THE EFFECT OF SUBSTRATE BIAS ON THE GROWTH OF VANADIUM OXIDE THIN FILMS

A Thesis in
Engineering Science and Mechanics
by
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Submitted in Partial Fulfillment of the Requirements for the Degree of Master of Science

May 2014
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Current portable high performance thermal imaging devices are possible as a result of uncooled focal plane arrays of microbolometers. In order to increase efficiency, portability and performance over their cooled counterparts, uncooled thermal imaging utilizes materials able to operate at room temperature. These thin film detectors absorb incoming thermal radiation, resulting in a temperature change and a corresponding resistivity change of the thin film imaging layer. This resistivity change is measured by the CMOS read-out circuitry the microbolometers are fabricated on, and converted to an image. One of the most widely used materials is a vanadium oxide thin film due to its low resistivity, high temperature coefficient of resistance, and low noise characteristics. While these films have been manufactured commercially for years using ion beam deposition, this study concentrates on thin film vanadium oxide films deposited using magnetron sputtering.

In this study, vanadium oxide thin films are deposited using pulsed DC reactive magnetron sputtering of a metallic vanadium target. Various properties of these films were studied in order to get a better understanding of the structural and electrical characteristics of the films. In particular, this study looked at the effect on the film properties of a substrate bias applied to the thin film during deposition. The vanadium oxide thin films in this study were deposited in an argon atmosphere at various oxygen partial pressures with total flow rates between 15 and 45 sccm at pressures of 2.5 and 5 mTorr. RF as well as both positive and negative DC substrate biases were applied to the films during deposition. Structural characteristics of the films were studied using spectroscopic ellipsometry, grazing incident x-ray
diffraction and transmission electron microscopy. Electrical properties such as resistivity and
the temperature coefficient of resistivity were also studied.

As seen in previous works, the cathode current at the target, as well as various electrical
properties, exhibited a hysteresis effect between films made at increasing %O$_2$ and decreasing
%O$_2$. These films have been shown to have resistivites on the order of 1 ohm-cm with TCR
values as large as $-4\%/K$. GIXRD has been used to show that these films consist of FCC rock salt
nanocrystallites in an amorphous matrix. The application of a substrate bias during deposition
has been shown to increase the TCR to resistivity ratio of the films, reduce their process
hysteresis, densify the films, and, through the use of TEM images, form a nanocrystalline
columnar structure containing micro-twins embedded within an amorphous vanadium oxide
matrix. The substrate bias has been shown to dramatically change the structure of the films as
well as to improve numerous film properties critical to their application as imaging layers in
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ACKNOWLEDGEMENTS

The work shown in this thesis was only possible due to the support and experience of the MURI group. I would like to thank Dr. Bryan Gauntt, Dr. Nik Podraza, Nicole Wonderling, Dr. Jing Li, Michael Moytka, Chandru Venkatasubramanian, Myung-Yoon Lee, and Hitesh Basantani for their assistance throughout my time at Penn State.

I would like to thank the MRL support staff, most especially William Drawl for all of his help and guidance with the KECK sputtering tools.

I would like to thank Dr. Srowthi S. N. Bharadwaja for his support and patience, without which this research would never have been completed.

I would most especially like to thank Dr. Mark Horn for his constant support and guidance as my thesis advisor. Without Dr. Horn this research would never have been possible.

This research was made possible due to the sponsorship by the U.S. Army Research office and the U.S. Army Research Laboratory and was accomplished under the Cooperative Agreement Number W911NF-0-2-0026.
Chapter 1  Introduction

1.1  Night vision

Night vision technology was originally developed for military use, but has also begun to be used extensively in various commercial applications. This technology is used widely for everything from strategic military advantage to security, surveillance and search and rescue. The original bulky optical technology has been heavily researched, developed and improved through the advancement in image intensification technology.

There are currently three basic night vision technologies [1]. The initial type of night vision technology was an active system designed to convert infrared light into visible light. This required the use of an infrared light source, such as lasers or filtered flashlights, detector, and processing technology. While revolutionary, this initial technology was range limited and easily detectable.

The remaining two types of night vision technology utilize either thermal imaging or image intensification technology. Both technologies are passive systems that respond to naturally available light. Image intensification technology converts incoming light, typically visible, into electrons, amplifies them, and then converts them back into a visible light image. Due to the amount of light amplification, very little light is needed in order to observe an object. Thermal imaging on the other hand only responds to available infrared light, typically in the 8 to 14micron wavelength range. Infrared
detectors use a special lens to focus incoming infrared light on to a focal plane array which converts the signal to electrical impulses. These impulses are then processed and finally displayed, like most CCD cameras, into an image scene that depends on the intensity of the infrared light. Due to the fact that infrared light is emitted, not simply reflected, by nearly everything to some degree, thermal technology performs equally well in both well and poorly lighted environments. Lastly, since thermal energy does not dissipate from an object immediately, thermal technology is able to detect where heat sources have been, which can be very important in some applications.

1.2 Thermal Imaging

Thermal imaging can be broadly categorized into two main types, cooled and uncooled infrared image detectors. Cooled infrared detectors utilize various photodetector materials. Since the detection mechanism of these materials utilizes a small semiconductor bandgap, at room temperature there is so much dark current generated in the system that it swamps the incoming light. In order to prevent this, the material needs to be vacuum-sealed and cryogenically cooled. While these cooling systems are bulky, expensive and power-intensive, cooled infrared cameras provide the highest IR image quality and sensitivity available, typically better than uncooled infrared cameras. Uncooled infrared cameras on the other hand use a detector material which operates at room temperature. These cameras utilize a MEMS membrane structure, a microbolometer, in a focal plane array (FPA) in order to have enough sensitivity. The microbolometer absorbs infrared radiation, thus heating the detector material and
changing its resistance. Through the comparison of these changes, along with the internal temperature of the detector, an image can be computed. Uncooled means that these detectors are able to perform without bulky and expensive cooling equipment. This makes uncooled infrared cameras significantly smaller and cheaper than their cooled counterparts, resulting in significantly higher portability and energy efficiency. Although the resolution of these devices is not as good as cooled systems, it is still good enough to be used in many military and commercial applications.

1.2.1 Microbolometers

A microbolometer is a sensing device used in thermal imaging cameras to measure the energy of incoming electromagnetic radiation. The device consists of an absorbing detector layer connected to a heat sink, as shown in Figure 1.1. In this way, any incidental infrared energy will be absorbed by the detector layer. The increase in energy results in an increase in temperature of the detector layer. This change in temperature can be measured and converted into an image. This is typically done at video frame rates (30-60Hz). A microbolometer is a single pixel of many in the focal plane array of the imaging equipment. In infrared imaging devices, a lens focuses incident light onto the focal plane array where each individual microbolometer absorbs the thermal radiation associated with that pixel in the imaged scene. In this way, the more microbolometers in a give focal plane array, the higher the subsequent resolution of the final image.
Figure 1.1. Schematical overview of a single pixel microbolometer. Consists of a thin film suspended over the surface of a ROIC.

The thin films that have been fabricated and evaluated in this thesis were specifically for use as the resistive imaging layer of a microbolometer. When infrared radiation falls on a resistive microbolometer, the detector layer, in this case the vanadium oxide thin film, absorbs the radiation. This energy increases the temperature of the thin film which also results in a resistance change. A readout integrated circuit (ROIC) is used to track and convert these resistivity changes through digital image processing in order to form an image.

The microbolometer bridge design originated with Honeywell Inc. in the 1980’s [2]. Once declassified, the research into microbolometers and desirable sensing materials increased greatly. Uncooled infrared cameras consist of many pixels constructed into a two-dimensional focal plane array. Each of these pixels contains a single microbolometers depicted in Figure 1.1. The bridge type microbolometer,
designed and originally prototyped by Honeywell Inc., is composed of a free-standing thermally isolated thin film detector layer suspended over the underlying silicon substrate. The bridge is suspended over the substrate through the use of two electrically conductive yet thermally insulating legs. In order to increase the efficiency of the design by reflecting any unabsorbed radiation back to the detector, a thin-film metal reflector layer is deposited on the underlying substrate. Another way found to maximize the efficiency of the design is to produce a quarter-wave resonant cavity between the substrate and the absorption layer. This cavity is known as the vacuum gap because once the assembly is vacuum packaged, this gap acts to thermally isolate the sensing layer and the read out integrated circuitry (ROIC).
Chapter 2: Background

2.1 Thin Film Vanadium Oxide

Vanadium oxide thin films are the most widely used sensing material for a resistive microbolometer due to vanadium’s high Temperature Coefficient of Resistance (TCR), low room temperature resistivity, and low 1/f noise. Other materials used and researched as possible detector layers include amorphous silicon [3] and polycrystalline SiGe [4]. Vanadium oxide is also desirable as a sensing material due to its capacity to be processed at low temperatures, making it compatible with current CMOS integrated circuits. The vanadium oxide thin films were first developed and patented by R. A. Woods [5] while at Honeywell Inc. Woods’ original thin films were fabricated using ion-beam sputter deposition. This method is still the most commonly employed method for commercial production of VO\textsubscript{x} for infrared focal plane array applications.

Vanadium is a transition metal that is able to form numerous oxides due to its many variable valences, which include +2, +3, +4, and +5. Vanadium oxide compositions with these valence states include VO, V\textsubscript{2}O\textsubscript{3}, VO\textsubscript{2}, and V\textsubscript{2}O\textsubscript{5}. The vanadium oxide composition reported for films used in microbolometers is VO\textsubscript{x}, where x is approximately 1.8. As seen from Figure 2.1 [6], due to the multivalent nature of the vanadium ion, it is difficult to obtain such an exact composition and precise crystal structure. This difficulty arises from the fact that there are many mixed phases of vanadium oxide which exist in a range of differing and non-exclusive crystal structures.
Obtaining such a precise composition reproducibly requires very stringent control of the deposition system being used to make the films. Typical process variables for reactive magnetron sputtering are: total power, total pressure, oxygen partial pressure, deposition time, substrate temperature and substrate bias. Additionally, complications arise due to the fact that vanadium is one of numerous metals that form compounds with oxygen, known as Magnéli phases. Magnéli phases, named after Arne Magnéli, have the general formula $V_nO_{2n-1}$ and exist between $VO_2$ and $V_2O_3$ on the vanadium phase diagram below [26]. Some examples of Magnéli phases of vanadium include $V_4O_7$, $V_5O_9$, $V_6O_{11}$, $V_7O_{13}$ and $V_8O_{15}$.

![Figure 2.1. Various phases of bulk vanadium oxide.](image-url)
Some vanadium oxide phases also exhibit metal-insulator transitions at certain temperatures. For example, VO$_2$ changes from a semiconductor with a monoclinic structure to a metal with a tetragonal rutile structure at 67 °C. These phase transitions make certain phases of vanadium oxide undesirable as detector layers due to drastic property changes associated with the change. For example, above 67 °C the resistivity is over 4 orders of magnitude different than below the transition temperature. Since this falls inside of the desirable operating temperature range, crystalline VO$_2$ would not be a desirable vanadium oxide phase for use in microbolometers. While the transition temperature of VO$_2$ excludes its use in microbolometers, there are numerous other phases of vanadium oxide whose transition temperature falls outside the range of operating temperatures and are therefore still of interest.

The Pennsylvania State University has been part of the Multidisciplinary University Research Initiative, MURI, from 2006 to the present through the sponsorship of the Army Research Office. The goal of the group at Penn State has been to find alternative fabrication methods and sensing materials for the imaging layer in uncooled microbolometers and to better understand the VOx that is currently being used in commercial products. This thesis is based on and built upon a number of other publications from the research group at Penn State.
Before the MURI was even awarded, John Petrilli started to investigate VO$_x$ deposited by pulsed DC magnetron sputtering as the topic for his senior thesis [7]. Since 2006, multiple papers have been published by the Penn State group on VO$_x$. A chronological summary of this work follows.

Early work on vanadium oxide thin films was done by Kerry Wells via deposition and analysis of vanadium oxide thin films fabricated by the pulsed DC reactive magnetron sputtering of a V$_2$O$_3$ target [8]. The main purpose of this work was to better understand the effects of various growth parameters on the optical, electrical and microstructural properties of vanadium oxide thin films. The growth parameters that were varied include total pressure, oxygen partial pressure, deposition time, temperature and thickness. While the fabricated films showed high TCR values, -3 to -5% K$^{-1}$, this was accompanied by resistivity values that were too high to make the films integratable with current ROIC technology. The resistivities and TCR of the films both decreased with increased thickness. It was also shown that both the resistivities and TCR of the films increased with increased oxygen partial pressure. The work also determined that the films were reproducible as well as stable over the course of the experiments. Cross sectional FESEM images showed that both low total pressure and low oxygen partial pressure result in primarily amorphous films. As the oxygen partial pressure and total pressure were increased the films began to develop distinct grain boundaries. Most importantly, it was shown that the microstructure and electrical properties of the films could be controlled through changes in varies process parameters. It is interesting to note that spectroscopic ellipsometry showed that some
films with similar electrical properties had variations in the dielectric functions due to the varied oxygen content of the films.

Chandrasekaran Venkatasubramanian studied pulsed DC magnetron sputtered vanadium oxide thin films using a metallic vanadium target for use in microbolometer applications. Venkatasubramanian showed that the cathode current during deposition exhibited a hysteresis behavior between the forward and reverse directions for changes in the oxygen partial pressure as well as the total flow rate [9]. Thin films were deposited along various points of the hysteresis curves and then their electrical and structural properties were characterized. Since current microbolometer arrays require a material with both a high TCR and low resistivity, films were deposited under low total pressure and low oxygen partial pressure. In this way vanadium oxide thin films with electrical properties comparable to films deposited by ion beam deposition were made. These films showed a microstructure change from columnar to multi-grained as the flow rates during deposition were increased. Transmission electron microscopy has also shown that these films contain nano-crystallites in an amorphous matrix. A linear relation between TCR and the log of resistivity, with higher resistivities resulting in higher TCR, was also seen.

Venkatasubramanian explored post-deposition techniques in order to try and improve the electrical characteristics of the deposited films. The sputtered films were introduced to either an oxygen or a nitrogen environment at various temperatures and periods of time. Films that were annealed in the oxygen environment showed both an
increase and decrease in resistivity depending on the annealing temperature. At lower annealing temperatures the resistivity of the films decreased while the TCR increased, but the films were unusable due to the irregularity of the TCR over the temperature range of interest. At higher annealing temperature of 400 °C and 500 °C the resistivity of the films increased up to several orders of magnitude due to the formation of less conductive oxide states, making the films unusable because the resistivity was now too high to be used current readout circuitry. On the other hand, annealing in a nitrogen environment reduced the resistivity of the films with increasing temperature. The TCR of these films also either stayed the same or increased up to 20%, with a lowering of the resistivity. By annealing the films in a nitrogen environment at 300°C, the films were able to be made with significantly better TCR values.

Nick Fieldhouse studied pulsed DC magnetron sputtered films using a metallic vanadium target being deposited at various temperature and oxygen partial pressures. Grazing incidence x-ray diffraction showed the films to be mostly amorphous while containing a VO crystal structure [10]. This indicated that both the temperature and oxygen partial pressure variations during deposition did not alter the films’ crystal structure. On the other hand, electrical characterization showed that increasing the temperature during deposition reduced films’ resistivities by an order of magnitude while only marginally lowering the TCR. In this way, films with high TCR values, but previously too high resistivities, could now be deposited at a higher temperature with a resulting lower resistivity capable of being used in current microbolometer readout
circuitry. It was suspected that with some further research, pulsed DC sputtering should be capable of producing films with comparable electrical properties as those currently grown in industry by ion beam deposition.

Bryan Gaunt investigated the structural properties of thin film vanadium oxide, deposited by pulsed DC magnetron sputtering of a metallic vanadium target in an oxidizing environment. By altering the processing conditions during deposition, Gaunt was able to study the correlation between the microstructure and the resultant properties of the thin films. The deposited vanadium oxide thin films were able to be divided into three distinct groups by differing microstructure: an amorphous columnar structure, a polycrystalline structure with nanometer-sized grains, and a composite structure of nano-crystalline vanadium oxide in an amorphous matrix [11]. Once the electrical properties were studied, it was found that the vanadium oxide films having a nano-composite structure were the most promising for use in microbolometer applications. These composite films usually contained VO FCC nano-crystals.

This nano-composite structure helped to explain the relationship between the room temperature resistivity and the thermal coefficient of resistivity of the vanadium oxide films. It was found that the volume fraction of the nano-crystalline phase of the structure acted to reduce both the resistivity and the TCR of the resultant films. Through the use an empirical mixing-rule analysis of the electrical properties, Gaunt was able to deduce several theoretical ways of improving both the resistivity and the TCR of films with this nano-composite structure:
- Provide a microstructure that resembles a series resistance circuit where the readout current is forced to travel through both phases in series. This could be accomplished with a microstructure composed of columnar nano-crystalline grains separated by very small volume fractions of a higher resistivity amorphous phase.

- Grow nano-crystallite FCC VO$_x$ where $x$ is greater than one. In this high oxygen nano-crystalline phase the TCR is increased while the resistivity remains relatively unchanged.

- Tailor the amorphous phase of the nano-composite structure, which inherently has a large TCR value, to have a lower resistivity. Gaunt was able to grow such an amorphous vanadium oxide thin film and reduce its resistivity through the use of a RF substrate bias applied during deposition.

Gaunt was also able to study the effect of oxygen incorporation during the film growth by eliminating the rotation of the substrate during deposition. The resultant film contained numerous vanadium oxide phases ranging from the very low oxygen content sub-oxide phases up to the oxygen rich FCC VO$_x$ phase. It was found that some of the oxygen-rich phases contained nano-twinned FCC VO$_x$ [11]. The absence of this nano-twinned structure in lower oxygen content film suggests that this nano-twinned structure is formed to accommodate the excess oxygen. It was also seen that through the application of an RF substrate bias during growth the resulting films were denser and contained high concentrations of nano-twins. It was observed that the RF biased
vanadium oxide films showed similar microstructure and electrical properties to ion beam deposited vanadium oxide. This suggests that the energetics at the surface of the film during its growth determine the films properties rather than being process specific.

Hitesh Basantani and Mike Motyka were the last students to publish theses from the Penn State MURI group. Hitesh Basantani deposited vanadium oxide thin films using pulsed DC reactive magnetron sputtering. Hitesh focused on improving the electrical characteristics of the sputtered vanadium oxide films, in comparison to ion beam deposited films, through the application of an rf substrate bias. Through the application of an rf substrate bias, the microstructure of the vanadium oxide changed from nanocrystalline to a columnar microtwin structure. This columnar microtwin microstructure, which is commonly present in ion beam deposited films, is believed to be responsible for the improved electrical properties, including low resistivity, high TCR, and reduced 1/f noise. Films with a resistivity range of $2 \times 10^{-4}$ and 0.6 Ω.cm, TCR in the range of $-0.29\%/\text{K}$ and $-2.85\%/\text{K}$ and a normalized Hooge's parameter as low as $1 \times 10^{-25}$ cm$^3$ were deposited [13]. Hitesh demonstrated that films deposited using pulsed DC reactive sputtering with the application of an rf substrate bias are comparable to ion beam deposited films. Substrate bias was also shown to help improve the degree of control over the amount of oxygen incorporated into the film during deposition. This control is able to be used to deposit films with relatively specific resistivities.
Michael Motyka deposited vanadium oxide thin films using pulsed DC reactive magnetron sputtering in an oxygen and argon environment in order to obtain a reference database of the electrical and optical properties via spectroscopic ellipsometry. Mike worked to obtain initial representative models of these nanocrystalline volume fractions within the nanocomposite vanadium oxide thin films. It was seen that many deposition parameters, such as oxygen flow rates, substrate temperature, substrate bias, and the substrate surface affect the overall growth of the thin films. It was also discovered that the type of substrate greatly affects the overall crystallinity, phase, and structural evolution of the thin films [14]. Mike was also able to use real time spectroscopic ellipsometry in order to study the growth and evolution of the vanadium oxide in situ.

2.2 Pulsed DC Reactive Magnetron Sputtering

Sputtering is a thin film deposition method where energetic particles are directed towards a target material in order to eject atoms from the target material. While Ion Beam Deposition is widely used in microbolometer technology, pulsed DC reactive magnetron sputtering is being researched as an alternative in order to study its potential ability to deposit bolometer-quality films at higher deposition rates. It also has the potential advantage of being used in a cluster tool configuration.

Sputtering is a plasma-based physical vapor deposition method that requires a vacuum system. The sputtering chamber is typically evacuated by a combination of a
turbomolecular pump and a backing pump. The sputter deposition tool primarily used in this thesis employs a sputter-up configuration where the substrate is secured downward-facing in the chamber (see Chapter 3). The sputtering process cathode is the sputtering gun and associated target, while the substrate and chamber walls are the anode for either an rf or dc deposition.

Once the substrate is secured and the chamber has been pumped down to a high vacuum, an inert sputtering gas, typically argon, is pumped into the chamber at a given rate. A negative voltage is then applied to the cathode, the target, in order to create an electric field between the target and the anode, which is the rest of the chamber. The electric field and low pressure create a plasma which ionizes the sputtering gas. The resulting positive ions are accelerated towards the cathode by the electric field. These ions impact the target and eject material to be deposited, i.e. sputtering. The key parameters that affect this deposition process are the power to the target, pressure, target-to-substrate distance, gas ambient, and method by which the power is applied. The plasma consists of electrons, neutrals, radicals, metastables, and ions and the ejected material can arrive at the substrate with a wide variation in energy depending upon the plasma conditions used. The ejected material is deposited around the whole chamber, not necessarily uniformly, resulting in a thin film of the target material on the chamber and the substrate.

Magnetron sputtering incorporates magnets in the target cathode assembly, often referred to as the sputtering gun, in order to confine the electrons close to the target. By confining the electrons close to the target there will be a greater number of
collisions near the target and more ionization resulting in higher sputtering rates. A disadvantage, however, is that the target has non-uniform erosion.

The reactive magnetron sputtering process is identical to non-reactive magnetron sputtering except for the introduction of a reactive gas, such as oxygen. When the target is metallic and the reactive gas used is oxygen, the target often oxidizes, which can result in a dielectric formation on the target and even sputtering failure when using a dc source. The oxidation of the target material can cause a charge buildup on the surface of the target resulting in a bias. This oxidation of the target is often referred to as the poisoning of the target. When this charge buildup approaches the sputtering bias, the plasma cycle fails and sputtering stops. In order to overcome this problem, a short positive electrical pulse can be applied to the target periodically to neutralize the charge buildup. This is known as pulsed-dc sputtering, and when combined with magnets in the target, it is known as pulsed-dc magnetron sputtering.

2.3 RF/DC Bias during growth of metal oxide

The effect of applying a substrate bias during the reactive RF magnetron sputtering deposition of vanadium oxide is being studied in this thesis. In order to gain a better understanding of the effect on the resulting vanadium oxide thin films, the following is a summary of some examples of past films where the effect of a substrate bias during reactive magnetron sputtering deposition has been investigated.
Thermochromatic vanadium dioxide has been deposited by reactive RF sputtering while a dc bias is applied to the substrate [15]. As the substrate bias is increased during deposition, the collision energy of the ions increases, which can result in both increased surface energy and greater damage due to ion bombardment. This increase in ion bombardment can result in both increasing resputtering and densification of the films. As a result, the deposition rate decreases as the negative substrate bias is increased. Through XPS measurements, it was also shown that the substrate bias was able to provide some control of the valence state of the vanadium in the films.[14] The XPS measurements showed that a bias of 0 to -60V applied to the substrate reduced the valence state of the vanadium in the deposited films. Further bias showed a continued, but smaller, reduction in the vanadium valence in the films. The bias resulted in an increasing amount of resputtered vanadium and oxygen during the growth of the film due to Ar ion bombardment [15].

Titanium nitride is another material where applying a substrate bias during deposition results in interesting property changes. Titanium nitride is known for its hardness, high melting point, and chemical inertness. These properties make titanium nitride ideal for protective and anti-corrosive thin film coatings. The negative dc substrate bias applied during deposition results in the densification of the films, until the negative bias is great enough, which leads to the resputtering of high energy ions from the film [16]. The range of negative substrate bias in this study can be divided into two regions: a smoothing region below a certain bias voltage, followed by a roughening region at higher biases. During the smoothing region, the ion current density and the
ion bombardment energy increase. This extra incident energy provides added mobility to the titanium and the nitride atoms leading to the development of a more densely packed, but thicker and smoother, crystalline structure. At higher substrate biases, the thickness of the film decreases due to the increasing amount of resputtering of the deposited film. The surface roughness of the films followed a similar pattern as the thickness, decreasing at lower bias voltages and increasing at higher bias voltages. Nano-hardness of the films also followed a similar non-linear trend with film hardness increasing during the smoothing region and decreasing during the roughening region. Studies have shown a nonlinear trend of surface morphology, RMS roughness and nano-hardness. These properties were optimized for coating applications at a substrate bias of -100V.

Tantalum oxide deposited by dc reactive magnetron sputtering in the presence of oxygen and an applied substrate bias has also been studied. High permittivity dielectrics, such as titanium oxide and tantalum oxide, are studied intensely for use in integrated circuits. Tantalum oxide is rather unique among other high index materials due to its superior thermal stability and mechanical resistance. It was shown that as the negative substrate bias was increased, the crystallinity of the films also increased [17]. The substrate bias also provided the positive ions with much higher energy, which resulted in a higher diffusion of deposited particles and a densification of the film. Biasing also reduced the leakage current of the resultant films by reducing both oxygen vacancies and bond defects during the deposition. This increase in both packing density and crystalinity of the films, along with the increase of the negative bias, resulted in an
increase in the dielectric constant. Compared to the unbiased films, the biased films showed an increase in the optical band gap, refractive index, dielectric constant, and the transmittance of the films.

Titanium oxide is widely used in both optical and electrical applications due to its high refractive index and dielectric constant. Ion bombardment is often used during deposition in order to densify and improve the structure of the thin film as well as improving adhesion. In order to produce such results, a negative substrate bias was applied during film deposition. As the negative bias power increased, the deposition rate of the films decreased [18]. At low bias powers, the surface of the film was ioni-
cally cleaned. Higher bias powers led to densification of the films and eventually resputtering of the films. Biasing also resulted in a decrease in the RMS roughness of the films. Finally, the packing density and the refractive index of the films increased with bias, achieving maximum values at intermediate bias powers.

Indium tin oxide is widely used as a transparent conducting coating in optoelectronic devices. In such applications high optical transmittance and low electrical resistivity are optimal. Typical ITO films are heated during deposition to get the required properties. ITO films were deposited with an applied substrate bias in order to see if similar results were possible though increased ion bombardment. Negative dc substrate bias resulted in greater crystallinity. The increased ion bombardment due to the biasing led to a reduction of contaminates in the film, resulting in reduced sheet resistance. The lattice parameter, which is an important indicator of stress in thin films, decreased with increasing bias power. At high negative
bias power the film resistivity began to increase. Positive substrate bias was also applied during deposition leading to a decrease in sheet resistance but an increase in film stress. Negatively biasing the substrate during deposition of ITO resulted in films with both increased transmittance and reduced resistivity.

Cuprous oxide is a well-known p-type semiconductor with high optical transparency in visible wavelengths. It is also non-toxic and cheap, making it a desirable material for many applications. Negative substrate biasing during deposition resulted in increased deposition rates at low bias powers and decreased deposition rates at high bias powers [19]. Biasing also lead to both an increase in film crystallinity as well as an orientation change from a (111) orientation to a (200) orientation. Lattice parameter, grain size, and film stress all showed a similar trend as deposition rate with the application of the negative substrate bias. The increase in the crystallite size in the biased films helped to improve their electrical properties as well as decrease the optical band gap.

It is clear that the application of a substrate bias during deposition can result in drastic differences in a variety of film properties. The use of a negative DC substrate bias has been shown effect many film properties including the deposition rate, density, sheet resistance, surface roughness, crystallinity, leakage current and transmittance, among others. While nearly all of these effects were obtained using a DC substrate bias, an RF substrate bias also affects many of the same properties. In order to gain a more comprehensive understanding of the effect of substrate bias during deposition, both DC and RF substrate biases were explored.
3.1 Experimental Procedure

Vanadium oxide thin films were deposited by pulsed DC magnetron sputtering. The films were deposited under various RF and DC substrate biases. The films were then characterized using grazing incidence x-ray diffraction, GIXRD, to determine the crystalline nature of the films, and ellipsometry, to determine film thickness. Contacts were deposited in order to extract electrical properties, such as resistivity and temperature coefficient of resistance, TCR. This last process is explained in the following chapter.

3.1.1 Sample Preparation

The VO<sub>x</sub> films were grown on <100> silicon with either a native oxide or a 500Å silicon nitride coating. In each case a quarter of a 6-inch wafer was used. These wafers were mounted onto a stainless steel substrate holder using Kapton tape, and blown clean with nitrogen gas. No special precleaning was used as the wafers were taken directly from the box and cleaved into quarters before being introduced into the chamber.

3.1.2 Deposition Procedure

Films were deposited by reactive pulsed DC magnetron sputtering using a Kurk J Lesker CMS-18, located in the Material Research Laboratory and shown in Figure 3.1. The
Keck system is a computer integrated three-target sputtering tool. The Keck system features a 10-inch throw distance, which is the distance between the substrate and the Vanadium target, a downward-facing rotated substrate holder, and three upward-facing 3-inch diameter targets. For all depositions a single 3-inch 99.99% pure vanadium target was used.

![Figure 3.1](image)

**Figure 3.1.** Schematic of the deposition chamber and a picture of the Kurk Lesker CMS-18 sputtering system used for depositions [20].

Films produced via pulsed DC sputtering used a MDX-1K 1KW DC Plasma Generator. The vanadium oxide films were deposited using a power of 300W and a pulse frequency of 20kHz for 900 seconds. The pulse profile of the deposition is shown in Figure 3.2.
A shutter was used to cover the vanadium target during the presputtering step of the deposition. Three different mass flow controllers were used to control the system input gases. The system features a load lock to speed up the total deposition process and reduce contamination. The system is also equipped with a rotating substrate holder in order to improve film uniformity due to the unsymmetrical chamber geometries.

Total pressure, total flow rate, and oxygen partial pressure were all varied throughout the study. Depositions were carried out at total pressures of both 2.5 and 5mTorr. The total flow rate of argon and oxygen was varied between 15, 25 and 45sccm.
depending on the run. The percent oxygen was also varied depending on the run (4% = 1sccm oxygen / 25sccm total). Pressure and flow rates were all controlled manually in order to ensure consistent operating values. Films were deposited under four different categories of substrate bias: no bias, RF bias, negative DC bias, and positive DC bias.

3.2 Characterization Methods

3.2.1 Ellipsometry

Spectroscopic Ellipsometry is a powerful optical technique for the investigation of the dielectric properties of thin films from which film thickness and surface roughness can be extracted. Ellipsometry is very useful due to the fact that it is both nondestructive and does not require any contacts to be deposited. Polarized light is directed at the surface of a thin film at an angle. The incident beam reflects off of the sample films. The changes to the amplitude and polarization state can be analyzed and fit to models in order to extract the dielectric function and thickness of each layer in the sample.
In this study a J. A. Woollam multichannel, dual-rotating compensator RC2 spectroscopic ellipsometer was used, as shown in Figure 3.3. The sample film is placed onto a stage. Polarized light is then directed onto the sample at an angle. These measurements were done at incident angles of 55°, 70°, and 85° over a spectral range of 0.75 to 6.5 eV. The change in the polarization of the beam of light when reflected from the sample surface through the complex electric field vector, $E_\nu$, is measured. This complex electronic field vector is the sum of two perpendicular vectors, $E_p$ and $E_s$. Using these component vectors and the following equations, the parameters $\Psi$, amplitude, and $\delta$, phase shift difference, can be determined. Here $r_p$ and $r_s$ are the complex amplitude coefficients and $\delta_p$ and $\delta_s$ are the phase shifts for each corresponding polarized plane.
Equation 3.1

\[ r_p = \frac{E_r^p}{E_i^p} = |r_p| \exp(\varphi_p) \]

Equation 3.2

\[ r_s = \frac{E_r^s}{E_i^s} = |r_s| \exp(\varphi_s) \]

Equation 3.3

\[ \frac{r_p}{r_s} = \frac{|r_p|}{|r_s|} \exp(\varphi_p - \varphi_s) = \tan \Psi \exp(\Delta) \]

Data from the ellipsometry measurements are then fitted to a model of the sample depicted through various representative layers. Once a model is developed for a certain kind of film, SE can routinely be used to determine the film thicknesses as long as the films do not deviate significantly in their optical properties from the films used to develop the model. In this thesis, known models from the MURI group were employed to get accurate thickness measurements for the films (discussed in Chapter 4).

### 3.2.2 GIXRD

Grazing Incidence X-Ray Diffraction, GIXRD, is a spectroscopy method that helps to determine the structure and composition of a thin film. Similar to ellipsometry, GIXRD is a nondestructive and contactless spectroscopy method. XRD works by angling an incident x-ray beam onto a sample and then measuring the reflected or transmitted x-rays at a range of angles. XRD measures the angle and intensity of the diffracted x-rays. These measurements can be compared to various standard XRD profiles in order to obtain information about the composition of the thin film.
GIXRD is a more specific type of XRD in which the x-ray source must remain stationary while the detector rotates over the samples. In this study a PANAnalytical PRO X’Pert MPD with Cu Kα1 (λ = 1.54 Å) radiation was used to analyze the structure of the deposited films. Diffraction patterns were collected for 2θ values between 30° and 75° with a 2θ glancing angle, and a scan rate of 1.2° per minute. Using MDI Jade V9.0 database software, the peak positions and intensities were compared to bulk vanadium oxide standard 2θ values in order to determine the crystalline phase and the lattice parameter.

3.2.3 Electrical Contacts

Once the nondestructive methods of characterization have been performed, the sample wafers were broken up in order to deposit contacts on the samples. These contacts are needed in order to gain information about the electrical properties of the films. A nearly identical Kurk Lesker CMS-18 system was used to deposit a layered titanium and platinum contact. Shadow mask contacts were deposited on approximately 1cm x 1cm squares of the deposited silicon wafers. An example of the contact spacing is shown in Figure 3.4.
3.2.4 IV Measurements for TCR and Resistivity

TCR and resistivity are two important metrics used in evaluating the utility of a microbolometer sensing material. Desirable films have high TCR while maintaining a low resistance. Current-voltage, I-V, characteristics were measured by sourcing the voltage from -1 volt to +1 volt with a step height of 0.2 volts. A Hewlett Packard 4140B DC voltage source connected to a 2-probe system, and a LabVIEW program were used to collect the data. Factoring in the contact spacing and cross sectional area, the resistance was extracted from the slope of the current voltage curves. The calculation of the resistivity values for each film consisted of a simple conversion involving the film thickness and resistance. The TCR is defined as the percentage change in resistance per unit change in temperature and is given by

$$ TCR = \frac{1}{R} \frac{dR}{dT} $$

Equation 3.4
where $R$ is the resistance of the film at the reference temperature.

To calculate the TCR of the film the I-V data was collected for temperatures between 30°C and 65°C in 5°C increments. The following equation along with the activation energy was used to calculate the TCR of the film

$$ TCR = \frac{d \ln(\rho)}{dT} = -\frac{E_a}{kT^2} $$

Equation 3.5

where TCR is the temperature coefficient of resistance ($\%$/°K), $E_a$ is the extracted activation energy from the resistance versus temperature data (in eV), $K$ is the Boltzmann’s constant (in eV/°K) and $T$ is 298°K.

3.2.5 Scanning Electron Microscopy

The scanning electron microscope, or SEM, is a type of microscope that uses a high-energy particle beam of electrons to image a sample surface. The beam of electrons scans the sample’s surface in a raster scan pattern, similar to graphics patterns in television and computer bitmap image systems. The SEM is able to gather information about the sample’s topography, composition and certain electrical properties.

An SEM can contain many different types of detectors in order to detect secondary electrons, back scattered electrons, x-rays, light, specimen current and transmitted electrons. Each detector measures a different characteristic of the sample. The most common detector is for secondary electrons. This detector is able to produce very high-resolution images of a sample surface. Back scattered electrons and x-rays are
used to determine the composition and measure the abundance of certain elements of the sample.

3.2.6 Transmission electron microscopy (TEM)

Transmission electron microscopy involves the observation and recording of electrons that have been scattered by the sample in a similar way as scanning electron microscopy. Scattered electrons can be recorded either by the way that they scatter spatially in images, the way they interfere after scattering in diffraction patterns, or by the amount of energy they lose by scattering in electron energy loss spectra [12].

The TEM images in this thesis were prepared and taken by Jing Li. The TEM was performed using three different microscopes: a Philips CM420 operated at 120 kV, a JEOL 2010 with a LaB$_6$ emitter operated at 200 kV, and a JOEL 2010-F operated at 200 kV [12].
4.1 Hysteresis

One important characteristic of the reactive sputtering process is the target current hysteresis [9]. Figure 1 shows the variation of the cathode (target) current vs. the oxygen flow rate (shown as a percentage in terms of total argon and oxygen flow rates) in the chamber, without substrate bias, for different total flow at a total pressure of 2.5mTorr. Each of the curves in Figure 1 show that at low oxygen percentages, the current at the target remained steady at approximately 0.95 A. The region where the cathode current remains steady is a stable “metallic” sputtering zone. Once the oxygen percentage is increased to approximately 10% – 12%, the cathode current begins to drastically decrease to approximately 0.7A. This drastic decrease in cathode current is due to the formation of a vanadium oxide layer on the surface of the target [9]. Once the amount of oxygen that flows into the chamber increases sufficiently, the target oxidation rate is relatively constant and results in a reduced sputtering rate. This effect is often known as target poisoning.

Once the oxygen percentage is increased enough, the target current once again remains steady indicating another stable sputtering zone. Once the oxygen percentage is reduced in the chamber to a certain point, the cathode current once again begins to increase. At lower oxygen percentages, the target oxidation rate decreases resulting in an increase in the sputtering rate and therefore the cathode current. Once again at low percentages the cathode current stabilizes at approximately 0.95A. This zone is often
referred to as the metallic zone. It is important to note that the region between the stable metallic zone and the stable target oxidation zone is unstable, especially at lower total flow rates. When oxygen percentages are in this intermediary unstable zone the cathode current drifts. Over the course of a single deposition, the cathode current could drift in excess of 20%. This amount of variability would not only reduce the quality of the films but also make the whole deposition nearly unrepeatable. Note that at higher total flow rates the residence time in the chamber is shorter, which results in a faster transition between the metallic and oxidized zones.

![Graph](image)

**Figure 4.1.** Variation of the cathode current as a function of oxygen percentage in the chamber for 3 different total flow rates at a total pressure of 2.5 mTorr.
Figure 4.2, shown below, shows the same hysteresis runs as in Figure 4.1 except in terms of the total oxygen flow in sccm. As one can see, the curves at each flow rate show similar metallic, unstable, and target oxidation zone characteristics. While each has these similar characteristics, each curve is consistently different from the others. For one, the position of the unstable zone in terms of total oxygen varies at the different flow rates. For lower flow rates, such as the 15 sccm curve, the width of the process hysteresis is much larger than at higher flow rates. Increasing the total gas flow rate during deposition results in a decrease in the width of the process hysteresis as well as shifting the whole hysteresis curve to the right, towards higher total oxygen flow rates. Another important difference is the slope of the process hysteresis. At higher flow rates the slope of the curve, within the unstable zone, is lower. It is interesting to note that the combination of both a thinner process hysteresis, the flatter curve, and a low pressure of 2.5mTorr, results in a unique mostly-stable intermediate zone.

In all three of the curves, even though the total gas flow rates vary for each, the unstable region begins at an oxygen flow rate of approximately 2.5sccm. This would suggest that for this specific system geometry and parameters, an oxygen flux of 2.5 sccm is sufficient to oxidize the target [9]. This shows that while the amount of argon in the system does affect the hysteresis curve, it has little effect on the location of the beginning of the unstable zone on the forward hysteresis curve. The amount of argon does seem to affect the backward hysteresis curves. Higher total argon flow rates, and therefore an increase in the turbine pump speed of the chamber, results in much faster de-oxidation of the target. The increase in total gas flow over the substrate
results in a thinner hysteresis loop, which indicates a much faster recovery of the oxidized target. This is due to the extra argon helping to decrease the amount of oxygen gas around the target. At lower flow rates, on the other hand, the lower argon gas flow is not able to remove as much oxygen as quickly which results in a much wider hysteresis loop. In order to make up for the reduced amount of argon flowing into the system, the recovery of the target depended on a much larger decrease in the oxygen flow rate.

The change in the oxidation characteristics of the target, reflected in the cathode current, can also be explained by the residence time of the $O_2$ gas in the system. At lower flow rates the oxidation of the target is “more efficient,” whereas at higher flow rates some of the oxygen is unutilized. In order to overcome this underutilization a higher total amount of oxygen is needed to cause the cathode current to decrease. Additionally, it appears that the extent of the $O_2$ oxidation based on the cathode current is less at high flows than low flows.
The target current is most affected by the total oxygen flow into the system, while the argon gas flow into the system changes little. As described in [22], the reactive sputtering process of a metallic target can be broken up into three main operating zones. These zones are determined by the total oxygen flow into the system. The first region is the elemental zone. This zone is characterized by low oxygen flow into the system. The small amount of oxygen that does enter the system is incorporated into the film, oxidizes vanadium on the walls of the chamber, or is pumped.
out of the chamber. The vanadium target is affected very little in the elemental zone.

The next zone is known as the intermediate zone. As the amount of oxygen flowing into the system increases, the amount of oxygen that interacts with the target begins to increase, reducing the sputtering rate of the vanadium. The final zone is known as the oxidized zone. As the name implies, this zone is characterized by high oxygen flow rates and an oxidized target. Once the target oxidizes, resulting in an increased resistance of the target, the cathode current stabilizes.

Figure 4.3. Variation of cathode current as a function of the total oxygen flow in the chamber at two different pressures, 2.5 mTorr and 5 mTorr.
Figure 4.3 shows two hysteresis curves for 25 sccm total gas flow rate, but at two different pressures, 2.5mTorr and 5mTorr. The first apparent difference is that once the pressure in the chamber is decreased, the width of the hysteresis decreases. More oxygen is needed in the chamber to start poisoning the target at the lower pressure. The separation of the curves at high O$_2$ flow rates also suggests that at lower pressures, less oxygen is able to interact with the target therefore reducing the amount of oxidation of the target at higher oxygen contents. Both of these can be accounted for by the reduction in residence time in the chamber from the reduction in pressure from 5mTorr to 2.5mTorr.

Similar hysteresis loops have been determined for a wide variety of system parameters. Total pressure, oxygen and argon gas flow rates, and substrate bias were all varied. Hysteresis curves for various substrate biases will be shown in later sections. Overall, the hysteresis loops show similar characteristics as those already described. Films were then deposited at parameters corresponding to some of these curves and their structural and electrical properties were then characterized.

4.2 Deposition Rate

The deposition rate, or more commonly known as growth rate, of the vanadium oxide films is another important film characteristic that helps to explain what is happening in the films. The thickness of each film was determined through the use of spectroscopic ellipsometry explained in the previous section. Unless indicated, all films were deposited for 900 seconds at a constant power of 300W. The deposition rate of
the various thin films was determined by simply dividing the thickness of each film by the deposition time. Figure 4.4 shows that in general the deposition rate of the films decreases with increasing oxygen partial pressure. This decrease in deposition rate as the oxygen partial pressure is increased can be attributed to target poisoning. As the oxygen content in the chamber increases, the target begins to oxidize, reducing the effective sputtering rate of the target. It is possible that if the oxygen content is high enough, the oxidation rate of the target could surpass the sputtering rate and the deposition will stop. This reduction, and eventual failure, of the sputtering due to target oxidation is common in reactive sputtering of metallic targets.

Figure 4.4. Variation of the deposition rate (A/s) as a function of the oxygen percentage in the chamber with a 25 sccm flow rate at a pressure of 5mTorr.
As seen in Figure 4.4, there is a deposition rate hysteresis present in much the same way as the hysteresis of the target current, as seen in Figure 4.1. While less apparent due to the fewer number of data points, there is still a noticeable difference between the deposition rate at a given oxygen percentage depending on whether the oxygen content of the chamber is being increased from an oxygen starved initial condition or decreased from an oxygen rich initial condition. This deposition rate hysteresis shows that not only is the oxygen percentage an important variable in the film processing, but that the conditions of the chamber prior to deposition also have an impact on the film. This suggests that with more stringent chamber conditioning prior to deposition, this process hysteresis could be minimized.

Figure 4.5 shows a similar film series that was deposited at a lower total pressure and a higher gas flow rate, 2.5 mTorr and 45sccm, respectively. This means that reactions and changes in the chamber occur much more quickly. This is apparent in that there is little to no hysteresis seen. Since the chamber changes much faster under these conditions, the previous chamber conditions do not affect the deposition of the film as significantly as films deposited at either a higher total pressure or a lower gas flow rate. Similar to previous films, the deposition rate decreases as the oxygen percentage increases, with the exception of low oxygen conditions. In the low oxygen, or metallic, region there is a noticeable maximum value in the deposition rate at which point either decreasing or increasing the oxygen content will decrease the deposition rate.
Figure 4.5. Variation of the deposition rate (Å/s) as a function of the oxygen percentage in the chamber with a 45 sccm flow rate at a pressure of 2.5mTorr.

4.3 TCR and Resistivity

Metal contacts were deposited in order to measure the resistivity and TCR of each film. Each film was measured using a 2-probe system as described in Chapter 3. A small piece of wafer, approximately 1 cm by 1 cm, was cleaved from the deposited wafer, covered with a stencil mask and TiPt contacts were DC sputtered on. These contacts were deposited under similar conditions, and with a similar Kurk Lesker CMS-18, as vanadium oxide, and consisted of 300Å titanium, in order to facilitate increased adhesion, and 1000Å platinum. All films exhibited linear I-V behavior between -5 to 5 V. As seen in
Figure 4.6 below, both the resistivity and the TCR decreased with decreasing oxygen. As the oxygen content increased, the TCR of the films increased marginally while the resistivity rose over an order of magnitude. This is understandable since as the oxygen content in the chamber increases, the oxidation rate of the target increases resulting in a decrease in both the total sputtering rate as well as the cathode current. This results in both a chamber with a higher oxygen to vanadium ratio as well as a more oxygen-rich and resistive film. Notice that two films deposited under the same conditions had similar TCR and resistivity indicating that for these conditions the process was repeatable.

![Graph showing variation of TCR vs. resistivity for different oxygen partial pressures](image)

**Figure 4.6.** Variation of the TCR of a set of films as a function of resistivity. Films where grown under varying oxygen partial pressures.
4.4 XRD

Glancing incidence x-ray diffraction, or GIXRD, was performed on a number of samples grown under various conditions. GIXRD results showed a variety of small sharp peaks as well as some very broad less distinguishable peaks. These peaks are called Bragg peaks and their location can shed a lot of information on the composition of the sample. The number, location, width, and intensity of these peaks are unique for certain crystal structures and can provide a great deal of information about the films characteristics. For example, diffraction patterns with sharper and more intense peaks indicate film crystallinity. It should be noted that the sharp peak around $2\theta = 55$ is a result of the silicon substrate and is not a characteristic of the film itself.

While peaks indicate film crystallinity, the lack of any significant peaks in Figure 4.7, presumably, indicates a large amount of amorphous VO$_x$. The films in the following figure were deposited at a pressure of 5 mTorr with a total flow of 25 sccm. The films were deposited under both increasing and decreasing oxygen conditions. The figure shows the hint of peaks in films deposited under low oxygen content, while at higher oxygen content the curves smooth out. This indicates that at lower oxygen flows, or lower total flow, the crystallinity of the film increases. This also implies that the pressure and gas flow play a large role in the microstructure of the deposited films.
4.5 Bias Hysteresis

Figure 4.8 shows a series of runs deposited at 5 mTorr with a total gas flow of 25 sccm. During deposition an RF substrate bias of 0W, 10W, 25W and 50W was applied in order to see the effect on the cathode current at various oxygen percentages. The RF substrate bias of 10W, 25W, and 50W correspond to DC self bias of -125V, -250V, and -400V respectively. As seen in the figure, the RF substrate bias increased the cathode current at all oxygen percentages when compared to having zero bias. Changes in the RF substrate bias power did not seem to significantly affect the cathode current in the...
metallic region. Increasing bias did, on the other hand, seem to have an effect the width of the hysteresis and the oxidized cathode current. At increased biases, the width of the hysteresis decreased relative to both reduced bias and non-bias curves. In terms of how this affects the processing of films, the application of RF substrate biases results in a stable metallic region existing at higher oxygen percentages. In other words, films deposited at oxygen percentages that were originally in the oxidation zone can be grown in the metallic zone through the application of a substrate bias. The effect on film properties is discussed subsequently.

Figure 4.8. Variation of cathode current as a function of the total oxygen flow in the chamber. Films were deposited under varying RF substrate biases with a 25 sccm flow at a pressure of 5 mTorr.
Figure 4.9 shows the cathode current in terms of oxygen percentage for runs deposited at 3 different positive DC substrate biases with a 45 sccm flow rate at a pressure of 2.5 mTorr. As seen previously, the higher flow rate combined with the reduced pressure results in a more gradual transition from metallic to oxidized and a thinner hysteresis. This is due to the more rapid environment changes as a result of the process conditions. Figure 4.9 also shows that the DC substrate bias affects the cathode current in a similar way as the RF substrate bias. An increase in the DC substrate bias results in an increase in the cathode current in the metallic region. Increasing DC substrate biases also reduce the width of the hysteresis.

**Figure 4.9.** Variation of cathode current as a function of the total oxygen flow in the chamber. Films were deposited under varying DC substrate biases with a 45 sccm flow at a pressure of 2.5 mTorr.
4.6 Deposition Rate for Samples with DC Substrate Bias

In order to see how DC substrate biasing affects the deposition rate of vanadium oxide, 5 sets of samples were deposited under a pressure of 2.5 mTorr with a total flow rate of 45 sccm and a power of 300W. Two series were grown under a negative DC substrate bias and another two series were grown under a positive DC substrate bias, while the last series was left unbiased. These samples’ thicknesses were then measured using spectroscopic ellipsometry.

Figure 4.10 shows the deposition rate of the unbiased series and the two negatively biased series in terms of the oxygen percentage of each film. All series show similar trends as previously seen for unbiased samples. As the oxygen percentage increases, the deposition rate generally decreases. As previously explained, the increase in oxygen begins to oxidize the target, reducing the deposition rate. The application of the negative DC substrate bias shows an overall trend of reducing the deposition rate of the films. This decrease in the deposition rate is thought to be due to an increase in density of the films rather than a true reduction of the target deposition rate due to oxidation. There is also the possibility that some of the weaker bonds at the substrate are broken, resulting in less net film growth.
Figure 4.10. Variation of the deposition rate (A/s) as a function of the oxygen percentage in the chamber with a 45 sccm flow rate at a pressure of 2.5mTorr. Film under DC substrate bias.
Figure 4.11 shows the same unbiased series with the two series grown at a positive DC substrate bias. The curves exhibit the general trend of decreasing deposition rate due to increase oxygen percentage in the chamber. Unlike the negative DC substrate bias, this positive DC substrate bias appears to slightly increase the deposition rate of the films in comparison to the unbiased curve. It also appears that increasing the DC bias further does not change the deposition rate proportionally.

Figure 4.11. Variation of the deposition rate (A/s) as a function of the oxygen percentage in the chamber with a 45 sccm flow rate at a pressure of 2.5mTorr. Film under DC substrate bias.
4.7 Bias TCR and Resistivity

Figure 4.12. Variation of the TCR as a function of the resistivity. Films deposited with a 45 sccm flow rate at a pressure of 2.5 mTorr with a DC substrate bias.

Figure 4.12 above shows the resistivity vs. TCR for three series of films deposited at 0V, -50V and -122V DC substrate bias. All films were deposited under a 45 sccm flow rate at a pressure of 2.5 mTorr. The films were deposited at various oxygen percentages, with the oxygen percentages remaining consistent between sets.

As can be seen, as the negative DC substrate bias is applied, there is a general shift down and to the left. The bias generally reduces both the TCR and the resistivity of the films, with a stronger bias resulting in a greater shift. While both the TCR and the resistivity are reduced, the TCR values only marginally decrease while the resistivities...
are reduced by orders of magnitude. This suggests that with only a marginal change in TCR, the resistivity can be controlled through the application of a DC substrate bias.

One important thing to note is that with the application of the negative DC substrate bias, the differences in TCR and resistivity between films deposited in the forwards and reverse directions becomes significantly more apparent. For example, under both of the negative DC biases the films with the lowest resistivity, yet not the lowest TCR, are those films deposited at an oxygen percentage of 4% (1.8sccm) in the reverse direction. Without any bias the least resistive film was deposited in the forward direction, yet the least resistive films deposited with bias was deposited in the reverse direction. That many of the films deposited in the reverse direction show greater TCR and lower resistivity compared to the forward direction suggests that through the use of the DC bias in conjunction with a properly conditioned chamber in the reverse direction, a whole new set of data points are possible. This means that the initial oxygen condition of the chamber is another important process condition that greatly changes the film properties. This is more apparent in Figure 4.13.
Figure 4.13. Variation of the resistivity as a function of the oxygen percentage. Films deposited with a 45 sccm flow rate at a pressure of 2.5 mTorr with no DC substrate bias. Data labels are film TCR values.

Figure 4.13 depicts a set of films deposited with no DC substrate bias with a 45 sccm flow rate under a pressure of 2.5 mTorr. As seen previously, without any substrate bias the differences between the forward and reverse directions are minimal. Films with corresponding oxygen partial pressures show very similar TCR and resistivity in both directions. Without bias the forward direction shows a slightly better TCR to resistivity ratio.
Figure 4.14. Variation of the resistivity as a function of the oxygen percentage. Films deposited with a 45 sccm flow rate at a pressure of 2.5mTorr with a DC substrate bias of -50V.

Figure 4.14 depicts a similar set of films, 45 sccm flow rate under a pressure of 2.5mTorr, except with a DC substrate bias of -50V. As is readily apparent, the difference between the forward and reverse directions is much greater. The films deposited in the reverse direction show a trend of having lower resistivities at similar oxygen partial pressures. It is interesting to note that the films with the lowest resistivity was deposited at one of the highest oxygen partial pressures and has one of the highest TCR values. The films with the most desirable TCR to resistivity ratio were deposited in the reverse direction.
As seen in the previous figure, Figure 4.15 shows a set of films deposited at 45 sccm flow rate at a pressure of 2.5mTorr with a DC substrate bias of -122V. Once again the difference between the forward and reverse directions are much greater than without any substrate bias. The films with the lowest resistivities were deposited in the reverse direction and have some of the highest TCR values. This suggests that films deposited in the reverse direction under a DC substrate bias show improved TCR and resistivity values.
Figure 4.16 shows the TCR in terms of the resistivity of films grown under different DC substrate biases with a 45sccm flow rate at a pressure of 2.5mTorr. All films were deposited at an oxygen percentage of 2.5% and 3.2% in the forward direction. As shown the general trend remains similar to other biases where increased substrate bias reduces both the TCR and resistivity of the films resulting in a general shift towards the lower left. For example, the application of a -122 V DC substrate bias resulted in a film with a TCR 13% lower and with a resistivity 93% lower, compared to the unbiased film.

The following figure is also a good comparison between the negative and positive DC substrate bias. It should be noted that due to equipment limitations the substrate bias magnitudes are as comparable as possible. As can be seen from the figure, the 7V bias had little effect on the TCR or resistivity, while the -122V bias resulted in the largest shift, as expected. The positive and negative DC substrate bias affected the TCR and resistivity of the deposited films in a similar fashion. Both reduced the TCR of the films while reducing the resistivity to a much larger extent. The only apparent difference comes from the magnitudes of the bias with a larger bias resulting in a larger shift, for both negative and positively biased films. The 13V and the -50V films showed a remarkably similar shift in values, which suggests that while a positive and negative bias results in similar shifts, they are not directly comparable.
Figure 4.1. Variation of the TCR as a function of the resistivity. Films deposited with a 45 sccm flow rate, a pressure of 2.5mTorr, an oxygen percentage of 2.4%, and a DC substrate bias.

Figure 4.17, below, also shows the TCR in terms of the resistivity of films grown under different DC substrate biases with a 45sccm flow rate at a pressure of 2.5mTorr. All 5 of these films were deposited at a higher oxygen percentage of 4.0%. As shown, the general trend remains similar to other biases where substrate bias reduces both the TCR and resistivity of the films. For example, the application of a -122 V DC substrate bias resulted in a film with a TCR 7% lower and a resistivity 99% lower, compared to the unbiased film. What makes figure 4.17 interesting is that the films were all deposited in the reverse direction. While the previous figure showed a nearly linear shift in values towards the lower left, the films deposited in the reverse direction show a much
different shift. The films resulted in a nearly identical TCR, only 3.5% decrease compared to 13%, while resulting in an even greater reduction of resistivity, a 97% decrease compared to 93%. This results in a nearly 4 times greater reduction in resistivity for a similar decrease in the TCR. This suggests that a substrate bias used in conjunction with the reverse direction can greatly reduce the resistivity without a significant decrease in TCR.

Figure 4.17 also shows a more distinct difference between the positive and negative DC bias. The -50V and -122V DC bias resulted in an order of magnitude decrease in resistivity greater than the 7V and 13V DC bias. This is a distinct difference from the forward biased films in the previous figure.

Figure 4.17. Variation of the TCR as a function of the resistivity. Films deposited with a 45 sccm flow rate, a pressure of 2.5mTorr, an oxygen percentage of 4.0%, a DC substrate bias, and in the reverse direction.
Figure 4.18 shows three sets of two films each deposited at a pressure of 2.5mTorr. Each set has a film deposited under no bias and a film deposited with a 25W RF substrate bias. The sets were each deposited in their respective metallic zones, between 3.5 and 7% oxygen at total flows of 15, 25 and 45sccm. As expected, each film set contains an unbiased film and a biased film that is shifted down and to the left. The TCR and the resistivity were both decreased with the application of the RF substrate bias, consistent with other biased films.

![Figure 4.18. Variation of the TCR as a function of the resistivity. Films deposited at a pressure of 2.5mTorr, with and without an RF bias. All oxygen partial pressure are between 3.5-6%, which is located in the metallic zone of each different total flow.](image)
Figure 4.19. Variation of the TCR as a function of the resistivity. Films deposited at a pressure of 2.5mTorr, a total gas flow rate of 45 sccm, with and without substrate bias. All oxygen partial pressures are between 2.5-3%.

Figure 4.19 shows 6 sets of films deposited at various substrate bias. All films were deposited at a pressure of 2.5mTorr and a total gas flow of 45 sccm. All oxygen percentages are between 2.5 and 3%. The type and magnitude of the substrate bias was varied as shown. Both the positive and negative DC substrate bias, as well as the RF substrate bias resulted in a similar change in TCR and resistivity with just the magnitude differing. With only the application of a substrate bias, the films' resistivities were able to be controlled over a range of 2 orders of magnitude.
4.8 Bias GiXRD

Figure 4.20 shows XRD results of a group of films deposited during the application of an RF substrate bias. The bias was increased from 0 to 50W. The films were all deposited at 4.5% oxygen with a total flow of 25sccm under a pressure of 5mTorr. As expected there is a sharp peak which corresponds to the silicon substrate. These curves indicate that these films were mostly x-ray amorphous. Some of the curves indicate that some of the films contain some sort of crystal structure. The few peaks that are apparent are near $2\theta = 38, 44, \text{ and } 65$ that closely match a VO phase. XRD results indicated the presence of only two material phases in the films, an x-ray amorphous phase occurring at high oxygen partial pressures, and a matrix of FCC VO$_x$ nano-crystals in an amorphous matrix occurring at low oxygen partial pressures.

As the RF substrate bias was increased, the crystallinity of the films would be expected to increase. As can be seen from the figure, as the bias increases, the peaks begin to grow in intensity. This indicates the growing presence of a crystal structure within the primarily amorphous film. Peak patterns with sharper and more intense peaks contain nano-crystals with increased size. The three peak pattern that begins to grow as the bias is increased correlates to the FCC VO$_x$ phase. This shows that besides the gas flow and pressure, the substrate bias is also able to exert some limited control over certain aspects of the film microstructure.
Figure 4.20. X-ray diffraction patterns of films deposited at a pressure of 5 mTorr, total flow of 25sccm, and oxygen percentage of 4.5.

It is worth noting that for many of these vanadium oxide films, grazing incident x-ray diffraction did not detect any crystallinity in films that electron diffraction has shown to be nano-crystalline [12]. Due to the limited sensitivity to small crystals, x-ray diffraction is not always the best technique in determining film stoichiometry. While electron diffraction is much more time consuming, it gave a much more accurate indication of a film's crystallinity. Another technique that is used in order to determine film stoichiometry is Rutherford backscattering spectrometry. RBS is used in order to determine the stoichiometry of a material by measuring the backscattering of a beam of high energy ions impacting the sample. This technique is useful for materials that contain oxygen, such as VO_x, by determining what x is.
Figures 4.21 and 4.22 are TEM images of a DC biased vanadium oxide thin films. The film was deposited under a pressure of 2.5 mTorr and a flow rate of 45 sccm. Oxygen percentage was 2.4%, or 1.1 sccm. During deposition the film was under a -122V, 4mA DC substrate bias. The resulting film was approximately 1125Å thick with a resistivity of 0.16 Ω.cm and a TCR of -2.3 %/°K.

![TEM micrograph showing cross sectional dark field image of vanadium oxide.](image)

**Figure 4.21.** TEM micrograph showing cross sectional dark field image of vanadium oxide. Film deposited with a 45 sccm flow rate, a pressure of 2.5mTorr, an oxygen percentage of 2.4%, and a DC substrate bias of -122V, 4mA.
Figure 4.21 shows a TEM micrograph of a cross sectional dark field image of the film deposited under DC substrate bias. The TEM image shows the formation of columnar nano crystals containing nano-twins with a diameter of 10nm and a sub-nanometer scale twin spacing. Films deposited under low pressure, below 5mTorr, and films deposited with a low oxygen flow, below 5%, result in nano-crystalline growth and exhibit the FCC VO$_x$ phase [12]. Note that nano-twins were present in many of the biased films deposited at low pressures, but were particularly distinct for the DC biased films.

Figure 4.22. TEM micrograph showing a selective area electron diffraction of vanadium oxide thin film. The film was deposited with a 45 sccm flow rate, a pressure of 2.5mTorr, an oxygen percentage of 2.4%, and a DC substrate bias of -122V, 4mA.
Figure 4.22 is another TEM micrograph of the same substrate biased vanadium oxide thin film. The image is a selective area electron diffraction of vanadium oxide which shows evidence of nano-twins. One of the main indications of nano-twinning is reciprocal rods which result from a highly periodic twin defect structure [23, 24]. There is significant evidence that this micro-twinning effect is a result of the incorporation of excess oxygen in the FCC VO$_x$ phase [12]. This is a common feature in bolometer grade VO$_x$ films deposited by ion beam deposition. Films deposited by reactive pulsed dc magnetron sputtering with a DC bias at low pressures have been shown to exhibit a nanocrystalline columnar microstructure with nano-twins embedded in an amorphous vanadium oxide matrix [25]. These films exhibit similar electrical properties as microbolometer grade VO$_x$ deposited using ion beam deposition.
Chapter 5 Conclusion

This thesis focused on the deposition of vanadium oxide thin films using pulsed dc reactive magnetron sputtering and the application of a substrate bias. The substrate bias has been shown to dramatically change the structure of the films as well as to improve numerous film properties critical to their application as imaging layers in uncooled IR microbolometer arrays. Also, films deposited with an applied substrate bias have shown electrical and microstructural properties similar to that of bolometer grade vanadium oxide films deposited by ion beam deposition.

One of the initial results of the application of substrate bias during deposition was the effect it had on the process hysteresis of vanadium oxide. Both RF and DC substrate bias increased the operating cathode current of the target during the deposition of the thin films. This resulted in an overall reduction of the process hysteresis, but more importantly resulted in a larger stable metallic region existing at higher oxygen percentages. In other words, through the application of a substrate bias, films can be grown in the metallic zone at higher oxygen percentages than otherwise possible. Furthermore, application of substrate bias enables better control over the amount of oxygen in a film, and therefore the resistivity of the films.

The application of a RF substrate bias also appears to reduce the overall deposition rate of the films. This reduction in deposition rate is believed to be a combination of an increase in overall density of the films and a reduction in the target deposition rate due to increased oxidation. Unexpectedly, the application of a positive
DC bias resulted in the opposite, an overall increase in the deposition rate. This may be due to an enhanced oxygen uptake as a result of negative oxygen ion impingement or enhanced ionization of deposited species leading to more oxygen incorporation into the growing film.

Substrate bias also greatly affected the resistivity and the TCR of the films. The bias generally reduces both the TCR and the resistivity, with a larger bias resulting in a greater decrease with respect to unbiased films. While both are reduced, the resistivity of the films generally decreases by an order of magnitude more than the decrease in TCR. This indicates that with only a marginal change in TCR, the resistivity can be controlled through the application of a substrate bias.

Interestingly, vanadium oxide films deposited in the reverse direction, i.e. from higher to lower oxygen flow, with a substrate bias resulted in a smaller decrease in TCR. This was the result of the condition of the chamber at the beginning of deposition. This was most apparent during the application of the negative DC substrate bias. The initial condition of the chamber plays a much more significant role in the films properties with the application of a substrate bias. In one instance, this resulted in a 2 order of magnitude drop in resistivity while TCR remained nearly unchanged.

Lastly, the application of a substrate bias resulted in a change in the microstructure of the films from a mixture of nanocrystalline and amorphous VO$_x$ to a mixture containing columnar microtwins. This microstructure is a prominent feature of microbolometer sensing films made by ion beam deposition. These microtwins are
thought to be responsible for the significantly improved electrical properties of these films.

Overall, the application of substrate bias during deposition of pulsed dc sputtered vanadium oxide results in both improved electrical and structural properties over unbiased films and shows conclusively that films made by this deposition technique are comparable to commercially produced vanadium oxide films deposited by ion beam deposition method.
Chapter 6 Future Work

While this thesis has shown some of the possible benefits that the application of a substrate bias during the deposition of vanadium oxide thin films by pulsed dc reactive magnetron sputtering, it has also brought up a number of issues that are worth investigating further.

Though this thesis has demonstrated the usefulness of substrate bias, the effect of both RF and DC substrate bias during deposition has only begun to be explored. With a more comprehensive setup, both the magnitude and application of the bias should be further tested.

Additionally, the work done to condition the deposition chamber before each deposition has been shown to greatly affect the resulting film. Throughout the research conducted for this thesis, it became apparent how difficult it was to replicate certain films. Due to numerous constantly changing factors, including the state of the vanadium oxide target as well as the condition of the chamber walls, even with identical deposition conditions it was difficult to produce films with identical electric properties. Further testing along with extensive monitoring of chamber conditions would help a great deal in better understanding magnetron sputtered vanadium oxide thin films.

Similarly, the physical chamber setup itself plays a significant role in the resulting films. One important observation over the course of this research was the effect of the gas ring and shutter configuration on the resulting plasma inside of the chamber. Due to the physical configuration of the processing chamber, the gas ring was positioned
around the substrate while the shutter was placed over the target. This resulted in a need for the plasma to reach a new equilibrium state once of shutter was removed and the deposition started. If the shutter was placed over the substrate instead of the target, the plasma would be able to reach an equilibrium closer to its operation equilibrium prior to the start of the deposition. A small window of time was noted at the beginning of most depositions during which the plasma and deposition indicators varied greatly before reaching an equilibrium. This shutter set up also greatly affected the amount of initial chamber conditioning that could be done before each deposition. Unfortunately, one of the seemingly only consistently successful ways to properly condition the chamber is to actually deposit an entire film.

Lastly, for this technique to be manufacturable, the run-to-run reproducibility would have to be verified as well as the long-term stability of the films after deposition. Future work should include assessing how these films are affected by post-deposition processing such as thermal annealing and what affect deposition temperature has on film properties.
BIBLIOGRAPHY


