_x$ with (a) $x < 1$ and (b) $x > 1$. From reference [64]

Conduction at all temperatures and at all values of $x$ appears to be via a two channel mechanism, whereby the ability of delocalized bands to carry either holes or electrons (depending on the stoichiometry) is augmented by the ability of trapped states to enable hopping from defect to defect. Depending on the temperature one or the other dominates. At $x < 1$ the Fermi level is above the gap and electrical conduction results from electron conduction in the itinerant band due to V-V orbital overlap. The conductivity magnitude is metal-like yet electron mobility is low due to the high concentration of trap states resulting from the trapped holes on cation sites. It is important to note that the TCR of $x < 1$ VO$_x$ is still negative, meaning the conductivity is not via free electrons and either the number of carriers or the carrier mobility increases with increasing temperature. At $x > 1$, the Fermi level is in the lower band, below the gap, and conduction is dominated by hole transport in the lower band, where localized defects act as acceptor states[64]. At low enough temperature, the conductivity is dominated by electrons hopping from defect state to defect state.

Across the whole range of $x$, the activation energy increases with increasing oxygen concentration; however the rate at which it increases changes dramatically at $x > 1$, in other
words the increase in lattice parameter with increasing $x$ (i.e. the increase in V-V separation) has a larger effect on the activation energy above $x = 1$. The increase in activation energy appears consistent with the increase in lattice parameter resulting in an increased gap between delocalized states. Across the range $0.99 < x < 1.30$ the resistivity on a Log$(\rho)$ vs $1/T$ plot is not linear. For the Banus, Reed and Strauss data the activation energy was extracted from the range $155 \, K < T < 300 \, K$. At low temperature the Log$(\rho)$ behavior is proportional to $T^{-n}$; however the exponent varies from -0.075 to -0.56 from $x=0.99$ to $x=1.30$.

According to Banus [58], effective activation energies for conduction increase with increasing oxygen concentration and V-V separation distance, suggesting a decrease in V-V orbital overlap and hence a decreased density of states in the gap region is responsible for the increased activation energy.

Thermoelectric power was found to switch from negative to positive with increasing oxygen concentration near a stoichiometry of $x=1$[58]. Similar behavior in the thermoelectric power as the stoichiometry approached $x=1$ was found elsewhere [62]. The sign change of the Seebeck coefficient is consistent with the presumed change in the transport at $x = 1$ from electron dominated below $x = 1$ to hole dominated above $x = 1$.

The assumption that the energy $U$ is not equal to 0 may not be the source of the gap between the delocalized states [65]. In that case the splitting, implied by the transport data (specifically the increase in $E_s$ with $x$), may result from the significant cation vacancy concentration. With such a large concentration of vacancies, the basis orbitals used to form bands may more appropriately belong to V-V pairs rather than crystal field split local cation orbitals, in which case the V-V separation distance is even more critical to the transport.
As discussed by Mott, the aperiodic nature of the cation vacancy distribution (the structure is disordered) results in a non-periodic potential throughout the material, which closely resembles an amorphous material[72].

2.3.2 Amorphous vanadium oxide (a-VO<sub>5</sub>)

The stable crystalline phases present on the V-O phase diagram[4] between VO and V<sub>2</sub>O<sub>5</sub> can be viewed in terms of a VO<sub>6</sub> octahedron wherein a central V ion is coordinated by six neighboring oxygen ions. The case of V<sub>2</sub>O<sub>5</sub> is extreme as there are 5 oxygen ions that form a square pyramid about the vanadium ion with a very long sixth oxygen ion located perpendicular to the pyramid base. Whether or not this oxygen is considered part of a highly distorted octahedral arrangement is a bit subjective. As all the compounds can be viewed as octahedral arrangements, the stoichiometric variation from VO to V<sub>2</sub>O<sub>5</sub> is achieved by the sharing of common octahedral corners, edges, and faces, thereby increasing the number of oxygen anions with respect to each vanadium. It is clear that in pure vanadium-oxygen compounds there is a preference for octahedral coordination, and that trend likely transfers to the amorphous counterparts. Zachariasen[73] predicted that V<sub>2</sub>O<sub>5</sub> was the only one of the vanadium oxides capable of forming a glass. The other vanadium valence states require either common edges and faces, or are too highly coordinated with oxygen atoms. At the time of Zachariasen’s prediction, V<sub>2</sub>O<sub>5</sub> had not yet been made in a glassy state; however, it was years later[55] and now constitutes the majority of literature concerning amorphous vanadium oxide.

Amorphous vanadium pentoxide (a-V<sub>2</sub>O<sub>5</sub>) has been studied extensively, and is considered a model system for studying the small polaron hopping mechanism [72]. It has typically been deposited via splat cooling of molten glass[55-56, 74-75]; however, it has also
been deposited via gel-based techniques[76], CVD[24], RF sputtering[75], and evaporation[77]. IR spectroscopy revealed spectra with the same number of bands at the same frequencies for both amorphous and crystalline $V_2O_5$, both of which were representative of 5-coordinated V with a distant oxygen atom[78]. Electron spin resonance (ESR) of the $V^{4+}$ ion in both amorphous and crystalline $V_2O_5$ suggests there is little change in the local structure between the crystalline and amorphous phases[78]. This result was confirmed by Kahn[79] who interpreted both amorphous and crystalline spectra, which suggested the axial anisotropy of the $V^{4+}$ sites is conserved between the crystalline and amorphous oxides.

Amorphous $V_2O_5$, like its crystalline counterpart, is considered an oxygen-deficient semiconductor, resulting from thermal decomposition during high temperature processing, and for every atom of oxygen evolved, two electrons are left behind[55]. These electrons can either be singly trapped separately on two $V^{5+}$ centers resulting in two $V^{4+}$ centers, or doubly trapped resulting in one $V^{3+}$ center. The conductivity is considered to occur by the small-polaron hopping mechanism and is described as dependent on both the concentration of $V^{4+}$ centers and their separation distance[55, 80].

ESR of crystalline $V_2O_5$ suggests the 3d electron is delocalized on 4 V ions, while the hyper-fine structure in amorphous $V_2O_5$ appears to point at the localization of the 3d electron to one V ion[79]. The TCR for amorphous $V_2O_5$ is very large, varying from –2.5 to -4.4 % K$^{-1}$ for the glassy material and -0.979 % / K for polycrystalline $V_2O_5$[55].

While there is no shortage of scientific literature concerning amorphous $V_2O_5$, there are few reports of amorphous vanadium oxides with varying stoichiometry. Kennedy et al. in 1969 deposited what they believed to be amorphous VO$_2$ and V$_2$O$_3$[81]. Below 66 °C the amorphous VO$_2$ film had a resistivity below that of its crystalline counterpart, and it lacked the metal-to-
The a-V$_2$O$_3$ film also had a room temperature resistivity below that of its crystalline counterpart and also lacked the metal-to-insulator transition. Heat treatment of both films at 600 °C for 24 hours in argon resulted in crystallization to the expected phases; however, the resistivities in both cases were still higher than they were prior to crystallization. The authors report that the resistivities in each case resembled the high-temperature values and proposed that during growth, which occurred when the substrate temperature was above the metal-to-insulator transition of both VO$_2$ and V$_2$O$_3$, the short-range order that formed more closely resembled the thermodynamically stable high-temperature, lower resistivity structures. As conductivity is generally influenced by short-range order, this could explain why the amorphous films exhibited such low resistivity values. The authors did not attempt to form amorphous films at substrate temperatures below the metal-to-insulator transitions to test their hypothesis, and their results highlight the difficulty in ascertaining the crystallinity of amorphous material. Without the careful use of either high brilliance X-rays or high energy electrons it is difficult to be certain the material under study is truly amorphous. It is possible that the “amorphous” films made by Kennedy were in fact nano-crystalline films. Nano-crystallinity, even in the presence of amorphous material, could explain the anomalously low resistivities that they measured.

Duchene et al. reported the deposition of amorphous VO$_2$ using reactive RF sputtering[30]. They found the presence of amorphous vanadium oxide when flowing 10% or more oxygen. The resulting amorphous films were found to have resistivity in the $10^3$-$10^4$ Ω cm range with activation energies around 0.29 eV. The authors were not attempting to make amorphous material and did not characterize the amorphous compositions either chemically or structurally.
Both Griffiths[17] and Kusano[16] report that amorphous films were deposited when low substrate temperature and high oxygen flow were used, in agreement with previous findings. Neither paper highlighted properties nor characteristics of the amorphous films as they were attempting to deposit and study crystalline VO\textsubscript{2} films. Miyazaki also reported the deposition of amorphous films with increasing oxygen pressure, resulting from target oxidation during deposition[28].

The lack of information in the literature regarding amorphous vanadium oxides other than a-V\textsubscript{2}O\textsubscript{5} makes it difficult to understand how stoichiometry affects the local arrangement of atoms in other amorphous vanadium oxide phases. Local atomic arrangement greatly influences V-V orbital overlap, which in turn directly affects whether or not electrons in V 3d states are itinerant or localized[65]. It may not be possible to form delocalized bands in such disordered material, regardless of stoichiometry, in which case transport in all amorphous vanadium oxide would be through a hopping mechanism.
Chapter 3

Experimental methods

This chapter contains the experimental methods used in this work to both deposit and analyze thin-film vanadium oxide. Each section describes the necessary theory for each technique and how the technique was implemented in this work. Specific experimental conditions will be included alongside results in later chapters; however, general parameters will be included in the following sections.

3.1 Pulsed direct current (DC) magnetron sputtering

Pulsed direct current (DC) sputtering is often employed in reactive sputtering processes when the reaction products are electrically insulating and therefore cause charge buildup on the surface of the target. When charge has built up enough to create a bias approaching the DC sputtering bias, the plasma is effectively quenched, as there is no attraction of charged ions towards the target. The charging issue can be overcome by the introduction of a brief positive pulse which draws electrons to the charged target, neutralizing any built-up charge. When the negative bias is returned to the target, the positively charged gas species are again accelerated towards the sputtering target. In asymmetric pulsed dc sputtering, the negative bias on the target due to the pulse and the negative bias resulting from the charged surface add to make an even larger bias on the reacted surface of the target. The greater bias results in increased
sputtering energy and preferential sputtering of the dielectric material[82]. Asymmetric pulsed DC biasing is shown schematically in Figure 3-1.

![Figure 3-1 Schematic of asymmetric pulsed DC sputtering. During the negative portion of the pulse the Ar ions (purple arrows) are attracted to the target and sputtering occurs. During the positive portion of the pulse electrons (black arrows) are drawn to the target to neutralize any built-up charge. From reference [47].](image)

### 3.1.2 Reactive sputtering

Non-reactive sputtering is performed in moderate vacuum (2-100 mTorr) with a target biased with respect to the anode (typically the remainder of the chamber). A plasma discharge is initiated by a single free electron being accelerated by the potential from anode to cathode. This accelerated electron has sufficient energy to ionize the gas in the chamber (typically argon) generating more free electrons and gas ions. This process cascades until a stable plasma discharge is present in front of the target. The ionized gas, upon acceleration by the potential on the cathode, is capable of knocking atoms from the target into the gas phase from which they deposit onto the chamber walls/substrate.

Reactive sputtering is mechanistically no different than non-reactive sputtering except for the introduction of a reactive gas capable of forming compound materials with the target. This reactive gas can also participate in sputtering, and the ionization of the reactive gas makes
it more reactive with respect to the un-reacted target material [83]. Parameters that influence the reaction at the target, thereby influencing the film composition, include relative reactive gas flow, ion current density, and sputtering power. With increasing reactive gas flow, the target surface becomes more and more reacted until the entire surface of the target has transformed into compound material. The compound material may have stronger bonds and becomes more difficult to sputter from the target, so increasing reactive gas flow can result in decreased sputtering rate.

A mechanistic model describing reactive sputtering was developed by Berg in the mid 1980’s [48] and has been extended over the years [49]. The Berg model is generalized and consists of a target, the substrate (which includes the chamber), a reactive gas influx, and the pumping system, which removes un-reacted gas. The target and substrate are further broken down into regions covered with either un-reacted or reacted compound. The Berg model accurately reproduces experimental results [49], suggesting the relevant parameters have been included.

Because reactive gas flow is generally not controlled by a feedback system in reactive sputtering processes, the complex behavior elucidated by the model in the transition region is not typically observed experimentally. The Berg model shows that with increasing mass flow of reactive gas, the rate of deposition decreases drastically at the onset of target oxidation exhibiting a complicated “s-shaped” behavior, shown in Figure 3-2. In the reverse direction, i.e. decrease in mass flow of the reactive gas, the deposition rate follows the same path. The “s-shaped” behavior is lost in experimental studies, and a hysteresis between the deposition rate and the mass flow of the reactive gas is observed because the partial pressure of the reactive gas varies non-linearly with the flow of the reactive gas, the history of the chamber, and the
history of the target. In the transition region there are two deposition rates for a given reactive gas mass flow, one for the increasing flow direction and a lower deposition rate for the decreasing mass flow direction.

In a concise review, Sproul points out the fundamental realities behind reactive sputter deposition and the constraints imposed by target oxidation [47]. With increased oxygen flow, the PO$_2$ of the system changes only slightly until the target is fully oxidized, at which point the PO$_2$ increases rapidly. This sudden increase occurs because the growing film, which was capable of gettering the increased oxygen flow when in a metallic state, is less effective at gettering the added mass flow of oxygen once it has oxidized. After oxidation of the target and substrate, further oxygen injection merely follows a linear behavior determined by the pumping capabilities of the system. Reducing the flow causes the PO$_2$ to decrease linearly to a much lower reactive gas flow than in the increasing case, finally plummeting after the oxide has been sputtered clean from the target. The hysteresis appears because it takes longer to sputter the oxide from the target due to the increased PO$_2$ which results from the lack of gettering by the substrate.

Reproducibility is enhanced in the oxidized state because the target composition is predictable and stable. With increased pumping speed the hysteresis be avoided and PO$_2$ will increase linearly with reactive gas flow; however, this comes at a cost, as the additional pumping requirements can become costly [47]. Attempts to directly control the partial pressure of the reactive gas have been carried out by monitoring and building feedback loops on the optical emission signal of the un-reacted species, partial pressure measurement from a mass spectrometer, and the cathode voltage, with the latter resulting in adequate control of a nitridation but not an oxidation process [47]. Control of the partial pressure of the reactive gas
can result in disappearance of the target hysteresis, and subsequent ability to deposit films in the previously “forbidden” zone in the parameter space. Typical mass flow controllers are not fast enough to respond to feedback signals, and the use of fast-acting valves to control the injection of gas is often necessary [47].

![Figure 3-2 Characteristic relationship between the sputter erosion rate, represented by the optical emission spectra (OES) peak height, and the reactive gas flow ($Q_{\text{tot}}$). A processing hysteresis occurs between the direction of increasing or decreasing the reactive gas flow rate. This hysteresis results in two different target conditions at the same reactive gas flow [49].](image)

In reactive DC magnetron sputtering of TiO$_x$, increased total sputtering pressure caused a decrease in the intensity of x-ray diffraction peaks accompanied by a slight increase in grain size [84]. Increased pressure also resulted in continual changes in film morphology from compact films at low pressures to porous films at higher pressures. This morphological change may result from lower adatom mobility, as sputtered species lose considerable energy through multiple scattering in the higher pressure atmosphere. Deposition rate decreases as collisions in the gas phase backscatter sputtered species, and the formation of compound materials, with increased bond strength, causes a sputtering yield decrease as well with increased sputtering pressure.
Reactive sputtering can be performed with a variety of biasing techniques including RF, DC and pulsed DC. In the case of reactive sputtering of alumina, increasing oxygen partial pressure resulted in both increased oxidation of the deposited material and increased disorder in the films. Initially, at low partial pressure, the films exhibited co-deposition of Al metal and γ-Al₂O₃, with increased partial pressure the films were composed of pure γ-Al₂O₃ with increasing lattice parameter, then increasingly amorphous material at high partial pressures. It was found that RF sputtered material had superior hardness, owing to film densification resulting from a biased substrate, but the expense and low deposition rates proved pulsed-dc sputtering to be a better compromise in terms of cost/time/properties when wear-resistant Al₂O₃ layers are desired [85].

With increasing oxygen partial pressure in the reactive sputtering of vanadium oxide, four distinct sputtering regimes, as shown in Figure 3-3 [86]. 1. In the oxygen-depleted zone, the growing film (on the substrate and surface of the chamber) is able to getter the injected oxygen at a sufficient rate to avoid oxidation build-up on the target. Because the target is not being affected, the deposition rate does not decrease, and the mass deposition rate increases due to the addition of oxygen into the growing film. 2. Additional injected oxygen begins to react with the target, decreasing sputtered vanadium flux sufficiently to reduce the deposition rate of the growing film. 3. Oxidation of the target increases abruptly, further decreasing the deposition rate as the oxygen reaction rate is greater than the rate of oxide sputtering. 4. The target and film are saturated with oxygen, and additional oxygen injection does not affect target or film composition. Reaction with oxygen at the target is ion-assisted and therefore leads to more stable vanadium-oxygen species, whereas the reaction at the growing film is thermally activated and likely results in metastable phases. Two mechanisms cause a decrease in sputter
yield, one is the less effective nature of sputtering by O\(^+\) compared to Ar\(^+\), and the other is the increased surface binding energy of V-O bonds compared to V-V bonds. The sputtering yield decreases 10 times as the target transforms from metal to oxide. The authors found that VO\(_2\) could only be grown in the transition region, and to form VO\(_2\) in a more stable manner would require altering the system geometry to change the composition of the film relative to the target.

![Graph showing discharge voltage vs. oxygen partial pressure](image)

Figure 3-3 Reactive sputtering of vanadium oxide thin film from reference [86].

In a closely related study, thin film vanadium oxides with stoichiometries varying from V\(_2\)O\(_3\) to V\(_2\)O\(_5\) were created in the transition region at elevated substrate temperatures (300-500 deg C) and a total pressure of 2.0 mTorr [87].

Reactive sputtering can also be performed in ion beam deposition systems wherein a high energy ion beam is aimed at a metal target, and reactive gas is introduced into the chamber. As with other reactive sputtering techniques, sputtered material is sensitive to the sputtering atmosphere. Increasing PO\(_2\) in the reactive ion beam sputtering of vanadium oxide
results in decreased deposition rate and increased oxygen content in the growing film [21]. XRD results of ion beam sputtered VO_x confirm the phases VO_x, VO_2 and V_2O_5 were all grown via changes in PO_2, providing evidence of the flexibility of this technique [88]. Increasing substrate temperature also allows for microstructural control, resulting in increased grain size and oxygen content with increasing temperature[20].

3.1.1 Sputtering equipment and general sputtering parameters

Reactive sputtering of a vanadium metal target (99.9% pure) was performed in two separate sputtering chambers. The primary chamber was a Kurt Lesker CMS-18 sputtering tool equipped with three sputtering guns, shown schematically in Figure 3-4. The system was equipped with a load lock in order to reduce contamination in the processing chamber and to reduce pumping time between consecutive runs. Prior to every set of film depositions, the chamber was “seasoned” by reactively sputtering for 30 minutes with a blank wafer loaded in the carrier. The “seasoning” run allowed the inner walls of the chamber to be coated with a composition near that of the desired films, which is extremely important in reactive sputtering work, as the inner walls of the chamber constitute an active part of the pumping system for low oxygen content depositions [49]. The secondary sputtering chamber was a generic, multi-port Huntingdon chamber that was not equipped with a load lock, and it will be referred to as the “Research Tool” throughout this thesis.

The geometry between the two sputtering chambers was significantly different; however, the throw distance between the substrate and the sputtering gun was 10 inches in each system. The CMS-18 was situated to hold the substrate so that it faces down and the sputtering guns face up, as shown in Figure 3-4, while the research tool was equipped with a
single sputtering gun oriented above the substrate, as shown in Figure 3-5. The means by which gas was introduced into each chamber was also very different. In the CMS-18, the gas was brought in via two separate paths. Ar was brought in via a gas-ring mounted on each sputtering gun in order to provide sufficient pressure near each gun to initiate a plasma discharge. A combination of Ar and O₂ was brought into a separate gas-ring located 3 inches below the substrate. In the Research Tool the reactive gas (O₂) and argon were brought in to a gas ring situated 1 cm below the sputtering gun.

Figure 3-4 Schematic of the sputtering geometry employed in the Kurt Lesker CMS-18 chamber. The chamber has a “sputter-up” geometry with the sputtering guns located in the bottom of the chamber. Each gun has its own gas-ring and there is a gas-ring that feeds the substrate region as well.

Figure 3-5 Schematic of the Research Tool chamber. Samples were loaded through the front chamber door because the system does not have a load-lock. Reactive and non-reactive gas are fed to a gas ring located just beneath the sputtering target surface.
For this work, pulsed DC sputtering of a metallic vanadium target was performed using either an Advanced Energy Sparc-le 20 power supply in a constant power mode with a pulse frequency of 25 kHz on the CMS-18, or an ENI RPG-50 plasma generator with a pulse frequency of 50 kHz. Most films were deposited using 300 W of power, which typically resulted in 1 amp of cathode current and a DC bias of 300 volts in a pure Ar atmosphere.

Substrates were typically rotated at 10 revolutions per minute (RPM) to provide increased uniformity across the six inch substrate holder. In several cases, which will be described in detail in Chapter 6, the substrate was intentionally not rotated, or rotated at a much slower rate.

All depositions were performed in an atmosphere of argon and oxygen, the relative flow rates of which were varied in order to achieve varying sputtering conditions. Both gas flow rates were controlled by mass flow controllers. In some cases, when O₂ flow rate was below 1% of the rated total flow of the O₂ MFC, a mixture of 10% O₂ in Ar was used. For all the films deposited in this work the O₂ flow rate was the main variable used to vary the composition of the sputtering atmosphere. The relevant control parameter was the relative oxygen flow rate ($\frac{\text{flow[O}_2\text{]}}{\text{flow[Ar]+flow[O}_2\text{]}}$), which will be reported from here on as the % O₂ (or $100 \times$ relative flow rate). This is an important distinction because in no way was the PO₂ controlled in these experiments, and it is likely that the PO₂ was changing during each deposition due to the reactive sputtering processes described previously. The presence of a changing sputtering environment was more likely in the Research Tool due to the lack of a load lock.

A substrate bias was not applied for the majority of films deposited for this work; however, the application of a substrate bias appears to be critical in depositing dense films with
properties comparable to those achieved in ion beam sputtered material. Chapter 7 contains results on samples grown with an applied RF substrate bias.

3.2 Transmission electron microscopy (TEM)

Transmission electron microscopy was used extensively in this work to collect both images and diffraction patterns from both cross-section and plan-view vanadium oxide samples. TEM requires specimen which are thin enough that they are transparent to high energy electrons (typically 100-300 keV). Extensive processing is required to make samples electron transparent, and the sample preparation techniques used in this work are discussed in section 3.2.1. In general TEM involves the observation and recording of electrons that have been scattered by the sample. Scattered electrons can be recorded either by the way they scatter spatially in images (section 3.2.2), the way they interfere after scattering in diffraction patterns (section 3.2.3), or by the amount of energy they lose by scattering in electron energy loss spectra (section 3.2.4).

3.2.1 Sample preparation

Two types of samples were used for this work: cross sectional samples which depict the sample in a plane perpendicular to the growth direction, and plan-view samples which depict the sample along the growth direction. Plan-view samples required no sample preparation as they were grown on Formvar® coated TEM grids, allowing a polymer support for the growing film which could be removed post deposition by exposure to chloroform. In most cases this provided a sample free from any defects that could potentially be introduced via processing;
however, this technique was only useful for samples under ~ 1000 Å in thickness. Cross sectional samples required extensive preparation which is described in Appendix A.

In order to achieve electron transparency, samples were ion-milled in a Fischione Model 1010 ion mill, cooled via liquid nitrogen to a stage temperature of at least -80 °C. The ion mill has two Ar ion guns, one on the top and one on the bottom, initially aimed at the specimen at an angle of 12 ° with respect to the plane of the specimen. The guns were run at 3kV and 5mA until perforation of the cross-sectional area was observed. The specimens were rocked ±30 ° throughout. After perforation, the milling angle was reduced to 8° with respect to the plane of the specimen and milled at a reduced current of 3 mA for an additional 10 minutes.

3.2.2 Bright-field and dark-field imaging

Imaging in the TEM is performed by magnifying the image plane of the main lens, the objective lens, which uses the TEM specimen as its object. Bright-field (BF) images are formed using either the central beam, which has undergone no or very slight scattering, or all of the diffracted beams. In bright-field images vacuum, i.e. the absence of sample, does not diffract electrons and appears “bright” in images. The contrast in these images results from both mass-thickness differences and diffraction effects. Mass-thickness contrast arises because both thicker portions and portions with greater average atomic mass diffract the central beam more strongly and appear darker in the bright-field image. Both contrast mechanisms can be exaggerated by the insertion of an aperture (the objective aperture) in the back-focal plane of the objective lens. The back-focal plane of the objective lens is where beams diffracted by the sample to the same angle come back to a focus. An aperture in this plane can thus exclude
beams diffracted outside of the central beam, keeping them from contributing to the bright-field image.

Dark-field (DF) imaging is the creation of an image using electrons that have been diffracted out of the central beam. This image can be created by placing the objective aperture around the diffraction spot produced by a crystalline portion of the sample. The aperture allows only the diffracted beams to contribute to the image and results in an image where vacuum, which cannot scatter the electrons through this aperture, appears “dark.” The best way to generate this image is to tilt the incident beam in such a way as to allow the diffracted beam to travel down the optic axis of the microscope, thereby avoiding the lens aberrations, the effects of which increase the further the electrons are from the optic axis. This technique is called centered dark-field imaging.

A modification of this technique, called hollow cone dark-field (HCDF) imaging, involves taking the tilted incident beam and rotating it azimuthally about this optic axis. The incident beam thus appears like a cone, with the cone tip at the sample and the cone angle determined by the scattering angle. This rotation allows for all of the beams diffracted to the same scattering angle to momentarily travel through the objective aperture. Using the hollow cone beam allows the image to more accurately represent polycrystalline samples in which the orientations of the grains are random.

3.2.3 Electron diffraction in the TEM

Electron diffraction in the TEM is performed by magnifying the back-focal plane of the objective lens. Because the sample sits at the object plane of the objective lens, the lens brings all of the electrons scattered in the same direction back to a point in the back-focal plane. In
order for a sample to diffract the electrons of the central beam, it must be oriented in such a way that electrons scattered from one atom of the unit cell are in phase with those scattered from another atom in the unit cell. The relationship among scattered beams is known as the structure factor, and it can be determined for any set of reflections within the crystal. Reflections with a structure factor of zero cannot contribute to the diffraction pattern. The scattering angles through which electrons are diffracted are determined by the inter-planar spacings of the crystal, as shown by the well known Bragg’s law in Equation 8.

$$\lambda = 2d_{hkl} \sin(\theta)$$

Equation 8

Electron diffraction in the TEM has the benefit of providing two dimensions of reciprocal space as opposed to the narrow window accepted by most powder or thin-film x-ray diffraction detectors. One benefit to this large amount of data is the ability to rotationally integrate the diffraction signal, thereby increasing the signal to noise ratio of the data. The rotational average also provides data in a format similar to X-ray diffraction 2θ patterns, making it easier to interpret and quantify the data.

3.2.4 Electron energy loss spectroscopy (EELS) in the TEM

Electron energy loss spectroscopy (EELS) is the dispersion and measurement of transmitted electrons based on the amount of energy they lost interacting with the sample. Electrons of a known energy are transmitted through the sample and lose energy by scattering, ejecting core electrons, and exciting plasmons to name a few mechanisms. The resulting spectrum is dispersed in energy via an L-shaped magnet, focused via a system of lenses, hexapoles, and sextapoles onto a scintillator, and recorded as an image via a CCD camera.
The spectrum can be divided into three parts: the zero-loss peak, the low-loss region, and the core-loss region. The zero-loss peak, at 0 eV energy loss by definition, constitutes the electrons that have not lost any energy while traversing the thickness of the sample. Any width in the zero-loss peak is due to the energy spread of the incident beam and the energy broadening due to the spectrometer. The full-width at half-maximum (FWHM) of the peak is often used as a measure of the resolution of the spectrum. The low-loss region, extending from 1-10 eV, typically exhibits low frequency oscillations generated by both the bulk and surface plasmons of the sample. This cloud of electrons is perturbed by the incident electrons and oscillates while returning to the ground-state. The oscillating charge in the sample results in oscillations in the low loss region of the spectrum. Typically metals have very large oscillations in the low loss region due to the large concentration of free carriers, while insulators have much smaller low-loss plasmon features. Finally the core-loss region, extending from ~10 eV on is composed of absorption edges due to the ejection of core-state electrons into the unoccupied density of states. In the absence of solid state effects, these edges would have a saw tooth shape; however, solid state effects resulting in a non-constant density of unoccupied states result in more complex features in the vicinity of the edge known as electron energy-loss near-edge structure (ELNES) [89].

3.2.5 Experimental details

TEM was performed on three separate microscopes: a Philips CM420 operated at 120 kV, a JEOL 2010 with a LaB₆ emitter operated at 200 kV, and a JEOL 2010-F operated at 200 kV. Only the 2010-LaB₆ was equipped with a hollow-cone generator. The 2010-F, equipped with a dedicated Gatan Enfina EELS spectrometer, was capable of collecting EEL spectra with a
resolution of 1 eV at a dispersion of 0.02 eV/channel. Every attempt was made to collect low-loss and core-loss regions with identical lens conditions; however, in the case of particularly thin samples, low loss spectra were too intense to be collected under identical conditions. In those cases the spot size was reduced for acquisition of the low loss region.

The 2010-LaB₆ was equipped with a Gatan Tridiem energy loss filter, commonly referred to as a Gatan imaging filter (GIF). The GIF allows the imaging of electrons that have lost a specified amount of energy by the insertion of an aperture in an energy-dispersive plane. The aperture has an adjustable width, so electrons falling within the energy window set by that width can progress through the remaining optics in the GIF to form an energy-loss image. The same treatment can be performed using the zero-loss peak resulting in a either a zero-loss image or an energy-filtered diffraction pattern. Filtering of the zero-loss peak in a diffraction pattern dramatically cuts down on the intensity at low scattering angle as shown in Figure 3-6. This is important when there are features of interest present in the diffraction pattern at low scattering angle.

![Image of graph showing the effect of zero-loss energy filtering on the intensity of a polycrystalline diffraction pattern.](image)

Figure 3-6 The effect of zero-loss energy filtering on the intensity of a polycrystalline diffraction pattern. The intensity at small scattering vector is reduced as the inelastically scattered electrons were filtered out of the pattern.
3.3 Rutherford backscattering spectrometry (RBS)

Rutherford backscattering spectrometry (RBS) is the analysis of thin films using a high energy beam of He$^{++}$ particles. The He$^{++}$ beam is focused onto the surface of the sample, and those ions that are backscattered and hit the detector contain information about the depth distribution of the elements in the sample. The mass and energy of the incident ion are known from the experimental parameters, and the geometry and energy of the scattered ion are measured. The physics underlying the elastic interaction between the probe ion and the target ion are well understood, and excellent descriptions can be found elsewhere [90].

Using the now classic simulation code RUMP[91] or one of the newer codes such as SIMNRA[92] or NDF DataFurnace [93], depth distributions of elements in the sample can be determined from an iterative procedure of guessing a sample configuration, simulating a spectra and calculating error between the experimental data and the simulation. Unfortunately, the older methods employed in RUMP and SIMNRA require apriori knowledge of the sample structure, and a certain amount of experience is necessary to make appropriate initial guesses of the starting sample structure [93].

3.3.1 Experimental details

RBS was used in this work to determine the film stoichiometry as other methods such as energy dispersive X-ray spectroscopy (EDS) and electron energy-loss spectroscopy cannot be used due to peak overlap between the oxygen and vanadium signals. Specifically, in EDS the O K peak (524.9 eV) and the V L$_{\alpha1,2}$ (511.3 eV) and L$_{\beta1}$ (519.2 eV) overlap within the energy resolution of the technique (~135 eV). In other words, the peaks with contributions from oxygen and
vanadium are indistinguishable. In EELS, the ionization edges for V L$_{2,3}$ and the O K can be distinguished; however, there is insufficient spacing between the edges to properly fit and remove the V L-edge background underneath the O K edge, a step necessary for quantification. X-ray photoelectron spectroscopy was also found to be inappropriate. As the vanadium to oxygen ratio was the main goal of the RBS measurement, separate films were grown for this analysis. Films grown on Si/SiO are subject to less accurate results due to the presence of oxygen in both the film of interest and the underlying thermal oxide. Vanadium oxide was grown on glassy carbon substrates to avoid the underlying oxygen and the overlap between the Si and O peaks.

RBS data was collected at two separate accelerator facilities. The first set of samples was analyzed using a 2.275 MeV He$^{++}$ beam at a backscattering angle of 160°. The experimental geometry is shown in Figure 3-7. All spectra were collected to a total accumulated charge of 20 micro-Coulombs. All subsequent data was collected on a 2.0 MeV He$^{++}$ accelerator located at Rutgers University in Piscataway, NJ. This data was collected to a total accumulated charge of either 10 or 20 micro-Coulombs with the detector located at a backscattering angle of 163°.

Figure 3-7 RBS experimental geometry. The 2 MeV He$^{++}$ beam is deflected into the RBS chamber where it is incident on the sample surface. The He$^{++}$ ions that are backscattered are collected on a solid state detector located at an angle of 17 with respect to the incoming beam. The solid angle of the detector is determined by the location of the detector with respect to the sample surface.
3.3.2 Data analysis using SIMNRA

For data collected at the Rutgers University accelerator, the program SIMNRA [92] was used for data analysis. SIMNRA is a code for the simulation of ion scattering experiments using Rutherford cross sections. The use of nuclear reactions can also be included in the simulation, hence the “N” in the code’s name. For this work, experimental parameters provided by the facility were input into the code. Estimates based on sample deposition parameters and known sample structure were used as first guesses for the sample structure.

3.4 Temperature coefficient of resistivity measurements

Resistivity was measured in one of two ways for this work. A 4D mapping four point probe instrument was used for films with a sheet resistivity below 800k Ω/square and in cases where resistance uniformity across large areas was desired. Resistivity was also measured using a two-probe technique with linear co-planar contacts deposited through a shadow mask. Ohmic contacts were made using Nickel metal, 300Å Ti/1000 Å Pt, and 300Å Cr/1000Å Au contacts. A HP 4140B picoammeter was used for two probe measurements, typically sweeping the voltage from -5 to +5 Volts with 0.5 Volt steps.

For TCR calculations, resistivity was measured from 20 to 80 °C at five degree increments with a precision of ± 0.2 °C. The resulting Resistivity(T) data was fitted using Equation 9, and both the resistivity prefactor (ρ₀) and the apparent activation energy(Eₐ) were extracted from the fit. In Equation 9, k is Boltzmann’s constant.

\[ \rho = \rho_0 \exp \left( \frac{E_a}{kT} \right) \]  

Equation 9
The derivative with respect to temperature of Equation 9 yields Equation 10, which rearranges to Equation 11, showing the connection between TCR and apparent activation energy.

\[
\frac{d\rho}{dT} = \left(-\frac{E_a}{kT^2}\right)\rho_0\exp\left(\frac{E_a}{kT}\right)
\]  

Equation 10

\[
TCR = \frac{1}{\rho} \frac{d\rho}{dT} = -\frac{E_a}{kT^2}
\]  

Equation 11

Using Equation 11, the TCR can be calculated at the desired temperature, typically 300 K, using the apparent activation energy relevant at the chosen temperature.
Chapter 4

The effects of sputtering conditions on microstructure, chemistry, and transport

Reactive sputtering results in the formation of a reaction product at the substrate, on the walls of the chamber, and at the sputtering target [48]. Complete oxidation of the target, commonly referred to as “poisoning,” [82] results in a sudden decrease in the deposition rate [86], as the vanadium-oxygen bonds require more energy to break than the vanadium-vanadium bonds. The onset of target oxidation is abrupt and typically results in a gap in the available film stoichiometries, as operating within the region between the metallic and oxidized zones is unstable [50]; however, it is possible to operate within the transition region given appropriate control over the actual PO$_2$ in the sputtering atmosphere [1].

For this work, vanadium oxide thin films were deposited using pulsed DC reactive magnetron sputtering. This chapter aims to describe the relationship between common sputtering parameters and the resulting film microstructures and properties.

4.1 Experimental details

Several distinct series of samples were deposited for this work in two separate sputtering systems, the details of which were discussed in Chapter 3. Each series was designed to independently study the effects of several relevant deposition parameters, including: sputtering pressure, relative oxygen flow rate, sputtering power, and substrate bias.
In order to investigate the effects of relative oxygen flow rate on the properties of vanadium oxide thin films, several series of films were deposited at constant total pressures of 2.5, 5, and 10 mTorr. Relative oxygen flow rate samples were deposited in both sputtering chambers, allowing for a broader sample set not specifically tied to any one deposition chamber.

The first set of samples was deposited in the CMS-18 chamber. Relative oxygen flow rate was varied from 2.5 to 30% of the total flow. Total sputtering pressure was usually held at 5 mTorr, total flow at 18 sccm, power at 300 W, and sputtering time at 900 seconds. All films were deposited on (100) crystal Si with 1000 Å of thermal oxide. Films were co-deposited on Formvar® coated Cu TEM grids for plan-view examination and glassy carbon substrates for RBS analysis. Table 4-1 shows the deposition parameters for the samples in this series (PO$_2$) as well as the total pressure series (P$_{tot}$), which was also deposited in the CMS-18 chamber.

Table 4-1 Deposition parameters for oxygen flow and total pressure samples deposited in the CMS-18 chamber. All samples were made with a total power of 300 W and a total sputtering time of 900 s.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total Pressure (mTorr)</th>
<th>% O$_2$ Flow (O$_2$/O$_2$+Ar)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO$_2$ – 1</td>
<td>5</td>
<td>2.5</td>
<td>609 ± 7</td>
</tr>
<tr>
<td>PO$_2$ – 2</td>
<td>5</td>
<td>5</td>
<td>534 ± 9</td>
</tr>
<tr>
<td>PO$_2$ – 3</td>
<td>5</td>
<td>6.7</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 4</td>
<td>5</td>
<td>8.3</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 5</td>
<td>5</td>
<td>10</td>
<td>722 ± 10</td>
</tr>
<tr>
<td>PO$_2$ – 6</td>
<td>5</td>
<td>15</td>
<td>236 ± 8</td>
</tr>
<tr>
<td>PO$_2$ – 7</td>
<td>5</td>
<td>30</td>
<td>142 ± 7</td>
</tr>
<tr>
<td>P$_{tot}$ – 1</td>
<td>2.5</td>
<td>5</td>
<td>403 ± 7</td>
</tr>
<tr>
<td>P$_{tot}$ – 2</td>
<td>7</td>
<td>5</td>
<td>579 ± 8</td>
</tr>
<tr>
<td>P$_{tot}$ – 3</td>
<td>10</td>
<td>5</td>
<td>882 ± 9</td>
</tr>
<tr>
<td>P$_{tot}$ – 4</td>
<td>15</td>
<td>5</td>
<td>896 ± 9</td>
</tr>
</tbody>
</table>

The second set of samples was deposited in the Research Tool at total pressures of 5 and 10 mTorr, with relative oxygen flows of 0, 2.4, 4.8, 7, and 9.1% of the total flow, corresponding to 0, 1, 2, 3, and 4 standard cubic centimeters (sccm) of oxygen. In these series of samples, the Ar flow rate was kept constant at 40 sccm. Total pressure was adjusted by
throttling the gate valve in front of the turbo pump until the pressure as read from the capacitance manometer was at the desired level. This pressure adjustment was different than in the CMS-18 chamber in which the gate valve was set at a fixed throttle position and the total flow rate of the Ar varied from run to run. Table 4-2 shows the deposition parameters for samples made with varying oxygen flow rates in the Research Tool at 5 mTorr (PO$_2$ – 2) and 10 mTorr (PO$_2$ – 3).

Table 4-2 Variable oxygen flow rate samples deposited in the Research tool chamber. All samples were sputtered for 900 s with 300 W of power.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Total Pressure (mTorr)</th>
<th>% O$_2$ Flow (O$_2$/O$_2$+Ar)</th>
<th>Thickness (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PO$_2$ – 2 – 1</td>
<td>5</td>
<td>0</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 2 – 2</td>
<td>5</td>
<td>2.4</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 2 – 3</td>
<td>5</td>
<td>4.8</td>
<td>2500 ± 14</td>
</tr>
<tr>
<td>PO$_2$ – 2 – 4</td>
<td>5</td>
<td>7</td>
<td>2280 ± 15</td>
</tr>
<tr>
<td>PO$_2$ – 2 – 5</td>
<td>5</td>
<td>9.1</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 3 – 1</td>
<td>10</td>
<td>0</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 3 – 2</td>
<td>10</td>
<td>2.4</td>
<td>Not measured</td>
</tr>
<tr>
<td>PO$_2$ – 3 – 3</td>
<td>10</td>
<td>4.8</td>
<td>2167 ± 15</td>
</tr>
<tr>
<td>PO$_2$ – 3 – 4</td>
<td>10</td>
<td>7</td>
<td>2430 ± 15</td>
</tr>
<tr>
<td>PO$_2$ – 3 – 5</td>
<td>10</td>
<td>9.1</td>
<td>413 ± 12</td>
</tr>
</tbody>
</table>

Total pressure variation experiments were performed in the CMS-18 sputtering chamber, keeping the relative oxygen flow rate fixed at 5% of the total flow rate while increasing the sputtering pressure by increasing the flow rates of both gases. The gate valve position for the chamber, and hence the pumping speed, was kept the same as for the partial pressure series; however, larger total gas flow rates were necessary to achieve the greater total pressures in the chamber.

For variable power experiments, the Research Tool was used. In order to eliminate the need for chamber pump-down prior to each run, a custom sample shutter allowing deposition on ¼ of a six inch Si wafer was installed 5 mm above the sample holder. The substrate shutter shielded the remaining ¾ of the wafer from exposure to sputtered species. Each experiment required only one initial pump-down to < 1 × 10$^6$ Torr prior to deposition of the initial sample in
the series. Subsequent depositions required only brief evacuation via the turbo-pump to return to a base pressure < $1 \times 10^6$ Torr. In this manner, four consecutive samples could be run in the time it would otherwise take to run one deposition. This configuration had the added benefit that the chamber was not exposed to atmosphere between depositions.

Variable sputtering power experiments were performed at a total pressure of 5 mTorr with 40 sccm Ar flow and either 3 or 4 sccm O$_2$ flow resulting in relative oxygen flow rates of 7% and 9.1%. Sputtering power was varied from 300 to 450 W in 50 W increments. Table 4-3 shows the deposition parameters for the two sets of variable power depositions.

Table 4-3 Deposition parameters for variable power series. All samples were deposited for 900 s at a total pressure of 5 mTorr.

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Power (W)</th>
<th>% O$_2$ Flow O$_2$/O$_2+$Ar</th>
<th>Thickness (Å)</th>
<th>Growth Rate (Å/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pow-1</td>
<td>300</td>
<td>7%</td>
<td>2280 ± 14</td>
<td>2.5</td>
</tr>
<tr>
<td>Pow-2</td>
<td>350</td>
<td>7%</td>
<td>2529 ± 12</td>
<td>2.8</td>
</tr>
<tr>
<td>Pow-3</td>
<td>400</td>
<td>7%</td>
<td>2315 ± 15</td>
<td>2.6</td>
</tr>
<tr>
<td>Pow-4</td>
<td>450</td>
<td>7%</td>
<td>2687 ± 14</td>
<td>3.0</td>
</tr>
<tr>
<td>Pow-5</td>
<td>300</td>
<td>9.1%</td>
<td>1132 ± 12</td>
<td>1.3</td>
</tr>
<tr>
<td>Pow-6</td>
<td>350</td>
<td>9.1%</td>
<td>1912 ± 10</td>
<td>2.1</td>
</tr>
<tr>
<td>Pow-7</td>
<td>400</td>
<td>9.1%</td>
<td>2877 ± 14</td>
<td>3.2</td>
</tr>
<tr>
<td>Pow-8</td>
<td>450</td>
<td>9.1%</td>
<td>3130 ± 15</td>
<td>3.5</td>
</tr>
</tbody>
</table>

4.2 The microstructural transition between amorphous and nanocrystalline growth

Throughout all of the depositions described in the previous section, only one crystalline phase was observed via both X-ray and electron diffraction. The FCC VO$_x$ phase was found in films deposited with either low oxygen sputtering atmospheres or high sputtering power conditions. Figure 4-1 shows glancing incidence X-ray diffraction (GIXRD) patterns from a subset of films deposited with increased relative oxygen content during growth. The oxygen content of the films in Figure 4-1 increases from A to F. As can be seen in the figure, the increased intensity of Bragg diffraction peaks reflects the increase in the crystallinity of the films with decreasing
oxygen content. The crystalline patterns designated A through E index to the FCC VO$_x$ phase, while the remaining film designated F is X-ray amorphous.

![GIXRD patterns](image)

Figure 4-1 GIXRD patterns from vanadium oxide films with increasing oxygen content. Both oxygen flow during deposition and oxygen content in the film increases from A to F.

The GIXRD patterns shown in Figure 4-1 are indicative of the types of patterns observed for all films deposited using the parameters described in section 4.1. The specific details of each sample in Figure 4-1 are shown in Table 4-4. It is clear from both the peak intensities and full widths at half max (FWHM) that both the amount and size of FCC VO$_x$ grains change with sputtering conditions. In other words, satisfying the growth conditions for FCC VO$_x$ does not result in the deposition of films with the same grain size or FCC VO$_x$ concentration. This result implies that there is control over certain aspects of the microstructure, certainly the grain size, by changing gas flow or total pressure.
Table 4-4 Deposition parameters and properties of nano-crystalline series

<table>
<thead>
<tr>
<th>Sample ID</th>
<th>Power (W)</th>
<th>Total Pressure (mTorr)</th>
<th>% O\textsubscript{2} Flow \textsubscript{O\textsubscript{2}/O\textsubscript{2}+Ar}</th>
<th>Thickness (Å)</th>
<th>Resistivity (Ω cm)</th>
<th>TCR (°C-1)</th>
</tr>
</thead>
<tbody>
<tr>
<td>NC-A</td>
<td>290</td>
<td>7.5</td>
<td>1965 ± 20</td>
<td>.029</td>
<td>0.37</td>
<td></td>
</tr>
<tr>
<td>NC-B</td>
<td>290</td>
<td>7.5</td>
<td>1955 ± 20</td>
<td>.16</td>
<td>0.56</td>
<td></td>
</tr>
<tr>
<td>NC-C</td>
<td>302</td>
<td>10.2</td>
<td>2000 ± 20</td>
<td>2.55</td>
<td>2.3</td>
<td></td>
</tr>
<tr>
<td>NC-D</td>
<td>272</td>
<td>5</td>
<td>1866 ± 19</td>
<td>0.66</td>
<td>1.5</td>
<td></td>
</tr>
<tr>
<td>NC-E</td>
<td>275</td>
<td>5</td>
<td>2232 ± 22</td>
<td>96.8</td>
<td>2.5</td>
<td></td>
</tr>
<tr>
<td>NC-F</td>
<td>282</td>
<td>10</td>
<td>2448 ± 24</td>
<td>263</td>
<td>2.2</td>
<td></td>
</tr>
<tr>
<td>NC-G</td>
<td>290</td>
<td>7.5</td>
<td>2000 ± 20</td>
<td>0.56</td>
<td>0.8</td>
<td></td>
</tr>
<tr>
<td>NC-H</td>
<td>280</td>
<td>7.5</td>
<td>2227 ± 22</td>
<td>954</td>
<td>2.90</td>
<td></td>
</tr>
<tr>
<td>NC-I</td>
<td>285</td>
<td>7.5</td>
<td>2347 ± 23</td>
<td>8870</td>
<td>2.91</td>
<td></td>
</tr>
<tr>
<td>NC-J</td>
<td>262</td>
<td>10</td>
<td>1668 ± 17</td>
<td>860</td>
<td>2.82</td>
<td></td>
</tr>
<tr>
<td>NC-K</td>
<td>272</td>
<td>5</td>
<td>2097 ± 21</td>
<td>15,300</td>
<td>3.13</td>
<td></td>
</tr>
</tbody>
</table>

The trend of increased crystallinity with increased oxygen content was also observed in the Research Tool at total sputtering pressures of both 5 and 10 mTorr. GIXRD patterns from films deposited in that chamber at both 5 and 10 mTorr are shown in Figure 4-2.

Figure 4-2 GIXRD patterns of 5 mTorr (left) and 10 mTorr (right) variable oxygen flow films (PO\textsubscript{2}-2 and PO\textsubscript{2}-3 series)

In both cases the relative oxygen flow rate was increased from 0 to 10% of the total flow, and in both cases two transitions in growth were observed, from vanadium metal to FCC VO\textsubscript{x} to X-ray amorphous vanadium oxide.

The patterns from the 2.5 % O\textsubscript{2} (1 sccm) films in between the vanadium metal and FCC VO\textsubscript{x} films have only one peak, which appears to be the (110) reflection from the metallic phase shifted to lower scattering angle. This shift is consistent with an increase in the lattice
parameter of the metallic phase due to dissolved oxygen[66]. At both 5 and 10 mTorr total pressure, the FCC VOₓ phase was deposited at a relative oxygen flow rate of 5% (2 sccm of O₂).

Increasing sputtering power has a similar effect to decreasing the oxygen flow rate. Figure 4-3 shows GIXRD patterns from films deposited in the Research tool with increasing sputtering power. The deposition conditions for the 300 W film in this series were chosen such that the resulting film was X-ray amorphous. Increasing the sputtering power in this condition resulted in increased film crystallinity as shown by the appearance of the FCC VOₓ Bragg peaks in the 400 W pattern shown in Figure 4-5. Increasing the power further to 450 W resulted in diffraction peaks with smaller FWHM values, indicating coherent scattering from larger domains of FCC VOₓ in the 450 W film.

Figure 4-3 GIXRD patterns from 5 mTorr variable sputtering power samples. With increased sputtering power the samples exhibit increased crystalline diffraction intensity.

The film microstructure was analyzed with the TEM. Figure 4-4 shows both a bright and a dark field image from a cross sectioned sample, a dark field image from a planview sample, and an electron diffraction pattern from a representative nano-crystalline film.
Figure 4-4 TEM data from a representative nano-crystalline film. (a) Bright field image. (b) Dark field image using the (200) diffraction ring. (c) Plan-view dark field image using the (200) diffraction ring. (d) Selected area diffraction pattern from the plan-view specimen.

As seen in Figure 4-4, the nano-crystalline films typically exhibit columnar growth which can start fine and coarsen with increased thickness. The grain size is typically on the order of 5-10 nm and depends on the sputtering conditions. The electron diffraction patterns, like the one shown in Figure 4-4d index to the FCC VO\textsubscript{x} “monoxide” phase.

Films that did not exhibit the FCC VO\textsubscript{x} phase were found to be “amorphous” via both X-ray and electron diffraction. It is worth noting that for many films, X-ray diffraction, even in glancing incidence geometry, did not detect crystallinity in many of the nano-crystalline films, and the use of electron diffraction was required to fully ascertain crystallinity. The lack of sensitivity to small crystalline domains is one potential reason that other “amorphous” VO\textsubscript{x} films reported in the literature are suspect, such as those described in section 2.3.2. Figure 4-5 shows a bright-field image and an electron diffraction pattern from a representative amorphous film. The bright field image shows voided columnar growth, while the selected area diffraction pattern (SADP) shows diffuse, radially symmetric rings indicative of an amorphous material. The voided columnar growth is expected in low temperature deposition [94].
Figure 4-5 TEM bright field image (left) and diffraction pattern (right) from a representative amorphous vanadium oxide film. The diffuse, radially symmetric rings in the diffraction pattern are indicative of an amorphous material.

Selected area diffraction patterns were used to ascertain crystallinity from plan-view, self-supporting samples when available. For the films deposited at a constant total pressure of 5 mTorr, increasing the relative oxygen flow caused a change in the film growth from nanocrystalline to amorphous between relative flow rates of 7 and 10%. Bright-field images of amorphous materials do not typically contain much contrast; however, the images from nanocrystalline samples clearly show dark regions due to diffraction contrast from the nanocrystalline phase. Figure 4-6 shows bright-field images of both the amorphous and nanocrystalline films and dark-field images of the nanocrystalline films utilizing the (220) diffraction ring.
Figure 4-6 Bright-field and dark-field TEM images of PO$_2$ and P$_{tot}$ samples. Films deposited under low oxygen flow or low total pressure conditions exhibit the FCC VOx phase, whereas those deposited at higher total pressure of higher oxygen flow are amorphous.

From the dark-field images it is evident the relative oxygen flow affects the size and distribution of the nanocrystalline phase, as was noted in the GI vaccinations results. All films exhibit mass-thickness contrast resembling columnar morphology, as is expected from the structure zone model [94]. The porosity predicted via the same model is also apparent in both nanocrystalline and amorphous films deposited with this technique.

Similar results were found for films deposited at lower pressure. Figure 4-7 shows dark-field TEM images of a set of films deposited at 2.5 mTorr total pressure with variable oxygen
flow rate. From left to right in Figure 4-7, the oxygen flow increases from 7.5 to 10 to 12.5% of the total flow. Note that the grain size and morphology changes with increased oxygen flow rate from large columnar grains to small dispersed equiaxed grains at higher oxygen flow.

Figure 4-7 Dark field TEM images of films deposited at 2.5 mTorr total pressure. From left to right the relative oxygen flow rate was increased from 7.5 to 10 to 12.5% of the total flow. Also from left to right the grain size of the nano-crystalline phase decreases, and the amount of amorphous material increases.

Deposition with either a low total pressure (< 5 mTorr) or a low relative oxygen flow (< 5 %O₂) resulted in nano-crystalline growth, while either higher total pressure or relative oxygen flow rate resulted in amorphous films. The parameter-structure relationship is mapped out in Figure 4-8, where a small region in the parameter space in which nano-crystalline films form becomes apparent.

The black curve in Figure 4-8 highlights a boundary, below which nanocrystalline material is deposited and above which amorphous material is deposited. Note that the set of samples traversing the % O₂ axis at a constant total pressure of 5 mTorr essentially follows the reactive sputtering process through target oxidation, which occurs very near the transition from nano-crystalline to amorphous growth.
Figure 4-8 Deposition parameter space and the nano-crystalline to amorphous transition at 300 W constant power. The black line denotes the transition in parameter space. Below the line films were found to be nano-crystalline and above the line films were found to be amorphous.

Increasing total pressure resulted in a similar nanocrystalline-to-amorphous transition in film growth between total sputtering pressures of 7 and 10 mTorr. As in the case of increasing relative oxygen flow rate, the amorphous films maintained a columnar structure. Increasing total pressure also appears to result in increased porosity in the films. In Figure 4-6 the 15 mtorr 5% film exhibits extensive porosity compared to the other amorphous films. In nanocrystalline films the grain size appears to correlate with the total pressure as well, with higher pressure films having smaller nanocrystallites compared to lower total pressure samples.

The amorphous to FCC VO$_x$ boundary described here is remarkably similar to the one observed by Griffiths[17] using reactive RF sputtering in a variable sputtering atmosphere. In that work, the transition extended up to ~150 °C substrate temperature before the amorphous phase was replaced with a “mixed” oxide material.

Aside from the microstructural changes, increasing the relative oxygen flow rate also resulted in an increase in the amount of oxygen incorporated into the films, as measured by RBS. Figure 4-9 depicts the amount of oxygen in each film (as x in VO$_x$) as a function of the
relative oxygen flow. Included in Figure 4-9 are the samples from the constant total pressure series as well.

Increasing total sputtering pressure resulted in increased oxygen content in the films from $x = 0.74 \pm 0.06$ for the 2.5 mTorr sample to $x = 2.24 \pm 0.14$ for the 15 mTorr sample. Similar to increasing relative oxygen flow rate at a fixed total pressure, film stoichiometry changed from $x = 0.74 \pm 0.06$ for the 2.5 mTorr film to $x = 2.0 \pm 0.12$ for the 5 mTorr film. Again it appears that depositing thin film $\text{VO}_x$ via reactive pulsed-DC sputtering between $x = 1$ and $x = 2$ is difficult.

![Figure 4-9 Oxygen content, as measured by RBS, as a function of $P_{O_2}$. Note that with increased oxygen flow the oxygen content in the films was found to increase. Also note the large range of film stoichiometries that was not realized in actual films. There is a large gap between $x = 1.3$ and $x = 1.8$ where no films lie. It is possible this range of stoichiometries is not available because they occur on the steep part of the target reaction curve.](image)

In the $P_{O_2} - 1$ series, moving from a relative oxygen flow of 2.5 to 5% resulted in an increase in $x$ from $1.2 \pm 0.08$ to $2.0 \pm 0.12$, meaning films between these stoichiometries were
not deposited, and deposition in this region may not be possible using this deposition technique. This is likely the result of target oxidation, below which lower oxygen contents are deposited and above which higher oxygen contents are deposited. Deposition on the steep part of the target oxidation curve could be made possible by controlling PO$_2$, as previously stated.

When the amorphous-to-nanocrystalline transition is viewed alongside the oxygen content in each film, depicted in Figure 4-8 as a number beside each $\times$, there is a dramatic correlation between the structural transition and the tendency to form material with the stoichiometry of VO$_2$. The formation of an amorphous VO$_2$ is somewhat unexpected as Zachariasen predicted that only the composition V$_2$O$_5$ would form a glassy phase[73]; however, these results resemble previous studies in which amorphous VO$_2$ was deposited via sputtering[34, 81]. Though many of the films with $x > 2.0$ are amorphous, there are films with the composition of VO$_2$ containing nanocrystalline FCC VO$_x$ as well.

It is important to note that the equilibrium FCC VO$_x$ phase field extends from $0.8 < x < 1.3$ in bulk polycrystalline material [4, 58, 62]. The same stability range was observed in epitaxially grown VO$_x$ [61], though there is no mention of an attempt to push that boundary. The films deposited in this work are neither polycrystalline bulk material nor epitaxial films; however, it is unlikely that the VO$_x$ nanocrystals within these films stabilize the increased concentration of defects that would result in a stoichiometry of VO$_2$, as the concentration of vanadium vacancies at the upper bound of $x = 1.3$ is $\sim$22%.
4.3 Vanadium oxide nano-composites of FCC VO\textsubscript{x} and amorphous vanadium oxide

There is another explanation for the discrepancy between the measured stoichiometry and the stoichiometry that can be accommodated by the observed crystalline phase. A secondary, oxygen-rich amorphous phase could accommodate sufficient oxygen to offset the x = 1.3 limit of the nano-crystalline phase. The presence of a secondary amorphous phase is supported by the electron diffraction data which shows a diffuse peak at low scattering angle. Figure 4-10 shows energy filtered diffraction data from a film with both nanocrystalline FCC VO\textsubscript{x} and amorphous VO\textsubscript{x}. The energy filtering allowed only the electrons that had lost only 10 eV of the original 200 keV beam energy to contribute to the diffraction pattern. This zero-loss filtering accentuates the scattering at low angle that is usually dominated by inelastic scattering events. The filtering makes the diffuse amorphous peak at low scattering angle more noticeable.

![Figure 4-10 A zero-loss filtered diffraction pattern (left) and the corresponding radially integrated diffraction data (right). At ~3.5 nm\textsuperscript{-1} there is a diffuse peak resulting from the amorphous vanadium oxide phase in the film. This diffuse intensity is superimposed on top of the nano-crystalline FCC diffraction pattern.](image)
Figure 4-11 shows radially integrated diffraction patterns from the \( P_{O2} \)-1 and \( P_{TOT} \) series of films. In both the nanocrystalline patterns and the amorphous patterns there are broad diffuse peaks at 3 nm\(^{-1}\) and 6.5 nm\(^{-1}\). The electron diffraction results suggest that even in nanocrystalline material with an overall stoichiometry of \( x = 1.2 \) there is sufficient disorder to result in amorphous-like diffuse scattering.

![Graph showing radially integrated electron diffraction patterns from \( P_{O2} \)-1 and \( P_{TOT} \) series.](image)

Figure 4-11 Radially integrated electron diffraction patterns from \( P_{O2} \)-1 and \( P_{TOT} \) series. Note that the diffuse peaks present in the amorphous films are also found in films with a nanocrystalline phase, signifying that many of the nano-crystalline films in this work contain both phases.

The presence of disorder in a nanocrystalline material is expected [95]. As the length-scale of the crystalline grains approaches the nanometer scale, the atoms on the surface of the grains, i.e. those at grain boundaries and free-surfaces, begin to approach the number of atoms within the repetitive structure of the grains themselves. In this case it appears that the amorphous material in the nanocrystalline films has short-range order similar to that of the
purely amorphous films, as evidenced by the agreement in peak location between the two types of samples, shown in Figure 4-12.

![Graph showing intensity vs. scattering angle](image)

Figure 4-12 Comparison of a completely amorphous film (lower pattern) and a film with both amorphous vanadium oxide and the FCC VO\textsubscript{x} phase (upper pattern). Note the agreement between the location of the diffuse intensity in both patterns at \~4.2 nm\textsuperscript{-1} and \~8 nm\textsuperscript{-1}.

Figure 4-13 shows TEM images of a plan-view sample that exhibited a diffraction pattern with both amorphous and nano-crystalline components. The image shown in Figure 4-13a was made using the unscattered electrons from the central beam, shown with a circled “A” in the diffraction pattern below. The image shown in Figure 4-13b was made using the electrons scattered to the (220) diffraction ring marked “B” in the diffraction pattern, therefore the bright parts in the image show the locations of nano-crystalline FCC VO\textsubscript{x} grains in the sample. The image shown in Figure 4-13c was made using the electrons scattered to the diffuse amorphous peak in the pattern, and the bright regions in this image show the location of the amorphous vanadium oxide phase.
Figure 4-13 Planview image of a nano-composite sample. Each image was formed using an aperture placed on the diffraction pattern shown below the images. (A) Bright field image. (B) Hollow cone dark field image. (C) Hollow cone image using the diffuse amorphous ring.

The dark field imaging of the diffuse ring supports the analysis of a nano-composite structure by proving that the intensity scattered to the diffuse peak originates from a delocalized secondary phase as opposed to originating from point defects within the nano-crystalline phase. The dark field image also suggests that in some samples the volume fraction of amorphous material is large enough to be considered a secondary phase and not merely disordered grain boundary material.

The increased structural disorder, or tendency for amorphous growth, increases with an increase in the relative oxygen flow, an increase in the total pressure, or a decrease in the sputtering power. In the case of increasing total pressure this can be explained by the coincident events of target oxidation, due to an increased mass flow of O$_2$ [84], and increased scattering of sputtered species due to the shortened mean free path. The target oxidation results in a similar effect, as the oxidized target material requires more energy to be sputtered,
resulting in sputtered species with less kinetic energy. Both mechanisms result in less adatom mobility and essentially a quenching of sputtered species as they land on the substrate.

Increasing the sputtering power has the effect of moving the target oxidation event to higher relative oxygen flow. One parameter that was not explored in this work is substrate temperature, which could largely affect the morphology of growing films by adding an addition source of energy for the mobility of adsorbed species.

4.4 The effects of microstructure and oxygen content on the temperature dependence of resistivity

The sputtering parameters discussed above affect the microstructure by either altering the stoichiometry of the films, the presence of FCC VO_x, or a combination of the two. Both the microstructure and chemistry of these films affect the charge transport, and separating the effects of each is non-trivial.

With increasing oxygen content both the resistivity and TCR of pulsed DC vanadium oxide increases, as shown in Figure 4-14, which shows all of the films for which oxygen content was measured via RBS. Note that the TCR has been plotted on a negative scale for clarity. The room temperature resistivity increases from 9.0×10^{-3} \Omega \text{ cm} at x = 1.2 to 6.5×10^{4} \Omega \text{ cm} at x = 2.5. Between those two extremes, the resistivity increases monotonically, as evidenced by the “linear” behavior on the log-scale in Figure 4-14. At x = ~2 the slope of the resistivity vs. oxygen content plot shifts to a larger value. This change in the resistivity relationship coincides roughly with the transition from films which are obviously nano-crystalline via GIXRD and those that are X-ray amorphous, i.e. the difference between the films labeled E and F in Figure 4-1.
Figure 4-14 Room temperature resistivity and TCR as a function of oxygen content (as $x$ in VO$_x$). Across the entire stoichiometry range the resistivity and TCR increase monotonically. At $\sim x=2$, the microstructure of the films transitions from nano-crystalline to amorphous.

Simplifying Figure 4-14 to show only the data from one particular series makes the transition more apparent, as in Figure 4-15. The GIXRD patterns for this set of samples are shown in Figure 4-16.

Figure 4-15 Resistivity and TCR as a function of oxygen content for films from a single sample series. The rapid change in the sample behavior is more evident in this plot, where the resistivity increases dramatically after $\sim x = 2$. 
Figure 4-16 GIXRD patterns from the films shown in Figure 4-15. Note the change in crystallinity between the film with $x = 2.0$ and the film with $x = 2.2$. Patterns with sharper and more intense diffraction peaks contain nano-crystalline domains with increased size.

Based on the GIXRD results in Figure 4-16 it appears there is an upper limit to the amount of oxygen that can be accommodated in the structure prior to eliminating the nano-crystalline phase, or at least driving the grain size small enough to be un-measurable using GIXRD.

Corresponding to the change in microstructure at $x = 2.0$ is a large change in the room temperature resistivity from $2.5 \, \Omega \, \text{cm}$ at $x = 2.0$ to $97 \, \Omega \, \text{cm}$ at $x = 2.2$. The increase in resistivity is accompanied by an unexpectedly small increase in TCR from $-2.7\% \, \text{K}^{-1}$ to $-2.9\% \, \text{K}^{-1}$. Interestingly the $x = 2.0$ sample was one of the few VO$_x$ films from this work which exhibited nano-twinning within the FCC VO$_x$ nano-crystals. The twinning occurs along (111) planes, and the twinned regions extend $\sim 10-15 \, \text{Å}$ before reverting back to the parent orientation. The limited spatial extent along the [110] direction results in smearing in reciprocal space which exhibits itself as streaks in the diffraction pattern. Figure 4-17 shows a comparison between a
non-twinned (d) and a twinned (c) FCC VOₓ sample. The main indication of the nano-twinning defects are the long streak-like features which run tangent to the (111) diffraction ring. Thorough analyses of ion beam sputtered VOₓ established both the presence of nano-twins in ion beam sputtered films and the corresponding features in the diffraction patterns [40-41]

![Comparison of a non-twinned (d) and a twinned (c) FCC VOₓ diffraction pattern.](image)

The presence of nano-twinned grains in the x = 2 sample is consistent with the claims that the nano-twin structure helps to accommodate increased oxygen concentration in the FCC VOₓ phase[41]. In this case it is proposed that oxygen in excess of the x = 1.3 limit for the FCC VOₓ phase is accommodated along the (111) twin planes which have a structure similar to V₂O₅, as shown in Figure 4-18. It is possible that the nano-twinned material is a stable and almost distinct phase in the V-O system, and is being observed in materials where additional oxygen is being incorporated in the growing film. The presence of twin defects in the sample with the highest oxygen content and the FCC VOₓ phase is indicative of the nano-twinned crystal’s stability in high oxygen growth atmospheres.
Figure 4-18 Comparison of the (111) twin boundary in FCC VO$_x$ and V$_2$O$_3$. Vanadium atoms are shown in red and oxygen atoms are shown in green. Note the similarity between the twin boundary and the V$_2$O$_3$ structure along this projection. The V$_2$O$_3$ structure stabilizes the ratio of $x = 1.5$, whereas a typical FCC VO$_x$ structure can only stabilize a ratio up to $x = 1.3$, hence twin planes in FCC VO$_x$ allow accommodation of more oxygen.

The resistivity and TCR of pulsed DC sputtered VO$_x$ appear to have a complex relationship on the log(Resistivity) vs TCR plot, somewhat similar to that previously observed for ion beam sputtered VO$_x$ material[7] at low resistivity values (< 1 $\Omega$ cm). Figure 4-19 shows the resistivity and TCR values for all films deposited via pulsed DC reactive sputtering in both chambers used in this work. Despite the scatter at certain points along the curve, the data show a unified trend regardless of the chamber used for deposition. Plotted along with the pulsed DC data are the bulk FCC VO$_x$ values from reference [58].
The relationship is complex with a different trend below and above ~ 1 Ω cm. The data as a whole begins around the low resistivity values for FCC VOₓ and increases monotonically up to the high resistivity, high TCR values of amorphous vanadium oxide.

The low resistivity film data from the pulsed DC films approach that of the bulk properties, but never replicate them. The behavior below ~10 Ω cm is monotonic on this plot. Between 10 Ω cm and 100 Ω cm the slope flattens out and then increases again between 100 Ω cm and 10⁵ Ω cm. The cutoff, as was shown in Figure 4-15, between films with obvious nano-crystalline content and those found to be X-ray amorphous is ~ 10 Ω cm. The drastic change in microstructure from nano-composite films to completely amorphous films is consistent with the change in slope on the ρ₃₀₀K vs TCR plot between 10 - 100 Ω cm. The behavior beyond 100 Ω cm thus represents the change in properties of amorphous vanadium oxide from amorphous VO₂ to amorphous V₂O₅.
The pulsed DC VO\textsubscript{x} does not compare favorably with ion beam sputtered VO\textsubscript{x}, as shown in Figure 4-20. For a given resistivity the pulsed DC TCR is always lower. Interestingly, both sets of data approach the bulk FCC VO\textsubscript{x} properties at low resistivity, as should be expected as they both contain nano-crystalline FCC VO\textsubscript{x}. Also worth noting is the similarity in slope between the ion beam and pulsed DC data between $10^{-2}$ and 1 $\Omega$ cm. In this resistivity region both materials exhibit both FCC VO\textsubscript{x} and an amorphous vanadium oxide phase. Due to the lack of overlap between the two populations of samples, it is clear there must be a microstructural or chemical difference between the two leading to the discrepancy. Microstructurally, the most obvious difference between the two sets of data is the morphology of the nano-crystalline phase. In ion beam sputtered films, there is a tendency for the nano-crystalline phase to grow in high-aspect ratio columns throughout the thickness of the film, whereas the pulsed DC films typically exhibit more equiaxed particles, often resembling columns that have been broken up along their length, as shown in Figure 4-21. The other main microstructural difference between the two populations of material is the presence of nano-twinned VO\textsubscript{x} in ion beam sputtered films, a feature typically absent in magnetron sputtered VO\textsubscript{x}. Nano-twinning in pulsed DC sputtered VO\textsubscript{x} is observed in either the presence of the appropriate partial pressure of oxygen or in the presence of an applied substrate bias, as will be discussed in further detail in Chapter 6 and Chapter 7.
Figure 4-20 $\rho_{300K}$ vs TCR plot of pulsed DC data including regions denoting microstructural character. Included in the plot is ion beam data from reference [7] and bulk FCC VO$_x$ data from reference [58].

Figure 4-21 Comparison of nano-crystalline morphology between ion beam sputtered material (a) and pulsed dc sputtered material (b). The normal to the growth direction is indicated in the dark field image in (a) with an arrow and the letter “n,” and indicates the relationship between the nano-crystalline column orientation and the growth direction. [41]
4.5 Electron energy loss spectroscopy of $\text{PO}_2$ and $\text{P}_{\text{TOT}}$ films

EELS was performed on the $\text{PO}_2$-1 and $\text{P}_{\text{TOT}}$ samples which were co-deposited on Formvar® coated TEM grids. For the EELS experiments, a 20 nm probe was focused on the plan-view sample in order to collect the spectrum from a larger area than the fully focused probe would allow. EEL core loss spectra of the V $L_{2,3}$ and O $K$ edges were aligned by setting the first inflection point of the O $K$ edge to 532 eV. Figure 4-22 is a typical core loss spectrum for a vanadium oxide sample showing both the V $L_{2,3}$ and O $K$ edges. The energy difference ($\Delta E$) between the inflection point of the V $L$ edge and the O $K$ edge, shown in Figure 4-22, can be used as a measure of vanadium valence state. Relative changes in $\Delta E$ between closely related samples thus represent a chemical shift due to the change in the chemical environment of the absorbing atoms. EEL spectra were collected from reference powders and used as reference values. It was assumed that the $\Delta E$ values for the reference powders VO, $V_2O_3$, VO$_2$ and $V_2O_5$ represented the formal valence states of $2^+$, $3^+$, $4^+$, and $5^+$, respectively. The formal valence states of the reference powders as well as the predicted valence states of the $\text{PO}_2$-1 and $\text{P}_{\text{TOT}}$ films are shown in Figure 4-23.
Figure 4-22 EEL spectra of a typical vanadium oxide thin film. The figure shows the energy split between the onset of the $V_{L_{2,3}}$ edge and the $O K$ edge. That energy split, $\Delta E$ correlates well with the increased valence on the V atoms.

Figure 4-23 EELS calibration curve and predicted formal valences of $P_{O2-1}$ and $P_{TOT}$ films. The energy split also correlates well with sample stoichiometry, with an increased energy split signifying a lower oxygen content.
Chapter 5

Microstructural evolution of pulsed DC sputtered VO$_x$

It can be seen in Figure 4-6 that the initial material in many of the vanadium oxide thin films deposited by pulsed DC sputtering appears different than the remainder of the film. This chapter focuses on the microstructural changes that occur throughout the thicknesses of these films and how microstructural changes affect the charge transport. Because the sensing layer thickness is somewhat restricted in microbolometer design, it is important to understand how sensitive the film properties are to the overall film thickness. In the ideal case, there would be no thickness dependence.

5.1 Experimental details

In order to probe the thickness-dependent properties of pulsed DC sputtered VO$_x$, a series of films with increasing thickness was deposited in a continuous fashion using a substrate shutter that shielded half of the substrate carrier. The custom substrate shutter is shown in Figure 5-1, as well as the sputtering geometry. One-inch square pieces of crystal Si with 1000 Å of thermal oxide were placed radially on the rotating substrate holder. Formvar® coated Cu TEM grids were placed on the corner of each substrate. During growth, the substrate pieces were rotated underneath the substrate shutter in order to quench their growth. The thinnest film, i.e. the first sample rotated underneath the substrate shutter was grown for 20 s while the thickest film was growth for 700 s.
Figure 5-1 Experimental setup used to make variable thickness series. The half-moons shaped substrate shutter was used to shield substrate pieces from the arrival of sputtered species. Periodically samples were rotated underneath the shutter, quenching their growth.

Metal (300 Å Ti / 1000 Å Pt) contacts were deposited onto each sample using a shadow mask, and room temperature resistivity and TCR were measured as previously described. Film thicknesses were extracted from a parameterized analysis of spectroscopic ellipsometric data. The vanadium oxide layer in each case was modeled with three Lorentz oscillators, which are described by Equation 12, where \( A \) is the amplitude, \( E_c \) is the center energy of the oscillator, and \( B \) is the broadening.

\[
\bar{\varepsilon} = \varepsilon_{1,\text{offset}} + \frac{AE_c}{E_c^2 - E^2 - iBE} \quad \text{Equation 12}
\]

The values for each oscillator are shown in Table 5-2 for each sample in the thickness series. Table 5-1 shows the relevant parameters for each film in the thickness series. The initial thin films have very large resistivity values, while the thicker films, starting at approximately 500 Å, show a drastic decrease in the resistivity.
Table 5-1 Thickness series samples

<table>
<thead>
<tr>
<th>Growth Time (sec)</th>
<th>Thickness (Å)</th>
<th>Resistivity (Ω cm)</th>
<th>TCR (% K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>76 ± 6</td>
<td>75,800</td>
<td>-5.5</td>
</tr>
<tr>
<td>40</td>
<td>154 ± 13</td>
<td>9,550</td>
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<tr>
<td>80</td>
<td>292 ± 12</td>
<td>2,330</td>
<td>-3.4</td>
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<tr>
<td>160</td>
<td>426 ± 2</td>
<td>13.3</td>
<td>-2.2</td>
</tr>
<tr>
<td>320</td>
<td>581 ± 2</td>
<td>.196</td>
<td>-0.8</td>
</tr>
<tr>
<td>540</td>
<td>988 ± 2</td>
<td>.127</td>
<td>-0.6</td>
</tr>
<tr>
<td>700</td>
<td>1434 ± 3</td>
<td>.121</td>
<td>-0.3</td>
</tr>
</tbody>
</table>

Table 5-2 Parameters for Lorentz oscillators used to describe each sample in thickness series

<table>
<thead>
<tr>
<th>Film thickness</th>
<th>Oscillator 1</th>
<th>Oscillator 2</th>
<th>Oscillator 3</th>
</tr>
</thead>
<tbody>
<tr>
<td>20</td>
<td>e1 offset = 2.8016</td>
<td>Amplitude = 1.6285</td>
<td>Amp = 0.56828</td>
</tr>
<tr>
<td></td>
<td>Energy = 4.4934</td>
<td>E = 2.5505</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Broadening = 1.1645</td>
<td>Br = 4.0621</td>
<td>E = 5.5961</td>
</tr>
<tr>
<td>40</td>
<td>e1 offset = 2.4981</td>
<td>Amp = 1.3735</td>
<td>Amp = 0.51663</td>
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<td></td>
<td>E = 4.4987</td>
<td>E = 2.3788</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Broadening = 1.6266</td>
<td>Br = 3.541</td>
<td></td>
</tr>
<tr>
<td>80</td>
<td>e1 offset = 2.5411</td>
<td>Amp = 1.5123</td>
<td>Amp = 0.51129</td>
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<tr>
<td></td>
<td>E = 4.8102</td>
<td>E = 1.8669</td>
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<td>Br = 1.6787</td>
<td>Br = 2.4514</td>
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<tr>
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<td>e1 offset = 2.2333</td>
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<td>Amp = 1.0271</td>
</tr>
<tr>
<td></td>
<td>E = 4.2533</td>
<td>E = 2.0693</td>
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<td>Amp = 1.4568</td>
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<td></td>
<td>E = 1.305</td>
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<td></td>
<td>Br = 3.2697</td>
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<td>Amp = 1.7976</td>
</tr>
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<td>E = 0.77734</td>
<td>E = 2.0359</td>
<td></td>
</tr>
<tr>
<td></td>
<td>Br = 2.6133</td>
<td>Br = 3.6457</td>
<td></td>
</tr>
</tbody>
</table>

5.2 Microstructural evolution: nucleation and growth of FCC VOₓ

The bright-field cross sectional TEM image shown in Figure 2-1a exhibits minimal contrast in the initial 15 nm of film growth, signifying the initial material is devoid of diffraction or mass-thickness contrast and likely does not contain measurable nanocrystalline grains. The lack of nanocrystalline grains is more evident in the dark-field image shown in Figure 5-2b in which there are no distinct grains in the initial 15 nm of material. Also evident from the dark-
field image is the increase in the size of the nanocrystals with increasing film thickness. Note that the topmost layer of the film was unintentionally amorphized by the focused ion beam sample preparation.

Figure 5-2 Cross sectional TEM images of thickest “thickness series” film. (a) Bright-field image and (b) Dark-field image showing the initial material is amorphous and nanocrystals nucleate and grow at ~150 Å.

Plan-view samples were used for TEM analysis of un-disturbed film specimens as they required no mechanical preparation or ion milling. Plan-view bright-field images are shown in Figure 5-3 as a function of film thickness. Unfortunately these samples are 2D projections of a 3D structure, and quantification of nanocrystal volume fraction cannot be performed. However, the images do show that at least the initial 80 seconds of material is amorphous, as evidenced by the mottled intensity in the bright-field image. In the thicker films, nanocrystalline domains can clearly be seen as dark circular objects. Accompanying the nanocrystalline phase is the continued presence of the disordered material found in the 80 second film and considerable porosity, indicated by the light filament-like features in the bright-field images. The pores appear to increase in both size and volume fraction throughout the series, making volume fraction quantification even more difficult.
Figure 5-3 Bright-field planview images as a function of film thickness. Nano-crystals are indicated by dark regions, and low density, or porous regions, are located in light regions.

Though plan-view dark-field images suffer from the same projection-related effects as bright-field images, they nonetheless help establish the microstructural differences between films deposited for short times and those deposited for long times, as shown in Figure 5-4.

Figure 5-4 Dark-field planview images of nanocrystalline films. Light regions in the images are nano-crystalline domains, whereas dark regions are the absence of nano-crystals.
Selected area diffraction patterns (SADPs) were collected from each plan-view sample, and those patterns are shown in Figure 5-5. The SADP from the 80 second film shows the diffuse, symmetric intensity typical of amorphous materials. With increased thickness the SADPs exhibit both the diffuse amorphous intensity as well as Bragg diffraction from the nanocrystalline phase.

Figure 5-5 SADPs as a function of film thickness. The 80 sec film shows a typical amorphous vanadium oxide diffraction pattern with no measurable evidence of a secondary crystalline phase.

To facilitate the direct comparison of diffraction patterns, the intensities in Figure 5-5 have been radially integrated and are shown in Figure 5-6. Note that each radially integrated pattern has been normalized using the maximum intensity of the first amorphous feature in the pattern, and then offset in order to provide qualitative insight regarding the ratio of amorphous to nanocrystalline material. The Bragg reflections index to the FCC VO$_x$ phase and are labeled with their respective Miller indices in Figure 5-6.
Figure 5-6 Radially averaged SADP’s as a function of film thickness. Each pattern has been normalized at the peak of the amorphous peak and offset. With increasing film thickness the nanocrystalline peaks increase in intensity with respect to the amorphous feature, indicating increased crystalline content.

It is clear from Figure 5-6 that the intensity from the nanocrystalline reflections increases with respect to the amorphous feature with increasing thickness. Unfortunately each thicker sample is a combination of the next thinnest sample and the new material added during the increased deposition time. This means that the diffraction patterns show the total scattering from the entire depth of the film and not just the newly added material. The increased intensity in the crystalline Bragg diffraction peaks however still indicates that the added material is more crystalline the thicker the film grows. As the film approaches 1000 Å the multiple scattering in the sample begins to cause widening of the crystalline peaks as electrons initially diffracted by the nanocrystals are re-diffracted by amorphous material or visa-versa.

Though oxygen content was not measured for this set of samples, electron energy loss spectra were collected from both plan-view samples and the thickest film of the series. As shown previously, EEL spectra from the vanadium L$_{2,3}$ and OK edges are useful in determining
average vanadium valence. To probe the potentially changing chemistry in the thickness series, linescans using the TEM in Scanning TEM (STEM) mode with a 1 nm probe size were analyzed as described previously to give an estimate of the vanadium valence, shown in Figure 5-7. The valence data suggests that the film begins to grow with predominantly $V^{3+}$ character and approaches $V^{2+}$ character with increased thickness. Figure 5-2 suggests that the grain size and/or volume fraction of the nano-crystalline phase increases with increasing thickness.

Figure 5-7 Vanadium valence estimated using EELS linescans. From the bottom of the film to the top the average valence changes from near 3+ towards 2+, signifying a change in the oxygen content from oxygen rich at the initial growth to oxygen depleted near the top of the film. The change in valence is consistent with an increasing concentration of $V^{2+}$ from the FCC VO$_x$ phase with increasing thickness.

The valence data from the plan-view samples describes the same trend but with increased estimated valence. The planview data represents the valence throughout the entire thickness of the sample and should always report a higher valence than the data from the linescans; however, the larger overall valence is likely the result of post deposition oxidation of
the freestanding TEM foil, which due to its large amount of surface area and limited thickness, was particularly susceptible to over-oxidation.

If we make the assumption that the FCC VO$_x$ nanocrystals in the film have a valence near 2$^+$ and the amorphous material in this set of samples has a valence near 3$^+$, as suggested by the measured valence of the initial amorphous material, then the linescan EELs data shown in Figure 5-7 is consistent with the claim that the volume fraction of the nanocrystalline phase increases with increased film thickness. This claim is also supported by the increased size and prevalence of nanocrystalline grains in the cross sectional TEM images shown in Figure 5-2. The reason this particular microstructure resulted can be explained in one of two ways, both of which involved a changing PO$_2$ throughout the film growth. The first explanation is that the system was contaminated with water from being opened to the ambient directly before the run. The water was removed from the walls of the chamber during the beginning of the deposition resulting in a large PO$_2$ or P$_{H2O}$ at the beginning of the run that gradual decreased throughout growth. The second explanation is that the reactive sputtering process itself was responsible as the initial PO$_2$ was reduced throughout growth by the gettering action of the growing film on the walls of the chamber. Either explanation results in a PO$_2$ that decreases throughout deposition. It was shown in Chapter 4 that films produced in a higher PO$_2$ are typically amorphous while those grown in a lower PO$_2$ are nanocrystalline. In the context of the thickness series this means that the initial material should be amorphous if the PO$_2$ was greater at the beginning of the deposition. Regardless of how the resulting microstructure developed, the set of samples in this thickness series represents a series of films with increased volume fraction of nanocrystals embedded in a disordered matrix.
5.3 Thickness dependence of charge transport

As can be seen from the data in Table 5-1 and again in Figure 5-8, film resistivity drops dramatically in the initial material until it is essentially converges at a thickness of ~500 Å. Likewise the TCR of the material drops as expected with decreasing resistivity.

The strong variation in resistivity and TCR with increasing thickness is strong evidence that the material is changing with increasing thickness. There are however several different material parameters that can be changing, and separating the effects of one from another is non-trivial. As shown in the previous section there is evidence that at least three parameters are changing: the overall chemistry of the film, the presence of a nancrystalline phase, and the size of the nanocrystals. Fortunately the presumed increase in volume fraction of the lower-valence nanocrystalline phase is consistent with the change in the average valence of the film.

![Figure 5-8 Resistivity and TCR as a function of film thickness. Both the resistivity and the TCR decrease with increased film thickness. These changes are consistent with an increasing volume fraction of a nano-crystalline phase with increased film thickness.](image)
Resistivity and TCR were measured using shadow mask deposited contacts on each of the seven samples. Those values thus represent the resistivity and TCR of the entire sample being probed and not necessarily the newly added material. It is likely however that if the newly deposited material is much lower in resistivity than the existing material that the measurement current would travel mainly through the newly added material. Incremental resistivity and TCR values were calculated for each sample as described below in order to better understand how the volume fraction of the nanocrystalline phase affects the charge transport.

Incremental resistances were calculated by treating each sample as a layered structure composed of the thinner films in the series, as shown in Figure 5-9. The resistance of the thickest sample can then be represented as the sum of the inverses of the resistances of all the layers as described by Equation 13. In such a way the resistances of the component layers can be calculated using the measured resistances from the films in the thickness series.

\[
\frac{1}{R_{Total}} = \sum_{i=1}^{7} \frac{1}{R_i}
\]

Equation 13

The incremental resistivity was calculated using the difference in thickness between two consecutive samples. This value represents the resistivity of the newly added material and more appropriately reflects the charge transport in that layer.

Figure 5-9 Schematic of the addition of new material to the existing film. The far left depicts the initial VO_x film growth, the middle depicts the film after additional film growth, and the far right depicts the incremental layer that grew in that additional time.
Incremental TCR values were calculated by using the resistance values of each sample at various temperatures. Film resistance as a function of temperature for each film in this series is shown in Figure 5-10. Resistance measurements at specific temperatures, i.e. 20, 30, 40 °C, were interpolated from the data shown in Figure 5-10. Those interpolated resistance measurements, at a given temperature, were then used to calculate an incremental resistivity for each of the layers. This process resulted in a set of resistivities for each incremental layer as a function of temperature. TCR was calculated from these sets of data for each incremental layer.

![Figure 5-10 Resistance as a function of temperature for samples with different thicknesses.](image)

In all cases the total film resistance measurements showed a negative TCR behavior, additionally increased film thickness resulted in a decreased resistance measurement for all samples.

The incremental TCR and resistivity values are plotted as a function of layer depth in Figure 5-11. Layer depth is defined as the midpoint of each incremental layer with respect to the SiO₂/VOₓ interface. According to Figure 5-11, the initial amorphous material has a room temperature resistivity of $10^5 \, \Omega \, \text{cm}$. Additional layers have greatly reduced resistivity, dropping
six orders of magnitude in the first 500 Å. Interestingly the resistivity levels off at that point and remains in the $10^{-1}$ Ω cm range.

According to the diffraction data in Figure 5-6 the additional material added in each incremental layer is more crystalline than the previous material. Each new layer has a larger nanocrystal volume fraction, so the trend of decreased resistivity with increased thickness is consistent with the addition of an increasing fraction of a lower resistivity nanocrystalline phase.

When plotted with TCR versus room temperature resistivity, shown in Figure 5-12, the data show the same behavior as the global behavior presented in Figure 4-19. Also apparent in Figure 5-12 is the difference between the thickest film values and the incremental values from the top, highly-crystalline material.

Figure 5-11 Incremental TCR and resistivity as a function of layer depth. Layer depth is defined as the midpoint of each incremental layer. The behavior is very similar to that for the total film thickness samples. Around 50 nm the film resistivities converge to roughly $10^{-1}$ ohm cm.
The incremental resistivity and TCR values can be interpreted in terms of a resistivity mixing rule, wherein a high resistivity amorphous phase is mixed with a low resistivity nanocrystalline phase in varying volume fractions. Unfortunately, the volume fraction of the nanocrystalline phase has not been measured experimentally, and it is a key variable in any mixing rule analysis.

5.4 Generic resistivity mixing rule analysis

The mechanism behind charge transport in semiconducting materials is very different than that for metallic materials. In metallic materials the conductivity can be described as the product of the number of charge carriers \( n \), their mobility \( \mu_n \), and their charge \( e \) as in Equation 14.
\[ \sigma = n e \mu \]

Equation 14

In metallic conductors there is a large number of carriers \((n)\) and their mobility decreases with increasing temperature due to electron-phonon interactions. As a result conductivity decreases (resistivity increases) with increasing temperature. This same positive temperature coefficient of resistance (PTCR) behavior has been observed in many composite systems including: inorganic polymer[96], carbon-black polymer[96], polymer metal-oxide[96], rare earth doped BaTiO\(_3\), Cu PVC[97], V\(_2\)O\(_3\) polymer[98], and conductive ceramic polymer composites[99]. The aforementioned composites all exhibit positive TCR and percolation-like behavior which appears in the TCR behavior and are unlike the materials discussed in this work.

The vanadium oxide films from this work exhibit no such percolation-like behavior in the resistance\((T)\) behavior and are much more like the negative TCR (NTCR) ceramics used in commercial-grade thermistors [100].

There are many ceramic systems that exhibit NTCR behavior including: Ag\(_2\)S, Fe\(_3\)O\(_4\), CoO, NiO, Cu\(_2\)O, Cu\(_2\)S, Sb\(_2\)S, and the systems: Ni-Mn-Cu, Ni-Mn-Cu-Co, Co-Mn-Cu, Fe-Ti, Ni-Li, Co-Li, Cu-Mn [100]. For oxide materials, the number of charge carriers is determined by the level of doping, whether it is intrinsic or extrinsic, and their mobility is temperature dependent [100].

The temperature dependence of resistivity in oxide semiconductors is well described by Equation 15.

\[ \rho = \rho_0 \exp \left( \frac{E_a}{kT} \right) \]  

Equation 15

In many oxide semiconductors the charge transport is believed to occur via charge hopping mechanisms in which the charges move from ion to ion, altering the local valence of the cation [101]. Both resistivity and TCR can be altered by doping with different cation atoms as
shown by Verwey [102]. When the charge is assumed to move from cations of the same element, i.e. from $V^{2+}$ to $V^{3+}$, the conductivity is described by Equation 16.

$$\sigma = c(1 - c)\frac{e^2a^2\nu}{kT}\exp\left(-\frac{E_\mu}{kT}\right)$$

Equation 16

$c = \text{probability that neighboring cation is of } \pm 1 \text{ charge}$
$v = \text{phonon frequency}$
$e = \text{electronic charge}$
$a = \text{transport distance}$
$E_\mu = \text{activation energy}$

The term “c” in Equation 16 directly affects the conductivity, and substitution of trivalent ions into multi-valent sites leads to a decrease in conductivity (and increase in TCR). The trivalent ion is incapable of participating in hopping because the valence is set [103].

Equation 16 is remarkably similar to Equation 17, which was proposed by Austin and Mott to describe the hopping conduction observed in amorphous transition metal oxides such as $V_2O_5$ [72, 104]. The main difference is that the tunneling dependence is exponential in Equation 17 whereas it is cubic in Equation 16.

$$\sigma = \left[\frac{\nu_0 e^2}{RkT}c(1 - c)\exp(-2\alpha R)\right]\exp\left(-\frac{w}{kT}\right)$$

Equation 17

$c = \text{fraction of low valent states}$
$\nu_0 = \text{phonon frequency}$
$e = \text{electronic charge}$
$\alpha = \text{rate of wavefunction decay}$
$R = \text{average hopping distance}$
$w = \text{activation energy}$

Banus and Reed showed that the resistivity of FCC VO$_x$ has a $1/T^n$ dependence with n varying from -0.075 to -0.56 with increasing oxygen content, suggesting that the charge transport in FCC VO$_x$ can be described by a hopping-related model [58]. Using the Banus and
Reed data, Mott concluded that FCC VO$_x$ with $x > 1$ adheres to a $T^{-1/4}$ behavior and likely conducts via the Mott hopping mechanism described by Equation 18 [105].

$$\sigma = C \exp\left(-\frac{A}{T^{1/4}}\right)$$  \hspace{1cm} \text{Equation 18}

It is clear that disordered vanadium oxide, either crystalline [55, 58, 105] or amorphous [55], has a tendency for temperature dependent mobility leading to negative TCR behavior. The interplay between these two phases must have an impact on the composite TCR behavior of the material, and according to Figure 4-20, a combination of two phases is necessary to achieve the desired properties.

Without knowledge of the volume fractions of the constituent phases the resistivity of a given composite cannot be exactly determined; however, a theoretical treatment using constituent phases with known transport properties allows for a deeper understanding of the desired volume fraction and morphology of each phase. A theoretical treatment also allows for the combination of ideal phases in ideal geometries, a situation that is difficult or impossible to enact in laboratory experiments, but which can provide guidance for desired microstructural features.

A general resistivity mixing rule, given by Equation 19, was used to simulate the resistivity of composite structures composed of a low resistivity ($\rho_{\text{cond}}$) and a high resistivity ($\rho_{\text{amorph}}$) phase. In the case of the vanadium oxide films described previously the conductive phase is the nanocrystalline FCC VO$_x$ and the high resistivity phase is the amorphous vanadium oxide.

$$\rho_{\text{mixture}}^\alpha = f \rho_{\text{cond}}^\alpha + (1 - f) \rho_{\text{amorph}}^\alpha$$  \hspace{1cm} \text{Equation 19}

In Equation 19, $f$ is the volume fraction of the nanocrystalline phase and $\alpha$ is an
exponent that can vary from -1 to +1. The variation of α allows for the combination of the two 
phases from the extremes of equivalent circuits representing resistors in parallel (-1) to those in 
series (+1), described schematically in Figure 5-13.

![Parallel conduction and Serial conduction](image)

Figure 5-13 Equivalent circuit representations

Composite resistivity as a function of the volume fraction of the conducting phase was 
calculated using values for the room temperature resistivities and activation energies previously 
determined from TCR measurements of the most resistive and most conductive of all of the 
films grown for this work. These values were chosen as they represent realistic constituent 
phases. Figure 5-14 shows the composite resistivity as a function of nanocrystal volume fraction 
using the parameters shown in Table 5-3, with the alpha parameter varying from -1 to +1.

<table>
<thead>
<tr>
<th>Phase</th>
<th>Resistivity$_{300K}$ (Ω cm)</th>
<th>TCR (-% K$^{-1}$)</th>
<th>$ρ_o$ (Ω cm)</th>
<th>$E_a$ (eV)</th>
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</thead>
<tbody>
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<td>Conductor</td>
<td>0.0027</td>
<td>0.14</td>
<td>0.0018</td>
<td>0.011</td>
</tr>
<tr>
<td>Insulator</td>
<td>$4.12 \times 10^6$</td>
<td>4.24</td>
<td>12.22</td>
<td>0.329</td>
</tr>
</tbody>
</table>

In the case analogous to parallel resistors ($\alpha = -1$) a volume fraction near zero is required 
to finally see the effect of the high resistivity phase on the composite resistance, whereas in the 
serial resistor case a volume fraction near 1 is needed in order to see the effect of the low
resistivity phase. This treatment of course ignores the possibility that a percolative network can form at very low volume fractions.

Figure 5-14 Composite resistivity as a function of nanocrystal volume fraction for different values of alpha. A large alpha value represents a serial circuit and requires an extremely large volume fraction for the resistivity of the crystalline phase to have any effect on the composite resistivity. A small alpha value represents a parallel circuit and requires an extremely low volume fraction of the crystalline phase to see the effects of the high resistivity phase.

In order to understand the effects of composite microstructure on TCR, temperature dependence was added to Equation 19 via the thermally activated conductivity of each phase described by Equation 9. Combining these terms with Equation 19 results in Equation 20.

\[
\rho^\alpha_{\text{mixture}} = f\left(\rho_{o,\text{cond}} \exp\left(\frac{E_{a,\text{cond}}}{K_B T}\right)\right)^\alpha + (1 - f)\left(\rho_{o,\text{amorph}} \exp\left(\frac{E_{a,\text{amorph}}}{K_B T}\right)\right)^\alpha
\]

Equation 20

Utilizing Equation 20 with the values from Table 5-3, resistivity as a function of TCR can be plotted for varying alpha values, as shown in Figure 5-15. These TCR versus \(\rho_{300K}\) curves were
calculated by simulating the temperature dependent resistivity of a composite structure with a given volume fraction and alpha value. The resulting resistivity as a function of temperature data was then fit in the same way that TCR was calculated per Appendix B. The resulting TCR value and the room temperature resistivity were then used to create a single data point on the plot in Figure 5-15. The same process was carried out for each alpha value, varying the volume fraction from 0 to 1 in each case. Specific details of the procedure can be found in Appendix C.

![Diagram](image.png)

Figure 5-15 TCR as a function of room temperature resistivity. Alpha varies from -1 to +1, spanning the $\rho_{300K}$ vs TCR plot with sub- to super-linear behavior. The behavior observed in actual sets of samples is mimicked by either alpha very near zero or very slightly negative.

The resistivity vs. TCR behavior resulting from the generic mixing rule approach is bounded on the high and low resistivity sides by the resistivities and TCRs of the constituent phases. The behavior between the end-members is determined by the alpha value. It is clear from Figure 5-15 that increasing alpha from -1 to +1 leads to a higher TCR for a given resistivity. According to the equivalent circuit analysis this means the closer the microstructure resembles serial resistors ($\alpha = +1$), the higher a TCR for a given resistivity composite. One way to
implement this trend in terms of a real microstructure is to grown columnar crystalline grains separated by amorphous grain boundary material. It is necessary however to keep the columns from being able to communicate electronically with one another. Whether this means it is sufficient to keep them separated by a grain boundary, or significantly more disordered intra-columnar material remains to be seen. Both FCC VO\textsubscript{x} \cite{105} and amorphous VO\textsubscript{x} \cite{75} have been shown to conduct via hopping mechanisms, and in granular metal systems, i.e. systems where metal particles are suspended in an insulating matrix, transport can occur via hopping from one metallic grain to another \cite{106}. This intra-granular hopping could impose an additional grain separation requirement in a material composed of aligned columnar grains.

Also seen in Figure 5-15 is that linear behavior, when plotted on a log(\rho) scale such as this, is only accomplished over a very narrow range of alpha values, specifically near alpha = 0. It is easy to interpret results requiring an alpha = 1 or an alpha = -1. It is difficult to understand what an alpha value near zero implies about the spatial distribution of the two phases. An alpha near zero certainly implies a lack of interconnectivity between the more conductive domains; however it does not rule out a case intermediary to both serial and parallel analogs. Perhaps a model including both serial and parallel pathways more closely resembles electronic structure of these vanadium oxide nanocomposites.

The data presented in Figure 5-15 can lead to a misinterpretation without knowledge of how the volume fraction is changing throughout the available resistivity range. Figure 5-16 shows the TCR vs resistivity\textsubscript{300K} behavior for composites composed of the same volume fraction of each phase, superimposed on the curves from Figure 5-15. Moving from the left to the right side of the plot along constant volume fraction curves follows the change from alpha = -1 to +1. In other words, for a given resistivity the TCR does increase with increasing alpha values but the
increase in TCR also requires an increase in the volume fraction of the low resistivity phase.

Composite structures with the same resistivity can be created with varying volume fractions as long as alpha can be changed as well.

Figure 5-16 TCR vs. resistivity_300K behavior for constant volume fraction composites. The percent volume fraction of the crystalline phase is shown in the legend. Three different constant nanocrystal volume fraction composites were calculated while varying the alpha value.

Figure 5-17 shows the TCR vs. resistivity behavior of the data extracted from the thickness series discussed previously. It is evident when plotted in this manner that the data from this set of samples mimics the global behavior seen in the entire collection of samples analyzed for this work by traversing the TCR versus resistivity plot from low resistivity and low TCR values to high resistivity and high TCR values in a monotonic fashion. As such, the thickness series data allows for a simplified analog to the entire dataset, helping to establish the usefulness of the following analysis.

Using the generic mixing rule with the incremental TCR and resistivity values from the end-member phases, shown in Table 5-4, with various alpha values, results in a calculation that
closely resembles the behavior observed in the data when alpha is between -0.1 and -0.01. The activation energy of the conductive phase (0.062 eV) is similar to the activation energy of bulk FCC VO$_{1.3}$ (0.054 eV) [58], while the activation energy of the insulating phase is similar that observed in amorphous VO$_{2.24}$ (0.329 eV)[107]. The lack of agreement between the model and the data for the low resistivity samples with increased thickness is likely due to the fact that a phase between vanadium metal and FCC VO$_x$ can also be deposited in low oxygen conditions. That phase, as will be discussed in Chapter 6, has a low resistivity and a positive TCR. The evidence shown above that the valence continues to drop with increased resistance suggests that the formation of the sub-oxide phase is possible and likely causes the top layers of this thickness series to exhibit TCR with a decreased and eventually positive TCR.

Table 5-4 Parameters used to model thickness series data

<table>
<thead>
<tr>
<th>Phase</th>
<th>Resistivity$_{300K}$ (Ω cm)</th>
<th>TCR (-% K$^{-1}$)</th>
<th>$\rho_o$ (Ω cm)</th>
<th>$E_a$ (eV)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Conductor</td>
<td>0.08</td>
<td>0.8</td>
<td>0.0073</td>
<td>0.062</td>
</tr>
<tr>
<td>Insulator</td>
<td>$1.06 \times 10^5$</td>
<td>5.05</td>
<td>.0275</td>
<td>0.392</td>
</tr>
</tbody>
</table>

It is important to note that the end-members chosen for this calculation represent electrically distinct end-members and not necessarily microstructurally phase pure end-members. In other words, the end-member chosen for the low resistivity end of the mixture is not pure FCC VO$_x$, which is clear from the cross sectional images and EELS data which do not show evidence of purely nanocrystalline material at the top surface of the film. However, even when using values for the low resistivity phase representative of a metallic phase with a positive TCR, the mixing rule still provides results consistent with experimental data, as shown in Figure 5-18.
Figure 5-17 Thickness series TCR as a function of room temperature resistivity. Calculations using the most resistive values and the values from the first film to exhibit the converged resistivity are shown along with the experimental data. The alpha value was varied slightly for the calculations to show the effect of alpha on the curvature of the $\rho_{300K}$ vs TCR behavior.

Figure 5-18 TCR vs $\rho_{300K}$ calculation with metal-like secondary phase. The use of a secondary low-resistivity phase with a positive TCR also describes the data hinting that the FCC VO$_x$ phase is not a specific necessity but the use of a generic low resistivity phase is.

Because the mixing rules described by Equation 20 provide an empirical understanding of the behavior of this two phase system, further understanding of the interplay between the
two phases can be gleaned from calculations using idealized combinations of phases that may or may not be achievable in an actual deposition. As the goal is to understand which aspects of this composite microstructure have the most influence on the TCR for a given resistivity material, altering the phases independently provides insight to the effects of the end-member components. Figure 5-19 shows the change in TCR vs. $\rho_{300K}$ behavior when either the activation energy, i.e. the TCR of the lower resistivity phase, or the pre-factor are changed independently. Clearly the change in either TCR or resistivity of the particulate phase acts to move the low resistivity starting point for the low resistivity end-member phase. In other words the transport properties of the low resistivity phase act together to alter the lowest possible resistivity/TCR of the composite. Altering the pre-factor of the particulate phase, as shown in the right pane of Figure 5-19, results in an increase in TCR at a given resistivity. By altering this value, however, the lowest possible resistivity material is moved to a higher and higher resistivity value, which may result in material with too great of a resistivity to be used in the current implementation of resistivity microbolometer structures.

Figure 5-19 Effects of varying particle $E_a$(left pane) and prefactor(right pane) on the TCR vs. $\rho_{300K}$ behavior. Notice that varying the activation energy acts to move the composite behavior along the same curve while varying the prefactor acts move the low-resistivity starting point for the composite behavior.
Alternatively, the properties of the amorphous matrix can be altered independently, giving rise to the behavior shown in Figure 5-20. When the activation energy of the amorphous matrix is increased, the high resistivity end-member moves dramatically to higher TCR, effectively increasing the TCR at any given resistivity. Likewise, changing the pre-factor of the amorphous matrix has the same effect. Taken together, the results from Figure 5-19 and Figure 5-20 suggest that independent control over the amorphous matrix phase is more effective at providing higher TCR at a given resistivity than independently altering the lower resistivity phase, particularly when attempting to keep the lower bound at low resistivity.

Figure 5-20 Effects of varying $E_a$ (left pane) and pre-factor(right pane) of high-resistivity phase on the TCR vs. $\rho_{300K}$ behavior. Changing the activation energy of the high-resistivity matrix acts to provide more TCR for a given resistivity. Altering the prefactor has a similar but less pronounced effect on the composite curve, providing more TCR at a given resistivity with increasing prefactor.

The pre-factor and TCR are seldom independently adjustable, and observation of Meyer-Neldel behavior in similarly processed samples [46, 107] suggests they are coupled. It is instructive then to use values from the literature for the low-resistivity FCC VO$_x$ phase, as shown in Figure 5-21, which clearly result in the lower resistivity bound being moved both up in TCR and resistivity. Composites composed of 1000 $\Omega$ cm amorphous vanadium oxide mixed with
VO\textsubscript{0.8} instead of VO\textsubscript{1.3} have a lower TCR for any given resistivity except for the amorphous end-member. Likewise, mixing the VO\textsubscript{1.3} with a lower resistivity amorphous phase (54 $\Omega$ cm) acts to move the entire set of composites up in TCR with an almost constant offset on this Log plot. The behavior observed in Figure 5-21 is very similar to that seen in Figure 4-20 in which the pulsed DC data had a similar slope as the ion beam data but a negative displacement in terms of TCR. These calculations suggest that the end-members in the two sets of samples are considerably different, with the ion beam samples having an oxygen rich nano-crystalline phase and a lower resistivity amorphous phase than the pulsed DC films presented in Chapter 4.

![TCR vs Resistivity Curves](image)

Figure 5-21 TCR versus resistivity curves for composites of presumed amorphous VO\textsubscript{x} mixed with values for FCC VO\textsubscript{x} from reference [58]. The stoichiometry, and hence activation energy, of the FCC VO\textsubscript{x} phase is very important in moving the entire composite TCR vs. $\rho$\textsubscript{300K} curve up on the plot. The use of VO\textsubscript{1.3} offers superior TCR at a given resistivity compared to the use of VO\textsubscript{0.8} as the low-resistivity constituent.

The limitation of the empirical mixing rule is that it does not address the physics associated with the charge transport. Low temperature conductivity measurements of both FCC VO\textsubscript{x} [105] and amorphous V\textsubscript{2}O\textsubscript{5} [75] suggest transport in both is mediated through a hopping
mechanism. Recent measurements of films similar to those made for this study show the low
temperature conductivity in this mixed phase material is well described by Efros-Schlovskii
variable range hopping (VRH)[108]. The propensity for hopping mediated transport in both
phases complicates the analysis of these materials, and likely points at future direction for
theoretical work on this material system.
Chapter 6

Growth mechanism in a non-uniform sputtering environment

When viewed as a closed system, reactive sputtering is tractable and the outcome in terms of growth rate and even film chemistry can be defined and modeled [48-50]. In fact, the Berg model [49] is a concise and elegant description of reactive sputtering which accurately describes a generic reactive sputtering process in terms of the deposition rate dependence on the reactive gas partial pressure. The model highlights the necessity of controlling the partial pressure of the reactive gas as opposed to the mass flow of the gas, as the two do not have a linear relationship over the entire available mass flow scale, as shown in Figure 3-2.

The Berg model, however useful it is in understanding target oxidation and the related hysteresis, neglects the geometry of the sputtering system and the inherent non-uniformities that result. The non-uniformity of a given sputtering system can have direct impact on the resulting microstructure. It is the goal of this chapter to describe the relationship between the sputtering geometry of the CMS-18 chamber used for this work and the resultant microstructures. It will be shown that a non-homogeneous sputtering atmosphere likely benefits the growth of low resistivity, high TCR vanadium oxide films when the substrate is rotated during growth.
6.1 Experimental details

As discussed in Chapter 4, films were typically deposited while rotating the substrate holder at ten rotations per minute throughout growth. The rotation was performed in order to increase sample uniformity across the six inch diameter of the substrate holder. The rotation also served to mask the non-homogeneity of the sputtering atmosphere across the surface of the substrate carrier.

Figure 6-1 depicts the sputtering geometry used in the CMS-18 sputtering chamber. As shown in the left pane of Figure 6-1, the chamber utilizes a “sputter-up” geometry with the reactive gas entering the chamber through the gas-ring located 3 inches below the substrate surface. The gas ring located just above the vanadium target supplies only argon. This particular gas introduction scheme has a profound impact on the spatial non-uniformity of the growing film. The non-uniformity is further compounded by both the orientation of the gas ring and the location of the turbo pump inlet, both of which serve to create a non-uniform availability of reactive gas at the substrate surface.

Figure 6-1 Sputtering geometry of the CMS-18 chamber
The non-rotated samples discussed below were deposited at 2.5 mTorr total chamber pressure, with target power maintained at 300 W. The sputtering time for both the rotated and non-rotated samples was kept constant at 900 seconds. Samples of both types (non- and rotated) were made with and without a 25 W RF substrate bias. The details of the depositions are shown in Table 6-1.

Table 6-1 Growth parameters for homogeneity experiments

<table>
<thead>
<tr>
<th>Type of deposition</th>
<th>Total pressure</th>
<th>% O₂</th>
<th>Substrate bias</th>
</tr>
</thead>
<tbody>
<tr>
<td>Non-rotated</td>
<td>2.5 mTorr</td>
<td>7%</td>
<td>0 W</td>
</tr>
<tr>
<td>Rotated 10 RPM</td>
<td>2.5 mTorr</td>
<td>7%</td>
<td>0 W</td>
</tr>
<tr>
<td>Non-rotated</td>
<td>2.5 mTorr</td>
<td>10%</td>
<td>25 W</td>
</tr>
<tr>
<td>Rotated 10 RPM</td>
<td>2.5 mTorr</td>
<td>10%</td>
<td>25 W</td>
</tr>
<tr>
<td>Rotated 10 RPM</td>
<td>5 mTorr</td>
<td>5%</td>
<td>0 W</td>
</tr>
<tr>
<td>Rotated 1 RPM</td>
<td>5 mTorr</td>
<td>5%</td>
<td>0 W</td>
</tr>
</tbody>
</table>

Wafer sheet resistance was measured using the 4D four-point probe mapping instrument using a minimum of 25 locations on each wafer. Prior to cleaving for TCR measurement, X-ray diffraction patterns were collected from some of the wafers as a function of distance across the diameter.

6.2 Analysis of non-rotated growth

The outcome of this particular sputtering geometry in terms of spatial non-uniformity is highlighted by the sheet resistance maps shown in Figure 6-2, and the optical image shown in Figure 6-3. The right pane of Figure 6-2 shows the rotated counterpart of the non-rotated sample. It is evident in the rotated sample that non-uniformity exists as well; however, the non-uniformity has been homogenized through the rotating action of the substrate holder. The result is radial non-uniformity with lower resistivity material in the center giving way to higher resistivity material around the edge of the wafer.
Figure 6-2 Sheet resistance maps from a non-rotated (left) and rotated (right) deposition on a six inch wafer performed at 2.5 mTorr with 7% relative oxygen flow.

Figure 6-3 Image of central section of non-rotated wafer. From left to right the wafer transitions from oxygen-rich to oxygen-deficient material.

As shown above, the material changes dramatically across the diameter of the wafer as evidenced by both the large change (four orders of magnitude) in sheet resistance shown in Figure 6-2 and the drastic change in appearance shown in Figure 6-3. The film changes appearance from reflective and metal-like to rust-colored. Figure 6-4 shows the orientation of the above sheet resistance map with respect to the chamber geometry. It is clear from the wafer orientation that sheet resistance increases towards the source of reactive gas and away from the direction of the vanadium target. Figure 6-5 depicts the sheet resistance and TCR across the wafer in the direction of greatest resistance change. The resistivity and TCR measurements shown in Figure 6-5 were taken from the samples shown in Figure 6-3.
Figure 6-4 Orientation of non-uniformity with respect to sputtering geometry. The low-
resistivity material was deposited near the v-target, and the gradient to high resistivity material
occurred along the line between the target and the beginning of the substrate gas-ring.

The resistivity across the wafer continually increases from $7.5 \times 10^{-4}$ Ω cm on the metal-
like side to 1.9 Ω cm on the oxide side. As expected from previous results, the TCR and
resistivity are correlated, with a decrease in TCR accompanying a decrease in resistivity. At
approximately 30 mm across the wafer from the metallic side, the TCR changes from positive on
the metallic side to negative towards the oxide side. The change to a positive TCR was evidence
of a different crystalline phase than the FCC VO$_x$ as positive TCR has not been observed in other
studies on FCC VO$_x$ [58, 62].

When the TCR versus room temperature resistivity is plotted, as in Figure 6-6, the result
is similar to what was observed throughout the thickness variation samples from Chapter 5. The
relationship between the resistivity and the TCR reflects the global behavior of the total
population of pulsed DC sputtered VO$_x$. 
Figure 6-5 Sheet resistance and TCR as a function of distance across the six inch wafer. There was a transition from positive to negative TCR at ~40 mm from the metallic side. There was also a distinct change in the TCR behavior at ~90 mm, at which point the TCR began to increase more rapidly with cross-wafer distance.

Table 6-2 Non-rotated samples from 2.5 mtorr 7% O₂ non-biased wafer

<table>
<thead>
<tr>
<th>Sample number</th>
<th>Distance (mm)</th>
<th>Thickness (Å)</th>
<th>Resistivity (Ω cm)</th>
<th>TCR (%K⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3</td>
<td>32</td>
<td>1016</td>
<td>8.455E-4</td>
<td>0.109</td>
</tr>
<tr>
<td>4</td>
<td>45</td>
<td>1005</td>
<td>0.00109</td>
<td>-0.081</td>
</tr>
<tr>
<td>5</td>
<td>61</td>
<td>1094</td>
<td>0.00385</td>
<td>-0.088</td>
</tr>
<tr>
<td>6</td>
<td>81</td>
<td>1068</td>
<td>0.01396</td>
<td>-0.23</td>
</tr>
<tr>
<td>7</td>
<td>88</td>
<td>1061</td>
<td>0.05955</td>
<td>-0.95</td>
</tr>
<tr>
<td>8</td>
<td>107</td>
<td>1081</td>
<td>0.28193</td>
<td>-1.35</td>
</tr>
<tr>
<td>9</td>
<td>120</td>
<td>1038</td>
<td>0.49887</td>
<td>-1.90</td>
</tr>
<tr>
<td>10</td>
<td>132</td>
<td>1001</td>
<td>1.20764</td>
<td>-2.15</td>
</tr>
</tbody>
</table>

Because the set of samples resulting from the non-rotated run so closely resembles the global behavior, the changes in both the microstructure and chemistry across the non-rotated sample likely reflect changes taking place in the entire population of pulsed DC sputtered films.
Figure 6-6 Non-rotated samples plotted with total pulsed DC film population. When the non-rotated samples are compared to other non-substrate biased samples there is an interesting agreement between the TCR vs. $\rho_{300K}$ behavior, possibly signifying that the non-rotated samples act as a combinatorial source of samples representative of rotated counterparts.

X-ray diffraction patterns collected along the diameter of the wafer from the metal-like to oxide-side are shown in Figure 6-7. The pattern from the metal-like side of the wafer does not index well to the FCC VO$_x$ structure, as the lattice spacing from the (111) reflection is too small to be consistent with the FCC VO$_x$ structure at $a = 3.97$ Å. The structure of this phase appears to be consistent with a tetragonally distorted variant of the FCC VO$_x$ structure due to a slight decrease in the (100), (010) or (001) lattice spacing. The tetragonal distortion results in a break-down in the degeneracy of the (200) and (220) reflections while leaving the <111> family of planes degenerate. This results in a broadening of the (200) and (220) reflections towards the high 2θ side and a shift to smaller lattice spacing (higher 2θ) of the (111) reflection. This is a likely distortion as the “sub-oxides” between metallic vanadium and the FCC VO$_x$ structure are tetrahedrally distorted variants of either the BCC or the FCC structure [51, 66].
Figure 6-7 Glancing incidence XRD of non-rotated non-biased 2.5 mTorr 7% O₂ sample. The numbers in the legend correspond roughly to one inch steps across the wafer, hence the pattern labeled “3” was from the center of the wafer.

The remaining XRD patterns index to the FCC VOₓ structure, and the lattice parameter increases from the metal-like side to the oxide side. The increasing lattice parameter is consistent with increasing oxygen content in the VOₓ phase [58, 62-63]. The FWHM of the peaks is minimized at the midpoint across the wafer, suggesting the grains are largest in the center of the wafer and are smaller at either edge.

TEM specimens were made from both edges and the center of the wafer. Figure 6-8 shows TEM micrographs from samples taken from the metal-like side, the center, and the oxide side. The bright field images confirm that the thickness is essentially constant across the wafer and that grain size does appear to be largest in the center of the wafer.
Figure 6-8 TEM micrographs from non-rotated wafer. From top to bottom the samples were taken from the oxygen-deficient side, the center of the wafer, and then the oxygen-rich side. For each sample there is a bright field image on the left and a dark field image on the right.

Selected area diffraction patterns from each film are shown in the top part of Figure 6-9, with the corresponding rotationally averaged intensity, note that the intensity values are offset.
Figure 6-9 Selected area diffraction patterns from non-rotated TEM samples. The bottom pane shows the radially integrated intensity from each pattern above. The rotationally averaged data was generated by choosing the center of each pattern and then integrating the intensity about that center. Note the presence of an amorphous feature in the oxygen-rich pattern, and the lack of the same feature in the other patterns.

It is evident from the diffracted intensity that the lattice parameter increases from the oxygen-deficient to the oxygen-rich side of the wafer. It is also evident that the samples from the oxygen-deficient edge and the center do not contain a diffuse peak at low scattering vector indicative of a secondary amorphous phase. The sample from the oxygen-rich side of the wafer does contain the diffuse peak at ~3 nm⁻¹, suggesting there is a secondary amorphous phase.
accompanying the FCC VOx. Not evident in the rotationally integrated data is the unique defect structure present in the non-rotationally integrated diffraction data. The SADP from the oxide side of the wafer shown in Figure 6-10 has both the expected FCC VOx diffraction rings and streak-like features running tangential to the (111) diffraction ring. The streak-like features are called reciprocal rods, and they result from a highly periodic twin defect structure [40-41].

![Image of SADP from oxygen-rich side of non-rotated wafer. Long streak-like reciprocal rods are present in the pattern, running tangential to the (111) diffraction ring. The rods result from highly periodic (111) twin plane defects.](image)

Figure 6-10 SADP from oxygen-rich side of non-rotated wafer. Long streak-like reciprocal rods are present in the pattern, running tangential to the (111) diffraction ring. The rods result from highly periodic (111) twin plane defects.

It remains to be seen if this structure is a critical microstructural component in microbolometer-grade vanadium oxide. The nano-twin defect structure is commonly observed in vanadium oxide thin films deposited by ion beam sputtering for use in current generation VOx based microbolometers, and thus represents a microstructural feature present in actual device material [41]. It has been proposed that this defect structure allows for the accommodation of oxygen in excess of the equilibrium limit of x = 1.3 for this phase [41].
This series of samples is evidence that the nano-twinned defect structure results from vanadium oxide growth in an oxygen-rich atmosphere. The twin structure is not typically seen in magnetron sputtered films in the absence of a substrate bias because the range in $P_{O_2}$ over which the phase is stable is likely very narrow. In this case oxygen-rich refers to an excess of oxygen compared to what is needed to grow non-twinned FCC $VO_x$. Sample oxygen content clearly increases from one side of the wafer to the other, though actual oxygen content has not been measured for these samples. The lattice parameter increases from the metal-like to the oxide side is consistent with the addition of oxygen to the FCC $VO_x$ phase across the wafer.

Additionally, the vanadium valence extracted from EELS data collected from the samples shown in Figure 6-8 give values of 2.0 for the sample labeled 2, 2.25 for the sample labeled 5, and 2.74 for the sample labeled 10. The increase in valence across the wafer is further evidence that the oxygen content increases from the oxygen-deficient side to the oxygen-rich side. Finally, the resistivity and TCR increase observed in the data is consistent with the results reported in Chapter 4 in which there was an increase in both resistivity and TCR with increasing oxygen content.

These trends all suggest that the samples from this non-rotated experiment represent a slice of a thin-film V-O phase diagram from below the equilibrium $VO_x$ phase field (in sub-oxide region) to beyond the upper limit (and into the amorphous plus FCC $VO_x$). It is proposed here that the “center” FCC $VO_x$ sample resulted from growth in the near-ideal atmosphere for the formation of that phase and that in either direction along the $PO_2$ gradient, the bounds for the successful growth of that phase were reached. The bound in the oxygen-deficient direction begins with the formation of the sub-oxide phase, and the bound in the oxygen-rich direction begins with the formation of the nano-twinned/amorphous composite material. It is possible
that between the center FCC VO$_x$ and the nano-twinned/amorphous material there is a purely nano-twinned VO$_x$ phase; however the range of oxygen accommodation in that phase is likely vary narrow as the twin boundary structure appears to stabilize a structure similar to V$_2$O$_3$ [109], which also has a very narrow phase field [52]. It is proposed that additional oxygen, beyond the accomodation of the nano-twinned structure, results in the formation of the secondary amorphous phase. If the material further in the oxygen-rich direction could be probed it would likely grow totally amorphous.

The presence of the nano-twinned VO$_x$ in this non-rotated sample is further evidence that the twinning structure results from the stable incorporation of oxygen in excess of the $x = 1.3$ bound of the FCC VO$_x$ phase, and not from a growth process specific to the ion beam deposition method.

6.3 The homogenization of non-uniformity

The samples presented in section 6.2 are not discrete representations of different intentional growth parameters. They are representations of the microstructures that develop as a result of the non-uniform presence of reactive gas under a single set of growth parameters, i.e. total pressure, oxygen flow rate, argon flow rate, sputtering power, etc. As such they provide information on the available growth environments across the surface of the substrate holder. Rotation of the wafer causes any given portion of the wafer, aside from the center, to be continually swept through a varying growth environment. Figure 6-11 summarizes the relationship between the non-uniformity in the sheet resistance map and the corresponding microstructures and phases present across the diameter of the wafer. On the low resistivity side (red) there is not sufficient oxygen during film deposition to grow the FCC VO$_x$ phase. The result
is a small grained metal-like material with a low resistivity and a positive TCR. In the center of the wafer there is sufficient oxygen during deposition to grow the FCC VO\textsubscript{x} phase with a resistivity comparable to literature values and a small but negative TCR. On the high resistivity side there is too much oxygen during deposition for the FCC VO\textsubscript{x} phase to accommodate, resulting in the formation of both twinned FCC VO\textsubscript{x} and a secondary amorphous phase.

Figure 6-11 Corresponding microstructure/phases and non-uniformity in sheet resistance across six inch wafer. Shown on the right of the figure are dark-field images taken from the locations indicated by open circles on the sheet resistance map. Each sheet resistivity range thus represents a microstructurally distinct vanadium oxide thin film material.

The variety of growth environments a given location on the substrate holder is exposed to is related to the radial distance from the center of the substrate holder. The time spent in each growth zone is related to the rotation speed of the substrate holder.
The left part of Figure 6-12 shows the un-rotated wafer along with seven approximately different “growth-zones”. The particular microstructure and phase present in each zone is not entirely known; however, zones 1, 7, and 6 have been determined per Figure 6-11. On the right side of Figure 6-12 is the sheet resistance map of the rotated counterpart, which has also been divided into 5 distinct regions. The radial variation in the rotated version of the sample can be explained by the homogenization of the various “growth-zones” of the non-rotated sample.

Figure 6-12 Proposed multiple growth zone schematic. The various growth zones are based on arbitrarily chosen limits in the sheet resistance data. The left side of the figure shows the non-uniform regions of distinct vanadium oxide films, and the right side of the figure shows the rotationally homogenized vanadium oxide material that results from substrate rotation.

Rotation of the substrate holder exposes various parts of the growing film to constantly varying growth conditions. For example, the region labeled “A” in Figure 6-12 is near the center of the wafer and is only exposed to the growth-zone labeled “1” in the non-rotated variant. The region labeled “B” in the rotated sample is further from the center of rotation and is exposed alternatively to the “growth-zones” labeled “1” and “2” in the non-rotated variant. A region as far out as “E” is exposed to all available “growth-zones” at the surface of the substrate holder, including the lower resistivity zone “7.” The result is a radial non-uniformity in the rotated
sample as a result of each part of the film seeing a different oscillating growth environment. In this case the low resistivity zone “7” helps to mediate the effects of the high resistivity zones 5 and 6, limiting the non-uniformity.

6.4 “Grow-suppress” mechanism for nano-composite growth

In rotated samples, a particularly strange microstructure is often observed, as highlighted in Chapter 4, wherein nanocrystalline grains begin to grow and then stop growing, as shown in the middle and right panes of Figure 6-13. This result alone implies that for some reason the growth of that crystal becomes less energetically favorable compared to the growth of the surrounding amorphous material. In other films, typically in lower oxygen atmospheres, grains that nucleate grow throughout the thickness of the film, as seen in the leftmost pane of Figure 6-13.

Figure 6-13 Dark field TEM images with schematic representations. From left to right the oxygen concentration in the films increases. The scale in all three images is the same. Note that with increasing oxygen concentration during growth the size of grains that grow before being suppressed decreases. The far left pane represents growth conditions which allowed FCC VO$_x$ to grow across the majority of the substrate surface.
The resulting microstructures of rotated samples can also be explained in terms of film deposition in an oscillating growth environment. It is known from the microstructural analysis in the previous section that growth of FCC VO$_x$ is favorable in zone 1 of the non-rotated sample, as shown in Figure 6-11. It is also known that a suboxide phase grows in zone 7 and a mixture of highly defective (twinned) VO$_x$ and amorphous vanadium oxide is favored in zone 6. This means that FCC VO$_x$ is capable of nucleating and growing in zones 1-6, while a tetragonally distorted, oxygen deficient variant is capable of nucleating and growing in zone 7. This also means throughout growth, part of the substrate is exposed to a sufficiently oxygen-rich atmosphere in which amorphous vanadium oxide growth is possible.

During a typical rotated deposition, if the nominal conditions are chosen appropriately, FCC VO$_x$ is capable of nucleating over the majority of the substrate holder. The rotating action causes some parts of the wafer to be moved into a zone where oxygen content is too high for non-defective VO$_x$ growth, and disordered or amorphous growth can cause the suppression of the initially crystalline growth. The amount of time that the growing film spends in either a growth or a suppression zone is dependent on the radial distance from the center of rotation and the speed of rotation. Of course, rotation through a suppression zone does not necessarily imply a growing crystal will be terminated with amorphous vanadium oxide, as the VO$_x$ phase can still grow in oxygen-rich zones, as was the case in zone 6 of Figure 6-11.

It is proposed that the resulting microstructures seen throughout this work result from a “grow-suppress” mechanism, the details of which are determined by the gas distribution at the surface of the growing film. A schematic of this “grow-suppress” mechanism is shown in Figure 6-14, starting with the film exposed to a region that promotes crystal growth, and then moving to a region that suppresses it.
Figure 6-14 Schematic of the “grow-suppress” mechanism. “Growth” refers to nanocrystal growth and “suppression” refers to suppression of nanocrystal growth. In the first pane, nanocrystal growth occurs non-uniformly across the substrate. In the second pane the nanocrystalline growth that occurred is suppressed, and amorphous over-growth occurs.

A simplified model for this mechanism requires at the very least two distinct growth environments, one in which the crystalline phase grows and one in which the amorphous phase grows, as in Figure 6-15. At time zero, crystalline grains nucleate in the growth zone and amorphous material is deposited in the suppression zone. The substrate rotation brings some of the crystalline nuclei into the suppression zone where they are quenched. Grains that have only had a short amount of time to grow may not be large enough to be considered nano-crystals. Other parts of the film that originated in the growth zone, such as the point marked with an open circle in Figure 6-15, have sufficient time in the growth zone prior to being rotated into the quench zone to grow observable nano-crystalline grains.

Figure 6-15 Simplified model of grow-quench mechanism. In this schematic there are only two zones, one in which grains will grow and one in which they are suppressed. Grains that nucleate and spend a longer time in the “growth zone” will be larger, while grains that spend less time will be small or not-measurable.
The grain size \( s \) can be predicted given the growth rate \( G \) in Å/s of the crystalline phase, the rotation speed \( R \) in revolutions per minute, and the areal fraction \( f_g \) of the substrate surface exposed to an atmosphere that promotes grain growth. Assuming that grain growth is shut off completely outside of the growth zone, the grain size is given by Equation 21.

\[
s = f_g \frac{60 \cdot G}{R}
\]

Equation 21

This simplified model, with only two distinct zones, does not fully capture the behavior of a real system because the presence of additional oxygen over a brief timespan likely does not always suppress crystal growth. A more realistic model would likely contain additional parameters such as: the growth rate of the amorphous phase, the probability that a grain can nucleate in the time spent in a growth promoting zone, and the probability that a grain will be terminated in the growth-suppression zone. The situation is further complicated by the non-uniform flux of sputtered material arriving from the target, which results in an oscillatory growth rate [83]. Additional terms should be added to correct for the growth-rate dependence for each zone.

The “grow-suppress” mechanism allows for small isolated grains to grow alongside an amorphous matrix, creating a nano-composite structure from a single sputtering target. This growth mechanism allows for a great deal of diversity in engineering a nano-composite film, as the gas distribution and the rotation speed allow for two variable parameters which directly affect the resulting microstructure. The gas distribution determines what fraction of the wafer either promotes growth or suppresses it. In theory the volume fraction of each phase can be fine tuned by varying the fraction of the wafer that either suppresses or promotes growth. The grain size can then be independently controlled by varying the rotation speed, allowing for more
or less time spent in growth zones. Figure 6-16 shows the effect of rotation speed on the sheet resistance across six inch substrates. Changing the rotation speed by a factor of ten causes the cross wafer non-uniformity to change character. In the 1 RPM case the sheet resistance drops from the center outwards, while the sheet resistance increases from the center out in the 10 RPM case. In practice, controlling the gas distribution at or near the substrate is not straightforward, and providing zones that completely suppress crystalline growth is likely not possible.

Figure 6-16 Sheet resistance maps showing the effects of rotation speed. Both six-inch sheet resistivity maps were grown under the same processing conditions. The only parameter changed between the two samples was the rotation speed. The sample grown at 10 RPM shows low resistivity material on the perimeter of the wafer and high-resistivity material at the center while the 1 RPM sample shows the opposite behavior. This reversal in sheet resistivity behavior is likely due to the difference in times spent in “growth” or “suppression” regions of the chamber.
Chapter 7

Non-rotated growth with radio frequency substrate bias

The voided columnar structure observed in the un-biased, reactively sputtered films from Chapters 4-6 is representative of Zone I of Thornton’s structure zone model. Altering the energetics at the surface of the growing film can provide sufficient ion bombardment to sputter weakly bonded atoms, increase adatom mobility, and drive surface atoms into the bulk [83]. The resulting Zone T of the structure zone model is a denser, yet still columnar structure. A more dense structure could benefit the properties of VO$_x$ films as used in microbolometers.

The non-rotated samples presented in Chapter 6 supply a myriad of useful samples through one single deposition. Ideally each “sample” from the non-rotated wafer could be mapped to a set of deposition parameters that could provide a specific material across an entire substrate. In order to capitalize on the combinatorial nature on non-rotated growth in the CMS-18, several additional non-rotated wafers were deposited with VO$_x$.

7.1 Application of a substrate bias in pulsed dc sputtering of VO$_x$

Several initial experiments with an applied RF bias suggested improvement in the film properties, likely through a densification mechanism. The data from those initial runs, which included either a 10 or a 25 W bias are shown in Figure 7-1 alongside the data from the un-biased films discussed in Chapter 4.
Figure 7-1 TCR versus resistivity data for biased and non-biased pulsed DC vanadium oxide. Notice that the samples made with a substrate bias often have a higher TCR for a given resistivity. The substrate bias was a 25 W RF bias unless noted.

7.2 Non-rotated growth: a combinatorial approach

In order to better understand the effect of substrate bias over a larger portion of the resistivity scale shown in Figure 7-1, non-rotated biased samples were deposited in hopes of capitalizing on the combinatorial nature of the non-rotated deposition discussed in Chapter 6.

Figure 7-2 shows the TCR versus resistivity data of the rotated and non-rotated samples deposited with an RF substrate bias of 25 W. The samples were both made at 2.5 mTorr with 10% O₂. The TCR data from the RF biased samples was collected via the four-point-probe mapping instrument, which was modified to provide substrate heating during measurement. As such, the data in Figure 7-2 represents measurements from the entire non-rotated substrate and a diameter scan across the rotated substrate. Clearly the substrate bias of 25 W provides
superior TCR for a given resistivity. Interestingly, when plotted along with the Woods’ data, the RF biased samples fill in the lower resistivity data almost ideally, as shown in Figure 7-3.

![Figure 7-2](image1.png)

**Figure 7-2** Non-rotated and rotated TCR vs resistivity data for 25 W RF substrate bias 2.5 mTorr 10% samples plotted alongside un-biased pulsed DC data.

![Figure 7-3](image2.png)

**Figure 7-3** Non-rotated and rotated biased pulsed dc samples compared to the Woods ion beam data [7].
The overlap in the $10^{-2}$ Ω cm region helps to establish that pulsed dc magnetron sputtering is useful for creating what is arguably the “benchmark” data for thin-film vanadium oxide as used in infrared microbolometers. The pulsed DC data; however, appears to drop off in terms of TCR above $10^{-2}$ Ω cm. Pushing the oxygen content up further by altering the deposition conditions in a non-rotated run provided an additional set of data, shown in Figure 7-4. It is apparent from the data shown in Figure 7-4 does appear to have a lower TCR at a given resistivity than Woods’ data. Interestingly if the oxygen content is pushed even further under the substrate biased condition the resulting film is likely amorphous but with a very large TCR (−4.35 % K$^{-1}$) for a moderate resistivity (59 Ohm cm) for an amorphous vanadium oxide film. The data from Figure 7-4 is plotted along with the datum from the high oxygen content biased film in Figure 7-5.

Figure 7-4 Non-rotated biased samples with increased oxygen content compared to Woods’ ion beam data [7].
The nominally amorphous sample shown in Figure 7-5 is a remarkable result as it provides a realistic end-member with the needed properties to confirm the mixing rule results suggested in Chapter 6. Previous attempts to make amorphous vanadium oxide resulted in extremely large resistivity values, making the pulsed DC films deposited with a bias inferior to their ion beam deposited counterparts. The application of a bias clearly enables the dense lower resistivity material needed to increase the slope of the global data on the TCR versus Log(resistivity) plot.

Figure 7-5 Biased pulsed DC vanadium oxide compared to Woods data. The nominally amorphous film at ~60 Ohm cm has a very large TCR for the given resistivity, and likely represents the amorphous end-member that is mixed with crystalline VO$_x$ in the biased samples.

When compared to the non-biased pulsed dc data, the biased data clearly has superior properties, as shown in Figure 7-6. Interestingly the biased data comes back into coincidence with the non-biased data at ~1 Ohm cm.
Figure 7-6 All non-biased rotated samples compared to biased non-rotated samples.
Chapter 8

Conclusion

8.1 Summary

Thin-film vanadium oxide, with properties in the range of usefulness in pulse-operated microbolometer devices, was successfully deposited by reactive pulsed DC magnetron sputtering of a vanadium metal target in an oxidizing atmosphere. The films exhibited one of three distinct microstructures: polycrystalline with nanometer-sized grains, an amorphous often voided columnar structure, or a nano-composite structure composed of nano-crystalline vanadium oxide in an amorphous matrix.

Most often the nano-composite films contained nano-crystals of the FCC VO$_x$ “monoxide” phase; however there were films which exhibited a “sub-oxide” vanadium oxide phase, intermediate to the bcc metal and the fcc oxide structure. The nano-composite structure proved critical in understanding the relationship between the two material properties of interest: the room temperature resistivity and the thermal coefficient of resistivity.

It was found that VO$_x$ thin films in the range of interest have a nano-composite structure. The volume fraction of the nano-crystalline phase acts to both reduce the room temperature resistivity and the TCR. An empirical mixing-rule analysis of the electrical properties helped to confirm the meaningful microstructural aspects of the composite structures. It was found that there are several theoretical ways to improve the resistivity versus TCR behavior in these structures:
• Provide a microstructure that resembles a series resistance circuit, where the readout current is forced to travel through both phases in series. A real microstructure with this characteristic might be columnar nano-crystalline grains separated by a very small volume fraction of a higher resistivity amorphous phase.

• Tailor the nano-crystalline phase such that it is at the very high-oxygen end of the FCC VO_x phase field. When x > 1 the TCR of the nano-crystalline phase is enhanced without a significant change in the resistivity. The use of high-oxygen content FCC VO_x in a given structure acts to increase the TCR for any given resistivity, regardless of the way the phases are combined. In other words, whether the alpha value in the mixing-rule relationship is positive or negative, the TCR at any given resistivity value is larger when the low resistivity component is VO_{x>1}.

• Tailor the amorphous phase so that it has a large TCR (> 4% K^{-1}) but a moderate resistivity (in the 10's of Ω cm). This is easier said than done; however, for this work, amorphous vanadium oxide with a TCR of 4.35 % K^{-1} and a resistivity of 60 Ω cm was deposited with the use of an RF substrate bias.

The non-uniform atmosphere seen by the growing film results in a large change in the oxygen content of the film when not rotated. The non-uniformity results in a phase-diagram worth of samples from one side of the wafer to the other, in some cases spanning from the “sub-oxide” phases, lower in oxygen content than the FCC VO_x phase, up to and beyond the upper oxygen boundary of the FCC VO_x phase field. Nano-twinned FCC VO_x was observed in oxygen-rich portions of the sample, suggesting the phase grows under certain oxygen partial
pressures, specifically in conditions where un-twinned FCC VO\textsubscript{X} can no longer accommodate the excess oxygen.

It was postulated that the non-uniform growth environment can lead to a “grow-quench” mechanism when films are rotated during growth. In this model, grains that are able to nucleate and grow in one portion of the chamber can be quenched in oxygen-rich portions of the chamber where growth of the crystalline phase is no longer stable. The extremes of the sputtering environment thus act to establish the “end-member” phases that are homogenized through rotation. There is potential for altering the nano-crystalline and amorphous composite components independently through proper engineering of the gas delivery system.

Applying an RF bias during sputtering resulted in denser films with improved properties and the frequent observation of nano-crystals with a high concentration of nano-twins. The non-rotated growth with an applied RF bias resulted in sufficient non-uniformity in both TCR and resistivity across the six inch substrate holder to fill in the TCR versus resistivity data between the data from Woods and the data from the bulk FCC VO\textsubscript{X} study reported by Banus and Reed, providing further evidence that the empirical mixing-rules are both useful in this system and point at the nano-composite structure of these films as a necessity. The extension down to the bulk FCC data also supports the proposed nano-composite structure with the FCC VO\textsubscript{X} phase as an “end-member” component.

The significant overlap between the RF bias magnetron sputtered VO\textsubscript{X} and the ion beam sputtered VO\textsubscript{X} suggests that the properties observed for ion beam sputtered films are not process specific, but rather they are related to the energetics at the surface of the growing film.
8.2 Conclusions

Prior to this work and the related studies [40-41, 44, 107, 110-113], the microstructure of vanadium oxide films with the combination of TCR and room temperature resistivity needed for use in microbolometer devices was unknown. The similarities between the microstructural components in both the films from this work and the films currently used in vanadium oxide based infrared cameras extends the usefulness of this work because it provides microstructural insight relevant to a more generalized system.

The determination of the nano-composite microstructures of both ion beam sputtered material[41] and pulsed DC sputtered material provides the scientific basis from which new processing routes can be developed, or current processing routes can be intelligently modified. Is it critical that vanadium oxide is used in these structures, or could a different conductive, nano-crystalline phase be embedded in a similar higher resistivity matrix and provide the same results? The difficulty in using vanadium in a reactive process is the remarkable flexibility of the vanadium atom to take on multiple valence states. Avoiding the reactive aspects of either pulsed DC or ion beam sputtering would provide additional predictability and reproducibility. Separating the deposition of the amorphous phase from that of the nano-crystalline phase by using a co-sputtering technique could provide reproducibility and fine-tuning in the constituent phases that is not easily available in a single-target reactive sputtering process.

The re-creation of the benchmark Woods’ data via an alternative technique opens up many additional processing routes or equipment choices for device manufacturers.
8.3 Future Work

This dissertation has raised several new questions worth answering:

- Can the single target reactive sputtering process be replaced with a dual target, non-reactive process? In other words, could an oxide target be used to create the high-resistivity constituent and a metallic target be used to create the low resistivity constituent? This opens up new possibilities for fine-tuning the flux of either species hitting the growing film, and would likely increase the control over the volume fractions of the constituent phases. It is worth attempting to separate the reactive process into these two separate processes to determine the feasibility of a co-sputtering process.

- Does the combination of any resistive and conductive phase in a manner similar to these films result in a high TCR material? The mixing-rule model suggests that the nano-crystalline phase can be any low resistivity phase, not just FCC VO$_x$. The incorporation of a different metallic phase in a high TCR, high resistivity matrix would likely result in a composite with a tunable resistivity vs. TCR behavior. Exploring other constituent phases for use as high TCR materials could lead to novel materials useful for microbolometer-based devices. Certainly the inclusion of an actual metal would increase absorption in the sensing layer, and moving away from the vanadium-oxygen system would simplify the processing as the multi-valent nature of vanadium makes the reactive process particularly complex in terms of the resulting oxide phases.

Additional exploration of the reactive process in a non-uniform oxygen atmosphere needs to be performed in order to understand how oxygen non-uniformity affects the resulting nano-
crystalline microstructure. The proposed “grow-suppress” mechanism has far-reaching implications in terms of growing nano-structured composites and further development of the model could aid in understanding how to utilize non-uniform reactive gas distribution to achieve novel nanostructured composites.
Appendix A

TEM cross-section sample preparation

For cross-sectional sample preparation the samples were first cleaved into manageable pieces approximately 1 × 1 cm square. Those pieces were glued film-side to film-side using Gatan G-1 two part epoxy and placed in a Thermolyne 48000 box furnace set at 60 °C for 1 hour. Upon cooling the sandwiched samples were mounted to a glass slide using Crystalbond 509, a temporary adhesive that dissolves in acetone, and diced into small pieces approximately 3 × 1 mm. These small pieces were released from the slide by soaking in acetone and then attached to the glass mounting stub of a South Bay Technology Bi-pod polishing tool (Model 595) using cyanoacrylate superglue.

Once on the polishing tool, the samples were ground down using diamond embedded polymer films starting with 15 μm grit size and moving down in grit size from 9 to 6 to 3 to 1μm. After grinding with the 1 μm film, the samples were polished using a proprietary polishing film called True Blue made by South Bay Technology. The samples were then released from the stub by soaking in acetone and glued once again, polished-side down, onto the glass stub of the polishing tool. The same grinding procedure described above was used, with the slight adjustment that the sample was initially ground on the 15 μm film until very thin and then ground on the 9 μm film until transparent to white light. At that point the sample was carefully polished to a 1 μm finish and released from the stub by soaking in acetone onto a piece of filter paper inside a small Pyrex dish. The acetone was removed from the dish, and the specimen was allowed to dry.

The specimen was then picked from the filter paper using a 2 × 1mm copper slot grid onto which two small strips of the Epotech XX epoxy had been drawn using the splinter from a
fragmented toothpick. The specimen and grid were placed again into the box furnace at 60 °C and allowed to cure until a witness drop of the epoxy was hard to the touch.

Figure A-1 Schematic of TEM cross sectional sample preparation.
Appendix B

Thermal coefficient of resistivity measurement protocol

Current-voltage curves were measured from room temperature to 70 °C in 5 °C increments. The resistance was extracted from linear fits to the I-V curves. Resistivity was calculated using film thickness and the geometry of the linear contacts.

The conductivity data for all samples fit a simply activated model shown by Equation 22. Taking the natural log of Equation 22 results in Equation 23.

$$\sigma = \sigma_o \exp \left(-\frac{E_a}{K_B T}\right)$$ \hspace{1cm} \text{Equation 22}

When $\ln(\text{conductivity})$ is plotted against $1/T(K)$ the slope of the resulting plot is $E_a/K_B T$.

With knowledge of the activation energy ($E_a$), the TCR can be calculated using Equation 11 with $T = 300$ K.

$$\ln(\sigma) = \ln(\sigma_o) - \frac{E_a}{K_B T}$$ \hspace{1cm} \text{Equation 23}
Appendix C

Modeling of TCR from mixing-rule model

The following is the Mathematica script used to model the TCR versus resistivity data from Chapter 5. For each phase a temperature dependent resistivity was calculated based on both a prefactor (RhoHnot and RhoLnot) and an activation energy (ActivH and ActivL). Those values were fed into the mixing rule expression (RhoMix), and a composite resistivity was calculated for varying temperature (Temp) and alpha values.

The following is the Mathematica script used to both calculate and display the TCR for each composite determined from the above expression. A table (Woods) was built up of room temperature resistivities, calculated from the above RhoMix expression with a temperature of 300 K. For a given volume fraction composite, resistivity was calculated over a range of temperatures (300 to 360 K). The resulting resistivity(T) data was fit using the expression:
R*Exp[b/x], where R is a pre-factor for resistivity and b is the activation energy/Boltzmann’s constant. The value “b” was extracted from each fitting routine and used to calculate a room temperature resistivity. The resulting table of data is a room temperature resistivity value paired with a calculated TCR value in (-% K⁻¹). In this particular example that table is exported as the file, “FCC1pt3VO_xgoodaVOX.dat.”

```
Clear[{VolFrac, alpha, RTRho, Woods, alf, data, i, Temp, b, R, x}]
Woods = Table[
    alf = -.07;
    data =
        Transpose[{300 + Range[60] - 1, RhoMix /. {VolFrac -> i, alpha -> alf, Temp -> 300 + Range[60]}}];
    FitRho = FindFit[data, R*Exp[b/x], {R, b}, x];
    b /. FitRho,
    {i, 0, 1, .001}];

RTRho = RhoMix /. {VolFrac -> .001 + (Range[1001] - 1), alpha -> alf, Temp -> 300};

WoodsPlot = Transpose[{{RTRho, 100*Woods/300^2}}];

Export["FCC1pt3VO_xgoodaVOX.dat", WoodsPlot]
```
References


14. Wood, R.A., *Camera for producing video output signal, infrared focal plane array package for such camera, and method and apparatus for generating video signals from*
passive focal plane array of elements on a semiconductor substrate, USPTO, Editor. 1995, Honeywell Inc.: USA.


39. Wada, H., et al., *VO<sub>x</sub> film, wherein X is greater than 1.875 and less than 2.0, and a bolometer-type infrared sensor comprising the VO<sub>x</sub> film*. 1998, Masahiro Ota, Director General, Technical Research and Development, NEC Corporation (Tokyo, JP): United States.


VITA

Bryan D. Gauntt

Bryan was born on June 20, 1980 in Bryan, Texas to Randall O. Gauntt and Susan E. Tibbs, both graduates of the nearby Texas A&M University. They transplanted to Albuquerque, NM where Bryan graduated from high school and then attended the University of New Mexico from 1998 to 2002. He earned a B.S. in Biochemistry and graduated magna cum laude. Throughout his tenure at UNM he was working as a student intern for Sandia National Laboratories at the Advanced Materials Lab. After completion of his B.S. he decided that he would rather pursue a career in materials science. He worked for two years as a research technician before deciding to continue his education in the field of materials science. He began an M.S. program in the fall of 2004 at The New Mexico Institute of Mining and Technology (New Mexico Tech) and performed his M.S. research on glass composite fuel cell seals.

In the summer of 2005 he married his lovely wife Sarah Engdahl, now Sarah Gauntt. In the summer of 2006 he completed his M.S. in Materials Science and Engineering and in the fall he and his wife moved to State College, Pennsylvania so that he could pursue a Ph.D. in Materials Science and Engineering at The Pennsylvania State University. On October 20, 2008 he and his wife Sarah welcomed their daughter Emma Claire into the world. In December 2010 he defended his Ph.D. research just in time to welcome his second daughter Allison Hailey into the world on January 6, 2011. He and his family will be returning to Albuquerque, New Mexico where he will take a TEM Postdoc position at Sandia National Laboratories.